energy for gelatinization compared with non-waxy one because of it's dense crystalline structure and that in the waxy type there may be upper limit of the energy required for gelatinization (for example approximately 15 J/g in rice) though the gelatinized temperature differs from one crop to another. Therefore there might be formed no relationship between Tp and enthalpy. However, this estimation cannot be confirmed until relationships with the structure of amylopectin, particle density and so on are clarified.


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# The Effects of Enzyme Hydrolysis on the Properties of Potato, Cassava and Amaranth Starches


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X-ray diffraction method and differential scanning calorimetry were used to study the effects of enzyme hydrolysis on physico-chemical properties of potato, cassava and amaranth starches. Various hydrolysis procedures and different sources of enzymes were employed. The highest percentage of hydrolysis was obtained using the bacterial thermostable α-amylase following by the saccharification with amyloglucosidase. Enzyme treatment showed decrease in the degree of crystallinity of all hydrolyzed starch samples of A-type crystals. B- and C-types were weakened upon enzymatic hydrolysis at 60°C and completely dissappeared at 100°C. The gelatinization endotherm decreased for samples with low degree of crystallization and disappeared in samples with amorphous stage.

**Die Einflüsse der enzymatischen Hydrolyse auf die Eigenschaften von Kartoffel-, Cassava- und Amaranthstärken.** Zur Untersuchung der Einflüsse der enzymatischen Hydrolyse auf die physikalisch-chemischen Eigenschaften von Kartoffel-, Cassava- und Amaranthstärken wurden die Röntgen-Beugungsmethode sowie der Raster-Differential-Kalorimetrie angewendet. Verschiedene Hydrolyseverfahren und unterschiedliche Enzymherkünfte wurden angewendet. Der höchste Prozentsatz der Hydrolyse wurde bei Verwendung von bakterieller thermostabiler α-Amylase erreicht, gefolgt von der Verzuckerung mit Amyloglucosidase. Die Enzymbehandlung führte zu einer Verringerung der Kristallinität aller hydrolysierter Stärkeproben der A-Typ-Kristalle. Die B- und C-Typen waren durch enzymatische Hydrolyse bei 60°C abgeschwächt und verschwanden bei 100°C vollständig. Die Verkleisterungsisotherme verringerte sich bei Proben mit niedrigem Kristallisationsgrad und verschwand in Proben im amorphen Zustand.


## 1 Introduction

The conversion of cassava, potato and other starches into ethanol has attracted the attention of many researches world over. But not too many were interested in the glucose and fructose products [1, 2, 3]. As can be seen from the very recent literature review that the use of potato, cassava and amaranth has documented in liquefaction with thermostable endo-amylase following saccharification with soluble and immobilized amyloglucosidase [4, 5, 6, 7, 8, 9, 10].

Bacterial α-amylase, being an endo-enzyme, catalyzes hydrolysis only of 1,4 α-glucosidic linkages located in the inner regions of the molecules of amylose and amylopectin. Fungal α-amylase also hydrolyzes 1,4-α-glucosidic linkages in the process of

saccharification. These enzymes don't hydrolyze the 1,6- α-branch points in amylopectin, but can bypass them [11]. Glucoamylase coacting in liquefied starch during saccharification, being an exo-enzyme, hydrolyzes all glucosidic linkages.

Cassava (*Manihot esculenta*) represents a popular crop in Taiwan. This plant is one of the main sources of starch [12, 13, 14]. Considering that the starch from different sources as potato, cassava and amaranth have proven acceptable for an enzyme hydrolysis process in the production of glucose or fructose, it would be of value to explore the possibility of implementing an appropriate technology for more efficient application of these starch sources.

Some preliminary kinetic studies on starch enzymatic hydrolysis and its nutritional indices were conducted in our previous work [15, 16].

There are some investigations about the heat-moisture treatment of different starches, which change dramatically their properties [17, 18, 19]. The role of the residual starch after gelatinization and saccharification processes becomes very important. It is interesting to study the composition of residual starches after a strong enzymatic attack.

Very little has been reported of the effect of different α-amylases and amyloglucosidases on the crystallinity of the residual starches during treatment at high temperatures.

This study aims to investigate the structure of potato, cassava and amaranth residual starches through their crystallinity, endothermic properties and degree of hydrolysis. The emphasis is done on intensive attack of enzymes at high temperatures, using different α-amylases with and without amyloglucosidase.

## 2 Materials and Methods

Starches Commercial cassava starch (Wu-Chin-Tzu) was purchased from Pu-Li Byproduct Factory, Taiwan Sugar Corp. (Pu-Li, Nantou, Taiwan). Potato starch was imported from The Netherlands. *Amaranthus cruentus* starch and amylaceous fraction from air classification of whole amaranth seed flour [20] were given by National Institute of Agricultural Research, Mexico.

Potato, cassava and amaranth starches were washed with distilled water several times to remove impurities and dried in an oven at 40°C before being used. The pure starches as well as the amylaceous fraction of amaranth were used for hydrolysis studies. The following enzymes were used: Bacterial α-amylase from *Bacillus subtilis,* type III-A, activity 52 units/mg (EC3.2.1.1); Fungal α-amylase from *Aspergillus oryzae,* type X-A, activity 100–200 units/mg (EC 3.2.1.1); Amyloglucosidase from *Aspergillus niger,* activity 5 000–8 000 units/ml (EC 3.2.1.1); Protease from *Bacillus subtilis,* activity 7–15 units/mg. All these enzymes were supplied by Sigma Chemical Co.

Termamyl 120L, a thermostable bacterial α-amylase, activity 120 KNU/g was produced by Novo-Industri A/S, Denmark, and was donated for this project. The moisture, fat and protein contents, swelling power and solubility, water binding capacity, amylograph viscosity, and gelatinization temperature were performed according to conventional methods of analysis [21, 22].

The gelatinization temperature range in starches was measured at the loss of birefringence of 2%, 5% and 98% using a polarized light microscope with *Kofler* hot stage and designated as initial, midpoint and end point values, respectively. A differential scanning calorimeter (DSC-DU PONT 1090B Thermal Analysis/Data System V2.0.E I. Du Pont de Nemours and Co., Inc. Wilmington, DE) was employed for gelatinization determination. Samples of about 6 mg weighed to 0.1 mg were hermetically sealed in metal pans (E.I. Du Pont de Nemours and Co., Inc. Wilmington, DE) and placed on one side. The other, or reference, side held an empty sealed pan. The instrument heated both pans equally for gelatinization from 20°C to 130°C at a rate of 10°C/min, and for retrogradation from 10°C to 130°C at the same rate. The endothermic peak area and peak temperature were recorded for each sample. All samples were analyzed in triplicates with 6% experimental error [17].

The following methods for starch hydrolysis were compared:

13 combinations with different enzymes at different incubation conditions were carried out (Table 2, experiments a-m). 7 g of starch (potato, cassava, amaranth and amylaceous fraction of amaranth) were incubated with 2.8 ml of Termamyl 120L, at 100°C for 30 min at pH 6.0. (respectively samples (a), (i), (l), (Table 2). Instead of Termamyl 120L potato starch was treated with 28 mg of α-amylase from *Bacillus subtilis* (Sample b, Table 2) or with 36 mg of α-amylase from *Aspergillus oryzae*-sample (c) at 100°C for 30 min at pH 6.9. Samples (d), (j), (k) and (m) were treated with 2 enzymes. The first one was under the same conditions as samples (a), (i) and (1). Then the slurry was cooled and 7 ml of amyloglucosidase from *Aspergillus niger* was added, and the sample was incubated at 60°C for 30 min at pH 4.5. Sample (e) was treated under the same conditions as samples (a), (i), (1), but instead ot Termamyl 120L 28mg of α-amylase from *Bacillus subtilis* were added. Potato starch as a reference was treated with various α-amylases at two different temperatures (60°C and 100°C) with and without amyloglucosidase. Therefore samples (f) and (d); (g) and (e); (h) and (e) were nearly equal in their composition, but the incubation with Termamyl 120L; α-amylase from *Bacillus subtilis* was at 60°C during 30 min. After appropriate time of incubation the sample was cooled in ice-water, centrifuged at 9000 rpm for 30 min at 4°C, then the precipitate was incubated with protease for proteolytic treatment at 37°C overnight in phosphate buffer (pH 7.5). Then the residues were centrifuged, washed and freeze-dried [19, 23]. Aliquots of supernatants were removed and the content of reducing sugars as glucose were determined according to the Somogyi- Nelson method [24]. A dilution of 1:10 was made and glucose released was measured. Carbohydrates were determined by the phenol-sulfuric acid method [25]. The residual starches were analysed for differential scanning calorimetry and X-ray diffraction.

Brabender viscoamylograms of starches were determinated by the use of a Brabender viscoamylograph according to Mazurs et al. [26]. The conditions of operation were with a 700 cmg sensitivity cartridge and at a speed of 75 rpm. 5% of potato and cassava, and 8% of amaranth were applied. The temperature increment was 1.5°C/min from 35°C to 95°C and 35°C.

X-ray diffractograms of raw and hydrolyzed starches were recorded by a Rigaku (MAX-IIIA, Rigaku Keisoku Co., Ltd, Japan) powder X-ray diffractometer according to *Hizukuri's* method [27]. The X-ray, $CuK_\alpha$, irradiation was performed with a monochrometer. The operating conditions were the following: voltage 35 kV; current 25 mA; scanning speed 1°/min; chart speed 5mm/min; time constant 4 s. Samples were densely packed on a glass plate using an aluminium frame. Values of intensities were read from the curves over the angular range 4°–30° which includes most of the crystalline peaks. Percent crystallinity was determined by an integral method. "d" spacings were computed by Bragg's law using that $\lambda = 2d \sin\Theta$, where $\lambda$ = wave length of the X-ray beam = 1.5405Å, d = spacing between unit cell edges of specific crystal needed to be studied, $\Theta$ = angle of diffraction. Some data were analyzed for statistical significance by the least significant difference (LSD) test at the 5% level of probability [28]. The quantitative measurement of crystallinity was undertaken according to *Nara* et al. [29]. Each point of minimum intensity on the X-ray diffractograms of potato, cassava and amaranth starches was joined by a smooth curve.

The upper region under the most prominent peaks in raw starch was the area of 100% crystalline fraction. The diffraction area of a corresponding treated sample with non shown peaks was taken as 100% amorphous substance.

## 3 Results and Discussion

Proximate composition and some physico-chemical properties of raw potato, cassava and amaranth (pure and amylaceous fraction) starches are given in Table 1.

The proximate composition (fat, nitrogen and carbohydrates), gelatinization temperatures, swelling power, solubility, water binding capacity and amylograph consistencies feel within the range of values reported in literature [5, 9, 10, 12, 13, 20, 30]. Potato and cassava starch had a lower gelatinization temperature range than the amaranth starch, which can be attributed to their higher amylose content and larger starch granule size.

Table 2 shows changes in reducing sugars (RS) during enzymatic hydrolysis of potato, cassava and amaranth starches. At 100°C significant ($p < 0.05$) increases in RS were observed in all

Tab. 1.
Composition of Raw Starches

| Indices | Starches Potato | Cassava | Amaranth | Amylaceous |
|---|---|---|---|---|
| Moisture (%) | 16.37 | 12.49 | 12.30 | 12.34 |
| N (%) | 0.01 | 0.02 | 0.02 | 0.96 |
| Protein (%)[1]) | 0.10 | 0.15 | 0.97 | 6.00 |
| Fat (%) | 0.04 | 0.05 | 0.39 | 2.60 |
| Carbo-hydrates (g/100g d.b) | 1.16 | 1.14 | 1.13 | 0.65 |
| Initial gelatinization temperature (°C) | 62 | 57 | 66 | – |
| Mid-point gelatinization temperature (°C) | 64 | 62 | 71 | – |
| End-point gelatinization temperature (°C) | 68 | 65 | 76 | – |
| Swelling power at 30°C | 2.17 | 2.88 | 3.42 | 2.45 |
| Solubility at 30°C (%) | 0.24 | 1.16 | 1.5 | 5.87 |
| Water binding capacity (%) | 1.17 | 1.85 | 2.37 | 1.31 |
| Amylograph consistencies (B.U.) | | | | |
| at peak | 980 | 287 | 400 | 375 |
| at 95°C | 930 | 205 | 310 | 275 |
| after 60 min at 95°C | 320 | 64 | 300 | 240 |
| on cooling to 35°C | 465 | 173 | 390 | 370 |
| after 60 min at 35°C | 540 | 170 | 380 | 355 |

[1]) % Protein = % Nitrogen × 6.25

Tab. 2.
Reducing Sugars (RS) in Raw and Hydrolyzed Starches.

| Starch | Enzymatic treatment | Number of samples treatment | RS (g/100g) |
|---|---|---|---|
| Potato | Raw | A | 0.09 |
| | Term. (l) | a | 87.61 |
| | *Bac. subt.* (2) | b | 27.73 |
| | *Asp. oryz.* (3) | c | 19.85 |
| | Term. (1) + AMG. S. (4) | d | 126.68 |
| | *Bac. subt.* (2) + AMG. S. | e | 89.91 |
| | Term. (5) + AMG. S. | f | 76.78 |
| | *Bac. subt.* (6) + AMG. S. | g | 73.82 |
| Cassava | RAW | B | 0.08 |
| | Term. (1) | i | 93.85 |
| | Term. (1) + AMG. S. | j | 104.69 |
| Amaranth | RAW | C | 0.13 |
| | Term. (1) + AMG. S. | k | 62.00 |
| Amaranth[7]) | RAW | D | 1.11 |
| | Term. (1) | l | 70.87 |
| | Term. (1) + AMG. S. | m | 82.69 |

(1) Termamyl 120 L, incubation at 100°C;
(2) α-amylase from *Bacillus subtilis*, incubation at 100°C;
(3) α-amylase from *Aspergillus oryzae*, incubation at 100°C;
(4) Amyloglucosidase Sigma, incubation at 60°C;
(5) Termamyl 120 L, incubation at 60°C;
(6) the same as (2), incubation at 60°C;
(7) amaranth amylaceous fraction.

samples treated with Termamyl following by saccharification with amyloglucosidase. Overall rate of starch hydrolysis was the highest for cassava, following by potato and amaranth starches, indicating that the susceptibilities of raw starch granules to amylases depend on the starch species and the origins of the enzymes [18, 30]. The calculated "d" spacings of enzymatically

Tab. 3.
X-ray Diffraction Spacings and Relative Crystallinity in Raw and Hydrolyzed Starches.

| Samples (1) | | Interplanar spacings d, Å – very strong (vs); strong (s); medium (m); weak (w); and broad (br) intensities (2) |
|---|---|---|
| Potato | A | 16.98 (m); 7.89 (w); 6.06 (s); 5.34 (vs); 4.67 (m); 4.07 (s); 3.80 (s) 3.48 (m) |
| | a | 3.90 (br) |
| | b | 5.34 (w); 4,07 (m) |
| | c | 5.34 (w); 4,67 (m); 4.07 (s); 3.80 (s) |
| | d | 4.35 (br) |
| | e | 4.35 (br) |
| | f | 5.34 (s); 4.67 (w); 4.07 (m); 3.80 (w) |
| | g | 5.34 (s); 4.07 (m) |
| Cassava | B | 7.76 (w); 6.06 (s); 5.27 (vs); 5.06 (s); 4.53 (w); 3.93 (vs); 3.42 (m) |
| | i | 4.87 (br) |
| | j | 4.87 (br) |
| Amaranth | C | 7.96 (w); 5.98 (s); 5.23 (s); 5.04 (vs) 4.57 (w); 3.90 (vs); 3.42 (w); 3.11 (w) |
| | k | 3.90 (s) |
| Amaranth | D | 5.98 (m); 4.57 (w); 3.90 (w) |
| | l | 5.04 (w) |
| | m | 5.04 (w); 3.90 (s); 3.42 (w) |

[1]) see Table 2 for samples composition

hydrolyzed samples, which correspond to the original native starch were included in Table 3. Fig. 1 shows the X-ray patterns for raw starches and enzymatically treated with three types of enzymes. As can be seen on Fig. 1 that raw starch samples reflected the following patterns: amaranth (type A), potato (Type B) and cassava (type C).

The treatment with thermostable α-amylase at 100°C has clearly destroyed the crystallinity of raw potato starch in sample (a) and cassava starch in sample (i), and decreased for amaranth starch in sample (l). Samples (d), (j), (k) and (m) treated with the same enzyme at the same temperature following saccharification with amyloglucosidase showed minor crystallinity to compare with the previous ones. Samples (a), (d), (i) and (j) had only one broad peak between 3.90 and 4.87 Å. Sample (e) was similar to sample (d), but sample (e) was treated in the first stage with α-amylase from *Bacillus subtilis* and after this with amyloglucosidase at the same conditions as sample (d). Samples (d) and (j) showed some minor crystallinity than the corresponding amorphous ones (a) and (i). Probably presence of glucose during saccharification affected the phase separation of the starch and water. The treatment of sample (A) with α-amylase from *Bacillus subtilis* at 100°C had clearly decreased its crystallinity in sample (b). This sample showed the presence of some additional peaks in comparison with sample (A) at medium intensity mainly between 21° and 24° at 4.07; 3.98; 3.91; 3.86 and 3.50 Å and two weak ones at 5.40 and 5.09 Å.

The enzymatic hydrolysis of sample (A) with α-amylase from *Aspergillus oryzae* changed the crystal type which is shown in sample (c). New minor peaks appeared at 8.58; 5.34; 5.18; 4.74; 3.97; 3.56; 3.40; 3.30 and 3.08 Å. The strongest peaks were located between 19 and 24° with "d" spacing corresponding to 4.44; 4.09 and 3.80 Å.

Peaks at 3.20 and 3.00 Å were with medium intensity. The functional form of the crystals in sample (c) is quite different from those in samples (A) and (b). This development of crystallinity in sample (c) can't be explained by the enzymatic action of α-amylase from *Aspergillus oryzae* at 100°C which showed even low activity at 30°C and was inactivated at 50°C. The type of crystals in sample (c) was different to that observed

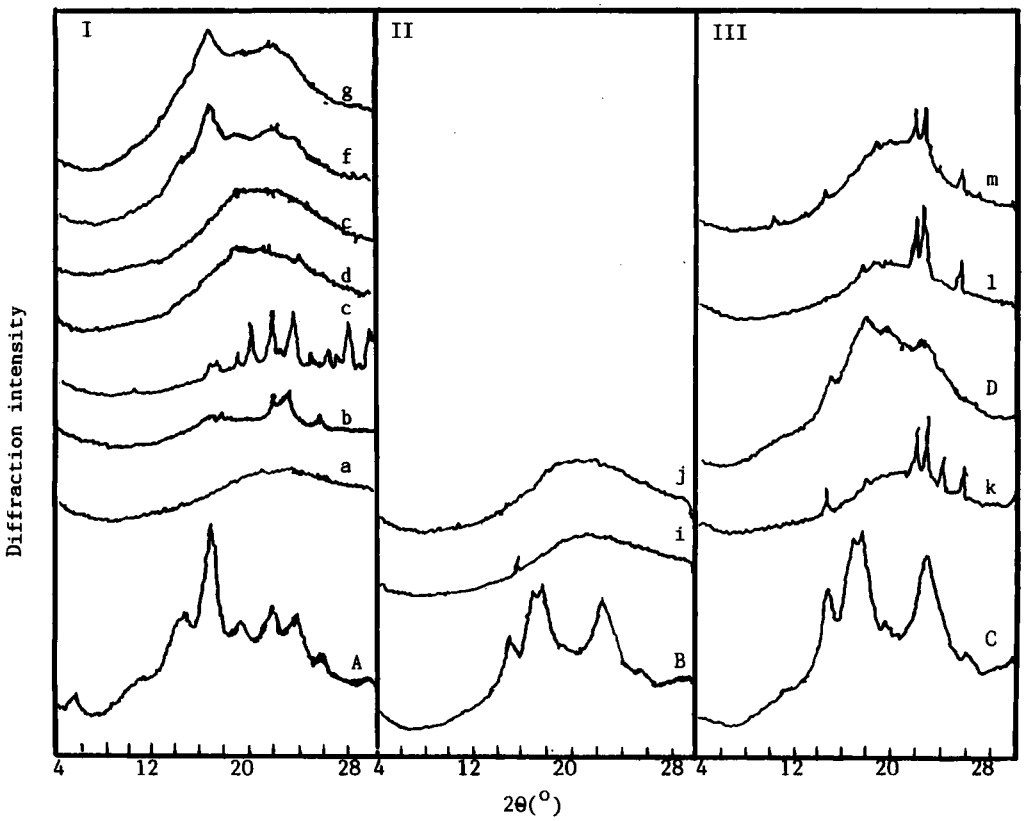


Figure 1. X-ray diffraction patterns of potato (I), cassava (II) and amaranth (III) starches with different hydrolysis treatments. A, a, b, c, d, e, f, g; B, i, j; C, k, D, l, and m respectively raw and hydrolyzed starch samples. See text, Table 2 for their composition.

for all other samples and can be explained on the basis of reorganization of molecules. Samples (f) and (g) were treated respectively with the same enzymes as samples (d) and (e), but at 60°C sample (f) showed higher crystallinity than (g). The activity of thermostable α-amylase at 60°C was lower than for α-amylase from *Bacillus subtilis*. In samples (b), (c), (f) and (g) the prominent peaks corresponding to raw starch appeared in different intensity, but at the same "d" spacings 5.34, 4.07 and 3.80 Å. Their relative crystallinity was measured taking into consideration these three strongest peaks in raw starch (Fig. 1, position I). Their crystallinity was respectively 12.7, 28.7, 38.3 and 43.5%.

In the case of amaranth starch (Fig.1, position III) sample (D) differed from the raw one. Sample (D) showed some additional peaks with medium intensity at 5.90; 4.98; 4.53 and 3.97 Å. Sample (k) had six peaks with medium intensity concentrated at 6.06; 5.27; 3.68; 3.46 and strong ones at 4.04 and 3.90 Å. Sample (l) showed the presence of two minor peaks at 5.04 and 3.74 Å; one medium at 3.62 and two strong ones at 4.06 and 3.91 Å. Similar spectra were recorded in sample (m) with fewer peaks at 8.67; 6.06; 5.04; 4.72; 3.71; 3.30; one medium at 3.62 and two strong ones at 4.04 and 3.90 Å. The X-ray patterns of samples (k), (l) and (m) were similar. The peaks in (l) and (m) appeared sharper than in their original raw starch sample (D). All treated amaranth samples with slight exception showed common peaks at 5.04 and 3.90 Å. The relative crystallinity of samples (D), (k), (l) and (m) was calculated in relation to these peaks and was respectively 51.9; 8.0; 64.7 and 6.2%. Amaranth starch only reduced the crystallinity but did not change the crystal type, which is in agreement with some literature data which reflected heat-moisture treatment, but not the intensive attack of enzymatic hydrolysis [18].

Cassava and amaranth starches displayed very similar X-ray diffraction patterns, characterized as type A. Amaranth starch, treated with enzymes, displayed curves with better defined peaks than the corresponding raw starch – sample (D), which is in agreement with other investigators [5, 18, 31]. Probably enzymatic attack was done throughout the amorphous granular areas.

A summary of DSC analysis of raw and hydrolyzed potato, cassava and amaranth starches is given in Table 4 and in Fig. 2. Differences in $T_o$ and $T_e$, and statistically ($P < 0.05$), the same

Tab. 4.
DSC Thermogram Values of Raw and Hydrolyzed Potato Cassava and Amaranth Starches (1).

| Samples (2) | | endothermic transition (C°) | | | Enthalpy of gelatinization | |
|---|---|---|---|---|---|---|
| | | $T_o$ | $T_p$ | $T_e$ | (j/g) | (Cal/g) $\Delta H_g$ |
| Potato | A | 52.920 | 60.600 | 79.550 | 5.370 | 6.42 |
| | a | – | – | – | – | – |
| | b | 29.000 | 37.100 | 43.870 | 2.480 | 2.96 |
| | c | 31.310 | 39.050 | 51.340 | 3.450 | 4.13 |
| | d | – | – | – | – | – |
| | e | 28.500 | 37.400 | 46.640 | 0.364 | 0.34 |
| | f | 58.570 | 66.000 | 73.240 | 1.014 | 0.80 |
| | g | 56.780 | 63.830 | 73.250 | 1.316 | 1.21 |
| Cassava | B | 52.250 | 63.100 | 74.050 | 2.770 | 3.31 |
| | i | – | – | – | – | – |
| | j | 32.470 | 39.450 | 46.400 | 1.300 | 1.04 |
| Amaranth | C | 58.750 | 66.300 | 79.370 | 2.630 | 3.14 |
| | k | 34.500 | 41.400 | 48.790 | 2.145 | 2.56 |
| Amaranth | D | 60.850 | 67.300 | 76.750 | 1.138 | 0.91 |
| | l | 27.500 | 37.600 | 57.920 | 5.240 | 4.17 |
| | m | 27.750 | 36.050 | 46.550 | 2.190 | 1.74 |

(1) Data are means of triplicate determinations.
$T_o$, $T_p$, $T_e$ = initial, peak and end endothermic temperatures.
(2) See table 2 for samples composition.

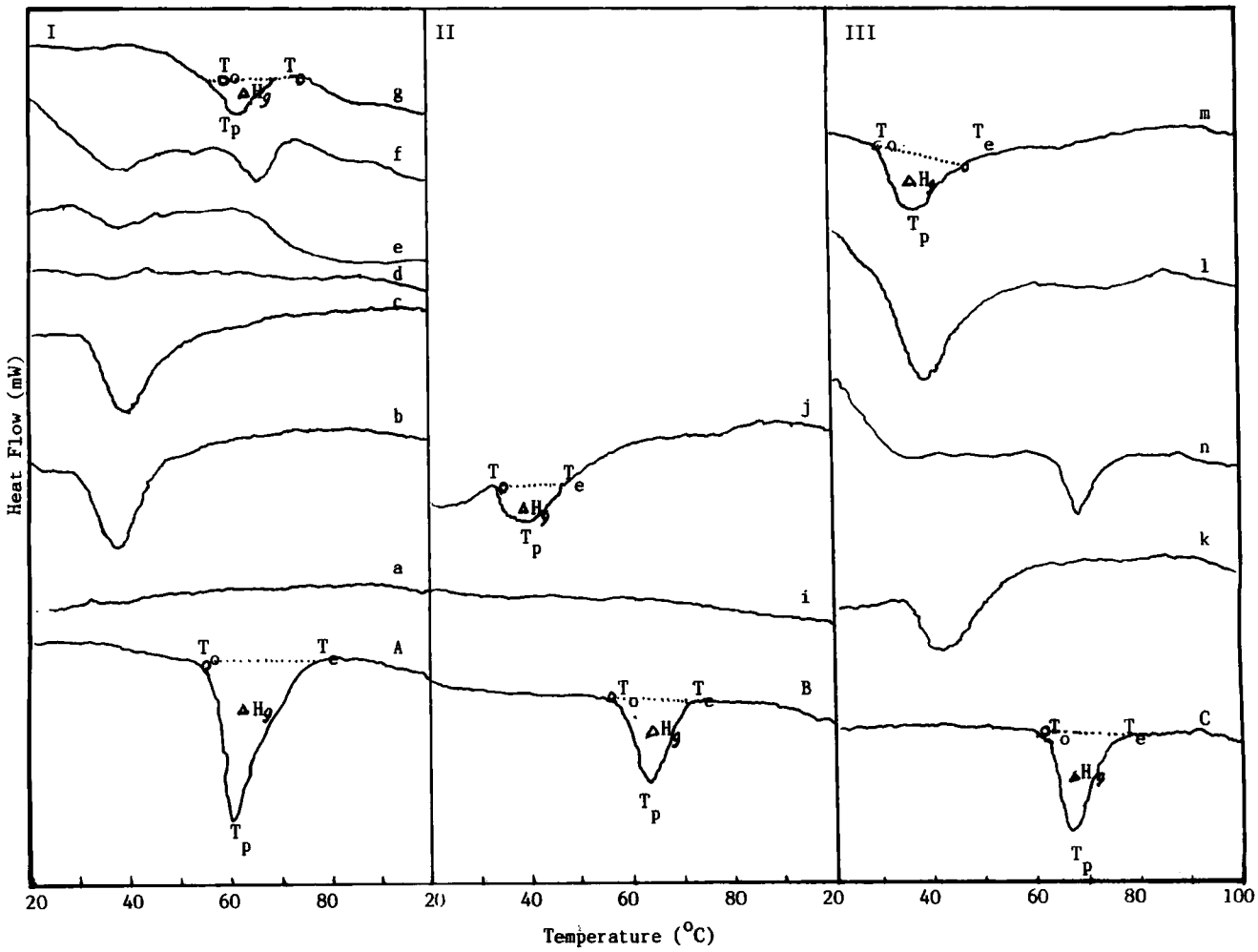


Figure 2. Differential scanning calorimetric thermograms of potato (I), cassava (II) and amaranth (III) starches with different hydrolysis treatments.
A, a, b, c, d, e, f, g; B, i, j; C, k, D, l, and m respectively raw and hydrolyzed starch samples. See text, Table 2 for their composition. $T_o$, $T_p$, $T_e$ = initial, peak and end endothermic temperatures. $\Delta H_g$ – enthalpy of gelatinization.

$T_p$ were found for hydrolyzed starches as compared to raw ones. As expected, $\Delta H_g$ decreased ignificantly ($p < 0.05$). Significant ($p < 0.05$) decreases were shown by these three endotherm temperatures during the hydrolysis in comparison with raw ones. *Griffin* and *Brooks* [32] showed that amylases produce maltodexrins with different proportions of high- and lowmolecular weight saccharides during the change of the hydrolyzing temperature. Sucrose decreased $\Delta H_g$ and $T_p$ as its concentration was increased. Samples (a), (d) and (i) did not show any endothermic peak during DSC measurements. $T_o$ and $T_e$ were not affected by sucrose level. Sugars with longer chain lengths delayed gelatinization more than did shorter-chain sugars. [33, 34]. Probably, the samples during enzymatic hydrolysis contained different proportions of low- molecular weight carbohydrates and residual starch. This is in agreement with others [30].

## 4 Conclusions

This study shows the potential of practical and commercial importance, since it demonstrates that the physical-chemical properties can be regulated by enzyme process.
The four starches are listed in order of increasing resistance to thermostable α-amylase: cassava, crude amaranth, pure amaranth and potato. The highest percentage of hydrolysis was obtained using the bacterial thermostable α-amylase and amyloglucosidase. Samples treated with thermostable α-amylase appeared largely amorphus. The samples treated with α-amylase and amyloglucosidase showed only minor crystallinity.The effectiveness of the bacterial and fungal α-amylases in reducing the crystallinity followed the order: Termayl > *Bacillus subtilis* > *Aspergillus oryzae*. The level of B-type crystallization was changed to another form with fungal α-amylase. DSC studies on raw and hydrolyzed samples showed that gelatinization temperatures and transition enthalpies decreased during enzyme attack. All treated starches gelatinized over broader and lower temperature ranges than the corresponding untreated control starches, exept samples (f) and (g).
The higher the amount of moisture used during the treatment, the higher were the initial and the final gelatinization temperatures. Similar effects on final gelatinization temperature and its ranges were observed for heat moisture treated cassava by *Lorenz* and *Kulp* [18].


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# Synthesis and Characterization of Starch-Glycidyl Methacrylate-Acrylic Acid Cation Exchange Composites

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The synthesis of starch/glycidyl methacrylate/acrylic acid cation exchange composites was achieved by bulk polymerizing of acrylic acid (AA)/glycidyl methacrylate (GMA) mixtures in presence of starch using sodium peroxydisulphate/sodium sulphite initiating redox system. The effect of the concentration of each of sodium peroxydisulphate sodium sulphite, AA and GMA as well as polymerization temperature on the formation of the composites was investigated. Five kinds of composites of different carboxyl contents were prepared and characterized by investigating their potentiometric titrations, durabilities to use, as well as water swellabilities and solubilities.

**Synthese und Charakterisierung von Stärke-Glycidyl-Methacrylat-Acrylsäure-Kationenaustauscher-Zusammensetzungen.** Die Synthese von Stärke-Glycidyl-Methacrylat-Acrylsäure-Kationenaustauscher-Zusammensetzungen wurde durch Massenpolymerisierung von Acrylsäure(AA)-Glycidyl-Methacrylat-(GMA)-Mischungen in Gegenwart von Stärke unter Verwendung eines Natrium-Peroxydisulfat-Natriumsulfit-Redoxsystems als Initiator durchgeführt. Die Wirkung der Konzentration an Natrium-Peroxydisulfat, Natriumsulfit, AA und GMA sowie die Polymerisationstemperatur bei der Bildung der Zusammensetzungen wurde untersucht. Fünf Zusammensetzungen mit unterschiedlichen Carboxylgehalten wurden dargestellt und durch potentiometrische Titrationen, Verwendungsdauer sowie hinsichtlich ihrer Wasserquellbarkeiten und -löslichkeiten untersucht.

## 1 Introduction

Current studies in this division have been concerned with the synthesis and characterization of starch/ion exchange composites, such as starch/melamine formaldehyde/citric acid cation exchange composite [1], starch/N-methylolacrylamide/methacrylic acid cation exchange composites [2], and starch/methylenebisacrylamide/dimethylaminoethyl methacrylate anion exchange composites [3]. The present work is a continuation of these studies, with the objective of synthesizing starch/

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