

Synthesis and property characterization of cassava starch grafted poly[acrylamide-*co*-(maleic acid)] superabsorbent via γ -irradiation

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Abstract

Graft copolymerizations of acrylamide and maleic acid onto cassava starch by a simultaneous irradiation technique using γ -rays as an initiator were carried out. Various important parameters of total dose, dose rate, monomer-to-cassava starch ratio and maleic acid content were studied. Addition of 2% w w⁻¹ diprotic acid of maleic acid into the reaction mixture yields a saponified starch graft copolymer with a water absorption in distilled water as high as 2256 g g⁻¹ of its dried weight. The water absorption of these saponified graft copolymers in saline and buffer solutions was also measured. The water absorption depends largely on the cationic type and concentration of these solutions in terms of ionic strength. This research explains a charge transfer mechanism for graft copolymerization of maleic acid and acrylamide onto cassava starch, and describes the influential parameters that affect grafting efficiency and water absorption. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: γ -irradiation; Cassava starch; Maleic acid

1. Introduction

During the last two decades, hydrogel research has made remarkable progress owing to the strenuous efforts by researchers from many different fields. Hydrogel is used for agricultural purposes as retainers of water and solutes. The gels keep the materials moist but absorb unnecessary excess water and are useful for efficient transportation and storage. Soft contact lenses, artificial lenses, artificial vitreous, and materials used in plastic surgery are made of hydrogel. Hydrogel is also used in control delivery systems for drugs and perfumes [1]. Disposable diapers and sanitary napkins use hydrogel as a superabsorbent polymer. About 90% of all superabsorbent materials are used in disposable articles. As most of them are disposed of landfills or by incineration, there is a perceived environmental problem with superabsorbent polymers. Use of starch as an extender and replacement for synthetic polymers is currently an active research area. Incorporation of starch into other synthetic polymers not only reduces our dependence on petrochemical-derived monomers but also provides materials in which the starch portion can biodegrade rapidly in the

environment. In the present article, we investigate the synthesis method and property characterization of saponified cassava starch grafted poly[acrylamide-*co*-(maleic acid)] superabsorbent, emphasizing the additional effect of a small amount of maleic acid on water absorption.

2. Experimental

2.1. Materials

Cassava starch containing 13.5% moisture was provided by Thai Wah Co., Ltd, (Bangkok, Thailand), acrylamide (AM) from Siam Resin and Chemical Co., Ltd, (Bangkok, Thailand), and they were all used as received. Methanol, commercial grade from BDH (Poole, England) was purified by fractional distillation at atmospheric pressure. Boric acid (analar grade) was also obtained from BDH (Poole, England). Maleic acid (MA), hydrochloric acid, sodium chloride, magnesium chloride and tri-sodium phosphate (analytical grade) were all obtained from Merck (Darmstadt, Germany). Calcium chloride and citric acid were purchased from Carlo Erba (Milan, Italy). Potassium hydroxide obtained from J.T. Baker (Phillipsburg, USA.) was used as received. A Cobalt 60 source, Gamma Beam 650 of

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42,750 Ci was from Nordion International Inc., Toronto Canada.

2.2. Procedure

Graft copolymerization of AM and MA onto cassava starch by γ -irradiation was carried out as follows:

2.2.1. Gelatinization of cassava starch

Cassava starch (10 g) was mixed with 200 cm³ of distilled water in a 500 cm³ reaction flask. The mixture was stirred at 400 rpm and heated at around 85 ± 3 °C for 1 h to form a paste-like slurry.

2.2.2. Graft copolymerization of acrylamide and maleic acid onto cassava starch by simultaneous irradiation

The gelatinized starch was then cooled to room temperature. Acrylamide (20 g) and 2% w w⁻¹ maleic acid (based on the total weight of acrylamide) were added into the gelatinized starch. The mixture was stirred at 400 rpm at room temperature for 30 min. The gelatinized starch mixture was removed into a 250 cm³ aluminum tube, the inner wall of which was covered with aluminum foil. The tube was closed tightly with the foil and paraffin film, and nitrogen gas was purged into the mixture for 20 min. The tube was then irradiated under γ -rays according to the desired total dose and dose rate. The reaction product was washed with distilled water, and separated. It was dewatered with methanol and dried in a vacuum oven at 65 °C for 24 h.

2.2.3. Effect of monomer-to starch ratio on graft copolymerization

Various amounts of acrylamide, 10, 15, 20, 25 or 30 g (at the monomer-to-starch ratios of 1:1, 1.5:1, 2:1, 2.5:1 or 3:1, respectively) and 2% w w⁻¹ maleic acid were added to each tube of the gelatinized starch samples. The reaction mixture was irradiated by γ -rays at the optimum total dose and dose rate. The reaction product was characterized for grafting characteristics and water absorption.

2.2.4. Effect of total dose and dose rate on graft copolymerization

Various dose rates of 1.71, 4.34, or 11.0 kGy h⁻¹ to various total doses of 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, or 12.0 kGy were used to irradiate 20 g of AM, 2% w w⁻¹ MA (based on the acrylamide concentration), and the gelatinized cassava starch mixture, in order to observe the effect on grafting efficiency and water absorption.

2.2.5. Effect of maleic acid concentration on graft copolymerization

Maleic acid of concentrations 0, 1, 2, 3, 4, 8 or 12% w w⁻¹ were each added to the reaction mixture of gelatinized cassava starch and acrylamide. Each sample was irradiated to the optimum total dose and dose rate as

mentioned earlier. The effect of the acid additive on grafting behavior and water absorption was evaluated.

2.3. Characterization of the polymers

2.3.1. Identification of functional groups by IR spectroscopy

The infrared spectra of cassava starch, graft cassava starch, and saponified cassava starch were identified by IR spectroscopy on a FTIR spectrophotometer using a KBr pellet.

2.3.2. Determination of optimum time and temperature for saponification of acrylamide and maleic acid moieties

For a series of reaction times at 30, 60, and 90 min, and a series of reaction temperatures at room temperature, 50 and 75 °C, a 5% KOH solution was applied to hydrolyze the starch-g-poly[acrylamide-co-(maleic acid)] samples, having 2% w w⁻¹ MA, prepared by a dose rate of 1.71 kGy h⁻¹ to the total dose of 6.0 kGy. The saponified samples were subjected to a determination of nitrogen content by elemental analysis (CHNS/O analyzer, Perkin Elmer PE 2400 Series II, USA).

2.3.3. Determination of percentage conversion

The polymer product, usually comprising the graft copolymer and the homopolymer, was weighed. The total amount of polymer obtained from the weight of monomer charged was calculated to yield the percentage conversion.

2.3.4. Removal of homopolymer and free copolymer

The dried product (about 10 g) was ground into a powder form. It was stirred in 1500 cm³ of distilled water at room temperature for 24 h. The mixture was centrifuged to separate the graft copolymer, then the graft copolymer was washed twice and centrifuged again to obtain the pure grafted product. The supernatant was precipitated with methanol (a non-solvent), filtered, and dried in a vacuum oven at 65 °C for 24 h. It was weighed to determine the amount of homopolymer and free copolymer.

2.3.5. Saponification of the graft copolymer

The starch graft copolymer (5 g) was mixed with 125 cm³ of 5% potassium hydroxide solution in a 500 cm³ reaction flask. The mixture was stirred gently with a mechanical stirrer at 400 rpm at room temperature for 90 min. The reaction mixture was washed with distilled water until pH 7 was achieved. The product was dewatered with methanol and dried at 65 °C in the vacuum oven for 24 h. It was then ground into a powder form.

2.3.6. Determination of percentage gel content

The dried product (1 g) was extracted by water in a Soxhlet extractor for 24 h. Then the solution was separated and precipitated with methanol, filtered, and dried to a

constant weight in the vacuum oven at 65 °C for 24 h. It was weighed to determine the amount of the gel content.

2.3.7. Water absorption capacity in distilled water, sodium chloride, magnesium chloride, and calcium chloride solutions, and in buffer solutions

Water absorption of the saponified starch-*g*-poly[acrylamide-*co*-(maleic acid)] was determined in distilled water. Similarly, the water absorption of the graft copolymer was detected under isotonic conditions of 0.9% w w⁻¹ of sodium chloride, magnesium chloride, and calcium chloride solutions.

Buffer solutions of pH 3–11 were prepared by mixing 0.20 M boric acid, 0.05 M citric acid, and 0.10 M tri-sodium phosphate as described by Shugar and Dean [3]. Water absorption of the polymer in the buffer solutions was carried out as mentioned earlier.

2.3.8. Effect of particle size on water absorption

The cassava starch graft poly[acrylamide-*co*-(maleic acid)] particles were ground to a specific size ranging from 150 to 600 μm by a mesh sieve classification (30–50 meshes). Their water absorption was investigated.

2.3.9. Water absorption under load of the copolymer

The test apparatus consists of a plastic cylinder of 2.6 cm inside diameter, with 100-mesh wire cloth fastened across the bottom of the cylinder. A piece of filter paper is placed on a wire net to ensure a good contact of the liquid with the polymer. A sample of saponified cassava starch graft copolymer (30–50 mesh) weighing 1 g is loaded into the plastic cell, and different weights (typically 54, 108, 162, 216, and 270 g calibrated for 1, 2, 3, 4 and 5 kPa loads, respectively) are placed on top of the sample. The weight (in g) of pick-up fluid after 60 min under load divided by the weight of the sample is called an AUL value, which is in g of fluid picked up per gram of the sample (g g⁻¹) [4]. Note that one atmospheric pressure equals 101.32 kPa.

3. Results and discussion

3.1. Spectroscopic characterization

The FTIR spectra of the reaction product indicates the presence of cassava starch, cassava starch-*g*-poly[acrylamide-*co*-(maleic acid)] and saponified cassava starch-*g*-poly[acrylamide-*co*-(maleic acid)]. The results show that the IR spectra of cassava starch-*g*-poly[acrylamide-*co*-(maleic acid)] before and after the extractions give all the characteristic absorption peaks of cassava starch [3397 cm⁻¹ (broad), 2929 cm⁻¹ (weak), 1455 cm⁻¹ (weak), 1421, 1366 cm⁻¹ (weak) and 1017 cm⁻¹ (strong) for the O–H stretching, C–H stretching, C–H bending, O–H bending and C–O stretching, respectively] acrylamide [3192 cm⁻¹ (broad), 1664 cm⁻¹ (sharp), 1607 cm⁻¹ (weak), 1324 and 1352 cm⁻¹ (weak) indicated the N–H stretching, C=O, N–H bending and C–N stretching, respectively, which are the characteristics of the –CONH₂ group] and additional peaks at 2786 cm⁻¹ (weak); 1664 cm⁻¹ (strong); 1206 cm⁻¹ (weak), and 937 cm⁻¹ (weak) for the O–H stretching, C=O stretching, C–O stretching and O–H bending of the –COOH group contained in maleic acid, respectively. When starch-*g*-poly[acrylamide-*co*-(maleic acid)] was saponified, the stronger peak at 1383 cm⁻¹ of C=O stretching of the carboxylate ion indicated that acrylamide and maleic acid moieties have been converted to the acrylate group.

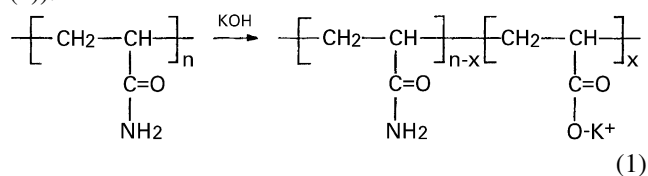
3.2. Effect of saponification time and temperature on degree of saponification

The degree of saponification depends on the reaction time, temperature, and concentration of alkaline solution [5]. The degree of saponification of starch-*g*-poly[acrylamide-*co*-(maleic acid)] is presented in terms of the nitrogen content and water absorption capacity as shown in Table 1. The grafted poly[acrylamide-*co*-(maleic acid)] undergoes an extensive saponification at a longer time and higher temperature. The amide groups on the grafted poly[acrylamide-*co*-(maleic acid)] chains change to the carboxylate

Table 1
Effect of reaction time and temperature on degree of saponification and water absorption

Temperature and duration of saponification	Elemental composition (%)			Water absorption (g g ⁻¹)
	C	H	N	
Unsaponified sample	43.956	5.178	11.922	81 ± 6
Room temperature, 30 min	42.855	6.526	10.780	592 ± 30
Room temperature, 60 min	41.420	6.055	9.629	1057 ± 21
Room temperature, 90 min	41.194	6.405	9.251	1216 ± 14
50 °C, 30 min	37.206	5.691	6.153	934 ± 54
50 °C, 60 min	37.902	5.692	5.935	946 ± 12
50 °C, 90 min	38.003	5.391	5.899	972 ± 28
75 °C, 30 min	36.434	5.620	4.905	960 ± 10
75 °C, 60 min	36.664	5.607	4.723	1296 ± 41
75 °C, 90 min	36.879	5.519	4.579	1159 ± 19

groups through the following chemical reaction (Reaction (1)).



From Table 1, the water absorption increases with increasing degree of saponification up to a nitrogen content of 9.25%. Thereafter, water absorption did not increase until the percentage nitrogen content was 4.7%. At low degrees of saponification, the number of carboxyl groups is very low and randomly distributed, so any hydrogen bonds formed are unable to sustain a stable intramolecular complex. At a higher degree of saponification, an increase in the number of acid groups on the acrylamide chain enhances intramolecular bonding between the amide and acid groups of the same molecule. The decrease in water absorption can be attributed to the decreased mobility of the saponified starch grafted poly[acrylamide-*co*-(maleic acid)] chains due to intramolecular hydrogen bonding [6]. It was then concluded that 90 min of saponification at room temperature would be used in the remainder of the present study.

3.3. Effect of total dose and dose rate on graft copolymerization of AM and MA on cassava starch

The effects of total dose and dose rate on the grafting of

AM and MA on cassava starch are presented in terms of the conversion of monomer, gel content, homopolymer and free copolymer formed, grafting efficiency, percentage add-on, and water absorption as shown in Table 2.

We found that for graft copolymerization of AM and MA onto starch at a dose rate of 1.71 kGy h⁻¹, the conversion of the monomer increases with an increasing total dose up to 8 kGy. For a total dose higher than 8 kGy, the conversion of the monomer decreases. However, at the dose rates of 4.34 and 11.0 kGy h⁻¹, the percentage conversion increases with an increase in the total dose up to at least 12 kGy. An increase in the total dose enhances the formation of radicals in the reaction mixture and induces a higher conversion for both the homopolymer and the graft copolymer. However, when the total dose is higher than 8 kGy at the dose rate of 1.71 kGy h⁻¹, the decrease in the percentage conversion could be the chain scission effect of the polymer at a longer reaction time. Increasing the dose rate slightly reduces the percentage conversion, especially at a lower total dose.

Increasing the dose rate increases the radical density, and radical recombination can probably occur. In addition, the effect of high dose rate enhances the degradation of the starch backbone [7]. When increasing the total dose, the gel content increases. The gel content is related to the cross-linking density. A cross-linking reaction of the graft copolymer is formed rapidly during the initial period of irradiation. Increasing the dose rate reduces the percentage gel content, because the cross-linking reaction occurs at a

Table 2

Effect of total dose and dose rate on the graft copolymerization of acrylamide and maleic acid onto cassava starch (DR: dose rate; TD: total dose; Conv: conversion; Gel: gel content; Homo: homopolymer; GE: grafting efficiency; WA: water absorption; AM-to-starch ratio: 2:1; MA = 2% w w⁻¹ of the acrylamide monomer, italics indicate optimal cases)

DR (kGy h ⁻¹)	TD (kGy)	Conv (%)	Gel (%)	Homo (%)	Add-on (%)	GE (%)	WA (g g ⁻¹)
1.71	0.5	80.8	55.7	77.7	40.9	10.5	808 ± 7
	1.0	90.8	65.8	66.7	49.9	19.9	866 ± 11
	2.0	96.6	69.3	48.4	54.6	36.8	1877 ± 16
	4.0	97.7	77.3	30.8	60.5	57.6	2026 ± 18
	6.0	98.7	78.9	22.9	60.8	67.2	1216 ± 14
	8.0	99.9	81.2	17.8	61.9	74.1	645 ± 5
	10.0	98.4	82.3	16.0	63.2	76.8	661 ± 18
	12.0	98.5	87.1	14.9	67.9	79.5	620 ± 37
4.34	0.5	68.4	28.7	82.1	26.6	5.4	718 ± 13
	1.0	86.5	42.2	79.4	31.6	7.6	748 ± 6
	2.0	89.8	52.8	70.8	36.6	13.0	1059 ± 9
	4.0	93.0	67.6	45.2	51.3	38.3	1229 ± 9
	6.0	94.4	68.0	29.7	58.0	57.9	1357 ± 7
	8.0	96.1	75.7	24.7	59.7	64.6	1123 ± 10
	10.0	96.5	76.6	21.4	62.2	69.6	941 ± 17
	12.0	97.4	81.5	18.7	59.1	72.0	857 ± 7
11.0	0.5	56.3	27.8	88.5	26.7	3.4	608 ± 7
	1.0	75.6	32.9	83.8	30.1	5.5	667 ± 5
	2.0	84.2	45.3	79.0	34.1	8.4	1071 ± 47
	4.0	91.9	45.8	73.9	38.8	12.0	1249 ± 39
	6.0	94.6	47.8	57.6	45.6	25.1	1540 ± 22
	8.0	95.8	59.3	47.3	51.5	36.4	1887 ± 9
	10.0	96.6	62.3	43.1	54.3	41.8	1700 ± 17
	12.0	97.5	64.9	36.4	58.0	50.3	1690 ± 24

Table 3

Effect of monomer-to-starch ratio on the graft copolymerization of acrylamide and maleic acid onto cassava starch (AM/St: acrylamide-to-starch ratio; Conv: conversion; Gel: gel content; Homo: homopolymer; GE: grafting efficiency; WA: water absorption; MA = 2% w w⁻¹ of monomer with a dose rate of 1.71 kGy h⁻¹, and a total dose of 4.0 kGy. Italics indicate the optimal solution)

AM/St ratio	Conv (%)	Gel (%)	Homo (%)	Add-on (%)	GE (%)	WA (g g ⁻¹)
1:1	80.4	51.0	38.0	32.2	34.5	682 ± 12
1.5:1	86.1	57.4	31.3	48.3	51.5	1582 ± 30
2:1	97.7	69.3	30.8	60.5	57.6	2026 ± 18
<i>2.5:1</i>	<i>96.6</i>	<i>72.5</i>	<i>24.5</i>	<i>63.2</i>	<i>66.1</i>	<i>2256 ± 25</i>
3:1	97.9	74.3	22.4	69.6	70.7	2037 ± 21

lower dose rate of gamma irradiation, but there is molecular chain scission takes place at a higher dose rate, especially in polysaccharides. The homopolymer decreases, but the grafting efficiency and the percentage add-on increase when increasing the total dose. This is because at a higher total dose, many active sites on the starch backbone are produced and many monomers can diffuse to graft on the starch backbone. However, when the total dose is higher than 10 kGy at the dose rate of 4.34 kGy h⁻¹, the percentage add-on is found to decrease. This could be due to the formation of small fragments of OH[·] and e_{aq}⁻ to form the homopolymer at the expense of the graft polymer. When increasing the dose rate at a fixed total dose, the percentage homopolymer increases and the grafting efficiency and the percentage add-on decrease. Generally, a lower dose rate produces a higher grafting efficiency. The monomer molecules and/or radicals are available at all active grafting sites on the starch backbones. At a higher dose rate, there are only a few free radicals available to start the graft copolymerization. Most radicals undergo recombination or initiate homopolymerization [8].

At the total dose of 4 kGy and dose rate of 1.71 kGy h⁻¹, the highest water absorption of the saponified product is obtained. The swelling of the polymer depends on the fine structure of the polymer network and primarily on the cross-linking density. High water absorption is affected positively by the percentage add-on, grafting efficiency, and conversion. The homopolymer formation has a strong negative effect on water absorption.

3.4. Effect of monomer-to-starch ratio on graft copolymerization

The effect of the monomer-to-starch ratio on the grafting of AM and MA onto cassava starch is presented in terms of the conversion of monomer, gel content, homopolymer and free copolymer formed, grafting efficiency, percentage add-on, and water absorption as shown in Table 3. The percentage conversion and the percentage gel content increase with an increasing monomer-to-starch ratio. During the irradiation, a temperature rise was detected. The increase in temperature may lead to a broader distribution of primary species and thereby an increase in G_R values of H[·], OH[·] or e_{aq}⁻, a decrease in G_M values of molecular hydrogen, H₂, or

H₂O₂ [5] and the occurrence of imidization, which usually takes place in the polymerization of acrylamide in a concentrated solution and at high temperatures or very long reaction times [9]. This results in a higher yield and higher cross-linking formation of polymers when a higher quantity of AM monomer is irradiated. However, the percentage conversion does not change when the ratio of the AM/starch ratio is higher than 2:1.

The percentage of homopolymer formed decreases but grafting efficiency and percentage add-on increase with increasing the monomer-to-starch ratio, because more monomers can react at grafting sites in the starch trunk polymer. However, at a high monomer-to-starch ratio, the percentage homopolymer may not be correctly determined simply by extraction, because a semi-IPN could be formed, either chemically or physically, with cassava starch. Homopolymers of PAM along with ungrafted, free copolymers of AM/MA could be formed [2] and sacrificed the graft copolymer.

The highest water absorption is detected in the super-absorbent polymer prepared with the monomer-to-starch ratio of 2.5:1 resulting in the higher grafting efficiency. However, at a monomer-to-starch ratio higher than 2.5:1, the water absorption somewhat decreased. This may be due to the higher cross-linking density at a higher monomer concentration. The equilibrium swelling is inversely related to the cross-linking density [10]. The polymer chains are restricted in swelling by elastic retraction forces of the network. The more the chains separate from each other, the more stiffness of the originally coiled polymer chains becomes.

3.5. Effect of maleic acid content on graft copolymerization

The effect of maleic acid content on starch-*g*-poly[acrylamide-*co*-(maleic acid)] prepared at the dose rate of 1.91 kGy h⁻¹ to the total dose of 4.0 kGy, the acrylamide-to-starch ratio of 2.5:1 and saponified at room temperature for 90 min with 5% KOH solution is shown in Table 4. The increasing amount of maleic acid does not increase the conversion of the reaction significantly as it approaches nearly 100% conversion. The percentage gel content decreases with increasing maleic acid content. This result indicates that maleic acid does not behave as a cross-linking

Table 4

Effect of maleic acid content on the graft copolymerization of acrylamide and maleic acid on to cassava starch (MA content: maleic acid content; Conv: conversion; Gel: gel content; Homo: homopolymer; GE: grafting efficiency; WA: water absorption; Acrylamide-to-starch ratio = 2.5:1 with a dose rate of 1.71 kGy h⁻¹, and a total dose of 4.0 kGy. Italics indicate the optimal solution)

MA content (%)	Conv (%)	Gel (%)	Homo (%)	Add-on (%)	GE (%)	WA (g g ⁻¹)
0	95.7	84.2	13.4	67.0	81.2	1679 ± 16
1	96.6	79.9	20.6	65.9	71.7	1637 ± 15
2	96.6	72.5	24.5	63.2	66.1	2256 ± 25
3	95.4	71.8	29.1	62.7	60.5	2166 ± 6
4	95.1	71.4	32.5	61.4	56.0	2020 ± 12
8	96.4	69.5	39.4	59.1	47.6	1972 ± 10
12	98.4	62.4	45.6	56.5	40.2	1718 ± 9

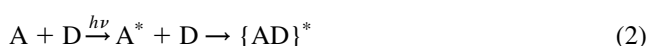
agent and both monomers prefer to copolymerize as an ungrafted free copolymer rather than a grafted copolymer onto the starch backbone, indicated by the decreasing grafting efficiency.

The percentages of the homopolymer and free copolymer increase when the grafting efficiency and percentage add-on decrease. Comparing the radical copolymerization of AM(*M*₁) – MA(*M*₂) with *r*₁ = 2.2 and *r*₂ = 0 [11], maleic acid cannot self-polymerize to obtain the homopolymer. Thus, the increasing homopolymer content may be from the formation of polyacrylamide or the random copolymerization of AM and MA radicals with the monomers, leading to the formation of the ungrafted, free copolymer of AM and MA. The percentage grafting efficiency and percentage add-on thus decrease could be caused by an increase in these non-grafted polymers in the solution phase, compared with a heterogeneous phase grafting between the two monomers with the gelatinized starch.

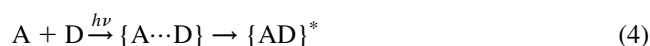
In aqueous solutions, several characteristic properties have been observed: conformational transition, a two-step dissociation process of dicarboxylic groups, binding of counterions, etc. These properties of maleic acid copolymers are attributed to two factors: (a) a hydrophobic interaction of non-polar side chains, and (b) a short-range electrostatic interaction of a pair of nearest-neighbor carboxylate groups [12,13]. The highest water absorption occurs at the quantity of maleic acid of 2% w w⁻¹ based on the weight of acrylamide. At a lower maleic acid concentration, the water absorption increases with increasing maleic acid content. This could be due to copolymerization reactions via the charge transfer (CT) complex of a monofunctional acceptor (A) and a donor (D). A detailed series of papers has discussed the background theory of the role of CT complexes in photopolymerization, and in particular their participation in UV curing systems under photoinitiator-free conditions has been explained [14–16]. This CT concept for UV grafting has also been extended to ionizing radiation system [16].

Typical mechanisms for the formation of an excited state DA complex are depicted in reactions (2)–(4).

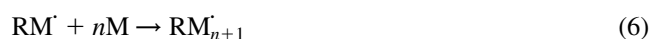
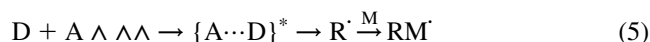
Formation of the exciplex type of AD*:



Formation of an AD* from a ground state CT:



The acrylamide, containing an electron-rich vinyl group as a donor, and the maleic acid becoming maleic anhydride on heating and dehydration via irradiation, and containing an electron-poor vinyl group as an acceptor, interact to yield CT complexes. Then gamma irradiation can directly cause a grafting reaction of the CT complex. The more energetic ionizing radiation can rupture bonds indiscriminately in the substrate, solvent, monomer or DA complex to create grafting sites and initiate polymerization [16]. Homopolymer formation may also be observed as a competing reaction during these grafting processes (Reactions (5) and (6)), where D is the electron-rich donor, A is the electron-poor acceptor and M is a monomer like acrylamide. Maleic acid itself is also an acceptor so many residual acids could complex with acrylamide and react as such



The number of hydrophilic groups of poly[acrylamide-co-(maleic acid)] is higher than that of the polyacrylamide, so the swelling of starch-g-polyacrylamide is obviously lower than that additionally contains the maleic acid moiety. However, at the maleic acid content higher than 2% w w⁻¹, the water absorption decreases. Bajpai proposed that the lower water absorption may be due to a predominant role of a hydrophobic character of the unionized maleic acid [17], leading to the increase in homopolymer and decreases in grafting efficiency and percentage add-on.

3.6. Effect of salt solution on water absorption

Table 5 shows the swelling of starch-g-poly[acrylamide-co-(maleic acid)] superabsorbent in the salt solutions. The highest superabsorbent copolymer was selected to test the salt effect in isotonic fluids of 0.9% w w⁻¹ of NaCl, MgCl₂, and CaCl₂ solutions. The water absorption decreases due to the ionic strength (*I*) of the salt solution. At a low ionic

Table 5
Effect of salt solution on water absorption

Solution	Ionic strength ^a (mole-ion dm ⁻³)	Water absorption (g g ⁻¹)
Distilled water	–	2256 ± 25
0.9% w w ⁻¹ NaCl solution	0.1540	94 ± 11
0.9% w w ⁻¹ MgCl ₂ solution	0.2832	64 ± 7
0.9% w w ⁻¹ CaCl ₂ solution	0.2433	47 ± 5

^a $I = 1/2(\sum(C_i Z_i^2))$, where I , C_i , and Z_i are the ionic strength, the ionic concentration, and the charge on each individual ion, respectively [17].

strength, repulsion is a long-range interaction, and the gel expands to minimize the repulsion free energy. When the ionic strength rises, the expansion of the network decreases because of the screening effect of the ionic charges bound to the network and the decrease of the osmotic pressure difference between the gel and the external solution [18]. The ionic strength of the solution depends on both the mobile ions' concentration and their oxidation state. Small quantities of divalent or trivalent ions can drastically decrease the swelling values. In addition, the divalent Mg²⁺ and Ca²⁺ ions may cross-link the gel by salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer. Consequently, the cross-linking density of the network increases [19,20].

3.7. Effect of pH on water absorption

Table 6 shows the influence of the solution pH (3–11) on the water absorption capacity of the synthesized graft copolymer, which has the highest water absorption in distilled water (2256 ± 25 g g⁻¹). When the pH of the external solution increases beyond 5.0, the ionization of carboxylic groups in the gel matrix causes a sudden increase in swelling due to increased ion osmotic swelling pressure as well as chain relaxation resulting from the electrostatic repulsion among carboxylate groups inside the polymer matrix [16]. In addition, the maximum extent of swelling is reached at pH 5, this being due to the complete dissociation of acidic groups of maleic acid at this pH value. The first and second dissociation constant of maleic acid are pK_{a1} = 1.85 and pK_{a2} = 6.06, respectively [21]. With further increases 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, which ultimately reduces the equilibrium swelling capacity of the superabsorbent polymer [17].

3.8. Effect of particle size on water absorption

We used the gravimetric swelling capacity method to determine the swelling extent for collections of small particles; the additional mass of interparticle, unabsorbed liquid was included in the swelling ratios. The water absorption of the superabsorbent polymer versus particle size is shown in Table 7. Water absorption values from this study are typically larger than those obtained with methods where interparticle moisture is excluded. The particle size distribution of the sample and the modulus of the swollen polymer affect the way in which the liquid drains from the gel [22]. The absorption increases when the particle size decreases due to the higher amount of interparticle liquid, because the small particles have a higher surface area per mass than the larger particle size at the same quantity.

3.9. Absorption under load

Superabsorbent polymers in personal care articles must resist deformation and deswelling under an external load because this ability has been correlated with improved performance in pad analysis and in diapers. When a uniaxial compression is applied to the swelling polymer particle, it is forced to change its shape. The magnitude of the deformation depends on the modulus, which in turn depends on the initial cross-linking density and extent of swelling.

Fig. 1 shows the gel swelling versus applied compression for seven different maleic acid contents. When the applied load increases, the absorbency under load decreases because liquid can be removed from a swollen superabsorbent gel by application of pressure. This deswelling occurs because the application of pressure to the system causes an increase in

Table 6
Effect of pH on water absorption

pH of buffer solution	Ionic strength ^a (mole-ion dm ⁻³)	Water absorption (g g ⁻¹)
3	0.0061	67 ± 7
5	0.0134	115 ± 6
8	0.0212	106 ± 3
11	0.0272	83 ± 5

^a $I = 1/2(\sum(C_i Z_i^2))$, where I , C_i , and Z_i are the ionic strength, the ionic concentration, and the charge on each individual ion, respectively [17].

Table 7
Effect of particle size on water absorption

Particle size (μm)	Water absorption (g g^{-1})
600	1939 ± 10
300	2226 ± 20
180	2527 ± 13
150	2653 ± 25

its free energy and in the chemical potential of any species that can diffuse into or out of the system. The increase in chemical potential serves as a driving force to expel water from the gel into the surroundings when the gel is compressed. The effect of adding pressure to the gel is similar to adding additional cross-links to the gel to increase the hydrostatic pressure in the gel phase and to reduce the maximum swelling. The limitation of swelling under pressure and the related deswelling behavior are thus related to the osmotic pressure of the gel, which acts as a polymer solution confined inside a semi-permeable membrane [23].

The absorbency under loading at the higher loads increases with increasing maleic acid content even though the equilibrium swelling capacity at zero loading decreases. More rigid gel particles at the high maleic acid content maintain their swelling capacity better under load than do particles of the same size distribution for a softer and more deformable gel. Regarding the swelling time under loading, all the starch-*g*-poly[acrylamide-*co*-(maleic acid)] without and with 1, 2, 3, 4, 8, or 12% maleic acid reaches a constant water absorption within 30 min. Actually, the water absorption under load (AUL) increases rapidly at the beginning of the test, increases slightly after 10 min, and becomes constant at 30 min.

3.10. Surface morphology of the copolymers

The surface appearance and structure of the saponified graft copolymer of saponified cassava starch-*g*-poly[acrylamide-*co*-(maleic acid)] were observed using scanning electron microscopy (SEM). The microphotographs taken

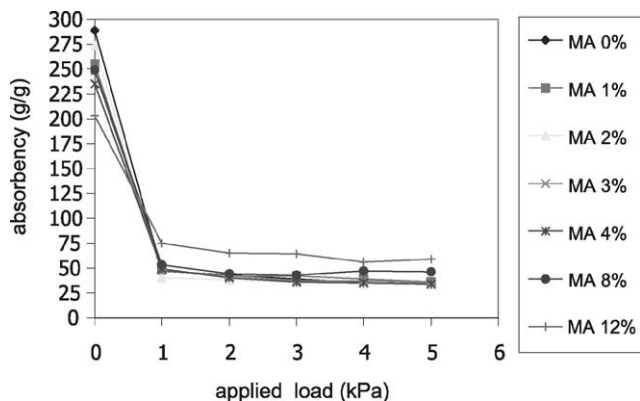


Fig. 1. Gel swelling versus the applied compression for seven different maleic acid contents.

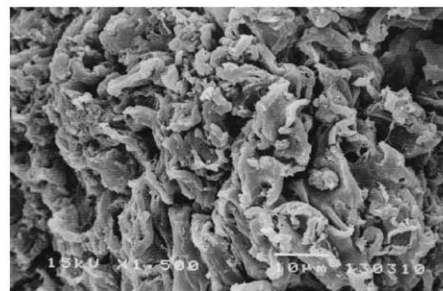
by the electron microscope of the saponified starch graft copolymers are shown in Figs. 2–5.

SEM photographs of the saponified starch-*g*-polyacrylamide (Fig. 2) and saponified starch-*g*-poly[acrylamide-*co*-(maleic acid)] that gives less water absorption (Fig. 3) show that they have a less porous, non-cellular structure. On the other hand, SEM photographs of saponified starch-*g*-poly[acrylamide-*co*-(maleic acid)] that has the higher water absorption (Fig. 4) show that it has more pores with a semi-cellular structure. It is believed that these pores are the regions of water permeation, in which the interaction of the hydrophilic groups with water makes the saponified copolymer a high water absorption material.

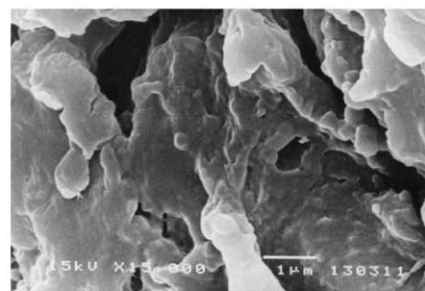
Fig. 5 shows an SEM photograph of starch-*g*-poly[acrylamide-*co*-(maleic acid)] that has a high percentage gel content and perhaps a higher cross-linking density. A fine network with smaller pore structures is observed, which could be the result of imidization of the acrylamide moiety. The fine network structure is one of the reasons for rapid water absorption.

4. Conclusions

Radiation grafting copolymerization of gelatinized cassava starch with acrylamide monomer in the presence of a small amount of diprotic acid of maleic acid was performed. Effects of the dose rate to various total doses on the graft copolymerization in terms of grafting performance and water absorption were investigated. The addition of a few percent of maleic acid, based on the weight of

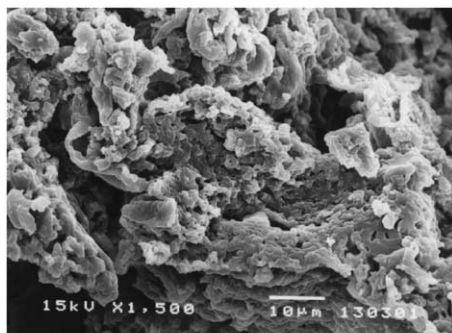


(a)

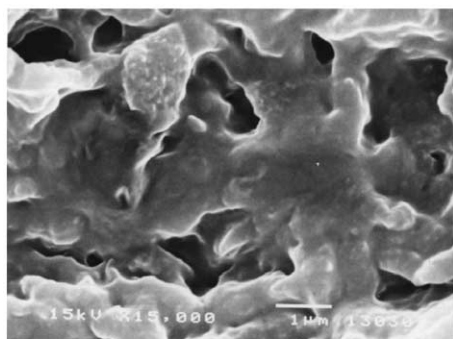


(b)

Fig. 2. SEM photograph of the saponified starch-*g*-polyacrylamide (WA = $1679 \pm 16 \text{ g g}^{-1}$).

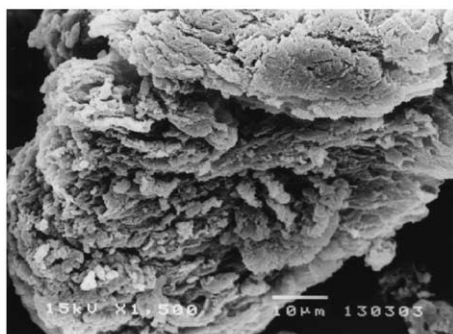


(a)

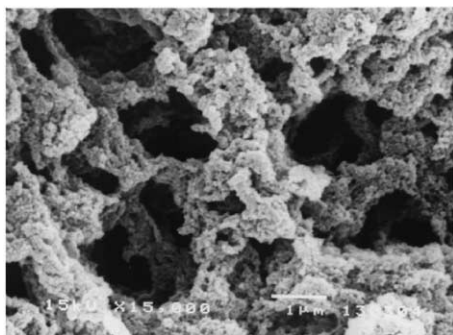


(b)

Fig. 3. SEM photograph of the saponified starch-g-poly(acrylamide-co-maleic acid) at DR 11.0 kGy h⁻¹ to the TD 0.5 kGy (WA = 608 ± 7 g g⁻¹).



(a)



(b)

Fig. 4. SEM photograph of the saponified starch-g-poly(acrylamide-co-maleic acid) at DR 1.71 kGy h⁻¹ to the TD 4.0 kGy (WA = 2256 ± 25 g g⁻¹).

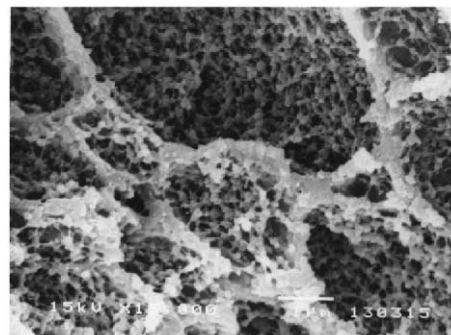


Fig. 5. SEM photograph showing the cellular structure of the saponified starch-g-poly(acrylamide-co-maleic acid) at the acrylamide-to-starch ratio of 3:1 (WA = 2037 ± 21 g g⁻¹).

acrylamide, yielded the optimum grafting efficiency and increased the water absorption of the resulting superabsorbent polymer. The grafting of the copolymer of acrylamide and maleic acid onto the starch backbone was proposed to take place via a charge transfer complex based on various previous research works on photopolymerization and ionizing radiation. In addition, analysis and property characterizations of the anionic superabsorbent polymers were also carried out in the areas of liquid absorption in isotonic saline solutions or buffered pH solutions, and absorption under loading. We have found it as a pH sensitivity, and the samples are affected by the ionic strength of the medium. The morphology of the superabsorbent polymers reveals some relationships between the porosity, network structure and extent of water absorption.

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