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Synthesis and properties of sodium alginate/Na$^+$rectorite grafted acrylic acid composite superabsorbent via ^{60}Coγ irradiation

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ABSTRACT

Sodium alginate/Na$^+$rectorite-graft-poly acrylic acid (SA/Na$^+$REC-g-PAA) composite superabsorbent was prepared via ^{60}Coγ irradiation in methanol solution and nitrogen protection. The effect of the preparation conditions on graft ratio, graft efficiency and absorption of water were investigated. The structure and morphology were analyzed by IR, XRD, TEM and SEM. The results showed that the optimal condition was that the amount of Na$^+$REC was 2 wt%, the ratio of SA/Na$^+$REC to AA was 10 wt%, total dose was 9.0 kGy and volume ratio of methanol to water was 8:2. SEM showed that it is much easier to obtain porous products through ^{60}Coγ irradiation than chemical initiator. The mechanism of graft copolymerization via ^{60}Coγ irradiation was discussed. The water absorption of the graft copolymer in salt solutions of different ionic strengths was also measured, from which the superabsorbent properties are found to be saline sensitive. Ionic strength markedly decreased the water absorption of the sodium alginate grafted superabsorbent composites.

1. Introduction

Superabsorbent polymers are lightly crosslinked networks of hydrophilic polymer chains, which can absorb very large amount of water and retain water even under pressure, so these polymers have been not only found extensive commercial applications as sorbents in personal care products such as infant diapers, feminine hygiene products, and incontinence products, but also gained considerable attentions for a variety of more specialized applications including enzyme immobilization, agricultural mulches and controlled release devices, etc. (Chang, Duan, Cai, & Zhang, 2010; Chen, Liu, Tan, & Jiang, 2009; Jamshidi, Ahmad Khan Beigi, Kabiri, & Zohuriaan-Mehr, 2006; Toshio, Ikumi, Yuko, & Rumiko, 2005). Superabsorbent polymers include synthetic and natural polymers, although synthetic polymers have large water absorbing capacities, those prepared from natural graft copolymers have a greater demand in industry due to their low cost, bio-degradability, low toxicity and friend-environmental nature (Li, Zhang, & Wang, 2007; Pourjavadi, Harzandi, & Hosseinzadeh, 2004; Toshio et al., 2005; Wang & Wang, 2009; Zhang, Shen, Li, & Fang, 2003). Recently, extensive attention has been directed toward polymer/clay composite superabsorbent due to their relative low production cost, high gel strength, excellent thermal stability, high water absorbency and resistance to salt, etc. Li et al. (2007) prepared starch/attapulgite superabsorbent composite, which has excellent water absorbency and water retention under load. Zhang et al. (2003) synthesized poly(methyl methacrylate)/OMMT nanocomposites, which exhibits improved storage modulus and glass transmission temperature.

Sodium alginate (SA) is a kind of polysaccharide in nature, which is mainly composed of (1–4)-linked β-D-mannuronic acid units and α-L-guluronic acid units (Teli, Gokavi, & Aminabhavi, 2007). The gel forming property, biocompatibility, nontoxicity and biodegradability of SA suggest it would have application prospects, as medical materials, sanitary materials, tissue engineering materials, controlled-release devices, and matrices for enzyme immobilization, etc. (Caykaraa, Demircia, Eroglub, & GuvenSuh, 2005; Smitha, Sridha, & Khan, 2005).

Rectorite has a layered structure and is easily available in China. In addition, REC exhibits good mechanical and thermal properties as well as excellent UV resistance, etc. (Toshio et al., 2005). A single rectorite layer has a thickness of about 2 nm and has reactive –OH groups on its surface, making it possible to prepare polymer/REC composites (Wang, Du, Luo, Lin, & John, 2007; Wang, Sabina, Du, & Kjell, 2010).

As an extension of our previous work on SA/Na$^+$REC composite (Yang, Liang, Zhang, He, & Wang, 2009), SA/Na$^+$REC-g-PAA composite superabsorbent was obtained by ^{60}Coγ-irradiation. The mechanism of graft copolymerization via ^{60}Coγ irradiation was preliminary studied. The main factors affecting the preparation

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of SA/Na$^+$REC-g-PAA composite superabsorbent via ^{60}Coγ irradiation were discussed. The structure, morphology and properties of the composite superabsorbent were investigated. Compared with superabsorbent polymer prepared by initiator, SA/Na$^+$REC-g-PAA composite superabsorbent prepared via ^{60}Coγ irradiation has the advantages of easy control of processing, no necessity to add any initiators or cross-linkers which may be harmful and difficult to remove.

2. Experimental

2.1. Materials

SA was obtained from Kemiou Chemical Co. Ltd. (Tianjing, China). REC was purchased from Hubei Zhongxiang Rectorite Mine (Wuhan, China), its cationic exchange capacity (CEC) is 45 mequiv./100 g, and its d-space value is 2.1225 nm; acrylic acid was made at Shanghai Wulian Chemical Factory (Shanghai, China); sodium pyrophate was purchased from Tianjin Boddy chemical Co. Ltd. (Tianjing, China). Glycerine was obtained from Tianjin Daqiuzhuang Froth Plastics plant (Tianjing, China); the cobalt-60 source was from The Second Woolen Mill of Shanxi (Xianyang, China).

2.2. Synthesis of Na$^+$REC

REC was calcined in 850 °C for 4 h to increase its white degree and improve its activity (Castelein, Soulestin, & Bonnet, 2001; Chandrasekhar & Ramaswamy, 2002). Then calcined REC was treated with sodium pyrophate in order to intensify insertion effect of SA. The synthesis of Na$^+$REC was performed as following steps. Firstly, 10.0 g of REC was dissolved in deionized water to obtain 15 wt% suspending solution. Secondly, 0.3 g sodium pyrophate was added into the suspending solution with stirring and maintained at the condition for 0.5 h to obtain a mixture. Thirdly, the mixture was slowly heated to 60 °C and maintained at that temperature for 12 h. Fourthly, the mixture was cooled to 30 °C, then it was filtered on a Buncher filter and dried. The product is coded as Na$^+$REC.

2.3. Preparation of SA/Na$^+$REC composite

SA/Na$^+$REC composite was prepared via a solution-mixing processing technique. The preparation was performed by following steps. Na$^+$REC was dissolved in deionized water to obtain 3 wt% suspending liquid through ultrasonic dispersion for 10 min. SA was dissolved in deionized water to form a homogeneous solution of 3 wt% polysaccharide. The SA solution was slowly mixed into the Na$^+$REC suspending liquid using homogenizer for 5 min, then glycerine (10%, w/w based on SA) as the plasticizer was dropped into the mixture. The mixture was stirred with a high speed shear mixer for 3 h and salivated on a dust-free glass plate with a uniform thickness for curing by a procedure of 50 °C for 5 h. After dryness, the resultant material is milled to get SA/Na$^+$REC composite with a particle size in the range of 160–200 mesh (Yang et al., 2009).

2.4. Preparation of SA/Na$^+$REC-g-PAA composite superabsorbent

A weight quantity of SA/Na$^+$REC composite and distilled water was put into a 250 mL three-necked flask equipped with a stirrer, a condenser, and a nitrogen line. The solution was heated to 60 °C for 30 min under a nitrogen atmosphere, acrylic acid which was neutralized to the extent of 85% (molar percent) by the addition of 40% NaOH solution (mass percent) and 10 mL methanol solution were added, and then irradiated under gamma-rays. The mixture after irradiation was dried in a vacuum oven at 56 °C for 24 h to obtain crude product. The resultant material is milled and riddling to get SA/Na$^+$REC-g-PAA superabsorbent with a particle size in the range of 40–80 mesh.

2.5. Measurements

The crude product was extracted in a Soxhlet's extractor with methanol for 24 h. The extracted product was dried in a vacuum oven at 65 °C for 24 h and weighed to determine the amounts of the graft copolymer. The grafting ratio (% G), grafting efficiency (% E) were calculated by using the following formulas:

$$G\ \ (\%) = \left(\frac{W_2}{W_0}\right) \times 100\% \qquad (1)$$

$$E\ \ (\%) = \left(\frac{W_2}{W_1}\right) \times 100\% \qquad (2)$$

where W_0, W_1, and W_2 denote the weight of SA/Na$^+$REC, crude product and graft copolymer, respectively.

The absorbency (Q) of superabsorbent composite was measured by following procedure: a weighted quantity of the superabsorbent composite was immersed in distilled water or saline solutions (0.9 wt% NaCl, 0.9 wt% $CaCl_2$, 0.9 wt% $FeCl_3$, 0.9 wt % Na_2SO_4 and 0.9 wt% Na_3PO_4) at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtration over 300 mesh screen. The absorbency (q_v) of superabsorbent composite was determined by weighing the swollen samples, and calculated using the following formula (Li et al., 2007; Toshio et al., 2005; Zhang et al., 2003):

$$q_v = \frac{W_2 - W_1}{W_1} \qquad (3)$$

where W_1 is the weight of the dry sample and W_2 is weight of the water-swollen sample.

Water retention of the swollen superabsorbent composites was determined by a heating oven test at 40 °C for 24 h.

The gel modulus was determined by following steps. The swollen hydrogels were compactly placed into a glass tube with one end sealed with a 280 mesh fabric, then a gradually enlarged pressure was loaded on until gel rupture.

The ultraviolet resistance was measured after the sample was radiated by short wave ultraviolated radiation, Model ZF-1 (Shanghai, China) for one month, the radiated power was 6 W, the distance between the sample and the light source was 0.1 m.

The structures of composite superabsorbent were investigated using DPmax23C X-ray diffraction (XRD) instrument (Rigaku, Osaka, Japan) with Cu K$_\alpha$ (λ = 0.154 nm) radiation source. The X-ray generator operated at 35 kV and 50 mA, the reflection angle 2θ was monitored from 2.0° to 30° at a scanning speed of 2°/min and a step size of 0.02°.

FT-IR spectra of composite superabsorbent were recorded with KBr pellets on a Fourier transform infrared spectrometer (Model VECTOR-22, Shimazu, Kyoto, Japan).

The morphology of product was observed using scanning electron microscopy (SEM) (KYKY1000B, Scientific Instrument Factory CAS, Beijing, China). Prior to observation, samples were arranged on metal grids by using double-sided adhesive tape, in addition, samples were coated with gold under vacuum.

The exfoliation and molecular dispersion of clay layers in nanocomposites were observed using a Hitachi H-800 transmission electron microscopy (TEM) instrument (Hitachi, Japan) with an acceleration voltage of 150 kV, and the ultra-thin samples with a thickness of less than 1 μm were microtomed in liquid nitrogen using LKB Bromma 2088 cutter.

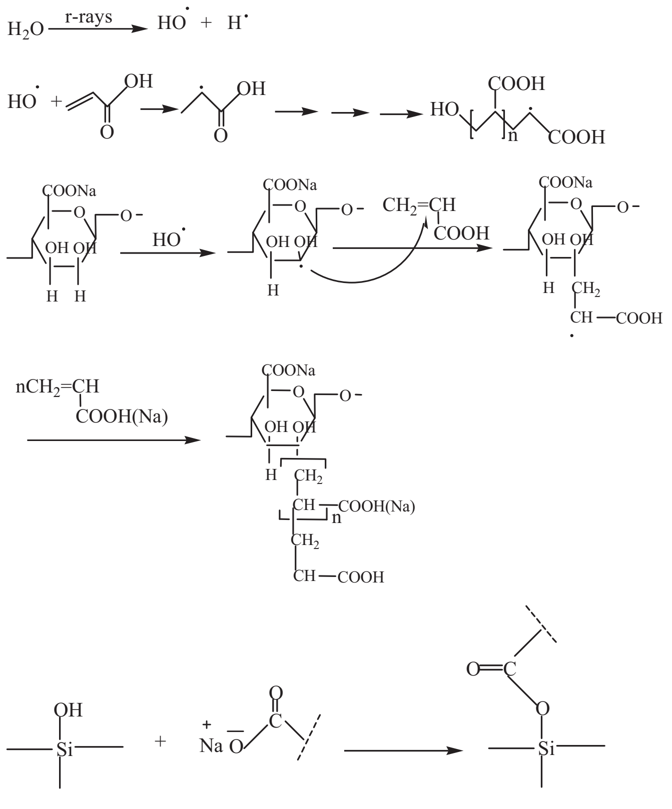


Fig. 1. Scheme of graft-copolymerization of SA, AA and Na$^+$REC.

3. Results and discussion

3.1. Mechanism of irradiation graft

Graft copolymerization of poly acrylic acid (PAA) onto the backbone of SA via ^{60}Coγ-radiation attributes to free radical reaction. The mechanism for polymerization process is showed in Fig. 1. First, most of the irradiation energy is absorbed by the water to produce hydroxyl radicals. Initiation occurs mainly by an indirect effect. Second, Hydroxyl radical was added to one side of the acrylic acid double bond leading to the formation of an unpaired spin on the other side of a vinyl bond (Bardajee, Pourjavadi, Soleyman, & Sheikh, 2008; Ge, Pang, & Luo, 2006; Suda, Kanlaya, & Manit, 2002), then acrylic homopolymerization started. At the same time hydroxyl radical attacks SA leading to the breakage of C–H bond to form SA-based radical, then it will react with acrylic acid molecule, followed by propagation leading to growth of a branched chain, following the network was formed via crosslinking. In addition, the carboxylate groups of the grafted poly (acrylic acid) can react with the –OH groups on the Na$^+$REC surface to produce ester. It also can be confirmed by absorption band at 1719 cm^{-1} from FTIR spectra of SA/Na$^+$REC-g-PAA composite superabsorbent. These reactions should lead to the formation of poly acrylic acid grafted onto SA and Na$^+$REC.

3.2. Effect of Na$^+$REC amount on the graft copolymerization

Fig. 2 shows the influence of Na$^+$REC amount on the grafting ratio, grafting efficiency and water absorption of SA/Na$^+$REC-g-PAA composite superabsorbent. The results showed that grafting ratio, grafting efficiency and water absorption of the composite increase with increasing Na$^+$REC content when the amount of Na$^+$REC was less than 2 wt% (based on SA). The reason lies in low concentration Na$^+$REC is well dispersed in the SA matrix so that SA and AA can be intercalation into layers of Na$^+$REC, and then enhance graft copolymerization. Furthermore OH on the surface of Na$^+$REC could react with acrylic acid, which could improve the polymeric network. However the aggregation of Na$^+$REC clusters at higher Na$^+$REC content causes the grafting ratio and grafting efficiency of composites decrease. At the same time Na$^+$REC clay mineral particle in network acted as crosslinking point, which caused the formation of an additional network and decreased the available free volume within the superabsorbent composite. Additionally, the content of hydrophilic groups is lower at a higher Na$^+$REC content, and then the osmotic pressure difference decreases, which also results in the shrinkage of the composite (Wu, Wei, Lin, & Lin, 2003; Zhang, Wang, & Wang, 2007). The optimal amount of Na$^+$REC was 2 wt%.

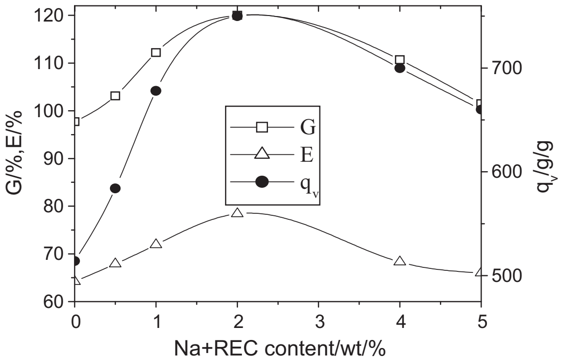


Fig. 2. Effect of Na$^+$REC content on the graft copolymerization.

3.3. Effect of the ratio of SA/Na$^+$REC to AA on the graft copolymerization

The effect of the ratio of SA/Na$^+$REC to AA on the grafting ratio, grafting efficiency and water absorption of product is summarized in Fig. 3. When the weight ratio of SA/Na$^+$REC to AA is in the range of 0–10 wt%, the grafting ratio increase. Beyond 10 wt%, the grafting ratio decreases. Firstly, the main function of SA/Na$^+$REC composite is to afford backbone for the graft copolymerization. When the amount of SA/Na$^+$REC gradually increases, the number of the active grafting sites on the sodium alginate and Na$^+$REC increase, leading to more number of monomers can diffuse to graft onto the SA and Na$^+$REC. However, with further increasing SA/Na$^+$REC composite content, the viscosity of the system improves, resulting in restriction of decentralization of SA/Na$^+$REC and the restricted movement of AA in the system and the inhibition of the propagating chain radicals, so the grafting ratio, grafting efficiency and water absorption decrease. The optimal ratio of SA/Na$^+$REC to AA was 10 wt%.

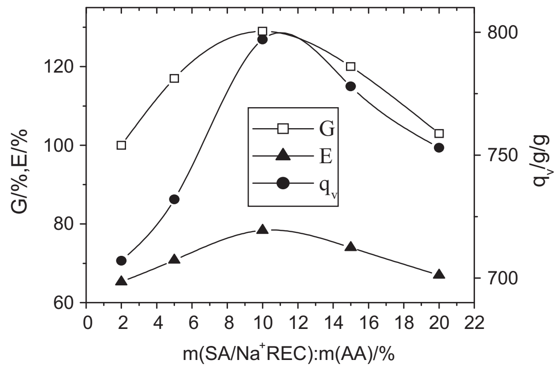


Fig. 3. Effect of the ratio of SA/Na$^+$REC to AA on the graft copolymerization.

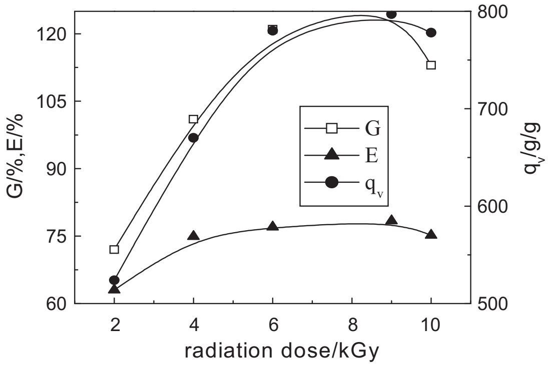


Fig. 4. Effect of the total dose on the graft copolymerization.

3.4. Effect of the total dose on the graft copolymerization

Fig. 4 shows the effect of the total dose on the grafting ratio, grafting efficiency and water absorption of SA/Na$^+$REC-g-PAA composite superabsorbent. Increasing the total dose increases the hydroxyl radical density, which increase the number of active grafting sites on the sodium alginate backbone. However, when the total doses are higher than 9.0 kGy, the homopolymer content increases and grafting efficiency decreases with increasing total dose. This may be because the higher irradiation dose gives a large amount of radiolysis products, leading to initiate homopolymerization rather than grafting reaction. Moreover too high concentration of the radicals tends to terminate through recombination before obtaining adequate grafting. In addition, too high total dose, the radiation may degrade naturally occurring sensitive trunk polymers like SA as well as graft copolymer. The optimal total dose is 9.0 kGy.

3.5. Effect of irradiation susceptivity intensifier on the graft copolymerization

It can improve the grafting ratio of product that adding methyl alcohol solution in reaction system, which is sensitive to irradiation and can swell polymer. The reason lies in methyl alcohol can produce a great deal of unstable hydrogen atoms, which make new active grafting sites.

$$CH_3OH_2{}^{+}\xrightarrow{\gamma\text{-rays}}CH_3OH+H^{\bullet}$$

Fig. 5 shows the effect of the volume ratio of methanol to water on the grafting ratio, grafting efficiency and water absorption of SA/Na$^+$REC-g-PAA composite superabsorbent. Initially, higher the volume ratio of methanol to water leads to higher grafting ratio, grafting efficiency and the water absorbency, but when the volume ratio is higher than 8:2, the parameters above mentioned of the composite superabsorbent decline. This is because more content of methanol can initiate more H$^{\bullet}$ resulting in more active grafting sites. However too high volume ratio causes the produced polymer be difficult to swell in methanol holding back stretch of macromolecule chain. The optimal volume ratio of methanol to water was 8:2.

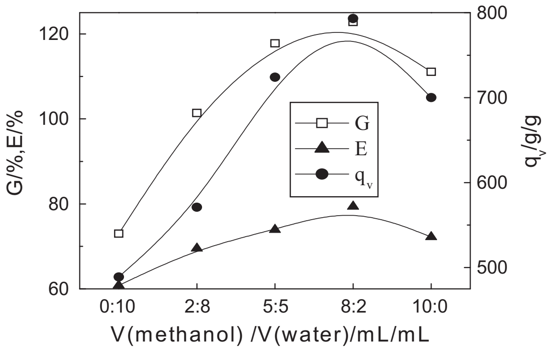


Fig. 5. Effect of irradiation susceptivity intensifier on the graft copolymerization.

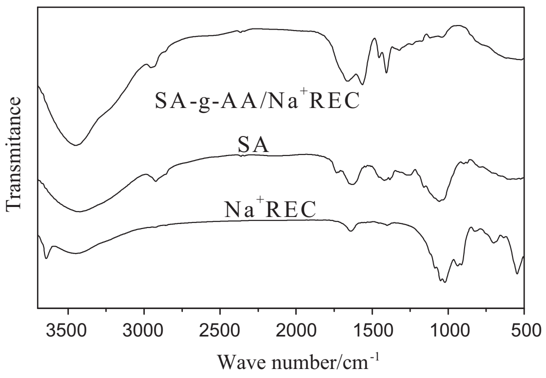
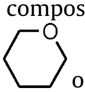


Fig. 6. FTIR spectra of Na$^+$REC, SA and SA/Na$^+$REC-g-PAA.

3.6. Structure and morphology of SA/Na$^+$REC-g-PAA composite superabsorbent

Fig. 6 shows FTIR spectra of Na$^+$REC, SA and SA/Na$^+$REC-g-PAA. Comparing with Na$^+$REC, the intensity of the absorption bands at 3431 cm^{-1} ascribing to the bending vibration of–OH increases in the spectrum of SA/Na$^+$REC-g-PAA, and the absorption band at 3616 cm^{-1} of Na$^+$REC disappears, implying that the OH groups on Na$^+$REC participate in the reaction with acrylic acid monomers. Absorption band at 1719 cm^{-1} also indicates esterification reaction between Na$^+$REC and poly (acrylic acid). By comparison with the infrared spectra of SA and superabsorbent composite, the absorption peak at 998 cm^{-1} attributed to C–H of  on SA still exists, suggesting that the ring of SA was not opened in the reaction, gamma-rays only produce free radicals at active site of C-2 or C-3 hydroxyl of the sodium alginate backbones (Fig. 1). New absorption bands at 1456 cm^{-1} (C–H), 1405 cm^{-1} (symmetric –COO– stretching) appear in the spectrum of SA/Na$^+$REC-g-PAA, indicating the existence of PAA chains (Wu et al., 2003; Zhang et al., 2007). The IR analysis results indicated that the graft copolymerization of acrylic acid monomer on both Na$^+$REC and SA took place during polymerization process and the resulting product was a composite based on PAA incorporating with Na$^+$REC and SA.

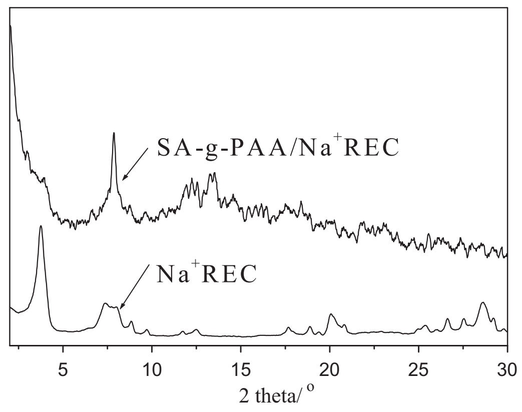


Fig. 7. X-ray diffraction patterns of Na$^+$REC and SA/Na$^+$REC-g-PAA.

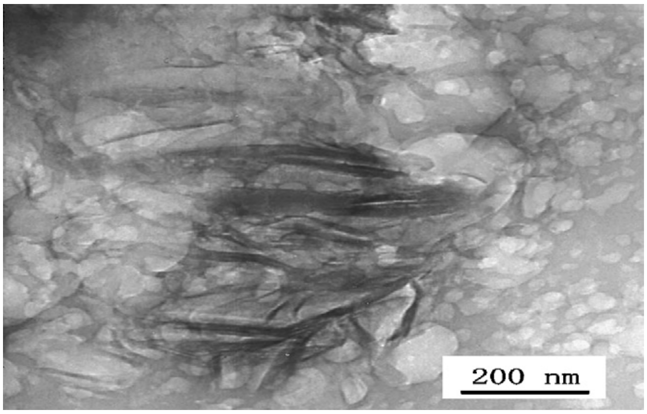


Fig. 8. TEM photograph of SA/Na$^+$REC-g-PAA composite superabsorbent.

Fig. 7 shows X-ray diffraction patterns of Na$^+$REC and SA/Na$^+$REC-g-PAA. A strong peak corresponding to a basal spacing of 2.2073 nm is observed in the X-ray diffraction pattern of Na$^+$REC, which shifts to low angle range, and the (0 0 1) diffraction pattern almost can not be observed in the X-ray diffraction pattern of SA/Na$^+$REC-g-PAA, implying that the morphology of SA/Na$^+$REC-g-PAA composite superabsorbent is a combination of intercalation and exfoliation. The conclusion can be confirmed by TEM micrograph.

TEM was also used to visually evaluate the degree of intercalation and the amount of aggregation of clay clusters. Fig. 8 shows TEM micrograph of SA/Na$^+$REC-g-PAA composite superabsorbent, in which the gray areas represent the silicate layers in the polymer matrix (bright). From the TEM results, the clay mineral platelets were well dispersed into matrix indicating a nanocomposite hydrogel. After careful observation, it can be also seen from Fig. 8 that intercalated and exfoliated structures coexist in the polymer matrix thus preventing the extending of cracks and reducing the volume shrinkage of polymer matrix during the coagulating course.

The SEM photographs of SA/Na$^+$REC-g-PAA composite superabsorbent initiated by kalium persulphate and that via ^{60}Coγ-radiation are shown in Fig. 9. It can be seen that SA/Na$^+$REC-g-PAA composite superabsorbent initiated via ^{60}Coγ-radiation exhibits loose structure and a lot of homogenous micro-pores can be seen. The porous structure gives one explanation that SA/Na$^+$REC-g-PAA composite superabsorbent prepared via ^{60}Coγ-radiation has higher swelling ability.

3.7. Properties of SA/Na$^+$REC-g-PAA composite superabsorbent

Properties of SA/Na$^+$REC-g-PAA composite superabsorbent obtained from optimum conditions of gamma irradiation (the product is coded as S_1) and that by kalium persulphate (the product is coded as S_2) are investigated and results are listed in Table 1. Compared to SA-g-PAA initiated by kalium persulphate, the absorbency for water and salt resistant, anti-ultraviolet property, the retention ability of hydrogel and the gel modulus of S_1 and S_2 are improved, suggesting that the addition of Na$^+$REC would endow the SA/Na$^+$REC-g-PAA composite superabsorbents with good comprehensive performances. Reasons lie in the following aspects. Firstly, in acid environment (acrylic acid was neutralized to the extent of 85%), Si–O bonds of rectorite are broken and attract H$^+$ and OH$^-$ in octahedron slices so as to make the surface of rectorite submitted positive charge, which attract with –COO– group of AA, resulting in the improvement of the polymeric network. Secondly, The cationic exchange capacity of Na$^+$REC is high, so it exhibits good property of salt resistant. Thirdly, rectorite is a kind of good dispersant, which improves the decentralization of polymer in water. Fourth, rectorite has high heat resistance and can reduce and decompose ultraviolet radiation due to being separated into nano slice layer.

In addition, compared to S_2, S_1 has greatly increased absorption in water and many water/inorganic salt solutions. The reason is that swelling capacity of hydrogels can be affected by the crosslinking density. Hydrogels prepared by irradiation have less crosslinking density and therefore possess the larger water-absorbing capacity (Zhang, Chen, & Wang, 2005). Furthermore porous and loose structure of S_1 accelerate the penetration of water molecules into the polymeric network.

It can be also seen from Table 1 that S_1, S_2 and SA-g-PAA are very sensitive to the salt nature of absorbed solution. The order of the swelling capacity of the hydrogels in saline is NaCl > $CaCl_2$ > $FeCl_3$.

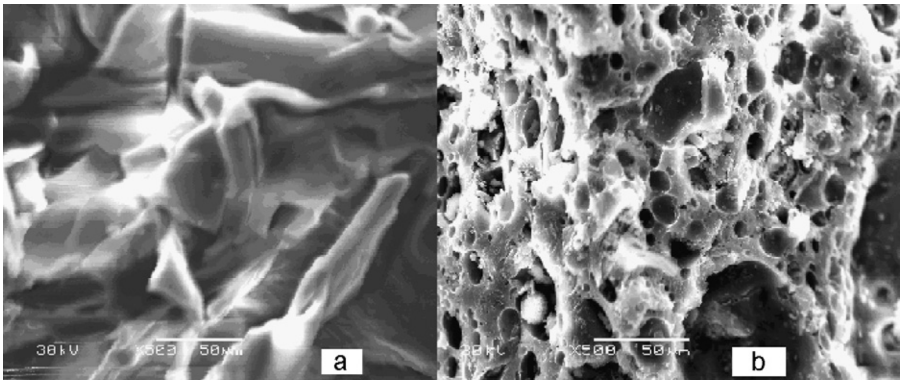


Fig. 9. SEM photographs of SA/Na$^+$REC-g-PAA composite superabsorbent (a) initiated by kalium persulphate and (b) that via ^{60}Coγ-radiation.

Table 1
Properties of SA-g-AA, S_1 and S_2.

Samples	Retention rate (%)	Gel modulus (Pa)	Mass loss ratio of dry resin by UV (%)	q_v (g/g)					
				H_2O	NaCl	$CaCl_2$	$FeCl_3$	Na_2SO_4	Na_3PO_4
S_1	29.7	1.51×10^{-5}	74.3	779	121	116	81	130	139
S_2	31.1	1.55×10^{-5}	73.2	641	115	97	69	120	127
SA-g-AA	26.5	1.25×10^{-5}	77.4	514	101	76	58	105	111

In case of salt solutions with same Na^+, the order of the swelling capacity of the hydrogels in saline is $Na_3PO_4 > Na_2SO_4 > NaCl$. This is consistent with the reports (Abad, Relleve, Aranilla, & Dela Rosa, 2003; Suda et al., 2002; Zhang et al., 2003).

4. Conclusions

SA/Na^+REC-g-PAA composite superabsorbent was prepared by ^{60}Coγ-radiation, its optimum synthesizing condition is: the amount of Na^+REC was 2 wt%, the ratio of SA/Na^+REC to AA was 10 wt%, total dose was 9.0 kGy and volume ratio of methanol to water was 8:2, respectively. The morphology of SA/Na^+REC-g-PAA superabsorbent composite prepared by ^{60}Coγ-radiation is a combination of intercalation and exfoliation. Compared to SA-g-PAA, SA/Na^+REC-g-PAA composite superabsorbents have good comprehensive properties and S_1 has more loose morphology and absorbency in water and many water/inorganic salt solutions.

In this paper, SA is intercalated into the interlayers of Na^+REC to prepare SA/Na^+REC composites followed by grafting acrylic acid onto SA/Na^+REC to obtain SA/Na^+REC-g-PAA composites with superabsorbency via ^{60}Coγ irradiation. The studies are very important for further increasing added value of rectorite, enriching basic theory of clay modifying polymer and study on degradable superabsorbent composite. In the meantime, compared with superabsorbent polymer prepared by initiator, SA/Na^+REC-g-PAA composite superabsorbent prepared via ^{60}Coγ irradiation has the advantages of easy control of processing, no necessity to add any initiators or cross-linkers which may be harmful and difficult to remove.

Acknowledgements

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