

Preparation of Acrylic Acid and AMPS Cointercalated Layered Double Hydroxide and Its Application for Superabsorbent

Shuxian Shi,¹ Fang Guo,¹ Yuzheng Xia,¹ Zhiqiang Su,¹ Xiaonong Chen,¹ Min Wei²

¹Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

²State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT: This article reports the cointercalation of acrylic acid (AA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) in the interlayer region of Mg₂Al layered double hydroxide (LDH) and the application of this inorganic-organic composite material in the field of water superabsorbent. The monomers of AA and AMPS were cointercalated into galleries of Mg₂Al-LDH (denoted as AA-AMPS/LDH) with various molar ratios by ion-exchange method, which was confirmed by powder X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), and elemental analysis. The polymer-based superabsorbent was prepared through *in situ* free-radical aqueous copolymerization of AA and AMPS, with AA-AMPS/LDH as additive, *N,N'*-methyl-

lenebisacrylamide (NMBA) as crosslinker and potassium persulfate (KPS) as initiator. The composition of this poly (AA-co-AMPS)/LDH was demonstrated as a good water superabsorbent. The LDH content, water absorbency, thermal stability, and swelling rate of this superabsorbent were also investigated in detail. Results showed that the incorporation of a 5 wt % AA-AMPS/LDH into polymer matrix increased its water absorbency significantly by 27.7% (in water) and by 51.5% (in 0.9 wt % NaCl solution). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1661–1668, 2011

Key words: AA; AMPS; LDH; cointercalation; copolymerization; superabsorbent

INTRODUCTION

Superabsorbent polymer hydrogels are lightly cross-linked hydrophilic polymers that can absorb, swell, and retain aqueous solutions up to thousands of times their own weight.¹ They have a markedly higher absorption capacity than traditional water-absorbing materials, such as cotton, pulp, sponge, etc. Because of their excellent characteristics, superabsorbents are widely used in many fields, such as agriculture, horticulture, sanitary goods, and medicine.^{2–4} As a typical kind of superabsorbents, polyacrylate (PAA)-based ones play an important role in practical application. However, the use of superabsorbents is limited because of low gel strength, poor stability, and high production cost. Much effort has been made to modify these shortages since the first superabsorbent was reported in 1961.⁵

In recent years, polymer/clay composite has attracted much attention. Clays are natural, abundant, and inexpensive materials with high mechanical strength and hydrophilic characteristic. The incorporation of these mineral powders into polymer will accelerate the generation of new superabsorbents for special applications.^{6,7} They can not only reduce production cost, but also improve the properties of superabsorbents, such as swelling ability, gel strength, mechanical and thermal stability. Recently, clays such as montmorillonite,⁸ attapulgite,⁹ mica,¹⁰ bentonite,^{11,12} and hydrotalcite¹³ have been widely studied for the preparation of composite superabsorbents.

Layered double hydroxides (LDH), a family of lamellar clays, are a large type of naturally occurring and synthetic materials, which can be described by the general formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{z+}A^{n-}_{z/n}yH_2O$. M^{II} and M^{III} are divalent and trivalent metal cations respectively, while Aⁿ⁻ is the anion which compensates for the positive charges of the hydroxide layers. The interlayer anion can also be exchanged by other inorganic or organic anions through a variety of methods. In recent years, LDHs have received considerable attention because of their applications as catalyst,^{14–16} drug delivery carrier,^{17–19} optical

Correspondence to: S. Shi (shisx@mail.buct.edu.cn) or Y. Xia (xiayz@mail.buct.edu.cn).

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material,²⁰ molecular reactor,²¹ as well as additive of organic/inorganic nanocomposites.^{22,23}

Because of the hydrophilic characteristic, LDH materials are also suitable for use in superabsorbents as additives. However, the inorganic and organic phases are quite incompatible, resulting in the occurrence of phase separation. Therefore, the organic-modification of the inorganic components is a very effective solution before the preparation of polymer/clay nanocomposite superabsorbents. Furthermore, the organic-modification inhibits the formation of aggregates of inorganic component and thus enables high dispersion of LDH in polymer matrix.²⁴

In this work, LDH was chosen as an additive to prepare polymer/LDH nanocomposite superabsorbents. The whole process involves two steps. First, the organic-modification of LDH was performed by coinertalation of both AA and AMPS into LDH galleries (denoted as AA-AMPS/LDH). Second, the nanocomposite superabsorbents were obtained by *in situ* copolymerization of AA and AMPS with the AA-AMPS/LDH as additive, in aqueous solution using *N,N'*-methylenebisacrylamide (NMBA) as crosslinker and potassium persulfate (KPS) as initiator. It was found that the superabsorbent containing AA-AMPS/LDH showed a significant improvement on thermal stability, swelling rate, and water absorbency in deionized water as well as in saline solution, compared with the pristine superabsorbent. Therefore, this work provides a novel method to obtain new polymer-based superabsorbents with AA-AMPS/LDH as additive.

EXPERIMENT SECTION

Materials

2-Acryloylamido-2-methylpropanesulfonic acid (AMPS) was supplied by Tokyo Kasei Industrial Ltd. *N,N'*-Methylene-bisacrylamide (NMBA) as a crosslinking agent, was obtained from Tianjin Chemical Reagent Corp (Tianjin, China). Potassium persulfate (KPS), acrylic acid (AA, distilled under reduced pressure before use), and other reagents were purchased from Beijing Chemical Reagent Factory. Deionized and decarbonated water was used in all experiments.

Preparation of NO₃-LDH

The precursor, NO₃-LDH, was synthesized by a procedure similar to that reported previously.²⁵ A solution of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O (molar ratio 2 : 1) in deionized water, was added dropwise to a solution of NaOH with vigorous agitation under a nitrogen atmosphere. The mixture was aged at 70°C for 24 h after the solution pH was adjusted to 10.0. The resulting precipitate was sepa-

rated by centrifugation, washed thoroughly with deionized water, and dried at 70°C for 24 h.

Preparation of AA-AMPS/LDH

The AA-AMPS/LDH samples were prepared via ion-exchange method. AA/AMPS with different molar ratios were neutralized by 2 mol/L NaOH in ice bath, and then the proper amount of NO₃-LDH was dispersed in the above solution with vigorous agitation under nitrogen atmosphere. The mixtures were stirred at 65°C for 48 h. The resulting precipitate was obtained as described above.

Preparation of poly(AA-co-AMPS)/LDH nanocomposite

In a typical procedure, appropriate amounts of AA and AMPS with a fixed neutralization degree of 90% (neutralized with 2 mol/L KOH) was introduced into a 250-mL four-necked flask, equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen line. Then the proper amount of AA-AMPS/LDH and NMBA (NMBA/total monomer ratio was 0.05/100) were added into the solution. After being purged with nitrogen for 30 min to remove the dissolved oxygen, the mixed solution was heated to 75°C gradually and then the initiator, KPS (KPS/total monomer ratio was 0.1/100), was introduced into the flask. The solution was stirred vigorously under nitrogen atmosphere for 3 h to complete the polymerization. The product was washed with water and dried in an oven at 100°C until the weight of the product was constant.

Two series of poly(AA-co-AMPS) superabsorbents incorporated with different type and content of LDH were synthesized by *in situ* polymerization as described above. In each series, LDH content was varied as 1, 3, 5, 7, and 10% (wt) in the total superabsorbent. NO₃-LDH as additive in superabsorbent denotes one series (hereafter named as A-1, A-3, A-5, A-7, and A-10, respectively), and AA-AMPS/LDH as additive in poly(AA-co-AMPS)/LDH ($n_{AA} : n_{AMPS} = 6 : 4$) represents the other series (named as B-1, B-3, B-5, B-7, and B-10, respectively). As a comparison sample, poly(AA-co-AMPS) superabsorbent without LDH was also prepared (named as C-0).

Characterization techniques

The XRD patterns were obtained on a Shimadzu XRD-6000 diffractometer under air condition, using Cu K α radiation ($\lambda = 0.154184$ nm) at 40 kV, 30 mA with a scanning rate of 10°/min, a step size of 0.02°/s, and a 2 θ angle ranging from 3 to 70°. The Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vector22 spectrophotometer

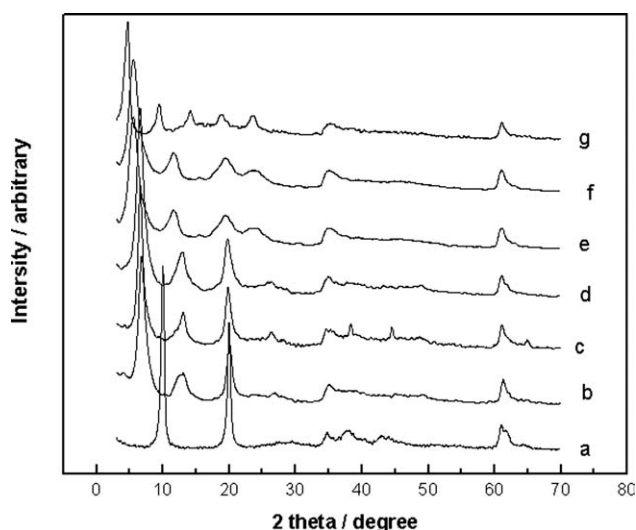


Figure 1 XRD patterns of Mg_2Al-X/LDH samples: (a) $X = NO_3^-$; (b) $X = AA$; (c–f): $X = AA/AMPS$ ($n_{AA} : n_{AMPS} = 9 : 1, 8 : 2, 7 : 3, 6 : 4$, respectively); (g) $X = AMPS$.

in the range $4000\text{--}400\text{ cm}^{-1}$, and the standard KBr disk method (1 mg of sample in 100 mg of KBr) was used. Analysis of metals was performed by inductively coupled plasma-mass ICP atomic emission spectroscopy on a Shimadzu ICPS-7500 instrument using solutions prepared by dissolving the samples in dilute hydrochloric acid. Carbon, hydrogen, and nitrogen analysis were carried out using a Perkin-Elmer Elementarvario elemental analysis instrument. Thermogravimetric (TG) and differential thermal analysis (DTA) were measured on a PCT-1A thermal analysis system under ambient atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$.

Measurement of equilibrium water absorbency and swelling rate

For the measurement of the water absorbency, a proper amount of the dry hydrogel (0.5 g) was immersed in distilled water or in various saline solutions ($NaCl$, $CaCl_2$, $FeCl_3$) with different concentrations at the ambient temperature to reach the swelling equilibrium. The resulting hydrogel was filtrated with a nylon meshwork and its surface water was removed

by blotting the sample. The water (or saline water) absorbency of the superabsorbent Q (g/g) was calculated according to the following equation:

$$Q = (M - M_0)/M_0 \quad (1)$$

where M and M_0 are the weights of swollen sample and dry sample, respectively.

Swelling rate of the superabsorbent was measured according to the following process. The sample was poured into to 500 mL distilled water. At certain time intervals, the water absorbency of the sample, Q_t , was measured based on eq. (1). The measurement condition is the same as that for equilibrium water absorbency.

RESULTS AND DISCUSSION

Characterization of AA-AMPS/LDH

XRD patterns

X-ray diffraction patterns for $MgAl-NO_3-LDH$ as well as the series of intercalated LDHs are shown in Figure 1. In each case, the XRD pattern exhibits the characteristic reflections of the LDH structure with a series of (001) peaks appearing as narrow, symmetric, strong lines at low angle. The diffraction pattern for the $MgAl-NO_3-LDH$ [Fig.1(a)] shows a typical layered structure with a basal d_{003} value of 0.89 nm, comparable with that of previously reported in the literature.²⁶ The basal spacing expanded to 1.31 nm when NO_3^- was replaced by AA in an ion-exchange reaction [Fig.1(b)]. The basal spacing increases gradually with the increase in molar ratio of AMPS/AA (Table I), with the (003) reflection progressively shifts to lower 2θ values, due to the larger size of AMPS than AA. In the case of AMPS intercalated LDH [Fig.1(g)], the d_{003} value reaches the maximum, 1.91 nm. Furthermore, the (110) reflection at about 60° 2θ shows no obvious shift after intercalation, indicating that no significant change occurred in the LDH host layers.^{27,28} XRD patterns indicate that the AA and AMPS monomers have been successfully intercalated respectively, or cointercalated into the galleries of LDH.

TABLE I
Chemical Composition, 2θ Value, and Basal Spacing of NO_3^- -LDH, AA-AMPS/LDH Samples with Different Molar Ratios

Sample	$n_{AA} : n_{AMPS}$	Chemical composition	$2\theta/^\circ$	d_{003} Spacing/nm
NO_3^- -LDH	–	$Mg_{0.68}Al_{0.32}(OH)_2(NO_3)_{0.32} \cdot 0.77H_2O$	9.98	0.89
AA-LDH	–	$Mg_{0.68}Al_{0.32}(OH)_2(AA)_{0.30}(NO_3)_{0.02} \cdot 0.62H_2O$	6.81	1.31
AA-AMPS/LDH	9 : 1	$Mg_{0.68}Al_{0.32}(OH)_2(AA)_{0.29}(AMPS)_{0.03} \cdot 0.65H_2O$	6.60	1.33
AA-AMPS/LDH	8 : 2	$Mg_{0.66}Al_{0.34}(OH)_2(AA)_{0.29}(AMPS)_{0.05} \cdot 0.67H_2O$	6.46	1.35
AA-AMPS/LDH	7 : 3	$Mg_{0.66}Al_{0.34}(OH)_2(AA)_{0.23}(AMPS)_{0.11} \cdot 0.75H_2O$	5.68	1.58
AA-AMPS/LDH	6 : 4	$Mg_{0.66}Al_{0.34}(OH)_2(AA)_{0.17}(AMPS)_{0.17} \cdot 0.74H_2O$	5.46	1.62
AMPS-LDH	–	$Mg_{0.66}Al_{0.34}(OH)_2(AMPS)_{0.34} \cdot 0.81H_2O$	4.58	1.91

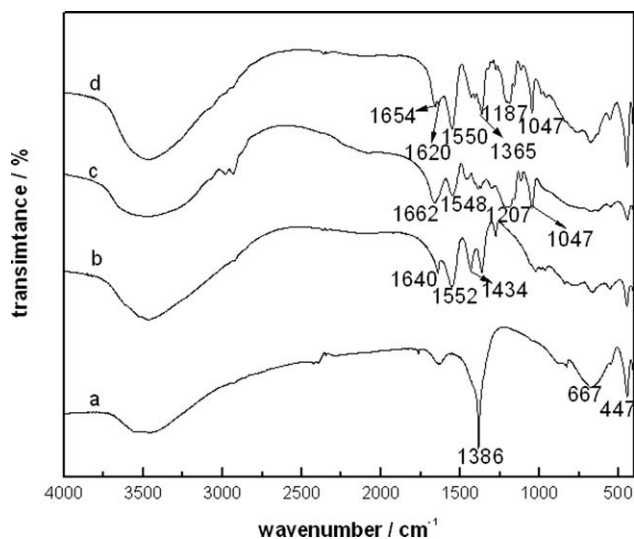


Figure 2 FTIR spectra of Mg_2Al-X/LDH samples: (a) $X = NO_3^-$; (b) $X = AA$; (c) $X = AMPS$; (d) $X = AA/AMPS$ ($n_{AA} : n_{AMPS} = 6 : 4$).

Elemental analysis

In agreement with the XRD results, elemental analysis of AA-AMPS/LDH confirmed the cointercalation of AA and AMPS into the LDH (Table I). The Mg/Al molar ratio was in well accordance with the normal ratio of 2. As shown in Table I, the AA/AMPS molar ratios for the samples are close to the expected values, i.e., close to the initial input ratio of AA/AMPS. This indicates that the coprecipitation in the presence of organics was complete leading to a single phase in each case as shown in XRD. The results also reveal that the relative contents of the cointercalated guests in LDH could be controlled by changing the initial input ratio.

IR-spectroscopy

The FTIR spectra of NO_3^- -LDH, AA-LDH, AMPS-LDH, and AA-AMPS/LDH (with AA/AMPS molar ratio of 6 : 4) are displayed in Figure 2. A broad absorption band between 3600 and 3200 cm^{-1} associated with the stretching mode of hydrogen-bonded hydroxyl groups from both the hydroxide layers and interlayer water are observed in all the spectra. For the NO_3^- -LDH [Fig. 2(a)], the absorption centered at 1386 cm^{-1} is assigned to the presence of nitrate anions within the structure. For the AA-LDH [Fig. 2(b)], the appearance of acrylate anion vibration at 1640 cm^{-1} ($\nu_{C=C}$) is noted and NO_3^- almost disappears. The symmetric and asymmetric stretches of $RCOO^-$ at 1552 and 1434 cm^{-1} , respectively, are also evident. For the sample of AMPS-LDH [Fig. 2(c)], $\nu_{C=C}$ (1624 cm^{-1}), C=O stretching (1662 cm^{-1}), N-H bending (1548 cm^{-1}),

asymmetric and symmetric stretching of S=O (1207 and 1047 cm^{-1}) appear. In the case of AA-AMPS/LDH [Fig. 2(d)], the absorption bands of C=C stretching (1620 cm^{-1}), C=O stretching (1654 cm^{-1}), N-H bending (1550 cm^{-1}), asymmetric and symmetric stretching of S=O (1187 and 1047 cm^{-1}) as well as $RCOO^-$ (1550 and 1365 cm^{-1}) are all observed, indicating that AA and AMPS are co-intercalated into galleries of LDH. The typical vibrations of M-O and M-OH (M=Mg, Al) in the LDH appear at around 447 and 667 cm^{-1} in both the NO_3^- -LDH and the intercalated LDH samples, which indicates that the layered structure was maintained after the cointercalation of AA and AMPS.

Measurement of poly(AA-co-AMPS)/LDH superabsorbents

XRD analysis

XRD patterns of the B-5 (with 5 wt % AA-AMPS/LDH) and B-10 (with 10 wt % AA-AMPS/LDH) superabsorbents are shown in Figure 3, with the AA-AMPS/LDH ($n_{AA} : n_{AMPS} = 6 : 4$) as a comparison sample. Compared with Figure 3(c), it was found that no reflection corresponding to the LDH structure was observed for both of the two superabsorbent composites [Fig. 3(a,b)]. The absence of reflections of LDH structure indicates that the LDH layers are exfoliated or highly expanded in superabsorbent composites. The expansion mechanism probably originates from the growing polymer chains by interlayer monomers pushing apart the layers when polymerization occurs.²⁹ This result is in conformity with Zhang's study in the chitosan-g-poly(acrylic acid)/montmorillonite superabsorbent nanocomposite.³⁰

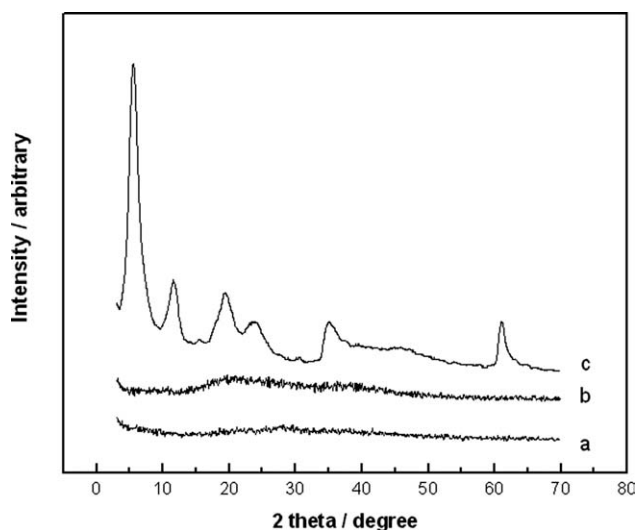


Figure 3 XRD patterns of (a) B-5, (b) B-10, (c) AA-AMPS/LDH ($n_{AA} : n_{AMPS} = 6 : 4$).

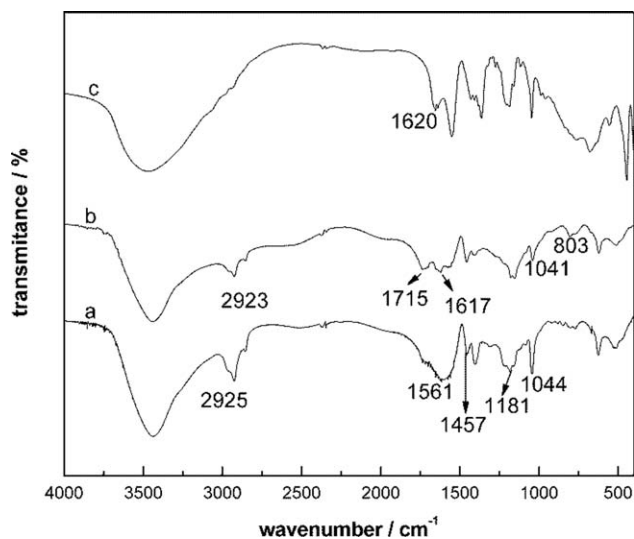


Figure 4 FTIR spectra of (a) C-0, (b) B-10, and (c) AA-AMPS/LDH ($n_{AA} : n_{AMPS} = 6 : 4$).

FTIR spectra

FTIR spectra of C-0, B-10 superabsorbent and the AA-AMPS/LDH are shown in Figure 4. The characteristic absorption band around 1561 cm^{-1} in the spectrum of C-0 is attributed to the C=O stretching vibrations of the carboxylic group, while the absorption bands at 1044 , 1181 , and 1457 cm^{-1} belong to symmetric and asymmetric stretching vibrations of the S=O and C(N group of AMPS, respectively). The characteristic band of $-\text{CH}_2-$ stretching of AA and AMPS appears at 2925 cm^{-1} , and no absorption band of C=C stretching can be observed in the spectrum. All of these indicate the existence of poly(AA-co-AMPS) copolymer for the sample of C-0 [Fig. 4(a)]. The main differences between B-10 and C-0 are the appearance of Al-O at 803 cm^{-1} , and some band shift (for example, the symmetric stretching vibration of the S=O shifts from 1044 cm^{-1} to 1041 cm^{-1}) in the spectrum of B-10 [Fig. 4(b)], indicating the coexistence of LDH additive. Compared with AA-AMPS/LDH [Fig. 4(c)], the C=C stretching at 1620 cm^{-1} disappears in the spectrum of B-10 [Fig. 4(b)], which indicates that free radical polymerization of the monomers in and out of the galleries of LDH occurs in the preparation process of B-10. This is in accordance with the XRD results that the LDH layers were exfoliated or highly expanded. The results above clearly show that interactions exist between the AA-AMPS/LDH and polymer matrix, and poly(AA-co-AMPS)/LDH nanocomposite was obtained by *in situ* copolymerization.

TG-DTA

TG-DTA method was used to evaluate the thermal stability of the superabsorbent and the results are

displayed in Figure 5. As can be seen from the thermal grams of C-0 and B-5 nanocomposite, the decomposition for the two samples is somewhat similar, showing three weight loss stages. The first step below 200°C corresponds to the loss of moisture existed in the samples. The second step (300 – 450°C) is due to the thermal decomposition of the poly(AA-co-AMPS) chains backbone, with the sharp weight loss of B-5 starting at about 350°C , 50°C higher than that of C-0 (ca. 300°C). In the DTA curves, the exothermic peak of sample C-0 appeared at 350°C , while the peak of sample B-5 was observed at a higher temperature (400°C). The third step (450 – 700°C) is attributed to the further decomposition of the sample. The TG-DTA results reveal that the sample of B-5 possesses higher thermal stability than that of C-0, indicating that AA-AMPS/LDH as an additive can improve the thermal stability of the poly(AA-co-AMPS)-based superabsorbent.

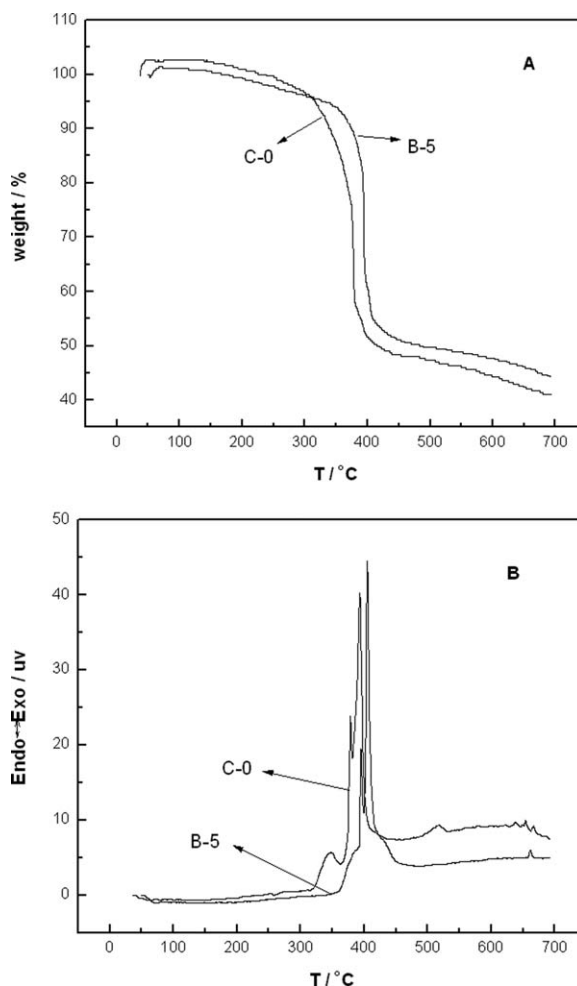


Figure 5 TG (A) and DTA (B) curves for the C-0 and B-5 superabsorbents.

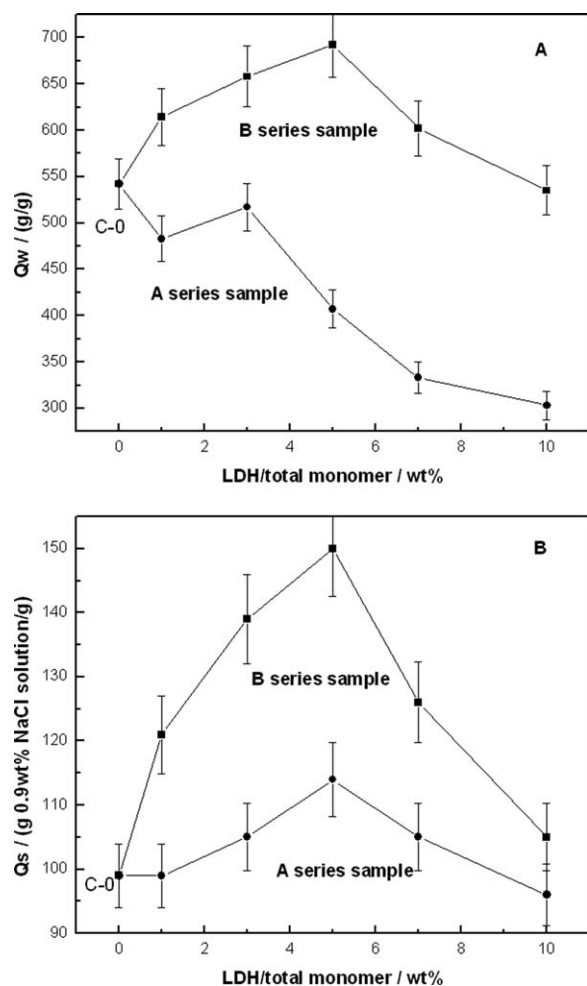


Figure 6 Water absorbency of poly(AA-co-AMPS)/LDH nanocomposite superabsorbents: (A) in pure water; (B) in 0.9 wt % NaCl solution. The swelling time was 30 min.

Study on the properties of the superabsorbents

Effects of LDH type and content on equilibrium water absorbency

Figure 6 presents the variation of equilibrium water absorbency for the poly(AA-co-AMPS)/LDH superabsorbent composites in deionized water and in 0.9 wt % NaCl solution respectively, with two different LDHs (i.e., NO₃-LDH as A series and AA-AMPS/LDH as B series) as additives and different LDH contents. It can be seen that the LDH type has a great effect on water absorbency, i.e., the water absorbency of the B series is much higher than that of A series in both pure water and saline solution. As referred in the introduction part, the cointercalation of AA and AMPS into LDH galleries makes it easier for exfoliation compared with the NO₃-LDH. This exfoliation could increase the particle surface area and result in an increase in the interaction between the poly(AA-co-AMPS) matrix and LDH dispersed phase. Furthermore, the cointercalated AA and AMPS can also provide a compatible

organic/inorganic nanocomposite through the reaction between the vinyl groups of the AA and AMPS monomers inside and outside LDH.³¹

It can be also found that the water absorbency at equilibrium in deionized water gradually increases as the AA-AMPS/LDH content increases from 0 to 5 wt % and decreases upon its further increase [Fig. 6(A,B series)]. The optimum absorbency is 692 g/g, increased by 27.7% than that of C-0 (542 g/g). The explanation for this is straightforward. When a small amount of AA-AMPS/LDH (lower than 5 wt %) is introduced, it acts as an additional crosslinking network point^{32,33} in the composite, and thus improves the hydrophilic network by increasing the length of the polymeric chain. However, further increasing AA-AMPS/LDH amount result in the generation of more crosslink points, leaving less space for water molecules to enter. Additionally, the amount of hydrophilic groups in the composite decreases as the content of AA-AMPS/LDH rises, leading to the decrease both in hydrophilicity of the composites and in the osmotic pressure difference between the polymeric network and external solution.³⁴ Therefore, a superabundant amount of LDH reduces the absorbency of the composite.

The tendency and principle of water absorbency in saline solution (0.9 wt % NaCl solution) for the superabsorbent composites are similar to those of in distilled water, except with a lower absorbency [Fig. 6(B)]. The ionic intensity in saline water largely reduces the infiltration pressure of the polymer network and hence reduces the water absorbency of the superabsorbent. The addition of AA-AMPS/LDH improves the water absorbency significantly, and the maximum was observed with 5 wt % LDH, increased by 51.5% compared with the pristine superabsorbent (C-0). More interestingly, the water absorbency in saline solution was also increased by adding NO₃-LDH with respect to that of C-0 (with the optimal addition of 5 wt %), but the efficiency is much lower than that of AA-AMPS/LDH as additive.

Effects of LDH type on equilibrium water absorbency in various saline solutions

It is well known that water solutions usually contain various salts at most circumstances. To expand the applications of this superabsorbent, especially for horticulture, hygienic products and industrial applications, the water absorbency of the as-obtained superabsorbents incorporated with different LDH was investigated in various saline solutions. Table II illustrates the relationship between swelling capacity of the A-5 and B-5 superabsorbents and concentration of salt solutions (NaCl, CaCl₂, and FeCl₃). It can be seen that water absorbency for the two composites in various external saline solutions with the

TABLE II
Water Absorbency in Salt Solutions with Various Concentrations

Salt concentration (mmol/L)	Water absorbency (g/g)					
	A-5			B-5		
	NaCl	CaCl ₂	FeCl ₃	NaCl	CaCl ₂	FeCl ₃
1.5	312	264	212	412	292	288
3.0	292	192	144	404	224	188
5.0	232	132	124	340	152	140
7.0	212	96.0	84.0	320	132	124
22.5	144	52.0	37.0	200	71.0	59.0

same concentration is always in the order of B-5 > A-5, which is similar to that of in deionized water. Moreover, the type and concentration of the salt added to the swelling medium have great effects on absorbency capacity of superabsorbents. Water absorbency for the two composites decreases in the order NaCl > CaCl₂ > FeCl₃. This may be related both to the different complexing ability of the hydrophilic groups in the superabsorbent network as well as the valence of the cations. According to the formation constants with EDTA (ethylenediamine tetraacetic acid) of the three cations (the complexing ability follows the order: Fe³⁺ > Ca²⁺ > Na⁺), the water absorbency decreases with the increase of complexing ability.

Furthermore, water absorbency for the two superabsorbent composites decreases upon increasing the concentration of various external saline solutions (shown in Table II). This can be attributed to the difference in ionic osmotic pressure between the gel and the external solution, which decreases with an increase of ionic strength of the salt solutions. In addition, the penetration of counterions (Na⁺, Ca²⁺, Fe³⁺) into the anionic polymeric network leads to the screening effect on hydrophilic group (–COO[–]), which also decreases water absorbency of the superabsorbents.

Study on swelling rate of the superabsorbents in deionized water

The absorption rates in deionized water for the samples of C-0, A-5, and B-5 were also studied respectively, and the results are presented in Figure 7. It has been reported that the swelling rate of superabsorbent is mainly determined by swelling ability, surface area, particle size and density of the polymer.³⁵ It can be seen from Figure 7(A) that the sample of B-5 shows both much faster swelling rate and larger water absorbency than those of C-0 and A-5. Figure 7(B) also reveals that the initial swelling rate (0 to 30 min) is in the order B-5 > A-5 > C-0. Initial swelling rate is primarily due to the penetration of water into the polymeric network through diffusion

and capillarity according to Lee et al.¹³ A higher initial swelling rate in distilled water is obtained when AA-AMPS/LDH is introduced into the poly(AA-co-AMPS) matrix. This is possibly because the capillarity is more evident in the network with the addition of AA-AMPS/LDH, which accelerates the penetration of water molecules into the polymeric network.

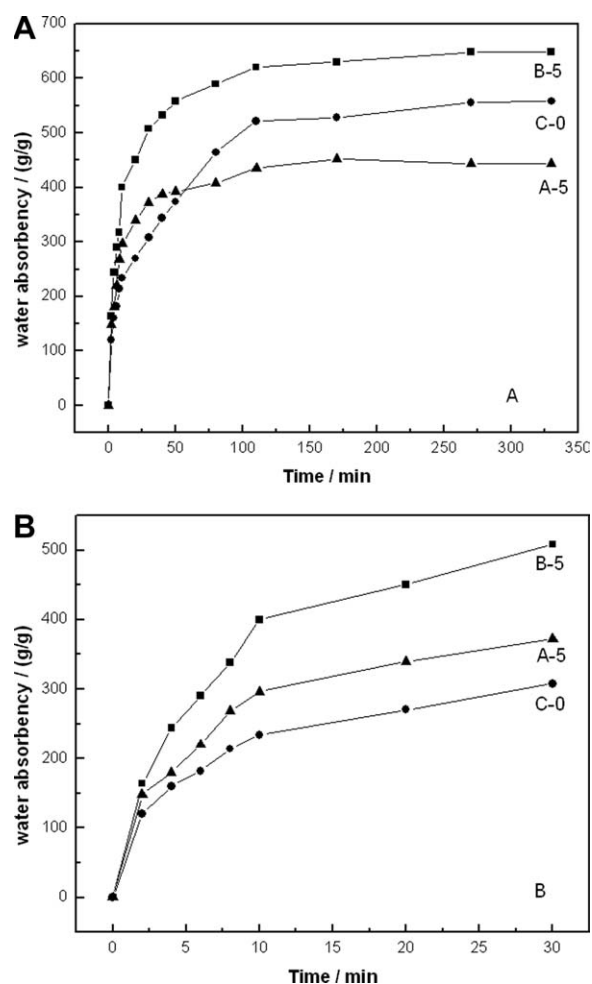


Figure 7 Swelling rates in deionized water for C-0, A-5, and B-5 superabsorbent composites in the time range: (A) 0–330 min; (B) 0–30 min.

CONCLUSIONS

The monomers of AA and AMPS were cointercalated into galleries of Mg₂Al (LDH with different molar ratios by ion-exchange method. A novel kind of polymer-based nanocomposite superabsorbent was prepared through *in situ* free-radical aqueous copolymerization of AA and AMPS, with AA-AMPS/LDH as additive, *N,N'*-methylenebisacrylamide (NMBA) as crosslinker and potassium persulfate (KPS) as initiator. The sample with 5 wt % AA-AMPS/LDH was demonstrated as a water superabsorbent in detail by comparison study. The B-5 sample exhibits a water absorbency of 692 g/g in distilled water and 150 g/g in 0.9 wt % NaCl solution, increased by 27.7% and 51.5% compared with the pristine poly(AA-co-AMPS) matrix. In addition, the samples of B series (with AA-AMPS/LDH as additive) show much higher water absorbency and faster swelling rate than those of A series (with NO₃-LDH as additive). Based on the results above, it can be concluded that the addition of AA-AMPS/LDH into the poly(AA-co-AMPS) matrix can not only enhance equilibrium water absorbency both in distilled water and in various saline solutions, but also improve its thermal stability and swelling rate, compared with the pristine superabsorbent.

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