

# Synthesis and Characterization of Acrylamide-Based Aluminum Flocculant for Turbidity Reduction in Wastewater

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**ABSTRACT:** Polymeric flocculants of aluminum hydroxide-poly[acrylamide-co-(acrylic acid)], AHAMAA, were prepared by solution polymerization using aluminum hydroxide as a coagulant in the presence of acrylamide (AM) and acrylic acid (AA) as a comonomer pair with *N,N'*-methylenebisacrylamide as a crosslinking agent. The crosslinking was initiated by ammonium persulfate with *N,N,N',N'*-tetramethylethylenediamine as an initiator. The water absorbency of crosslinked poly[AM-co-AA] was always higher than that of AHAMAA and was found to be correlated to the storage modulus of the polymers, which was higher for AHAMAA than that of crosslinked

poly[AM-co-AA]. The residual aluminum concentration of AHAMAA (0.09–0.2 mg L<sup>-1</sup>) indicated the stability of the polymer flocculant which was in good agreement with the observed  $\tan \delta$  and the higher  $G''$  and  $G'$  values. Both the crosslinked poly[AM-co-AA] and AHAMAA satisfactorily reduced the turbidity of kaolin suspensions, but the latter gave a better reduction performance. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2564–2575, 2009

**Key words:** hydrogel; clay; crosslinking; swelling; viscoelastic properties

## INTRODUCTION

Superabsorbent polymers (SAPs) are the crosslinked networks of flexible polymer chains that have the ability to absorb, hold and release large amounts of water. With this excellent property, they are used in many fields of application such as infant diapers, agriculture,<sup>1,2</sup> wastewater treatment,<sup>3–6</sup> and so forth.

Polyacrylamide is one of the SAP generally used in water treatment.<sup>4</sup> Cationic polyacrylamide with a very high molecular weight and low charge density achieved 91% water recovery and 99% total suspended solids removal after a 30 min setting period, whilst anionic polyacrylamide can be used as a coagulant aid to improve the setting velocity.<sup>5</sup>

In water and wastewater treatment processes, alum (aluminum sulfate) has been used generally as

an inorganic coagulant because of its low cost and high efficiency. Alum can remove a broad range of impurities from water, including dissolved organic matter with two distinct mechanisms: charge neutralization of the positive charge of hydrolysis products of alum, and the negative charge of colloidal particles in the water and the incorporation of impurities in an amorphous hydroxide precipitate. However, limitations are that the precipitation process is sensitive to changes in the pH<sup>7</sup> and that water treated with aluminum sulfate or aluminum complexes may induce medical ailments in those people with retarded renal functions such as osteomalacia, encephalopathy, microcytic anemia, and perhaps Alzheimer's disease, if there is a free aluminum ion or residual alum/aluminum complex in the water.<sup>8–10</sup> The types of coagulant, such as alum and poly(aluminum chloride), the pH of the water and the dose of the coagulant, all affect the amount of the residual alum/aluminum complex.<sup>11,12</sup> One method for reducing the amount of aluminum residue in treated water is to combine a coagulant and a polymeric flocculant with the wastewater treatment. Thus, polymeric flocculants have become particularly attractive. Polymeric flocculants can be

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TABLE I  
The Synthesis Parameters for the Crosslinked Poly[AM-co-AA] and AHAMAA

Reactants	Contents	
	poly[AM-co-(AA)]	AHAMAA
Acrylamide : acrylic acid ( $\times 10^{-3}$ mol)	100 : 0, 98 : 2, 96 : 4, 94 : 6, 92 : 8, 90 : 10	100 : 0, 98 : 2, 96 : 4, 94 : 6, 92 : 8, 90 : 10
N-MBA ( $\times 10^{-4}$ mol)	1.2, 2.3, 4.6, 9.2	1.2, 2.3, 4.6, 9.2
APS ( $\times 10^{-4}$ mol)	0.8, 1.6, 3.1, 6.2	0.8, 1.6, 3.1, 6.2
TEMED ( $\times 10^{-4}$ mol)	1.5, 3.0, 6.0, 12.0, 24.0, 36.0, 96.0, 145	1.5, 3.0, 6.0, 12.0, 24.0, 36.0, 96.0, 145
Synthesized Al(OH) <sub>3</sub> suspension (mL)	–	42.5

nonionic, anionic, cationic, or amphoteric polymers with an ionized form as a soluble polyelectrolyte. As mentioned above, polyacrylamide, a polymeric flocculant, has been used for increasing the size of flocs and to accelerate flocculation of flocs by a bridging mechanism.<sup>7</sup> The flocculation efficiency of the synthesized hybrid aluminum hydroxide-polyacrylamide (HAPAM) was found to be much better than that of the commercial PAM or the mixed PAM/AlCl<sub>3</sub> blend used for a kaolin suspension because the flocs were denser and larger in the presence of HAPAM.<sup>13</sup>

In this research, a novel polymeric flocculant of hybrid aluminum hydroxide-poly[acrylamide-co-(acrylic acid)], AHAMAA, was synthesized by suspension polymerization. Evaluation of the water absorbency and the level of residual acrylamide monomer and free aluminum in soaking water for AHAMAA and poly[acrylamide-co-(acrylic acid)] were performed. The efficiency of both polymers on the turbidity reduction of a kaolin suspension was investigated.

## EXPERIMENTAL

### Materials

Acrylamide (AM) monomer was kindly supplied by the Siam Chemical Industry Co. Ltd., Bangkok, Thailand. Acrylic acid (AA), *N*, *N*'-Methylenebisacrylamide (N-MBA), and *N*, *N*, *N*', *N*'-tetramethylethylenediamine (TEMED) were purchased from Fluka (Buchs, Switzerland). Ammonium persulfate (APS) was purchased from Merck (Hohenbrunn, Germany). Sodium carbonate and aluminum sulfate were supplied from BDH (analytical grade, Poole, UK). Kaolin (BDH, Poole, UK), with a Zeta potential of  $-50$  mV measured by a Zetasizer (Nano ZS, Malvern, UK), was used as received. Deionized water was processed from Elga Deionizer (Model LA611, Buxinghamshire, UK).

### Synthesis of aluminum hydroxide

A suspension of aluminum hydroxide (Al(OH)<sub>3</sub>) was prepared by slowly dropping 22.5 mL of 0.2 M sodium carbonate into 20 mL of 0.1 M aluminum

sulfate at a constant rate while stirring by a magnetic stirrer at room temperature. The Al(OH)<sub>3</sub> suspension obtained was then used as it was.

### Synthesis of crosslinked poly[acrylamide-co-(acrylic acid)]

Monomers of AM and AA were added into a 500-mL four-necked round-bottomed reaction flask equipped with a mechanical stirrer, a condenser and an inlet tube for feeding nitrogen gas. Immersed in a water bath at a controlled temperature of  $45 \pm 2^\circ\text{C}$ , the mixture was stirred with a small-bladed propeller at 250 rpm in a nitrogen gas atmosphere, fed constantly through the gas inlet tube at 10 mL/min, for 30 min. The crosslinking agent (N-MBA), initiator (APS) and co-initiator (TEMED) were sequentially added in that order (Table I for amounts) and stirred for another 30 min. The crosslinked poly[acrylamide-co-(acrylic acid)] or poly[AM-co-AA] was filtered, dehydrated with acetone, cut into pieces of approximately  $1 \times 1$  cm square and dried in a vacuum oven at  $50^\circ\text{C}$  for 24 h to a constant weight. The dried pieces were then milled and sieved through a 50–100 mesh screen.

### Synthesis of polymeric flocculants of aluminum hydroxide-crosslinked poly[acrylamide-co-(acrylic acid)]

Polymeric flocculants of aluminum hydroxide-crosslinked poly[acrylamide-co-(acrylic acid)], or AHAMAA, were synthesized by polymerization of acrylamide and acrylic acid with the Al(OH)<sub>3</sub> suspension in a 500-mL reaction flask as above and using the same procedure used for preparing the crosslinked poly[AM-co-AA]. The synthesis conditions of crosslinked poly[AM-co-AA] and AHAMAA are summarized in Table I.

### Characterization

IR spectra of the synthesized products were recorded using KBr pellets by Fourier Transform Infrared Spectroscopy (FTIR, model PerkinElmer). The forms of aluminum ion in Al(OH)<sub>3</sub> and

AHAMAA were examined by  $^{27}\text{Al}$  nuclear magnetic resonance ( $^{27}\text{Al}$ -NMR, model Unity Inova-500, Switzerland).

#### Determination of the aluminum concentration in AHAMAA

Aliquots of AHAMAA weighing 0.04 g were each suspended in a mixture of 10 mL concentrated HCl and 10 mL HF and then heated on a hot plate until dry. This procedure was repeated three times. A mixture of 6 M  $\text{HNO}_3$  and 6 M HCl was then added and heated until dry, cooled, and then transferred to a 50 mL volumetric flask and made to the mark with deionized water. The aluminum ion concentration in the suspension was determined by an ICP-AES technique (PerkinElmer model PLASMA-1000).

#### Determination of the leaking aluminum ion concentration

The free aluminum ion of the AHAMAA gel was determined by adding portions of AHAMAA, at 0.04 g per beaker, into 1000 mL of deionized water. The beakers were covered with lids and kept at room temperature for one of 15, 30, 45, or 60 days, respectively, and then the swollen gel was filtered through a 100-mesh aluminum screen sieve. The filtrate was collected and the aluminum ion concentration, defined as the leachate, was determined by the ICP-AES technique.

#### Determination of residual acrylamide or *N*, *N'*-methylenebis acrylamide monomers

The crosslinked poly[AM-*co*-AA] was stirred in 300 mL deionized water and filtered. The filtrate was used to determine the residual acrylamide monomer concentrations by a bromination reaction of acrylamide monomer to form 2,3-dibromopropionamide as described,<sup>14</sup> the concentration of which was then determined by gas chromatography (model GC-7AG, Shimadzu, Kyoto, Japan).

#### Surface morphology

The surface morphologies of poly[AM-*co*-AA] and AHAMAA, and the element distribution of AHAMAA, were investigated using a scanning electron microscope (SEM, model JSM-6400, Japan) without cross-section. The samples were scanned at an accelerating voltage of 15 kV. Detailed morphology of the surface structures and mapping densities of the carbon and the Al ions were studied by SEM/Energy Dispersive X-ray Spectroscopy (EDXS, JSM-T 220A JEOL) without cross-section. The thickness of gold coated on the copolymers was 25 nm.

#### Equilibrium water absorbency

Water absorbencies of the crosslinked poly[AM-*co*-AA] copolymer and hybrid AHAMAA were evaluated with deionized water at room temperature in a closed system to minimize water evaporation. Deionized water (200 mL) was added to 0.1 g of the dry crosslinked poly[AM-*co*-AA] or AHAMAA and allowed to reach equilibrium swelling for 24 h. Then, the swollen gel was filtered through a 100-mesh aluminum sieve screen for 2 h. The water absorbency was determined for each crosslinked poly[AM-*co*-AA] or AHAMAA and calculated from eq. (1)<sup>15</sup>:

$$\text{Water absorbency}(Q) = (W_s - W_d)/W_d \quad (1)$$

where  $W_d$  = the weight of dry crosslinked poly[AM-*co*-AA] or AHAMAA (g), and  $W_s$  = the weight of the equilibrium swollen gel (g). The results for the evaluation of water absorption are shown as the average of three replications with one standard deviation.

#### Rheological study

The rheological experiments of the swollen gel particles having an irregular shape were carried out in a strain-controlled rheometer (ARES, TA, New Castle) equipped with a solvent trap to prevent water evaporation during measurements. The experiments were operated at 25°C using parallel plate geometry (50 mm diameter, 1 mm gap) made of stainless steel. The strain sweeps, at a fixed frequency of 1 rad s<sup>-1</sup>, were conducted in the range of 0.1–100% for determining a linear viscoelastic (LVE) range, where  $G'$  (storage modulus) and  $G''$  (loss modulus) are independent of the strain amplitude. After a strain sweep test, the dynamic frequency sweeps were performed within the determined LVE range. The samples were prepared as follows. The dry superabsorbent (0.1 g of the crosslinked poly[AM-*co*-AA] or hybrid AHAMAA) was dispersed in 200 mL deionized water and allowed to swell for 24 h to reach equilibrium swelling. The swollen superabsorbent was filtered through a 100-mesh aluminum screen for 2 h. Pieces of tissue papers were used to rub off the unabsorbed water at the bottom of the screen until the swollen gel did not flow when the screen was held vertically. Then, the swollen gel particles were removed from the screen to investigate their rheological behavior.

#### Turbidity reduction of kaolin suspension

Turbidity reductions by the crosslinked polymer and hybrid flocculant were carried out in a jar testing apparatus (Vekp Scientifica Model FC6S, Milan, Italy). Kaolin powder weighing 0.1% w w<sup>-1</sup> with an

average particle size of 2  $\mu\text{m}$  and a negative charge of  $-50$  mV was used to prepare a stock kaolin suspension which was placed at 600 mL beaker into four beakers per assay. The first beaker was left as a no sample control, whereas the other three beakers were for samples, and their pH was adjusted to precisely 2, 6, and 10, respectively. The dry crosslinked poly[AM-co-AA] and AHAMAA samples, weighing 0.24 g each, were individually placed one sample in each beaker and then all beakers were stirred by a mechanical stirrer at 120 rpm for one min. The speed was then reduced to 30 rpm for 20 min and finally the beakers were set aside for 45 min with no stirring. The final turbidity in each beaker was measured using a portable turbidity meter (Model 2100P, Hach, CO).

Other flocculation experiments were carried out in a 100-mL graduate cylinder with the same concentration of kaolin powder. The cylinder was inverted 10 times. After mixing, the cylinder was set upright for 3, 9, 15, and 24 h. The turbidity of the samples was measured using a portable turbidimeter (Model 2100P, Hach, CO). The sample having the turbidities of less than 10 units were allowed to cool to room temperature before analysis. The turbidity of the original sample was then computed from the turbidity of the diluted sample and the dilution factor. The relative turbidity of the crosslinked poly[AM-co-AA] and AHAMAA was calculated by eq. (2):

$$\text{relative turbidity} = \frac{\text{final turbidity}}{\text{initial turbidity}} \quad (2)$$

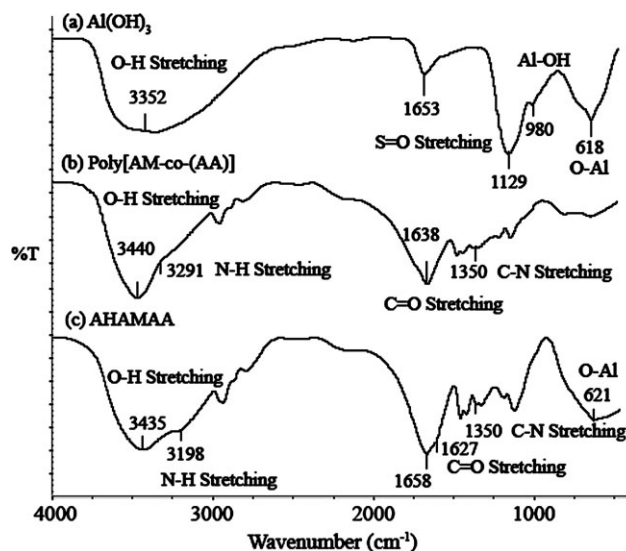
#### Effect of flocculation time on agglomeration of kaolin particles

The dry crosslinked poly[AM-co-AA] or AHAMAA samples, each weighing 0.08 g, were individually mixed with 0.1% w w<sup>-1</sup> of the kaolin in 200 mL water. Each suspension was agitated by stirring at 100 rpm for 5 min. Floc formation was observed at 15, 20, 25, 30, 60, 120, 300, and 1440 min, where a drop of the floc suspension was taken from the beaker, placed on a slide and covered gently with a cover glass. The floc size was roughly measured with an optical microscope coupled with a CCD-digital camera (Olympus, model SZH 10, Tokyo, Japan) in a bright field mode.

## RESULTS AND DISCUSSION

#### Characterization of functional groups by FTIR spectroscopy

The FTIR spectra of the synthesized  $\text{Al}(\text{OH})_3$ , cross-linked poly[AM-co-AA] and AHAMAA are shown in Figure 1. The  $\text{Al}(\text{OH})_3$  FTIR spectrum shows a peak of



**Figure 1** FTIR spectrum of (a)  $\text{Al}(\text{OH})_3$ , (b) the cross-linked poly[AM-co-AA] and (c) AHAMAA.

—OH stretching ( $\sim 3352$   $\text{cm}^{-1}$ ) which indicates the presence of the hydroxide group. In addition, it also shows peaks of Al—OH and O—Al at 980 and 618  $\text{cm}^{-1}$ , respectively.<sup>16</sup> This strongly supports that the hydrolysis product of aluminum sulfate was aluminum hydroxide and that the absorption peaks of the sulfate group, at 1129 and 1653  $\text{cm}^{-1}$ , are thus residual aluminum sulfate residues within the  $\text{Al}(\text{OH})_3$ .<sup>17</sup> The crosslinked poly[AM-co-AA] in the FTIR spectrum confirms the presence of the carboxylic acid group (3440 and 1638  $\text{cm}^{-1}$ ) and carboxamide group (3291 and 1350  $\text{cm}^{-1}$ ) in the copolymer.<sup>16</sup> The AHAMAA FTIR spectrum shows evidence of the coordination between the carboxylate anion and the metal ion (aluminum ion) at the strong absorption peak of 1658  $\text{cm}^{-1}$ , which indicates a complex formation of the copolymer and  $\text{Al}(\text{OH})_3$ .<sup>16</sup>

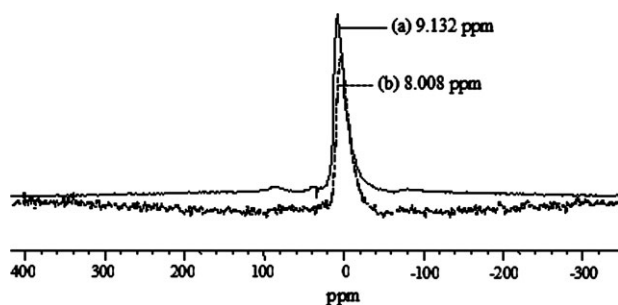
#### Characterization of $\text{Al}(\text{OH})_3$ and AHAMAA by <sup>27</sup>Al-NMR

The <sup>27</sup>Al-NMR spectra of  $\text{Al}(\text{OH})_3$  and AHAMAA are shown in Figure 2. The signal near 0.0 ppm represents the monomeric specie. The octahedral form of the Al ion shows a signal at around 6–8 ppm.<sup>18</sup> Thus, the  $\text{Al}(\text{OH})_3$  (at 9.132 ppm) and AHAMAA (at 8.008 ppm) are the monomeric species and octahedral form, respectively. From this result, it is possible to indicate that the aluminum atom in the AHAMAA is in a six-coordination.

#### Determination of residual aluminum ion concentration of AHAMAA in treated water

The residual aluminum ion concentration in water (Table II) was found in the range of 0.09–0.2  $\text{mg L}^{-1}$





**Figure 2** The  $^{27}\text{Al}$ -NMR of (a)  $\text{Al}(\text{OH})_3$  and (b) AHAMAA synthesized with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS and  $12 \times 10^{-4}$  mol TEMED.

regardless of the soaking time which suggests that the stability of the aluminum in the AHAMAA is high. Furthermore, this concentration range of free aluminum ions is not likely to be harmful to human health because the maximum contaminant level of aluminum ions in the human body is higher than  $0.2 \text{ mg L}^{-1}$ .<sup>19</sup> Indeed, the current World Health Organization No Adverse Effect Limit (NOAEL) for acrylamide monomer ingestion is  $500 \text{ mg kg}^{-1}$  wet body weight  $\text{day}^{-1}$ . Therefore, with respect to leaching (release) of free aluminum ions, the AHAMAA obtained in this experiment is likely to be relatively harmless and safe to be used as a polymeric flocculant in wastewater treatment.

#### Determination of residual acrylamide monomer

The residual level of acrylamide monomer can be directly related to the conversion of acrylamide monomer, which is a major component of the super-absorbent polymer composite, to polymer. On the basis of the relative reactivity ratios of the three monomers ( $r_{\text{AM}} = 0.58$ ,  $r_{\text{AA}} = 1.38$ , and  $r_{\text{N-MBA}} = 1.77$ ),<sup>20</sup> we presume that the N-MBA was used up earlier in the crosslinking reaction due to its higher reactivity. Therefore, acrylamide should be the only monomer that reacts with bromine solution in the bromination reaction. However, since any deviation

from this assumption will result in an overestimate and not an underestimate of free acrylamide levels, we consider from a safety point of view (see below) this to be a valid measurement method.

Table III indicates that the conversion of acrylamide monomer was relatively high at 99.93%. However, since the residual acrylamide monomer was found in the range of  $43\text{--}77 \text{ mg L}^{-1}$  (0.10%) which is significantly above the level permitted ( $0.0005 \text{ mg L}^{-1}$ ) as a contaminant in drinking water,<sup>21</sup> this residual concentration might impose potential health problems in drinking water and is unsuitable. Acrylamide monomers are reported as both human carcinogens and inheritable genetic damage. Cumulative extraction and purification of these polymeric flocculants with hot water must be carried out to remove the unreacted acrylamide and the extractable and soluble polyacrylamide.

#### Surface morphology of crosslinked poly[AM-co-AA] and AHAMAA and the density distribution of elements in AHAMAA

The SEM micrographs of crosslinked poly[AM-co-AA] show two different surface morphologies, i.e., a smooth and a porous surface [Fig. 3(a,b)]. The different surfaces can result from different solubility's between the crosslinked and soluble portions. Thus, removal of the soluble portion by washing leads to a porous surface, whilst the smooth surfaced insoluble portion results from the cyclization and the multiple crosslinking reactions at pendant vinyl groups of N-MBA, which also leads to the lower water absorption.<sup>16</sup> The SEM micrograph of AHAMAA [Fig. 3(c)] shows different surface structures for AHAMAA from that of crosslinked poly[AM-co-AA]. Most notably, is that AHAMAA has several agglomerations of white particles on the smooth surface, which may imply a different chemical environment.

The density distribution of carbon and aluminum elements on the surface of AHAMAA, as detected by EDXS, reveal different distribution maps of

**TABLE II**  
Aluminum Ion Concentration in AHAMAA and Residual Aluminum Ion (leachate) Levels in the Treated Water

Sample condition	Al in AHAMAA ( $\text{mg L}^{-1}$ )	Residual aluminum ( $\text{mg L}^{-1}$ ) retained in the treated water after the indicated treatment times (days)			
		15	30	45	60
A <sup>a</sup>	$9.99 \pm 0.51$	$0.15 \pm 0.03$	$0.10 \pm 0.01$	$0.13 \pm 0.03$	$0.17 \pm 0.03$
B <sup>b</sup>	$11.28 \pm 0.78$	$0.19 \pm 0.01$	$0.14 \pm 0.02$	$0.18 \pm 0.02$	$0.14 \pm 0.02$
C <sup>c</sup>	$13.51 \pm 0.38$	$0.16 \pm 0.03$	$0.10 \pm 0.01$	$0.15 \pm 0.01$	$0.13 \pm 0.02$
D <sup>d</sup>	$10.38 \pm 0.55$	$0.15 \pm 0.03$	$0.11 \pm 0.01$	$0.16 \pm 0.02$	$0.14 \pm 0.01$

<sup>a</sup>AA  $4 \times 10^{-3}$  mol, N-MBA  $4.6 \times 10^{-4}$  mol, APS  $3.1 \times 10^{-4}$  mol, TEMED  $12 \times 10^{-4}$  mol.

<sup>b</sup>AA  $4 \times 10^{-3}$  mol, N-MBA  $2.3 \times 10^{-4}$  mol, APS  $3.1 \times 10^{-4}$  mol, TEMED  $12 \times 10^{-4}$  mol.

<sup>c</sup>AA  $4 \times 10^{-3}$  mol, N-MBA  $2.3 \times 10^{-4}$  mol, APS  $1.6 \times 10^{-4}$  mol, TEMED  $12 \times 10^{-4}$  mol.

<sup>d</sup>AA  $4 \times 10^{-3}$  mol, N-MBA  $2.3 \times 10^{-4}$  mol, APS  $1.6 \times 10^{-4}$  mol, TEMED  $12 \times 10^{-4}$  mol.

Data are shown as the mean  $\pm$  S.D. and are derived from four independent repeats.

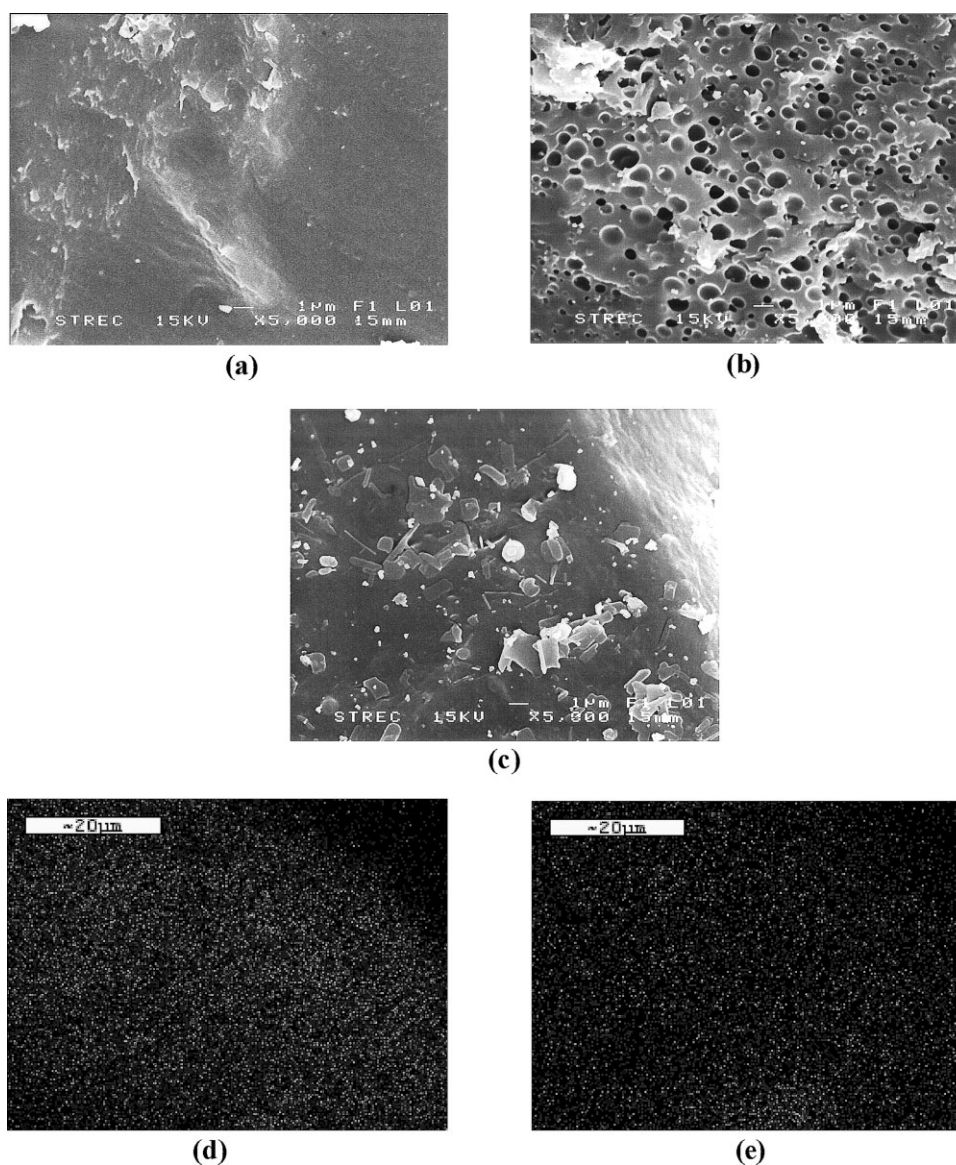
**TABLE III**  
**The Level of Residual Acrylamide in the Crosslinked Poly[AM-co-AA]<sup>a</sup>**

Sample AM : AA	AM content (mol)	Initial acrylamide concentration (mg L <sup>-1</sup> )	Residual acrylamide (mg L <sup>-1</sup> )	Residual acrylamide (%)
100 : 0	0.090	63,970	43	0.1
98 : 2	0.092	65,390	77	0.1
96 : 4	0.094	66,820	63	0.1
94 : 6	0.096	68,240	68	0.1
92 : 8	0.098	69,650	64	0.1
90 : 10	0.100	71,080	63	0.1

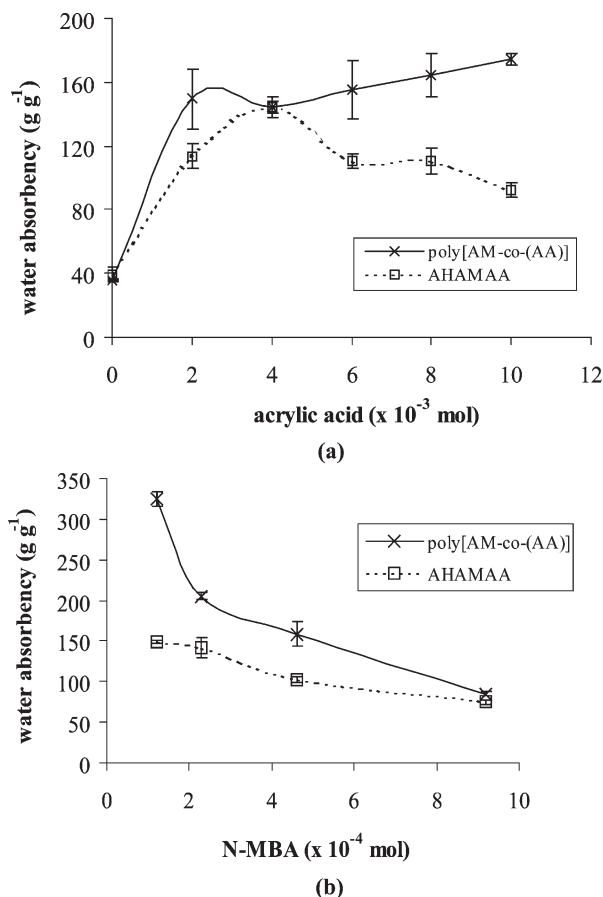
<sup>a</sup>Polymerization reaction was carried out with  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS,  $12 \times 10^{-4}$  mol TEMED, 250 rpm, at 45°C and 1 h polymerization time.

carbon and aluminum elements on the surfaces [Fig. 3(d,e)]. The carbon elements comprise some 38.4% of the surface, which is much higher than that of alu-

minum at 0.46–0.61%. Most of the aluminum and carbon densities are overlapped. This distribution indicates that aluminum hydroxide is dispersed into



**Figure 3** SEM micrographs prepared with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS and  $12 \times 10^{-4}$  mol TEMED for (a & b) the crosslinked poly[AM-co-AA]; (c) AHAMAA; and the EDXS of AHAMAA for (d) carbon and (e) aluminum elements.



**Figure 4** The effects of (a) acrylic acid and (b) N-MBA contents on the water absorbency ( $Q$ ) of the crosslinked poly[AM-co-AA] and AHAMAA synthesized with  $3.2 \times 10^{-4}$  mol APS,  $12 \times 10^{-4}$  mol TEMED, 250 rpm, at  $45^\circ\text{C}$  and 1 h polymerization time. Data are shown as the mean  $\pm 1$  S.D. and are derived from three independent repeats.

the matrix of the acrylamide-acrylic acid superabsorbent polymer. The degree of aluminum ion dispersion in the polymer controls the performance of the polymer composite in water treatment.

#### Effect of monomer pair and crosslinking agent on water absorbency

The water absorbency of polymers made from crosslinked poly[AM-co-AA] and AHAMAA with various acrylic acid contents from 0 to  $10^{-2}$  mol is shown in Figure 4(a). The water absorbency values of crosslinked poly[AM-co-AA]s were always higher than those of AHAMAA and increased with increasing acrylic acid content. This is likely to be due to the fact that increases in the ionic content in the polymer network increase the hydrophilicity of the superabsorbent polymer.<sup>22</sup> The higher hydrophilicity reflects the increasing amount of carboxylate groups in the polymer chains,<sup>23</sup> the higher the repulsion between the carboxylate groups in crosslinked polymer chains and the greater the water absorbency.<sup>24</sup> Like-

wise, AHAMAA hybrid polymers with various acrylic acid contents displayed a high and dose-dependent water absorbency. The highest water absorbency of AHAMAA was  $145 \pm 6 \text{ g g}^{-1}$ . Increasing the acrylic acid contents above this level reduced the water absorbency. This is primarily caused by more interactions between the carboxylate anion and the aluminum counter ion through a complex formation to construct a more rigid chain. The complex formation between aluminum ions and carboxylate anions behaves like another type of crosslinking reaction, as shown in Scheme 1a, and so it reduces the anionic repulsion, osmotic pressure, and thus reduces the water absorption.<sup>25,26</sup>

The N-MBA crosslinker was employed to improve the strength of the swollen gel. However, high crosslinker content does reduce the water absorbency of the resultant polymer because of the increasing rigidity of the crosslinked chains.<sup>27</sup> The water absorbency of crosslinked poly[AM-co-AA], summarized in Figure 4(b), is of course higher than that of AHAMAA because the crosslinked poly[AM-co-AA] has only the N-MBA crosslinking sites, whereas the AHAMAA has both the N-MBA crosslinking sites and the coordination between the aluminum ion and the carboxylate anion which reduces the electrostatic repulsion significantly, leading to a decrease in water absorbency.<sup>25</sup> Both crosslinked poly[AM-co-AA] and AHAMAA gave the highest water absorbency of  $322 \pm 13$  and  $148 \pm 2 \text{ g g}^{-1}$ , respectively, using the same amount of N-MBA, and its water absorption decreased with increasing N-MBA contents thereafter.

#### Effect of initiator couple on water absorbency

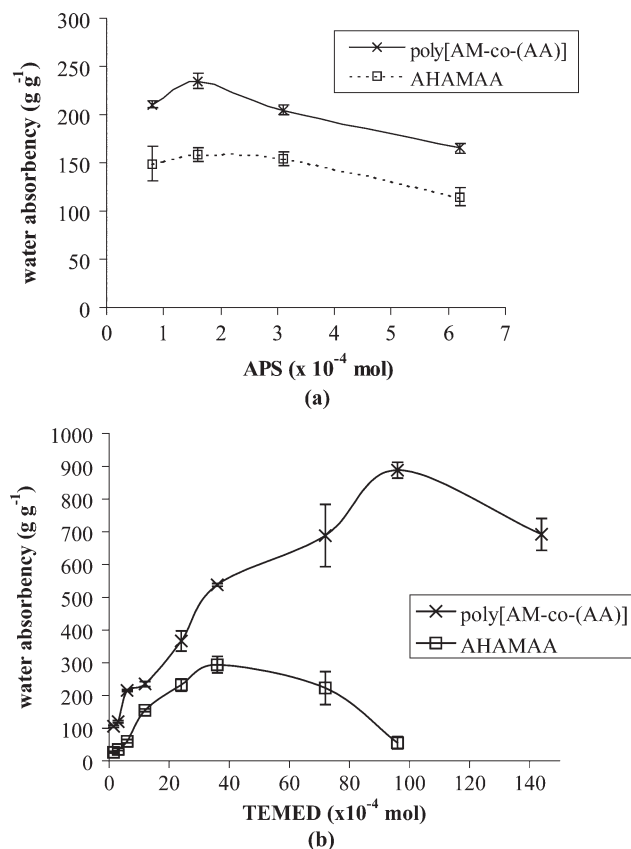
When a relatively low amount of APS initiator at a fixed amount of TEMED was used in the polymerization reaction, the water absorbency was low. However, at higher APS contents, the water absorbency decreased. At lower APS contents, a few radicals were generated and a low conversion was thus obtained to yield short polymer chains and low anionic repulsions. At higher APS contents, too many radicals were generated yielding again short polymer chains because the superabsorbent polymers could not swell to such a larger extent due to the lower repulsion level attributed by the small amount of carboxylate groups.<sup>27</sup> The water absorbency of AHAMAA was lower than that of crosslinked poly[AM-co-AA] at all APS values [Fig. 5(a)] because of the complexation between the aluminum ion and the carboxylate anion leading to a reduction of the electrostatic repulsion. However, the highest water absorbency of crosslinked poly[AM-co-AA] was, like that for AHAMAA, achieved at the same amount of APS. The crosslinked poly[AM-co-AA] and



The content of the TEMED co-initiator significantly affects the water absorbency of the attained polymer [Fig. 5(b)]. For both the crosslinked poly[AM-*co*-AA] and AHAMAA, the water absorbency increased with increasing co-initiator content. The TEMED accelerates the production of free radical generation and results in longer polymer chains. In a redox initiated polymerization of APS and TEMED pair, TEMED generally acts as a reducing agent to generate electrons to reduce the APS, an oxidizing agent. In other words, TEMED is a co-initiator or a starter to induce the decomposition of the APS ini-

tiator. When the TEMED content was low, the activated TEMED molecules were not sufficient to produce hydroxyl radicals. Thus, short rather than long polymer chains were produced with resultant low water absorbency. For the crosslinked poly[AM-*co*-AA], the maximum water absorbency was  $888 \pm 24 \text{ g g}^{-1}$  at a high TEMED content because the higher TEMED content produced many longer and flexible copolymer chains to facilitate water absorption. In the case of AHAMAA, the highest water absorbency ( $294 \pm 25 \text{ g g}^{-1}$ ) was achieved when the TEMED content was 2.6 folds lower than that for the crosslinked poly[AM-*co*-AA]. Similarly, the water absorbency decreased when too high a TEMED



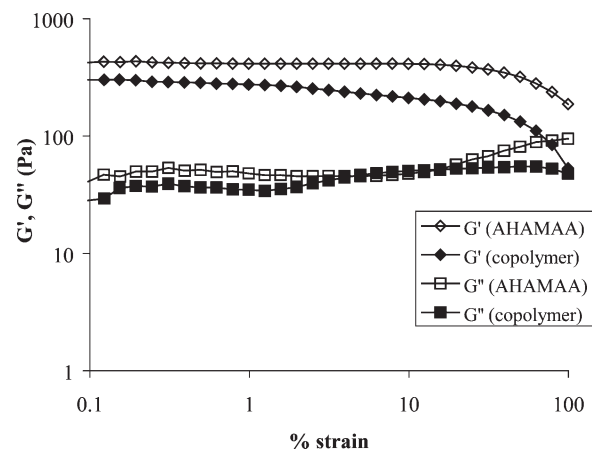


**Figure 5** The effects of the (a) APS content and (b) TEMED contents on the water absorbency ( $Q$ ) of crosslinked poly[AM-co-AA] and AHAMAA synthesized with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA, 250 rpm, at 45°C and 1 h polymerization time. Data are shown as the mean  $\pm$  1 S.D. and are derived from three independent repeats.

content was used. We postulate that the carboxylate anion in the long polymer chains can act as a coordination donor to the reaction site of the aluminum ion, leading to many more crosslinking sites in the polymer chain. This would then be one reason attributed to the very low water absorption. From these results, the possible structures for AHAMAA and crosslinked poly[AM-co-AA] are proposed in Scheme 1 a and b, respectively.<sup>28,29</sup>

### Rheological study

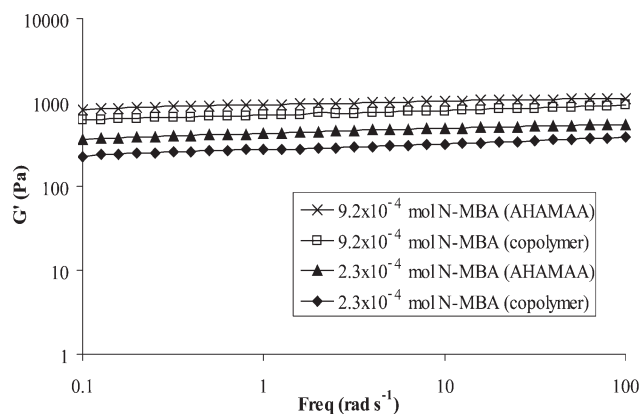
The superabsorbent polymers were tilted to drain off the excess water to confirm that inter-particle water was drained out. We did not see air bubbles during loading of the gel and duplicate experiments gave the same result. Plots of the storage modulus  $G'$ , and the loss modulus  $G''$ , as a function of the strain amplitude of the superabsorbent poly[AM-co-AA] copolymer and hybrid AHAMAA flocculant indicate that both systems show an elastic response since the  $G'$  values of crosslinked poly[AM-co-AA] and AHAMAA are higher than their respective  $G''$



**Figure 6** The strain sweep of crosslinked poly[AM-co-AA] and AHAMAA at a constant frequency ( $0.1 \text{ rad s}^{-1}$ ). Data are representative of two repeats.

values (Fig. 6). This indicates that the elastic response of the gel is stronger than the viscous response.<sup>30</sup> Both  $G'$  and  $G''$  are independent of the applied strain in the LVE range. The copolymer had an LVE range below 2% strain, whereas AHAMAA presents an LVE range up to 10% strain. Rheologically, it means that the AHAMAA superabsorbent polymer behaves as a stronger gel than the neat superabsorbent copolymer, in as much as that the AHAMAA flocculant is still elastic and can withstand a larger deformation.<sup>31</sup>

At a constant crosslinking agent content ( $2.3 \times 10^{-4}$  mol), the  $G'$  value of crosslinked poly[AM-co-AA] was in a range of 227–388 Pa which is much lower than that of AHAMAA (361–553 Pa) (Fig. 7). The chelate formation between the carboxylate anion and the aluminum ion in AHAMAA (Scheme 1a) is suggested to play its role to induce chain rigidity, which results in higher storage moduli. Both the crosslinked poly[AM-co-AA] and AHAMAA synthesized with a



**Figure 7** The effect of the crosslinking agent content of crosslinked poly[AM-co-AA] and AHAMAA on the storage modulus at a constant strain (1% strain). Data are representative of two independent trials.

**TABLE IV**  
The Effect of pH on Turbidity Reduction by the Crosslinked poly[AM-co-AA]<sup>a</sup> and AHAMAA<sup>b</sup>

pH of kaolin suspension	Turbidity (NTU)		
	Control	Poly(AM-co-AA)	AHAMAA
2	71	52	32
5.8	653	562	368
10.5	1560	1440	1455

<sup>a</sup>Polymerization reaction was carried out with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS,  $12 \times 10^{-4}$  mol TEMED, 250 rpm, at 45°C and 1 h polymerization time.

<sup>b</sup>Polymerization reactions were carried out with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS,  $12 \times 10^{-4}$  mol TEMED, 42.5 mL Al(OH)<sub>3</sub>, 250 rpm, at 45°C and 1 h polymerization time.

higher N-MBA content ( $9.2 \times 10^{-4}$  mol) have a lower water absorption than those synthesized with a lower N-MBA content ( $2.3 \times 10^{-4}$  mol). This supports the notion that low water absorption directly results from the higher crosslinking reaction. Thus, an increase in an appropriate amount of N-MBA in both systems increases the elastic modulus due to an increase in network junctions because the higher crosslinking agent content joins more main chains together with many more molecules of the crosslinking agent to become parts of the crosslinked polymer chains.<sup>27</sup> This result is inversely related to the water absorption, as illustrated in Figure 4(b), because the increase in the crosslinking points typically restricts the network capability to expand in water. During the hydration-dependent swelling, the network chains are forced to loosen the chain entanglements and become more elongated and expanded by repulsive forces. In contrast, the dissociated carboxylate groups increase the osmotic pressure in the gel for absorption whilst the nearby crosslinking junctions restrict “infinite swelling” by elastic retraction forces.

### Turbidity reduction of a kaolin suspension

The pH of the suspension has a significant effect on floc formation due to the change in the face and edge surface charge densities and the polarity of kaolin. At pH 2, the turbidity after a 45 min settling time was low (71 NTU) even if the flocculant was not used, as shown in Table IV. This faster settling of the kaolin suspension is because of the positive charges of kaolin that predominate at pH 2.2 (a point of the zero charge).<sup>31</sup> On the other hand, the turbidity for 45 min settling at pH 10 was very high (1560 NTU), caused by the electrostatic repulsion of anions between the kaolin particles. The higher the negative charge density was, the higher the amount of stable suspension was formed. Thus, the turbidity for the 45 min settling period at pH 5.8 was lower than that of pH 10 because of the lower negative charge density.<sup>31</sup> When crosslinked poly[AM-co-AA] or AHAMAA was used as a flocculant in the kaolin suspension, it was found that these flocculants did not affect significantly the turbidity reduction at pH 2 and 10. However, at pH 5.8, AHAMAA reduced the turbidity some 44% (from 653 to 368 NTU), whereas crosslinked poly[AM-co-AA] only reduced the turbidity  $\sim 14\%$  by the jar test. Moreover, AHAMAA allowed a better reduction in turbidity by the cylinder method attaining up to 95% reduction after a 24-hour settling period compared with only a 84% turbidity reduction attained with the crosslinked poly[AM-co-AA] under the same conditions (Table V).

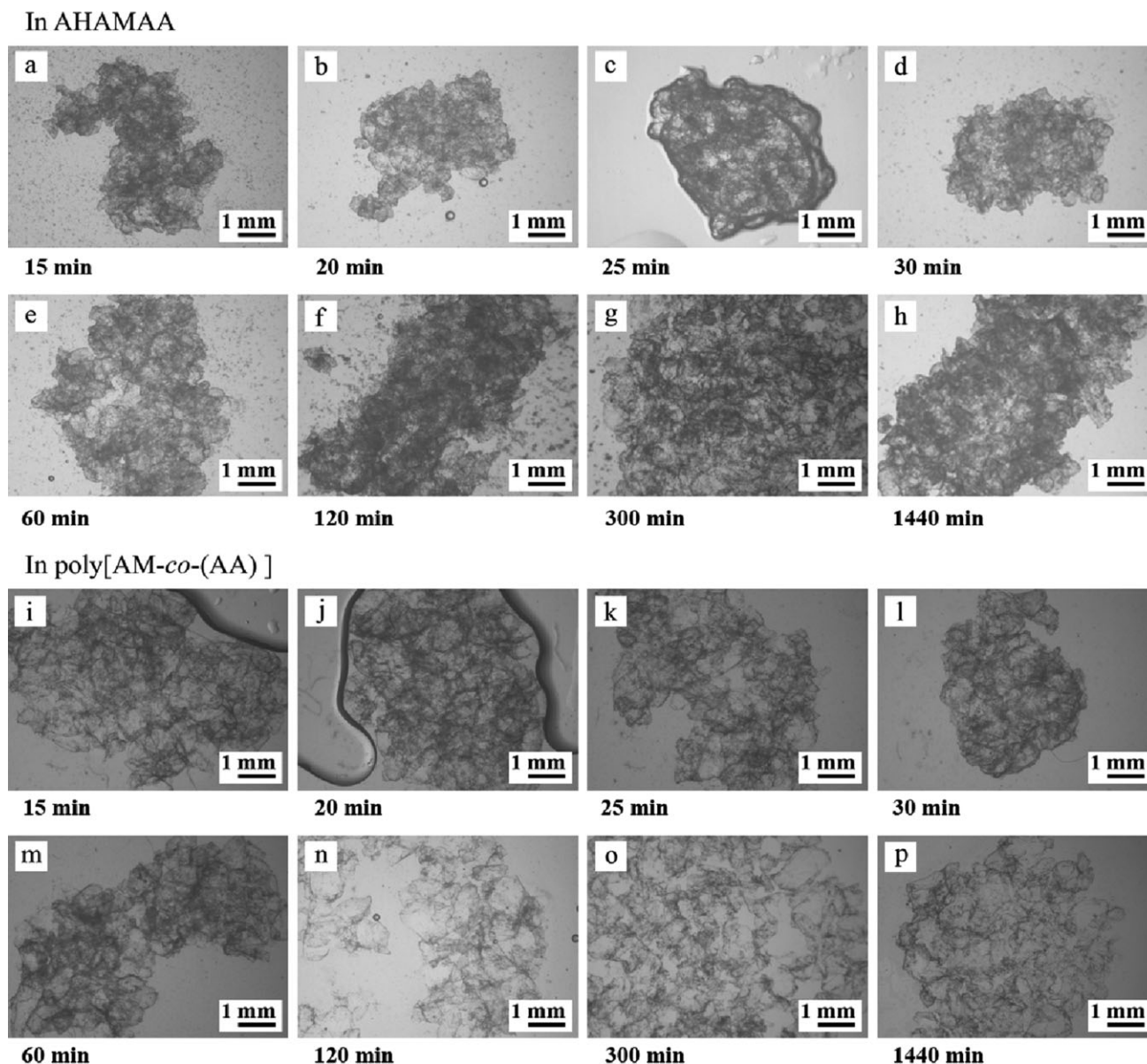
The turbidity reduction by poly[AM-co-AA] could take place via a polymer bridging flocculation mechanism. At pH 5.8, polymer bridging between poly[AM-co-AA] with kaolin particles would be formed through hydrogen and/or chemical bonds on the kaolin surfaces. That is, the surface hydroxyls in the alumina layer of kaolin could bind with the oxygen atoms in the carbonyl groups of the flocculant,

**TABLE V**  
The Relative Turbidity of the Kaolin Suspension by the Synthesized Poly[AM-co-AA]<sup>a</sup> and AHAMAA<sup>b</sup>

Flocculation time (hours)	Relative turbidity of kaolin		% Reduction in turbidity	
	Copolymer	AHAMAA	Copolymer	AHAMAA
0	1.00 $\pm$ 0.18	1.00 $\pm$ 0.16	–	–
3	0.18 $\pm$ 0.06	0.15 $\pm$ 0.01	82	85
9	0.18 $\pm$ 0.04	0.12 $\pm$ 0.03	82	88
15	0.17 $\pm$ 0.05	0.08 $\pm$ 0.02	83	92
24	0.16 $\pm$ 0.04	0.05 $\pm$ 0.01	84	95

<sup>a</sup>Polymerization reaction was carried out with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS,  $12 \times 10^{-4}$  mol TEMED, 250 rpm, at 45°C and 1 h polymerization time.

<sup>b</sup>Polymerization reactions were carried out with  $4 \times 10^{-3}$  mol AA,  $2.3 \times 10^{-4}$  mol N-MBA,  $1.6 \times 10^{-4}$  mol APS,  $12 \times 10^{-4}$  mol TEMED, 42.5 mL Al(OH)<sub>3</sub>, 250 rpm, at 45°C and 1 h polymerization time.



**Figure 8** The effect of flocculation time on kaolin particles in AHAMAA and the crosslinked poly[AM-co-AA] in the Jar test. Slides shown are representative of two samples from two independent trials.

and by oxygen atoms on the silica layer via hydrogen bonding with the  $H^+$  of the amino group ( $-NH_2$ ).<sup>32</sup>

Since kaolin possesses a net negative surface charge (net Zeta potential of  $-50$  mV), AHAMAA can bridge the kaolin particles together through charge neutralization, because of the positive charge of  $Al^{3+}$ , with a relatively high coagulation power of more than 1000 to accelerate charge neutralization.<sup>23</sup> Moreover, the presence of negatively charged segments along the polymer chain of AHAMAA can significantly enhance the bridging flocculation.

#### Effect of flocculation time on agglomeration of kaolin particles

The effect of flocculation times of on the degree of floc formation and the appearance of the kaolin par-

ticles in crosslinked poly[AM-co-AA] and AHAMAA polymers after 15 to 1440 min of coagulation time are depicted in Figure 8. AHAMAA flocculants formed denser flocs with more compact sizes and sooner than did the poly[AM-co-AA] (e.g., compare 25 min and 30 min in Figure 8(c,l)). Again, this is likely to be due to the flexible chains in the cross-linked poly[AM-co-AA] and the better water absorption, where the floc sizes in the crosslinked poly[AM-co-AA] were initially expanded and became loose. Dense and compact sizes of the flocs were found at 25- and 30-min flocculation for AHAMAA and poly[AM-co-AA], respectively. Moreover, the flocs from AHAMAA were still denser and more compact [6 mm in diameter, Fig. 8(c)] than that of crosslinked poly[AM-co-AA] [7 mm in diameter in Fig. 8(l)]. Longer flocculation times could not retain



the compact and dense flocs because the flocs with diameters of greater than 10  $\mu\text{m}$  were subsequently found in all time points. Nevertheless AHAMAA still gave denser and tighter flocs at each time point than the crosslinked poly[AM-co-AA] [Fig. 8(f–h) for AHAMAA and in Fig. 8(m–p) for the crosslinked poly[AM-co-AA]]. For charge neutralization in AHAMAA, which has electrostatic interactions, particles were linked by rather rigid bonds and floc breakage occurred more readily and was a reversible process.<sup>23</sup> One of the important properties for polymer flocculants is their gel strength to produce floc strength. As discussed above, the AHAMAA superabsorbent polymer flocculant behaved as a stronger gel withstanding larger deformations,<sup>33</sup> than the crosslinked poly[AM-co-AA] and so AHAMAA maintained stable flocs for a longer time than did the crosslinked poly[AM-co-AA].

## CONCLUSIONS

Crosslinked poly[AM-co-AA] and AHAMAA have been successfully prepared by a radical chain polymerization. The FTIR spectra of  $\text{Al}(\text{OH})_3$ , poly[AM-co-AA] and AHAMAA indicated the peaks for the Al–O portion and the poly[AM-co-AA] portion. The  $^{27}\text{Al}$ -NMR spectra of  $\text{Al}(\text{OH})_3$  confirmed the monomeric and/or dimeric species for Al ion in  $\text{Al}(\text{OH})_3$  and the octahedral coordination in AHAMAA spectra. Rheological studies demonstrated that both polymers were strong gels having higher elastic than viscous responses. The AHAMAA possessed a larger storage modulus due to the additional formation of physically crosslinking points through the chelate formation between the carboxylate anion from acrylic acid in the crosslinked poly[AM-co-AA] and the aluminum ion. The superabsorbent polymers with more crosslinking junctions imparted a higher storage modulus and lower water absorption capacity. TEMED controlled the water absorption of crosslinked poly[AM-co-AA] and AHAMAA at a given APS content, with a highest water absorbency of  $888 \pm 24$  and  $294 \pm 25 \text{ g g}^{-1}$ , respectively. The residual aluminum concentration of AHAMAA in water was in the range of  $0.1\text{--}0.2 \text{ mg L}^{-1}$  indicating a high stability of AHAMAA. The turbidity reduction of kaolin suspension by AHAMAA was better than the crosslinked poly[AM-co-AA], which gave 95% reduction in turbidity achievable from AHAMAA whereas only 84% turbidity reduction was provided by the crosslinked poly[AM-co-AA]. AHAMAA has good performance as mentioned above. Thus, AHAMAA can be a candidate to polymeric flocculant for turbidity reduction in wastewater treatment.

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