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Synthesis and characterisation of starch grafted superabsorbent via 10 MeV electron-beam irradiation

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ABSTRACT

A starch-*graft*-polyacrylamide (St-*g*-PAM) superabsorbent crosslinked by *N*,*N*′-methyl bisacrylamide (MBA) was prepared using 10 MeV simultaneous electron beam irradiation at room temperature and subsequent alkaline hydrolysis. The effects of the irradiation dose, acryliamide-to-anhydroglucose unit (AM-to-AGU) ratio and crosslinker amount on the properties of the obtained polymers were evaluated. The structure of the graft copolymer was confirmed by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Optimisation treatments were carried out and found for a total dose of 8 kGy, an AM-to-AGU ratio of 4.5 mol mol^{-1} and a crosslinker-to-AM ratio of 0.4% mol mol^{-1}. The obtained superabsorbent polymer showed the maximum absorptions of 1452 g g^{-1} and 83 g g^{-1} for distilled water and saline solution, respectively (relative to its own dry weight). The results suggest 10 MeV electron beam irradiation is more efficient than γ-ray irradiation due to its higher energy and dose rate.

1. Introduction

Superabsorbent polymers are a type of moderately crosslinked hydrophilic polymer network that can uptake and retain a large amount of aqueous liquid, as high as 1000 times its weight, which is difficult to remove even when applying heat or pressure (Wu, Wei, Lin, & Lin, 2003; Zhai, Yoshii, Kume, & Hashim, 2002; Zhang, Li, & Wang, 2006; Zohuriaan-Mehr & Kabiri, 2008). The potential applications of such polymers have been reported in many fields, including hygienic products, drug-delivery systems, as well as water-blocking and fertiliser releasing materials for soil environments (Buchholz & Graham, 1997; Omidian, Rocca, & Park, 2005; Wu, Zhang, Liu, & Yao, 2012).

In the development of superabsorbent, polysaccharides, particularly starch, have been heavily studied for their use as the back-bones of these super networks. The —OH on the anhydroglucose unit of the starch chain can interact with the initiator to form redox pair complexes, which can subsequently dissociate to produce carbon radicals through the homogeneous cleavage of the anhydroglucose as the radical centre of the vinyl monomer and crosslinker propagation, leading to the formation of complicated copolymer networks. Initiator extraction of the hydrogen atom from the —OH of the anhydroglucose to form the radical centre on the polysaccharide backbone is another way to explain the process of starch grafting copolymerisation (Zou et al., 2012).

The initiation systems of polymerisation, such as the thermal decomposition of initiators, redox initiation, photochemical initiation, ionising irradiation systems et al. have been reviewed before (Odian, 2004). Chemical copolymerisation (Chen et al., 2005; Ge, Pang, & Luo, 2006; Lanthong, Nuisin, & Kiatkamjornwong, 2006; Zou et al., 2012) and γ-ray methods (Chen, Zhang, Luo, & Fang, 2004; Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002; Lv et al., 2013) have also been applied to form these superabsorbent. In recent years, irradiation processing for materials and other chemical industry has drawn public attention and achieved some commercial success.

Compared with γ-ray irradiation, electron beam accelerator technologies are more frequently utilised in materials areas, including coatings and other thin reactions, due to its higher irradiation efficiency and mechanical flexibility. Most previous researches on the EB inducing reactions in this field have also been conducted with lower energy of less than 5 MeV (Ibrahim, El Salmawi, & Zahran, 2007; Zhai et al., 2002). As reported by Cleland, Galloway, Genin, and Lindholm (2002) an EB with energy up to 10 MeV and power > 10 kW has several advantages over low energy EB ($E \leq 5$ MeV) and γ-ray, i.e., it has higher dose rate, wider range

Abbreviations: St, starch; AGU, anhydroglucose unit; AM, acrylamide; *N*,*N*-MBA, *N*,*N*-methylene bisacylamide; EB, electron beam; SAP, superabsorbent polymers; GR, grafting ratio; GE, grafting efficiency; E, energy; ICP-AES, inductively coupled plasma-atomic emission spectrometer; D, irradiation dose.

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and consequently it's more efficient for polymerisation synthesis (Cleland et al., 2002). Moreover, the electron energy deposition of 10 MeV EB is much higher, which would lead to the variations of absorbed dose and secondary particles yields (*G* value), and result in different effects on the starch grafting copolymerisation.

In this study, a series of St-*g*-PAM superabsorbent composite was prepared by a linear electron accelerator with energy of 10 MeV. The formation mechanism was explored and the structure of the obtained polymers was characterised. The swelling behaviours of the crosslinked hydrogels with respect to the total irradiation dose, AM-to-AGU ratio and crosslinker amount on the properties of the obtained polymers were evaluated.

2. Experimental

2.1. Materials

Cassava starch (Sahnghai Heyu), acrylamide and *N*,*N*′-methyl bisacrylamide (Sinopharm Chemical) were used as received without further purification. The samples were irradiated using an electron beam generated by a linear electron accelerator (E = 10 MeV, power > 10 kW) from Ishikawajima-Harima Heavy Industries Co., Ltd., Japan. The FTIR spectra were recorded on a Bruker V22 FTIR spectrometer. The SEM images were obtained on a Philips XL30-ESEM SEM microscope. Elemental analysis of C, H and N was performed on a Therm Finnigan elemental analyser (Flash EA 1112). The content of Na was measured on a Jarrel. Asm ICP-AES (Atom Scan 2000).

2.2. Synthesis of the cassava starch grafted polyacrylamide

Cassava starch was mixed with distilled water in a 250 cm^3 three-necked flask by an electric blender at 400 rpm with refluxing. The mixture was gelatinised at 85 ± 2 °C for 30 min in a water bath to form a paste. The gelatinised starch was then cooled to room temperature, and predetermined amounts of the monomer and crosslinker dissolved in deionised water were added to the cooled starch paste. The mixture was then stirred at 400 rpm at room temperature for 10 min. All of these procedures were performed under nitrogen. The paste was then transferred into a 100 cm^3 glass tube and bubbled with nitrogen for 10 min. The tube was irradiated with a 10 MeV electron beam for various doses, as needed. After polymerisation, the product was washed, dehydrated with 95% ethanol and dried at 70 °C in a vacuum oven to constant weight. The monomer conversion of this irradiation polymerisation was determined according to the following equation:

$$\text{Conversion} = \frac{W_1 - W_0}{W_M} \times 100\% \quad (1)$$

where W_0, W_1 and W_M are the weight of the raw cassava starch, the weight of the polymer products and the weight of acrylamide, respectively.

2.3. Removal of the free polymers

The dry cassava St-*g*-poly (AM-*co*-MBA) was washed in 50 mL methanol/water (v/v, 4/1) and acetone/water (v/v, 4/1) solutions for 60 min and 3 times with an ultrasonic extractor. The extracted polymer was dried in a vacuum oven at 70 °C to a constant weight. The grafting ratio and grafting efficiency of the polymer were determined according to the following equations:

$$\text{GR} = \frac{W_2 - W_0}{W_0} \times 100\% \quad (2)$$

$$\text{GE} = \frac{W_2}{W_1} \times 100\% \quad (3)$$

where W_0, W_1 and W_2 are the weight of the raw cassava starch, the weight of all the polymers (including the free polymers and the starch grafted copolymers) and the weight of St-*g*-poly (AM-*co*-MBA), respectively.

2.4. Hydrolysis of the cassava starch grafted polyacrylamide

The St-*g*-poly (AM-*co*-MBA) was swollen by NaOH aqueous solution with a concentration of 5% (w/w) and put into a three-necked flask equipped with an electric blender and reflux condenser. The gel was stirred at 75 °C for 1 h at 200 rpm. The hydrolysed gel was extracted with 50 mL ethanol/water (v/v, 3/2) solution in an ultrasonic bath three times for 60 min. The extracted polymer was dehydrated with anhydrous alcohol and dried at 70 °C in a vacuum oven to a constant weight. The dry samples were subsequently grinded and sieved to obtain particles with diameters of 150–300 μm.

2.5. Swelling test of the superabsorbent

The samples were immersed in distilled water and left to stand for 1 h. The expanded hydrogel was then filtrated with a 100-mesh sieve to remove any water that was not retained. The weight-dependent swelling ratio was calculated according to the following equation:

$$Q = \frac{W_H - W_S}{W_S} \quad (4)$$

where W_H and W_S are the weights of the swollen hydrogel and the dry sample, respectively. The swelling tests in a 0.9% NaCl solution were measured using the same method.

2.6. Characterisation

KBr pellets were used for FTIR analysis to determine the results of the irradiation polymerisation. The inner and surface morphology of the starch and grafted polymers were observed using a SEM with an accelerating voltage of 20 kV. The hydrolysis degree of the St-*g*-poly (AM-*co*-MBA) is presented in terms of the nitrogen and sodium contents in the SAP. Elemental analyser and ICP-AES were used to determine the SAP elemental composition.

3. Results and discussion

3.1. Characterisation of the polymers

3.1.1. Functional group analysis of the copolymers

The FTIR technology is adopted to prove that the acrylamide was successfully grafted onto the backbone of the cassava starch as a result of electron beam irradiation, and the amide groups were partially hydrolysed in aqueous alkaline solution. Fig. 1 shows the FTIR spectra of cassava starch, St-*g*-poly (AM-*co*-MBA) and the hydrolysed St-*g*-poly (AM-*co*-MBA). In the cassava starch spectrum, a broad band can be observed in the region of 3200–3600 cm^{-1} that is due to the–OH stretching vibration, and a small peak at 2926 cm^{-1} is attributed to the C-H stretching, both of which can also be observed in the St-*g*-poly (AM-*co*-MBA) spectrum and in the hydrolysed St-*g*-poly (AM-*co*-MBA) spectrum. The triplet peaks at 1012, 1086 and 1158 cm^{-1} are assigned to the C—O—C stretching of the starch, and the peak at 1643 cm^{-1} is attributed to water molecules. In the St-*g*-poly (AM-*co*-MBA) spectrum, the peaks found at 3450, 1658 and 1611 cm^{-1} indicate N—H stretching, C=O stretching and the N—H bending modes, respectively, which

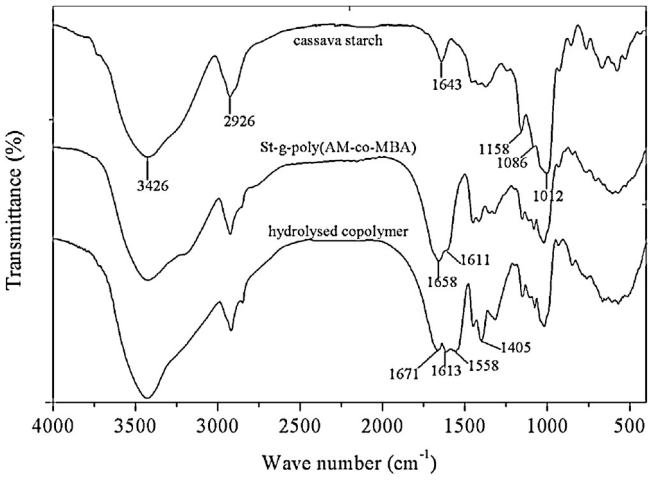


Fig. 1. FTIR spectra of (a) cassava starch, (b) St-*g*-poly (AM-*co*-MBA) and (c) hydrolysed St-*g*-poly (AM-*co*-MBA).

are characteristic of the acrylamide grafted on cassava starch. A band at 1672 cm^{-1}, which is attributed to a shift in the C=O stretching vibration, was observed in the spectrum of the hydrolysed St-*g*-poly(AM-*co*-MBA), which was caused by the superposition of the amide group absorption (1658 cm^{-1}) and the C=O stretching in —COONa (1710 cm^{-1}) (Wu et al., 2012). Furthermore, the band at 1558 cm^{-1} corresponds to the asymmetric —COO^- stretching, which indicates that the —$CONH_2$ was hydrolysed to —COONa (Zou et al., 2013).

3.1.2. Surface morphology of the copolymers

The surface morphology and structure of the cassava starch (a), St-*g*-poly (AM-*co*-MBA) (b) and the hydrolysed St-*g*-poly (AM-*co*-MBA) (c) were observed using SEM, as shown in Fig. 2. The photographs indicate that the starch particles (a) show a smooth and approximately spherical surface before the grafting reaction, while the St-*g*-poly (AM-*co*-MBA) (b) shows a loss in smoothness due to the grafted PAM. However, it is more rigid and non-cellular than the hydrolysed St-*g*-poly (AM-*co*-MBA). The hydrolysis of —$CONH_2$ changes the St-*g*-poly (AM-*co*-MBA) to a polyelectrolyte, thus giving the network a multiporous structure and ionisable characteristic. It has been reported that these pores give channels for water permeation to the network, and the interaction of the hydrophilic groups with water endows the hydrolysed copolymer with its high water absorption properties (Kiatkamjornwong et al., 2002).

3.2. Synthesis of the cassava starch superabsorbent composite

3.2.1. Effect of the irradiation dose on the copolymerisation

The effects of the reaction conditions on the grafting of AM onto cassava starch were examined by analysing the grafting ratio, grafting efficiency, monomer conversion and absorption capacity in water and a 0.9% NaCl solution, as shown in Figs. 3–5.

The effect of the total irradiation dose on the cassava starch grafting AM copolymerisation is shown in Fig. 3. It was found that the monomer conversion and grafting ratio increase with increasing irradiation dose and a conversion rate of about 100% was achieved when the total dose is higher than 10 kGy, while the grafting efficiency decreases along with the irradiation dose (Fig. 3a). The absorption capacities of the grafting copolymer in both distilled water and saline increased with increasing total dose up to 8 kGy and decreased with higher dose (Fig. 3b).

Most irradiation polymerisations are radical polymerisations. The chemical effect of EB irradiation was quantitatively different, but qualitatively similar to other radiation processes (Odian, 2004). In this starch grafting copolymerisation, the anhydroglucose unit of the starch, the monomer and the solvent water are excited or ionised by the ejection of an electron and the formation of radicals by the higher energy electron beam. The excited molecule would subsequently break into radicals due to homogeneous cleavage. Moreover, the ejected electron, e^-, can be captured by H_2O to form e_{aq}^-. All of these short life radicals can propagate at or as the radical centre to initiate polymerisation.

Increasing the total dose promotes the generation of radicals in the reaction solution. Increasing AGU· density enhances the grafting polymerisation with the AM acting as the active sites, thus increasing both the grafting ratio and the monomer conversion. However, at high irradiation doses ($D > 10$ kGy), more H·, OH· and e_{aq}^- are also produced by water radiolysis, which initiates homopolymer formation rather than the desired grafting reaction. In addition, the radicals from water radiolysis act as the chain transfers to terminate the polymer growth reaction with the combination of radicals (Kiatkamjornwong, Chomsaksakul, & Sonsuk, 2000). A greater amount of homopolymer formed directly results in a lower grafting efficiency, as shown in Fig. 3a.

The EB dose rate in this experiment was approximately 8.44 kGy s^{-1}, which is over 1000 times greater than the rate observed in experiments performed with γ irradiation. The higher dose rate increases the radical density and enhances the recombination of radicals. Additionally, the high total dose and dose rate of EB irradiation may induce the chain scission of the starch backbone (Kiatkamjornwong, Chvajarernpun, & Nakason, 1993). Each of the above mechanisms would most likely lead to a decrease in the grafting efficiency.

The swelling of the polymer depends on the fine structure of the polymer network (Kiatkamjornwong et al., 2002), which is primarily dictated by the amount of hydrophilic groups on the polymer chains and the crosslinking density. In most cases, the absorption ratio increases with the concentration of hydrophilic moieties, which can also be described in terms of the grafting ratio. When the irradiation dose was higher than 8 kGy, the absorption, of both water and a 0.9% NaCl solution decreased with increasing grafting ratio. As reported before, under high-dose irradiation, PAM tends to undergo crosslinking rather than degradation in concentrated solution (Biswal et al., 2007; Kiatkamjornwong et al., 2002; Nishii & Hayashi, 1975; Xu et al., 2008). The high crosslinking density of the polymer would occur because of the high total dose, and this made the network too tight to hold an optimal amount of aqueous material.

3.2.2. Effect of AM-to-AGU ratio on the copolymerisation

The effect of the AM-to-AGU ratio on the graft copolymerisation is presented in Fig. 4. The monomer conversion increased with increasing AM-to-AGU ratio, but the grafting efficiency did not continue to rise when the ratio was increased above 4.5 mol mol^{-1} (Fig. 4a). The absorbing properties of the SAP (Fig. 4b) initially increased with increasing AM-to-AGU. A maximum was reached at a ratio of 4.5 mol mol^{-1} and then continuously decreased.

The probability of molecular contact became higher with increasing monomer concentration. More AM molecules reacted at the radical centre of the AGU· and PAM·, resulting in the propagation of the active chain. This reaction was presented as the monomer conversion and grafting ratio, continuously increasing with the monomer to starch ratio. However, when the AM-to-AGU ratio was over 5.0 mol mol^{-1}, the grafting efficiency of the polymerisation decreased slightly. When the monomer concentration was over an appropriate value, the probability of chain transfer to monomer would increase, which made the molecular weight of the grafted PAM decrease. Increasing the monomer concentration

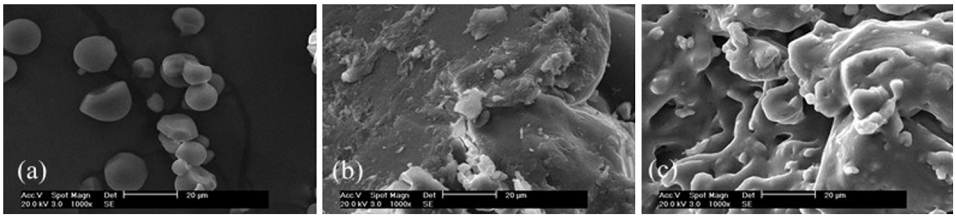


Fig. 2. SEM images of (a) cassava starch, (b) St-*g*-poly (AM-*co*-MBA) and (c) hydrolysed St-*g*-poly (AM-*co*-MBA).

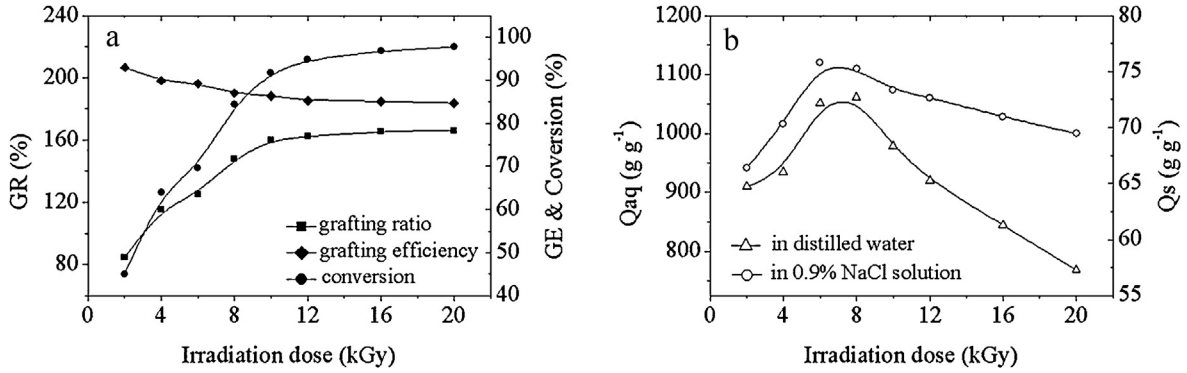


Fig. 3. Effect of irradiation dose on the graft copolymerization and absorption properties.

also enhanced the homo polymerisation (Pourjavadi, Farhadpour, & Seidi, 2008). Moreover, the viscosity of the reaction system, which blocked the movement of free radicals and monomer, may further strengthen this effect. All the above reasons made the grafting efficiency decrease with increasing AM-to-AGU when too much AM was irradiated.

The monomer to starch ratio has a great impact on the structure of the hydrogel network by affecting the hydrophilic moieties on the grafted chain. As the AM-to-AGU ratio increased, the grafting ratio of the polymer increased. This result led to the enhanced swelling capacity of the hydrogel network. When the AM-to-AGU ratio was larger than 4.5 mol mol^{-1}, the self-crosslink via imidisation made the grafted copolymer over-crosslinked for the concentrated acrylamide (Thomas, 2004), which resulted in a decrease in the swelling properties.

3.2.3. *Effect of the amount of crosslinker on the copolymerisation*

To illustrate the effect of the amount of crosslinker on the cassava St-*g*-poly (AM-*co*-MBA) synthesised with an EB dose of 8 kGy, an AM-to-AGU of 4.5 mol mol^{-1} and hydrolysed at 75 °C for 60 min with 5% NaOH aqueous solution is shown in Fig. 5. It can be observed that increasing the amount of crosslinker resulted in a slight increase in all of the grafting parameters, but this increase was not significant. The slight increase in the grafting ratio, grafting efficiency and monomer conversion with increasing crosslinker may be ascribed to the homopolymer or free polymer not being extracted from the semi-IPN structure of the over crosslinked network (Kiatkamjornwong et al., 2002).

Superabsorbent polymers have to be crosslinked to a certain extent to prevent the polymer chain from dissolving in aqueous media (Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004). The copolymer in this work showed its highest swelling ratio at a 0.4% crosslinker to monomer ratio. When the crosslinker was below the optimum value, the less crosslinking in the hydrogel makes more dissolved hydrophilic chains in aqueous media. At higher crosslinking densities, the hydrogel was enhanced with a higher strength but showed a small expansion range that did not hold a large quantity of water. Compared to other methods, the amount of crosslinker used in this work was far less than that used in chemical initiating systems because the self-crosslinked grafted PAM was particularly concentrated (Lanthong et al., 2006).

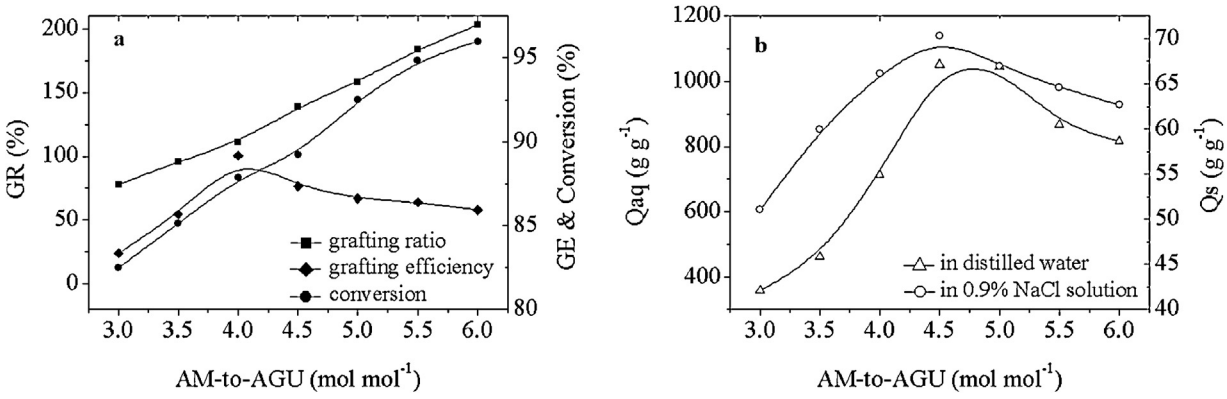


Fig. 4. Effect of AM-to-AGU ratio on the graft copolymerisation and absorption properties.

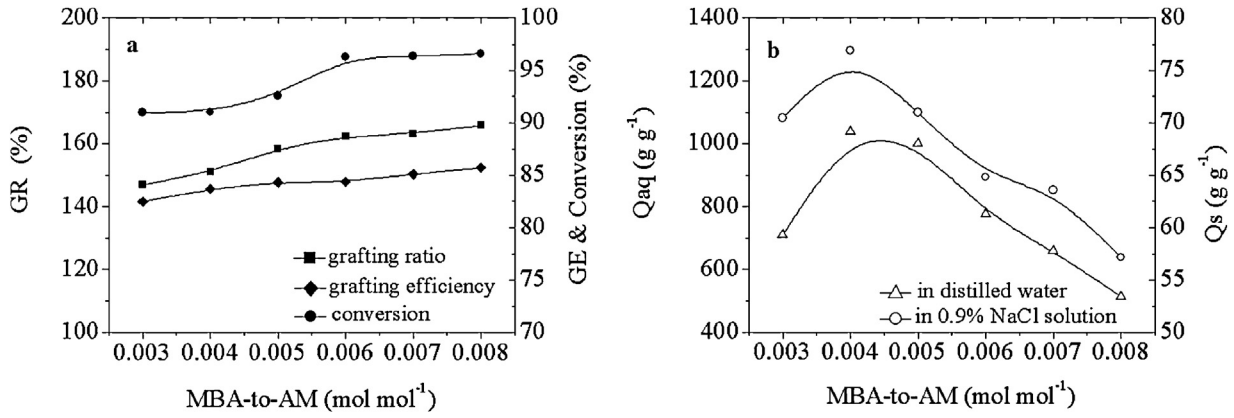


Fig. 5. Effect of the amount of crosslinker on the graft copolymerisation and absorption properties.

Table 1
Effect of temperature and time on the hydrolysis degree and absorption properties.

Temperature and time of hydrolysis	Elemental composition (%)					Qaq [a]/(g g^{-1})	Qs [b]/(g g^{-1})
	Nitrogen	Carbon	Hydrogen	Sodium			
Unhydrolysed sample	11.73 ± 0.09	44.49 ± 0.13	7.19 ± 0.05	–	–	25 ± 2	18 ± 1
60 min	25 °C	7.49 ± 0.14	41.53 ± 0.24	6.96 ± 0.07	3.12 ± 0.04	256 ± 5	45 ± 1
	45 °C	5.18 ± 0.03	38.71 ± 0.29	6.58 ± 0.05	5.99 ± 0.06	370 ± 7	53 ± 1
	60 °C	4.06 ± 0.13	36.78 ± 0.25	6.26 ± 0.03	7.75 ± 0.14	526 ± 10	62 ± 1
	75 °C	3.92 ± 0.03	38.13 ± 0.27	6.34 ± 0.13	8.33 ± 0.04	1049 ± 7	73 ± 1
	90 °C	3.79 ± 0.02	35.88 ± 0.37	6.35 ± 0.09	8.62 ± 0.04	1106 ± 30	80 ± 1
75 °C	30 min	4.04 ± 0.06	37.36 ± 0.35	6.24 ± 0.10	8.01 ± 0.10	947 ± 25	72 ± 1
	60 min	3.98 ± 0.12	37.19 ± 0.29	6.34 ± 0.03	8.47 ± 0.08	1056 ± 26	75 ± 2
	90 min	3.94 ± 0.07	37.69 ± 0.45	6.08 ± 0.11	8.50 ± 0.06	1227 ± 18	80 ± 2
	120 min	3.82 ± 0.11	37.70 ± 0.39	6.04 ± 0.10	8.60 ± 0.08	1452 ± 25	83 ± 1
	150 min	3.78 ± 0.13	36.70 ± 0.51	6.09 ± 0.07	8.97 ± 0.07	1283 ± 43	76 ± 1
	180 min	3.73 ± 0.11	37.27 ± 0.58	5.89 ± 0.03	9.07 ± 0.10	1196 ± 14	74 ± 1

[a] Qaq = quantity of water SAP absorbed, g g^{-1}.
[b] Qs = quantity of saline solution SAP absorbed, g g^{-1}.

3.2.4. *Effect of time and temperature on the hydrolysis degree*

The hydrolysis degree of —$CONH_2$ is presented in terms of the nitrogen and sodium contents in the chains and the absorption properties, as shown in Table 1.

In strong alkaline and high-temperature environments, the amide groups on the grafted PAM chains react to become carboxylate groups via the following reaction (Scheme 1) (Mahdavinia et al., 2004).

It's generally accepted that the random distribution of carboxylate groups in the network increases with the degree of hydrolysis. As shown in Table 1, gradually decreased nitrogen and increased sodium contents were observed with increasing temperature and reaction time, indicating the enhancement of the hydrolysis reaction. The more extensive hydrolysis attributes to an increase in the amount of hydrophilic groups, —COO^-, on the chain, which results in disparity in the osmotic pressure into and out of the network.

The hydrolysis degree has important effects on the absorption properties of the superabsorbent by regulating the hydrophilic groups on the chains. However, Table 1 indicates that the water absorption does not show a positive correlation with the amount of —COONa. That result may be attributed to the intermolecu-

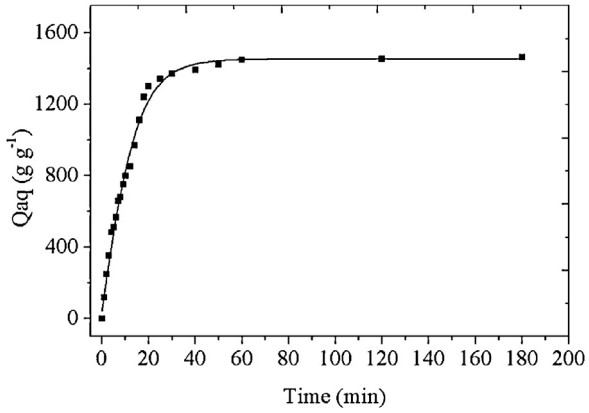
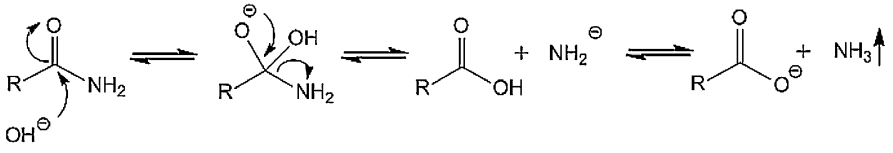


Fig. 6. Swelling rate of the hydrolysed St-*g*-poly (AM-*co*-MBA) under the preparation conditions of AM/AGU = 4.5 mol mol^{-1}, D = 8 kGy, MBA/AM = 0.4% mol mol^{-1} and hydrolysed for 60 min at 75 °C.



Scheme 1. Hydrolysis mechanism of the grafted polyacrylamide.

lar hydrogen bonding that decreases the segmental mobility of the hydrolysed St-*g*-poly (AM-*co*-MBA) with its large amount of hydrophilic groups on the chains (Maltesh, Somasundaran, Kulkarni, & Gundiah, 1991).

3.2.5. Swelling rate of the superabsorbent

The swelling rate of the hydrolysed copolymer was determined with the results shown in Fig. 6. The curve of the swollen water quantity to the soak time indicates that the water absorbency of the composite initially increases with time and reaches 1300 g g^{-1} for water within 20 min. A swelling equilibrium of 1450 g g^{-1} for water is observed within 60 min. All of the above results show that the superabsorbent composite in this work has comprehensive absorbency properties with a relatively fast swelling velocity.

4. Conclusion

Radiation grafting copolymerization of cassava starch with acrylamide was carried out using a higher energy (10 MeV) electron beam irradiation as the initiator. The total irradiation dose, the AM-to-AGU ratio and the crosslinker amount demonstrated significant influences on the properties of the obtained polymers. Attributed to its higher energy and dose rate, the EB irradiation of 10 MeV can significantly promote the polymerisation reaction efficiency. The optimisation polymerisation was observed at a total dose of 8 kGy, an AM-to-AGU ratio of 4.5 mol mol^{-1} and a crosslinker-to-AM ratio of 0.4% mol mol^{-1}. The obtained superabsorbent polymer showed excellent water absorbability, with the maximum absorptions of 1452 g g^{-1} and 83 g g^{-1} for distilled water and saline solution of its dry weight, respectively.

Acknowledgements

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