Preparation, swelling, and stimuli-responsive characteristics of superabsorbent nanocomposites based on carboxymethyl cellulose and rectorite

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Utilization of naturally available raw materials for the fabrication of eco-friendly functional materials has long been desired. In this work, a series of superabsorbent nanocomposites were prepared by radical solution copolymerization of sodium carboxymethyl cellulose (CMC), partially neutralized acrylic acid (NaA), and rectorite (REC) in the presence of initiator ammonium persulfate (APS) and crosslinker N,N'-methylene-bis-acrylamide (MBA). The optimal reaction variables including the mass ratio of acrylic acid (AA) to CMC, MBA concentration, and REC content were explored. FTIR spectra confirmed that NaA had been grafted onto CMC and REC participated in polymerization. REC was exfoliated and uniformly dispersed in the CMC-g-PNaA matrix without agglomeration as shown by XRD, TEM, and SEM analysis. The thermal stability, swelling capabilities, and rate of the nanocomposites were improved after introducing REC, and the gel strength greatly depended on the concentration of crosslinker MBA. The nanocomposite showed excellent responsive properties and reversible On–Off switching characteristics in various saline, pH, and hydrophilic organic solvent/water solutions, which provided great possibility to extend the application domain of the superabsorbent nanocomposites such as drug delivery system. Copyright © 2010 John Wiley & Sons, Ltd.

**Keywords:** carboxymethyl cellulose; rectorite; superabsorbent nanocomposite; swelling; stimuli-responsive

**INTRODUCTION**

Organic/inorganic nanocomposites are functional materials derived from the nanoscale modification of fully organic polymers by the incorporation of inorganic nano- or microparticles.\cite{1} Polymer/clay hybrids are representative nanocomposites because they frequently exhibit excellent performance superior to those of the components, cost-efficient characteristics, and extended applications.\cite{2,3} Superabsorbents are functional materials with a unique 3-D hydrophilic network structure and highly water-swellable property, which have raised continuous interest and have found extensive application in many fields such as hygienic products,\cite{4} agriculture,\cite{5,6} wastewater treatment,\cite{7,8} coal dewatering,\cite{9} catalyst supports,\cite{10} communication cable,\cite{11} and drug-delivery systems,\cite{12} etc. However, these applications encounter some limitations because the superabsorbents are mainly petroleum-based synthetic polymers with high production costs and poor environmental characteristics.\cite{13} Thus, new types of multi-component superabsorbents by introducing naturally available raw materials as additives have long been desired.

Recently, polysaccharide-based materials have attracted considerable interests because they show low-cost, renewable, biodegradable, non-toxic, and biocompatible characteristics.\cite{14–16} The composites or nanocomposites of polysaccharides with abundant, cost-efficient, and eco-friendly inorganic clay minerals also exhibited outstanding hybrid performance and have been honored as one of the material families “in greening the 21st century materials world”\cite{17} Thus, considerable efforts have been made to develop novel superabsorbent by the compounding of polysaccharide with clay minerals.\cite{18–21} Among numerous polysaccharides, cellulose is potentially useful because it is the most abundant natural polymer with excellent biodegradability and biocompatibility. However, the poor solubility and reactivity of cellulose make it difficult to directly modify and produce other useful materials. Carboxymethyl cellulose (CMC) is a representative cellulose derivative with carboxymethyl groups (-CH\textsubscript{2}-COONa) bound to some of the hydroxyl groups on the cellulose backbone; it can be easily produced by the alkali-catalyzed reaction of cellulose with
chloroacetic acid. The polar carboxyl groups render the cellulose soluble, chemically reactive, and strongly hydrophilic, and so the application of CMC in superabsorbent fields becomes attractive.[22] Rectorite (REC) is a particular clay mineral. It is a sort of regularly interstratified clay mineral with alternate pairs of a non-expansible dioctahedral mica-like layer and an expandible dioctahedral smectite-like layer existing in a 1:1 ratio.[23] REC has a water-swelling property similar to that of montmorillonite, and it is possible to form monolithic REC layers with the thickness of a single REC platelet, about 2 nm, and to prepare nanocomposites by exfoliation and intercalation techniques.[24] It is expected that the type and number of hydrophilic groups, as well as the network structure of the superabsorbents, could be improved by the nanoscale composite of CMC with REC clay.

Based on the above background, in this work, the series of sodium carboxymethyl cellulose-g-poly(sodium acrylate)/rectorite (CMC-g-PNaA/REC) superabsorbent nanocomposites were prepared by the nanoscale combination of CMC and REC. The structure and morphologies of the developed nanocomposites were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Thermogravimetric Analysis (TGA) techniques. In addition, the swelling properties and stimuli-responsive behaviors of the nanocomposites were evaluated systematically.

**EXPERIMENTAL**

**Materials**

Sodium carboxymethyl cellulose (CMC, CP, 300 ~ 800 mPa·s (25 g/L, 25 °C)) was from Sinopharm Chemical Reagent Co., Ltd, China. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure prior to use. REC micropowder (Mingliu Colloidal Co., Hubei, China) was milled and passed through a 320-mesh screen prior to use. Ammonium persulfate (APS, Analytical grade, Xi'an Chemical Reagent Corporation, China) was used as received. The other reagents used were of analytical grade and all the solutions were prepared with distilled water.

**Preparation of CMC-g-PNaA/REC nanocomposites**

CMC (1.20 g) was dissolved in 30 ml distilled water in a 250 ml four-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen line. The resultant solution was heated in an oil bath at 60 °C and purged with N₂ for 30 min to remove oxygen. Then, an aqueous solution (5 ml) of the initiator APS (0.1008 g) was charged to the flask under continuous stirring and kept at 60 °C for 10 min. After cooling to 50 °C, a solution of 7.2 g of AA neutralized by 8 ml 8.8 mol/L NaOH solution, crosslinker MBA (21.6 mg), and REC powder (0.45 g) was added, and the temperature was slowly raised to 70 °C, and maintained for 3 hr to complete polymerization. Continuous purging of nitrogen was used throughout the reaction period. The gel products were dried to a constant mass at 70 °C and ground and passed through 40–80 mesh sieve (180 ~ 380 μm).

**Measurements of equilibrium water absorption and swelling kinetics**

0.05 g of superabsorbent particle was immersed in an aqueous solution at room temperature for 4 hr to reach swelling equilibrium. The swollen gels were filtered using a 100-mesh sieve and then drained for 10 min until no free water remained. After weighing the swollen gels, the equilibrium water absorption (Qₑ, g/g) was derived from the mass change of samples before and after swelling.

Swelling kinetics of superabsorbents in aqueous solutions was measured as follows: 0.05 g samples were placed in 200 ml aqueous solution set intervals. The swollen gels were filtered by a sieve and then the water absorption at a given time was calculated according to the mass changes of sample before and after swelling. In all cases three parallel samples were used and the averages were reported in this paper.

**Evaluation of stimuli-responsivity**

NaCl, MgCl₂, and AlCl₃ solutions with various molar concentrations (0.01, 0.1, 1, 10, 20, 30, and 100 mmol/L) and mixtures of methanol, ethanol, and acetone/water with various volume concentrations (5, 10, 30, 40, 50, 60, 70, 80, and 90 v/v%) were prepared by dissolving calculated amounts of the corresponding solutes in distilled water. Buffer solutions with various pHs were prepared by combining KH₂PO₄, K₂HPO₄, H₃PO₄, and NaOH solution. Ionic strengths of all the buffer solutions were adjusted to 0.1 M with NaCl solution. The pH values were determined by a pH meter (DELTA-320). The equilibrium water absorption (Qₑ) in each solution was determined by a method similar to that in distilled water. The saline-, pH-, and hydrophilic organic solvent-reversibility of the nanocomposite were investigated in terms of its swelling and deswelling in each media. Typically, the sample particle (0.05 g, 180 ~ 380 μm) was placed in a 100 mesh sieve and adequately contacted with 100 mmol/L saline solutions, pH 2.0 buffer solution, or 90 v/v% hydrophilic organic solvents/water mixtures until equilibrium was reached. Then, the swollen samples were soaked in 0.01 mmol/L saline solutions, pH 7.2 buffer solutions, or 5 v/v% hydrophilic organic solvents/water mixtures for set time intervals. The swollen samples were filtered, weighed, and the water absorption of nanocomposite at a given moment was calculated according to the mass change of samples before and after swelling. The time interval is 15 min for each cycle, and the same procedure was repeated for five cycles. After every measurement, each solution was renewed.

**Determination of gel strength**

The gel strength of the swollen nanocomposites was determined with the Physica MCR 301 rheometer (Germany) at 25 °C according to a previously developed method.[25] The tested samples were fully swollen in 0.9 wt% NaCl solution. The strain amplitude was chosen as 0.5% and the angular frequency ω was defined in the range of 0.1 ~ 100 rad/sec. The results were the average of at least three measurements.

**Characterizations**

FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm⁻¹ region using KBr pellets. XRD analyses were performed using a X-ray power diffractometer with Cu anode (PAN analytical Co. X’pert PRO), running at 40 kV
and 30 mA, scanning from 3° to 10° at 3°/min. TEM was performed on a JEM1200EX (Japan) instrument, and the powdered specimen was placed on the copper grids after sonicating a suspension in ethanol and drying for 30 min. The morphologies of the samples were examined using a JSM-5600LV SEM instrument (JEOL) after coating the sample with gold film. Thermal analysis of samples was carried out on a Perkin–Elmer TGA-7 thermogravimetric analyzer (Perkin–Elmer Cetus Instruments, Norwalk, CT), within a temperature range of 25–800°C at a heating rate of 10° C/min, using dry nitrogen purge at a flow rate of 50 ml/min.

RESULTS AND DISCUSSION

FTIR spectra analysis

FTIR spectra of REC, CMC, CMC-g-PNaA, CMC-g-PNaA/REC (5 wt%), and the physical mixture of CMC-g-PNaA with REC (m/m = 18:1) are shown in Fig. 1. The characteristic absorption bands of CMC at 1061, 1115, and 1159 cm⁻¹ (stretching vibrations of C–OH groups) were obviously weakened after reaction (Fig. 1(b–d)). New bands at 1714 cm⁻¹ (C=O stretching of –COOH), at 1576 and 1572 cm⁻¹ (asymmetric stretching of –COO– groups), and at 1455 and 1410 cm⁻¹ (symmetric stretching of –COO– groups) appear in the spectra of CMC-g-PNaA and CMC-g-PNaA/REC (Fig. 1 (c, d)). This revealed that NaA had been grafted onto CMC macromolecular chains. The strong absorption of CMC at 1613 cm⁻¹ (asymmetric stretching vibration of –COONa groups) can be observed in Fig. 1(b), but it overlapped with the absorption bands of –COO– groups of grafted PNaA chains and appeared as a broad band (Fig. 1 (c, d)). The –O–H stretching vibration of REC at 3638 cm⁻¹ and the –OH bending vibration at 1634 cm⁻¹ disappeared in the spectrum of the physical mixture of CMC-g-PNaA with REC (Fig. 1(e)). The absorption bands of REC at 1049 cm⁻¹ (Si–O–Si asymmetrical stretching) and 1022 cm⁻¹ (–Si–O asymmetrical stretching), at 938 cm⁻¹ (Si–O–Si symmetrical stretching) and 915 cm⁻¹ (–Si–O symmetrical stretching), as well as at about 546 and 489 cm⁻¹ (Si–O(H) bending vibration) appear in the spectrum of CMC-g-PNaA/REC with a weakened intensity (Fig. 1(d)), but can be clearly observed in the spectrum of the physical mixture of CMC-g-PNaA and REC with considerable intensity (Fig. 1(e)). This information indicates that REC participated in the graft copolymerization reaction through its active silanol groups.[26]

XRD analysis

REC showed a strong (001) reflection at 2θ = 3.60° with a basal spacing (d) of 2.46 nm (Fig. 2a), but no REC reflections could be observed in the XRD patterns of the nanocomposites, even if the content of REC reached 15 wt% (Fig. 2(c, d)). Thus, REC may be exfoliated and the REC platelets thoroughly dispersed in the polymer matrix.[27] A similar observation was made for superabsorbent nanocomposites based on starch grafted PAA-co-AM/MMT.[28]

TEM and SEM analysis

TEM observation (Fig. 3) revealed good dispersion of REC in CMC-g-PNaA/REC (5 wt%). Due to the correspondingly greater interlayer spacing of REC, the rectorite particles exfoliated during the polymerization reaction and distributed in the polymeric matrix in the form of exfoliated platelets. This result is in accordance with the XRD analysis.

The SEM micrographs of CMC-g-PNaA and the CMC-g-PNaA/REC nanocomposites with 5, 10, and 20 wt% of REC are shown in Fig. 4. CMC-g-PNaA only exhibits a smooth and dense surface; while CMC-g-PNaA/REC nanocomposites show a correspondingly coarser surface (Fig. 4(b)). This implies that the incorporation of

Figure 1. FTIR spectra of (a) REC, (b) CMC, (c) CMC-g-PNaA, (d) CMC-g-PNaA/REC (5 wt%), and (e) the physical mixture of CMC-g-PNaA with REC (m/m = 18). This figure is available in color online at wileyonlinelibrary.com/journal/pat
REC improved the surface structure of superabsorbent. Also, it was observed that the REC is almost embedded and dispersed within the CMC-g-PNaA matrix (Fig. 4 (c)), with a homogeneous composition and without the flocculation of REC particles. This observation is consistent with the results of XRD and TEM.

**Thermal stability**

Figure 5 depicts the TGA curves of CMC-g-PNaA hydrogel and CMC-g-PNaA/REC (5 wt%) nanocomposite. It is obvious that REC has great influence on the thermal stability; the weight-loss rate was slowed after introducing REC. The weight loss about 21 wt% below 219°C for CMC-g-PNaA and about 18 wt% below 327°C for CMC-g-PNaA/REC (5 wt%) can be ascribed to the removal of absorbed water, the dehydration of saccharide rings, and the breaking of C–O–C bonds in the chain of CMC.

The weight loss of about 17 wt% (219/C242°C) for CMC-g-PNaA and about 16 wt% (327/C2432°C) for CMC-g-PNaA/REC (5 wt%) can be attributed to the elimination of water molecule derived from the two neighboring carboxylic groups of the grafted PNaA.
chains due to the formation of anhydride. The weight losses about 24 wt% (431 ~ 508 °C) for CMC-g-PNaA and about 18 wt% (432 ~ 512 °C) for CMC-g-PNaA/REC (5 wt%) are due to main-chain scission and the destruction of the crosslinked network structure. In comparison with CMC-g-PNaA matrix, CMC-g-PNaA/REC nanocomposite showed slower weight-loss rate and lesser total weight loss, which indicated that the incorporation of REC enhanced the thermal stability of superabsorbent.

Effect of mass ratio of AA to CMC on water absorption

The water absorption (Fig. 6) increased as the mass ratio of AA to CMC is enhanced, reaching a maximum at 7, and then decreasing. Because the dosage of initiator APS is definite in the reaction system, the number of free radicals generated by the decomposition of APS is constant. Thus, the dosage of monomer may directly determine the reaction rate as well as the amount of hydrophilic groups in polymer network. Enhancing the mass ratio of AA to CMC, more monomer can participate in the grafting reaction in the vicinity of active sites of CMC. As a result, the hydrophilicity of the polymeric network was improved due to the grafting of PNaA chains. Moreover, the osmotic pressure difference derived from the dissociation of –COONa groups and the repulsive interaction derived from the negative –COO– groups also increased with increase in the dosage of AA, which is also responsible for the enhancement of water absorption. However, a high ratio of AA in the reaction system causes a shrinkage of the water absorption. This is because a higher monomer concentration will increase the number of free radicals generated during the chain transfer reaction process, which results in an increase in the crosslink density and a decrease in the water absorption.

Effect of MBA concentration on water absorption and gel strength

As shown in Fig. 7, the crosslinker concentration exhibits more notable effects on water absorption than others. It is obvious that water absorption rapidly decreases with an increase in the crosslinker concentration from 3.59 to 10.74 mmol/L. A power law relation between the equilibrium water absorption ($Q_{eq}$, g/g) and the concentration of crosslinker MBA ($C_{MBA}$, mol/L)

![Figure 5. TGA curves of CMC-g-PNaA and CMC-g-PNaA/REC (5 wt%) superabsorbent nanocomposite. This figure is available in color online at wileyonlinelibrary.com/journal/pat](image)

![Figure 6. Effect of the mass ratio of AA to CMC on water absorption. APS concentration, 6.07 mmol/L; MBA concentration, 3.59 mmol/L; Neutralization degree of AA, 70%; REC content, 5 wt%; Reaction temperature, 70 °C. This figure is available in color online at wileyonlinelibrary.com/journal/pat](image)

![Figure 7. Effects of crosslinker concentration on water absorption in distilled water and 0.9 wt% NaCl solution. APS concentration, 6.07 mmol/L; Mass ratio of AA to CMC, 7; Neutralization degree of AA, 70%; REC content, 5 wt%; Reaction temperature, 70 °C. The inset illustrations are the plots of Ln($Q_{eq}$) against Ln(1/$C_{MBA}$). This figure is available in color online at wileyonlinelibrary.com/journal/pat](image)
was expressed according to Eqn (1) and its logarithmic form (Eqn (2)).

\[ Q_{eq} = kC_{MBA}^{-n} \]  
\[ \ln(Q_{eq}) = \ln k + n\ln(1/C_{MBA}) \]  

\( k \) and \( n \) are constant for an individual superabsorbent. The plots of \( \ln(Q_{eq}) \) against \( \ln(1/C_{MBA}) \) give perfect straight lines with good linear correlation coefficient \((R > 0.9939)\), and the \( k \) and \( n \) values can be calculated through the slope and intercept of the straight line. For CMC-g-PNaA/REC nanocomposite, the effect of crosslinker concentration on equilibrium water absorption follows the relation \( Q_{eq} = 5.08C_{MBA}^{-0.8461} \) in distilled water and \( Q_{eq} = 10.87C_{MBA}^{-0.3063} \) in 0.9 wt% NaCl solution.

Figure 8 showed the dependence of storage modulus (\( G' \)) of the swollen superabsorbents on angular frequency \((\omega = 0.1 \sim 100 \text{ rad/sec}; \gamma = 0.5\% )\) and the concentration of crosslinker MBA. The storage modulus (\( G' \)) of the nanocomposites increased with increase in the angular frequency and concentration of crosslinker MBA. The maximum \( G' \) of the nanocomposite reached 2340 Pa \((\gamma = 0.5\%, \omega = 0.1 \text{ rad/sec})\) and 2980 Pa \((\gamma = 0.5\%, \omega = 100 \text{ rad/sec})\) when the crosslinker concentration is 10.78 mmol/L, and the \( G' \) also reached 632 Pa \((\gamma = 0.5\%, \omega = 1 \text{ rad/sec})\) and 789 Pa \((\gamma = 0.5\%, \omega = 100 \text{ rad/sec})\) even at a low concentration of crosslinker (3.59 mmol/L).

**Effect of REC content on water absorption**

As depicted in Fig. 9, the water absorption of the nanocomposite containing 5 wt% of REC increased by 62% in contrast to the REC-free sample. The greater improvement in the water absorption can be attributed to the following: REC can participate in the polymerization reaction through the active silanol groups on its surface or edges of the platelet, which improve the network structure and surface morphologies of the superabsorbent. Also, the incorporation of rigid REC platelets may prevent entanglement of polymer chain, weaken the hydrogen-bonding interaction among hydrophilic groups, and decrease the physical cross-linking degree. These factors facilitate the improvement in water absorption. However, the addition of excessive amounts of REC (> 5 wt%) into polymeric network induced the reduction in water absorption. This is because the excess of REC platelets may physically fill in the network voids. On the one hand, the amount of hydrophilic groups such as \(-\text{COOH}\) and \(-\text{COO}^-\) in unit volume was reduced and the hydrophilicity of nanocomposite was decreased; on the other hand, the physically filled REC platelets in polymer network plugged up some network voids used for holding water. These factors lead to the shrinkage of water absorption of the nanocomposite. The similar tendency can also be observed in Starch-graft-acrylic acid/Na-MMT. As discussed above, REC may exist in polymer network by chemical bonding and physical filling as shown in Scheme 1.

**Swelling kinetics**

Figure 10 represents the swelling kinetics curves of the superabsorbent nanocomposites with various amounts of REC in distilled water. It can be seen that the swelling rate of the nanocomposites is faster within 1200 sec and then reached a plateau. In this section, the swelling kinetics can be expressed by
Schott’s pseudo second order kinetics model (Eqn (3)).\[33\]

\[
t/Q_t = 1/K_i + (1/Q_\infty) t
\]  

(3)

Qₜ is the water absorption at a given swelling time t (s); Q_∞ (g/g) is the power parameter, denoting the theoretical equilibrium water absorption; Kᵢ is the initial swelling rate constant (g/g•s). As shown in Fig. 10(b), the plots of t/Qₜ versus t exhibited a perfect straight line with a good linear correlation coefficient, which indicates that the swelling kinetics of the nanocomposites follow the pseudo second order model. By fitting experimental data using Eqn (3), the values of Kᵢ and Q_∞ can be calculated through the slope and intercept of the above lines and are listed in Table 1. According to the obtained values of Kᵢ and Q_∞ for each superabsorbent, it can be concluded that the initial swelling rate decreased in the order: CMC-g-PNaA/REC (5 wt%) > CMC-g-PNaA/REC (10 wt%) > CMC-g-PNaA/REC (20 wt%) > CMC-g-PNaA. PNaA. This indicates that the incorporation of moderate amount of REC contributes to improvement in the swelling rate.

**Saline-responsive behaviors**

The osmotic pressure difference between the interior gel network and exterior swelling media is a driving force for the swelling of superabsorbent, and so the phase transition occurs after contact with the electrolyte solution. As shown in Fig. 11, the water absorption remains almost constant at low concentration of saline, but it rapidly decreases after reaching a critical concentration (about 0.5 mmol/L), and the decrease in the tendency follows the order of Na⁺ < Mg²⁺ < Al³⁺. This may be ascribed to

![Scheme 1. Schematic network structure of the superabsorbent nanocomposite.](#)

**Figure 10.** (a) Swelling kinetic curves of the superabsorbents with various contents of REC and (b) the plots of t/Qₜ against t for each superabsorbent. This figure is available in color online at wileyonlinelibrary.com/journal/pat
the screening effects of cations on negative charges of polymer chains. However, the relatively strong screen effects and additional complexing interaction of Mg$^{2+}$ or Al$^{3+}$ cations with the $-\text{COO}^-$/COOH groups make the water absorption decrease faster than monovalent cation. For evaluating the reversibility of saline stimuli-responsive behavior, the swelling–deswelling behavior of the nanocomposite was circularly measured between 0.01 and 100 mmol/L of saline solution. It was observed that the nanocomposite showed better On–Off switching properties in NaCl solution, but this property was decreased in MgCl$_2$ solution and disappeared in AlCl$_3$ solution. For evaluating the effect of multivalent cations on $-\text{COOH}$ and $-\text{COO}^-$ groups, the FTIR spectra of the nanocomposite after swelling in NaCl, MgCl$_2$, and AlCl$_3$ solutions were obtained and are shown in Fig. 12. The characteristic absorption bands of $-\text{COOH}$ and $-\text{COO}^-$ groups show no obvious change after swelling in NaCl solution, indicating no interaction between $-\text{COO}^-$ and Na$^+$. After swelling in MgCl$_2$ solution, the characteristic absorption bands of $-\text{COOH}$ and $-\text{COO}^-$ groups shifted to 1708 and 1562 cm$^{-1}$, respectively, which implied that Mg$^{2+}$ was complexed with $-\text{COO}^-$ groups. Different from the situation in NaCl and MgCl$_2$ solutions, the characteristic absorption band of $-\text{COOH}$ shifted to 1717 cm$^{-1}$ with increased intensity and the absorption of $-\text{COO}^-$ group shifted from 1572 to 1617 cm$^{-1}$ after swelling in AlCl$_3$ solution. The $-\text{COO}^-$ groups are not only complexed by Al$^{3+}$, but also protonated by the acidic AlCl$_3$ solution. In this process, a portion of the $-\text{COO}^-$ groups are transformed into $-\text{COOH}$ groups, which increases the physical crosslinking degree of the hydrophilic network. These lead to the collapse of gel network in AlCl$_3$ solution and the collapsed nanocomposite hydrogel is not recovered. In MgCl$_2$ solution, Mg$^{2+}$ has correspondingly weak complexation with $-\text{COO}^-$ groups, and so the gel network can re-expand to some degree and exhibit weak reversibility.$^{[34]}$ In NaCl solution, the On–Off switching swelling behavior of the nanocomposite is reversible.

### pH-responsive behaviors

Figure 13 shows the variation of the water absorption for CMC-g-PNaA/REC nanocomposite with pH of the external buffer solution (0.1 mol/L). It is evident that the water absorption is lower at pH $< 4$, but sharply increases until a plateau is reached at
pH > 4. As an anionic superabsorbent, the nanocomposite contains numerous hydrophilic –COO¯ and –COOH groups that can interconvert. In acid medium (pH < 4), most of –COO¯ groups transform into –COOH groups. Consequently, the hydrogen bonding interaction among hydrophilic groups and the correlative physical crosslinking degree is increased, and the water absorption is reduced. As pH increases beyond 4, a contrary process occurs. The hydrogen bonding interaction is broken and the electrostatic repulsion among negatively charged polymer chains is increased, and so the polymer network tends to swell more. The evident change of water absorption with altering of the pH of external buffer solution confirmed the excellent pH-responsive characteristic of CMC-g-PNaA/REC nanocomposite. For evaluating the pH reversibility of the nanocomposite, the swelling–deswelling behavior was investigated in 0.1 mol/L buffer solution of phosphate at pH 2 and 7.2 (Fig. 13(b)). The nanocomposite exhibited higher swelling capability at pH 7.2, but the swollen gel rapidly shrinks at pH 2 due to the protonation of –COO¯ groups. The intriguing On–Off switching behavior was observed. After five On–Off cycles, the nanocomposite still exhibited responsivity. This suggested pH reversibility and render the nanocomposite suitable candidates for controlled drug delivery systems.

**Hydrophilic organic solvent-responsive behaviors**

Besides external saline and pH, the nanocomposite showed excellent phase transition and responsivity to hydrophilic organic solvents (Fig. 14(a)). It can be noticed that the water absorption is almost constant at low concentration of hydrophilic organic solvent, but sharply decreases after a critical concentration (40 v/v% for methanol and ethanol, 30 v/v% for acetone), and the tendency in acetone/water solution is more obvious than in methanol or ethanol. This behavior can be attributed to the change in dielectric constant of solution due to the addition of organic solvents.[35] For evaluating the reversibility of the gel phase transition, the swelling–deswelling cycles were made between 5 v/v% and 90 v/v% hydrophilic organic solvents/water mixtures (Fig. 14(b)). Interestingly, the nanocomposite showed excellent On–Off switching behavior and better reversibility.

**CONCLUSIONS**

As a part of the endeavor to minimize the consumption of petroleum resource and the environmental impact resulting from...
industrial polymers and to extend the application of superabsorbents, the novel superabsorbent nanocomposites were prepared by radical solution polymerization using CMC as matrix and REC as an inorganic component. FTIR, XRD, TEM, SEM, and TGA analyses indicated that (i) the PNaA chains had been grafted onto CMC main chains and REC participated in the polymerization reaction through active –OH groups; (ii) REC has been exfoliated after polymerization and equably embedded within the CMC-g-PNaA matrix by the nanoscale platelets with no flocculation; and (iii) the thermal stability of the superabsorbent was enhanced due to the introduction of REC. The incorporation of REC improved the water absorption and swelling rate of the superabsorbent. The superabsorbent nanocomposite exhibited excellent saline-, pH-, and hydrophilic organic solvent-responsive characteristics and better reversibility can also be observed for each responsivity cycle. Besides the water absorption properties, the additional responsivity of the nanocomposite contributes to the extend the application of superabsorbent in other fields such as drug delivery carrier. Thus, superabsorbent nanocomposites based on renewable and biodegradable CMC and abundant REC showed enhanced swelling capability, swelling rate and excellent saline-, pH, and organic solvent-responsivity, which can be used as potential water-manageable materials for agriculture or suitable candidate for the controlled release carrier of drugs.

REFERENCES