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Pasting and leaching properties of irradiated starches from various botanical sources

[1*]Mohd Adzahan, N., [1]Mat Hashim, D. [1]Muhammad, K., [1]Abdul Rahman, R., [2]Ghazali, Z. and [2]Hashim, K.

[1]*Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia*
[2]*Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor Darul Ehsan, Malaysia*

Abstract: Changes to the physicochemical properties of wheat, sago and tapioca starches subjected to gamma ray, electron beam and microwave irradiations and the conditions that lead to wheat starch having leaching behaviour similar to sago or tapioca starch were studied. The properties were characterised through swelling and leaching behaviours of the starch granules and retrogradation following pasting. The leaching of wheat starch increased tremendously and resulted in amylose to amylopectin ratios in the leachate similar to that of native sago and tapioca starches. This observation is significant as wheat starch is known to have a leachate composition of mostly amylose. This opens up the possibility of utilising wheat starch in snacks where tapioca and sago starch are commonly used. It was observed that the required conditions for such changes were exposure to microwave for 8 and 10 minutes, electron beam at 5 and 10 kGy and gamma ray at 5 kGy.

Keywords: Pasting properties, irradiation, starch, leaching, amylose-amylopectin ratio

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Introduction

Sago or tapioca starch is known to have high leaching and swelling abilities when cooked. This ability allows the application of both starches in expanded snack product made of starch-protein mixture. On the contrary, such leaching and swelling ability is rather restricted in a wheat starch system where the protein and lipid contents are higher. The mechanisms involved in maintaining the starch, that is amylose and amylopectin, within the deformed heated granules could be affected by the amount of proteins present in the granules; and the viscoelastic properties of the granule envelope that helps retain the starch within the starch granules (Han *et al.*, 2004; Israkarn *et al.*, 2007). Preliminary work in our laboratory has shown that microwave, electron beam and gamma ray irradiation resulted in higher leaching and swelling of wheat starch. Irradiation is known to not only preserve food, but also to modify the physical and chemical properties of these foods and the components as starch that are present in these food systems. Starch is made up of amylose and amylopectin and both polymers are responsible for different functional properties in the food systems (Jane and Chen, 1992). Ohmic heating has been shown to reduce the pasting temperature for commercial rice starch, resulting in a starch

*Corresponding author.
Email noraadzahan@food.upm.edu.my
Tel:+603-89468392; Fax:+603-89423552

that swelled faster (An and King, 2006). Starch gels formed by heating using microwave energy had significantly different properties than those heated using conduction. The lack of granule swelling and the resulting soft gel are two key observations that highlight the differences in the two modes of heating (Palav and Seetharaman, 2007).

Gamma irradiation is capable of hydrolyzing chemical bonds, thereby cleaving large molecules of starch into smaller fragments of dextrin that may be either electrically charged or uncharged as free radicals (Wu *et al*., 2002; Urbain, 1986). These changes may affect the physical and rheological properties of irradiated starches, resulting in changes to the solubility, swelling power and relative viscosity of starch paste.

A vast amount of research has been done on starch irradiation. However, the purpose for such treatment in these studies was for inactivation and preservation purposes and not for functional modification reasons (snack expansion properties). They focused on swelling properties and polymer contents in the granules and did not study the leachate content. In this work, leachate content and the ratio of starch polymers are presumed to be the key factors that will lead to the expansion properties during frying of the intended product. This study was carried out to determine the irradiation conditions necessary for the wheat starch to have leaching and swelling values which are similar to those of sago or tapioca starch. The irradiation techniques employed were microwave, electron beam and gamma ray irradiations.

Materials and Methods

Experimental

Three types of starches from different botanical sources, that is, sago (stem), tapioca (tuber) and wheat (cereal) were used and three types of irradiation treatments (gamma ray, electron beam and microwave) were applied at different intensities or dose rate on the starches.

Raw materials

*Sago (*Metroxylon sagu*) and tapioca starches (*Manihot esculentus*) used in this study were provides by Ajinomoto. Wheat starch (*Triticum aestivum*) was purchased from Roquette Starch Co., France and BDH Chemicals, Inc.*

Irradiation

Heating was done in a microwave oven having a 900W power (Sharp Corporation) and emitting a 2450 MHz microwave frequency. Starch weight 10g in powder form was spread as a thin layer in a Pyrex dish (6 in x 9 in) and exposed to microwave using the highest power level for duration of up to 10 minutes with 2 minutes interval.

Starch was put in sealed polyethylene bags, prior for irradiation. Starches were irradiated using electron beam machine (EBM) up to 30 kGy with 5 kGy intervals. Ionizing radiation processes were carried out at Malaysian Nuclear Agency (Nuclear Malaysia) using EBM having following specification: accelerate voltage 3 MeV (0.5 - 3.0 MeV) ± 2% stability, beam current 30 mA (1 - 30 mA) ± 2% stability, beam width 120 cm (30 – 120 cm), dose uniformity ± 5% and conveyer speed of 1 – 20 m/min.

In the case of gamma irradiation, starch in a sealed polyethylene bags were irradiated at room temperature using the J.L. Shepherd Gammacell (Model 109 Irradiator) at Nuclear Malaysia, with total dosage reaching 20 kGy, with 5 kGy intervals. The dose rate of gamma irradiator used in this study was 9.08 kGy/hour, and total absorb dose was determined by the Harwell Amber Perspex Dosimeter (Type 3042 Batch H).

Moisture content

Moisture contents of native and irradiated starches were determined according to the AOAC standard method (1984).

Pasting profile

Pasting characteristics of the starches were measured using a Brabender Viskograph® (PT100, Model no. 801260, Duisburg, Germany) with a 700cmg-sensitivity cartridge. The bowl speed was 75 rpm. The starch slurry (400 ml at 6% starch solids) pasted at a heating rate of 1.5^{o}C/min from 30^{o}C to 90^{o}C, held at 95^{o}C for 30 minutes, cooled at 1.5^{o}C/min from 95^{o}C to 50^{o}C, and held at 50^{o}C for 30 minutes. Paste viscosity could be identified from the peak of viscograph curve. The viscograph will reveal gelatinization temperature, torque and temperature at maximum viscosity, torque at the start of holding and cooling period and torque at the end of holding period. Pastes obtained were stored for 24 hours for gel strength determination.

Swelling volume

The swelling volume (Mat Hashim et al., 1992; Griffiths, 1997) was determined by heating starch pastes (1% w/v) at 95^{o}C in a water bath for 30 minutes. During the first 5 minutes of pasting, the starch suspensions were agitated to ensure that they were homogenously dispersed. After pasting, the starch pastes were cooled to room temperature (25°C), and then centrifuged at 2,200 rpm for 20 minutes. The swelling volume was obtained directly by reading the volume of sediment in the tube. The swelling volume was expressed as volume of sediment per 100 ml of starch solution.

Leaching of carbohydrates

The amount of carbohydrates leached from the starch granules was measured using the method of Dubois *et al.* (1956). Starch (20 mg) was suspended in distilled water (5 ml) and heated at 95^{o}C in a water bath for 30 minutes. During the first 5 min of pasting the starch suspensions were agitated to ensure that they were dispersed. After cooling and centrifugation (3500 rpm, 10 minutes), 1 ml of the supernatant was pipetted and diluted 50 times. 1 ml of the diluted supernatant was mixed with 1 ml 5% phenol solution in a screw-capped test tube and followed by rapid addition of 5 ml concentrated sulphuric acid (stream of acid directed against liquid surface rather than against the side of the test tube to get good mixing). The mixture was set aside for 10 minutes in a water bath at 20^{o}C - 30^{o}C before readings were taken. It was then shaken with the Vortex Shaker and the absorbance of the yellow-orange colour mixture was measured at 490 nm with distilled water as blank; using a UV-VIS Spectrophotometer (Ultrospec 3000, Pharmacia Biotech). The amount of sugar was determined with reference to a standard curve.

Leaching of amylose

20 mg of starch in a narrow-bottom 20 ml centrifuge tube was mixed with 5 ml 85% (v/v) methanol and heated in water bath at 60^{o}C for 30 minutes. Following centrifugation, the supernatant was discarded and this extraction was repeated three times. Water (5 ml) was added to the sample and heated heated at 95^{o}C in a water bath for 30 minutes. To determine the amount of amylose in the leached carbohydrate, the procedure followed was as previously reported (Hoover and Vasanthan, 1994). One ml of the supernatant was withdrawn and its amylose content determined (Chrastil, 1987). The amount of amylose leached was determined with

reference to a standard curve. Amylose used for the standard was from Sigma Chemical Co. (Sigma A0512).

Statistical analysis

Analysis of variance was done using the SAS method (SAS Institute, Inc., 1985). Duncan's Multiple Range test (Duncan, 1955) was used to determine significant differences among means. Linear regression curves for correlation studies were drawn using the Tool Pak Analysis in Microsoft Excel® (version 5.0).

Results and Discussion

Conversion of units

Unit for amount of energy absorbed during irradiation depends on the source of irradiation and is expressed in the unit of Joule (J). The rate at which energy is utilised is expressed in units of Watts (W). The power absorbed during microwave heating is determined using the following equation (Buffler, 1993):

$$P(W) = \frac{70 \times V\,(L)\,\Delta T\,(^{o}C)}{t(min)} \quad \text{Equation 1}$$

where P = power absorbed
70 = multiplication factor
V = volume of the sample
ΔT = temperature rise
t = time that microwave power is applied

Since Watt is the power of joule per second, energy absorbed is multiplied by the duration of exposure to irradiation (in seconds). The quantity of ionising radiation energy absorbed by the food as it passes through the radiation field during processing is called radiation dose. The SI unit for radiation dose is measured as Gray (Gy), where 1 Gray is 1 joule per kg. The conversion of energy unit is shown in Table 1.

Moisture content

Moisture content of irradiated starches was found to be less than the native starch especially for microwave treated samples as this process involves heating of water molecules. Energy absorption during microwave treatment is attributed to two-principle process: elevation of starch temperature and vaporisation of water. Although some vaporised water condensed was reabsorbed by the starches as they were cooled, the net moisture loss was substantial (Yoshida and Kajimoto, 1994). After 10 minutes of heating, the effect of microwave heating was more pronounced in wheat starch samples with approximately 18% loss of moisture compared to 11.5% loss of moisture in sago and tapioca starches. Gamma ray irradiated starches had the least amount of moisture loss, followed by the electron beam irradiated starches but the loss was not significant (P>0.05). The Gamma Cell was equipped with a cooler, which maintained the temperature (~40°C) of the samples throughout the process while the electron beam system does not have a cooling system.

Pasting characteristics

In general, pasting profile of starches exposed to microwave irradiation was not altered significantly. However, electron beam and gamma-irradiated sago and tapioca starches showed higher peak viscosity and a breakdown. Breakdown illustrates stability of paste during cooking (Table 2). Irradiated wheat starches have similar pasting profile to that of native starch, which is typical of cereal starch. However, viscosity of the pastes was significantly affected by microwave irradiation. Lewandowicz *et al*. (1997) reported that tuber starches changed their swelling behaviour from high, rapid increase in viscosity within a narrow temperature range coupled with the occurrence of a

Table 1. Absorbed energy of irradiated starches

TREATMENT	CODE	ENERGY (J)
Native (N)	N	0
Microwave (M)		
2 min	M2	30,240
4 min	M4	34,020
6 min	M6	34,650
8 min	M8	35,280
10 min	M10	37,170
Electron beam (E)		
5 kGy	E5	8,000
10 kGy	E10	16,000
15 kGy	E15	24,000
20 kGy	E20	32,000
25 kGy	E25	40,000
30 kGy	E30	48,000
Gamma ray (G)		
5 kGy	G5	10,000
10 kGy	G10	20,000
15 kGy	G15	30,000
20 kGy	G20	40,000

* Codes for treatments are used throughout the write up in discussions, figures and tables.

viscosity peak to medium swelling behaviour which is, closer to the profile of a cereal starch. Starches of 30% moisture content heated for 60 minutes had an increase in the pasting temperature and a drop in viscosity of wheat and corn starches as a result of microwave radiation (Lewandowicz *et al*., 2000).

From the viscographs, significant ($P<0.05$) changes in gelatinization temperature, peak viscosity, breakdown, setback and consistency values were observed for all starches when compared to the native starch. Setback and consistency exhibit the cold paste viscosity's tendency to retrograde. The tuber starches (sago and tapioca) had maximum peak viscosity in the 8 minute-treated starches and a drastic reduction was observed in the 10 minute-treated starches. Peak viscosities in microwave treated starch increased gradually as the time of exposure to microwave increased. It is believed that the exposure to microwave have caused these starches to undergo slight swelling, which resulted in the granules being more porous. When the starch suspension is cooked, the more porous granules tend to imbibe more water and thus swell better and leach more soluble materials and thus produced a more viscous solution. High viscosity is not only caused by the properties of the individual swollen granules, but is also attributed to the release of exudates from the granules. The importance of exudation is pointed out through an explanation on the increased peak viscosity. The maximum viscosity of starch suspension heated occurred after most of the granule swelling had ceased (Miller *et al*., 1973).

However, breakdown of SM10 and TM10 were less pronounced and there were significant ($P<0.05$) reduction in viscosities (Table 2). The difference in viscosity reflects the lack of ability of the granules to swell. Amylopectin, being a polymer with bushy structure is responsible to promote swelling. Therefore, the decreased viscosity reveals the lack of ability of amylopectin to hold the granule during the imbibition of water. The reason for this is possibly attributed to the amylopectin branches bei

Table 2. Pasting Characteristics of Native and Irradiated Starches

Starch	Gelatinization Temperature (^{o}C)	Viscosity (BU)				Break down (P-H)	Setback (C-P)	Consistency (C-H)
		Peak (P)	At 95^{o}C	30 min, 95^{o}C (H)	At 50^{o}C (C)			
NT	66.0^{h}	1204^{c}	524b	362^{b}	535^{b}	842^{c}	-669^{l}	173^{b}
TM2	65.6^{i}	1126^{d}	437^{e}	305^{e}	401^{e}	821^{d}	-725^{n}	96^{e}
TM4	66.0^{h}	1108^{e}	446^{d}	321^{d}	429^{d}	787^{e}	-679^{m}	108^{d}
TM6	64.9k	1272^{b}	450^{c}	337^{c}	447^{c}	935b	-825^{o}	110^{c}
TM8	65.3^{j}	1537^{a}	634^{a}	444^{a}	661^{a}	1093^{a}	-876^{p}	217^{a}
TM10	68.6^{a}	802^{f}	367^{f}	205^{f}	280^{f}	597^{f}	-522^{k}	75^{f}
TE5	66.4^{g}	392^{h}	149^{h}	97^{h}	118^{h}	295^{i}	-274^{h}	21^{g}
TE10	66.8^{f}	188^{k}	49^{j}	24^{i}	26^{i}	164^{k}	-162^{f}	2^{i}
TE15	67.5^{d}	100^{m}	21^{k}	11^{j}	13^{j}	89^{m}	87^{d}	2^{i}
TE20	67.5^{d}	66^{n}	12^{j}	7^{k}	9^{k}	59^{n}	-57^{c}	2^{f}
TE25	67.9^{c}	40^{o}	8^{m}	4^{j}	4^{j}	36^{o}	-36^{b}	0^{j}
TE30	68.3^{b}	26^{p}	4^{n}	2^{m}	1^{m}	24^{p}	-25^{a}	-1^{j}
TG5	66.4^{g}	558^{g}	223^{g}	132^{g}	159^{g}	426^{g}	-399^{j}	7^{h}
TG10	66.8^{f}	375^{i}	63^{i}	23^{i}	24^{i}	352^{h}	-351^{i}	1^{ij}
TG15	67.1^{e}	236^{j}	20^{k}	10^{j}	12^{j}	226^{j}	-224^{g}	2^{i}
TG20	67.1^{e}	141^{l}	10^{l}	6^{k}	9^{k}	135^{l}	-132^{e}	3^{j}
NS	71.6^{f}	1217^{b}	598^{c}	338^{c}	507^{d}	879^{b}	-710^{o}	169^{d}
SM2	71.6^{a}	1062^{e}	514d	306^{e}	455^{e}	756^{e}	-607^{n}	149^{e}
SM4	71.6^{a}	1112^{d}	512^{d}	308^{d}	516^{c}	804^{d}	-596^{m}	208^{c}
SM6	70.9^{c}	1164^{c}	611^{b}	355^{b}	612^{a}	809^{c}	-552^{l}	257^{a}
SM8	71.3^{b}	1397^{a}	630^{a}	381^{a}	596^{b}	1016^{a}	-801^{p}	215^{b}
SM10	70.1^{d}	397^{f}	265^{e}	169^{f}	257^{f}	228^{i}	-140^{f}	88^{f}
SE5	72.0^{e}	326^{h}	105^{g}	49^{h}	67^{h}	277^{h}	-259^{i}	18^{h}
SE10	72.4^{d}	252j	67^{h}	28^{I}	36^{i}	224j	-216^{h}	8^{i}
SE15	72.8^{c}	139^{l}	35^{i}	14^{k}	16^{k}	125^{l}	-123^{e}	2^{jk}
SE20	73.1^{b}	77^{m}	17^{k}	7^{m}	8^{m}	70^{m}	-69^{d}	11^{k}
SE25	73.5a	47^{o}	10^{kl}	5^{n}	5^{no}	42^{o}	-42^{b}	0^{l}
SE30	73.1^{b}	42^{p}	7^{l}	3^{o}	4^{o}	39^{o}	-38^{a}	11^{k}
SG5	72.0^{e}	466^{f}	131^{f}	52^{g}	72^{g}	414^{f}	-394^{k}	20^{g}
SG10	72.4^{d}	316^{i}	61^{h}	21^{j}	23^{j}	295^{g}	-293^{j}	$2j^{k}$
SG15	72.8^{c}	199^{k}	28^{j}	11^{l}	14^{l}	188^{k}	-185^{g}	3^{j}
SG20	73.5^{a}	68^{n}	9^{l}	4^{no}	6^{n}	64^{n}	-62^{c}	$2j^{k}$
NW	86.3^{c}	206^{f}	163^{e}	205^{d}	554^{d}	-1^{ab}	348^{c}	349^{b}
WM2	85.1^{h}	269^{e}	185^{c}	269^{cb}	443^{f}	0^{ab}	174^{e}	174^{d}
WM4	85.3^{g}	277^{d}	163^{e}	291^{cd}	446^{e}	-14^{a}	169^{f}	155^{d}
WM6	86.5^{b}	285^{c}	178^{d}	299^{ab}	560^{c}	-14^{b}	275^{d}	289^{c}
WM8	86.0^{e}	300^{b}	194^{b}	308^{ab}	689^{b}	-8^{b}	389^{b}	397^{ab}
WM10	85.9^{f}	312^{a}	196^{a}	313^{a}	720^{a}	-1^{ab}	408^{a}	407^{a}

N = Native T = Tapioca, S = Sago, W = Wheat,

$^{a-p}$: Means within a column with different letters are significantly different ($P<0.05$)

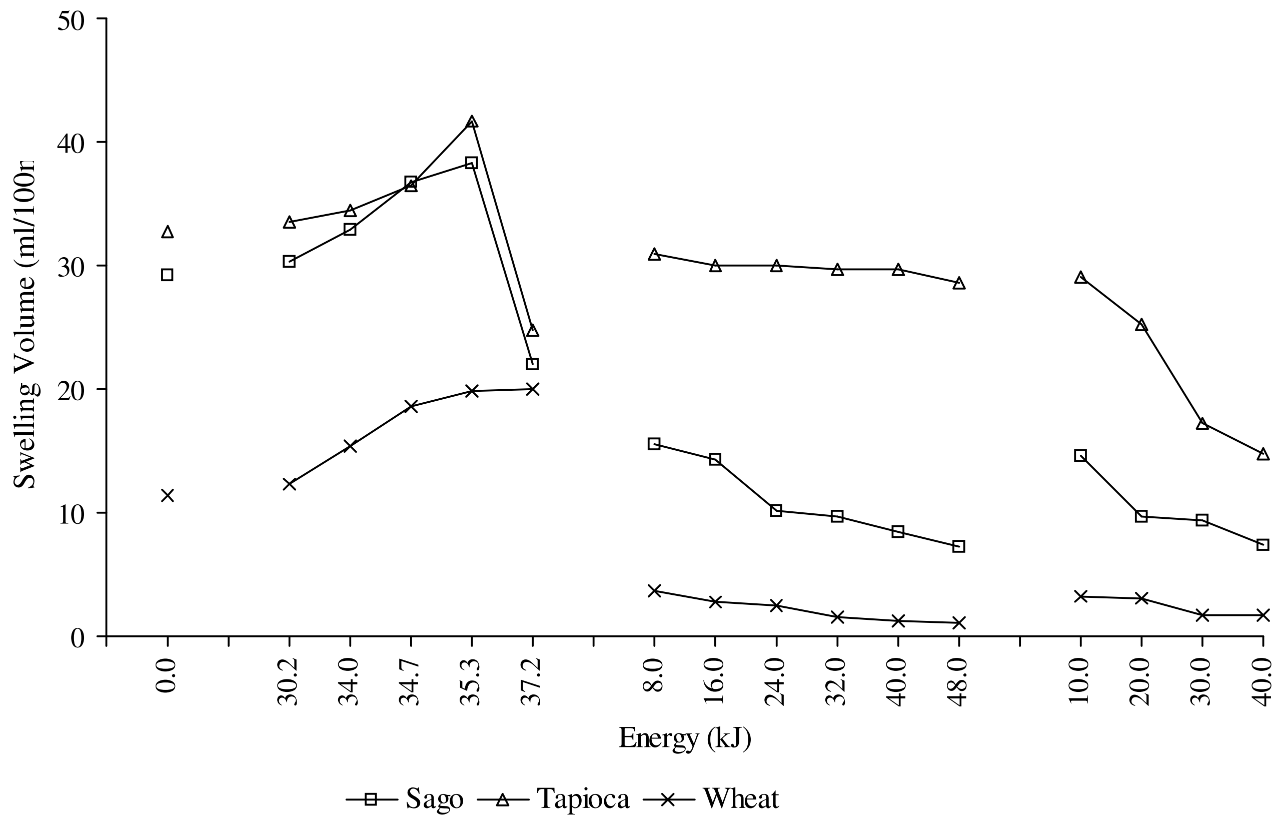

Figure 1. Swelling volume of starches exposed to different energy levels from various irradiation source *Swelling volume*

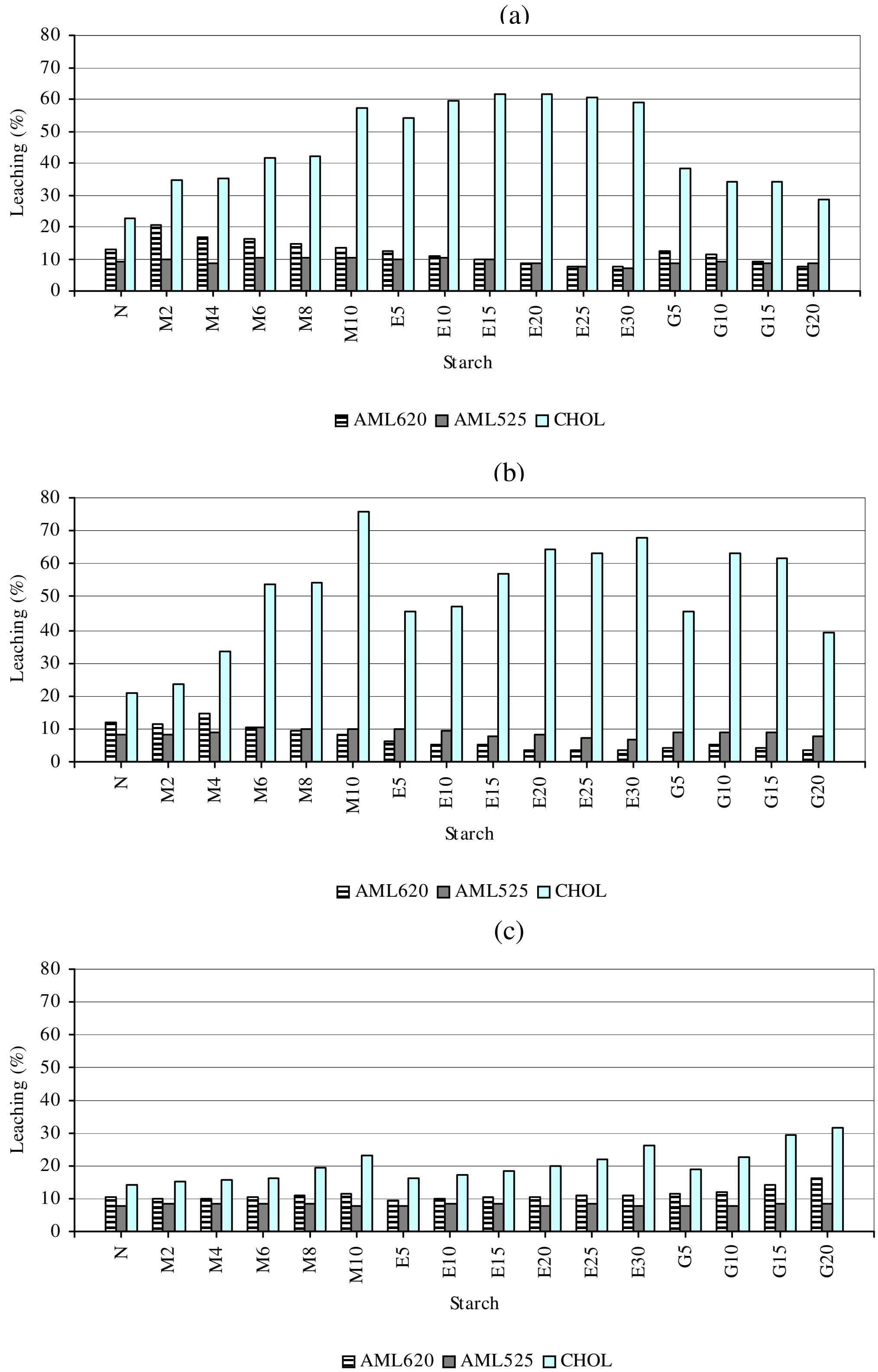

Figure 2. Leaching properties of (a) sago b) tapioca (c) wheat starches after exposure to various irradiation conditions (AML: Amylose in leachate, 620 / 525: wavelength (nm), CHOL: carbohydrate in leachate).

cleaved by the energy from the microwave and irradiation for 10 minutes is believed to be sufficient to do so. This agrees with Lewandowicz *et al*. (2000) that microwave radiation was proven to cause a shift in the gelatinization range to higher temperature, and a drop in crystallinity and solubility. According to the European Patent (Patent No. 0059050), the viscosity decreased with increasing exposure to Ultra High Frequency (UHF) radiation. A characteristic feature of UHF radiation treatment is that, though the crystallinity of the starch is reduced or destroyed, the granular nature of the starch is not modified. UHF treatment may result in breaking some branches at the α-1,6 linkages; that is to say, the side chains bonded to the main chains may be separated and thus made more accessible to the action of chemical reagents or enzymes. Only an activation of the H-OH dipoles can cause this kind of result without involving the complete destruction of the granule structure within a reasonably short time at a temperature below 100^{o}C.

Upon cooling, the treated starches showed almost similar patterns as for the hot paste. Generally, the viscosity increased as the duration of exposure to microwave is increased. This is probably due to significantly high amount of linear polymers in the continuous phase. It is possible that some of the amylopectin remain in the granules even though the branches have been cleaved. The granules act as fillers and amylose, being a gel-forming component re-associates with one another to form network, which resulted in an increased viscosity of the paste.

Energy produced at 10 minutes of exposure to microwave was sufficient to chop the α-1,6 linkages to form smaller fractions of amylopectin. This means after the linkages have been chopped, linear chain polymers were produced. It is known that the branched fraction amylopectin contains several hundred short linear branches with an average length of 25 glucose units (Pomeranz, 1987). These linear chain polymers have fewer sugar molecules (glucose units) in the chains. In other words, the molecular weight of the polymers were lower and thus, capable to seep out from the starch granules easily. With more of these small linear and branched fractions existing in the continuous phase, it interferes with re-association of amylose molecules to form network and this resulted in a dilute solution. This explains the low cold paste viscosity of TM10 and SM10 starches.

For the electron beam and gamma irradiated starches, the viscosity was markedly decreased and there were significant shifts in the pasting temperature, which were higher than the native starch (Table 2). The effect was most severe for irradiated wheat starch as no viscosity values were detected (values not within detectable limits) by the viscograph during the hot paste cycle. However, viscosity values were detected during the cold paste cycle even though the values were very low. The increase in viscosity during cooling was attributed to retrogradation or re-association of the amylose fractions in the paste. As the dosage of irradiation is increased, the viscosity decreased. These drastic reductions in viscosity for the gamma and electron beam irradiated starches were caused by cleavage of the glycosidic bonds through free radical formation to form smaller carbohydrate units or dextrins of varying lengths, leading to a reduction in the molecular weight (Urbain, 1986) and solubility increase (MacArthur and D'Appolonia, 1984). Unlike microwave radiation, ionizing radiation causes scission in the glycosidic chains randomly. Therefore, scissions of the chains probably produce short amylose chains, short linear chains from the branches of amylopectin or small-branched fraction of the amylopectin. Starch granules loss their ability to swell during cooking and therefore no significant imbibation of water occurred. The soluble materials leaching out from the granules were degraded and of lower molecular weight and thus, did not contribute to viscosity increase. The consistency values were very low and these illustrate the retrogradation behaviour of the pastes. Retrogradation of amylose was possibly inhibited by the small fractions of cleaved amylopectin.

Swelling volume

Swelling pattern of irradiated starches was almost similar to the pattern shown in the pasting profile. Microwave irradiated starches showed an increase in swelling volume when compared to the native starch, except for SM10 and TM10 (Figure 1). Maximum swelling was achieved with approximately 9% increment from the native starches. However, gamma and electron beam irradiated starches showed significant reduction as the irradiation dosage is increased, especially in starches treated with gamma ray. This is in agreement to published findings, irradiation decreases the overall swelling power of bean and wheat starch (Rayas-Duarte and Rupnow, 1994; MacArthur and D'Appolonia 1984). The decrease in swelling power can possibly be attributed to depolymerization of the starch due to irradiation. The lower molecular weight fractions formed are not able to bind water for swelling and gel formation as a result of being more soluble in water (MacArthur and D'Appolonia, 1984). Amylopectin acts as a skeleton to the granule. Although the amylopectin branches may have been cleaved, some are still entangled in the granules, supporting or giving structure to the granules. With the existence of the entangled polymers, but with less branched structure, the granules could imbibe more water than the native starch. This allows further swelling during cooking. Until a certain extent, the cleaved fractions were small enough to be leach out from the granules, leading to the decreased swelling volume in SM10 and TM10 starches. In wheat starch, 10 minutes of heating did not cause drastic changes to the swelling volume. This is because the granule did not swell much as the amylose-lipid complex existing naturally in the granules inhibits swelling. It is also possible that the surface of the granules might have been damaged by the microwave energy, in the form of crack or tear. As the surface of granules (in dry form) already has damages made by the microwave energy, cooking somehow caused further damage to it. This complies with a published article which mentioned that the granules become increasingly susceptible to shear disintegration as they swell, and they release soluble material as they disintegrate (Dengate, 1984). The botanical source of starch is another factor that contributes to the difference (Pomeranz, 1991). Differences in lipid and amylose contents and in granular organisation are among the other factors to cause the varied swelling volume (Dengate, 1984). Swelling in wheat starch is inhibited by the amylose-lipid complex, which exists naturally in wheat starch granules (Leach *et al*., 1959).

Leaching properties

Leaching of carbohydrate in this study refers to the amount of polysaccharide (amylose, amylopectin or both) existing in the continuous phase of cooked starch as detected by colorimetric method. Leaching of amylose refers to the quantitative determination of amylose by means of its colour reaction with iodine. Amount of amylopectin leached from the granules was obtained from the difference between the amount of carbohydrate and amylose leached; assuming that the starch is a mixture of just two pure components, amylose and amylopectin.

Figures 2(a)–(c) illustrates the leaching properties of native and irradiated starches. Amylose leached was measured at two wavelengths, 620 nm and 525 nm to determine iodine-complexed and free amylose, respectively. Leaching of carbohydrates in irradiated starches increased significantly ($P<0.05$) as the exposure to radiation increased. This is attributed to degradation of the starches, leading to a decrease in the molecular weight of the cleaved fractions. The highest amount of carbohydrate leaching was observed for TM10 (75.98%), SE15 (61.88%) and WG20 (31.79%) for tapioca, sago and wheat starch, respectively (Figure 3). These values are high compared to the leached carbohydrate in native tapioca (20.73%), sago (21.6%) and wheat (14.35%) starches. However, the gamma irradiated sago and tapioca starches showed a decreasing pattern even though the values were higher than native starch. The reason for this was not understood as the D-glucose was used to construct the standard curve. Degradation of the starch chain as a result of gamma irradiation would not possibly be the reason since D-glucose is the simplest sugar.

Significant increase of amylose leached in wheat starch occurred only in the WG10 (12.27%), WG15 (14.33%), and WG20 (16.29%) starches. This is considered good when compared to the amount of amylose leached in native wheat starch (10.39%). Limited leaching was due to the amylose forming complexes with lipids existing naturally in the granules. Leaching of amylose for sago and tapioca decreased with increasing exposure to radiation, accredited to the decreased colour produced, resultant of the degraded starch chains. Amylose forms complex with iodine to produce colour change. The colour produced depends on the number of helix turns and therefore on the chain length of the linear chain. Free amylose detected at 525 nm remained unchanged as irradiation become more severe. This proves that no additional free amylose occurred as a result of irradiation, indicating that all the leached amylose have formed complex with iodine. However, leaching of amylose is believed to have reached the maximum point, but decreased as the exposure to irradiation extended the limit. This assumption is based on the amylose content of the native starches as compared to the highest amount of leaching achieved. The greatest leaching (14.89%) in tapioca starch was achieved after exposure to microwave for 4 minutes (TM4). For sago starch, microwaving for 2 minutes caused the highest amount of leaching (20.60%). These values are close to amylose content in respective starches i.e., 15.4% for tapioca and 26.2 % for sago. Greatest

Table 3. Ratio of Amylose and Amylopectin in Leachate after Exposure to Various Irradiation Treatments

Treatment	Amylose/Amylopectin Ratio		
	Sago	Tapioca	Wheat
N	1.31[i]	1.45[a]	2.62[a]
M2	2.42[e]	0.97[b]	1.83[c]
M4	2.93[d]	0.81[c]	1.81[d]
M6	1.70[g]	0.40[g]	1.86[b]
M8	1.66[h]	0.39[g]	1.31[g]
M10	0.84[j]	0.25[k]	0.97[l]
E5	0.63[m]	0.51[ef]	1.46[f]
E10	0.54[n]	0.49[f]	1.31[g]
E15	0.50[o]	0.37[h]	1.28[h]
E20	0.49[p]	0.32[i]	1.16[j]
E25	0.76[l]	0.32[i]	0.99[l]
E30	0.80[k]	0.29[j]	0.74[m]
G5	2.16[f]	0.51[e]	1.50[e]
G10	3.36[c]	0.32[i]	1.20[i]
G15	3.45[b]	0.33[i]	0.96[l]
G20	9.67[a]	0.65[d]	1.05[k]

[a-p]: Means within a column with different letters are significantly different ($P<0.05$)

amylose leaching for irradiated wheat starch was achieved at 20 kGy in which the amount was 16.29% from a total of 24.6% amylose content. More information is needed to identify the profile of materials in aqueous phase, i.e. the chain length and the structure of the chains. Measuring the intrinsic viscosity and having knowledge of the molecular weight would lead to a clearer picture and a better understanding on the leaching properties of irradiated starches.

Amylose-amylopectin ratio

Assuming that total leaching of amylose has been achieved, the amount of amylopectin can be determined. In general, irradiation has significantly increased the leaching of amylopectin (APL) as compared to the native starch. Many reports have been published on the amylose and amylopectin ratio in starch granules from various botanical sources (Medcalf and Gilles, 1965; Pomeranz, 1991; Kearsley and Dziedzic, 1995) but not much has been discussed on the ratio in the aqueous phase or amount of both polymers that leached from the starch granules and its importance to or effect on an end product. Table 3 shows the ratio of amylose to amylopectin. Generally, as the exposure to irradiation is increased, the ratio of amylose to amylopectin is reduced. In other words, when severity of exposure is higher, amounts of both the amylose and amylopectin leached are high. This information will provide an indication to the kind of end product expected when the treated starch is to be applied later on. The ratio of amylose to amylopectin leaching observed was 1.31, 1.45 and 2.62 for native sago, tapioca and wheat starches respectively. Native sago and tapioca starches have been used in fish cracker production because of their good expansion properties. Wheat starch, on the other hand was not used in the cracker production due to its poor expansion properties. Wheat starch seems to have a higher ratio of amylose to amylopectin in the leachate when compared to sago and tapioca starches. Leaching and expansion of fish cracker correlates positively (Kyaw *et al*., 1999). It is believed that the lower the ratio (higher amount of amylose relative to amylopectin) in the continuous phase, the better the expansion. There is possibility that expansion is best in a specific range of AM/AP ratio.

For expansion of crackers to happen, starch polymers must be leached out of the granules when the fish-starch dough was steamed. In fish cracker processing, steaming is a processing step before cooling and frying. The leached materials will re-associate during cooling of the dough and forms a network around and between the granules. Puffing will only take place when water in the network is converted to steam (during frying) once in contact with the hot oil. The escaping steam helps expand the network into a porous texture. Irradiation can help increase polymer leaching. The more polymers being leached, the better the expansion but the length of the leached polymers will also dictate the level of expansion.

Wheat starch treated with M8, M10, E5, E10 and G5 had ratios of leaching similar to native sago and tapioca starches. The energy value is equivalent to 35,280 J, 37,170 J, 8,000 J, 16,000 J and 10,000 J for the respective treatments (Table 1). This means that amylopectin leached from the granules has increased. From the same table, the amylopectin leaching of these three starches increased to at least double the amount of amylopectin leaching in the native starch. Therefore, these starches would probably produce fish crackers with better expansion than those produced by native wheat starch. However, without the availability of information on the expansion of fish crackers this assumption is not confirmed.

Conclusion

The effects of irradiation energy on the physico-chemical properties of starches vary in different ways, depending on the type of starch. The leaching ability of wheat starch was improved through irradiation by bringing its amylose to amylopectin leaching ratio closer to the ratio in native sago or tapioca starches. Wheat starch having properties close to those of native tapioca or sago starches were those exposed to microwave for 8 and 10 minutes, electron beam at 5 and 10 kGy and gamma ray at 5 kGy. These modified wheat starches are expected to produce expanded fish-starch snacks with similar expansion properties compared to those made from the native sago and tapioca starches.

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