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Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents

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Abstract

Biodegradable superabsorbent polymers were synthesized by graft copolymerization of acrylamide (AM)/itaconic acid (IA) onto cassava starch via a redox initiator system of ammonium persulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TEMED), in the presence of N,N'-methylenebisacrylamide (*N*-MBA) crosslinking agent, sodium bicarbonate foaming agent, a triblock copolymer of polyoxyethylene/polyoxypropylene/polyoxyethylene as a foam stabilizer. The acrylamide-to-itaconic acid ratio, the starch-to-monomer ratio, and concentrations of the crosslinking agent and initiator, on the water absorption of the superabsorbent polymers were investigated. The swelling of starch-*g*-PAM was 39 g g⁻¹ while the starch-*g*-P(AM-*co*-IA) with the IA content of 0.02–0.15% mole gave the water swelling value in the range of 70–390 g g⁻¹. By-products of the reaction were removed by water extraction. The starch grafted composites were characterized by FTIR and SEM. Thermal gravimetric analysis was also used for determining the percentage of grafting ratio. Biodegradation of the starch grafted copolymer was carried out using α -amylase. After the α -amylase hydrolysis, the amount of reducing sugar was quantified by DNS method. The hydrolyzed solution gave a negative test with iodine solution and a positive test by Benedict's solution, an indication of the existence of glucose units.

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1. Introduction

Biodegradable polymers have been attracting much attention owing to concerns related to environmental pollution by plastics waste. As a result, attempts have been made to solve these problems by including biodegradability into polymers in everyday use through slight modifications of their structures (Chandra & Rustgi, 1998). Thailand is the world's leading producer of cassava roots and is the world's largest exporter of cassava products. Besides its low cost and availability, its biodegradability has gained even more importance in this environmentally sensitive era. A reliable process to use cassava starch to increase its commercial value by modifying its chemical structure to produce superabsorbent polymers (SAPs) for various applications (Ichikawa & Nakajima, 1996) is needed.

SAP or hydrogel is an important class of partially crosslinked polymeric materials that are able to absorb large quantities of fluids, generally water. Commercially, SAPs are mostly produced with acrylic acid as a major component. However, acrylic polymer cannot be easily biodegraded. Many attempts have been made to use natural polymer such as a starch, and their derivatives in the synthesis of hydrogel. Besides grafting with acrylonitrile in the early days of invention of superabsorbent polymers (Fanta, 1973a), starch-based superabsorbent polymers are also developed by grafting starch with acrylic monomer, acrylamide (Athawale & Lele, 1998; Karadağ, Uzum, & Saraydin, 2005; Mostafa, 1995), and ε -caprolactone (Chen et al., 2005a). They can be formed by chemical

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copolymerization (Athawale & Lele, 2000; Chen, Park, & Park, 1999, 2005b) and the use of γ -ray irradiation (Caykara, Bozkaya, & Kantoglu, 2003; Kiatkamjornwong, Chomsaksakul, & Sonsuk, 2000, 2002).

Superabsorbent polymer or hydrogel transition (volume changes) takes place in response to changing environmental conditions. The behavior of a highly swollen hydrogel is, therefore, a function of the network characteristics, such as degree of swelling, diffusion parameters, crosslinking density, pH, and so on (Sen, Yakar, & Güven, 1999). Acrylamide and itaconic acid are water-soluble and can provide polymer chains with amide and carboxylic groups (diprotic acid), respectively. The side chains may increase the hydrophilic character of the copolymer.

In this research, the starch-based superabsorbent polymers are achieved by grafting of poly[acrylamide-co-(itaconic acid)] onto starch, where the starch and poly[acrylamide-co-(itaconic acid)] ratio is in the range of 1:4–2:1. Their absorption capacity differs from the amount of itaconic acid and starch content. Our aim for the present work is to develop starch-based superabsorbent polymers containing starch contents for water absorption and biode-gradability. The effects of temperature, initiator and co-initiator content, and crosslinking agent amount were studied. The biodegradation of graft copolymer was investigated by enzymatic method using α -amylase. After hydrolysis by enzyme, the amount of reducing sugar was determined by DNS method.

2. Experimental

2.1. Chemicals

Acrylamide (AM, Siam Resin and Chemicals, Thailand) and the anionic comonomer, itaconic acid (IA, Merck, Hohenbrunn, Germany), were used as monomers. N,N'-Methylenebisacrylamide (N-MBA, Fluka, Buchs, Switzerland) was used as a crosslinker. Ammonium persulfate (APS, Merck, Hohenbrunn, Germany) and N,N,N', N'- tetramethylethylenediamine (TEMED, Fluka, Buchs, Switzerland) were used as a redox initiator pair. For a graft polymer of cassava starch-g-poly(acrylamide-co-acrylic acid), cassava starch was supplied from Thai Wah Co., Ltd. Thailand, derived from tapioca cultivated in summer. containing 13.5% moisture, 0.20% ash, pH range of 4.0-7.0, and viscosity of 550 B.U. The foam formation reagent of sodium bicarbonate (NaHCO₃, Sigma-Aldrich, St. Louis, USA) and 0.05% V⁻¹Lutrol F[®] 127 foam stabilizer, a triblock copolymer of polyoxyethylene/polyoxypropylene/polyoxyethylene, (BASF, Ludwigshafen, Germany), with a molecular weight range $9800-14600 \text{ g mol}^{-1}$ were used as received and their concentrations were held constant for the whole experiment. α -Amylase (EC 3.2.1.1) from *Bacillus* species with an enzymatic activity of 1600 IU mg^{-1} was supplied by Sigma-Aldrich (St. Louis, USA). One unit is defined as the amount of enzyme liberating 1.0 mg maltose from starch in 3 min at pH 6.9 at 20 °C.

2.2. Procedure

A preparative scheme outlining the main starch graft copolymers and side reaction products is presented in Scheme 1.

2.2.1. Gelatinization of cassava starch

Cassava starch (4.0 g) was mixed with 30 cm³ of distilled water in a 500 cm³ four-necked round bottom flask. The system was mechanically stirred at 250 rpm under heating within the temperature range of 80 ± 2 °C (Kiatkamjornwong et al., 2000) for 30 min under the nitrogen atmosphere to form a homogeneous, soft and opaque paste or gelatinized starch.

2.2.2. Graft copolymer of poly[acrylamide-co-(itaconic acid)] onto cassava starch

The gelatinized starch was then cooled to 45 °C (Kiatkamjornwong & Wongwatthanasatien, 2004). The mixture of water (100 cm³) containing 0.90 mol acrylamide, 0.10 mol itaconic acid, 1.0 wt% monomer of *N*-MBA, 1.0 wt% monomer of ammonium persulfate, 0.05 g of Lutrol F^{\circledast} 127, 2.0 g of NaHCO₃, and 0.35 cm³ TEMED was added into the reaction. The reaction mixture was



Scheme 1. Preparative flow chart for starch grafted PAM and P(AM-co-IA).

Table 1 Parameters of graft copolymerization of cassava starch and acrylamide/ itaconic acid

Composition	Ratio (w/w, $g g^{-1}$)
Weight ratio of the monomer, AM:IA	100:0-85:15
Weight ratio of starch-to-monomer	1:2-3.5:2
Ammonium persulfate (wt%) of monomers	0.5-2.0
Temperature (°C)	45
Stirring rate (rpm)	250

stirred under the nitrogen atmosphere for 30 min to allow the reaction to take place until completion to get a semiviscous solution. The reaction product was precipitated with methanol and dried at 65 °C. A product with the highest water absorption capacity could be obtained by investigation of the influential effects on graft copolymerization. Various reaction parameters of grafting characteristics and water absorption were investigated as shown in Table 1.

2.3. Characterizations

2.3.1. Removal of free polymers

The dried product (1.0 g) derived from the above sections that was ground previously into a powder form was stirred in 300 cm³ distilled water at room temperature for 24 h. The mixture was centrifuged to separate the graft copolymer. The graft copolymer was washed with distilled water and centrifuged to obtain another separation of grafted copolymer. Then it was dehydrated with methanol to give fine precipitate. It was then dried in the oven at 65 °C for 24 h and it was weighed to examine the amount of the free polymers. The weights of polymer after removal of a free polymer were calculated for the amounts of free polyacrylamide, poly(itaconic acid), and poly[acrylamide-co-(itaconic acid)] produced as by products. Grafting performance in terms of percentage addon, percentage grafting ratio and grafting efficiency was determined. The supernatant was evaporated, dried and ground to fine powder. The powder was investigated by IR spectroscopy for the existence of soluble free homopolymer or copolymer.

2.3.2. Percentage add-on

In a 125-cm³ Erlenmeyer flask mounted with a condenser, 0.5 g of the grafted copolymer was refluxed in 50 cm³ of 1 M HCl for 2 h at 100 °C. The polymer was filtered and washed with distilled water until pH 7 was reached and then it was dried. The residual starch (substrate) after the acid hydrolysis was checked with iodine solution to observe the completion of reaction. The weight in percentages of polyacrylamide, poly[acrylamide-*co*-(itaconic acid)] in the graft copolymer or the so called "percentage add-on" was computed from the weight difference between the graft copolymer and soluble starch, which had been previously removed by the acid hydrolysis.

2.3.3. Percentage grafting ratio

The weights of the polymer in grafts and the substrate (starch), which was considered as the percentage of grafting ratio, were calculated as shown in Eq. (1).

%Grafting ratio =
$$\frac{\text{Weight of starch grafted polymer}}{\text{Weight of starch}} \times 100.$$
 (1)

2.3.4. Percentage grafting efficiency

The percentage of the total synthetic polymer formed that had been grafted to starch or the so called "percentage grafting efficiency" was computed. It can be calculated by Eq. (2).

%Grafting efficiency

$$= \frac{\text{Weight of starch grafted polymer} \times 100}{\text{Weight of free polymers} + \text{Weight of polymer grafted}}.$$
 (2)

2.3.5. Water absorption capacity of superabsorbent polymer

Water absorption capacity of dry superabsorbent polymers was carried out at ambient temperature using distilled water until the polymer gel was completely swollen (Kiatkamjornwong et al., 2000). The swelling measurements of the copolymer were carried out in water at room temperature. Distilled water 200 g was added to 0.1 g of the dry copolymer in a 400-cm³ glass beaker with a glass cover. The polymer was allowed to swell for 24 h. The fully swollen gel was then separated from unabsorbed water by filtering through a 100-mesh sieve aluminum screen for 1 h in a room temperature and the swollen copolymer gel was weighed. The water absorbency was calculated as shown in Eq. (3). The water absorption capacity was determined three repeats for each sample and its value was expressed as mean \pm SD.

Water absorbency
$$(Q) = (W_1 - W_0)/W_0$$
, (3)

where W_0 is the weight of the dry polymer (g), W_1 is the weight of the water swollen gel (g).

2.3.6. Functional group by FTIR spectroscopy

The functional groups of the cassava starch, extracted homopolymer and copolymer and grafted copolymers were examined by Fourier transform infrared spectroscopy (FTIR), on Nicolet Impact 410 using a KBr pellet. Nicolet Omnic Interface Software was connected to the Nicolet FTIR in a data acquisition system.

2.3.7. Surface morphology of the copolymer

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

2.3.8. Grafting amount of graft copolymer determined by thermal gravimetric analysis (TGA)

The grafting amount of the graft copolymer was investigated using thermal gravimetric analysis (TGA, Netzsch STA 409 C), in nitrogen atmosphere at a flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$. The temperature range investigated was from ambient temperature to 600 °C at a heating rate of 10 °C min^{-1} .

2.4. Enzymatic hydrolysis of the graft copolymers

In a 125-cm³ Erlenmeyer flask, the dried graft copolymer (0.05 g) was soaked in 50 cm^3 of phosphate buffer, pH 7.0 for 30 min, and then 2.0 cm³ of α -amylase enzymatic solutions was added. The graft copolymer and phosphate buffer, pH 7.0 without α -amylase were used as a control. The mixture was incubated and shaken at 70 rpm, 37 °C for 24 h. Then, the samples were taken and investigated using the dinitrosalicylic acid (DNS) method, iodine test, and Benedict's test. The buffered enzyme solution was replenished every 24 h to ensure that enzymatic activity remained at a desired level throughout the experiment. The incubation time was varied at 1, 2, 3, 4, and 5 days. For each sample studied, this procedure was repeated for three times, and the values are reported as an average of the three runs. Finally, the degraded copolymer was heated to destroy the enzyme, and cooled at room temperature. The mixture was centrifuged to separate the degraded copolymer. The degraded copolymer was washed with distilled water and centrifuged to get another separation of the grafted copolymer. Then it was dehydrated with methanol to give fine precipitate. The precipitate was dried in the oven at 65 °C for 24 h and then weighed.

2.4.1. The amount of reducing sugar from enzymatic degradation

To obtain the amount of glucose liberated, a standard (calibration) curve was plotted. The standard glucose solution was obtained by preparing a mixture of an initial standard glucose solution containing 0.5 g dm^{-3} , and filled up with distilled water to give a fixed volume. The blank solution comprises 1.0 cm^3 of distilled water and 1.0 cm^3 of DNS solution. The mixture was heated at 100 °C for 5 min. After cooling to room temperature, 10 cm^3 of distilled water was added.

The absorption of the standard glucose solution of different concentrations was determined with a UV/vis spectrophotometer (Spectronic-20, model Genesys, USA). The UV/vis measurement was done at a wavelength of 540 nm. Subsequently, the amount of glucose liberated was obtained from the standard curve. The plot should be linear. A spreadsheet and linear regression were used to obtain the standard curve.

The reducing sugars in the degradation solution were quantified by the DNS method (Miller, 1959) The DNS solution of 1.0 cm^3 was added to 1.0 cm^3 of the sample in a test tube. The mixture was heated at 100 °C for 5 min to develop the color and to let it cool to room temperature. After the cooling, 10 cm^3 of distilled water was added and the solution was measured at the absorbance of 540 nm. In each case, three replicas were experimented. The amount of

reducing sugar was reported as the average concentration of the three replicas calibrated by the standard curve.

The amount of reducing sugar was calculated in g dm^{-3} as follows:

Reducing sugar (g dm⁻³) =
$$\frac{\text{Absorbance at 540 nm}}{\text{Slope}}$$
. (4)

2.4.2. Surface morphology of the copolymer

The surface morphology of the degraded copolymers was revealed by scanning electron microscopy (JEOL, model JSM-6400, Japan).

3. Results and discussion

3.1. Characterization of the functional groups of the copolymers by FTIR

The synthesized copolymers were characterized by the functional groups using FTIR technique. The IR spectra for starch, starch-g-PAM before and after water extractions, and after the acid hydrolysis are presented in Fig. 1. The results show that the IR spectra of cassava starch display the O-H stretching absorption in the region of $3550-3200 \text{ cm}^{-1}$ (broad, s), the C-H stretching at 2930 cm^{-1} (m), and the wave numbers of 1158, 1081, and 1015 cm^{-1} (s) for the C–O–C stretching (a triplet peak of starch). The IR spectra of starch-g-polyacrylamide for both before and after extractions give all the absorption peaks of cassava starch. Additionally, the peaks found at 3400, 1650, and 1600 cm^{-1} indicate the N-H stretching, the C=O stretching and N-H bending of the amide bands, respectively, which are characteristics of the -CONH₂ group containing in the acrylamide. In addition, the peak at 1411 cm⁻¹ is for the -C-N stretching and 765–710 cm⁻¹ for the weak band N-H out of plane bending. These are the typical absorption bands of the amide. After the acid hydrolysis, the following observed absorption peaks confirm the occurrence of PAM as follows. The NH stretching O=C-NH (amide band), the C=O stretching, the NH bending and at 1452 cm^{-1} for the -C-N stretching and the NH out of plane bending at 672 cm^{-1} . There is a small characteristic peak found at 2330 cm⁻¹ which is the $-C \equiv N$ peak, an intermediate peak from the acid hydrolysis of the amide group to carboxylic group (Khali, Farag, Fattach, & ABD, 1995).

In the case of starch-g-poly[acrylamide-co-(itaconic acid)], the IR spectra before and after extractions give the identical absorption peaks of cassava starch and acrylamide, and the additional itaconic acid. The IR spectra in Fig. 2 illustrate the strong peak of the COO– group at 1650–1580 cm⁻¹, the C–N stretching overlapping with that of starch at 1500–1410 cm⁻¹ and the C–O–C peak at 1024 cm⁻¹, and the two broad peaks of N–H at 3442 cm⁻¹ of primary amide and the hydrogen bonded OH of carboxylic acid at 2610–2600, 1644, and 1452 cm⁻¹ for the weak –C–O–H in plane bending interaction. The



Fig. 1. IR Spectra of starch, starch-g-PAM before and after water extraction and after acid hydrolysis.

weak peak at 1710 cm^{-1} indicates the formation of dimer attributed to the shift in the stretching vibration and hydrogen bonded directly to the C=O carbon atom (Karadağ, Saraydin, & Güven, 2001). It is therefore confirmed that both acrylamide and itaconic acid have been grafted onto the cassava starch.

In addition, the IR spectra for the water extracted polymers are shown in Fig. 3. The extraction main products are the starch mixed with the grafted mixed the grafted PAM and starch mixed with the grafted P(AM-*co*-IA) which was the solid precipitated from the reaction fluid. The water extractable products are the uncrosslinked polymers



Fig. 2. IR spectra of starch, starch-g-P(AM-co-IA) before and after extraction, and starch-g-P(AM-co-IA) after acid hydrolysis.



Fig. 3. IR spectra of PAM after water extraction and P(AM-co-IA) after water extraction.

or homopolymer. Basically, the solubility of PAM in water is greater than in other solvents such as ethylene glycol and it becomes solvophilic in acetone, ethanol, and dimethyl formamide, i.e., PAM is immiscible with these solvents (Wu & Shanks, 2004). The crosslinked starch grafted PAM is insoluble in water. On the other hand, the IA portion is more hydrophilic due to its dicarboxylic acid functionality. The uncrosslinked starch-g-P(AM-co-IA) is thus found in the water extract.

IR spectra in Fig. 3 shows the absorption peaks for starch/PAM after water extraction and starch/P(AMco-IA). The absorption peaks at 3411, 3209, 1664, 1614, 1449, and 1353 cm⁻¹ are for PAM (a little shift from what have been described earlier) while the peaks at 1116, 1024, 932, 762, 621, 572, and 523 cm⁻¹ are for starch. The similar absorption peaks are found for the AM/IA portion as follows: 3408, 3212, 1664, 1611, 1448, 1416, and 1348 cm⁻¹ are for the PAM/PIA while the peaks at 1150, 1081, 1021, 932, 762, 572, and 523 cm⁻¹ are for the starch portion. The crosslinked starch graft copolymers with either PAM or PAM/PIA are free from by products.

The acid hydrolysis of the carboxamide to carboxylic acid cannot occur significantly because the acidity is not

so high (1 M HCl) and its main effect under the current condition is mainly on the starch component of poly(acrylamide)-starch graft copolymer or poly[acrylamide-*co*-(itaconic acid)] which indicated that the reaction ceased at the amide group step not the carboxylic step (Khali et al., 1995). Although the $-C \equiv N$ peak appeared at the 2330 cm⁻¹ indicates the effect of acid conversion of carboxamide to carboxylate via cyano-complex formation, its peak intensity is very weak and can be neglected.

3.2. Effect of acrylamide-to-itaconic acid ratio on graft copolymerization

The effect of acrylamide-to-itaconic acid ratio on starchg-poly[acrylamide-co-(itaconic acid)] is shown in Table 2. This result indicates that itaconic acid alone does not behave as a grafting monomer and both monomers prefer to copolymerizing as an ungrafted free copolymer rather than becoming a grafted copolymer onto the starch backbone, indicated by the decreasing grafting efficiency. The free polyacrylamide is lower than the free polymer from AM and IA. The optimal ratio of AM:IA giving the highest water absorption could be due to copolymerization

 Table 2

 Effect of acrylamide-to-itaconic acid ratio on graft copolymerization

AM:IA ratio	FP (%)	GE (%)	Add-on (%)	GR (%)	WA $(g g^{-1})$
100:0	11.0	84.4	59.9	149.5	39 ± 1
98:2	11.9	82.3	55.6	125.2	70 ± 2
96:4	10.4	83.3	51.8	107.3	115 ± 0
94:6	17.1	74.5	49.8	99.2	249 ± 1
92:8	23.2	68.3	49.9	99.6	264 ± 6
90:10	25.0	66.8	50.3	101.4	379 ± 10
88:12	30.8	60.1	48.7	95.2	298 ± 1
85:15	39.0	55.1	47.7	91.4	222 ± 4

FP, free polymers; GE, grafting efficiency; GR, grafting ratio; WA, water absorption; starch-to-monomer ratio, 1:2; APS, 1.0 wt%, and *N*-MBA, 2.0 wt%, at 45 °C, 250 rpm, 30 min.

reactions via the charge transfer (CT) complex from a donor (oxidant) to an acceptor (reductant), i.e., from the electron-rich AM to the electron-poor IA (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002). We found that when incorporating IA concentration of 0.1% mole to the AM before graft copolymerization, the resulting starch-g-P(AM-co-IA) possesses significantly high water absorption. The current finding is in agreement with the recent works discussed by Karadağ et al. (2001), Kiatkamjornwong et al. (2002), Solpan, Duran, and Güven (2002). Both of them utilized radiation grafting. In the case of starch-gpoly[acrylamide-co-(maleic acid)], the addition of a small amount of maleic acid or itaconic acid having many hydrophilic groups into the reaction mixture of starch-acrylamide, the water absorption increases from 1600 to 2300 g g^{-1} . Solphan reported that the radiation – produced acrylamide-acrylic acid hydrogels, the swelling capacities of the copolymer of poly[acrylamide-(acrylic acid)] are in the range of 1000-3000% while polyacrylamide hydrogels themselves swelled in the range of 450-700% only. It is possible to conclude that the presence of a small amount of hydrophilic vinyl monomer enhances the water absorption of the acrylamide-based superabsorbent polymers.

The copolymerization of AM can form imidization because the imidization takes place in polymerization of AM in concentrated solutions and at high temperatures or very long reaction times (Bikales, 1973). The result so obtained is evidenced with the higher gel strength than those without this reaction because of the cyclic imide structures (Kiatkamjornwong et al., 2000) as observed as a medium peak at 1710 cm^{-1} shown in Fig. 2. This C=O absorption band indicates that the carboxylic groups form a dimer (Arndt et al., 1999). In the present system, gel strength can be enhanced by crosslinking the relatively hydrophobic acrylamide monomer with N-MBA for elastic modulus and increase in water absorption by inclusion of a more hydrophilic monomer like itaconic acid, a diprotic vinyl monomer having two polar groups (Vallés, Durando, Katime, Mendizábai, & Puig, 2000) to bound to the network, which increases the hydrophilic character of the graft copolymer.

The percentages of the homopolymer and free polymer increase when the grafting efficiency and percentage addon decrease. The increasing homopolymer content may be caused by the formation of polyacrylamide or the random copolymerization of AM and IA radicals with the monomers, leading to the formation of the ungrafted, free copolymer of AM and IA. The percentage of grafting efficiency and percentage of add-on thus decrease which could be caused by an increase in the non-grafted polymers in the solution phase, compared with a heterogeneous phase grafting between the two monomers with the gelatinized starch.

The water absorbency increases with the increasing number of hydrophilic and ionic functional groups. The reactivity ratios of AM and IA are 0.77 and 1.36 (a double-fold increase), respectively (Uyanik & Erbil, 2000), which render that the structure of the copolymer should contain more IA units than AM units especially if the monomer feed concentrations are equal. The structure of the copolymer consisting of more itaconic acid units gives a graft copolymer with more hydrophilic groups i.e., the IA monomer was used up quickly. Although the IA concentration in this case is much lower than that of AM, the IA still plays an important role in copolymerizing to promote the higher water absorption value. Another important point is that IA portion could be neutralized by NaHCO₃ foaming agent, its additional role of sodium itaconate in polymerization is out of the scope of this work. The graft copolymer must have an optimum ratio of AMto-IA in order to have balance of hydrophilic or ionic functional groups and chain flexibility to produce the graft copolymer with an optimum (high) water absorption capacity. The starch grafted superabsorbent polymer with the ratio of AM:IA of 90:10 can absorb distilled water as highest as $379 \pm 10 \text{ g s}^{-1}$. However, at the AM-to-IA ratios higher than 90:10, the water absorption unfortunately decreases. The lower water absorption may be due to a predominant role of the hydrophobic characters of the acrylamide and the unionized IA, leading to increases in homopolymer or free copolymer, and decreases in grafting efficiency and the percentages add-on (Bajai, 2001).

3.3. Effect of the starch-to-monomer ratio on graft copolymerization

The effect of the starch-to-monomer ratio on the grafting of acrylamide and itaconic acid onto cassava starch is presented in terms of homopolymer formed, grafting efficiency, the percentage of add-on, grafting ratio, and water absorption as shown in Table 3. When increasing the quantity of the starch content, the percentage of free polymer formed increases but the grafting efficiency, the percentage of add-on, and grafting ratio decrease gradually. At a higher amount of starch, a small number of monomers can diffuse to graft onto the starch backbone. Most of the monomers are used for free polymer formation through collisions due to the viscous grafting substrate and the greater bulk volume of the aqueous phase. However, the highest water absorption was found in this work at a P. Lanthong et al. / Carbohydrate Polymers 66 (2006) 229-245

 Table 3

 Effect of the starch-to-monomer ratio on the graft copolymerization

			-		
Starch:monomer	FP (%)	GE (%)	Add-on (%)	GR (%)	$WA (g g^{-1})$
1:2	25.0	66.8	50.3	101.4	379 ± 10
1.5:2	28.1	64.5	51.1	104.5	237 ± 2
2:2	28.6	53.5	33.0	49.2	209 ± 7
2.5:2	28.7	47.12	25.7	34.7	170 ± 2
3:2	33.5	31.7	15.5	18.4	118 ± 9
3.5:2	47.2	13.8	7.6	8.2	114 ± 3

FP, free polymers; GE, grafting efficiency; GR, grafting ratio; WA, water absorption; AM-to-IA ratio, 90:10; APS, 1.0 wt%, and *N*-MBA, 2.0 wt%, at 45 °C, 250 rpm, 30 min.

minimum AM/IA ratio to starch of 2:1, where the AM-to-IA ratio was 9:1. The graft copolymerization with a higher grafting efficiency gives the graft copolymer containing the higher amount of hydrophilic segment. Thus, the swelling increases due to the increase of the differential osmotic pressure between inside and outside the gel membrane (Buchholz, 1998). In addition, the swelling also increases because the increasing hydrophilic fraction of the polymer chain tends to disperse better in the aqueous phase.

3.4. Effect of the initiator concentration on graft copolymerization

Ammonium persulfate and N, N, N', N'-tetramethylethylenediamine were used as the redox initiating system. The reaction between APS and TEMED produces the trimethyl ethylene methylene diamine radical and hydrogen sulfate free radical. The kinetic chain length decreases with increasing initiator concentration, which directly affects the molecular weight of the polymer. The mechanisms of the graft copolymerization via the redox system involved the chain transfer reaction. Since free radicals on the starch are not formed initially, but they are produced through the chain transfer reaction with an existing free radical, significant amounts of homopolymer or free copolymer are often formed by the reaction of initially formed radicals with monomer(s) before chain transfer to starch can occur (Fanta, 1973a). Therefore, the percentage of free polymers increases with increasing concentration of the redox initiator.

In expression of the percentage of grafting efficiency, add-on, and grafting ratio tended to increase with increasing the concentration of initiator, reached an optimum value and then decreased. Free radicals were generated as a result of decomposition of APS in various reactions in the polymerization media to initiate, propagate, and terminate the growing polymer chains. An increase in the concentration of the initiator increases the chance of hydrogen abstraction from the starch backbone, and chain transfer reaction of the copolymer chain with starch rendered the graft yield to increase. However, the excessive increase in the concentration of APS produced free radical species from the decomposition of APS and TEMED to

Table 4	
Effect of ammonium persulfate on graft	copolymerization

			÷ .		
APS (%)	FP (%)	GE (%)	Add-on (%)	GR (%)	WA $(g g^{-1})$
0.5	26.7	64.0	47.4	90.3	243 ± 1
1.0	16.9	74.2	48.9	95.5	300 ± 2
1.5	29.0	58.1	40.2	67.2	230 ± 4
2.0	29.5	57.4	39.8	66.2	212 ± 1

FP, free polymers; GE, grafting efficiency; GR, grafting ratio; WA, water absorption; Starch-to-monomer ratio, 1:2, AM-to-IA ratio, 90:10, and N-MBA, 1.0 wt%, at 45 °C, 250 rpm, 30 min.

give the termination reaction with starch macroradicals or the growing polymer chain or a combination reaction between them. Consequently, the grafting yield decreased.

The water absorption of the grafted copolymer synthesized by 1.0 wt% APS gave the highest water absorption of $300 \pm 2 \text{ g g}^{-1}$. Considering the characteristics of swollen gel, flexibility and size of the swollen gel decreased with increasing APS concentration. When APS concentrations are higher than 1.0 wt%, the gel strength is reduced because the low-molecular weight branches are grafted on starch backbone (Fanta, 1973b). The effect of APS concentration is presented in Table 4.

3.5. Effect of the crosslinking agent concentration on graft copolymerization

The *N*-MBA crosslinker concentration (wt% of monomers) vs. the grafted copolymer is presented in Table 5. The crosslinking reaction takes place through any site in growing polymer chains and opening the double bonds of the two vinyl groups of the crosslinker. The free polymer contents decrease with the increasing amount of crosslinker because the majority of the monomers were used up in the crosslinking copolymerization, which decreased the residue monomer concentration in the reaction mixture. The extent of the copolymerization depended on the crosslinker-to- monomer concentration ratios.

An expression for water absorption of the starch graft copolymer is that the percentage of grafting efficiency, add-on, and grafting ratio tend to increase with increasing the percentage of crosslinker since the bifunctionality of the crosslinker could be significantly used for reacting with the polymer radicals of the starch substrate. The grafted

Table :	5						
Effect of	of the	crosslinker	concentration	on	graft	copolymerization	

N-MBA (%wt)	FP (%)	GE (%)	Add-on (%)	GR (%)	WA $(g g^{-1})$
0.5	64.3	20.5	16.6	19.9	221 ± 6
1.0	16.9	74.2	48.9	95.5	300 ± 2
1.5	18.9	72.9	50.8	103.5	298 ± 3
2.0	25.0	66.8	50.3	101.4	379 ± 10
2.5	34.4	57.9	47.2	89.5	326 ± 6

FP, free polymers; GE, grafting efficiency; GR, grafting ratio; WA, water absorption; AM-to-IA ratio, 90:10; starch-to-monomer ratio, and 1:2; ammonium persulfate 1.0 wt%, at 45 °C, 250 rpm, 30 min.

copolymer which gave the highest water absorption capacity was synthesized with 2.0 wt% of *N*-MBA. At 2.5 wt% *N*-MBA, too many crosslinking points of the crosslinking reaction enhanced the higher gel strength and reduced its water absorption (Buchholz, 1990) because of the rigid chain reducing the osmosis pressure of the gel and the external solution.

3.6. Effect of salt solution on water absorption

The graft copolymer with the highest water absorbency was selected to test for the effect of isotonic salt solution of 0.9% w v⁻¹ NaCl, MgCl₂, and CaCl₂ solutions as shown in Table 6. The water absorption capacity decreases with increasing the ionic strength of the saline solutions. The presence of ions in the solution surrounding the network counteracts the mutual repulsion of the fixed ion on the network itself, and the decrease of the osmotic pressure difference between the gel and the external solution (Grignon & Scallan, 1980). The salt type and concentration can be expressed in the terms of ionic strength. The effect of the ionic strength on the water absorbency can be expressed by Flory's equation (Ichikawa & Nakajima, 1996).

$$Q^{5/3} = \left[(i/2v_{\rm u}S^{*1/2})^2 + (\frac{1}{2} - \chi_1)/v_1 \right] / (v_{\rm e}/V_0), \tag{5}$$

where Q is the degree of swelling, i/v_u is the charge density of polymer, S^* is the ionic strength of solution, $(1/2 - \chi_1)/v_1$, is the polymer-solvent affinity, v_e/V_0 is the crosslinking density.

According to Eq. (5), when the ionic strength of saline solution increases, the water absorbency decreases. The ionic strength of the solution depends on both the mobile ions and their valence or oxidation state. Small quantities of divalent or trivalent ions can drastically decrease the swelling values. The decreases are more significant by Mg^{2+} or Ca^{2+} ions, which can be additionally caused by the complex formation ability of carboxamide or carboxylate groups including intramolecular and intermolecular complex formations, or because one multivalent ion is able to neutralize several charges inside the gel. Consequently, the crosslink density of the network increases while water absorption capacity decreases (Castel, Ricarb, & Audebert, 1990).

Table 6	
Effect of salt solutions on water absorption	

Solution	Ionic strength (mol-ion dm ⁻³)	Water absorption $(g g^{-1})$
Distilled water	_	379 ± 10
$0.9\% \text{ w v}^{-1}$ NaCl solution	0.154	36 ± 1
$0.9\% \text{ w v}^{-1} \text{ MgCl}_2$ solution	0.2836	11 ± 1
$0.9\% w v^{-1} CaCl_2$ solution	0.2433	4 ± 2

 $I = \frac{1}{2}\sum_{i} (C_i Z_i^2)$, where *I*, C_i , and Z_i are the ionic strength, the ionic concentration, and charge on each individual ion, respectively (Christian, 1986).

3.7. Effect of the pH buffer solution on water absorption

The influence of solution pH (3-11) on the water absorption capacity of synthesized graft copolymer having the highest water absorption in distilled water is shown in Table 7. The starch-g-poly[acrylamide-co-(itaconic acid)] contains carboxylate and carboxamide groups which are the majority of anionic-type superabsorbent polymer. An anionic-type superabsorbent polymer normally ionizes at a high pH but unionizes at a low pH. At a high pH where the gel is ionized, the equilibrium degree of swelling increases. Consistent with polyelectrolyte behavior, swelling of superabsorbent polymers was found to increase with pH. When the pH of the external solution increases beyond 5.0, the ionization of the carboxylic groups in the gel matrix also increases. This sudden increases in swelling due to increased ion osmotic swelling pressure as well as chain relaxation resulting from the electrostatic repulsion among caboxylate groups inside the polymer matrix (Kiatkamjornwong et al., 2000). In addition, the extent of swelling was found constant at pH 7-11, this being due to the complete dissociation of acidic groups of itaconic acid at these pH values. The first and second dissociation constants of IA are $pK_{a1} = 3.85$ and $pK_{a2} = 5.44$, respectively (Sen et al., 1999). Even through the ionic strength of pH 7 to 11 is higher than those at pH values of 3-7, water absorption is a bit higher. Because the superabsorbent polymer exposed to high alkalinity medium for a longer time can hydrolyze acrylamide moiety to acrylic acid moiety, which is also the anionic type superabsorbent polymer. Thus, water absorption at the higher pH values could be somewhat higher. At high pH values, the concentration of anionic groups in the polymer network increases (Tasdelan, Kayaman-Apohan, Güven, & Baysal, 2004). With further increase in pH, the ion swelling pressure begins to drop again. Because of the increase in ionic strength of the swelling medium, the ion osmotic swelling pressure decreases and ultimately reduces the equilibrium swelling capacity of the superabsorbent polymer (Kiatkamjornwong et al., 2002).

We anticipated that under acidic conditions, the carboxylate groups are protonated and the graft copolymer network shrinks significantly. In general, starch can be

Table /					
Effect of pH	buffer	solution	on	water	absorbency

Table 7

pH of buffer solution	Ionic strength (mol-ion dm^{-3})	Water absorption $(g g^{-1})$
3	0.0061	22 ± 1
5	0.0134	35 ± 4
7	0.0190	40 ± 1
9	0.0236	40 ± 1
11	0.0272	39 ± 2

 $I = \frac{1}{2} \sum (C_i Z_i^2)$, where *I*, C_i , and Z_i are the ionic strength, the ionic concentration, and charge on each individual ion, respectively (Christian, 1986).

hydrolyzed in acidic solution. For the present cases, it is possible that some portion of the starch graft AM/IA copolymer could be hydrolyzed to give the shorter grafted chains. The shorter grafted chains can reduce the extent of water absorption.

3.8. Grafting characteristics of graft copolymer by thermal gravimetric analysis (TGA)

The results of thermogravimetric analysis (TGA) technique employed to characterize the thermal properties of the obtained graft copolymers as shown in Fig. 4 revealed that the percentage of the weight loss at the decomposition temperatures of starch, itaconic acid, and acrylamide presented in the starch-g-poly[acrylamide-co-(itaconic acid)] thermograms. The weight loss can be used to calculate the grafting characteristics expressed as the percentages of add-on and grafting ratio.

The thermal decompositions of poly[acrylamide-co-(itaconic acid)] and starch-g-poly[acrylamide-co-(itaconic acid)] are clearly exhibited in the thermograms. The percentage of grafting ratio gives information about the extent of a synthetic polymer grafted onto the backbone polymer and hence it is a preferred parameter to study thermal stability of the grafted polymer. The thermal stability of graft copolymer can be compared at the onset temperature of decomposition and the percentage of weight loss for different stages of the decomposition.

One can point out that there are three similar main degradation steps in all formulations. At about 100 °C, there is a 10% weight loss which is assigned to water evaporation. At about 259 °C, a 12% weight loss was found to be the decarboxylation of IA coupled with the chain scission (McNeil & Sadeghi, 1990) while at about 319 °C, a 44% weight loss in the third or main stage of decomposition can be assigned to the degradation of acrylamide portion. Finally, at a temperature higher than 400 °C, a rapid decomposition to carbon dioxide and volatile hydrocarbons was found.

Pure starch shows a two-step characteristic thermogram, wherein the major weight loss (75%) takes place in the second step within the temperature range of 233–368 °C, the temperature for a maximum decomposition was 308 °C (Athawale & Lele, 2000).

In case of starch grafted with poly[acrylamide-*co*-(itaconic acid)], four stages of decomposition were observed. (Fig. 4(a)). It is suggested that in an initial stage of the thermal diagram, when the temperature in a range from ambient temperature to about 150 °C, the weight loss is a result of the dehydration process of the water contained in such a hydrophilic superabsorbent polymer. At the second stage from 167 to 261 °C, there is a decomposition peak in the side groups and branches of the graft copolymer (carboxyl group in itaconic acid proportion). At the third stage from 261 to 328 °C, there is a degradation of starch in the graft copolymer. However, at the forth stage about 336 °C, the



Fig. 4. TGA thermograms of (a) starch-g-poly[acrylamide-co-(itaconic acid)] after acid hydrolysis, (b) poly[acrylamide-co-(itaconic acid)], and (c) starch-g-poly[acrylamide-co-(itaconic acid)] at different AM-to-IA ratios: AM:IA 90:10, and (d) AM:IA 98:2.

Table 8Thermogravimetric data of graft copolymer

Polymer	Number of decomposition stage	Temperature range (°C)	$T_{\max}(^{\circ}\mathrm{C})$	weight loss (%)
Starch	1	37–100	42	11.8
	2	233-417	308	75.5
P(AM-co-IA)	1	25-200	100	10.2
	2	200-289	259.3	12.1
	3	289-372	318.9	44.2
St-g-P(AM-co-IA) ^a	1	25-167	100	5.7
	2	167-261	253.9	6.6
	3	261-328	298.4	23.1
	4	328-400	338.7	31.1
St-g-P(AM-co-IA) ^b	1	25-200	100	11.9
	2	200-256	235.6	7.2
	3	256-322	295.4	17.5
	4	322-400	341.7	18.6
St-g-P(AM-co-IA) ^c	1	25-167	100	9.0
	2	167-300	229.4	10.8
	3	300-472	400.9	58.3

^a AM-to-IA ratio = 90:10.

^b AM-to-IA ratio = 98:2.

^c After acid hydrolysis.

weight loss was found as a result of the degradation of the polymer chain and matrices (degradation of acrylamide portion).

To compare the degradation characteristics, the data for starch and starch-g-copolymer were presented in Table 8. The degradation temperature of starch portion in the graft copolymer was found to decrease. When comparing between the starch-g-copolymers and the free copolymer (Figs. 4(a) and (b)), the graft copolymers have significantly higher thermal stability than that of the ungrafted copolymer, which was caused by the strong bonding between the grafting polymer chains and starch matrices in the graft copolymer and imidization.

In comparison between different compositions of AMto-IA ratio as shown in Figs. 4(c) and (d), the degradation temperature was shifted towards the decreasing IA contents in the graft copolymer. The attribute for this observation is a formation of the imide group by the cyclization of amide groups as evidenced by the presence of 1710 cm^{-1} peak in the IR spectrum (Singh, Sandle, & Varma, 1987). Fig. 4 also shows the thermogram of the grafted poly[acrylamide-co-(itaconic acid)], which was separated from the starch backbone by heating the graft copolymer under refluxing in acid solution. Strong acidic conditions used in the hydrolysis reaction of starch can lead to a progressive insolubilization of the reaction product in a form of an imidization of amide pendants in the copolymer as already shown in Eq. (5), resulting to very highly thermal stability (400 °C).

The thermogram data of starch-g-poly[acrylamideco-(itaconic acid)] were used to calculate grafting characteristics expressed as the percentage of add-on and grafting ratio as shown in Eqs. (6) and (7):

%Add-on =
$$\frac{\sum(\text{weight loss at decomposition stages 2 and 4}) \times 100}{\sum(\text{weight loss at decomposition stages 2, 3, and 4})}$$
,
(6)
%Grafting ratio = $\frac{\sum(\text{weight loss at decomposition stages 2 and 4}) \times 100}{\sum(\text{weight loss at decomposition stage 3})}$.

The calculated values were compared with the gravimetric method to verify the possibility of using the TGA method as a tool for determination of grafting characteristics of a graft copolymer. From the two techniques, TGA gave the higher values (%add-on and % grafting ratio) than the gravimetric method by 3.6 and 19.8, respectively, as shown in Table 9.

3.9. Biodegradation study of the graft copolymer

3.9.1. Enzymatic hydrolysis of the graft copolymers

Enzymatic hydrolysis is one pathway for biodegradation. Enzymatic hydrolysis of starch-g-polymer is accompanied by the liberation of glucose. Determination of the amount of reducing sugar (g dm⁻³) during exposure will therefore give an indication of the extent of biodegradation.

The dinitrosalicylic (DNS) assay is based on the reduction of 3,5-dinitrosalicylic acid by the sugar to 3-amino-5-nitrosalicylic acid which as a strong absorbance at 540 nm as shown in the following Eq. (8) (Chandra & Rustgi, 1998).



Table 9

Determination of %add-on and %grafting ratio by differential method in TGA

Grafting characteristics	Method	
	Gravimetric measurement	TGA
%Add-on	55.6	59.2
%Grafting ratio	125.2	145.0



Fig. 5. Effect of α -amylase concentration on the amount of reducing sugar.

3.9.1.1. Effects of the enzyme concentration and incubation *time.* The effect of the α -amylase concentration at the buffered phosphate pH 7 on the swollen superabsorbent gel of the starch graft copolymer incubated at 37 °C for 24 h is shown in Fig. 5. The increasing α -amylase concentration led to increases in the amount of reducing sugar. However, this relation leveled off after 20,400 U cm⁻³ of the enzyme had been added. Thus, a maximum amount of reducing sugar of 2.4352 g dm⁻³ was observed. The mode of interaction between the enzyme and the polymeric chains affects the kinetics of starch hydrolysis. The hydrolysis of starch composed of mainly insoluble fraction involves four steps (Rahmouni, Chouinard, Nekka, Lenaerts, & Leroux, 2001): (I) Diffusion of enzyme molecules from the bulk aqueous phase to the gel surface. (II) Adsorption of the enzyme onto the gel substrate, resulting in the formation of the enzyme-substrate complex. (III) Hydrolysis of the α -(1 \rightarrow 4)-glucose bond, and finally diffusion of the soluble degradation products from the gel substrate into the bulk aqueous phase.

The effect of incubation time (1, 2, 3, 4, and 5 days) on the degradation of the starch-g-copolymer in the phosphate buffer pH 7 containing 20,400 U cm⁻³ of α -amylase is shown in Fig. 6. When the incubation time is increased, the amount of reducing sugar is also increased. After 5 days of degradation, the amount of reducing sugar is 5.46 g dm⁻³. The enzymatic hydrolysis of the insoluble starch requires more time for the four steps of degradation mentioned above to take place completely.

3.9.1.2. Effects of mole percent of AM-to-IA ratio and starch-to-monomer ratio. The amount of reducing sugar released depends on the mole percent of IA in graft copolymer as shown in Fig. 7. Increasing the IA content decreases sharply the amount of reducing sugar. The reason of this decrease can be caused by an increase in a specific interaction (intermolecular hydrogen bonding) between the amino



Fig. 7. Effect of mole percent of acrylamide-to-itaconic acid ratio on degradation.

group of the enzyme molecules and the oxygen atom in the itaconic acid of the graft copolymer (Bayramoglu, Yilmaz, & Afica, 2004; Tumturk, Caykara, Kantoglu, & Guven, 1999), which decreases the enzymatic activity for the degradation. The activity of α -amylase on the starch-g-polyacrylamide is more effective than superabsorbent polymers containing only the itaconic acid moiety, which need more enzymatic activity to break the glucosidic chains.

The effect of starch-to-monomer ratio on degradation is shown in Fig. 8. The amount of reducing sugar increases with increasing the starch-to-monomer ratio, wherein the enzyme selectively hydrolyzes the starch, so the enzymatic activity increases with an increase in the starch content.

Other methods confirming the existence of a short chain of starch is iodine test and Benedict's test for glucose. Iodine solution is used for checking polysaccharide starch, if the sample contains polysaccharide, the solution will produce a blue color, a blue charge-transfer complex of polysaccharide with iodine, which is called a positive test. Benedict's solution is used for checking a reducing sugar. If the sample contains the reducing sugar, the solution will gave a red precipitate of cuprous oxide, which is then called a positive test. For the present research, after the enzymatic degradation, the iodine test gave the negative test for the



Fig. 6. Effect of time on the degradation of starch-g-poly[acrylamide-co-(itaconic acid)] at the starch-to-monomer ratio = 1:1 and AM:IA = 90:10.



Fig. 8. Effect of starch-to-monomer ratio on degradation.

non-existence of starch molecules while the Benedict's test was positive for the occurrence of glucose units. The Benedicts color reaction and the related starch-iodine intensities are correlated quantitatively to a certain extent by visual matching.

3.10. Surface morphology of the superabsorbent copolymer

The SEM photographs of starch, starch-g-polyacrylamide and starch-g-poly[acrylamide-co-(itaconic acid)] are illustrated in Fig. 9. The starch granules (Fig. 6a) have an irregular shape and varied particle sizes with smooth surface while the graft copolymers have a different surface morphology. The SEM photographs of the starch-g-polyacrylamide in Figs. 9(b)–(c), have coarse network and rather smooth surface, the water absorbency of the starch-g-polyacrylamide was lower than that of the starch-g-poly[acrylamideco-(itaconic acid)] in Figs. 9(d)–(f). The number of hydrophilic groups of starch-g-poly[acrylamide-co-(itaconic acid)] is higher than that of the starch-*g*-polyacrylamide. In addition, the acrylamide functional group is rather hydrophobic when comparing with itaconic acid. So the swelling of starch-*g*-polyacrylamide is obviously lower than the starch grafted with both acrylamide and itaconic acid. The coarse porous structure and broad network of starch-*g*-poly[acrylamide-*co*-(itaconic acid)] and semi-porous structure with thick struts between pores in Fig. 9(d) gave the higher water absorption. The less porous structures in Figs. 9(e–f) gave the lower water absorption. It is supposed that these pores are regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

3.10.1. Surface morphology of the degraded superabsorbent copolymer

The surface appearances of the graft copolymer and the degraded graft copolymer were viewed by scanning electron microscopy as shown in Fig. 10. The higher



Fig. 9. SEM photographs of (a) starch, (b) the starch-*g*-polyacrylamide: at a low magnification, and (c) at a high magnification (WA = $39 \pm 1 \text{ g g}^{-1}$), and the starch-*g*-poly[acrylamide-*co*-(itaconic acid)] at AM-to-IA ratios of (d) 90:10 (WA = $379 \pm 10 \text{ g g}^{-1}$), (e) 94:6 (WA = $249 \pm 1 \text{ g g}^{-1}$), and (f) 96:4 (WA = 115 g g^{-1}).



Fig. 10. SEM photographs of starch-g-poly[acrylamide-co-(itaconic acid)] incubated for 1 day in phosphate buffer (pH 7.0), containing α -amylase at different concentrations: (a) control, (b) 2040 U cm⁻³, and (c) 10,200 U cm⁻³ and starch-g-poly[acrylamide-co-(itaconic acid)] incubated in phosphate buffer (pH 7.0) containing α -amylase of 20,400 U cm⁻³ for: (d) control and non-degraded, (e) incubated for 2 days, and (f) incubated for 5 days.

 α -amylase concentration can remove more starch portions as shown in Figs. 10(a)-(c). Almost all of the starch particles were degraded, forming many small amorphous aggregates (Figs. 9(b)-(c)). Starch particles were removed randomly resulting from its degradation. Similar observations were noted when starch and acrylic grafted starch were biodegraded by Aspergillus niger fungus (Moreono-Chulim, Barahona-Perz, & Canche-Escamilla, 2003). They explained the observation through IR spectra of starch and acrylic grafted starch before and after the biodegradation. Only a small difference in the characteristic peaks (-C-O-C-) and (-OH-) and a small increase in the O-H stretching was found in the biodegraded starch from the degraded products of glucose dextrin and maltose which are resulted from the random degradation on the starch particles. We anticipated that the fungus can generate α -amylase slowly leading to a slow degradation evidenced by the small differences in the characteristic IR peaks. We detected a positive DNS test from the degraded products indicating the existence of glucose molecules. It has been reported that starch degradation takes place by hydrolysis of the α -1,4-linkage in amylose and amylopectin. Furthermore, the longer incubation time was needed for a complete removal of starch as illustrated in Figs. 10(d)–(f). As shown in most of the photographs, the surface of degraded graft copolymer however, is rougher with many cellular structures than that of the undegraded graft copolymer.

4. Conclusions

The biodegradable superabsorbent polymers were prepared by the graft copolymerization between the gelatinized starch and acrylamide/itaconic acid via foamed solution polymerization using APS and TEMED as an oxidation-reduction initiator and cointiator, respectively, while *N*-MBA as a crosslinking agent. We found that the presence of both acrylamide and itaconic acid is essential for the grafting reaction on the gelatinized cassava starch to obtain high absorbency such as the water absorption of $379 \pm 10 \text{ g s}^{-1}$ prepared from the optimum mole ratio of AM-to-IA of 90:10 and the optimum weight ratio of starch to the monomer of 1:2 to give the highest percentage of grafting efficiency and the highest water absorption. A higher amount of the monomers provided the higher grafting opportunity to starch grafting substrate in the other phase. Donoracceptor was used to explain the ratio of AM to IA. The concentration of the redox initiator APS: TEMED of 1:2 wt% of monomers gave the optimum result to achieve the highest water absorption. Increasing the crosslinking agent concentration in the graft copolymerization enhanced the percentages of grafting efficiency, add-on, and grafting ratio. The optimum condition of the crosslinking agent N-MBA of 2.0 wt% gave the highest water absorption. Increasing the ionic strength of the salt solutions decreased significantly the water absorption of the graft copolymer. The buffer pH solution with the high ionic strength decreased the water absorption of the graft copolymers. When the anionic superabsorbent polymer was immersed in the high pH buffered solution, the constant water absorption was observed.

The IR spectrum of polyacrylamide gives the characteristic absorption peaks of the $-\text{COONH}_2$ at 3443 cm⁻¹ (NH₂ stretching) and 1655 cm⁻¹ (C=O stretching). Imidization of the starch-*g*-P(AM-*co*-IA) shown at 1710 cm⁻¹ and the higher thermal stability the thermogram were found. The surface morphology of the graft copolymers studied by SEM reveals that graft copolymers having the higher absorbency are more porous. The TGA technique was employed to successfully characterize the weight loss and grafting ratio of the obtained graft copolymers.

The starch grafted copolymers can be biodegraded by α -amylase enzyme, which was monitored by measuring the amount of reducing sugar using DNS method. In addition, Benedict's test and iodine test applied after the enzymatic hydrolysis confirmed the degraded product of glucose, which indicates the biodegradation of starch and leaves the acrylamide–itaconic acid portions undegraded.

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