STRUCTURAL-FUNCTIONALITY CHANGES OF CORN STARCHES INDUCED BY GAMMA IRRADIATION

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ABSTRACT

The effects of gamma irradiation on the physicochemical and morphological properties of starch samples were investigated. Corn starches with different amylose content (waxy, normal, Hylon V, and Hylon VII) were treated with five doses of gamma irradiation (1 kGy, 5 kGy, 10 kGy, 25 kGy, and 50 kGy). Waxy samples showed an increase of amylose-like fractions when irradiated at 10 kGy. The reduction in apparent amylose content increased with amylose content when underwent irradiation at 25 and 50 kGy. The more drastic decrease in pH value and increase in carboxyl content were observed on Hylon V and VII samples indicated that starches with higher amylose content marked greater susceptibility towards oxidation effect of increasing radiation intensity. Low amylose starches lost their pasting ability when irradiated at 25 kGy and 50 kGy. Results from thermal behavior and pasting profile suggested that lower level of cross-linking effect occurred in Hylon VII samples irradiated at 5 kGy. Severe reduction in pasting properties, gelatinization temperatures and relative crystallinity with increasing irradiation intensity revealed that waxy samples were affected more by gamma irradiation; this also indicated amylopectin was the starch fraction most affected by gamma irradiation. Alteration level was portrayed differently when different kind of physicochemical properties were investigated, in which the pasting properties and crystallinity of starches were more immensely influenced by gamma irradiation while thermal behavior was less affected. Despite the irradiation level, the morphology and crystal pattern of starch granules were found remain unchanged by irradiation.

ABSTRAK

PERUBAHAN STRUKTUR-FUNGSI KANJI-KANJI JAGUNG DISEBABKAN OLEH SINARAN GAMMA

Kesan-kesan sinaran gamma terhadap sifat-sifat fizikokimia dan morfologi kanji jagung yang mempunyai nisbah amilosa ke amilopektin yang berbeza telah dikaji. Kanji jagung dengan kandungan amilosa yang berbeza (waxy, normal, Hylon V, dan Hylon VII) telah dirawat dengan lima dos sinaran gamma (1 kGy, 5 kGy, 10 kGy, 25 kGy, dan 50 kGy). Sampel waxy menunjukkan peningkatan pecahan-pecahan yang bersifat seperti amilosa apabila disinarkan pada 10 kGy. Pengurangan dalam kandungan amilosa jelas meningkat dengan nisbah amilosa ke amilopektin dalam kanji apabila menjalani penyinaran pada 25 kGy dan 50 kGy. Penurunan yang lebih drastik dari segi nilai pH serta peningkatan kandungan carboxyl pada sampel Hylon V dan VII menunjukkam kanji yang beramilosa tinggi adalah lebih mudah terjejas oleh kesan pengoksidaan daripada peningkatan keamatan radiasi. Apabila diradiasi pada 25 dan 50 kGY, sampel beramilosa rendah mengalami kehilangan kesan penampalan. Keputusan daripada analisis terma dan sifat pempesan mencadangkan bahawa kesan sambung-silang bertahap rendah telah berlaku pada sampel Hylon VII apabila disinarkan pada 5 kGy. Penurunan yang ketara berikutan dengan peningkatan dos penyinaran dalam sifat penampalan, suhu penggelatinan dan penghabluran relatif mendedahkan bahawa sampel waxy adalah lebih terjejas oleh sinaran gamma; fakta ini turut menunjukkan bahawa amilopektin merupakan bahagian dalam kanji yang lebih terjejas. Tahap pengubahan dicerminkan secara berbeza dalam pelbagai ciri-ciri fizikokimia yang disiasat di mana sifat-sifat penampalan dan penghabluran kanji terjejas lebih drastik oleh sinaran gamma manakala kajian haba adalah kurang terjejas. Walau bagaimanapun, morfologi dan corak kristal granul kanji didapati tidak berubah oleh kesan penyinaran.

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LIST OF ABBREVIATIONS

FAO	-	Food and Agriculture Organization
IAEA	-	International Atomic Energy Agency
WHO	-	World Health Organization
AAC	-	Apparent Amylose Content
DSC	-	Differential Scanning Calorimetry
RVA	-	Rapid Visco Analyzer
SEM	-	Scanning Electron Microscopy
PEF	-	Pulse Electric Fields
ADPGPase	-	ADP-glucose pyrophosphorylase
SS	-	Starch synthase
SBE	-	Starch branching enzyme
DP	-	Degree of polymerization
M_W	-	Molecular weight
IA	-	Iodine affinity
WRC	-	Water retention capacity
GBSS	-	Granule-bound starch synthase
GBSSI	-	Granular-bound starch synthase I
AM	-	Enzyme amylomaltase
CDase	-	Enzyme cyclomaltodextrinase
AKD	-	Alkenyl ketene dimer
OPT	-	Osmotic-pressure treatment
T_o	-	Onset temperature
T_p	-	Peak temperature
T_c	-	Complete temperature
w/w	-	Weight to weight

LIST OF SYMBOLS

±	-	Plus minus
°C	-	Degree Celcius
%	-	Percentage
>	-	More than
Gy	-	Gray
ΔH	-	Enthalpy
θ	-	Theta
nm	-	Nanometer
g	-	Gram
ml	-	Mililiter
L	-	Liter
min	-	Minute
J/g	-	Joule per gram
s	-	Second
mbar	-	Milibar

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Irradiation has been explored since decades ago as a new treatment on food that can produce a wide variety of beneficial effects. Such beneficial effects include prolonging shelf life, destruction of insects and parasites, inhibition of microorganisms, prevent sprouting of tuber crops and delay of ripening of fruits and vegetables. Food irradiation is a physical treatment of food involving direct exposure to electron or electromagnetic rays to enhance their preservation period as well as for the improvement of safety and quality (Urbain, 1986). The irradiation technology was first approved by FAO/IAEA/WHO joint committee on the wholesomeness of food and to-date there is more than 26 countries using food irradiation on a commercial scale (Lacroix and Ouattara, 2000). As the commercial use of food irradiation is getting more acceptance and recognition, the technology has also been utilized on food ingredients and ready-to-eat meals as well as agricultural products (Aliste, Vieira and Del Mastro, 2000).

As the major component in foods derived from plant sources, starch contributes widely to the textural properties of many foods and has many industrial applications as it can imparts and heightens structure, consistency, texture, and appeal to many food systems (Lee, Kim, Lim, Han, Kim and Kang, 2006; Chung and Liu, 2009). Owing to its practicality in different food products and to its nutritional benefit, starch is currently savouring utmost attention and used in many food and non-food applications. Nevertheless, due to the lack of wider functionalities such as low shear resistance, low thermal resistance, thermal decomposition, and high retrogradation tendency, starch is not ideal and optimal in some industrial food applications (Chung and Liu, 2009; Yoon, Yoo, Kim, Lee, Byun, Baik and Lim, 2010). For this reason, starches from different sources have been modified chemically, physically, or enzymatically to suit and obtain the desired functional traits at industrial levels.

Conventionally, most starches are modified chemically (acid and alkaline hydrolysis) and enzymatically (enzymatic digestion by amylolosic enzymes) to improve the functionality of starch and chemical modification is the mainstream of the modified starch over the last century (Bettaieb, Jerbi and Ghorbel, 2014). However, there is also a growing interest in the physical modification of starch, especially in food applications. Among physical modification techniques, irradiation, particularly using gamma rays has recently gained wider acceptance as no by-products of chemical reagents are present in the modified starch (Farkas, 1998). Advantages such as minimal sample preparation, non-thermal treatment , and have no dependence on any type of catalysts have made gamma irradiation of starch a safer, faster and more environmentally friendly modification method over conventional chemical modification (Farkas, 1998; Bhat and Karim, 2009).

Starches have been modified extensively using gamma irradiation in recent years to induce physicochemical transformations in starch granules, for example in wheat (MacArthur and D'Appolonia, 1984), rice (Bao and Corke, 2002), maize (Lee *et al.*, 2006; Chung and Liu, 2009), potato (Ciesla and Eliasson, 2007), bean (Rayas-Duarte and Rupnow, 1993), and cowpea (Abu, Duodu and Minnaar, 2006). Desired functional and processing traits like reduction of viscosity, high water solubility, reduction of gelatinization enthalpy and others can be attained through gamma irradiation of starch (Yu and Wang, 2007; Chung and Liu, 2009; Bhat and Karim, 2009). Kang, Byun, Yook, Bae, Lee, Kwon and Chung (1999) were able to produce modified corn starch with low viscosity and sufficient viscosity stability using gamma irradiation and addition of ammonium persulfate.

It has been reported that the high ionizing power of gamma rays treatment is able to generate free radicals that can induce molecular changes and fragmentation of starch by breakdown of glycosidic bonds (MacArthur and D'Appolonia, 1984). As such, this distinctive property has been suggested to be one of the important mechanisms underlying physicochemical and functionality changes in starch, typically on the reduction of viscosity and high water solubility (Bao and Corke, 2002; Lee *et al.*, 2006). Apart from their major applications in food industries, starches are also being modified under high doses of gamma irradiation to be utilized in paper and textile industries

1.2 Justification

Extensive studies on various starches reported different alterations by irradiation on the physicochemical properties. For example, the gelatinization enthalpy was found to decrease for gamma irradiated rice, corn, and potato starch up to 40 kGy (Ciesla and Eliasson 2002; Bao, Ao and Jane, 2005; Lee *et al.*, 2006), but no significant effect of gamma irradiation were recorded for grain amaranth starch irradiated up to 10 kGy by Kong, Kasapis, Bao and Corke (2009) and even on corn starch irradiated up to 50 kGy by Chung and Liu (2009). Also, Chung and Liu (2009) discovered that the crystallinity of corn starch remained unchanged at 2 kGy and reduced at 10 kGy but an increase of crystallinity in wheat (at 1 and 3 kGy) and rice starches (up to 9 kGy) was spotted in other studies (MacArthur and D'Appolonia, 1984; Bao *et al.*, 2005). Even within same type of starches, there is still controversy in the reported physicochemical properties. For instance, corn starch granules structure was found visually unchanged when irradiated up to 40 kGy (Lee *et al.*, 2006), but an increase in the starch granule surface roughness was spotted for corn starch treated with a dose of 10 kGy (Kweon, Kim, Lee, Lee, Kim, Kim and Byun, 2002).

It has also been found that the amylose-to-amylopectin ratio affects the sensitivity of starch toward gamma irradiation (Bhat and Karim, 2009; Chung and Liu, 2009). Various studies have been carried out on single type of starch with different amylose-to-amylopectin ratio to investigate the aforementioned relationship. For instance, Wu, Wang and Xia (2002) and Zuleta, Dyner, Sambucetti and de Francisco (2006) studied the effects of gamma irradiation (3 kGy) on physicochemical properties of various types of rice cultivars (with amylose content up to 26%). They discovered that amylopectin was the starch fraction most affected by gamma irradiation in rice cultivars and the apparent amylose content (AAC) of high amylose rice starches was not significantly affected by gamma irradiation. The rheological and physical properties of two cultivars of gamma irradiated grain amaranth starch with different amylose content (6.0% and 10.3%) irradiated up to 10 kGy have also been reported by Kong *et al.* (2009). However, all the studies mentioned only covered narrower range of amylose content (less than 30%) and with irradiation dosage up to 10 kGy only. With the acknowledgement of FAO/IAEA/WHO Study Group (1999) that food irradiated at any dosage is confirmed to be safe and wholesome, it is therefore important to understand the effect of gamma irradiation on starches at higher irradiation intensity. Since amylose and amylopectin also characterize the physicochemical properties of starches, thus it is crucial to find out the interaction between amylose and amylopectin in gamma irradiated starches when expose to higher irradiation dosages.

In addition, studies have shown that other than amylose-to-amylopectin ratio, factors like botanical origin of starches and irradiation conditions would critically influence the effect of gamma irradiation on starches. In their review on radiation processing on starches, Bhat and Karim (2009) pointed out that future research on gamma irradiation of starch should focus on setting standardized doses for each of the starch molecules, based on their origin. Therefore, this research served as a fundamental study to provide important insight into starch modification by gamma irradiation as well as to fill in the knowledge gap on structural-functionality changes of corn starches with different amylose content as induced by gamma irradiation.

1.3 Objective

This study reported is part of the attempt to elucidate the effect of gamma irradiation on the structural-functionality changes of corn starches with varying amylose content. The specific objectives of the study include:

i. To evaluate the effects of gamma irradiation doses on the structural properties of corn starches with different amylose-to-amylopectin ratio.

ii. To assess the effects of gamma irradiation doses on the functional properties of corn starch with different amylose-to-amylopectin ratio.

CHAPTER 2

LITERATURE REVIEW

2.1 Starch

Among food carbohydrates, starch holds a unique and special position. Besides playing a central role in human diet by providing 70-80% of the calories consumed by humans worldwide, starch is also one of the most important but flexible food ingredients which has been widely attributed for its innumerable industrial applications (Lee *et al.*, 2006). It is the major reserve carbohydrate in stems, roots, grains, and fruits of all forms of green leafed plants and starch existed in the form of tiny granules. Cereal grains, such as corn, wheat, sorghum, and tubers, and roots, such as potato, tapioca, arrowroot, etc., are some of the commercial sources of starch for industrial exploitation (Myllarinen, 2002). Starch has been associated significantly to the texture and sensory properties of processed foods and it exhibits a wide range of functional properties. Starch is also likely to be the most commonly used hydrocolloid. One third of total starch produced worldwide is utilized for a variety of industrial applications that take advantage of its unique properties. Presently, the modern life is more and more dependent upon processed and convenience foods; it is almost impossible to live without starch today (Myllarinen, 2002; Tharanathan, 2005).

2.1.1 Biosynthesis of Starch

Visser and Jacobsen (1993) postulated that in green plants, the starch synthesis happen in two steps. Transitory starch, leaf starch, is synthesized in the chloroplast during daylight when photosynthesis occurs; during the dark period when photosynthesis is inhibited, leaf starch is degraded, and sucrose is formed, which is then transported to sink tissues (Visser and Jacobsen, 1993; Matheson, 1996).

Starch granule synthesis in green plants occurs in amyloplasts. Amyloplasts are the organelles containing the enzymes necessary for the biosynthesis of starch