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# Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel

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ABSTRACT

Superabsorbents were synthesized by graft copolymerization of acrylic acid (AA)/acrylamide (AM)/2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) onto sodium carboxymethyl cellulose (CMC) and montmorillonite (MMT) by using potassium persulfate (KPS) as a free radical initiator, in the presence of N,N′-methylenebisacrylamide (MBA) as a crosslinking agent. The structure and morphologies of the superabsorbents were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). Superabsorbent comprised a porous crosslink structure of MMT and CMC with side chains that carry carboxylate, carboxamide and sulfate. The swelling behaviors of the superabsorbent were dependant on the pH of external solutions, particle size and the concentration of the salt solution. The effect of four cationic salt solutions on the swelling had the following order: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$.

## 1. Introduction

Superabsorbents are three-dimensional networks of hydrophilic polymers connected by chemical and/or physical crosslinking (Kuang, Yuk, & Huh, 2010). These networks are composed of homopolymers or copolymers and can absorb and hold a significant amount of water. Superabsorbents can be prepared with different functional groups such as carboxylic acid, amine, hydroxyl, amide and sulfonic acid groups (Zheng, Hua, & Wang, 2010). These groups attached onto the polymeric networks can be tailored easily for a specific application, such as agriculture (Puoci, Iemma, & Spizzirri, 2008), hygienic products (Kosemund et al., 2009), wastewater treatment (Kasgöz & Durmus, 2008) and drug release (Wang, Zhang, & Wang, 2009), etc. However, most of superabsorbents used as disposable particles are based on fully petroleum-based polymers with serious environment impact.

Superabsorbents prepared with natural material, such as cellulose (Chang, Duan, Cai, & Zhang, 2010), starch (Pourjavadi, Jahromi, Seidi, & Salimi, 2010) and chitosan (Zhang, Wang, & Wang, 2007), because of their abundant resources, low production-cost and biodegradability, have attracted great attention. Cellulose is the most abundant one. However, the strong intermolecular and intramolecular hydrogen bonds between the hydroxyl groups along the chain backbone not only limit the water solubility but also led to the poor reactivity of cellulose. Carboxymethyl cellulose (CMC) is a representative cellulose derivative, which is water soluble cellulose ether, manufactured by reacting sodium monochloroacetate with cellulose in alkaline medium.

Nanocomposites exhibit improved or even novel properties when compared to micro- and macro-composites. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of the virgin polymer Montmorillonite (MMT) is a layered aluminum silicate with exchangeable cations and reactive –OH groups on the surface. It is one of the most widely used layered silicates because its lamellar elements display high in-plane strength, stiffness, and high aspect ratio (Mansoori, Atghia, Zamanloo, Imanzadeh, & Sirousazar, 2010).

Our previous work, the acrylic polymer/MMT nanocomposite was prepared via in situ polymerization (Bao, Ma, & Wang, 2009) and polymer solution-intercalation (Ma, Gao, Lv, Chu, & Dai, 2007), respectively. In this paper, we report the preparation of a novel multi-component superabsorbent by graft copolymerization of vinyl monomers along the chains of CMC in the presence of MMT. Vinyl monomers are acrylic acid (abbreviated as AA), acrylamide (abbreviated as AM), and 2-acrylamido-2-methyl-propanoesulfonic acid (abbreviated as AMPS). These monomers were chosen due to the following reasons: AA and AM is anionic monomer and nonionic monomer, respectively. They are rather cheap, common monomer of preparing superabsorbent. AMPS is hydrophilic monomer containing nonionic and anionic groups. Increasing number of ionic groups in the superabsorbent is known to increase their swelling capacity. The nonionic groups can

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improve their salt tolerance. CMC shows environmental friendly characteristics. The incorporation of MMT can not only reduce production cost, but also improve the properties (such as swelling ability, gel strength, mechanical and thermal stability) of superabsorbents.

## 2. Experimental

### 2.1. Materials

Acrylic acid (AA), acrylamide (AM), sodium carboxymethyl cellulose (CMC) and potassium persulfate (KPS) were purchased from Tianjin Chemicals. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) supplied by Allplus Chemicals Limited, Nanjing. Montmorillonite (MMT) was provided by Qing-he Chemical Factory, Zhangjiakou. N,N′-Methylenebisacrylamide (MBA) was bought from Aoran Chemicals, Tianjin.

### 2.2. Procedure for graft copolymerization

CMC solution has been prepared by slow addition of weighted amount of CMC powder to distilled water in a 250-mL three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer. Then Na-MMT was added under continuous stirring to form a uniform sticky solution. The solution was heated to 60 °C. The calculated amount of initiator KPS was added and kept at 60 °C for 10 min to generate radicals. After cooling the reactants to 40 °C, the mixture of AA, AM, AMPS and MBA was added to the flask. The pH was adjusted by NaOH solution. The temperature was risen to 70 °C and maintained for 2 h to complete reaction. The obtained products have been precipitated by pouring it into the water/methanol mixture (ratio 1:5). The precipitate of graft copolymer has been separated, dried and weighed.

### 2.3. Method of characterization

#### 2.3.1. IR spectroscopy

The IR spectra of sodium carboxymethyl cellulose and grafted samples have been recorded with EQUINX55 in the range 500–4000 $cm^{-1}$ to provide the proof of the grafting.

#### 2.3.2. Thermogravimetric analysis

The thermograms have been recorded on NETZSCH-STA 449 F1 Jupiter thermal analyzer at from 0 to 1000 °C temperature range and with a heating rate of 20 °C/min in an atmosphere of nitrogen.

#### 2.3.3. Surface morphology of the superabsorbent hydrogel

The surface morphology of the copolymers was investigated using the scanning electron microscopy (SEM, JEOL, model JSM-6400, Japan).

### 2.4. Study of properties

#### 2.4.1. Swelling

The pre-weighted dry superabsorbent was immersed in excessive distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen superabsorbent was filtered using a 100-mesh sieve and drained for 20 min until no free water remained. After weighing the swollen superabsorbent, the equilibrium water absorption can be calculated by using the following equation.

$$Q_{eq} = \frac{w_2 - w_1}{w_1} \quad (1)$$

where $Q_{\mathrm{eq}}$ is the equilibrium water absorption defined as grams of water per gram of sample; $w_1$ and $w_2$ are the mass of sample before and after swelling, respectively.

#### 2.4.2. Water retention

The pre-weighted swollen gels ($w_2$) equilibrated in distilled water were taken at room temperature for 24 h. Then the mass of hydrogels were recorded and marked as $w_4$. The percentage water retention is calculated as follows:

$$\text{water retention} \quad (\%) = \frac{w_4}{w_3} \times 100 \quad (2)$$

#### 2.4.3. Swelling at various pHs

Individual solutions with acidic and basic pHs were prepared by diluting of NaOH (pH 13.0) or HCl (pH 1.0) solutions to achieve $pH \geq 6.0$ and $pH \leq 6.0$, respectively. The pH values were precisely checked by a pH meter. Then, 0.1 g of the dried hydrogel was used for the steady state swelling measurements according to Eq. (1).

#### 2.4.4. Swelling in salt solutions

Water absorbent capacity of superabsorbent hydrogel was determined in various saline solutions (NaCl, KCl, $CaCl_2$ and $MgCl_2$) with different concentration according to the above method described in Section 2.4.1.

#### 2.4.5. Effect of particle size on swelling

Water absorbent and water retention of superabsorbent hydrogels with different particle sizes were determined according to the above methods described in Sections 2.4.1 and 2.4.2.

## 3. Results and discussion

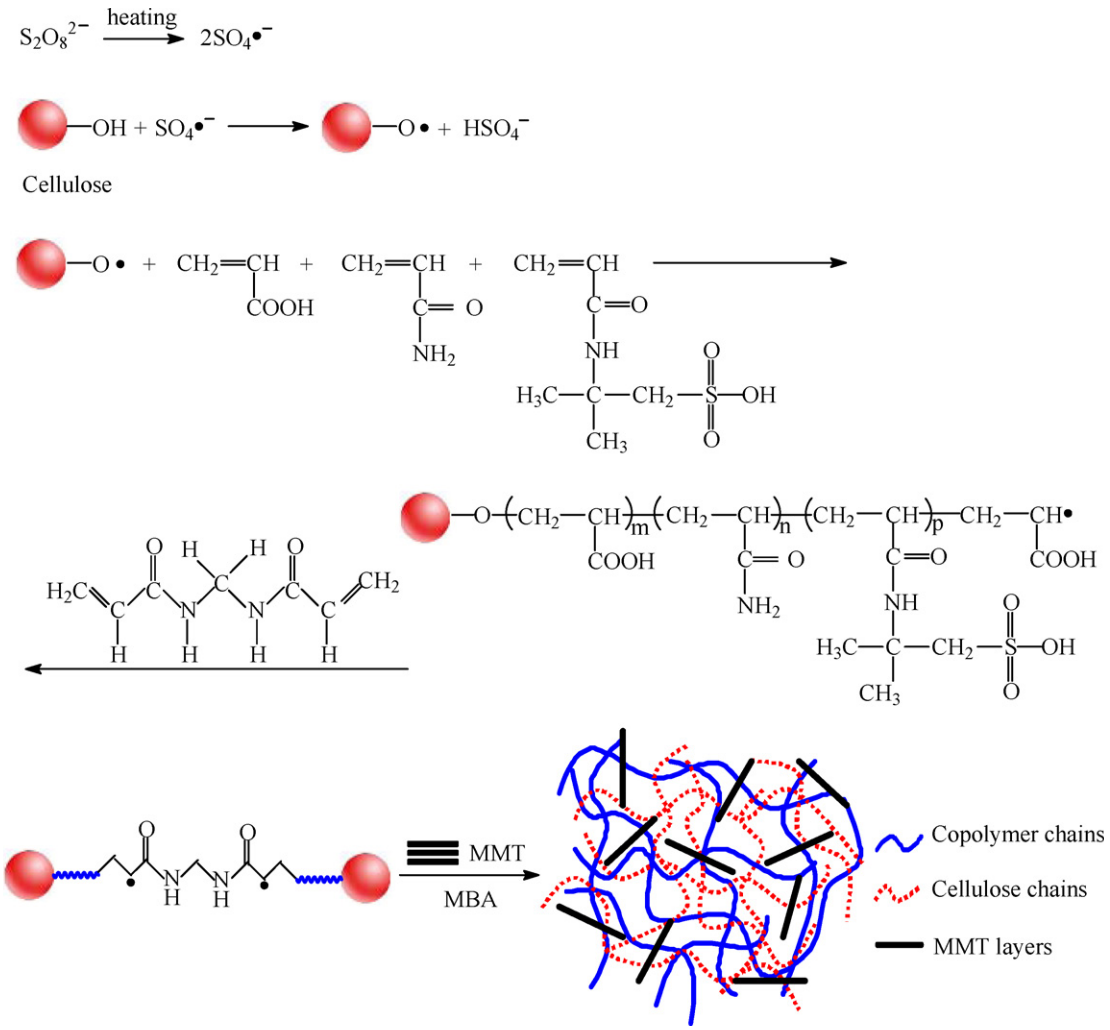
### 3.1. Mechanism of hydrogel formation

The superabsorbent composite was prepared by graft copolymerization of acrylic acid, acrylamide and 2-acrylamido-2-methyl-1-propanesulfonic acid onto sodium carboxymethyl cellulose in the presence of crosslinking agent and powdery montmorillonite. Potassium persulfate was used as a free radical initiator. The water absorption of the superabsorbent composite was 680.2 g/g, and increased by 107% compared with its counterpart polymer (328.2 g/g). The proposed mechanism for the grafting and chemically crosslinking reactions are outlined in Scheme 1.

Initially, the persulfate initiator is decomposed under heating to generate sulfate anion-radicals. The radicals extract hydrogen from the hydroxyl group of the sodium carboxymethyl cellulose to form alkoxy radicals on the substrate. The monomer molecules, which are in close vicinity of the reaction sites, become acceptor of carboxymethyl cellulose radicals resulting in chain initiation and thereafter themselves become free radical donor to neighboring molecules. In this way grafted chain grows (Pourjavadi, Barzegar, & Zeidabadi, 2007; Pourjavadi, Ayyari, & Amini-Fazl, 2008; Wang & Wang, 2010). Since a crosslinking agent, e.g. MBA, is presented in the system, the end vinyl groups of crosslinker MBA may react synchronously with polymer chains during the chain propagation. The copolymer is comprised of a crosslinked structure. The montmorillonite in the polymerization reaction can be considered as acting in one or both of two ways: (a) the MMT particles act as a crosslinking agent. (b) MMT particles prevent the polymer chains from growing by a chain transfer mechanism (Uthirakumar, Nahm, Hahn, & Lee, 2004).

### 3.2. FT-IR spectrum analysis

In the FTIR spectrum (see Fig. 1a) of MMT the broad band centered near 3400 $cm^{-1}$ is due to the –OH stretching mode of the interlayer water. The overlaid absorption peak in the region of 1640 $cm^{-1}$ is assigned to the –OH bending mode of adsorbed water. The characteristic peak at 1115 $cm^{-1}$ is due to the Si–O–Si stretching and out of plane Si–O–Si stretching mode for montmorillonite. The band at 1035 $cm^{-1}$ is assigned to the Si–O–Si stretching



**Scheme 1.** Proposed reaction mechanism for synthesis of cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel.

(inplane) vibration for layered silicates. The band in the region of 796 cm$^{-1}$ is due to the Si–O–Al stretching mode for montmorillonite. The FTIR peaks at 522 cm$^{-1}$ and 468 cm$^{-1}$ are assigned to the Si–O–Al and Si–O–Si bending vibration, respectively (Patel, Somani, Bajaj, & Jasra, 2007).

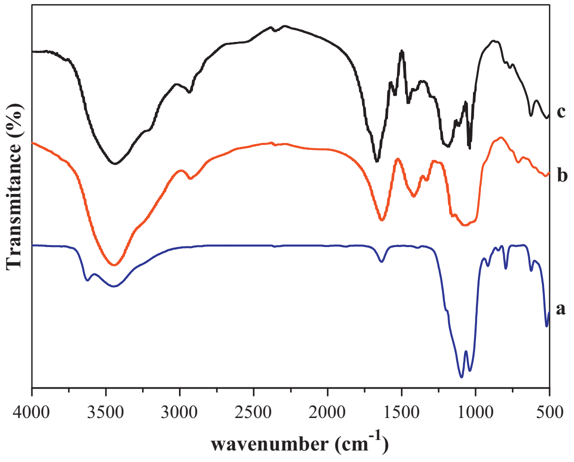


**Fig. 1.** FTIR spectra of (a) MMT, (b) CMC and (c) superabsorbent hydrogel.

In the FTIR spectrum (see Fig. 1b) of CMC a strong peak at 3443.8 cm$^{-1}$ is observed due to OH stretching vibration. The band in the range of 1000–1166 cm$^{-1}$ is assigned to the ether bonds. The absorption peak at 1635 cm$^{-1}$ is related to the carboxylate. The peak at 2926.8 cm$^{-1}$ is due to methylene.

On comparing the FTIR spectra of MMT, CMC and cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel, it has been observed that the spectrum of cellulose-g-P(AA-co-AM-co-AMPS)/MMT shows variations in intensity and shifting of peak from 3455.9 to 3437.8 cm$^{-1}$ appear due to OH stretching vibration of CMC. The characteristic absorption bands of CMC at 1000–1166.6 cm$^{-1}$ are obviously weakened after reaction. These indicate the participation of hydroxyl of CMC in chemical reaction. The –OH stretching of MMT in the range of 3400–3700 cm$^{-1}$ disappeared and the intensities of peaks due to Si–O and Al–O of MMT are reduced as shown in Fig. 1c. It has been reported by Zhang et al. that acrylamide could graft onto clays and form the polyacrylamide/clay superabsorbent composite (Zhang & Wang, 2007). –OH of MMT could react with acrylic monomer and MMT particles chemically bond with the polymer chains to form the CMC/polymer/MMT network. The very intense characteristic band at 1548 cm$^{-1}$ is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by peaks at 1457 and 1410 cm$^{-1}$ which is related to the symmetric stretching mode of the carboxylate anion. The absorption peak at 1670 cm$^{-1}$ is attributed to carboxamide. The characteristic absorption peak of AMPS units is shown at 1040 cm$^{-1}$

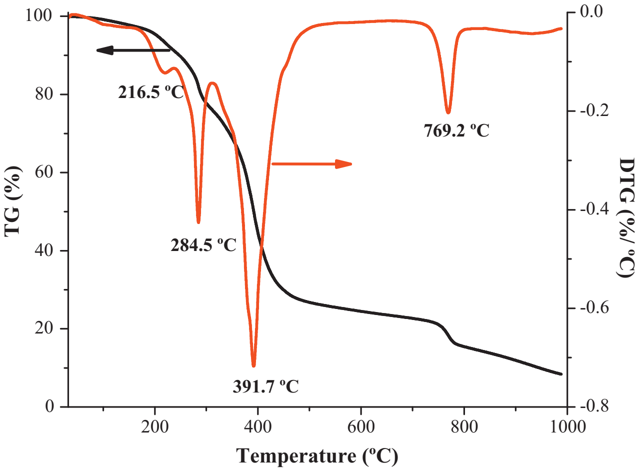


**Fig. 2.** Thermogravimetric analysis of superabsorbent hydrogel.

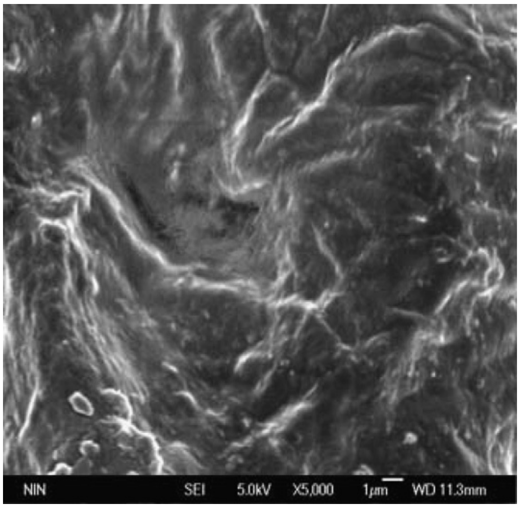


**Fig. 3.** Scanning electron microscopy picture of superabsorbent hydrogel.

due to S=O group. Therefore, the superabsorbent hydrogel product comprises a crosslink structure of MMT and CMC with side chains that carry carboxylate, carboxamide and sulfate.

### 3.3. *Thermogravimetric analysis*

Fig. 2 is the thermogravimetric curve of superabsorbent hydrogel. The degradation of cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel has four steps. At the initial stage, the minor weight loss about 6 wt% from 168 to 236 °C is ascribed to the dehydration of saccharide rings and the breaking of C–O–C bonds in the chain of CMC (Yang, Li, He, Ren, & Wang, 2009). The weight loss about 15 wt% within the temperature of 236–311 °C might be due to elimination of $CO_2$ molecule from the polymeric backbone (Sand, Yadav, & Behari, 2010). Temperature at which maximum degradation occur, i.e. $T_{max}$ has been found at 391.7 °C. The weight loss is about 50 wt%. This $T_{max}$ can be attributed to the elimination of the water molecule from the two neighboring carboxylic groups of the polymer chains due to the formation of anhydride, main-chain scission and the destruction of crosslinked network structure (Huang, Lu, & Xiao, 2007). The last stage at 769.2 °C might be due to elimination of $SO_2$ molecule from pendent chain attached to the polymeric backbone.

### 3.4. *Morphological analysis*

Hydrogels water absorbency and its retention rate depend on hydrogel porosity and mean pore size. Hence, one of the most important properties which should be considered is hydrogel microstructure morphologies. This porous microstructure brings about an increased surface area and capillary effect. SEM micrographs of cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel was observed and shown in Fig. 3. Obviously, the surface morphology of superabsorbent hydrogel has an undulant and coarse surface. This surface is convenient for the penetration of water into the polymeric network, and then may be of benefit to water absorbency of corresponding superabsorbent (Liang, Yuan, Xi, & Zhou, 2009).

### 3.5. *Equilibrium swelling at various pH solutions*

The cellulose-g-P(AA-co-AM-co-AMPS)/MMT contains carboxylate, carboxamide and sulfonate groups which are the majority of anionic-type superabsorbent. Ionic superabsorbent hydrogels exhibit swelling changes for a wide range of pHs. To investigate the sensitivity of the superabsorbent hydrogel to pH, firstly the equilibrium swelling (ultimate absorbency) of the hydrogel was studied at various pHs ranged from 2.0 to 12.0 (Fig. 4a). Because absorbency of superabsorbent is strongly affected by ionic strength, no additional ions (through buffer solution) were added to medium for setting pH (Chen, Liu, Tang, & Tan, 2010). Therefore, NaOH (pH 12.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

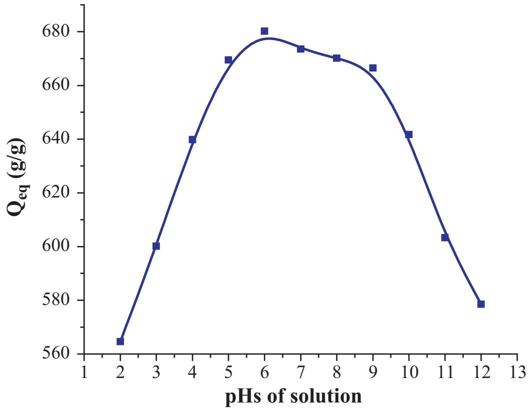
Under acidic pHs (pH < 5), most of the carboxylate and sulfonate anions are protonated. On the one hand, the hydrogen-bonding interaction among carboxylate and sulfonate groups was strengthened and the additional physical crosslinking was generated; on the other hand, the electrostatic repulsion among carboxylate and sulfonate group was restricted. So the network tends to shrink and consequently swelling values are decreased. At higher pHs (9 > pH > 5), some of the carboxylate and sulfonate groups are ionized. Consequently, the hydrogen-bonding interaction was broken and the electrostatic repulsion between $-COO^-$ and $-SO_3{}^-$ groups increased. So the polymer network tends to swell more. The reason for the swelling loss in the highly basic solutions (pH > 9) is due to the "charge screening effect" of excess $Na^+$ in the swelling media, which shields the carboxylate and sulfonate anions and prevents effective anion–anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems (Lanthong, Nuisin, & Kiatkamjornwong, 2006). The structure models of superabsorbent hydrogel at various pH solutions are seen in Fig. 4b.

### 3.6. *Effect of salt solution on water absorbency*

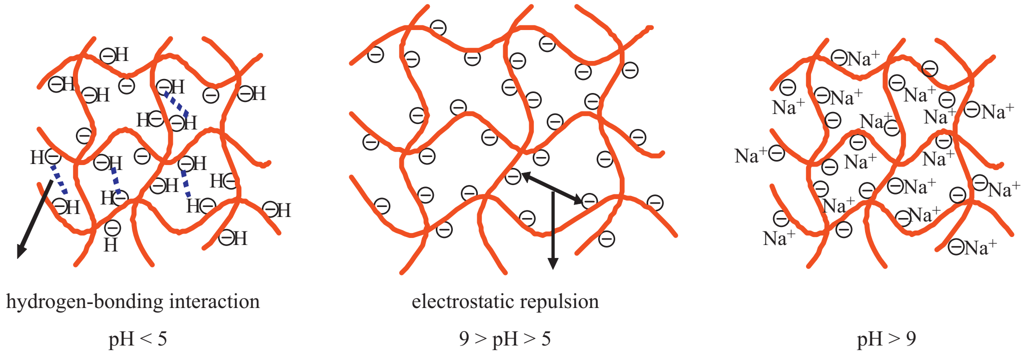
The characteristics of external solution such as charge valencies and salt concentration greatly influence the swelling behaviour of the superabsorbent polymers.

The swelling of the absorbents in saline solutions was appreciably decreased comparing to the values measured in deionized water. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels (Zhao, Su, Fang, & Tan, 2005), is often attributed to a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, led to a decreased osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution.

The effect of various cations on swelling can be concluded from Fig. 5 and Table 1. As shown, the absorbency of the hydrogel in the studied salt solutions from high to low is $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The salt type and concentration can be expressed in the terms of



a Water absorbency



b Structure models

**Fig. 4.** Water absorbency and structure models of superabsorbent hydrogel at various pH solutions.

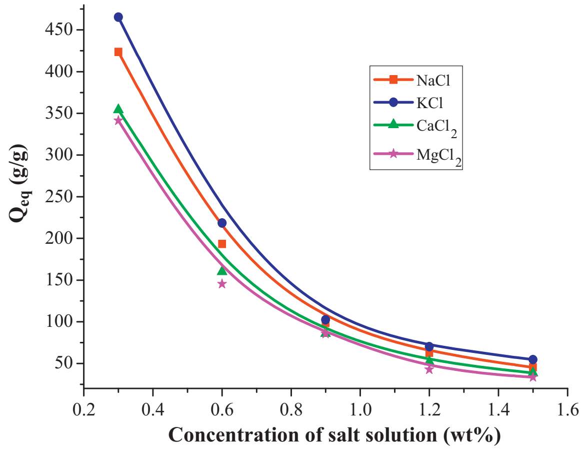


**Fig. 5.** Water absorbency of superabsorbent hydrogel in NaCl, KCl, $CaCl_2$ and $MgCl_2$ aqueous solutions.

**Table 1**
Effect of salt solutions on water absorption.

| Solution | Ionic strength[a] (mol ion/dm$^3$) | Water absorption (g/g) |
|---|---|---|
| 0.6 wt% KCl solution | 0.0805 | 218.3 |
| 0.6 wt% NaCl solution | 0.1026 | 193.4 |
| 0.6 wt% $CaCl_2$ solution | 0.1622 | 160.1 |
| 0.6 wt% $MgCl_2$ solution | 0.1895 | 145.3 |

[a] $I = 0.5\sum(C_iZ_i^2)$, where $I$, $C_i$, and $Z_i$ are the ionic strength, the ionic concentration, and charge on each individual ion, respectively.

ionic strength. From the Table 1, it can be seen the ionic strength of isotonic salt solution is $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$. According to the literature (Lanthong et al., 2006), the effect of the ionic strength on the water absorbency can be expressed by Flory's equation.

$$Q^{5/3} \approx \frac{(i/2V_uS^{1/2})^2 + (1/2 - x_1)/V_1}{V_E/V_0} \tag{3}$$

where $Q$ is the degree of swelling, $i/V_u$ is the charge density of polymer, $S$ is the ionic strength of solution, $(1/2 - x_1)/V_1$ is the polymer–solvent affinity, $V_E/V_0$ is the crosslinking density.

According to Eq. (2), when the ionic strength of saline solution increases, the water absorbency decreases. Therefore, the experimental results abide by Flory's equation. The absorbency of the hydrogel in salt solutions is monovalent > divalent cations. It may be additionally caused by complexing ability arising from the coordination of the bivalent cations with superabsorbent hydrogel groups (Zheng, Li, Zhang, & Wang, 2007). This ionic crosslinking mainly occurs at surface of particles.

The water absorbency decreased as the concentration of various external saline solutions increased. This phenomenon is mainly caused by the cations in various salt solutions. The osmotic pressure between polymeric network and external saline solution decreases with the increase of saline solution concentration (Murali Mohan, Keshava Murthy, & Mohana Raju, 2005). The penetration of counterions ($Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$) into polymeric network makes the screening effect of them on anionic group ($-COO^-$ and $-SO_3{}^-$) more evident, which also decreases water absorbency of these superabsorbents composites. In addition, the complexing ability of carboxylate groups on superabsorbent composite network can induce the formation of intramolecular and intermolecular com-

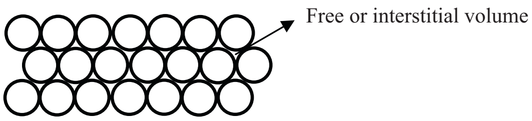


**Fig. 6.** A schematic diagram, showing interstitial volume between water-swollen particles.

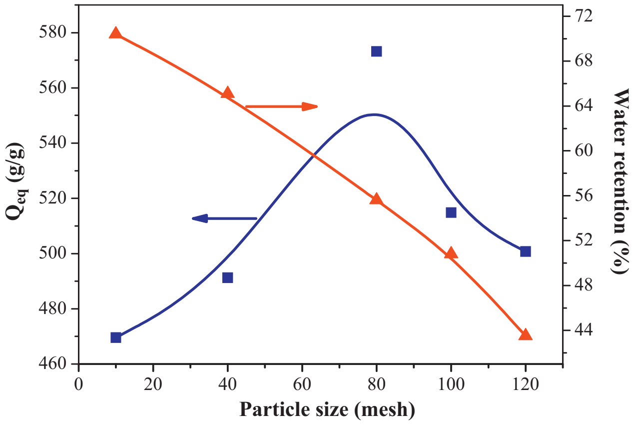


**Fig. 7.** water absorption and water retention for superabsorbent hydrogel with different particle size.

plex with divalent (such as $Ca^{2+}$ and $Mg^{2+}$). As a result, water absorbency decreases with increasing concentration of external saline solutions.

### 3.7. *Effect of particle size on water absorption and water retention*

Absorption of water for superabsorbent hydrogel is more rapid as the particle size is smaller. The reason would be expected from the increase in surface area with decreasing particle size (Omidiana, Hashemi, Sammes, & Meldrum, 1999). If the particles laid side by side, some space could be left between the swollen particles, whether the particles are coarse or fine. This space can be called free or interstitial volume which serves to accommodate additional water by a typical capillary action (see Fig. 6). The interstitial volume per unit mass of absorbent is bigger, the ultimate degree of absorption is higher.

The water absorption and water retention for cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel with different particle size are shown in Fig. 7. The water absorbency for superabsorbent hydrogel with particle sizes from 10 mesh to 80 mesh is increased under the same times. This may be because the rate of absorption for the absorbent with bigger particle size is slower than that for the absorbent with smaller particle size, the water absorption for the absorbent with bigger particle size may be unsaturated. With particle size continue decreasing, the interstitial volume is smaller. But the water absorption for all products is saturated. So the water absorbency for superabsorbent hydrogel with particle sizes from 80 mesh to 120 mesh is decreased. The water retention decreased as the particle size decreased. This phenomenon is mainly caused by higher surface area or contact area of the fine particles with water.

## 4. Conclusions

Cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogels were synthesized by using KPS as a free radical initiator, in the presence of MBA as a crosslinking agent. The results of FTIR spectra showed superabsorbent hydrogel product comprises a crosslink structure of MMT and CMC with side chains that carry carboxylate, carboxamide and sulfate. The TGA technique was employed to successfully characterize the weight loss and grafting information of superabsorbent. The surface morphology of superabsorbent hydrogel has an undulant and coarse surface. It is a typical porous microstructure. Water absorbency for this hydrogel showed buffer action in a pH value from 5 to 9 resulting from the –COOH and –$SO_3$H groups on the polymer chains. The impact of salts on water absorbency of cellulose-g-PAA-co-PAM-co-PAMPS/MMT superabsorbent hydrogel is relative to the concentration of salt solution and valence of cations. The swelling-loss behavior of the hydrogel occurred as the concentration of the external salt solution increased. The effect of four cationic salt solutions on the swelling has the following order: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The water absorbency for hydrogel is increased and then decreased, but the water retention is decreased as the particle size finer.

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