STUDY ON THE EFFECTS OF PARBOILING ON RICE AND RICE PRODUCTS OF ASSAM

A thesis submitted in partial fulfillment of the requirements for the degree of the Doctor of Philosophy

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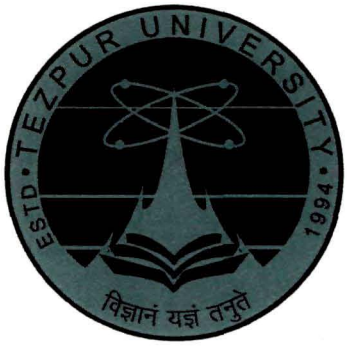

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Abstract

Introduction

Rice (*Oryza sativa*), the staple food of many Asian countries is mostly consumed in cooked form. About 90% of the dry weight of milled rice kernel is composed of starch, a semicrystalline biopolymer of D-glucose. Starch is composed of two components- amylose and amylopectin; their proportion directly influences the cooking properties of rice. On the basis of the amylose content, rice varieties are subdivided into basically four groups- high amylose (>25%), intermediate amylose (20-25%), low amylose (7-20%) and waxy/ glutinous (1-2%).[1] High amylose rice varieties give separated, non-sticky cooked grains while cooking of waxy varieties give a sticky mass; both types of rice have their own utility as food.

Parboiling is a unique hydrothermal treatment resulting in marked changes in the morphological, structural, physical and physicochemical properties of rice. Parboiling hardens the rice grain by sealing the lines of fracture on the kernel with gelatinized starch. Being harder, it requires greater force for milling and polishing and therefore the nutritive epidermal layers of the rice kernel are retained. The changes that occur in the rice kernel on parboiling are basically due to changes in the morphological, structural, physical and most importantly, the physicochemical and nutritional properties of its starch content.[2] The native crystallininity of rice starch lowers while newer crystalline polymorphs are formed after parboiling. The newer polymorphs, namely, gelatinized starch, retrograded amylopectin, crystalline amylose and amylose-lipid complex have different temperatures of melting than raw rice starch as revealed from Differential Scanning Calorimetry.[3,4] Accordingly, other properties like viscosity, water holding capacity and cooking behavior of the rice also change. Recent studies have also revealed the formation of therapeutically important resistant starches in the parboiled rice.[5]. Parboiled rice has been recently reviewed as a biological material with peculiar polymeric properties.[6]

The parboiling techniques been subdivided into three types, namely, conventional parboiling, pressure parboiling and dry-heat parboiling.[7] Although the three different parboiling methods are seen to be involving the basic three steps- soaking, heating and drying, the products are markedly different from each other. The significant variations in the product characteristics are attributed to the alteration in the starch properties of the

rice due to differences in parboiling methods and severity of treatment.[2,3,7] An optimum quality product hence needs optimum conditioning of the three steps of parboiling.

Assam, one of the North-Eastern states of India is naturally endowed with rice germplasm of wide genetic diversity.[8] The state grows high/intermediate-amylose rices that are mainly used in the staple diet. A distinct class of low amylose and waxy rice varieties collectively known as *chokua* and *bora* rice respectively are grown in the region and are consumed only after processing into rice products. Some of these processed food products have peculiar property of softening when soaked in water and therefore does not require any form of cooking. Unique parboiling practices are followed in the households for making the products. Absence of standard conditions of temperature and pressure for different stages of processing often results in non-uniformity of the product quality. Long processing times have also resulted in poor product output as well as product deterioration due to leaching, fermentation, etc. Scientific and systematic approaches towards the processing conditions and subsequent quality changes in Assam rices have not been undertaken. Apart from *Hurum*, no other rice products of Assam have been processed under laboratory conditions and analyzed for their properties.[10] Commercialization of the products has been initiated by some local companies, however digestibility pattern of the products are not known. Some of the local varieties like *Kola chokua* are pigmented and hence may prove to be having potential health benefits.[9] It was also felt necessary to profile their phytochemical content and antioxidant activities and their qualitative alterations after parboiling.

This PhD work therefore primarily dealt with the study of the physical, physicochemical and digestibility changes in high and low amylose as well as waxy rice varieties of Assam after parboiling with normal, pressure and dry-heat parboiling methods and understanding the nature of starch in these parboiled rices and rice products. Another part of the work dealt with characterization of two rice products of Assam, namely, *komal chaul* and *bhoja chaul* processed in the laboratory. A preliminary investigation on the effect of parboiling on phytochemical content and antioxidant activity of the milling fractions of pigmented *Kola chokua* paddy was also carried out.

Methodology of the present work

Paddy samples of *Ranjit* (high amylose), *Kola chokua* (low amylose), *Aghoni* and

Bhogali bora (waxy) varieties were purchased from the Regional Rice Research Station, Assam Agricultural University, Titabor and local farmer of the state. Steam parboiling with and without added pressure and dry-heat parboiling methods with variations in pressure, temperature and time conditions were carried out for the different rice samples.

The rice samples, after milling were analyzed for different morphological, structural, physical, physicochemical and digestive properties to understand the changes on parboiling.

Physical properties: Grain dimensions, density and porosity, grain hardness, head rice yield, grain color.

Morphological properties: Scanning Electron Microscopic analysis.

Physicochemical properties: Amylose content, Water absorption (Equilibrium moisture content on soaking kernels at room temperature and sediment volume of flour), pasting properties, cooked rice texture, crystallinity, thermal parameters and *in vitro* starch digestibility.

Phytochemical content and antioxidant activity of milling fractions: total phenolic and flavonoid content, radical scavenging activity and metal chelating activity.

Based on the results obtained and after further statistical analysis, the properties of starch in the raw and parboiled rice samples were elucidated.

The Thesis-

The thesis is divided into eight chapters which are briefly discussed below:

Chapter 1 presents the general introduction on rice and rice parboiling. Further, the properties of parboiled rice with special emphasis on changes in the status of starch were introduced. A few popular traditional parboiled rice products of Assam and their conventional processing techniques have also been detailed. A brief note on phytochemicals in rice bran has been added.

Chapter 2 reviews the important works conducted on parboiling and on characterization of starch in parboiled rice. It also reviews works on phytochemicals and antioxidants in raw and processed rice.

Chapter 3 includes a study on the effect of mild, moderate and severe steam parboiling at open and under steam pressure on physical, physicochemical and digestibility properties of four rice varieties differing in amylose content.

Chapter 4 presents a study on the effect of dry heat parboiling at two different temperatures for three different time periods each on physical and physicochemical and digestibility properties of three rice varieties differing in amylose content.

Chapter 5 deals with processing and characterization of *Komal chaul,* a low amylose and hydrothermally treated ready-to-eat rice product requiring no cooking. The product was processed by a laboratory-scale method under different temperature, pressure and time conditions and was characterized for different physical and physicochemical as well as digestibility properties. Special emphasis was given to the texture profile analysis using a texture analyzer to compare the product with cooked rice.

Chapter 6 includes a study of the physical, physicochemical and starch digestibility characteristics of *Bhoja chaul*, another traditional ready-to-eat rice product processed by an improvised laboratory-scale dry heat parboiling method under different temperature and time conditions. Changes in different properties of the rice on processing into the product were studied and the texture parameters important for the product's consumption were evaluated.

Chapter 7 includes a study on the phytochemical content and antioxidant activity of milling fractions of a pigmented parboiled rice variety, namely *Kola chokua.* Changes in color parameters, total phenolic and flavonoid content, radical scavenging activity and metal chelating activity were carried out by standard biochemical methods.

Chapter 8 concludes the thesis presenting the salient findings of the present investigation. The results of the work indicated that varietal difference, amylose content and parboiling methods and severity play very important roles in determining the physicochemical status of parboiled rice. Change in the colour of parboiled rice on steam parboiling is due to both pigment migration and formation of Maillard browning compounds. These compounds also add to antioxidant activities of pigmented parboiled rice as revealed from the study on milling fractions. Severity of dry heat parboiling resulted in cavity formation in the kernel that can be related to splitting of the kernel on treatment with alkali during alkali score test as was reported previously by other authors. Continuously rising pasting curves and altered digestibility after parboiling indicated targeted use of the low amylose and waxy parboiled rices and products. Amylose was observed to inhibit amylopectin melting during parboiling as was observed from crystallinity studies. Formation of amylopectin-lipid complexes in dry heat parboiled waxy samples was suggested by the thermal analysis results. *Komal chaul* obtained by the laboratory-scale method resulted in texture comparable to open cooked rice kernels.

Bhoja chaul processed by the laboratory method, when soaked in water at room temperature for 20 min gave better texture than cooked rice.

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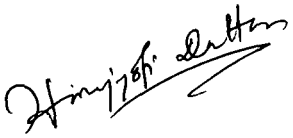
Declaration

I hereby declare that the thesis entitled "**Study on the effects of parboiling on rice and rice products of Assam**", submitted to the School of Engineering, Tezpur University in partial fulfillment of the requirements for the award of the Doctor of Philosophy in Food Engineering and Technology, is a record of original research work carried out by me. Any text, figures, theories, results or designs that are not of my own devising are appropriately referenced in order to give due credit to the original author(s). All the sources of assistance have been assigned due acknowledgement. I also declare that neither this work as a whole nor a part of it has been submitted to any other university or institute for any degree, diploma, associateship, fellowship or any other similar title or recognition.

Date: 18/06/2014

Place: Tezpur



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Certificate

This is to certify that the thesis entitled "**Study on the effects of parboiling on rice and rice products of Assam**", submitted to the School of Engineering, Tezpur University in partial fulfillment of the requirements for the award of the Doctor of Philosophy in Food Engineering and Technology, is a record of original research work carried out by Mr. Himjyoti Dutta under my supervision and guidance.

All help received by him from various sources have been duly acknowledged.

No part of the thesis has been submitted elsewhere for award of any other degree.

Charu Lata Mahanta

Signature of Supervisor: (Prof. Charu Lata Mahanta)
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List of abbreviations

AOAC	Association of Official Analytical Chemists
db	dry basis
DG	degree of gelatinization
DP	degree of polymerization
DSC	differential scanning calorimetry
EMC-S	equilibrium moisture content on soaking
FRAP	ferric reducing antioxidant potential
FTIR	fourier transform infrared
GPC	gel permeation chromatography
HPSEC	high performance size exclusion chromatography
HRY	head rice yield
IR	infra red
IRRI	International Rice Research Institute
MCC	metal chelating capacity
NMR	nuclear magnetic resonance
ppm	parts per million
RDS	rapidly digestible starch
rpm	rotations per minute
RS	resistant starch
RTE	ready-to-eat
RVA	rapid visco analyser
SDS	slowly digestible starch
SEM	scanning electron microscope
SV	sediment volume
TFC	total flavonoid content
TPA	texture profile analysis
TPC	total phenolic content
TS	total starch
w/v	weight per volume
w/w	weight by weight
WAXS	wide angle X-ray diffraction spectroscopy
wb	wet basis
XRD	X-ray diffraction

List of symbols

°C	degree Celsius
min	minute
s	second
h	hour
>	greater than
<	lesser than
=	equal to
%	percentage
mL	millilitre
μm	micrometre
μ	micron
A°	angstrom
N	normal
M	molar
nm	nanometre
kPa	kilo pascal
mg	milligram
g	gram
kg	kilogram
cm^{-1}	per centimetre
kV	kilo volt
K	constant for XRD machine
2θ	Bragg's angle of diffraction
mA	milli ampere
U	enzyme activity unit
j/g	joule per gram
Da	dalton
psig	per square inch of gauze
H	hue angle
C	chroma
L/B	length by breadth
ρ_b	bulk density
ρ_t	true density
ε	porosity
ΔH	change in entahlpy
To	onset temperature
Tp	peak temperature
Tc	conclusion temperature
mM	milli molar
	per

Chapter 1

INTRODUCTION

Parboiling, the process of pretreating paddy with water and heat, originated in India. Parboiled rice is widely consumed in India, Sri Lanka, Nepal, Bangladesh, Pakistan and also by Indian immigrants in many parts of the world. An estimated one-fifth of the world paddy production and more than half of the annual production in India undergo parboiling.[1] This post-harvest processing technique for paddy was developed for quality enhancement. Parboiling brings about major changes in the grain and it can be said that parboiled rice is distinct from normal raw rice. Raw rice loses its opacity and becomes glassy and translucent on parboiling. The hydration and cooking behaviour, the eating quality, and the product making quality are profoundly altered on parboiling. The flow and packing properties on parboiling are altered. Parboiling gives stable bran and the oil content in the bran is increased.[2]

1.1. Parboiling techniques and practices

Parboiling is an age-old traditional post-harvest processing technique for paddy meant for quality enhancement. Parboiling originated in India in times dating back to fourth or fifth century AD.[1] Today, about one-fifth of the world's paddy is parboiled. The general parboiling process involves basically three steps- soaking paddy in water followed by steaming and drying.[3,4,5] The traditional parboiling process involves soaking rough rice overnight or longer in water at ambient temperature to sufficiently moisten the paddy, followed by boiling it (at 100°C, atmospheric pressure) while the grains expand until the hull starts to split. The grains are then air or sun dried and milled. The modern pressure parboiling process, however involves soaking of the paddy at elevated temperatures (typically 70°C) for a few hours which results in sufficient saturation, followed by pressure steaming for a brief period and drying by both traditional and mechanized ways.[6,7] Another parboiling process, called as dry heat parboiling involves

only partial soaking of the paddy (18-20% moisture) followed by brief conduction heating using very hot sand or air instead of steam.[1] The third process is however employed only for making some speciality rice products. Fig 1.1 is the schematic diagram showing the three types of parboiling processes.

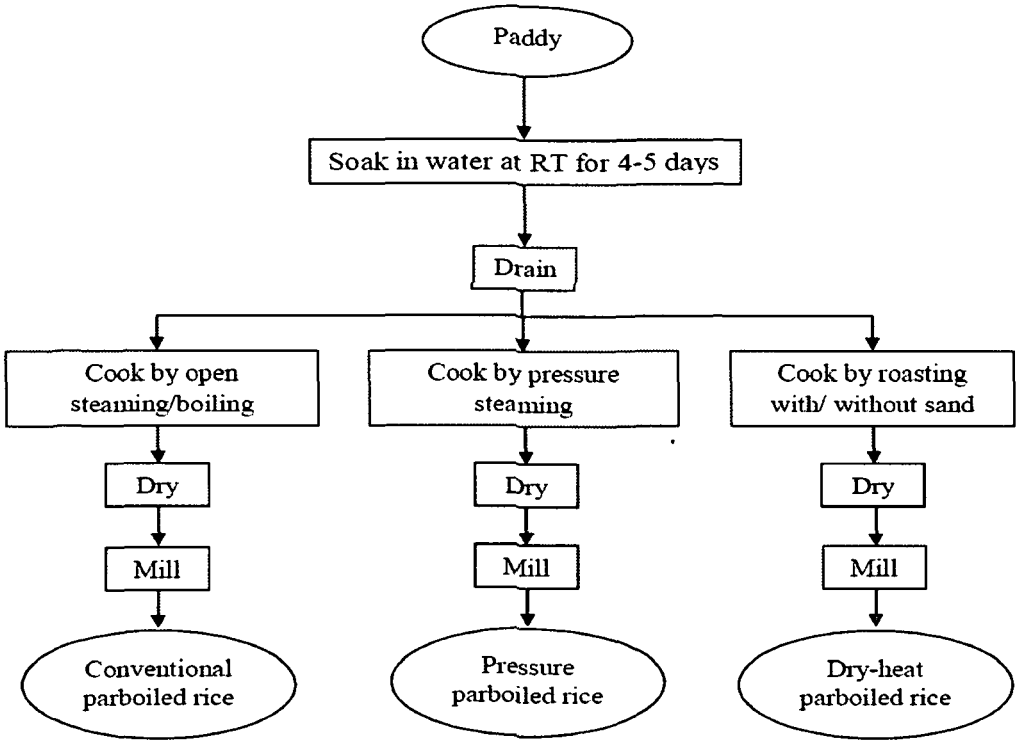


Fig. 1.1. The three basic parboiling processes (Source: Bhattacharya, 1985).[1]

Many variations in terms of parboiling conditions and techniques under these three basic processes have been practiced and studied.[4,7] Newer tools like modern dryers, microwaves, fluidized hot beds etc have reportedly made the drying step easier and efficient.[9,10]

1.2. Properties of parboiled rice

The most important property for commercial importance of parboiled rice is higher head rice yield and less broken kernels on milling, which gives higher economic return and better consumer acceptance. Parboiling influences the physical characteristics of the rice grains to a marked extent. Length to breadth (L/B) ratio of rice grains is an important commercial parameter. Parboiling is reported to change the L/B ratio.[11] With change in the dimensional ratio, other parameters like bulk density, true density, porosity,

flowability, packing properties etc also change. Milled parboiled rice kernels are glassy and translucent while raw kernels are opaque.[12,13] An insufficient soaking leads to formation of "white belly", which is a characteristic opaque core in the parboiled rice kernel.

The cooking properties of rice are highly altered upon parboiling. Cooked parboiled rice has a bold structure and firm texture. It exhibits lower water uptake during cooking and hence needs a longer time to cook to a soft consistency. However, the kernel shape is better retained; the rice becomes fluffier and less sticky during cooking as compared to the raw rice. The choice of cooked rice texture however varies from region to region depending upon consumer's acceptability. For evaluating texture profile of cooked rice, modern texture analyser is extensively used.[11,13]

The change in starch properties relate to the changed properties of the rice kernel. For measuring the change in crystallinity and identifying the crystallite types, quick and efficient tools like X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimeter (DSC) are popularly used.[15,16,17] The semicrystalline property combined with pasting property as determined by RVA can be utilized for understanding the status of starch and flour and their targeted industrial uses.

From the nutritional point, the reason for acceptance and recommendation of parboiled rice is mainly because of its nutritional quality. Parboiled rice is rich in B vitamins. The developed kernel hardness makes the polishing step less effective and the nutritive epidermal layers of the rice kernel are retained even after milling. Starch digestibility is another important nutritional parameter.[18] The increase or decrease of the rate of digestion after parboiling has however been a topic of controversy.[19,20,21]

1.3. Parboiled rice products

1.3.1. Steam parboiled rice product

Steam parboiled rice as discussed above is industrially produced, consumed and exported from almost all Asian countries. African countries like Nigeria, Ghana, Egypt, Niger and Benin are also significant producers of rice.[22]

1.3.2. Dry heat parboiled rice products

Dry heat parboiled rice products are speciality products which are not generally consumed as staple food. Dry heat parboiling has however never been considered or studied as a replacement of steam parboiling. Puffed rice and flaked rice are the most popular dry heat parboiled products but have been given limited scientific attention till date.

Puffed rice

Traditionally, paddy is soaked in warm water overnight and the soaked paddy is then roasted in sand on a *bhatti* (traditional firewood burner) in small batches to produce dry-heat parboiled paddy. The paddy is allowed to dry in mild sun or in air after spreading out. The dried paddy is then milled in a huller. The milled parboiled rice is gently heated on the *bhatti* without sand to reduce the moisture content to the appropriate level, then taken out and mixed with a proper amount of salt solution. After holding for some time, the parboiled rice is again roasted on *bhatti* in small batches with sand on a strong fire for a few seconds to produce the puffed rice.

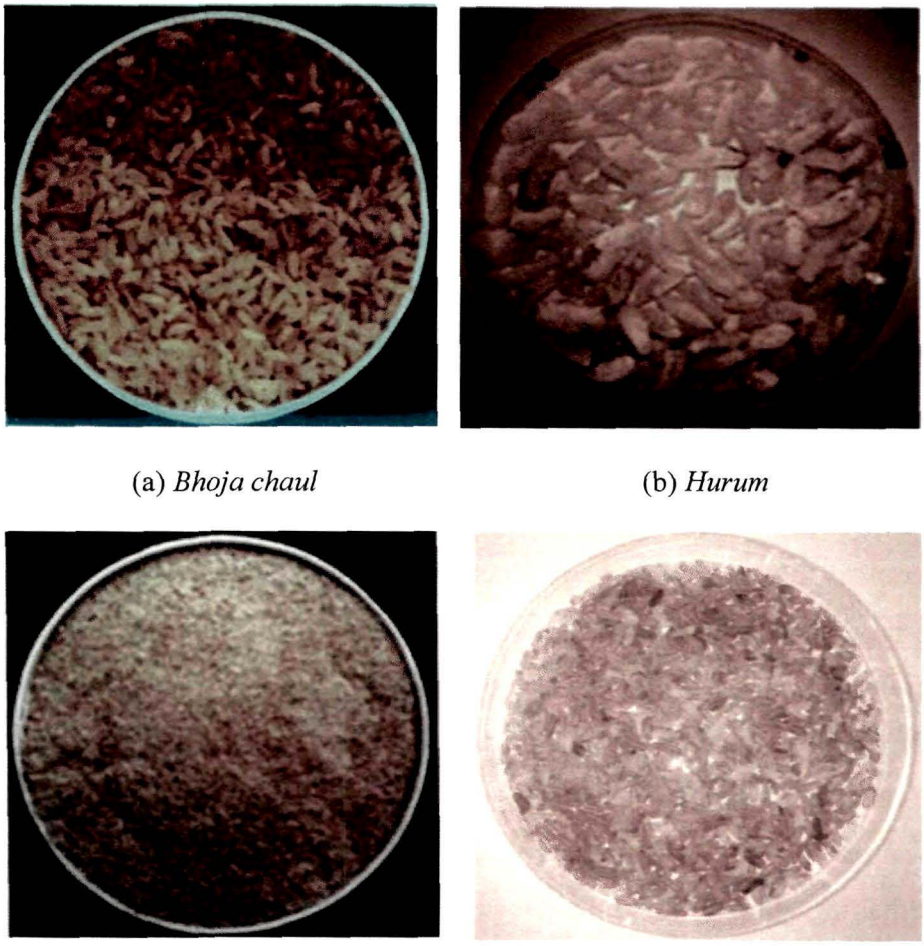
Flaked rice

For making flaked rice, soaked paddy is roasted and then flaked in an edge runner. The process also removes the brittle outer husk. In the edge runner, the roasted grain has to pass between the roller and pan edge repeatedly round and round. This severe abrasion at the edges of the grain along with grain breakage results in low product yield.

1.3.3. Parboiled rice products of Assam

Bhattacharya et al (1980) classified hundred Indian rice varieties collected from different parts of the country into eight groups.[23] Group I cooks flaky and hard while group VIII cooks extremely sticky and soft. Group IV consists of the aromatic rice varieties. It was observed that only Assam produced varieties from all the eight groups. Glutinous rice varieties of Assam and its adjoining states are unique in India. While the high and intermediate amylose rice varieties are consumed as staple foods, the low amylose and waxy varieties are processed to make speciality products. The low amylose

rices are called *chokua* rice and the waxy rices are called *bora* rice. Unique taste and texture are attained when the dry-heat parboiled rice products like *moori* (puffed rice) and *chira* (flaked/beaten rice) etc are prepared using the waxy varieties which are commonly eaten in Assam whereas *moori* and *chira* made from non-glutinous rice are popular throughout the Indian subcontinent. Further, there are certain speciality rice products which despite of having possible ethno-economic importance have not been studied and extensively researched on. Special parboiling treatments develop peculiar hygroscopic and sensory characteristics in these products. A few such products and their present status in the scientific scenario are detailed below.



(a) *Bhoja chaul* (b) *Hurum*

(c) *Sandahguri* (d) *Komal chaul*

Fig. 1.2. Traditional parboiled rice products of Assam

Bhoja chaul

Bhoja chaul in simple terms is a dry heat parboiled rice product (Fig 1.2a). *Bhoja chaul* grain does not undergo excessive structural and morphological disorganization during the process. Waxy paddy is soaked for 3-4 days at room temperature after which the water is drained out. The moistened paddy is roasted in an iron vessel over wood fire with constant stirring. Roasting is stopped when the grains sufficiently dry up. The roasted paddy is spread over mud floor to cool for about 30 min before milling in a *dheki* (a hand and foot operated pounding and milling device) to get *Bhoja chaul*. However, many variations can be seen in the time and temperature of soaking and roasting in different rural households. Soaking in hot water overnight or boiling the soaked paddy till very fine split in a few husks occur are also practiced by some. The roasting temperature is controlled by the intensity of the wood fire. The prepared *Bhoja chaul* is soaked in water at room temperature prior to consumption to let it hydrate sufficiently to an optimum level. The excess water is squeezed out with hand during which the sticky grains cling to one another forming an oval and flat shaped lump. These lumps are eaten with milk, cream, curd and jaggery. According to the rural household processors, the desirable characteristics of *Bhoja chaul* are the roasted aroma and colour, a sticky and chewy texture and appearance of the rice grains clinging together to form the lump.

Hurum

Hurum is an expanded rice product made from waxy *bora* rice of Assam (Fig 1.2b). The product is traditionally relished with milk and sugar or jaggery. It is distinctly different from the more popular *moori* both in the processing method and the product quality. The extensive expansion and translucency acquired during processing are the distinctive characteristics of *Hurum*. The basic traditional parboiling method comprises the following steps: full soaking of paddy, parboiling, dehusking at high moisture, immediate flaking, rubbing fat to the flaked rice and expansion in sand. This product can therefore be called as 'expanded flaked' rice. Mishra et al (2000) identified the essential steps of *Hurum* making in the laboratory using paddy processed by normal, dry-heat and pressure parboiling methods.[24] Based on the findings, a process was further optimized for cottage scale production of *Hurum*.[25] Instead of a longer soaking period and intermediate simmering in water, the authors soaked paddy overnight in freshly boiled

water and allowed for self-cooling to room temperature to allow optimum moisture absorption. It was directly followed by vigorous roasting in sand on the *bhatti* to bring the moisture content down to 21-23 % (db). The paddy was then simultaneously flaked and dehusked in an edge runner in a flaked rice mill. The flaked and dehusked kernels were rubbed with an optimum amount of hydrogenated oil. The oiled flaked rice was then roasted for a short time to obtain expanded *Hurum.*

Sandahguri

Sandahguri is obtained as a coarsely ground powder of parboiled rice (Fig 1.2c) involving a longer process. Although no specific type or rice variety is used for this product, *chokua* variety of rice is known to be preferred over others. Instead of soaking for long durations, a double parboiling method is traditionally employed. The paddy is cooked in water for 15-20 min until a few bubbles appear to indicate boiling. The vessel is then removed from fire and kept overnight to hydrate, after which the paddy is again boiled afresh till a few husks split. The water is drained out and paddy allowed to sundry. The dried paddy is stored and further processed into *Sandahguri* whenever needed. For that, the paddy is milled in *dheki* (the traditional hand and foot pounding machine) and roasted in iron pan without sand. The roasting is done either directly or after moisture treatment. Moisture treatment may be simple washing and draining or longer soaking for 15-20 min and draining. Roasting results in very slight puffing of the rice, now called *Karai.* This may be consumed as such or further powdered to obtain *Sandahguri.* The moisture content before roasting influences the extent of puffing of *Karai* which in turn determines the product quality of *Sandahguri.* High moisture gives lower puffing and therefore is roasted at lower flame for a longer time which gradually reduces the moisture and develops desirable flavour and aroma in the *Karai.* Lower moisture results in undesirably excessive puffing. The puffing should not be extensive as that gives an unsuitable end product quality. Roasting may be carried out for 2-20 min depending on the paddy used, followed by pounding using *dheki* to get lumpy or dry powdery textured *Sandahguri.* Traditionally, the powder is mixed with hot milk and stirred to a thick, slightly sticky, cohesive, porridge like consistency and consumed along with jaggery or sugar. A strong roasted aroma from the slightly particulate mixture is a desirable characteristic. Certain notable variations in the traditional process are also available. Instead of double boiling, many households use a standard dry-heat parboiling technique

with paddy soaked for 4-6 days. A practice of rubbing salt solution to the parboiled rice and sun drying for 20-25 min prior to roasting is also practiced by some for better puffing quality of *Karai.*

Komal chaul

Komal chaul (soft rice) is a whole grain, ready-to-eat product which needs no cooking and can be consumed after simply soaking in cold to lukewarm water (Fig 1.2d). It is a speciality rice product of Assam. The traditional parboiling technique is given in Fig 1.7b. Traditionally, *chokua* paddy is soaked in water at room temperature for 3-4 days to attain an acceptable moisture level. The excess water is drained and the paddy is put in fresh water and cooked over wood fire till the husks start splitting. The water is again drained and the paddy dried under the sun on the same day. Dried paddy is milled in *dheki*, the traditional hand and foot pounding machine to get the *Komal chaul* product. Drying of the boiled paddy is done on the same day so that there is negligible retrogradation and the milled product attains soft texture on simple soaking in water at room temperature.

1.4. Phytochemicals in rice

Phytochemicals are non-nutritive plant chemicals that have protective or disease preventive properties in humans. Although fruits and vegetables are considered to be rich in phytochemicals, cereals and cereal products are also reported to possess these compounds in abundance.[27] The phytochemicals have antioxidant activities and hence are nowadays popularly utilized for health enhancement and cancer treatment etc. Polyphenols constitute a large population of phytochemical compounds. While quantitative estimation of these compounds are measured as total phenolic content and total flavonoid content. Their qualitative antioxidant potentials are widely measured in terms of diphenylpicrylhydrazyl (DPPH) radical scavenging activity and metal chelation capacity, etc.[27] High performance liquid chromatography (HPLC) has also been used as a modern tool for identification and quantification of phytochemicals in plant extracts. Gas chromatography coupled with mass spectroscopic (GC/MS) analysis is carried out for structural charactertization and identification of these compounds.[28] In rice, most of the phytochemicals are located in the husk and bran layers and hence are removed during

milling.[29] Rice bran oil has hence been popularly used in health promoting formulations. [30] High temperature treatments like parboiling results in loss of their chemical structures and thereby lower their antioxidant capacities. Parboiling also results in migration of surface compounds into the starchy endosperm of the rice kernel.[13] Estimation of these compounds in the different milling fractions is hence necessary to understand their health benefits.

Though Assam is a reservoir of rice germplasms and rice varieties varying in amylose content are processed into different rice products, very limited studies have been carried out till date on the physicochemical and functional properties of the rice grains and their flours and the effect of processing on these properties have not been evaluated. The present thesis aimed to conduct an in depth study on the properties of rice varieties differing in amylose content and also to assess the changes in the physicochemical, morphological, thermal, textural, IR spectral, pasting and crystalline properties on processing into rice products.

1.5. Objectives

The following objectives were set for the research work:

- To study the effects of steam parboiling varying in time and pressure on the properties of parboiled rice varieties with different amylose content.
- To study the effects of dry heat parboiling varying in temperature and time on rice varieties with different amylose content.
- To characterize ready-to-eat *komal chaul* processed by a laboratory-scale steam parboiling method.
- To characterize ready-to-eat *bhoja chaul* processed by a laboratory-scale dry heat parboiling method.
- To study the changes in phytochemical content and antioxidant activity of the milling fractions of a pigmented paddy on parboiling.

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Chapter 2

REVIEW OF LITERATURE

Formal research on rice had started about nine decades back.[1] Kato et al (1928) first classified rice into its two subspecies, *indica* and *japonica*.[2] This was based on the geographical distribution, plant and grain morphology, hybrid sterility, and serological reaction. The role of starch in determining the functional properties of rice and consumer acceptability was however examined much later.[3] Work of Juliano (1979) resulted in the most scientific classification of rice varieties into groups based on their amylose contents.[4] Rice varieties with high amylose content cooks dry and fluffy and has high volume expansion. As amylose content decrease, the rice cooks moist and gives low volume expansion.[5,6,7,8]

Parboiling brings about distinct and significant changes in the physical and physicochemical properties of rice. The starch granules in the rice grains hence behave as to be in aqueous slurry inside the husks. When starch is heated in excess water, gelatinization occurs. The gelatinization process is again a combination of a few phenomenons. When the starch slurry is continuously heated, the granules start to swell due to uptake of water resulting in increased slurry viscosity. Simultaneous decoiling of the helices occurs with exposure of the hydrogen bonding sites to bind more water molecules. The amorphous fractions are hence believed to be mainly responsible for the initial water uptake.[9] The soluble fractions get released from the starch granules into the surrounding water.[10] Subsequently with increased temperature, the starch crystallites melt to diffuse into the amorphous phase and it is called the gelatinization temperature. This is an endothermic transition as revealed from numerous studies.[11] The swollen granules then disrupt completely causing the viscosity to drop continuously with any further rise in temperature. When this heated amorphous slurry is cooled, the suspended starch chains tend to recoil to regain the original semicrystalline conformation with simultaneous release of the entrapped water molecules. This reversible phenomenon is

called retrogradation and plays the major role in cooked starch products.[12] In parboiled rice, retrogradation starts just after the steaming step and continues throughout drying, milling and further storage. Hence, the conditions followed during these steps play an important role in the physicochemical properties of the end product. The gelatinised starch never regains its native properties.

2.1. Structure of rice kernel and head rice yield

Rice starch granules are the smallest among all starches with size ranging from 3 to 10 μm.[13] They are polyhedral in shape. The small size of rice starch granules and wide range of amylose contents have allowed its extensive commercial utilization.[14] In the kernel, the granules are abundantly packed and loaded inside amyloplasts of cells. The closeness of packing varies from variety to variety and also from tissue to tissue within the rice kernels.[15,16] Parboiling and cooking involving hydrothermal processing causes swelling and disruption of the native starch granules in the rice kernels.[17,18] Ogawa et al (1999) reported uneven levels of starch gelatinization in the cooked rice.[19] Climatic and processing stress forms fissures in the raw rice endosperm. The formation of molten and gelatinized starch during steaming fills up the weak lines of fractures in the rice kernels. This thereby helps in improving hardness and lowering grain breakage during milling. Typically, parboiled rice should give 100% head rice yield. However, moisture gradient developed in the parboiled kernels due to use of high and non-uniform temperature during the drying step may also result in formation of new kernel fissures.[20,21] Ogawa et al (2003)[19] and Horigane et al (1999)[22] reported formation of hollow voids in cooked rice, which were attributed to rapid pressure build-up (steaming) during steaming and subsequent expansion or localized explosion within the grain. Witek et al (2010) reported formation of micro and macropores in heat moisture treated rice.[23] Similar phenomenon may also arise during parboiling of paddy under pressure. An additional tempering step during drying reduces grain breakage in parboiled rice.[24] As per that, Igathinathane et al (2008) developed a moisture diffusion model using a multi-pass drying simulation with a vacuum system for process acceleration.[25] Temperature of water used for soaking paddy positively influenced the head rice yield of fragrant rice variety.[26] Although head rice yield is measured by general observational technique as proportion of intact kernels to that of the total milled rice, sophisticated image analysing tools have been developed for observing the kernel integrity prior to milling.[27,18] Dang

and Copeland (2004) reported a smoother cut surface of parboiled rice than raw rice in sections prepared for SEM analysis.[29] The smoother edges are supposedly formed by amylose that had leached out during gelatinization. SEM images of dry heat parboiled rice markedly varies from steam parboiled rice with formation of distinct porous texture with differential distribution of porosity with process variables.[30,31,32]

2.2. Colour

Another important physical change distinctly observed in parboiled rice is development of colour. While milled raw rice is white, milled parboiled rice is amber in colour. Bhattacharya and Rao (1966) reported progressive darkening of kernel colour with the severity of temperature in the soaking and steaming steps.[33] Quantitatively, high temperature soaking caused more severe change in colour than the steaming. Colour may be considered as an important indicator of the extent of rice parboiling. The authors mentioned that the changes in colour is due to Maillard type non-enzymatic browning, embedding of the bran layers into the endosperm and their browning and also penetration of husk pigments into the endosperm. Lamberts and Delcour (2008) however found that the carotenoids got reduced to trace levels after parboiling and hence do not contribute to the final colour of parboiled rice.[34] Elbert et al (2001) reported the impact of air temperature during drying on the browning of parboiled rice.[35] Developed techniques for judging colour of parboiled rice are being used over the simple visual method to evaluate its quality.[36] Bhattacharya (1996) used the Hunter system for colour determination of rice parboiled at different pressure and process times.[37] The development of colour was found to positively correlate with severity of pressure and time. Decreased lightness and greenness and increased yellowness were observed. The author suggested that the change in colour can be regulated by controlling the pressure and time of steaming. While the changes in lightness values followed first order kinetics, changes in the other two colour parameters followed zero order kinetics. Islam et al (2004) mentioned that lightness value may be considered as a suitable quality indicator to estimate the energy requirement in parboiling.[38] Lamberts et al (2006) found that while moderate parboiling affected the yellowness more than redness, severely parboiled samples showed an opposite trend. The brightness of parboiled milled rice was attributed to the migration of lipids from the inner to the outer bran layers. Starch gelatinization was also reported to be responsible for the marked difference in total colour. The principal involvement of browning reaction in

colour development was confirmed by evaluating the formation and loss of reducing sugars during steaming.[39]

2.3. L/B ratio, density and porosity

It is the ratio (L/B) of the kernel length (L) and breadth (B) that decides its shape. The shape further relates to the bulk density and porosity of the grain when packed. The more round the grain, the greater was the bulk density and the lower the porosity and vice versa.[40] L/B has therefore been considered as an important physical parameter for rice commercialization. Parboiling causes changes in the L/B ratio of rice kernels. Kurien et al (1964) observed increase in breadth with significant reduction in kernel length.[41] Contrary to this, Sareepuang et al (2008) reported increased lengths of rice kernels and simultaneous decrease in breadths when paddy was subjected to steaming after different temperatures of soaking.[26] Sowbhagya et al (1993) proposed that different parboiling conditions result in variable changes in the rice shapes.[42] Higher increase in values of L than B was reported for both steam parboiled and dry heat parboiled samples. This indicated rearrangement of the parboiled kernel material in a different order than the raw rice. However, no significant effect of parboiling on L/B ratio was observed by Saeed et al (2011) on six different Pakistani rice varieties.[43] While degree of milling greatly influences the kernel dimensions and thereby the packing properties, rice cultivars with higher L/B ratio showed higher degree of milling when milled for the same duration.[44]

2.4. Proximate analysis and amylose content

Parboiling has been reported to alter the proximate composition of rice. Chukwu and Oseh (2009) reported reduction in crude fibre, crude protein and vitamins and increase in ash, fat and total carbohydrate contents.[45] The significant decrease in protein content was attributed to sinking of the degenerated protein bodies into the compact mass of gelatinized starch grains during steaming, making it less extractable. The higher fat content is the result of the rupture of the fat globules present in the bran layers and distribution throughout the kernel. Increase in fat content was also reported.[26] The authors however reported significant increase in protein content too. Dors et al (2011) also reported increase in ash content which they attributed to migration of minerals from the husk and bran into the endosperm.[46] Amylose content plays an important role in

determining the quality of parboiled rice products.[47,48] Insignificant increase in amylose content of rice on parboiling has been reported.[49] Otegbayo et al (2001) however reported some loss in apparent amylose content which they attributed to molecular leaching during soaking and steaming of paddy.[50]

2.5. Microscopy

Light microscopy has been widely used for determination of structures of starch granules.[51] Microscopy under plane polarized light has been able to give higher insight into the development, structural organization and processing changes in starch granules.[52,53] The surface morphology of rice grains and starch however varies widely in nature. Starch can be modified in a lot of ways which results from minor morphological changes of granules to complete disintegration of the granular structures.[54-56] To observe these changes and study the changing patterns, a detailed observation can be made using the Scanning Electron Microscope (SEM). SEM is widely used due to the appreciably higher magnification down to nanometer scale and superior resolution. The sample to be observed is coated with a metallic coating (gold or platinum) uniformly throughout its surface and electrons are bombarded over it. The electrons that scatter back are called secondary electrons, which generate the SEM image. As revealed by SEM, it has been revealed that rice starch granules are the smallest known to exist, with size in the range of 2 to 7 μm and are polyhedral in shape.[57]

2.6. Water absorption

Ajisegiri et al (2007) studied the moisture sorption of locally parboiled rice and found a sigmoidal pattern of absorption, which is common for all cereal types.[58] Parboiled rice that has been soaked in water behaves differently with change in temperature. While at room temperature it absorbs water at a faster rate than raw rice, the opposite is experienced while cooking.[59] Parboiled rice therefore takes longer time to cook than raw rice. The relative humidity condition also plays a significant role in the extent of moisture absorption by the rice.[60,61] Equilibrium moisture content of rice on soaking in water at room temperature (EMC-S) is considered as an effective tool for identifying parboiled rice. A simple method of soaking paddy or milled rice in water at room temperature for a few hours to study the EMC-S was developed.[62] Unnikrishnan

and Bhattacharya (1987) used this method for parboiled rice samples differing in apparent amylose contents.[63] The results clearly indicated a negative correlation amongst amylose content and EMC-S. The most severely parboiled waxy varieties were reportedly not following the trend of change in properties as the rest of the varieties, which however could not be explained by the authors then. Another important test for hygroscopicity of rice flour is the test for sediment volume (SV). This test is closely associated with the cold slurry viscosity.[64] It also gives an idea of the status of starch as indicated by its affinity towards water. The authors reported that steam parboiled rice gives markedly higher SV than raw rice. The values are still higher for dry heat parboiled rice products because of the reduced amounts of retrograded starch.[64] SV was hence considered as an indicative factor for amount of pregelatinized starch in processed starchy flours. Similar findings were also reported by Chitra et al (2010) who opined that the highest value of SV in flaked rice amongst other products were due to the effect of different impact forces acting upon the starchy matter.[65]

2.7. Pasting properties

The viscosity changes exhibited by a starch paste when subjected to heating and cooling treatments suggests its cooking behaviour and also gives a measure of its molecular characteristics. Starch is used in many food and non-food applications which involve temperature treatments. The response of the polymer to such conditions influences the product properties. The viscosity profile of cooked and cooled starch paste is obtained by the modern Rapid Viscosity Analyzer (RVA) instrument.[66] The instrument has a a paddle that rotates in a stationary starch paste and the resistance to paddle movement is measured. The working principle in the RVA is that the torque required to turn an object in fluid is a function of the viscosity of the fluid. Different starch pastes show different viscosities at any particular temperatures and the molecular differences of those can be well understood from this.

The rice flour slurry viscosity while cooking is considered as one of the principal physicochemical attribute used to determine the nature of molecular arrangement in a particular flour sample. Amylose content acts as the key factor for determining the pasting pattern of any variety of rice. Varavinit et al (2003) studied the RVA pasting patterns of thirteen different rice cultivars falling under different groups as per their

apparent amylose contents.[67] The authors observed that the waxy rice varieties can be characterized by higher breakdown and lower setback values than those with higher amylose contents. This suggests that the starch granules in waxy rice flour disrupt more easily on cooking and shows a lower tendency towards retrogradation due to lower amylose reassociation. Setback viscosity of parboiled rice flour was reported to be related with cooked rice texture.[68] According to Juliano et al (1987), varietal differences in pasting characteristics of starch can be attributed to the differences in molecular structure of amylopectin rather than amylose.[69] Ashogbon, and Akintayo (2012) observed that rice varieties with higher amylopectin content also exhibited higher swelling observed during heating to its cooking temperature.[70] Varietal differences in pasting patterns often creates obstacle in industrial processing of starch. Lee et al (2012) hence classified twelve cultivars of rice into six groups based on their hydration and pasting properties to be used industrially.[71] Unnikrishnan and Bhattacharya (1983) used coaxial cylinder viscometer to find that slurry of parboiled rice flour at room temperature showed a markedly higher viscosity than the slurry of raw rice flour. They observed that the viscosities were proportional to the hydration power and slurry-sedimentation behaviour of the samples.[72] Brabender viscograms of rice samples processed under different parboiling conditions indicated drop in all pasting parameters and shifting of the peak viscosity to higher temperature with severity of parboiling. This suggested a decreased swelling ability of the starch granules in parboiled rice on heating.[73] Similar observation was also reported by Biswas and Juliano (1988).[48] However, waxy and low amylose varieties were found to be more resistant to loss in viscosity than the high amylose varieties. Many other workers using modern rapid viscosity analyser tool also have obtained similar findings.[74-77] Repeated steaming was found to cause gradual decrease in all viscosity parameters of two high amylose rice varieties.[78] This has been attributed to the disruption of the granular structure of starch which fails to swell again on heating.[75] Gunaratne and Hoover (2002) reasoned that amylose leaching reduces after parboiling as the hydrothermal treatment caused additional amylose–amylose and amylose–amylopectin interactions within the starch granule reducing the leaching ability.[79] This along with the restricted swelling of parboiled rice starch was attributed to the delay of onset of pasting in six high amylose rice varieties.[80] In a recent work, Mir and Bosco (2013) reported drop in peak viscosity with increased temperature of soaking.[81] Lai and Cheng (2004) prepared pregelatinized rice flour from rice varieties differing in amylose

content by gun puffing. Effect of pre-steaming prior to puffing and amylose content played the key role in the wide differences in pasting patterns of the product.[82] Use of infrared heating for simultaneous parboiling and drying also resulted in pasting patterns similar to steam parboiled rice slurry.[83] Derycke et al (2005) studied the effect of protein bodies on the pasting properties of rice slurry and suggested the presence of a protein barrier that affects starch swelling during cooking of both raw and parboiled rice.[84] Gelders et al (2006) extraneously added amylose-lipid complexes to rice flour samples prepared for RVA. The lipid molecules got released into the system during the heating step and altered the pasting profiles.[85] This clearly suggests the importance of the complexes in deciding the pasting properties of parboiled rice flour.

2.8. Cooked rice texture

RVA pasting parameters and setback in particular were found to be correlated with cooked rice texture as measured by sensory and instrumental methods.[86] Texture profile analysis (TPA) of cooked rice is considered as the most important quality attribute from the consumer's point of view. Conditions during post-harvest processing of paddy has great effect the TPA values.[87] Okabe (1979) developed a method for measuring hardness, stickiness and cohesiveness of rice and proposed a ratio between stickiness and hardness as a measure of acceptability of non-waxy rice varieties.[88] Although amylose content is considered as the principal factor responsible for deciding TPA parameters of cooked rice, it is not always true. While amylose determines the stickiness, the hardness was found to be correlated to gel hardness and gelatinization temperature.[30,89] Parboiling causes alteration of starch chain structures. Ong and Blanshard (1995) proposed that it is the proportion of the longest (DP = 92–98) and shortest (DP = 25) amylopectin chains in cooked parboiled rice that determines the TPA parameters.[68] The authors however also found that the hard cooking rice varieties also had higher amylose contents which they proposed were responsible for binding with other non-starch components that resulted in the firmer texture. Further, the authors reported correlation between leached amylose in cooking water and RVA setback value with the texture profiles of 11 cultivars of rice.[90] They found that the longest chains did not leach out and hence might be responsible for the observed hardness of the cooked kernels. Work of Bello et al (2006) involved standardization of a method for parboiling.[91] The optimum processing condition was evaluated to be soaking the paddy at 25°C for 24 h followed by additionally tempering at

25°C for 24 h in an adiabatic container and heating at 85°C for 174.4 min or at 93.7 °C for 45 min. The rice hence obtained was found to be less hard than traditional parboiled rice and less sticky than raw rice. Parboiled rice with a harder endosperm was found to give harder cooked rice texture than non-parboiled rice.[92] Contrary to this, Sareepuang (2008) reported softer and less sticky texture of hot soaked parboiled rice than non-parboiled brown rice after cooking.[26] Patindol et al (2008) parboiled rough rice and brown rice of the same variety and observed similar hardness and stickiness in severely processed samples of both forms of parboiled rice.[93] It indicated insignificant effect of the temperature gradient formed due to the husk during parboiling on texture parameters of cooked rice.

2.9. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique that uses a range of infra-red (IR) light waves to determine the functional groups in a compound, and thereby determine the molecular structure of the compound. The frequencies of vibration of the chemical bonds when subjected to light waves are functions of the atomic size and bond strength in the compound. When a radiation of a particular frequency is applied to it, the bond absorbs energy from it and vibrates at higher amplitude detectable by the detector of the FTIR. A particular bond absorbs only a particular set of IR frequencies. The mathematical software associated with the FTIR system gives intensities of absorption at different frequencies, called as wavenumbers in terms of separate peaks. By matching the peak positions and intensities with the available database, the existing bonds and functional groups can be identified. The molecular structure of carbohydrates is basically composed of only carbon, hydrogen and oxygen. However, different bonding patterns occur in between these atoms. FTIR has been widely used to understand the effect of different modifications in the molecular structure of starch. A total of sixteen IR wavenumbers for raw starch have been proposed based on a review of different previous works.[94] They are given in the Table 2.1. Although no report on spectroscopic study of rice flour as a whole was found in reported literature, any change in FTIR spectra on hydrothermal modification may be principally related to structural changes in the starch like starch chain conformation, helicity, crystallinity as well as water content.[95] The IR beams can penetrate into a depth of 2 μm into the granule.[96] The work of FTIR study by

Rubens et al (1999) on pressure induced gelation of starches resulted in the finding that a correlation exists between the molecular structure and the stability to gelation of the

Table 2.1. FTIR wavenumbers for starch.*

FTIR wavenumbers (cm^{-1})	Infrared band assignment
537	Skeletal modes of pyranose ring
581	
627	
711	
764	C-C stretching
850	C(1)-H, CH_2 deformation
930	Skeletal mode vibration of α-1,4 glycosidic linkage, (C-O-C)
1067	C(1)-H bending
1094	C-O-H bending
1163	C-O, C-C stretching
1242	CH_2OH (side chain) related mode
1344	C-O-H bending, CH_2 twisting
1415	CH_2 bending, C-O-O stetch
1642	Water absorbed in amorphous regions of starch
2800-3000	CH_2 deformation
3000-3600	O-H stretching

*Source: Kizil et al (2002)[94]

different starch types.[97] B-type starches were found to be more resistant than A- and C-type starches. However, for all the starch types, bands in the region 900–1300 cm^{-1} increased in intensity and changed position at high pressure. Goodfellow and Wilson (1990) from their study on starch gel retrogradation, suggested that amylose undergoes rapid formation of three-dimensional hydrated double helical structures upon cooling of an amorphous sol.[98] Helical structures were proposed to act as junction zones among the polymer chains, which on further lateral aggregation leads to formation of B-type crystalline structures. The IR bands at 1047 and 1022cm^{-1} have been shown to be associated with ordered and amorphous structures of starch, respectively.[95] The band at 1047cm^{-1} increases with increase in crystallinity whereas the band at 1022cm^{-1} increases with increase in amorphousness. Thus, the ratio of the heights of the bands at 1047 and 1022cm^{-1} expresses the amount of ordered starch to amorphous starch.[95,99] Chung et al (2009)[100] and Mutungi et al (2011)[101] reported decrease in the ratio between the characteristic bands at 1047 and 1022cm^{-1} in heat moisture treated corn and cassava starch respectively. This is related to loss in crystallinity which is revealed by wide angle X-ray scattering. Li et al (2008) found out that the loss in the short-range order of heated

rice starches from different origins is highest at the pasting onset temperature.[102] The short-range order of native waxy and medium grain rice starches was found to be higher than that of long grain rice starches by the authors. However, the loss of order was also higher for the former. This was attributed to amylose which restrained the swelling and disruption of starch granules during heating.

2.10. Wide angle X-ray scattering

Starch is semicrystalline in nature. X-ray diffractometer (XRD) is the equipment used for determining the crystalline nature of any substance. The crystalline regions in starch are mainly attributed to the branching structures of amylopectin and ordered helical structures of some amylopectin and amylose chains having ordered helical structures.[103] The amorphous fraction is composed predominantly of amylose long chains spread with unordered arrangements.[104] The water molecules trapped in the ordered helical arrangements of the starch chains also play a major role in determining the crystallinity of a particular starch.[105] The ordered nature of the crystallites in polymers like starch is due to the presence of repeating helices. When X-rays strike any such material, the crystallites diffract them while the amorphous regions allow them to freely pass through. The diffracted X-rays are detected by the XRD machine and gives corresponding peaks with variable intensities that are indicative of the presence and ranges of order of the crystalline domains respectively. The diffraction phenomenon is described by the Bragg's law. According to it, if an X-ray of wavelength 'λ' is incident on a plane at angle 'θ' and the distance between two planes of a crystal is 'd' then Bragg's equation says

$$\lambda = 2d \sin\theta \qquad \textbf{Eq. 2.1}$$

When running a test with XRD, the λ value is kept constant and the θ values are changed at a particular rate. From these, the value of d can be calculated. When d is smaller at a particular locus, crystallinity at that particular point is considered to be higher and the machine gives a higher and sharper peak and vice versa. For polymers like starch, a strong and sharp peak designates higher coiling of the chains at the particular locus and vice versa. The crystallinity of starch is hence determined by dividing the total area under the peaks by the total area under the XRD curve.[103]

% crystallinity = (Total area under the peaks / Total area under the curve) x 100 **Eq. 2.2**

Depending upon the X-Ray Difraction (XRD) pattern, starch has been primarily classified into A, B and C type.[106] The A-type starch is predominantly found in cereal grains and gives characteristic diffraction peaks at 2θ positions near 15.1, 17.1, 18.0 and 22.8 while B-type is predominant in roots and tuber crops showing peaks near 15.4, 17.1, 22.2 and 24.0. A-type starch has a closely packed arrangement of double helices with 4-8 water molecules entrapped per turn, B-type starch helices entrap 36 water molecules per turn. Because of the more packed structure, A-type starch is considered to be more stable than B-type.[107] Another polymorphic pattern known as the C-type is exhibited by starches derived from legumes and yam. The C-type XRD pattern gives peak characteristic which is a mixture of A and B-types. Hydrothermal treatment also forms another polymorphic form called V-type with XRD pattern showing a major peak at 2θ = 20.[108,109] This is due to the formation of amylose-lipid complexes in the hydrothermally treated starch. The crystallinity of rice flour is attributed to the semicrystalline starch component. Native rice starch exhibits A-type XRD pattern with characteristic peaks.[110-112] Amylopectin has been considered as the predominant crystalline component in starch granules, with the short-branched chains forming local crystalline structures.[113] Iturriaga et al (2004) studied XRD patterns of seven Argentine rice flours.[114] All the varieties exhibited A-type spectra, however with different peak intensities. The crystallinity of waxy genotypes was found to be higher (48%) than that non-waxy ones (37% to 40%). However, no significant differences in crystallinity were found among the non-waxy varieties with different amylose:amylopectin ratios. Similar results were also found by Ong and Blanshard (1995) while working on different non-waxy rice varieties.[68] The authors proposed that retrograded starch exhibits a mixed A+V type XRD pattern and not a B-type pattern. Tester et al (2000) reported that amylose may contribute to the crystallinity in high-amylose starches.[115] Singh et al (2007) attributed the differences in starch crystallinity to differences in proportions of amylose, short side-chain and long side-chain amylopectin.[116]

However, the native A-type crystalline structure of rice starch is often lost on parboiling.[108] This is explained by the fact that as the gelatinization process involves uptake of water with decoiling of helices and the retrogradation involves release of the water molecules with recoiling, the water transport system into and out of the system are

never strictly reversible. Water molecules associated with the starch polymer system plays the major role in its crystallinity and hence formation of complete or partial B-type polymorph has been reported from XRD studies by various authors.[108,117] The hydrothermally treated rice starch often exhibits developed moisture absorption properties than raw rice.[118] The native relative crystallinity is also not obtained due to insufficient formation of the crystallites during retrogradation. Mahanta et al (1989) development of V-type polymorph in parboiled rice, characteristic of formation of amylose-lipid complexes.[108] The lipid bodies, that are found in the outer bran layers get ruptured and with the recoiling of amylose long chains, form amylose-lipid complexes, a newer important crystallite in parboiled rice.[117] Breaking down of the glycosidic linkages due to thermal processing also results in dextrinization and formation of newer and simpler fractions resulting in changed status of starch in the kernel system.[82] Work of Hibi et al (1990) on cooked rice retrogradation revealed that these amylose-lipid complexes are metastable and may shift from V-type to more stable B-type during the course of retrogradation.[119] Manful et al (2008) reported gradual loss of starch crystallinity in parboiled rice with severity of soaking temperature and steaming time.[120] The most severely parboiled sample (soaking at 90°C and steaming for 12 min), showed no discernable change toward the V-pattern. Repeated cycles of pressure parboiling were found to increase the amount of retrograded amylopectin.[78] This was evidenced by progressive increase in the intensity of the peaks responsible for B-type XRD pattern. The samples hence showed a mixture of B and V-type starch crystallinity. Witek et al (2010) reported a mixture of A, B and V-type polymorph in heat moisture treated IR64 rice.[23] In parboiled rice starch, temperature gradient developed during different stages of the steaming and drying steps may be responsible for moisture transfer and hence be considered as a function of the pattern of crystallinity developed. Mohoric et al (2009) processed rice with different techniques with and without subsequent puffing.[121] While puffed rice made from raw milled rice showed mainly A-type crystalline starch, the non-puffed pressure parboiled rice samples clearly showed the presence of B-type polymorph. Polished raw rice cooked under atmospheric pressure gave still higher proportion of B-type starch. Formation of V-type starch was observed in all the samples to varied extents. Resistant starch isolated from autoclaved rice *in vitro* was found to contain B and V-type polymorphs with much lower intensity of XRD peaks than native rice starch. Such differences in polymorphic type in hydrothermally processed rice products have also been

reported.[122] Lamberts et al (2009) discovered the presence of amylose crystallites by hydrolysing the acid labile amorphous portions of parboiled rice starch. The amylose crystallites reportedly exhibited B-type diffraction pattern.[117]

2.11. Thermal profile analysis

Differential Scanning Calorimeter (DSC) is a key tool for measuring changes in heat flow into and out of a system with continuously changing temperature through heat input. It quantifies the heat flows associated with endothermic or exothermic transitions in materials as a function of time and temperature and thereby provides information about physical and chemical changes during these processes. The sample is taken in an aluminium pan and heated in an atmosphere controlled under a specific gas to increase the temperature at a constant rate with another pan which is empty. The empty pan is called the reference pan. At a particular temperature, a reaction or phase transition in the sample may occur with altered heat flow shown as positive or negative peaks by the software associated with the DSC system. An endothermic transition leads to positive heat flow into the sample and an exothermic heat flow results in negative heat flow out of the sample system. The area under the peaks generated gives the difference in heat flow between the sample and reference pan. Thermal properties of different starches have been extensively studied using DSC.[123-125] When an aqueous suspension of starch granules is heated sufficiently, the granules undergo an order-disorder endothermic transition known as gelatinization. Gelatinized starch is in a rubbery amorphous liquid form. Further cooling of gelatinized starch leads to retrogradation which is regaining of partial crystallinity by the polymer. It often leads to transition of the crystalline form from A to B and vice versa, resulting in shifting of the endothermic peak for crystallite melting.[126] The amylose-lipid crystallite complexes melt at temperatures near 100°C giving an additional endothermic peak in the DSC thermogram.[123,127]

Differential Scanning Calorimetry is often used along with XRD as an extremely valuable tool for qualitative and quantitative estimation of crystalline starch polymorphs. It primarily details the changes occurring during the molecular disassembling of starch when heated in excess of water. Mahanta et al (1989) reported that raw rice flour and starch gives a large endothermic peak for starch gelatinization and a small peak for amylose-lipid complex melting.[108] The gelatinization endotherm gradually decreased and eventually disappeared with increased severity of parboiling. Amylose-lipid

endotherm was visible in all parboiled samples. Parboiled rice starch was hence reported to be largely amorphous with very minor crystallinity. The authors however could not ascribe the endothermic pattern of parboiled rice to a definite polymorphic form of starch. Marshall et al (1993) reported similar findings with conventionally parboiled rice samples.[128] The authors reported much lower degree of gelatinization in parboiled rice. Microwave treatment, however failed to produce any significant parboiling effect in the two rice varieties. Shi and Seib (1992) reported that the major endothermic peak in gelatinized starch shifted towards lower temperature which as per the authors was due to melting of retrograded amylopectin formed during cooling of the starch gel.[129] Retrogradation results in reordering of the amylopectin branches but in less ordered manner, which explains the lower temperature of melting and lower melting enthalpy than gelatinization of the native starch.[130] The trend in lowering of gelatinization enthalpy may however be questioned from the findings of Manful et al (2008) who observed certain discrepancies in the results.[120] This created need for further insight into the phenomenon. Islam et al (2002) observed shift of the peak for melting of residual ungelatinized starch in parboiled rice to higher temperature.[121] The lower melting temperature fraction of starch was supposed to be gelatinized during the steaming stage resulting in the shift in gelatinization temperature in DSC. The peak temperature of gelatinization was hence considered as an indicator of the extent of parboiling. This shift in peak position of partially gelatinized starch in rice parboiling has been explained by Miah et al (2002) who stated that the amylose molecules which diffuse during the gelatinization reorients during retrogradation and surround the intact amylopectin.[132] On reheating, the retrograded amylose structures inhibit subsequent swelling of the starch material and hence take a higher temperature for gelatinization. Basically, two phase transitions were observed by DSC during starch gelatinization. They are the glass transition (Tg) of the amorphous regions and the melting transition of the crystalline regions.[133] Ojeda et al (2000) assumed that gelatinization initially affects the amorphous regions of starch.[134] Crystalline regions get gelatinized during the final phase involving further hydration and swelling of the molten crystallites accompanied by dissolution of the granules. In certain cases, this may however be also attributed to annealing effect as a result of soaking.[135,136] Waxy rices were found to swell more but solubilize less than non-waxy varieties at 96°C.[137] Perdon et al (2000) demonstrated that Tg increased as water content decreased from 27 to 3% (w/w).[138] Tg of native starch was significantly

higher than that of gelatinized starch in a low moisture content range (8–18%) which increased further with decreasing moisture content.[139] Gelatinisation onset (To), peak (Tp) and conclusion (Tc) temperatures are generally recorded from the DSC curve and gelatinization enthalpy (ΔH) calculated from the area under the endothermic peak. Vandeputte et al (2003) divided starch from different rice varieties into waxy (Tp = 65.2–65.8 8oC), normal low Tp starches (62.8–67.0 8oC), intermediate Tp (71.7–73.5 8oC) and high Tp (76.7–78.5 8oC) rice starches.[140] Lipids play a critical role in the thermal phase transition of starch as seen by a reduction in Tg after defatting of starch (Singh et al., 2000).[141] Amylose-lipid complexes may be indigenously present or may be formed during parboiling of rice.[84,85] Eliasson (1994) reported that different polymorphic forms of amylose-lipid complex exists. The author in this study also obtained indirect evidence on existence of amylopectin-lipid complex as presence of lipid decreased gelatinization enthalpy and also reduced retrogradation.[142] Iturriaga et al (2004) observed formation of these compounds in waxy rice samples despite of very low amylose contents.[114] They suggested that this complex could be originated in the longest amylopectin branches and extra granular complexing lipids. Existence of the amylopectin-lipid complex was also reported by Ong and Blanshard (1995) and further possibilities may be drawn from work of Tian et al (2010) who developed a newer amylose-beta cyclodextrin-lipid complex by extraneous addition of beta cyclodextrin into a cooked starch-water system.[90,143] The complex was found to retard retrogradation. This may be considered important for parboiled rice as severe temperature treatment may breakdown starch into simpler fractions which may further result in such phenomenon.[53,145] Karkalas et al. (1995) studied the thermal properties of potato amylose inclusion complexes with fatty acids. While type I amylose lipid amorphous complexes are formed at temperatures below 60°C and dissociate in the range of 96–104°C, type II crystalline polymorphs are formed at above 90°C and dissociate between 114 and 121°C.[145] Synthesis of these two types of complexes following exothermic transitions during cooling of starch gel in a DSC machine was revealed by using native rice starch-water system.[146] Derycke et al (2005) reported type II amylose-lipid complex melting endotherm in parboiled samples of two rice varieties.[84] Parboiling severity was found to increase the melting enthalpy in both the varieties. Lamberts et al (2009) observed the occurrence of amylose crystallites in parboiled rice which reportedly had a melting point of 135°C.[117]

More sophisticated techniques for probing the molecular structure of the starch polymer are now available. Chemical, enzymatic and NMR techniques describe the branching pattern and branch length profile.[147-149] Coupling these with prior chromatographic fractionation of starch gives better information.[150,151] The use of gel permeation chromatography (GPC) and its modernized form, high performance size exclusion chromatography (HPSEC) however remains to be the most trusted and accepted technique for determining molecular weight distribution of different starch fractions.[152-154] The technique is based on the principle that when a solution containing solutes with different molecular weights resulting in variable hydrodynamic volume is passed through a column packed with porous, microparticulate material, the larger molecules are excluded from some of the pores in the packing material and therefore elute faster through the column than the smaller molecules. In effect, the molecules are sorted by size, with the largest eluting first and the smallest last. For starch, amylopectin being the larger molecule elutes faster than the amylose fraction.[8,155]

2.12. Enzymatic hydrolysis and resistant starch

A great part of the modern research in food science involves works on digestibility. While the *in vivo* techniques involve use of the gastrointestinal system of live animals, *in vitro* techniques with higher popularity involve use of artificial conditions of pH, temperature and time created as per the human digestive system to assess the digestibility of a particular food product. It has been observed that, the rate of digestibility of all fractions of starch from a common source is uneven. While certain fractions get readily digested, certain fractions are slowly digested. Another fraction called resistant starch does not get digested and pass through the human alimentary canal unhydrolysed. Being indigestible, it plays an important role in glycemic control in humans and also exerts other positive health effects.[156] Evaluation of starch digestibility is very important as it may also thereby decide the targeted consumer group for a particular starchy food product. The formation or loss of resistant starch on parboiling has been a topic of controversy .[157,158] Being an important staple food of the world, study on glycaemic status of rice and rice products is important. Perera et al (2010) reviewed different protocols for measuring resistant starch and factors affecting it.[159] They proposed that factors like genetic differences in plants, processing material (meal versus

starch) and conditions of processing (partial versus complete gelatinization), modification and storage conditions significantly influence RS values. Amylose content has also been reported to significantly affect the digestibility of starch.[160,161] Differences in digestibility of rice flour with different amylose contents were studied by Zhu et al (2011).[162] Slowly digestible starch (SDS) content decreased and RS increased with the increase in amylose content. Similar findings were also reported by other authors.[92,163-168] Rapidly digestible starch (RDS) was found to be highest in varieties with higher amylose content than low amylose and waxy varieties, while SDS and RS gave opposite trends. Digestibility was found to be also significantly correlated with proportions of long and medium chain amylopectin, relative crystallinity as determined by FTIR spectroscopy, swelling factor, amylose leaching, onset temperature of gelatinization and gelatinization range, enthalpy, pasting temperature and viscosity parameters.[166] The proportion of RS varies with plant source, starch type and processing conditions.[169] Shi and Gao (2011) developed RS from waxy rice starch using autoclaving and pullulanase treatment.[158] The RS products were found to have higher apparent amylose content, B and V-type XRD patterns and of higher crystallinity than native starch. Zhou (2014) recently reported similar findings with indica varieties of rice.[126] A newly developed high-amylose variety (amylose = 55.4%) exhibiting B-type starch crystallinity was found to be most resistant to enzymatic digestion. This was attributed to great proportion of long chains in amylopectin, high gelatinization temperature, and semi-compound starch granules. However, flour of low-amylose rice (amylose = 16.1%) was found to have lower RS than waxy rice which was attributed to weaker crystalline structure in its starch granules as revealed by XRD and DSC studies. Pathiraje et al (2010) also reported GI values not in correlation with amylose contents.[170] Amylopectin chain length distribution and recrystallinity due to retrogradation induced by storing at 5°C contributed to the variation in the digestibility of starch extracted from three waxy rice varieties.[171] The authors claimed that the proportion of longer chains of amylopectin with DP = 17-29 had positive effect on resistance to enzymatic hydrolysis. Parboiling and hydrothermal modification of starch involving similar phenomenal changes have been reported to decrease digestibility by many authors. Larsen et al (2000) in their *in vivo* study found lower glycemic response in nine type2 diabetes patients fed with cooked pressure parboiled rice.[172] Amylose-lipid complex was considered responsible for the lowered digestibility rate. Similar reports were obtained from Pathiraje et al (2010).[170] Frei et al

(2003) evaluated the effect of retrogradation on starch digestibility.[171] While cooking resulted in high digestion rate in waxy varieties, retrogradation caused by cooling the cooked rice at 4°C for 24 h resulted in markedly lowered glycaemic response. This difference was reportedly highest for the waxy cultivars, which was also reported in the work of Hu et al (2004).[163] Temperature cycled retrogradation caused development of higher amount of SDS in waxy rice starch than isothermic storage. Temperature-cycling hence may be applicable for preparing slowly digestible starch from waxy starch.[174,175] Aromatic jasmine Paddy rewetted to 28-33% followed by drying at 135-150°C and room temperature with an intermediate tempering step was found to show lower glycaemic index than raw rice.[176] This was attributed to formation of amylose-lipid complexes which was a function of drying temperature. Rattanamechaiskul (2014) recently proposed that use of superheated steam to dry rice with high gelatinization temperature and hot or humidified hot air to dry rice with low gelatinization temperature may yield lowest GI rice.[157] High pressure parboiling was found to significantly increase the SDS content in both waxy and non-waxy rice.[177] This increase was more than that obtained in heat-gelatinized starch. The authors proposed that the amount of SDS formed does not correlate with the degree of retrogradation but may be attributed to imperfect crystallites formed because of it. Han and Lim (2009) reported that the temperature of water used for soaking japonica rice prior to cooking and the time of soaking results in differences in water uptake rate, which further creates differences in digestive properties.[179] Soaking in water at 50°C was found to give more readily digestible cooked rice than soaking at 25°C. Leached amylose during soaking was proposed to have re-interacted with gelatinized starch formed during cooking and retard digestibility. In another work involving parboiling with two-stage drying at 100°C and 60°C showed that parboiling process reduced *in vitro* starch digestibility from 62.31-78.63% to 35.52-49.74%. Parboiling process also reduced the GI of rice from 54.43-97.29 to 44.22-76.32.[49] Contradictory findings have also been reported in abundance. Zavareze et al (2010) and Gunaratne et al (2013) reported that rice flour become more susceptible to enzymatic hydrolysis after parboiling.[164,181] Zavareze et al (2010) reported increased susceptibility of heat moisture treated starch to hydrolysis by amylase which positively correlated with the moisture content.[164] Rewthong et al (2011) reported increased GI caused by retrogradation of cooked instant rice that was subjected to precooling at 4°C for 24 h prior to drying. Moistened waxy rice was dried by fluidized bed technique at temperatures ranging from

90-150°C followed by tempering and further drying with ambient air.[179] This led to damage of the amylopectin structures thereby increasing the digestibility of the rice to a marked level.[180] In a recent study, Gunaratne et al (2013) reported upto 50% reduction of RS in one rice variety after parboiling.[181] The authors suggested that with increase in swelling and rupture, starch granules become more susceptible to amylolysis and hence may be related to the viscosity parameters. Severity of dry heat parboiling markedly reduced the RS content.[182] Mujoo and Ali (1998) suggested that rice roasting resulting in gelatinization, causes exposure of starch component to enzymatic digestion.[183] However, the additional step of roller flaking for rice flake preparation causes formation of certain starch-protein complexes with molecular weights greater than 4 x 107 kDa. These complexes decrease the susceptibility of the product to enzymatic hydrolysis. Chitra et al (2010) worked on in vitro starch digestibility of popped rice, expanded rice and flaked rice prepared by sand roasting.[65] Lower starch content in the products than the raw rice was attributed to the adhering bran layers and formation of resistant starch in those. The products were hence suggested to for use in preparation of diabetic foods. Pre-roasting prior to boiling a mutant rice variety also resulted in marked increase in resistant starch content.[184]

2.13. Phytochemicals in rice

The phytochemical compounds in rice bran have purported health benefits as well as antioxidant characteristics for improving the storage stability of foods. Rice bran is also viewed as a potential source of these high-value antioxidants for use as additives in foods, pharmaceuticals, and cosmetics.[185] Several studies have reported the effects of rice bran oil on reduced plasma cholesterol in laboratory animals and humans.[186,187] Oryzanol reduces cholesterol absorption.[188] Komiyama et al (1992) and Nesaretnam et al (1998) reported anticancer activity associated with tocotrienols which constitutes approximately 1.7% (v/v) of the unsaponifiable fraction of the oil. (189-191) Approximately 1% is constituted by Vitamin E. Heat processing of rice bran to stabilize it against oxidation reduces the concentrations of many of these valuable compounds. Nicolosi et al (1994) found that 90% of the oryzanol and tocotrienols were lost during oil refining.[192] Varietal difference in rice bran is a key factor for this loss.[193] Lloyd et al (2000) collected rice bran from various milling breaks of a commercial system and found varying antioxidant levels. While oryzanol concentration was significantly higher in outer

bran layers, the fractions collected after milling break 2 had the highest levels of tocopherol and tocotrienol.[185] Defatted rice bran was analysed as a source of bioactive phytochemicals.[194] Various solvent extracts showed the presence of oryzanols, tocopherols, and ferulic acid. Methanol was found as the most effective extractant under the optimized conditions of a material–solvent ratio of 1:15 (w/v) and a time of extraction of 10 h. The yields of total phenols, oryzanols and ferulic acid from the defatted bran with methanol were 2204, 316, and 233 ppm, respectively. These compounds were further positively evaluated for antiradical efficacy by the same authors in a different study.[195] Methanol was also found as a suitable extractant for japonica rice bran phytochemicals by Lai et al (2009).[196] The colour of the rice pericarp positively correlated with TPC.[197-199] Among four types of rice ranked by color, black rice varieties emerged as those exhibiting the highest antioxidant activities, followed by purple, red, and brown rice varieties.[200] de Mira et al. (2009) found the TPC values were almost four times higher in pigmented than in non-pigmented rice genotypes (4246 and 1073 mg ferulic acid equiv. kg^{-1}, respectively).[197] Massaretto et al (2011) obtained similar differences and proposed that TPC in rice is composed largely of soluble phenolic compounds, represented by proanthocyanidins and anthocyanins. Soluble phenolics were considered to be predominantly responsible for inhibiting angiotensin I-converting enzyme thereby considered important for controlling high blood pressure in humans. Cooking reduced total phenolic content and changed the soluble : insoluble phenolics ratio.[201] The outer layers of non-parboiled brown rice contain beta-carotene, lutein, and/or lycopene.[33,39] which were partially attributed to colour development in parboiled rice by means of intra-kernel migration. Lamberts and Delcour (2008) however found that the carotenoids got reduced to trace levels after parboiling and hence do not contribute to the final colour of parboiled rice.[34] The rice germ, which is often found mixed in commercial rice bran was found to have superior antioxidant properties due to abundance of α-tocopherol and γ-tocopherol than the actual bran.[202] Despite of enormous research on phytochemicals of rice germ and bran layers, very few works have till been done on parboiled rice. From *in vivo* experiments on rats, Finamor et al (2012) reported much higher concentration of TPC in parboiled rice than white milled rice.[203] They thereby confered greater protection of parboiled rice against oxidative stress in the renal tissue of diabetic animals. This however is questionable as other works involving thermal processing produced contradictory results. Work of Lloyd et al (2000) involving steam expansion of rice bran

for separation resulted in 26% decrease in oryzanol content of rice bran.[185] However, no pronounced effect was seen on tocopherol or tocotrienol contents. Pascual et al (2013) performed a combined process of parboiling, storage and cooking that caused approximate 90% reduction in tocols.[204] Parboiling followed by storage resulted in an approximate 40% loss of γ-oryzanol. Cooking had almost no further effect over γ-oryzanol levels in parboiled rice previously stored for 6 months. Parboiling and cooking reduced the soluble portions of TPC in rice due to the loss of part of them in the processing water, thermal decomposition and, possibly, interaction with other components. This reduction is related to the lower antioxidant activity. [205]

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Chapter 3

EFFECT OF STEAM PARBOILING TREATMENT VARYING IN TIME AND PRESSURE ON THE PROPERTIES OF RICE VARIETIES WITH DIFFERENT AMYLOSE CONTENT

3.1. Introduction

Starch is a biopolymer of D-glucose units comprising of amylose and amylopectin. The ratio of the two fractions greatly influences the starch properties. On the basis of the amylose content in starch, rice can be classified into high amylose (>25 %), intermediate amylose (20-25 %), low amylose (7-20%) and waxy or glutinous (1-2 %) types.[1]

The physicochemical and functional properties attributed to the peculiar starch properties differ with variety and processing methods and thereby decide the applications of pregelatinized rice flours.[2] Rice parboiling is a unique hydrothermal processing technique and variations in parboiling steps and conditions also result in varied end product properties because of microstructural and molecular alterations in the starch granules.[3] Parboiled rice starch undergoes the phenomena of starch gelatinization and retrogradation.[4] The hygroscopic behaviour of the whole rice as well as flour is altered with hydrothermal treatment conditions and variety.[5] Viscosity profile obtained from the Rapid Visco Analyzer (RVA) is a key tool for determining the quality of raw and processed rice which is mainly dependent on the amylose content and micromolecular structure of the rice. On parboiling, appreciable changes occur in the pasting parameters due to the order-disorder transitions taking place at the molecular level. IR spectroscopy of gelatinized and retrograded starch indicated that the bands at 1047 cm^{-1} and 1022 cm^{-1} are characteristic of crystalline and amorphous zones of starch, respectively and their absorption ratio indicates the crystallinity of starch.[6] Wide-angle X-ray scattering

(WAXS) of raw rice starch and flour gives a typical A-type crystalline pattern which is reduced or destroyed during parboiling.[7-9] Formation of mixed A and B-type crystalline pattern due to retrogradation and formation of V-type pattern due to amylose-lipid complexes formed by 'in situ' crystallisation of amylose have been reported.[8,10]

Englyst et al (1992) classified the digestible starch fractions into two basic types on the basis of an *in vitro* technique developed to estimate the same.[11] While rapidly digestible starch (RDS) is the fraction that is hydrolyzed to glucose within 20 min, slowly digestible starch (SDS) gets converted in the next 100 min. SDS goes through a slow but complete hydrolysis in the small intestine and its potential health benefits are linked to a stable glucose metabolism, diabetes management, mental performance, and satiety.[12] The fractions remaining after that is considered as resistant starch (RS). It passes down the small intestine and gets fermented by the microflora of the large intestine to produce anti-carcinogenic compounds. The proportion of RS in starchy foods is hence clinically very important.[13] Parboiling has been reported to create alteration in the SDS and RS contents of rice. Although it has been employed for increased production of RS, contradictory results have also been reported.[14,15]

Due to the special agro-climatic conditions, the North-Eastern region of India including the state of Assam is endowed with large varieties of rice germplasm. This region possesses varieties with extreme physicochemical properties which could be categorized into eight rice types.[16] The low amylose and waxy rice varieties are generally consumed after special parboiling processes. Such hydrothermal processing makes the rice suitable for consumption by simple soaking in water without involving any heat treatment which has been discussed in chapter 5. The present study involved parboiling of four traditionally grown rice varieties of Assam with and without application of pressure and examining the changes in the physicochemical properties of the raw and processed rice samples.

3.2. Material and Methods

Pure line paddy samples of *Ranjit* (HR), *Aghoni bora* (WA) and *Bhogali bora* (WB) varieties from the recent harvest of 2009 were purchased from the Regional Agricultural Research Station, Assam Agricultural University, Titabor, Assam. *Kola chokua* (LK) variety paddy was purchased from local farmers of the region. The raw

paddy samples were cooled at room temperature for 24 h and stored at 4°C until processing. Enzymes, D-glucose and potato amylose standards were procured from Sigma Aldrich (St. Louis, Mo.,U.S.A.). Chemicals were procured from MERCK (India) and Sigma (US).

3.2.1. Processing and coding of samples

For parboiling, 400 g paddy of each sample was added to water raised to 70°C and kept for 18 h for hydration. The container was covered with a thick gunny bag to prevent rapid cooling of the water. The water was then decanted and the samples were immediately steamed in an autoclave (Equitron 7407ST, India) fitted with a pressure gauge for 10 min (mild), 15 min (moderate) and 20 min (severe treatment) at conditions of 0 psig (100°C/ open steaming) and 15 psig (121°C/ pressure steaming), respectively. The steamed paddy samples were then layered on a plain surface and air-dried at room temperature for 2-3 days to moisture levels between 11 and 13 % (wb). This was followed by milling (8 %, weight basis) in a dehusker and a polisher (Satake, Japan). A portion of each sample was ground into flour in a laboratory grain mill (Pulverisette 14, Fritsch, Germany) at 6000 rpm to pass through 100 μm sieve. Whole kernels and flour samples were stored in polypropylene pouches at 4°C for further analysis. The samples were coded as per the steaming conditions applied (Table 3.1).

Further in this chapter, open steaming and pressure steaming have been mentioned as the two parboiling conditions and time of steaming as the severity of parboiling.

3.2.2. Estimation of total starch, amylose, moisture, fat and protein in raw rice

Raw rice flour samples were analyzed for total starch content and apparent amylose content (%, db) by the methods described by Sadasivam and Manickam (2008) and Sowbhagya and Bhattacharya (1979) respectively.[17,18]

For estimation of total starch, 0.5 g of sample was repeatedly washed with hot 80% ethanol to remove sugars. Washing was repeated till the washing did not give colour with anthrone reagent. The residue was then dried over a water bath. Distilled water (5

mL) and 6.5 mL of 52% perchloric acid were then added to it before storing at 4°C for 30 min allowing starch extraction. Supernatant was collected after centrifugation (3000 rpm).

Table 3.1. Sample codes based on rice type, name, steaming pressure and temperature.

Variety	Variety codes	Steaming pressure (psig)	Steamingtime (min)	Sample codes
Ranjit	HR	-	-	HR(N)*
		0	10	HR-0-10
		0	15	HR-0-15
		0	20	HR-0-20
		15	10	HR-15-10
		15	15	HR-15-15
		15	20	HR-15-20
Kola chokua	LK	-	-	LK(N)
		0	10	LK-0-10
		0	15	LK-0-15
		0	20	LK-0-20
		15	10	LK-15-10
		15	15	LK-15-15
		15	20	LK-15-20
Aghoni bora	WA	-	-	WA(N)
		0	10	WA-0-10
		0	15	WA-0-15
		0	20	WA-0-20
		15	10	WA-15-10
		15	15	WA-15-15
		15	20	WA-15-20
Bhogali bora	WB	-	-	WB(N)
		0	10	WB-0-10
		0	15	WB-0-15
		0	20	WB-0-20
		15	10	WB-15-10
		15	15	WB-15-15
		15	20	WB-15-20

*Sample code followed by (N) represents raw samples

This step was repeated with the residue several times using fresh perchloric acid for maximum extraction. The volume of supernatant was made up to 100 mL. An aliquot of 0.2 mL was pipetted out and volume was made up to 1 mL. A standard curve was prepared using glucose (Sigma) at different concentrations and making up the volumes to 1 mL with distilled water. 4 mL anthrone reagent was added to each, heated for 8 min and intensity of colour was measured at 630 nm in a spectrophotometer (Cecil Aquarius 7400, England). The amount of glucose was calculated from the standard curve and converted to starch by multiplying by a factor of 0.9.

$$\text{Total starch (\%, db)} = \frac{(\text{Amount of glucose} \times 0.9)}{\text{Dry weigh of sample}} \times 100 \qquad \text{Eq. 3.1}$$

For estimation of apparent amylose content, rice flour samples (<100 μm) and amylose standards were exposed to 50% relative humidity for 24h. Hundred milligrams of the flour was taken in a stoppered conical flask, wetted with 1 mL ethanol and 10 mL of 1N NaOH was gently added. After keeping for 18h, the solution was heated in a boiling water bath (Voltam, India) for 2 min. The volume was made up to 100 mL and 20 mL of the alkaline dispersion was taken in a graduated glass cylinder. Petroleum ether (7 mL) was added to it and manually shaken for 10 min. The ether layer was sucked off with a water suction. This was repeated with 7 mL carbon tetrachloride and allowed to stand for 15 min. Carbon tetrachloride being heavier than water, settled as a layer below it. Five millilitres of the aqueous layer from the top was pipetted out and neutralized with hydrochloric acid. Two millilitres iodine reagent (0.2%) was added and volume made up to 100 mL with distilled water. The process was also carried out using the standard potato amylose. Two millilitres of the iodine solution made up to 100 mL served as blank for reading the colour of the solutions in a spectrophotometer (Cecil Aquarius 7400, England) at 630 nm after 20 min of dark incubation. The apparent amylose content was then estimated.

$$\text{Apparent amylose content (\%, db)} = \frac{R \times a}{A \times r} \times 20 \qquad \text{Eq. 3.2}$$

Where,
R = reading of rice flour dispersion
A = reading of standard amylose solution
a = amount of standard amylose weighed (mg)
r = amount of rice flour weighed

Other analyses viz., moisture, fat and protein contents (all in %, db) were done as per AOAC (2000) standard protocols.[19] Moisture content was determined by the vacuum oven drying method (925.09, AOAC). Briefly, milled rice sample was taken in previously dried and weighed covered dishes. The sample was allowed to dry in a vacuum oven at 100°C and vacuum pressure equivalent to 3 kPa till constant weight was attained. Weight of the dish containing sample was measured both before and after drying and moisture content was calculated.

$$\text{Moisture content (\%, db)} = \frac{\text{Initial weight - Final weight}}{\text{Final weight} - \text{Weight of emty dish}} \times 100 \qquad \textbf{Eq. 3.3}$$

For estimating crude fat in the rice flour samples, a soxhlet method (2003.05, AOAC) was used. Briefly, 5 g flour sample was taken in a cellulose thimble, dried to constant weight at 102°C and extracted with petroleum ether (boiling point = 60°-80°C) at 100°C for 2 h (Socs Plus, Pelican Equipment, India). After the extraction, solvent was allowed to evaporate at 200°C and was collected by distillation. The fat that collected in the extraction cup was then dried at 70°C to remove any trace of moisture, cooled in desiccator and weighed. Crude fat was quantified using the following formula.

$$\text{Crude fat (\%, db)} = \frac{\text{Weight of cup containing fat} - \text{Weight of empty cup}}{\text{Dry weight of sample}} \times 100 \qquad \textbf{Eq. 3.4}$$

Protein content was measured by the standard AOAC method (920.87) using a Micro-Kjeldahl apparatus ((KelPlus, Pelican Equipment, Chennai, India). Two grams flour sample was digested in a digestion flask by adding 0.7 g mercury (II) oxide, 15 g potassium sulfate and 25 mL of concentrated sulphuric acid followed by heating at 80°C for 2 h. The solution was then added with 1 M sodium hydroxide solution and the ammonia gas liberated was collected in a boric acid solution. The nitrogen content (N, %) was estimated by titrating the solution with 0.1 N hydrochloric acid using methyl red (1%, w/v) as indicator.

$$\text{N (\%, db)} = \frac{[0.1 \times (\text{Titrated volume of acid}) \times 0.014]}{\text{Dry weight of sample}} \times 100 \qquad \textbf{Eq. 3.5}$$

Amount of protein was calculated by multiplying it by a factor of 6.25.

$$\text{Protein (\%, db)} = \text{N} \times 6.25 \qquad \textbf{Eq. 3.6}$$

3.2.3. Degree of gelatinization (DG)

DG (%) was calculated by a method of Wootton et al (1971).[20] For this, 0.2g sample was dispersed in 100 mL distilled water with stirring for 5 min and centrifuged at 1500 rpm for 25 min. One milliliter supernatant was then diluted to 10 mL with distilled water and 0.1mL iodine solution was added. The method was repeated using 100 mL of 10 M potassium hydroxide instead of water and absorbance of both solutions were read at 600 nm in a Spectrophotometer (Cecil Aquarius 7400, England).

DG (%) = (Absorbance of fresh solution/ Absorbance of alkali solubilized solution) x 100

Eq. 3.7

3.2.4. Colour measurement

The colour of all samples was determined in a Colour Measurement Spectrophotometer (Ultrascan Vis, Hunter Color-Lab, Virginia). The result was expressed as L, a, b using corresponding native rice samples as reference. The chroma value (C) of parboiled rice was calculated.[21]

$C = (a^2+b^2)^{1/2}$ **Eq. 3.8**

3.2.5. Equilibrium moisture content on soaking at room temperature (EMC-S)

EMC-S (%, db) of polished whole rice kernels soaked at room temperature was determined by the method of Indudhara Swamy et al(1971).[22] Whole-grain milled rice (about 3-5 g) with 11 to 13% moisture content (db) was put in 50 mL water in a covered 100 mL beaker and left aside. The rice was strained through a wire strainer after 20-24 h and dried between Whatman No.1 filter paper sheets. The moisture content of the rice was determined by a drying method (AOAC, 2000) and EMC-S was calculated.[19]

EMC (%, db) = [Moisture evaporated / Dried weight of kernels (g)] × 100 Eq.3.9

3.2.6. Sediment volume (SV)

The method of Bhattacharya and Ali (1976) was used to determine the SV of the raw and processed rice flour samples at ambient temperature.[23] Briefly, 1 g each of desiccated flour samples was taken in a measuring cylinder and 15 mL of 0.05 N hydrochloric acid added to it with agitation after each 5 min for 1 h. The level of the flour sediment was observed after 4 h and was reported as the SV of the sample.

3.2.7. Pasting properties

The pasting profiles of flour suspensions (10 % w/w; 28 g total weight) were recorded using a Rapid Visco Analyser (RVA Starchmaster2, Newport Scientific Instruments, Australia). The Rice1 profile of Newport Scientific was used, where the samples were held at 50°C for 1 min, heated from 50C to 95°C, held at 95°C for 2.40 min followed by cooling to 50°C at and finally holding at 50°C for 1 min. The pasting temperature (PT), peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown (BD) and setback (SB) were recorded. HPV is the minimum viscosity at 95°C, CPV is the final viscosity at 50°C, BD is obtained after subtracting HPV from PV. SBt is obtained after subtracting PV from CPV.[24]

3.2.8. FTIR spectroscopy

Two milligrams of properly vacuum dried rice flour samples and 50 mg dessicated potassium bromide powder were thoroughly mixed in a mortar and pestle before pressing into a thin pellet. The infra-red absorption spectra of the sample pellets were obtained using a FTIR spectrometer (Nicolet Impact 410, Thermoscientific, United Kingdom) equipped with KBr optics and a DTGS detector. The equipment was operated with a resolution of 2.0 cm^{-1} and scanning range of 4000–450 cm^{-1}.

3.2.9. Wide angle X-ray scattering (WAXS)

The rice flour samples were conditioned at 50% relative humidity for 5 days prior to this experiment in order to attain uniform moisture content in the samples. WAXS diffractographs were obtained with an X-ray diffractometer (Rigaku Miniflex, Japan) with a K value of 1.54040 operating at 30 kV acceleration potential and 15 mA current with a copper target. The scanning range was 10–40° of 2θ values with a scan speed of 5°

2θ /min. The total area under the curve and the area under each prominent peak was determined using OriginPro 8.0 software (OriginLab Corp., UK) and the percentage crystallinity was determined.

% Crystallinity = (Area under peaks/ Total area under the XRD curve) x100 **Eq. 3.10**

3.2.10. Starch digestibility

Resistant Starch (RS) present in the flour samples were measured by a method slightly modified from Englyst et al (1992).[11] One hundred milligram flour was first incubated with 7 mL acetate buffer (5.2 pH) at 37°C for 20 min in a shaking water bath. The stoppered incubation tubes contained glass balls for proper disruption of the flour particles and guar gum for standardizing the viscosity of the solution. To this, 3 mL of an enzyme mixture comprising of invertase (220 U/mL), pancreatic α-amylase (3000 U/mL) and amyloglucosidase (15 U/mL) was added. After 20 min of incubation, an aliquot was taken out and estimated for rapidly available glucose (G_{20}) using a D-glucose oxidase-peroxidase assay kit (Robonik, India) and a standard curve prepared by similar manner with different concentrations of D-glucose. A second aliquot was similarly estimated for glucose after further 100 min incubation (G_{120}). Both these values were multiplied by a factor of 0.9 to measure the rapidly digestible starch (RDS) and slowly digestible starch (SDS) respectively and expressed as a percentage of dry matter.

$RDS = G_{20} \times 0.9$ **Eq. 3.11**

$SDS = (G_{120} - G_{20}) \times 0.9$ **Eq. 3.12**

RS is considered to be the undigested starch after the 120 min incubation and hence was calculated as the difference between total starch (TS) and the starch digested during the incubation period.[25]

$RS = TS - (RDS + SDS)$ **Eq. 3.13**

3.2.11. Statistical analysis

All the experiments were carried out in triplicates and means are reported. Pearson's correlation and significant differences between means by Duncan's multiple

range test at a significance level of 0.05 was performed using SPSS 11.5 (SPSS Inc., USA).

3.3. Results and Discussion

3.3.1. Estimation of total starch, amylose, moisture, fat and protein in raw rice

Total starch content was almost similar for all the polished rice samples (Table 3.2). Apparent amylose content of each sample clearly differentiated HR as high amylose, LK as low amylose and WA and WB as waxy rice varieties.[1] All the samples had almost similar moisture and protein contents. The fat content, however was markedly higher in the two polished waxy samples which was almost double the content in the LK(N) sample. Such varied contents of fat in different paddy samples have also been reported by other researchers and was also found in the traditional waxy rice varieties of North-East India in our laboratory.[26-28]

Table 3.2. Apparent amylose, moisture and fat contents in raw rice samples (mean± SD).

	HR(N)	LK(N)	WA(N)	WB(N)
Total starch (%,db)	84.3±0.12^a	85.6±0.89^b	85.8±0.41^b	84.2±0.72^a
Apparent amylose (%, db)	27.2±0.12^a	12.6±0.03^b	1.1±0.02^c	1.1±0.08^c
Moisture (%, db)	13.1±0.09^a	12.9± 0.04^b	13.1±0.06^a	13.1±0.04^a
Fat (%, db)	1.2±0.04^c	0.9±0.01^d	1.8±0.05^b	1.9±0.04^a
Protein (%, db)	5.7±0.66^b	5.8±0.52^a	5.4±0.72^c	5.8±0.48^a

a Means with the same superscript in a row do not differ significantly from one another ($P<0.05$)

3.3.2. Degree of Gelatinization

The values of DG (%) are given in Table 3.3. Gelatinized starch content increased with severity of parboiling in both open and pressure steamed samples and was markedly higher in the pressure parboiled samples. The greater extent of gelatinization with process severity may be attributed to higher water absorption during parboiling, as water absorption by rice kernel increases with time and pressure of steaming and to the increased temperature due to increase in pressure.[29]

3.3.3. Colour measurement

Colour change in parboiled rice kernels is an important indication of rice parboiling and is attributed to the migration of husk or bran pigments and non-enzymatic

Table 3.3. Degrees of gelatinization and colour values of raw and processed rice samples.

Samples	DG (%)	Colour values			
		L	a	b	C
HR(N)	-	46.67±1.31[a]	2.22±0.04[a]	10.54±0.10[a]	10.77±0.10[a]
HR-0-10	32.61±1.14[f]	42.44±1.71[b]	1.35±0.05[e]	7.69±0.11[b]	7.80±0.08[b]
HR-0-15	42.67±2.11[e]	41.18±1.32[c]	1.36±0.09[d]	7.64±0.07[c]	7.76±0.13[c]
HR-0-20	55.27±1.49[c]	38.76±1.38[e]	1.38±0.11[c]	7.60±0.08[d]	7.74±0.08[c]
HR-15-10	51.54±2.23[d]	39.78±1.26[d]	1.31±0.04[g]	7.11±0.14[f]	7.23±0.10[e]
HR-15-15	62.56±2.11[b]	37.11±2.12[f]	1.34±0.15[f]	7.13±0.07[e]	7.25±0.13[d]
HR-15-20	69.42±1.15[a]	34.74±2.15[g]	1.39±0.03[b]	7.11±0.13[f]	7.23±0.07[e]
LK(N)	-	57.5±1.38[a]	2.34±0.14[a]	10.29±0.13[a]	10.55±0.14[a]
LK-0-10	34.23±1.74[f]	45.51±2.15[b]	1.46±0.17[e]	7.75±0.05[c]	7.88±0.09[c]
LK-0-15	44.25±2.36[e]	44.42±2.17[c]	1.48±0.13[c]	7.75±0.07[c]	7.89±0.08[b]
LK-0-20	54.68±2.12[c]	43.82±2.13[d]	1.52±0.02[b]	7.75±0.11[c]	7.89±0.09[b]
LK-15-10	50.34±1.92[d]	43.30±1.35[d]	1.42±0.12[g]	7.62±0.08[d]	7.75±0.10[e]
LK-15-15	60.14±1.78[b]	40.14±2.17[e]	1.44±0.101[f]	7.62±0.09[d]	7.75±0.09[e]
LK-15-20	68.88±1.56[a]	37.89±2.11[f]	1.47±0.09[d]	7.64±0.14[b]	7.78±0.07[d]
WA(N)	-	66.71±1.75[a]	2.18±0.08[a]	11.23±0.07[a]	11.43±0.14[a]
WA-0-10	32.17±1.78[f]	47.82±1.37[b]	1.14±0.19[e]	7.34±0.15[b]	7.43±0.09[b]
WA-0-15	42.56±0.83[e]	46.54±1.34[c]	1.17±0.15[c]	7.32±0.14[b]	7.41±0.09[b]
WA-0-20	54.47±1.65[c]	44.14±1.36[d]	1.21±0.07[b]	7.37±0.06[b]	7.46±0.08[b]
WA-15-10	53.23±1.38[d]	44.44±2.17[d]	1.15±0.08[d]	7.31±0.09[b]	7.39±0.07[b]
WA-15-15	62.34±1.82[b]	41.05±2.15[e]	1.12±0.05[f]	7.34±0.07[b]	7.42±0.13[b]
WA-15-20	68.26±1.96[a]	37.78±2.11[f]	1.13±0.07[ef]	7.33±0.15[b]	7.41±0.10[b]
WB(N)	-	64.84±2.12[a]	2.35±0.13[a]	11.98±0.15[a]	12.20±0.14[a]
WB-0-10	34.42±0.57[e]	43.29±2.17[b]	1.32±0.06[e]	8.09±0.17[b]	8.19±0.02[b]
WB-0-15	44.12±1.42[d]	43.12±1.39[b]	1.37±0.16[c]	8.03±0.09[b]	8.14±0.08[b]
WB-0-20	54.39±0.98[c]	42.11±2.1[c]	1.44±0.08[b]	8.10±0.14[b]	8.22±0.14[b]
WB-15-10	53.32±1.89[c]	39.95±1.33[d]	1.29±0.09[f]	7.89±0.07[b]	7.99±0.10[c]
WB-15-15	64.37±1.13[b]	36.29±2.15[c]	1.32±0.11[e]	7.91±0.09[b]	8.01±0.14[ab]
WB-15-20	71.17±0.66[a]	32.28±1.72[e]	1.33±0.07[d]	7.89±0.14[b]	8.00±0.08[ab]

[a] Means with the same superscript in a row do not differ significantly from one another ($P > 0.05$)

browning taking place during processing.[30] All the three colour parameter values of the rice kernels changed appreciably on parboiling (Table 3.3). With processing severity, the 'L' value representing whiteness for all varieties fell gradually as was also reported for paddy soaked at elevated temperatures.[21] This fall was significant for the pressure parboiled rice samples. This may be attributed to the increased migration of husk and bran and severe non-enzymatic browning at the elevated temperature achieved during

steaming under pressure. The degree of redness represented by positive value of 'a' and attributed to the husk and bran pigments initially decreased drastically on mild parboiling at both processing conditions but again increased with further severity of processing indicating higher migration of pigments into the rice endosperm. The positive 'b' value indicating yellowness showed a drop for the mildly processed samples but remained almost unchanged with processing severity. The changes in colour values were more prominent in the high pressure processed samples. The drastic decrease in colour value 'C' was due to similar losses of the b value on processing. The changes in redness and yellowness were not found to be interrelated as indicated by the irregular patterns of changes in the B values of the processed samples. The decrease in L, a, b and C values of parboiled rice samples as compared to the raw could also probably be due to the translucent nature of the rice starch on account of gelatinization.

3.3.4. Equilibrium moisture content on soaking at room temperature

Both raw waxy samples, showed highest EMC-S (%, db) followed by the low amylose and high amylose samples, in that order, indicating a direct negative correlation of EMC-S with amylose content. EMC-S increased with process severity in both open steamed and pressure steamed samples (Fig 1.1a) indicating that hydrothermal processing definitely increased the water uptake capacity of the parboiled rice kernel.[23] High pressure treated samples from each variety showed distinctly higher EMC-S % than the raw and open steamed samples of the same variety. The kernel structures of moderate and severely pressure parboiled waxy samples, although showing a longitudinal split after the soaking period, did not lose kernel integrity. The highest EMC-S value of 256.8 % (db) was exhibited by WA-15-20 followed by WB-15-20 with a value of 248.5 % (db).

3.3.5. Sediment volume

SV showed a similar change in pattern as with EMC-S (%, db) for the open steam processed samples of all the varieties (Fig 1.1b). However, the high pressure processed samples indicated a milder increase which may be due to leaching of smaller starch fractions generated due to thermal degradation of the samples.[31] This was also indicated by development of turbidity in the acidic media used for the test (not shown) which

increased with process severity. This difference between EMC-S and SV also indicated that the kernels from the high pressure treated rice samples behaved quite differently from its flour when in aqueous suspension. Thus, particle size may play an important role in incorporating parboiled rice in other food uses.

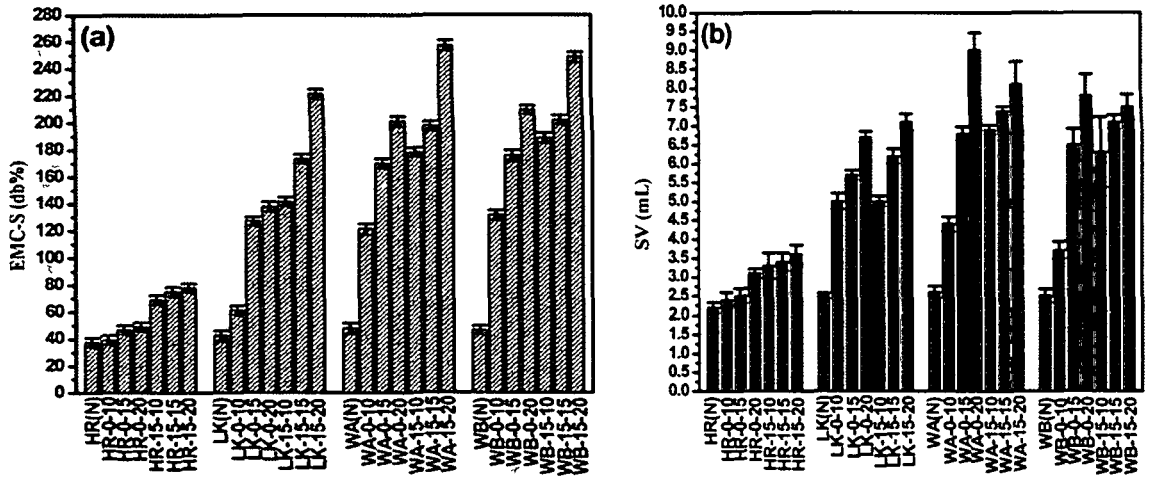

Fig.3.1. (a) EMC-S % (db) of raw and processed rice kernels; (b) SV of raw and processed rice flour.

3.3.6. Pasting properties

The pasting behaviour of amylose rice was different from the low amylose and waxy rices (Table 3.4). Viscosity values of the mildly parboiled rice under both processing conditions were low which increased with processing severity. It is well known that the water absorption ability of parboiled rice is low at temperatures above GT because of the effect of retrogradation. Being high in amylose, the amount of retrograded starch formed with increasing severity of processing is also greater and may have prevented the development of viscosity. However, extensive thermal breakdown of the starch in the pressure parboiled high amylose rice may have caused the very low viscosity values during both the heating and cooling phases. On the other hand, in the low amylose and waxy rices, the viscosity values of the open parboiled rice was higher than the corresponding raw rice due to the high content of amylopectin. The viscosity increased with increasing severity of parboiling. However, the viscosity of pressure parboiled rice was lower than the open parboiled rice. Parboiled rice of the low amylose and waxy rice were more resistant to shear in the cooking process and therefore showed lesser BD than

the high amylose rice. The ability of the cooked rice fractions to retrograde on cooling as studied from SB values revealed that low amylose rice had greater ability to retrograde than the high amylose rice. Probably the amylopectin chain length of the low amylose rice was long enough to enable retrograded fractions to develop. Parboiled waxy rices, on the other hand, due to their high amylopectin content did not show any SB.

The extent of changes in the viscosity patterns of processed samples showed clear relationship with the amylose contents. Increase in PT with processing as reported by previous workers was observed for the open steamed high amylose and low amylose varieties.[32] Pressure parboiled samples of all varieties showed variable fall in the PT with the waxy samples exhibiting a more drastic drop with process severity indicating rapid water absorption. In the case of HR sample, initial drop in viscosity parameters observed for mildly parboiled HR-0-10 sample, may be due to milder gelatinization (as also revealed from lower DG % and % crystallinity) resulting in molecular patterns that prevents water uptake. This was reversed in HR-0-15 and HR-0-20 due to higher gelatinised fractions of starch resulting in better water absorption and thereby higher viscosity. Severe pressure parboiling caused extensive loss of all pasting parameters indicating complete thermal degradation of these hygroscopic starch fractions with absolutely no tendency of gel formation.[12] This also indicates that although being harder in the native and cooked form the starch granules from high amylose HR are very sensitive to hydrothermal degradation on parboiling.[33]

On the contrary, the low amylose and waxy varieties exhibited distinct increase in viscosity on mild open steam processing followed by a marginal fall for the LK-0-15 and LK-0-20. SB values show that the low amylose rice properties stand in between those of high amylose and waxy varieties indicating that the raw rice amylose content plays the key role in the properties of parboiled rice. Pressure treated LK samples, however, showed a trend just opposite to the open steamed samples. After an initial drop in PV for LK-15-10, the value increased marginally for LK-15-15 and LK-15-20 samples accompanied with a very low BD. However, exceptionally high SB indicated very high tendency towards retrogradation with formation of higher thermostable hygroscopic fractions. Patterns for the two raw waxy samples were similar except for WA(N) showing a markedly lower PV than WB(N). This difference may be due to differences in amylose activities and in amylopectin fine structures. High pressure treated waxy samples had GT

values very close to the initialization temperature of the RVA profile used (50°C) indicating that the samples have taken up water to attain viscosity at a temperature below 50°C. As also found from the turbidity generated in the aqueous acidic media used for the SV study at room temperature (section 3.4), it can be said that in the pressure parboiled samples, there occurs destruction of starch to fractions that have greater tendency to bind to water causing low temperature pasting.[31] In addition, there may be formation of some fine structures, that leach out to the water in the suspension after attaining PV at high temperature (95°C in this case) as indicated by increased BD.[34] The loss of SB in these samples reflects the absence of retrogradation during the cooling phase of the RVA profile.

Table 3.4. Pasting parameter values of raw and processed rice flour samples.

Samples	PV (cP)	HPV (cP)	CPV (cP)	BD (cP)	SB (cP)
HR(N)	4219^{a}	3347^{a}	5990^{a}	872^{a}	1771^{c}
HR-0-10	659^{d}	603^{d}	1304^{d}	56^{d}	645^{d}
HR-0-15	2094^{c}	1996^{c}	4086^{b}	98^{c}	1992^{a}
HR-0-20	2119^{b}	2015^{b}	4074^{c}	104^{b}	1955^{b}
HR-15-10	149^{g}	139^{g}	200^{g}	10^{f}	51^{f}
HR-15-15	191^{e}	181^{e}	261^{e}	10^{f}	70^{e}
HR-15-20	167^{f}	156^{f}	243^{f}	11^{e}	76^{e}
LK(N)	1687^{c}	1287^{f}	2916^{g}	400^{b}	1229^{f}
LK-0-10	3720^{a}	2844^{a}	4357^{b}	876^{a}	637^{g}
LK-0-15	2540^{b}	2433^{b}	5379^{a}	107^{c}	2839^{a}
LK-0-20	1463^{f}	1338^{e}	3935^{d}	125^{d}	2472^{b}
LK-15-10	1403^{g}	1255^{g}	3583^{f}	148^{c}	2180^{e}
LK-15-15	1574^{e}	1512^{d}	3846^{e}	62^{f}	2272^{d}
LK-15-20	1605^{d}	1573^{c}	3965^{c}	32^{g}	2360^{c}
WA(N)	1723^{f}	1181^{f}	1565^{f}	542^{f}	-158^{a}
WA-0-10	3159^{c}	2181^{c}	2897^{c}	978^{d}	-262^{d}
WA-0-15	3461^{b}	2202^{b}	3236^{b}	1259^{b}	-225^{b}
WA-0-20	3687^{a}	2402^{a}	3443^{a}	1285^{a}	-244^{c}
WA-15-10	1563^{g}	891^{g}	1319^{g}	672^{e}	-244^{c}
WA-15-15	2647^{e}	1496^{e}	1898^{e}	1151^{c}	-749^{e}
WA-15-20	2768^{d}	1511^{d}	1969^{d}	1257^{b}	-799^{f}
WB(N)	3109^{e}	1809^{d}	2294^{d}	1300^{f}	-815^{c}
WB-0-10	3991^{c}	2075^{c}	2673^{b}	1916^{c}	-1318^{d}
WB-0-15	4285^{b}	2398^{a}	2622^{c}	1887^{d}	-1369^{e}
WB-0-20	4318^{a}	2319^{b}	2922^{a}	1999^{b}	-1396^{f}
WB-15-10	2037^{g}	1367^{g}	1736^{f}	670^{g}	-301^{a}
WB-15-15	2796^{f}	1477^{f}	2169^{e}	1319^{e}	-627^{b}
WB-15-20	3757^{d}	1536^{e}	2168^{e}	2221^{a}	-1591^{g}

[a] Values with the same superscript in a row do not differ significantly from one another ($P < 0.05$)

3.3.7. FTIR spectroscopy

The IR absorption spectra of the different rice flour samples are shown in. All the characteristic bands for starch as reported by Kizil, Irudayaraj,, and Seetharaman (2002) were observed in all the samples (Fig 1.2 a-d) with very minor and variable changes in intensities indicating definite changes in the molecular bonding parameters on processing.[35] The ratio of the intensities of the two bands (1047 cm^{-1}:1022 cm^{-1}) representing crystallinity showed irregular and dissimilar patterns for the different varieties and between the processed samples of the same variety (Fig 1.2 e-h).[6] These differences in the values also indicate differences in the helical and crystalline arrangements in the raw and processed samples of the different varieties. An interesting observation was that the pattern of changes in the ratio of band intensities at 2855 cm^{-1} and 2925 cm^{-1} (Fig 1.2 e-h) responsible for symmetric and asymmetric stretch of H-C-H respectively, showed good correlation with the 1047 cm^{-1}:1022 cm^{-1} ratio indicating shift of the stretching modes of the CH_2 group with retrogradation. This creates possibility of being another indicative parameter for the study of starch crystallization by FTIR. Retrogradation directly influences the vibrational mode of C-H bonds in starch and was confirmed by loss of intensity of small peaks at 866 cm^{-1} and 1344 cm^{-1}.[6] Indications of possible damage of the pyranose ring structure due to severe processing were also noticed by the loss of the sharp peak near 590 cm^{-1}.

3.3.8. Wide angle x-ray scattering

All the native rice flour samples exhibited the typical A-type starch crystalline pattern (Fig 1.3 a-d) with major peaks at Bragg's angle (2θ) positions near 15.2 (Peak 1), 17.4 (Peak 2), 18.1 (Peak 3) and 23.3 (Peak 4). A minor peak at 2θ = 20, was evident in all the raw samples indicating presence of crystallites, which supports the idea of 'in situ' amorphous amylose complex formation.[10] Development of major peaks (indicating V-type polymorph) in the same domain were seen in all processed HR and LK samples and in the high pressure In spite of the very low contents of amylose, there were distinct formations of the V-type polymorph in the pressure processed waxy rice samples. In addition to it, the gradual loss in intensity of peak 1 on severe parboiling with formation of a weak peak near 2θ of ~22 indicated superimposition of partial B-type spectra in all the pressure parboiled samples.[8] All the A-type peaks were retained in the open steamed waxy samples. Peaks 2, 3 and 4 were found in the open steamed samples of HR and LK.

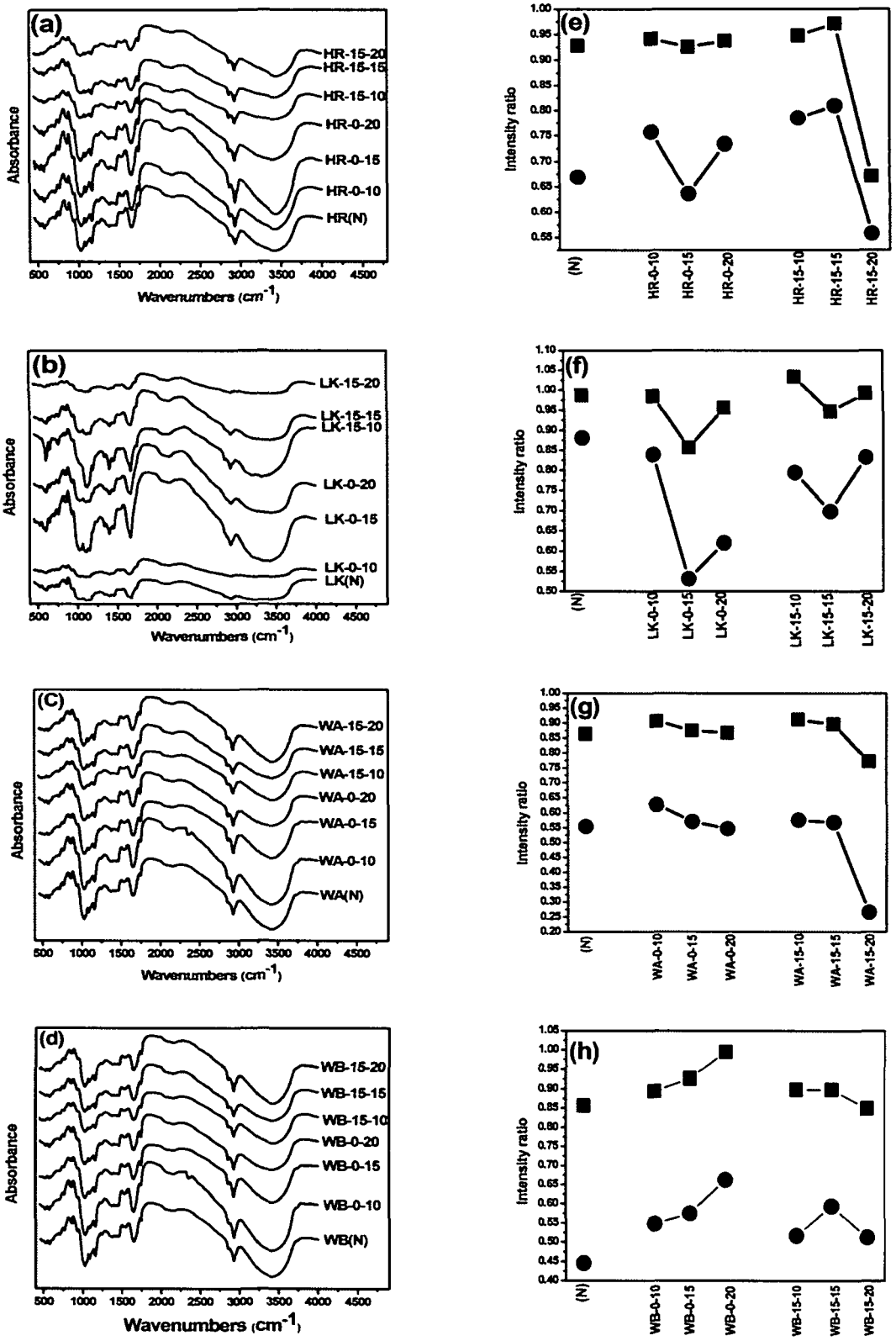

Fig. 3.2. (a,b,c and d) FTIR spectroscopic patterns of raw and processed HR, LK, WA and WB flour samples respectively; (e, f, g, h) changes in the ratio of IR absorption intensities 1047 cm^{-1}:1022 cm^{-1} and 2855 cm^{-1}:2925 cm^{-1} of the raw and processed samples.

Peak 2 and 3 were subdued in all the pressure parboiled samples. Hence, there were distinct superimposition of A and V-type patterns in open steamed high and low amylose samples and superimposed A, B and V-type patterns in all the pressure parboiled samples indicating formation of all the three main parboiled rice starch polymorphs. There were obvious losses in crystallinity as indicated by the loss of intensities of the major native peaks.[8,9] Highest % Crystallinity of 27.1% was exhibited by WB(N). Mild open steaming caused drastic loss of crystallinity in all varieties (Fig 1.3e).

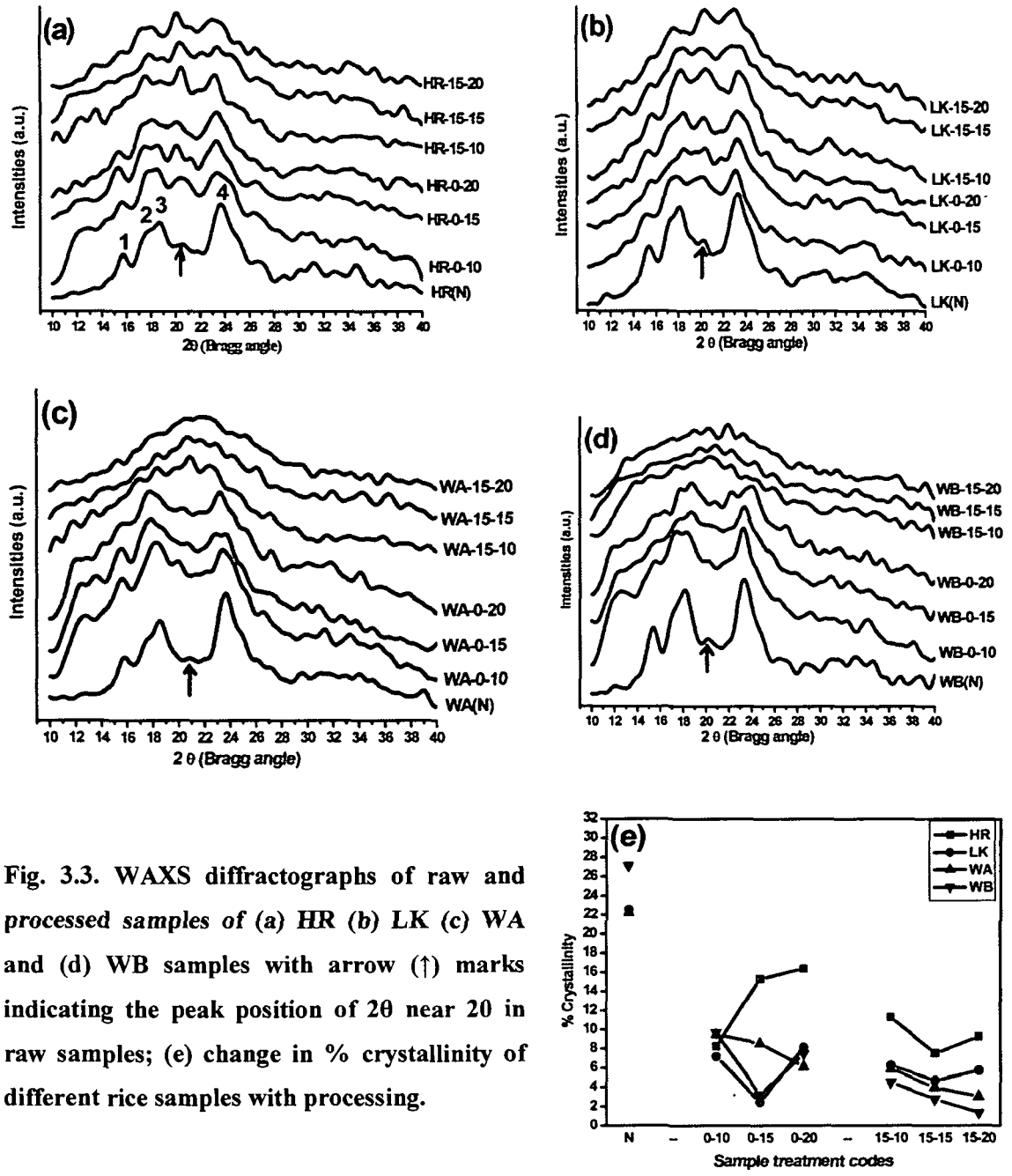

Fig. 3.3. WAXS diffractographs of raw and *processed samples of* (a) HR (b) LK (c) WA and (d) WB samples with arrow (↑) marks indicating the peak position of 2θ near 20 in raw samples; (e) change in % crystallinity of different rice samples with processing.

However, after moderate treatment, there was rise in the % Crystallinity values for HR and LK suggesting higher retrogradation with formation of crystalline polymorphs. This may be related to higher degree of gelatinization as previously mentioned (section 3.3.2) and subsequent retrogradation of the same leading to formation of retrograded crystallites. Similarly, for the pressure processed HR and LK samples, crystallinity drop was seen till moderate processing and recrystallization occurred after the severe treatment, thereby nullifying any direct relationship between DG (%) and retrogradation. Adding to it, for waxy samples, continuous loss in crystallinity was observed. Hence, the loss in crystallinity was higher in the processed waxy samples than HR and LK suggesting that the extent of recrystallization was dependent on the amylose content and the higher tendency of water absorption of the pressure parboiled waxy varieties as seen from the EMC-S%, SV and RVA studies is due to amorphous fractions of the rice starch rather than the crystallites present.[9] Again, no significant correlation was observed between the change in the % Crystallinity with the pattern of change of the FTIR band ratios $1047cm^{-1}$:$1022cm^{-1}$ which is obvious as the calculation of % Crystallinity considers only a small range (10-40°of 2θ in this case) of the whole diffractograph with major emphasis on the strong peaks, while the FTIR method considers the bonding vibrational modes at two band positions of the spectra.

3.3.9. Starch digestibility

The digestibility of the rice sample was found to be dependent upon the amylose content (Fig 1.4). Native and processed HR samples showed lowest levels of RDS, followed by LK, WA and WB samples. An opposite trend was observed for SDS values of the samples.[36] At least 50% (db) RDS and a maximum of 15% (db) SDS were present in all the samples. The differences in the digestible fractions were clearly reflected in their RS contents (%, db). Raw HR(N) showed the highest RS content of 7.42%, followed by LK(N), WB(N) and WA(N) with 6.83%, 4.24% and 4.39% RS, respectively. Zhu et al (2011) reported rice flour RS contents to range from 4.9% to 33.4% in four rice types differing in apparent amylose contents. In general, the RS content is positively correlated with the level of amylose.[37] Distinct drop in RS content with processing severity was observed for all the four varieties. These findings are in accordance with Juansang et al (2012)[38] but are contrary to reports of Li et al (2011).[26] The decrease in RS content was more extensive for the processed HR samples and was minimal for the processed LK,

WA and WB samples. Hydrothermal processing resulting in the breakdown of the starch polymeric chains and specially long chains of amylose, as also revealed by EMC-S, SV, RVA and WAXS results, must have resulted in the formation of simpler and more digestible fractions. However, the high digestibility of raw and processed LK samples, which is even more than those of the two waxy samples creates scopes for further research on its molecular structure and peculiar enzymatic hydrolysis pattern.

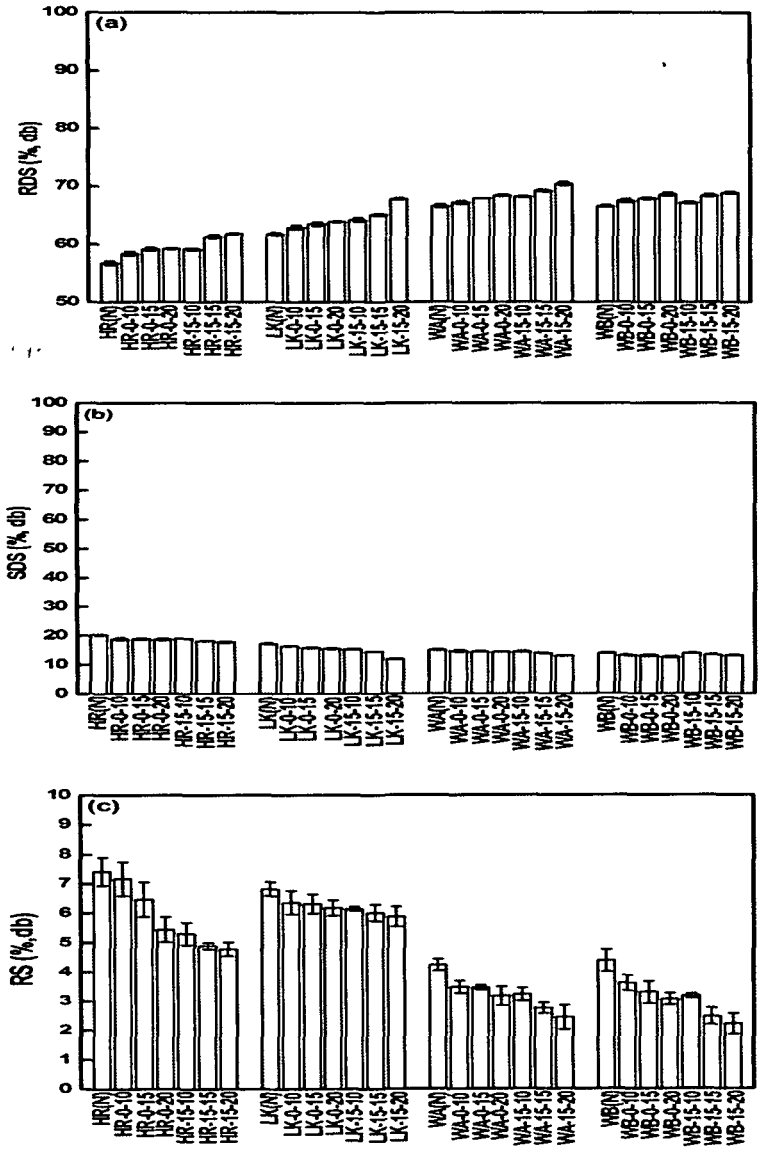

Fig. 3.4. (a) Rapidly digestible starch (RDS, % db), (b) slowly digestible starch (SDS, % db) and (c) resistant starch (%, db) in the native and processed rice flour samples.

3.3.4. Conclusions

This chapter has focussed on the effect of varietal differences and different hydrothermal processing treatments on the physicochemical properties of the parboiled rice. Degree of gelatinization was markedly high in the severely pressure parboiled samples. The very high EMC-S and SV of open steamed low amylose and waxy rices are indicative of altered cooking properties of these on processing. Pressure parboiled waxy samples showed extensive fall of gelatinization temperature and increased hydration at lower temperatures. Formation of short amylopectin fine structures in these samples was indicated by sediment volume and viscosity patterns. The pattern of change in the infrared spectroscopic bands may be due to shift in stretching mode. Wide angle X-ray diffractographs of raw samples showed peaks at 2θ values near 20 which indicated 'in situ' points for amorphous amylose complex formation. A, B and V-type polymorphs were seen in pressure parboiled samples and only A and V-type polymorphs were observed in open steamed samples. The existence of V-type crystalline pattern even in waxy parboiled rice needs to be further confirmed through investigation of the amylopectin chain length in a few waxy rice varieties of Assam. Loss in crystallinity with simultaneous increase in water uptake can be attributed to the amorphous fractions in parboiled rice. Low amylose parboiled rices of both processing conditions have high RS value and can be commercially exploited. Severe hydrothermal processing causes thermal degradation of starch.

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Chapter 4

EFFECT OF DRY HEAT PARBOILING TREATMENT VARYING IN TEMPERATURE AND TIME ON THE PROPERTIES OF RICE VARIETIES WITH DIFFERENT AMYLOSE CONTENT

4.1. Introduction

Rice is a major staple food crop. The physicochemical attributes of rice is determined by the status of the two basic fractions of the starch macromolecule, namely amylose and amylopectin. From the work of Juliano (1979), rice may be classified into high amylose (amylose content <25%), intermediate amylose (20–25%), low amylose (7–20%) and waxy or glutinous (1–2%) types.[1] Parboiling is an age-old technique applied for quality enhancement of rice. Steam parboiling has been widely practiced and investigated.[2] The rice variety, parboiling conditions and extent of gelatinization and retrogradation decides the properties of parboiled rice.[3] Parboiled rice gives higher head rice yield because of the filling up of the naturally occurring fissures in the kernels by gelatinized starch. However, an inefficient drying step can cause severe moisture gradient within the kernel even after an efficient steaming step that may induce kernel fracture during milling.[4] Drying involves lower temperature than steaming. At the molecular level, cooling causes rearrangement of the starch chains with release of water molecules. The crystallinity as determined by XRD is again developed due to retrogradation with formation of newer crystallites and permanent loss of the native ones.[5] Formation of amylose lipid complexes has been reported.[6] Thermal analysis of steam parboiled starch gives a peak for retrograded starch at temperature below the GT of raw rice and may give another peak at 90°C to 120°C for melting of amylose-lipid complexes.[7] The phenomenon of gelatinization and

retrogradation is well understood when the pasting profile of starch is studied in a Rapid Visco Analyser (RVA). The viscosity profile however markedly changes in parboiled rice which may be attributed to varietal differences, amylose content, parboiling severity, granular damage and retrogradation, amylose-lipid complexes and protein network formation during processing.[8-12] Parboiling increases the digestibility of rice starch.[13] Englyst et al (1992) classified starch in foods into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS).[14] While starch that gets digested under 20 min of incubation is considered as RDS, SDS is the starch that gets digested after another 100 min. RS comprises the residue remaining undigested after that. While RS has been considered suitable for incorporation in food for diabetics, a product with high RDS is suitable for person needing fast energy intake or non-residual digestion.[15]

Dry heat parboiling is another important technique that involves rapid roasting of sufficiently soaked paddy with heated sand.[16] It is comparatively a faster process than steam parboiling. The technique is generally applied for making speciality rice products, the popular being puffed rice.[17,18] Although there are possibilities, dry heat parboiled rice has not been studied to understand its quality as staple parboiled rice (other than steam parboiled rice). In the present study, three rice varieties belonging to high amylose, low amylose and waxy types were dry heat parboiled at two different temperatures for three different time periods each.[1] The changes in physical and physicochemical properties of the rice samples were analysed for determining desirable characteristics that can provide scope for possible food applications of the products.

4.2. Materials and methods

Pure line paddy samples of *Ranjit*, *Kola chokua* and *Aghoni bora* varieties with 27.2% (high amylose, HR), 12.6% (low amylose, LK) and 1.1% (waxy, WA) apparent amylose content respectively (as reported in the last chapter, section 3.2.2) from the harvest of 2012 were purchased from the Regional Rice Research Station of Assam Agricultural University at Titabor, Assam and local farmers of the region. The raw paddy samples were cooled at room temperature for 24 h and stored at 4°C for further processing. Enzymes, namely invertase from Baker's yeast (I4504), α-Amylase from porcine pancreas (A4268), amyloglucosidase from *Aspergillus niger* (A7095) and D-glucose standard (47829) were procured from Sigma-Aldrich (Missouri, USA).

4.2.1. Processing and coding of samples

Water (~2 L) was taken in an aluminium vessel and raised to 70°C over a burner. The flame was put off and 200 g paddy of each sample was immediately soaked in it. The temperature of water on addition of paddy immediately reduced to 60-62°C. The vessel was then covered with a gunny bag and kept for 18 h for hydration of the paddy. The excess water was then decanted and the soaked paddy was immediately roasted in a manually operated drum type roaster with sand (1:3 paddy to sand, 110-120 rpm). The sand particles (less than 3mm in diameter) were preheated to temperatures of 220°C and 270°C so that it came down to 140°C and 200°C, respectively after addition of the wet paddy. Temperature was maintained during processing by wrapping the drum of the roaster with a wet piece of gunny bag. The paddy samples were roasted under two conditions - low temperature for longer time (LTLT, 140°C for 11, 13 and 15 min) and high temperature for shorter time (HTST, 200°C for 3, 4 and 5 min). No popping of paddy occurred during processing. The roaster was tilted to take out the roasted paddy and sand. The hot sand was sieved out and the paddy was stored at room temperature (RT, 25±2°C) in a thin layer for 6 h allowing sufficient cooling down to RT. The samples were further stored at 4°C before milling in a dehusker and a polisher (Satake, Japan). The milled kernels (8-10% milling, w/w) were stored in polypropylene bags at 4°C for further analysis. For ease of identification, the rice varieties were coded as HR meaning high amylose *Ranjit*, LK meaning low amylose *Kola chokua* and WA meaning waxy *Aghoni bora*. HR, LK and WA suffixed with (N) indicated native raw rice. Processed sample code indicated variety code suffixed with roasting temperature and time of roasting. Thus, HR-140-11 indicates high amylose *Ranjit* paddy roasted at 140°C for 11 min.

4.2.2. Moisture content of raw, soaked and dry heat parboiled samples

Moisture content of raw paddy was estimated using a standard AOAC protocol (2000).[19] The moisture content of soaked paddy was determined after surface moisture was carefully removed with a blotting paper. For dry heat parboiled samples, portions were immediately collected after roasting in a pre-weighed moisture cup and weighed for moisture estimation. Briefly, milled rice sample was taken in previously dried and

weighed covered dishes. The sample was allowed to dry in a vacuum oven at 100°C and vacuum pressure equivalent to 3 kPa till constant weight was attained. Weight of the dish containing sample was measured both before and after drying and moisture content was calculated (925.09, AOAC).

$$\text{Moisture content (\%, db)} = \frac{\text{Initial weight - Final weight}}{\text{Final weight} - \text{Weight of emty dish}} \times 100 \qquad \textbf{Eq. 4.1}$$

4.2.3. Head rice yield (HRY)

HRY (%) was determined as the weight average percentage of intact kernels obtained after milling to that of total milled rice containing both intact and broken kernels.

HRY (%) = [Weight of intact kernels / Weight of total milled rice] x 100 **Eq. 4.2**

4.2.4. Kernel hardness and physical dimensions

Milled whole rice kernels were tested for hardness (H) using a Texture Analyzer (TA.HD.plus, Stable Micro Systems, UK) with a 25 kg load cell using single compression. A single kernel was compressed with a 2 cm diameter stainless steel probe along the thickness at a speed of 0.5 mm/min and returned to its original position. The test was repeated for 25 kernels from each sample and the mean was calculated. The maximum force indicated by the force-time curve generated by the inbuilt software (Exponent Lite) was taken as the hardness. The length (L) and breadth (B) of ten milled kernels from each sample were determined using a Seed dial calliper (Baker, India) and L/B ratios were determined.

4.2.5. Colour measurement

The colour values (L, a, b) of all the samples were determined with a colour measurement spectrophotometer (Ultrascan Vis, Hunter Color-Lab). Raw rice was taken as the reference. The chroma value (C) of parboiled rice was then calculated.[20]

$$C = (a^2+b^2)^{1/2} \qquad \textbf{Eq. 4.3}$$

4.2.6. Degree of gelatinization (DG)

DG (%) was calculated by the method of Wootton et al (1971).[21] For this, 0.2g sample was dispersed in 100 mL distilled water with stirring for 5 min and centrifuged at

1500 rpm for 25 min. One milliliter supernatant was then diluted to 10 mL with distilled water and 0.1mL iodine solution was added. The method was repeated using 100 mL of 10 M potassium hydroxide instead of water and absorbance of both solutions were read at 600 nm in a Spectrophotometer (Cecil Aquarius 7400, England).

DG (%) = [Absorbance of fresh solution / Absorbance of alkali solubilized solution] x 100

Eq. 4.4

4.2.7. Scanning electron microscopy (SEM)

Transverse sections of the milled raw kernels and samples roasted at 140°C and 200°C for 15 min and 5 min respectively were carefully cut using a sharp blade. The sections were then fixed using liquid nitrogen and sputter coated with gold before observing under a Scanning Electron Microscope (JEOL 6993V) operating at an acceleration voltage of 15 kV and magnifications of 30X and 2000X.

4.2.8. Equilibrium moisture content on soaking at room temperature (EMC-S)

The method of Indudhara Swamy et al (1971) was used to determine EMC-S(% db) of polished whole rice kernels.[19] Whole-grain milled rice (about 3-5 g) with 11 to 13% moisture content (db) was put in 50 mL water in a covered 100 mL beaker and left aside. The rice was strained through a wire strainer after 20-24 h and dried between Whatman No.1 filter paper sheets. The moisture content of the rice was determined by a drying method (AOAC, 2000)[22] and EMC-S calculated.

EMC-S (%, db) = [Moisture evaporated (g) / Dried weight of kernels (g)] x 100

Eq. 4.5

4.2.9. Sediment volume (SV)

The method of Bhattacharya and Ali (1976) was used to determine the SV of the raw and processed rice flour samples at ambient temperature.[23] Briefly, 1 g each of desiccated flour samples was taken in a measuring cylinder and 15 mL of 0.05 N hydrochloric acid was added to it with agitation after each 5 min for 1 h. The level of the flour sediment was observed after 4 h and was reported as the SV of the sample.

4.2.10. Pasting properties

Twenty eight gram flour (with 12% moisture content) was mixed with 25 mL water to make slurry. A Rapid Viscosity Analyser (RVA Starchmaster2, Newport Scientific Instruments, Australia) was used to measure the pasting profile. The prepared slurry was held at 50°C for 1 min, heated from 50°C to 95°C at 12°C/min, held at 95°C for 2.40 min followed by cooling to 50°C at 11.25 °C/min, and finally holding at 50°C for 1 min. The pasting curves obtained were compared and the pasting parameters, namely peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown (BD), and total setback (SBt) were recorded using the inbuilt software. PV is the maximum viscosity during heating, HPV is the minimum viscosity at 95°C, CPV is the final viscosity at 50°C, BD is obtained after subtracting HPV from PV. SBt is obtained after subtracting PV from CPV.

4.2.11. Wide angle X-ray scattering (WAXS)

An X-ray diffractometer (Rigaku Miniflex, Japan) with a λ value of 1.54 A° and operating at an acceleration potential of 30 kV with 15 mA current and copper target was used to obtain wide angle X-ray diffraction spectra of the flour samples. The scanning range was 10–40° of 2θ values in steps of 0.05°. The total area under the curve and the area under each prominent peak were determined and the percentage crystallinity was calculated.

% crystallinity = area under peaks / total area x 100 **Eq. 4.6**

4.2.12. Differential scanning calorimetry (DSC)

Flour slurries of raw rice and samples roasted at 140° and 200°C for 15 and 5 min respectively from each variety were analysed for thermal properties by a method modified from Liu et al (2009).[24] Slurries were prepared in aluminium pans by weighing 4 mg flour and adding 8 mg deionized water to it. The pans were then saturated for 1 h at 4°C before hermetic sealing followed by heating in a Differential Scanning Calorimeter (model DSC-60; Shimadzu, Japan) against an empty reference pan from 30°–130°C at a heating rate of 5°C/min under nitrogen atmosphere. The instrument was periodically calibrated with pure indium for heat flow and temperature. The onset (To), peak (Tp), and conclusion (Tc) temperatures and enthalpy of gelatinization (ΔH, in J/g) were obtained from the thermograms using TA-60WS software.

4.2.13. Starch digestibility

Resistant starch (RS) present in the flour samples was measured by a method modified from Englyst et al (1992).[14] One hundred milligrams of flour was first added to 7 mL of acetate buffer (5.2 pH) at 37°C for 20 min and incubated in a shaking water bath. Then, 3 mL of an enzyme mixture composed of invertase (220 U/mL), pancreatic α-amylase (3000 U/mL) and amyloglucosidase (15 U/mL) were added and incubated further for 20 min. An aliquot was taken out and estimated for rapidly available glucose (G_{20}) using a D-glucose oxidase-peroxidase assay kit (Robonik, India) and a standard curve was prepared in a similar manner with different concentrations of D-glucose. Another aliquot was similarly estimated for glucose after 120 min incubation (G_{120}). Both these values were multiplied by a factor of 0.9 to measure the rapidly digestible starch (RDS) and slowly digestible starch (SDS) respectively and expressed as a percentage of dry matter. The difference between total starch (TS) measured by the standard AOAC method (2000) and the starch digested during the incubation period of 120 min was calculated as RS.[25]

$$RDS = G_{20} \times 0.9 \quad \textbf{Eq. 4.7}$$

$$SDS = (G_{120} - G_{20}) \times 0.9 \quad \textbf{Eq. 4.8}$$

$$RS = TS - (RDS + SDS) \quad \textbf{Eq. 4.9}$$

4.2.14. Statistical Analysis

All the experiments were carried out in multiple replicates and means are reported. Significant differences between means were determined by Duncan's multiple range test at a significance level of 0.05. The tests were performed using SPSS 11.5 (SPSS Inc., USA).

4.3. Results and discussion

4.3.1. Moisture content of raw, soaked and dry heat parboiled samples

The moisture content of raw *Ranjit*, *Kola chokua* and *Aghoni bora* was between 12.5 to 13.0 % (wb) that increased to 34.6%, 35.2% and 35.1% respectively on soaking, indicating sufficient hydration of the rice endosperms. Dry heat parboiling significantly reduced the moisture content of the paddy samples (Table 4.1). It was observed that temperature severity played the crucial role in moisture reduction than processing time.

4.3.2. Head rice yield (HRY)

LTLT dry heat parboiling significantly improved the head rice yield of all the three varieties (Table 4.1) with values nearing 100%. HTST processed samples however exhibited HRY values in between raw and LTLT samples. This might be attributed to the development of higher temperature and moisture gradient within the kernels during initiation of roasting and during sudden release of the roasted mass to room temperature that created internal fissures and cracks resulting in kernel breakage during milling.[4] The pre and post-roasting temperature change hence needs to be controlled for getting a higher head rice yield out of the HTST samples.

4.3.3. Kernel hardness and physical dimensions

Dry heat parboiling increased kernel hardness of the three rice varieties (Table 4.1) and HTST processed samples were less hard than LTLT processed samples due to the development of internal fractures. All the three rice varieties were medium in size with L/B between 2.5 to 2.9. Reduction in kernel lengths with simultaneous increase in breadths of LK and WA samples resulted in marked reduction of L/B ratio making the dry heat parboiled rice bolder in shape. Possibly higher tension developed along the horizontal axis of the cylindrical kernels during starch gelatinization and drying. HR kernels however did not exhibit such notable changes indicating the effect of varietal differences.

4.3.4. Colour measurement

The reduction in L of the processed kernels was due to gelatinization of starch and inward migration of husk and bran pigments as was earlier observed in steam parboiled rice (Chapter 3, section 3.3.3). Similarly, the increased positive values of a and b were indicative of pigment migration and Maillard browning reactions (Table 4.1), as has been reported in steam parboiled rice.[26] The high temperature used in dry heat parboiling probably increased the C value of the samples which were higher than those reported for steam parboiled rice.

4.3.5. Degree of gelatinization

LTLT processing resulted in rice kernels with some ungelatinized starch fractions in the kernels (Table 4.1). However, HTST processing resulted in complete gelatinisation of starch suggesting higher efficiency of the method in attaining gelatinization. High heat applied in HTST must have reached the centre of the rice

kernels extensively to result in sufficient gelatinization throughout the kernel, which the lower heat in LTLT samples could not. Precisely, HTST processing could overcome the temperature gradient occurring between the external layers and the centre of the paddy than LTLT. Effect of this was indicated by the observations made from the following electron microscopic study (section 4.3.6).

4.3.6. Scanning electron microscopy

Distinct morphological differences in the surface integrity of the sections of rice kernels were observed (Fig 4.1). The loss in starch granular structure and sealing of naturally occurring fissures in the raw endosperms after starch gelatinization on dry heat parboiling was seen from the SEM at 2000x (dii, eii, fii, gii, hii, iii).[27] The effect of severity of gelatinisation was visible when HTST and LTLT samples were compared. Magnification at 30X however demonstrated development of a distinct cavity in radial direction of HTST kernels namely HR-200-5, LK-200-5 and WA-200-5 (gii, hii, iii). Probably, when suddenly subjected to very high temperature, the water in the soaked paddy simultaneously participated in starch gelatinization process as well as tried to migrate out of the gelatinized core of the endosperm. This releasing force pushed the softened kernel material in all directions creating a cavity in the middle of the kernel which because of instantaneous drying did not get sufficient scope to refill. The lower kernel hardness and head rice yield of the HTST samples may be attributed to this cavity formation. The characteristic splitting of dry heat parboiled rice kernel when subjected to alkali solution as reported elsewhere may also be related with this phenomenon.[28]

4.3.7. Equilibrium moisture content on soaking at room temperature

EMC-S (% db) was higher for both raw and dry heat parboiled WA and LK samples than the HR samples clearly indicating the role of amylose content (Fig 4.2a). Dry heat parboiling increased the water absorption capacities of the three rice varieties due to extensive starch gelatinization.[3] HTST treatment resulted in notably sharp increase in EMC-S than LTLT treated samples probably due to the accumulation of water in the cavity formed in the kernel.

Table 4.1. Moisture content, head rice yield, kernel hardness, L/B ratio, colour value and degree of gelatinization of raw and processed rice samples.

Samples	Moisture (% wb)	HRY (%)	H (N)	L (mm)	B (mm)	L/B	L	a	b	C	DG (%)
HR(N)	-	78.4±1.34^{c}	66.4±0.11^{b}	6.2±0.22^{b}	2.4±0.04^{b}	2.5±0.53^{c}	46.6±0.88^{k}	2.1±0.07^{a}	10.5±0.89^{a}	10.7±0.34^{a}	-
HR-140-11	11.9±0.87^{f}	99.3±0.91^{q}	87.4±0.68^{l}	6.2±0.13^{b}	2.4±0.07^{b}	2.6±0.24^{c}	37.3±0.27^{j}	2.6±0.03^{b}	10.7±0.13^{b}	11.0±0.41^{b}	92.4±0.02^{a}
HR-140-13	11.6±0.56^{e}	98.7±0.79^{no}	87.8±0.29^{m}	6.3±0.12^{c}	2.4±0.03^{b}	2.6±0.40^{c}	32.1±0.49^{h}	2.6±0.05^{c}	10.9±0.45^{d}	11.2±0.12^{d}	94.2±0.04^{c}
HR-140-15	11.5±0.29^{e}	98.8±0.47^{o}	89.1±0.48^{n}	6.3±0.17^{c}	2.4±0.07^{b}	2.6±0.26^{c}	26.6±0.59^{e}	2.7±0.03^{c}	10.9±0.39^{d}	11.2±0.27^{d}	95.1±0.07^{d}
HR-200-3	9.2±0.79^{c}	82.4±1.21^{g}	71.3±0.21e	6.2±0.14^{b}	2.4±0.08^{b}	2.6±0.17^{c}	29.7±0.46^{g}	2.5±0.01^{b}	10.8±0.19^{d}	11.1±0.22^{c}	98.6±0.09^{e}
HR-200-4	8.8±0.66^{b}	84.3±0.72^{i}	72.5±0.76^{f}	6.3±0.09^{c}	2.5±0.04^{c}	2.5±0.19^{b}	24.4±0.38^{d}	2.9±0.02^{d}	11.1±0.39^{e}	11.2±0.19^{d}	99.0±0.03^{f}
HR-200-5	8.6±0.44^{ab}	83.8±0.19^{h}	70.3±0.29^{d}	6.3±0.16^{c}	2.5±0.08^{c}	2.5±0.22^{c}	21.5±0.18^{a}	3.2±0.02^{e}	11.4±0.26^{g}	11.4±0.42^{e}	100.0±0.00^{g}
LK(N)	-	72.1±1.89^{a}	68.8±0.82^{c}	6.7±0.16^{f}	2.4±0.06^{b}	2.8±0.28^{d}	57.5±0.34^{l}	2.3±0.04^{c}	10.5±0.38^{a}	10.7±0.17^{a}	-
LK-140-11	11.4±0.18^{de}	99.5±0.12^{r}	84.3±0.04^{j}	6.5±0.14^{e}	2.6±0.04^{d}	2.5±0.32^{c}	32.1±0.38^{h}	2.6±0.02^{b}	10.8±0.34^{c}	11.1±0.09^{c}	93.0±0.06^{ab}
LK-140-13	11.2±0.55^{d}	98.2±0.27^{m}	86.5±0.29^{k}	6.5±0.18^{e}	2.6±0.07^{de}	2.5±0.24^{c}	28.6±0.18^{l}	2.9±0.05^{d}	10.9±0.42^{d}	11.3±0.18^{e}	94.2±0.12^{c}
LK-140-15	11.2±0.18^{d}	99.1±0.01^{p}	86.9±0.19^{j}	6.4±0.11^{d}	2.7±0.09^{e}	2.4±0.13^{a}	23.1±0.46^{fg}	3.2±0.04^{e}	10.9±0.29^{d}	11.4±0.25^{e}	94.4±0.06^{c}
LK-200-3	8.9±0.48^{ab}	80.6±1.81^{e}	74.2±0.61^{g}	6.3±0.14^{c}	2.6±0.03^{d}	2.4±0.44^{b}	27.7±0.33^{e}	2.8±0.03^{c}	10.8±0.28^{c}	11.2±0.16^{d}	98.7±0.05^{e}
LK-200-4	8.6±0.91^{ab}	82.4±0.38^{g}	77.5±0.44^{i}	6.3±0.19^{c}	2.7±0.03^{e}	2.3±0.62^{a}	24.1±0.28^{cd}	3.4±0.04^{g}	10.8±0.19^{d}	11.3±0.07^{e}	100.0±0.00^{g}
LK-200-5	8.5±0.71^{a}	79.8±1.31d	71.1±0.37^{e}	6.2±0.18^{b}	2.7±0.05^{e}	2.3±0.37^{a}	21.9±0.19^{a}	3.6±0.04^{h}	11.7±0.15^{h}	11.6±0.14^{f}	100.0±0.00^{g}
WA(N)	-	73.8±1.29^{b}	59.8±0.17^{a}	6.4±0.17^{d}	2.2±0.03^{a}	2.9±0.58^{e}	66.7±0.21^{m}	2.2±0.04^{b}	11.2±0.31^{e}	11.4±0.19^{e}	-
WA-140-11	12.1±0.39f	97.8±0.31^{l}	90.9±0.11^{o}	6.3±0.11^{c}	2.4±0.06^{b}	2.6±0.18^{d}	35.1±0.48^{i}	2.7±0.01^{c}	11.3±0.27^{f}	11.6±0.31^{f}	92.2±0.08^{a}
WA-140-13	11.6±0.19^{e}	99.7±0.11^{s}	86.9±0.28^{k}	6.2±0.15^{b}	2.5±0.07^{c}	2.5±0.28^{c}	28.8±0.22^{g}	2.8±0.03^{c}	11.7±0.16^{h}	12.0±0.28^{h}	93.2±0.03^{ab}
WA-140-15	11.4±0.20^{de}	98.6±0.19^{n}	87.6±0.33^{lm}	6.2±0.12^{b}	2.5±0.03^{c}	2.5±0.41^{b}	26.3±0.19^{e}	3.1±0.06^{e}	11.8±0.22^{i}	11.8±0.12^{g}	95.3±0.08^{d}
WA-200-3	9.1±0.17^{c}	84.5±1.82^{j}	72.3±0.21^{h}	6.2±0.18^{b}	2.5±0.04^{c}	2.5±0.47^{c}	28.1±0.29^{ef}	2.8±0.03^{d}	11.4±0.25^{g}	11.7±0.26^{f}	99.1±0.00^{f}
WA-200-4	8.7±0.24^{ab}	81.5±1.43^{f}	70.4±0.19^{f}	6.2±0.11^{b}	2.6±0.05^{d}	2.4±0.20^{b}	23.8±0.17^{c}	2.9±0.04^{d}	11.7±0.19^{h}	12.1±0.26^{i}	100.0±0.00^{g}
WA-200-5	8.7±0.71^{c}	88.6±1.76^{k}	74.8±0.13^{h}	6.1±0.11^{a}	2.6±0.05^{d}	2.3±0.23^{a}	21.7±0.41^{a}	3.3±0.03^{f}	11.7±0.24^{h}	12.1±0.09^{i}	100.0±0.00^{g}

[a] Means with the same superscript in a column do not differ significantly from one another ($p < 0.05$)

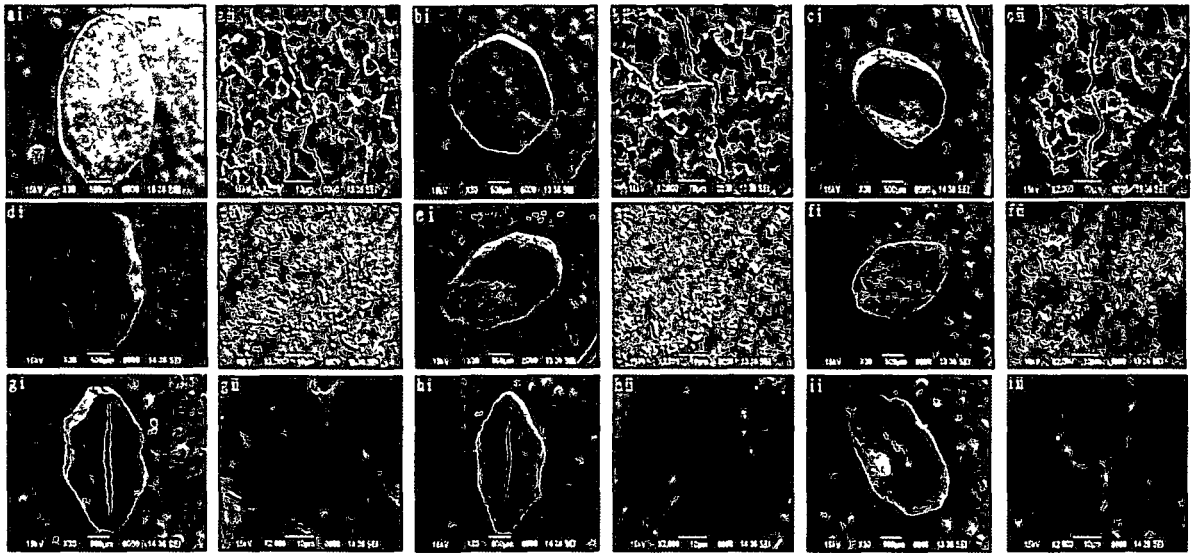

Fig. 4.1. Scanning Electron Microscopic pictures of (a) HR(N), (b) LK(N), (c) WA(N), (d) HR15, (e) LK15, (f) WA15, (g) HR5, (h) LK5 and (i) WA5 taken at 30x (ai, bi, ci, di, ei, fi, gi, hi, ii) and 2000x (aii, bii, cii, dii, eii, fii, gii, hii, iii) magnification.

4.3.8. Sediment volume

While EMC-S (%, db) was evaluated for whole kernels, sediment volume was determined for rice flour (Fig 4.2b). Although the pattern of increasing values was similar, the sharp rise in values observed for HTST treated samples in EMC-S test was not found in sediment volume test. This confirmed the role of the cavity in HTST treated rice kernel samples in accumulating water.

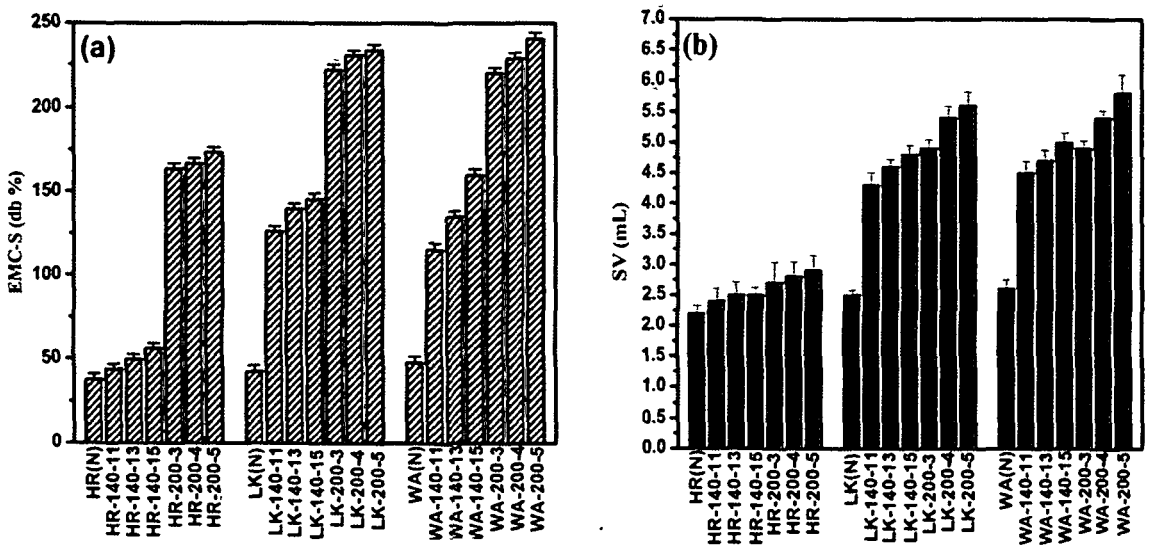

Fig. 4.2. (a) Equilibrium moisture contents on soaking at room temperature; (b) sediment volumes of the raw and dry heat parboiled HR, LK and WA samples.

4.3.9. Pasting properties

RVA pasting curves of the raw and processed samples of the three varieties are given in Fig 4.3 (a, b and c). The effect of amylose content in pasting pattern of raw rice was evident. HR(N) required longer time to attain viscosity than LK(N) and WA(N). High amylose wheat starch was reported to be slower in swelling on pasting.[29] Sang et al (2008) suggested it to be due to formation of amylose-lipid complex in the raw starch.[9] These complexes were found in native rice in very low proportion with no significant quantitative difference amongst the varieties.[10] Newer complexes are formed over process temperature above 50°C.[4] Its formation and differential influence

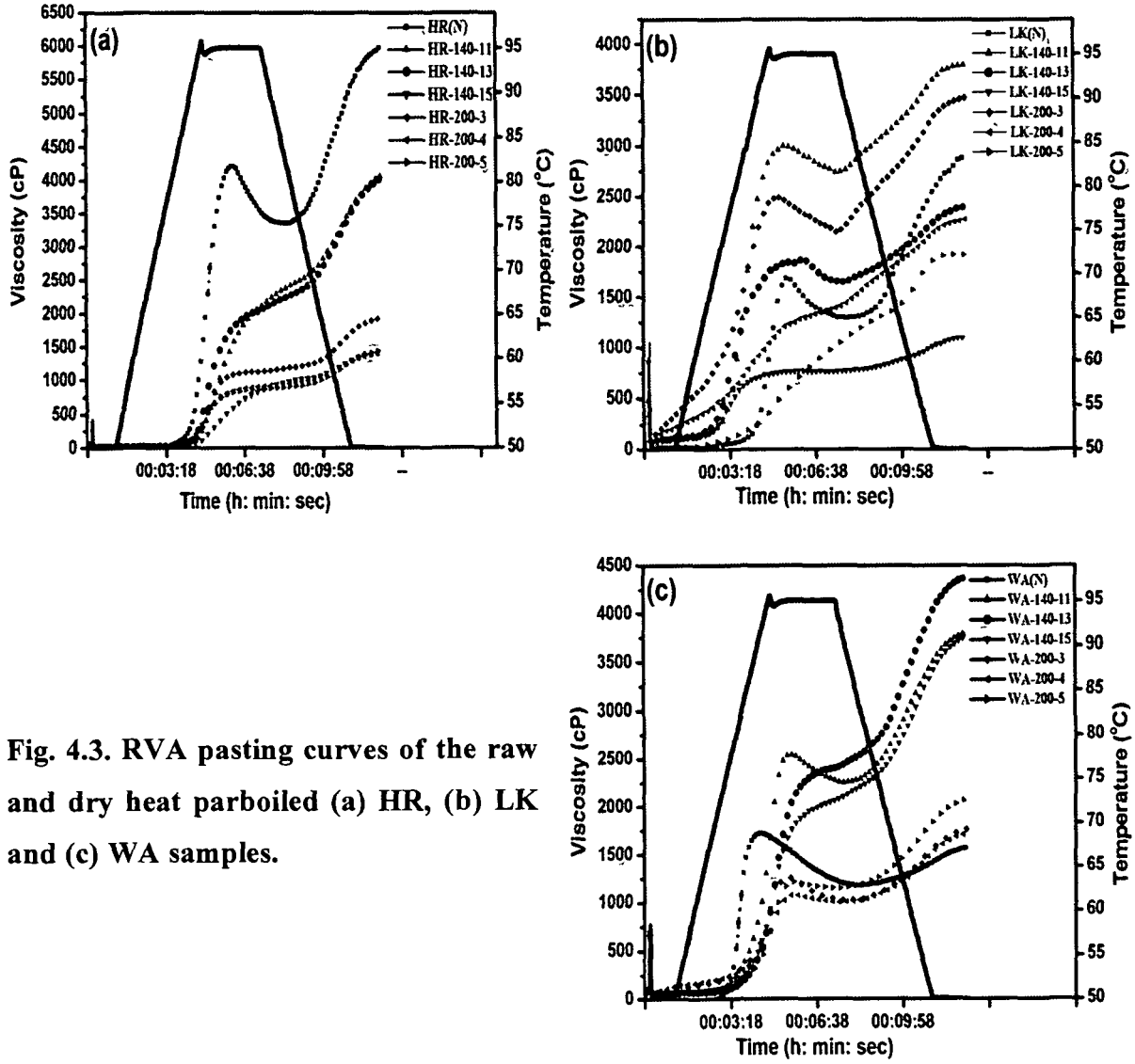

Fig. 4.3. RVA pasting curves of the raw and dry heat parboiled (a) HR, (b) LK and (c) WA samples.

on the raw rice samples can hence be nullified. The higher PV in HR(N) also does not imply any such inhibitory effect of amylose on the extent of starch swelling. Amylopectin may however be attributed to the rapid absorption of water. This branched structure being more susceptible to damage by increased temperature during the heating phase of RVA resulted in lower PV.[31] Probably, irreversible damage of the heat labile amylopectin structures and subsequent leaching out in processed LK and WA samples caused continuous rise of the pasting curves. The PV, HPV and CPV of the LTLT samples were even higher than the raw samples of LK and WA, indicating larger degraded fractions resulting in higher density of the heated slurry. The branched chains in waxy WA were probably longer than those of low amylose LK to explain for the highest value of CPV attained.[30] HTST caused further breakdown, bringing the overall slurry viscosity to lower values. In addition, amylose-lipid complexes and a protein network formed during the hydrothermal treatment also may have restricted the swelling of the flour pastes to a minor extent.[11] The low SB of all the processed samples indicated their scope for utilization in development of foods that particularly requires low cooked viscosity.

4.3.10. Wide angle X-ray scattering

The native A-type starch diffraction spectra of raw rice flours with major peaks at Bragg's angle (2θ) positions near 15.2 (Peak 1), 17.4 (Peak 2), 18.1 (Peak 3) and 23.3 (Peak 4) were distinctly yet variably altered on dry heat parboiling (Fig 4.4. a, b, c). The crystallinity was highest in WA(N) followed by LK(N) and HR(N) that was related to the amylopectin content.[31] Significant loss in crystallinity occurred on parboiling (Fig 4.4 d) owing to rapid amylopectin melting as was also observed in our work on steam parboiling of the same rice varieties (Chapter 3, section 3.3.8). This was also indicated by the DG values which were marginally higher for the HTST and LTLT treated WA and LK samples. Temperature severity results in breakdown of starch fractions.[24] As the process temperature was lower in the LTLT process, starch breakdown occurred to a lesser extent allowing rapid recrystallization of the broken chains. HTST process formed even shorter chains due to thermal degradation which failed to recrystallize to the same extent as LTLT samples, thereby giving lower values of % crystallinity. The characteristic spectra obtained for LTLT and HTST treatments were also specifically different from each other for all the

three varieties owing to the moisture content of the end product. Formation and development of newer crystalline polymorphic structures in parboiled rice starch leading to B-type WAXS for retrograded amylose and V-type for amylose-lipid complexes have been reported.[5,32] Lamberts et al (2009) reported presence of amylose crystallites in parboiled rice which also give B-type WAXS pattern.[7] LTLT roasting of the three varieties resulted in distinct superimposition of B- and V-type spectra with minor A-type as suggested by major peaks at 2θ positions of 17.5, 20.0 and minor peaks at 15.2, and 23.3. HTST roasting of HR also resulted in distinct superimposition of the three major types of spectra with peaks at 2θ values of 18.1 (A-type), 20.02 (V-type) and 22.1 (B-type). However, roasted LK and WA samples of HTST gave strictly V-type spectra with a single peak at 2θ positions near 20.02.

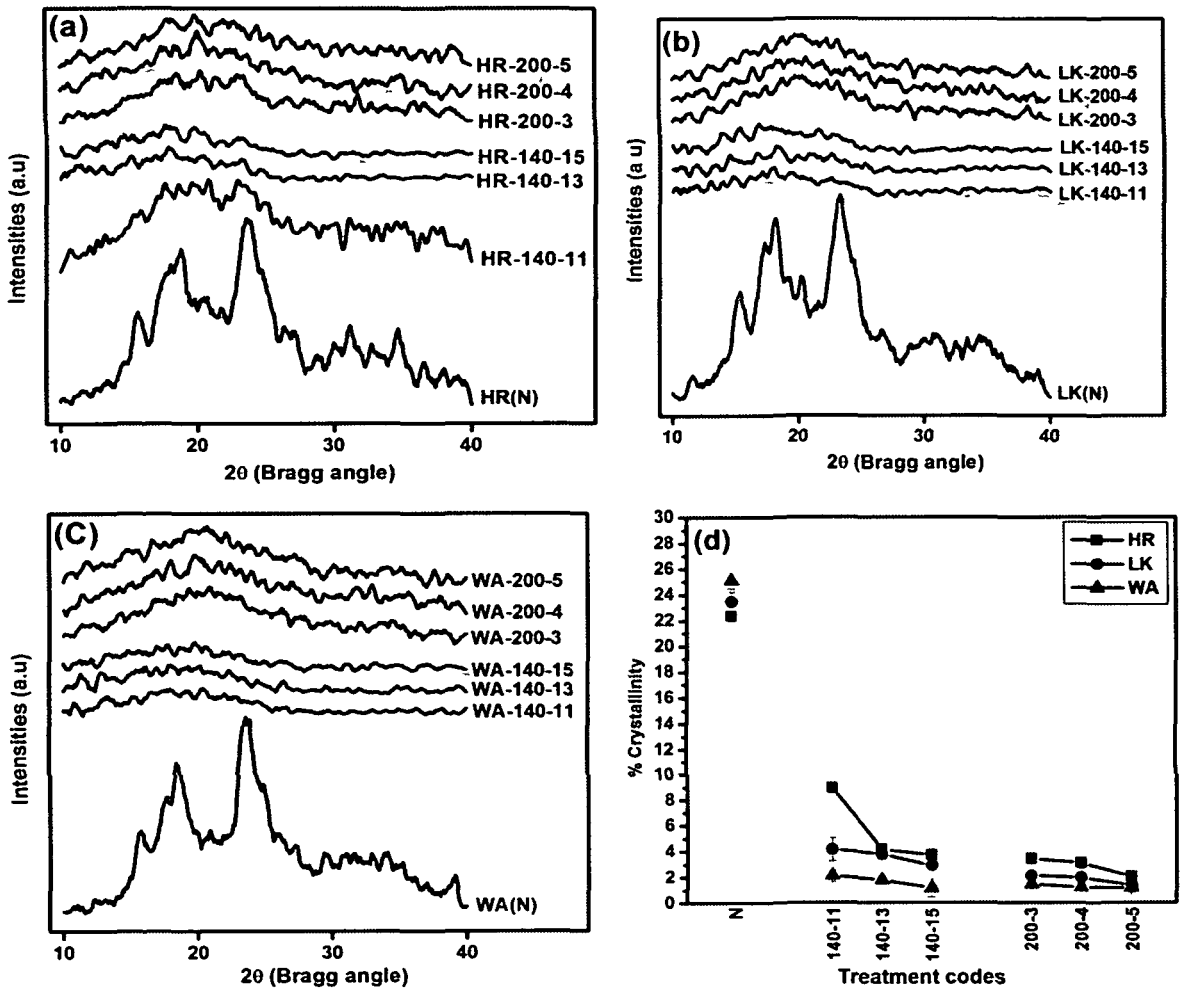

Fig. 4.4. (a), (b) and (c) Wide angle X-ray diffractinon patterns of raw and dry heat parboiled HR, LK and WA samples, respectively; (d) Changes in % crystallinity of different rice samples with processing.

Bhattacharya and Ali (1985) opined that as dry heat parboiling involved rapid bringing down of the moisture content of paddy to below 18%, storing the rice below room temperature thereafter does not produce retrograded starch because there is no free moisture to be released.[3] But in the present work, formation of partial B- and V-type spectra with traces of the native A-type was suggestive of occurrence of at least minor retrogradation or recrystallization and formation of amylose-lipid complexes.[5,7] However, WA(N) with very low amylose content (1.1%, db) exhibiting V-type WAXS spectra upon HTST treatment was suggestive of the binding of lipid with either amylopectin or long chains that are formed due to thermal degradation of amylopectin during dry heat parboiling.[2,5]

4.3.11. Differential scanning calorimetry

Raw rice starch shows a wide range of gelatinization temperature. Our study also supported the same (Table 4.2). The impact of amylose content on the gelatinization temperature has been strongly debated and impact of other factors like starch structures and nutritional composition of rice have been related to it.[33-35] Two distinct peaks could be observed in most of the thermograms (Fig 4.5 a, b and c). While peak 1 was representative of gelatinization of raw rice starch and/or retrograded starch, peak 2 emerging after 90°C represented melting of amylose-lipid complexes.[35] No peak for ungelatinized starch that as was earlier reported to be present from the test for DG was however observed in the DSC curves of the processed samples. This may be due the very low and undetectable amounts of these. Shi and Seib (1992) reported that this major peak shifted towards lower temperature after parboiling due to melting of retrograded amylopectin formed during cooling of the starch gel.[36] Retrogradation results in reordering of the amylopectin branches but in less ordered manner, which explains the lower temperature of melting and lower melting enthalpy than gelatinization of the native starch. Peak 1 for HR-140-15 and HR-200-5 and LK-140-15 was hence for retrograded starch which melted at temperatures of 55.1 °C, 54.1° C and 66.0°C respectively with melting enthalpies of 70.1, 68.8 and 33.3 J/g respectively. This is especially notable as it occurred even though there was excessive moisture reduction during dry heat parboiling. It also supports the observation from XRD patterns of LTLT treated HR samples that the gelatinized amylose in particular had a tendency toward recrystallization.[37] Those fractions may have retrograded during the 1 h saturation time prior to DSC analysis. Some portion of the added water must

have been used by the starch chains to recoil into B-type polymorphic structures representative of retrograded starch that encompasses higher number of water molecules than native A-type, has a weaker coil structure and hence can be easily formed.[38] Samples processed under HTST conditions however did not generate peak 1 in accordance with the WAXS results indicating formation of irreversibly gelatinized starch with no indication of retrogradation.[36] Emergence of peak 2 with minor enthalpy (9.3 J/g) in thermogram of HR(N) may be considered to have emerged or developed under hydrothermal condition similar to cooking during the experiment in the DSC system.[39,40] Peak 2 was not shown by the raw samples of the other two varieties which might be related to comparatively lower availability of free amylose in them. The peak however emerged with much higher intensity for all the three HTST treated samples with LK-200-5 and WA-200-5 giving even higher values of melting enthalpy (39.1 J/g and 38.5 J/g, respectively) than HR-200-5 (37.8 J/g). Extensive thermal breakdown of amylopectin during the high temperature roasting as observed in RVA profiles might have resulted in fractions that readily bind with the lipid bodies during cooling and storage after processing, which was also suggested by WAXS.

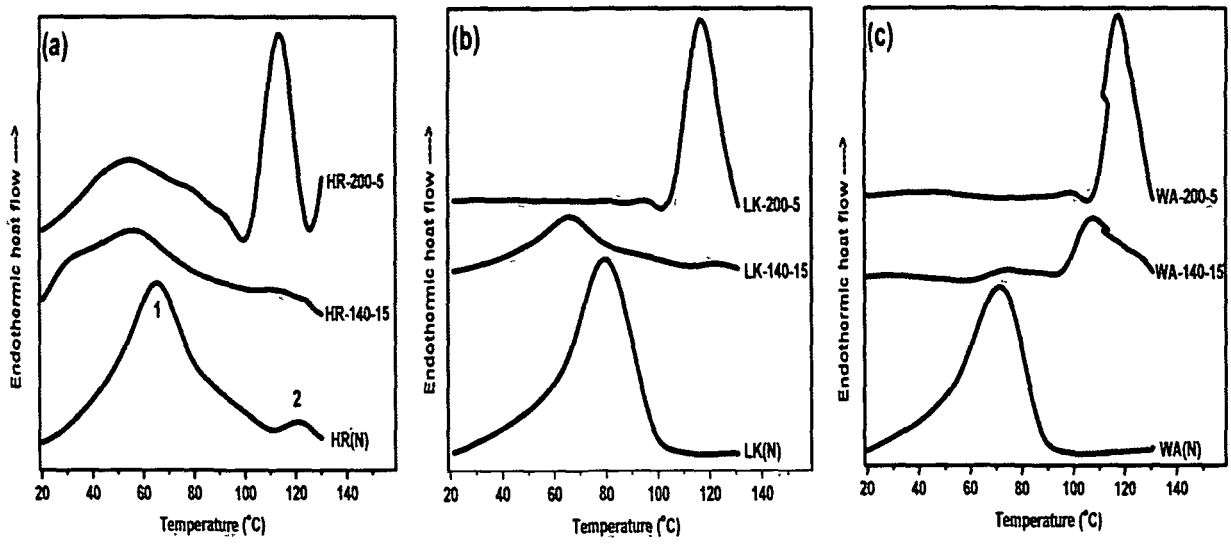

Fig 4.5. DSC thermographs of the flours of raw rice and samples dry heat parboiled at 140°C and 200°C for 5 and 15 min of (a) HR, (b) LK and (c) WA samples. 1 and 2 indicates DSC peaks emerging before and after 90°C that are representative of melting of the native and/or retrograded starch crystallites and of amylose-lipid complexes respectively.

Different polymorphic forms of amylose-lipid complex exist and indirect evidence on existence of amylopectin-lipid complex has also been reported.[41-43] Iturriaga et al (2004) suggested that amylopectin-lipid complex can originate in the very long long amylopectin branches and extra granular complexing lipids.[43]

Table 4.2. DSC thermal parameter values of the flours of raw rice and rice samples processed for 5 and 15 min

Samples	Peak 1[1]				Peak 2[1]			
	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)
HR(N)	44 8±1 31^{e}	65 0±0 98^{cd}	78 2±1 09^{d}	43 4±1 21^{e}	112 0±1 16^{e}	121 6±0 73^{f}	129 3±1 19^{bc}	9 3±0 26^{b}
HR-140-15	40 7±1 23^{b}	55 1±0 23^{b}	70 1±1 08^{b}	26 2±0 88^{c}	100 8±1 17^{bc}	114 5±1 38^{c}	124 7±1 31^{a}	11 7±0 45^{c}
HR-200-5	38 7±0 91^{a}	54 1±0 33^{a}	67 8±0 38^{a}	23 4±0 29^{b}	100 4±1 14^{bc}	113 3±1 16^{b}	125 5±0 84^{c}	37 8±0 56^{e}
LK(N)	56 4±0 88^{f}	79 2±0 18^{g}	99 1±0 72^{f}	48 9±0 44^{f}	-	-	-	-
LK-140-15	50 6±0 68^{d}	66 0±0 43^{d}	77 2±0 19^{c}	33 3±0 61^{d}	112 0±0 89^{e}	120 6±1 01^{e}	129 3±1 09^{bc}	6 8±0 06^{a}
LK-200-5	-	-	-	-	101 6±0 41^{c}	116 3±0 83^{cd}	129 0±1 18^{bc}	39 1±0 39^{g}
WA(N)	51 4±1 11de	71 4±0 76^{e}	87 9±1 01^{e}	49 1±0 34^{g}	-	-	-	
WA-140-15	62 2±0 49^{g}	73 9±0 48^{f}	87 6±0 92^{e}	13 6±0 41^{a}	95 8±0 94^{a}	107 2±0 92^{a}	125 2±1 33^{c}	28 7±0 45^{d}
WA-200-5	-	-	-	-	105 4±0 89^{d}	116 8±0 71^{cd}	129 8±1 44^{d}	38 5±0 28^{f}

[a] Means with the same superscript in a column do not differ significantly from one another ($p > 0.05$)
[1] Peak 1 and peak 2 are the peaks emerging before and after 90°C in the thermograms respectively

In dry heat parboiled samples, however, another hypothesis can be made drown. Gelatinization was accompanied with extensive cleavage in the amylopectin branched structures and formation of smaller branched fractions as suggested by RVA. Such short chains probably gets decoiled and possibly behaves like amylose chains which readily formed complexes with the available lipid molecules. Although present, the intensity of the representative peak for this complex in WAXS was not very sharp as is shown by the complex melting endotherm in DSC. Probably, additional formation of these complexes occurred in the aqueous environment used during DSC sample preparation. The free dehydrated starch fractions formed as a result of gelatinization and subsequent rapid drying were resoponsible for forming the newer structures. Dry heat parboiling followed by hydration can hence be further investigated as a tool for targeted formation of these complexes.

4.3.12. Starch digestibility

Quantified values of the different fractions of enzyme-hydrolysed starch are plotted in Fig 4.6. HR(N) samples exhibited lower *in vitro* digestibility indicated by lower RDS and higher RS than LK(N) and WA(N) implicating the effect of amylose. The RDS level significantly improved after parboiling for all varieties and was highest for

WA samples (66.6 to 94.8%). Extensive starch gelatinization along with molecular breakdown resulted in higher exposure of the starch fractions to the digestive enzymes as was also suggested by the DSC analysis.[44] The dry heat parboiled rice samples were hence quickly digestible. HTST treated WA samples showed highest RDS along with higher levels of SDS. Severity of dry heat parboiling markedly reduced the RS content.[45] RS reduced from 24.5% to 0.4% for HR, 21.2% to 1.9% for LK and 18.4% to 0.1% for WA making the samples almost devoid of RS. The findings indicate that the dry heat parboiled rice samples can have possible application in infant food formulae or may prove useful for post-operation recovery.

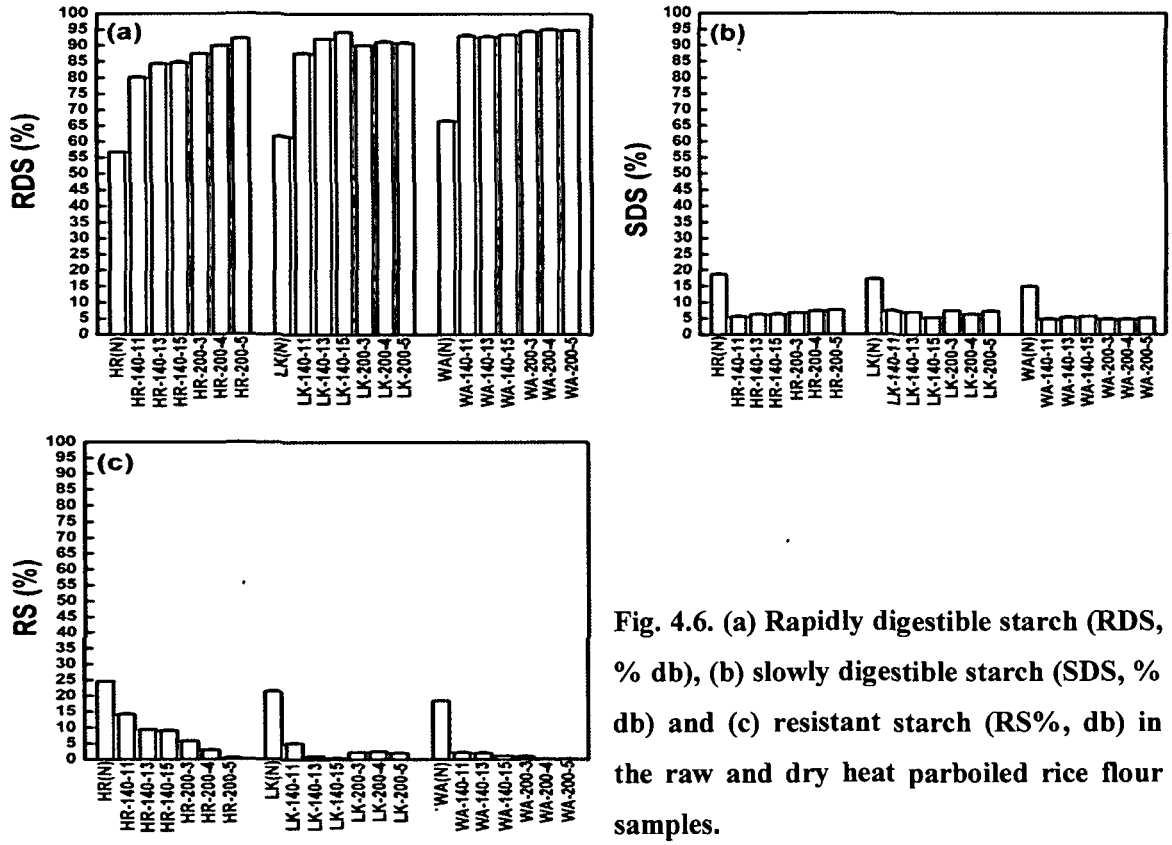

Fig. 4.6. (a) Rapidly digestible starch (RDS, % db), (b) slowly digestible starch (SDS, % db) and (c) resistant starch (RS%, db) in the raw and dry heat parboiled rice flour samples.

4.5. Conclusions

LTLT dry heat parboiling improved the HRY of rice near to 100%. The lower HRY in HTST was attributed to rapid development of temperature and moisture gradients within the kernel. Marked reduction of L/B ratio resulted in processed LK and WA kernels becoming bolder in shape than raw rice kernels. Varietal difference in

arrangement of kernel material after parboiling was hence suggested as L/B ratio of HR kernels were not as affected by the hydrothermal treatments. Biochemical analysis of DG suggested very limited occurrence of ungelatinizad starch in the LTLT processed kernels, which however were not detected by DSC. The dry heat parboiled samples were highly hygroscopic as revealed by EMC-S and SV values. The extensive gelatinization and molecular breakdown led to the development of peculiar physicochemical characteristics. XRD and DSC curves suggested formation of additional B-type retrograded starch in the high amylose HR variety. Although peaks for amylose-lipid complex formation were feeble in the curves of HR, amylopectin-lipid complex in processed LK and WA samples were clearly evident. This created scope for further research and application of the dry heat parboiling technique. The almost complete loss of resistant starch and increased cold paste viscosity may be exploited for targeted use of dry heat parboiled rice in food products specified for special population groups.

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Chapter 5

CHARACTERIZATION OF READY-TO-EAT *KOMAL CHAUL* PROCESSED BY A LABORATORY-SCALE STEAM PARBOILING METHOD

5.1. Introduction

Rice (*Oryza sativa* L.) is an important food crop and is a staple food in many countries.[1] Rice flour is an important ingredient of various food products.[2] About 90% of a polished rice kernel is composed of starch granules. Starch is a semicrystalline biopolymer of D-glucose and primarily composed of linear long chains of amylose and shorter branched clusters of amylopectin. While amylose consists of glucose monomers linked by α-1,4 linkages, amylopectin contains additional α-1,6 branch points. There have also been reports of some intermediate material whose structure falls in between these two fractions.[3] The ratio of amylose and amylopectin basically decides the peculiar properties of the starch granule. Based on the amylose content, Juliano (1979) classified rice into high amylose (>25 %), intermediate amylose (20-25 %), low amylose (7-20 %) and waxy or glutinous (1-2 %) types.[4] All the four types have distinctly different properties. Other factors like granule size, molecular chain length and coiling pattern etc. also play important roles in industrial uses of the polymer. Rice starch has been modified by different methods for different uses.[5,6] Hydrothermal modification is the most popular and widely studied due to the extensive changes brought about in the physical as well as physicochemical properties.[7]

Parboiling is a unique hydrothermal technique involving soaking of paddy in water followed by steaming, drying and milling. Temperature of water used for soaking and the soaking time play vital roles in properties parboiled rice.[8] Parboiled rice possesses many improved properties like higher nutrition, higher head rice yield, lower insect infestation, etc., however, with disadvantages of higher energy input for polishing,

lower keeping quality due to lipid oxidation, browning, etc.[9,10] Parboiled rice flour shows different properties from raw rice flour.[11] Gelatinization and retrogradation are the basic phenomena involved behind all these changes. The starch molecule takes up water when its slurry is heated up to its gelatinization temperature. The granules swell and the helical structures of the chains get decoiled, often accompanied with partial breakdown of the chains. When this gelatinized hot suspension is cooled, retrogradation occurs, involving formation of new crystallites with simultaneous release of the water molecules.[12] The extent of retrogradation is the principal factor for the end product quality.[1] Due to formation of newer polymorphic structures during retrogradation, the native structure is never regained. These molecular changes are reflected in the changed properties of the rice kernel as well as the rice flour. Physical properties of kernel like colour, appearance, kernel dimensions, density, cooking time, moisture absorption, etc. are very important for commercialization of the products.[13] The texture of the cooked rice kernels and the viscosity of the pastes made from their flours also are very important for the consumers' satisfaction and food uses. Bello et al. (2004) observed harder texture of parboiled cooked rice with lesser stickiness as compared to raw rice.[14] Leelayuthsoontorn and Thipayarat (2006) worked on cooked rice texture and reported that higher temperature cooking resulted in softer and stickier texture.[15] The pasting curve of the flour slurry obtained from the Rapid Viscosity Analyzer (RVA) also give an idea of the end product texture.[16] The crystallinity of the starch polymer which is lost after the hydrothermal treatment can be studied by the Wide Angle X-Ray diffractography (XRD) of the rice flour. The diffractograph of raw rice flour shows peaks at 2θ values near 15°, 17°, 18°, and 23°, which is called the typical A-type starch diffraction pattern.[17] However, parboiled rice flour shows altered diffraction patterns with formation of new peaks and loss of some A-type peaks indicating formation of new crystalline polymorphs as well as loss of a few native crystallites. A new peak generally reported at 2θ = 20 depicts formation of amylose-lipid complexes on parboiling treatments, which on thermal analysis using the Differential Scanning Calorimeter (DSC), gives an endothermic melting peak.[18,19] The B-type polymorphs formed after parboiling are characterized by the XRD peaks at 2θ values near 17.1, 22.0 and 24.0, resulting in a C-type (A+B) crystalline structure in the parboiled rice. Thermal analysis gives the amount of crystalline polymorphs present in the sample based on their melting enthalpies.[20] Pregelatinized and retrograded starches have different melting enthalpies

and DSC is an effective tool for this analysis.[21] Another important parameter for all starchy foods is the starch digestibility as the health effects of foods have become a primary concern of the consumers. Hydrothermal processing of starchy foods has been found to be effective in the formation of slowly digestible starch fractions, that lowers the glycemic response.[22] However, conflicting findings have also been reported.[23]

The ease of cooking along with economy in fuel and time consumption have made the instant cooking and quick cooking starchy foods much popular in recent times. A special quick cooking rice product called *komal chaul* is prepared in the Assamese households from ages following traditional parboiling techniques and eaten as a breakfast cereal.[24] *Komal chaul* is principally parboiled rice but the unique characteristic of this parboiled rice is that it does not need any cooking prior to consumption. *Komal chaul* is a whole rice product. Simple soaking of the *komal chaul* makes it soft enough to eat. In the present study, the traditional parboiling technique was improvised at the laboratory scale to obtain *komal chaul* and the important product qualities of the whole kernel and flour of *komal chaul* were characterized.

5.2. Materials and methods

Pure line *Kola chokua* (LK) variety paddy from the harvest of 2011 was purchased from the local farmers of Titabor, Assam (L indicates low amylose and K stands for *Kola chokua*). The rice variety falls under low amylose type with 12.6 % (db) apparent amylose content as was mentioned in chapter 3 (section 3.3.1). The samples were kept at room temperature for 24 h and then stored at 4°C until processing.

5.2.1. Processing and coding of samples

Initially, 400g paddy was added to 10 L water at 100°C in a vessel kept over flame and the water was constantly stirred for 1 min and 3 min. The temperature instantly fell down to 92±1°C and thereafter increased to 100°C in 2.5 min. The vessel was covered with a thick gunny bag and kept at room temperature (27±2°C) for 18 h to allow the paddy to hydrate. The excess water was decanted after 18h and the soaked paddy was immediately steamed in an autoclave (Equitron 7407ST, India) fitted with a pressure gauge for 10 (mild treatment), 15 (moderate treatment) and 20 min (severe treatment) at conditions of 0 psig (100°C, open steaming) and 15 psig (121°C, pressure steaming), respectively. Drying was carried out at room temperature for 48 h followed by milling (8 %, weight basis) in a Satake huller and polisher (Satake, Japan). A portion of each sample was

ground into flour in a laboratory grain mill (Fritsch Pulverisette 14) and passed through a 100 μm sieve. All the kernel and flour samples were stored in polypropylene pouches at 4°C for further analysis. The samples were coded as per the steaming conditions applied (Table 5.1). The raw and hot soaked but non-steamed samples were primarily coded as N, open steamed samples as O and pressure steamed samples as P. The primary codes were followed by time (in minutes) of hot soaking followed by the steaming time (in minutes). For examples, pressure parboiled paddy hot soaked for 1 min and steamed for 15 min was coded as P-1-15.

Table 5.1. Processing conditions and sample codes.

Broad classification	Soaking time at 100°C (min)	Steaming time (min)	Sample codes
N	-	-	N
N	1	-	N-1-0
O	1	10	O-1-10
O	1	15	O-1-15
O	1	20	O-1-20
P	1	10	P-1-10
P	1	15	P-1-15
P	1	20	P-1-20
N	3	-	N-3-0
O	3	10	O-3-10
O	3	15	O-3-15
O	3	20	O-3-20
P	3	10	P-3-10
P	3	15	P-3-15
P	3	20	P-3-20

5.2.2. Colour measurement

The Hunter 'L', 'a' and 'b' colour values of all kernel samples were obtained by a colour measurement spectrophotometer (Hunter Color-Lab Ultrascan Vis). From these values, the hue angle (H) and chroma (C) values were calculated as per previous reports.[25,26]

$H = \tan^{-1}(b/a)$ **Eq. 5.1**

$C = (a^2+b^2)^{1/2}$ **Eq. 5.2**

5.2.3. L/B Ratio

The length (L) and breadth at the midpoint (B) of the polished kernels were determined using a Vernier calipers and a screw gauge (Mitutoyo, Japan) respectively and the L/B ratio was calculated.

5.2.4. Porosity (ε) bulk density (ρb) and true density (ρt)

ρb and ρt were first determined for calculating ε. An established method was slightly modified for determining ρb.[13] Briefly, polished grains were allowed to fall into a measuring cylinder from a constant height up to a known volume. The top level was adjusted by gentle tapping. The weight of the filled grains was determined and ρb was calculated.

$$\rho b = \frac{\text{mass of grain}}{\text{volume occupied}} \qquad \text{Eq. 5.3}$$

True volume was determined by the toluene displacement method. Briefly, to a known volume of toluene (Merck, India) in a measuring cylinder, polished kernels of known weight were immersed and the volume displaced by the kernels was recorded and the density (ρt) was calculated.

$$\rho t = \frac{\text{mass of grain}}{\text{volume of toluene displaced}} \qquad \text{Eq. 5.4}$$

The porosity (ε) was determined from values obtained from Eq 5.3 and Eq 5.4.

$$\varepsilon\,(\%) = \frac{(\rho t - \rho b)}{\rho t} \times 100 \qquad \text{Eq. 5.5}$$

5.2.5. Cooking time (T)

Cooking time was determined by an objective method.[27] Kernels weighing 20 g were cooked in 200 ml water at 98°C on a hot plate. After 10 min of cooking, ten kernels were brought out from the middle of the cooked mass and pressed between two clean glass slides. The number of translucent kernels were counted and recorded. The pressing test was repeated after each minute and the time at which 90 % of the kernels were translucent was considered as the cooking time of that sample.

5.2.6. Equilibrium moisture content on soaking at room temperature (EMC-S)

Equilibrium moisture content (EMC-S, %, db) of polished rice kernels soaked at room temperature for 4 h were determined by the method of Indudhara Swamy et al

(1971).[28] Whole-grain milled rice (about 3-5 g) with 11 to 13% moisture content (db) was put in 50 mL water in a covered 100 mL beaker and left aside. The rice was strained through a wire strainer after 20-24 h and dried between Whatman No.1 filter paper sheets. The moisture content of the rice was determined by a drying method (AOAC, 2000)[29] and EMC-S calculated.

$$\text{EMC}\,(\%, \text{db}) = \left[\frac{\text{Moisture evaporated}}{\text{Dried weight of kernels (g)}}\right] \times 100 \qquad \text{Eq. 5.6}$$

5.2.7. Sediment volume (SV)

The test for SV gives an indirect indication of degree of gelatinization of pregelatinized rice flour.[30] Briefly, 1 g each of desiccated flour samples was taken in a measuring cylinder and 15 mL of 0.05 N hydrochloric acid was added to it with agitation after each 5 min for 1 h. The level of the flour sediment was observed after 4 h and was reported as the SV (ml) of the sample.

5.2.8. Cooked rice texture

Briefly, 20 g samples from both raw and processed rice kernels were cooked for their cooking times and texture profile analysis (TPA) of the cooked grains was performed using a Texture Analyzer (TA.HD.plus, Stable Micro Systems, UK). A 5 kg load cell fitted with a cylindrical probe of 2 cm diameter was used for performing the two-cycle compression test.[31] A single kernel was collected from the middle of the cooked rice mass and compressed to 70 % at 0.5 mm/s. The time between two chews was 3 s. All the TPA parameters, viz., hardness, fracturability, adhesiveness, springiness and chewiness were determined by the inbuilt software (Exponent Lite). Ten replicates for each sample were run and the mean values for each parameter taken. In addition to this, looking at the quick cooking nature of the product, the samples were soaked in excess water at 20°C and 50°C for 60 and 20 min respectively in a hot water bath (Labtech, India) and the TPA parameter values were compared.

5.2.9. Pasting properties

The pasting profiles of flour suspensions (12 % w/w; 28 g total weight) were recorded using a Rapid Visco Analyser (RVA Starchmaster2, Newport Scientific Instruments). The Ricel profile of Newport Scientific was used, where the samples were

held at 50°C for 1 min, heated from 50°C to 95°C at 12°C/min, held at 95°C for 2.40 min followed by cooling to 50°C at 11.25°C/min and finally holding at 50°C for 1 min. The pasting curves obtained were compared and the pasting parameters, viz., peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown (BD) and total setback (SBt) were recorded. PV is the maximum viscosity during heating, HPV is the minimum viscosity at 95 C, CPV is the final viscosity at 50°C, BD is obtained after subtracting HPV from PV. SBt is obtained after subtracting PV from CPV.

5.2.10. Wide angle X-ray scattering (WAXS)

WAXS difractograms were obtained using a Rigaku Miniflex X-ray diffractometer with a Cu target and 'K' value of 1.5404 A° operating at 30 kV acceleration potential and 15 mA current with a copper target. The scanning range was 10–40° of 2θ values in steps of 0.05°. The total area under the curve and the area under each prominent peak were determined and the percentage crystallinity was calculated (Singh et al., 2006).

$$\% \text{ Crystallinity} = \left(\frac{\text{Area under the peaks}}{\text{Total area under the XRD curve}}\right) \times 100 \qquad \text{Eq.5.1}$$

5.2.11. Thermal analysis

A Differential Scanning Calorimeter (model DSC-60; Shimadzu, Tokyo, Japan), periodically calibrated with pure indium for heat flow and temperature was used for thermal profile analysis of the flour samples. Flour to moisture ratio (1:2) was taken in an aluminium pan and saturated for 12 h at 4°C. The pan was then hermetically sealed and heated against an empty reference pan from 25°-150°C at a heating rate of 5 C/min under N_2 atmosphere. The onset (To), peak (Tp), and conclusion (Tc) temperatures and enthalpy of gelatinization (ΔH, J/g) were obtained from the thermograms using TA-60WS software.

5.2.12. Starch digestibility

The extent of enzymatic hydrolysis leading to release of glucose from starch gives an indication of digestibility of starchy foods. The amount of glucose liberated on hydrolysis gives a measure of digestible starch fractions present in it. The *in vitro* starch hydrolysis rates (Goni et al., 1996) of the rice flour samples were estimated.[33] A solution containing 1g of pepsin in 10 mL of HCl-KCl buffer (pH 1.5) was prepared and 0.2 mL of this solution was mixed with 50 mg of flour sample and kept for deproteinisation in a

shaking water bath at 40°C for 60 min. The volume was made up to 25 mL with Tris-Maleate buffer (pH 6.9). To this, 5 mL of a solution of in Tris-Maleate buffer containing 2.6 IU pancreatic α-amylase (Sigma-Aldrich) was then added to each sample and incubated at 37°C. One millilitre aliquot was taken out from each tube after each 30 min from 0 min up to 180 min to determine the hydrolysis rate at different times. The aliquots were boiled to inactivate the enzymes and stored under refrigeration for further analysis. Then 3 mL of 0.4M Sodium acetate buffer (pH 4.75) containing 60 μL of amyloglucosidase (Sigma-Aldrich) was added to each aliquot and incubated at 60°C for 45 min to hydrolyse the digested starch into glucose. The glucose liberated was estimated by the DNS (3,5-dinitrosalicylic acid) method and was converted to starch by multiplying by a factor of 0.9. The degree of hydrolysis was calculated as the percentage of starch degraded from the total starch content.

5.2.13. Statistical analysis

All the experiments were carried out in three or more replicates and the means are reported. Significant differences between the means by Duncan's multiple range test at a significance level of 95% were determined using SPSS 11.5 (SPSS Inc., USA).

5.3. Results and discussion

5.3.1. Colour measurement

It was observed that the lightness values (L) decreased on hot soaking alone compared to raw and further with extent of steaming (Table 5.2). The hue angle (H) value also exhibited a similar fall indicating increased redness in the samples.[34] These values indicating loss of whiteness and significant rise in the redness may be attributed to the migration of husk and bran pigments into the endosperm as the husk of the paddy LK was highly pigmented.[35] Additionally, there might have also occurred Maillard browning due to the high heat applied during soaking and steaming. The C value indicative of colour purity and clarity increased markedly with extent of processing indicating more uniform product appearance.[25,36] More drastic changes in the colour values were observed in a different study (Chapter 3, section 3.3.3) where similar steaming conditions were employed with the same paddy variety after the same soaking duration but without the short-term boiling step. An explanation for this may be that the hot soaking causes surface gelatinization of the rice starch accompanied by pigment migration. On cooling, the gelatinized surface starch retrogrades. The retrograded layer has a harder texture and

hence might have served as a partial barrier that lowered the migration of pigments during the steaming step.[1,37]

5.3.2. L/B ratio

Hot soaking caused increase in the grain L/B values (Table 5.2). While the L values of the kernels remained almost unchanged on open steaming, pressure steaming caused marked increase in the L values.[38] This was however accompanied by simultaneous decrease in the B values which was indicative of elastic stress development in the kernels during steaming and subsequent drying.[39,40] The pattern of increase in L/B ratio on parboiling was found to be variety dependent by Siddiquee et al (2002).[41] Saeed et al. (2011) have however reported general increase in the dimensional ratio during parboiling of five different rice varieties.[42] Increase in L/B ratio in the present study was more prominent in the pressure steamed samples than the open steamed samples.

5.3.4. Porosity

The pattern of change in porosity on parboiling is dependent on the rice variety and also on the final moisture content of the paddy.[43,44] The changes in bulk and true density were marginal; both properties increased with parboiling. The marginal decrease in porosity with increasing L/B ratio, however was not in accordance with Bhattacharya et al. (1972) who observed positive relationship of porosity (ε) with kernel length (L).[45] The decrease in porosity was higher for the pressure parboiled samples indicating better packing properties.

5.3.5. Cooking time

Table 5.2 shows the values of the cooking times of the different samples. T was highest for the raw LK(N) kernels. LK(N) required around 18 min to cook. Hot soaking only marginally lowered the T values, which was further reduced on both open and pressure steaming which reflected the effect of gelatinization of starch. LK3-15-10 exhibited the fastest cooking, with almost half the T value of LK(N). The very low cooking time of severely parboiled rice reflected the effect of both gelatinization and thermal degradation. Although, parboiling is said to increase the cooking time of rice kernels, reduction in cooking time in heat moisture treated starches have also been reported.[46,47] Further, the low cooking time of *chokua* parboiled rice may be attributed to the low amylose content of the rice. As amylose content is low in *chokua* rice, the extent of retrogradation of the gelatinised starch during drying was restricted, which was reflected in the cooking time.

5.3.6. Equilibrium moisture content on soaking at room temperature

Marked increases in EMC-S (%, db) were observed on processing (Fig 5.1a). Although LK1(N) and LK3(N) did not vary much in the EMC-S, both open and pressure steaming resulted in higher water uptake by the kernels. This increase was higher in the pressure steaming of 3 min hot soaked samples than 1 min hot soaked samples. EMC-S was highest for LK3-15-20 followed by LK1-15-20 with values of 259.9% and 236.6% respectively. The increased EMC-S was probably due to the thermally degraded starch in the samples.

5.3.7. Sediment volume

SV also showed a similar pattern as EMC-S, with higher volume increase by the rice flour in acidic solution with increasing severity of processing (Fig 5.1b). It was indicative of increased degree of starch gelatinization and subsequent thermal degradation with severity of processing.[30]

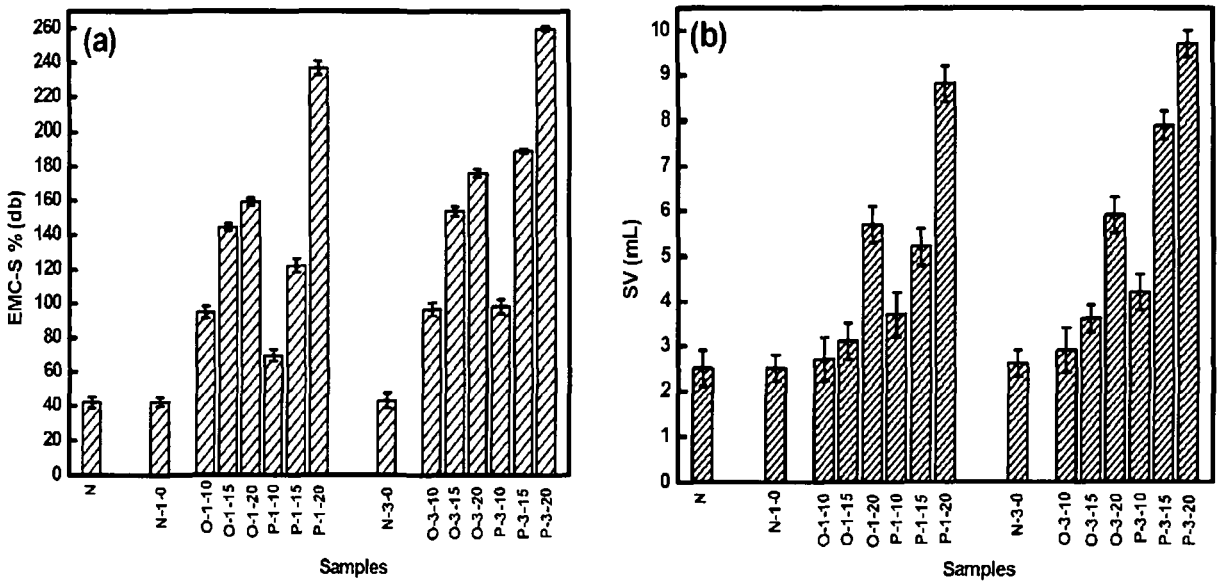

Fig. 5.1. (a) Equilibrium moisture contents on soaking (%, db) and (b) Sediment volumes (mL) of the raw and processed samples.

5.3.8. Cooked rice texture

The textural properties of open pan cooked (100°C) samples and samples soaked at 20°C and 50°C for 60 and 20 min respectively were studied (Fig 5.2). Hardness decreased

Table 5.2. Color values, L/B ratio, density, porosity and cooking time of the raw and processed rice kernels.

Samples	Color					L/B ratio			Bulk density	True density	Porosity	Cooking time
	L	a	b	H	C	L	B	L/B	ρ_b	ρ_t	ε (%)	T (min)
N	79.3±0.3^{o}	0.6±0.1^{a}	14.2±0.1^{a}	87.4±0.4^{o}	14.2±0.6^{a}	6.0±0.3^{a}	2.7±0.2^{a}	2.1±0.2^{a}	0.7±0.3^{a}	1.4±0.2^{a}	48.6±0.3^{j}	18.1±0.4^{o}
N-1-0	78.1±0.4^{n}	2.0±0.1^{b}	15.2±0.3^{b}	82.3±0.3^{n}	15.3±0.4^{b}	6.0±0.3^{a}	2.7±0.4^{a}	2.2±0.1^{b}	0.7±0.5^{b}	1.4±0.1^{a}	46.5±0.4^{e}	17.1±0.3^{n}
O-1-10	75.1±0.3^{m}	3.2±0.2^{d}	19.1±0.4^{d}	80.3±0.4^{l}	19.4±0.2^{d}	6.0±0.2^{a}	2.7±0.7^{a}	2.2±0.1^{b}	0.7±0.4^{bc}	1.4±0.2^{ab}	46.2±0.4^{d}	16.1±0.4^{l}
O-1-15	69.1±0.3^{i}	5.4±0.1^{h}	22.1±0.8^{h}	76.2±0.3^{h}	22.7±0.3^{h}	6.0±0.4^{a}	2.7±0.4^{b}	2.2±0.1^{b}	0.7±0.5^{bc}	1.4±0.1^{bc}	46.6±0.7^{f}	14.2±0.1^{j}
O-1-20	63.3±0.2^{e}	8.0±0.4^{l}	24.3±0.7^{k}	71.8±0.6^{d}	25.6±0.3^{k}	6.1±0.1^{b}	2.7±0.4^{b}	2.2±0.1^{b}	0.8±0.7^{cd}	1.4±0.1^{bc}	45.9±0.6^{b}	13.6±0.2^{f}
P-1-10	71.2±0.4^{k}	4.3±0.4^{g}	21.1±0.4^{g}	78.4±0.6^{i}	21.5±0.4^{g}	6.0±0.3^{a}	2.7±0.3^{b}	2.2±0.3^{bc}	0.7±0.3^{bc}	1.4±0.2^{bc}	46.6±0.4^{f}	14.2±0.4^{k}
P-1-15	66.9±0.4^{g}	6.4±0.5^{j}	22.4±0.5i	73.9±0.6^{f}	23.3±0.1^{i}	6.1±0.2^{b}	2.7±0.1^{b}	2.2±0.3^{bc}	0.8±0.4^{cd}	1.4±0.3^{bc}	45.9±0.3^{b}	12.8±0.4^{d}
P-1-20	57.8±0.4^{b}	9.6±0.6^{n}	25.1±0.6^{n}	68.9±0.5^{b}	26.9±0.2^{n}	6.1±0.2^{b}	2.6±0.4^{bc}	2.2±0.3^{bc}	0.8±0.3^{e}	1.4±0.1^{cd}	45.6±0.3^{a}	11.6±0.3^{a}
N-3-0	73.0±0.3^{l}	2.4±0.4^{c}	15.7±0.6^{c}	81.1±0.6^{m}	15.9±0.4^{c}	6.0±0.5^{ab}	2.6±0.2^{a}	2.2±0.1^{b}	0.7±0.1^{bc}	1.4±0.1^{a}	46.8±0.2^{h}	16.9±0.5^{m}
O-3-10	71.0±0.3^{j}	3.8±0.3^{e}	20.2±0.3^{e}	79.1±0.3^{k}	20.5±0.8^{e}	6.0±0.5^{ab}	2.6±0.2^{b}	2.2±0.1^{b}	0.7±0.1^{bc}	1.4±0.1^{bc}	46.6±0.2^{f}	14.1±0.4^{h}
O-3-15	64.4±0.6^{f}	5.8±0.2^{i}	23.6±0.3^{j}	76.1±0.4^{g}	24.3±0.3^{j}	6.0±0.3^{a}	2.6±0.3^{bc}	2.2±0.1^{b}	0.7±0.1^{bc}	1.4±0.2^{cd}	46.9±0.3^{i}	13.3±0.4^{e}
O-3-20	60.0±0.5^{c}	9.2±0.7^{m}	24.9±0.4^{m}	69.7±0.5^{c}	26.6±0.7^{m}	6.1±0.3^{b}	2.6±0.3^{c}	2.3±0.2^{d}	0.8±0.2^{cd}	1.5±0.1^{e}	46.6±0.1^{g}	14.1±0.2^{i}
P-3-10	67.7±0.3^{h}	4.0±0.3^{f}	20.8±0.3^{f}	78.8±0.3^{j}	21.2±0.4^{f}	6.0±0.3^{a}	2.6±0.7^{bc}	2.3±0.3^{d}	0.7±0.1^{bc}	1.4±0.2^{cd}	46.9±0.3^{i}	13.9±0.3^{g}
P-3-15	61.2±0.2^{d}	7.6±0.1^{k}	24.7±0.3^{l}	72.7±0.2^{e}	25.9±0.3^{l}	6.1±0.3^{b}	2.6±0.2^{c}	2.3±0.2^{d}	0.8±0.2^{cd}	1.5±0.1^{e}	46.6±0.3^{g}	11.8±0.4^{b}
P-3-20	54.1±0.7^{a}	12.7±0.3^{o}	29.8±0.4^{o}	66.9±0.3^{a}	32.4±0.5^{o}	6.1±0.1^{b}	2.5±0.2^{c}	2.3±0.1^{d}	0.8±0.1^{e}	1.5±0.1^{e}	46.0±0.1^{c}	9.3±0.5^{c}

The means followed by a common letter are not significantly different by Duncan's Multiple Range Test at $p<0.05$

progressively with extent of processing.[8] Adhesiveness of the cooked kernels increased on open steaming which might be attributed to formation of hot water soluble fractions[48] while pressure steaming exhibited decrease with severity of pressure steaming possibly due to thermally degraded starch. Springiness values, however, showed marked increase for both the processing types. The presence and type of amylose and amylopectin fine structures in the starch plays important role in the rice TPA parameters creating scope for further research in this area.[49] Soaking at 50°C for 20 min gave texture parameter values nearer to that of the open cooked samples as compared withsoaking in water at 20°C for 60 min. This similarity was more prominent for the pressure processed samples. From the TPA results, it is evident that just soaking at 50°C for 20 min of the hot water soaked and pressure steamed low amylose *chokua* rice gave similar textural as open pan cooking of such treated rice. Such processing conditions hence obviates the need of cooking and converts the processed *chokua* rice into ready to eat cereal.

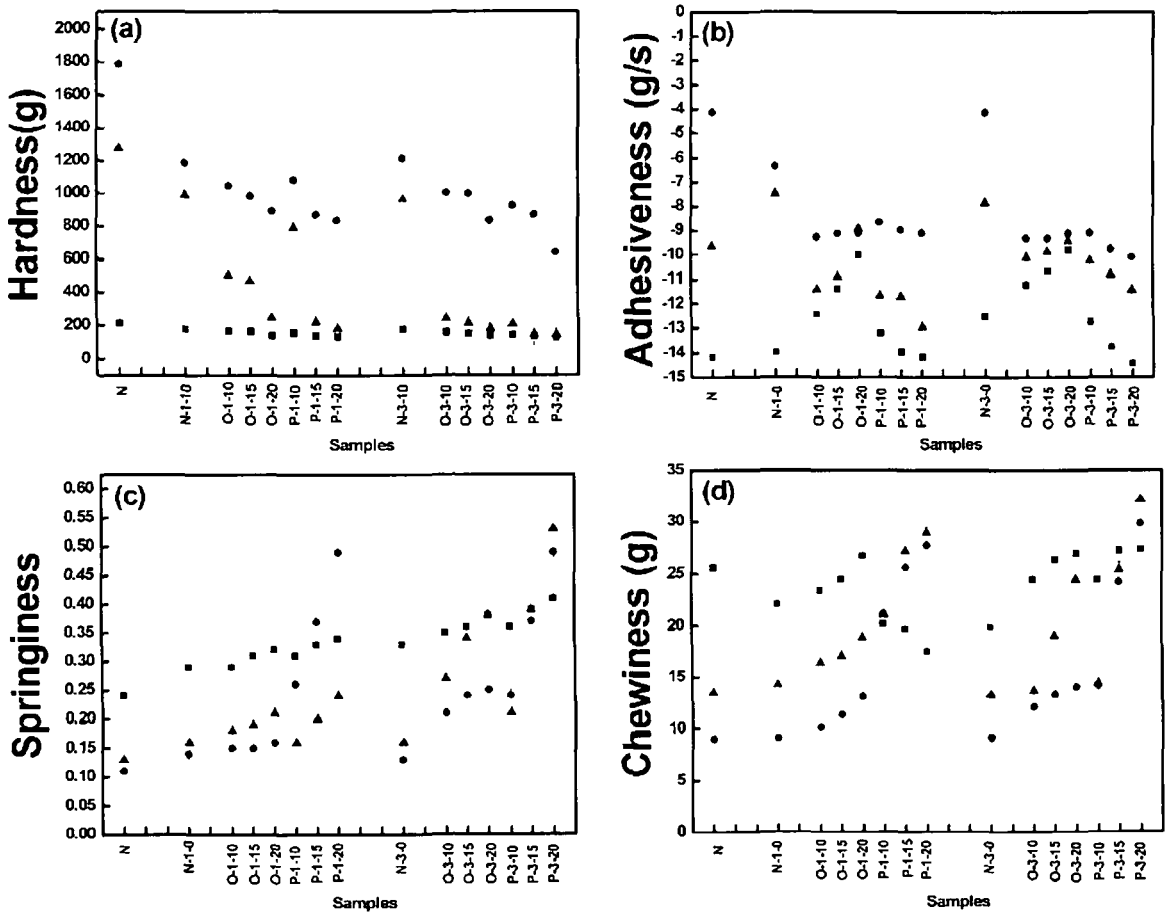

Fig. 5.2. The TPA parameter values viz (a) Harness (g) (b) Adhesiveness (g/s) (c) Springiness and (d) Chewiness (g) of the parboiled samples cooked at 100°C till done (■), 50°C for 20 min (▲) and 20°C for 60 min (●).

5.3.9. Pasting properties

Both 1 and 3 min hot soaked samples (not steamed) had pasting profile similar to the corresponding raw, however, the viscosity at PV, HPV, and CPV were considerably higher (Fig 4). PV for N-1-0 was 4.558 Pas and for N-3-0 was 3.932 Pas. On open steaming, while PV remained almost constant for the LK1 samples (3.577–4.646 Pas), minor drop was

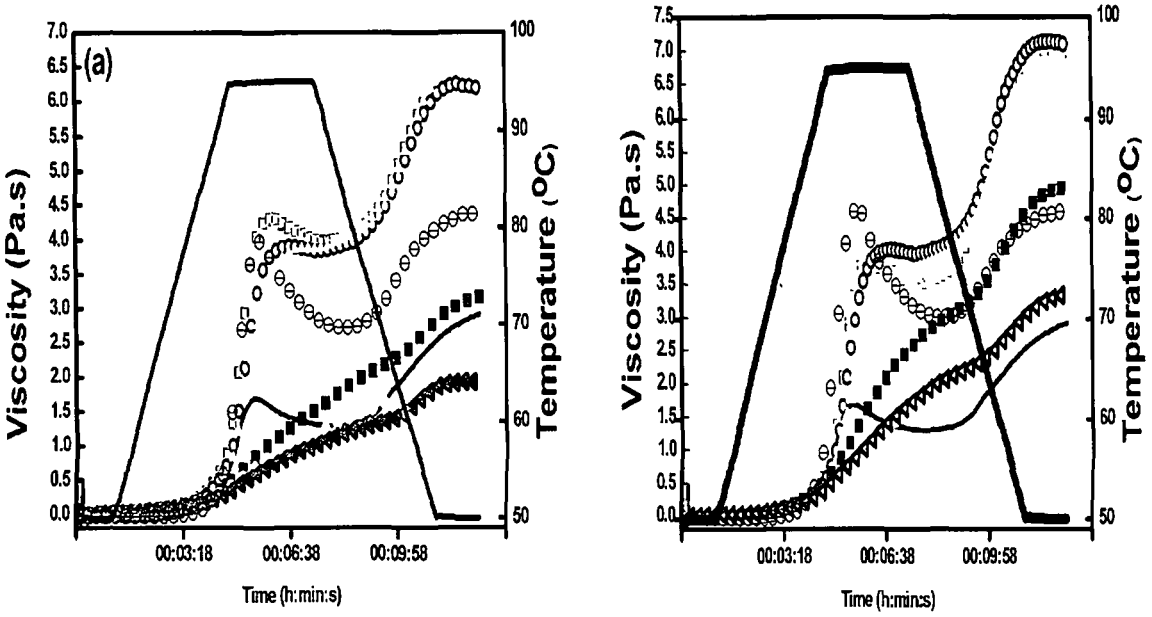

Fig. 5.3. RVA pasting curves of parboiled samples hot soaked for (a) 1 min and (b) 3 min. The representations of the symbolic curves are as follows: Native (-), hot soaked and non-steamed (θ), -0-10 (□), -0-15 (o), -0-20 (Δ), -15-10 (■), -15-15 (•) and -15-20 (◂).

observed for the processed LK3 samples (4.109–3.375 Pas), which was suggestive of lower thermal stability of the polymeric pattern developed on hot soaking. The CPV for the open steamed samples, O-3-10 (6.924 Pas), O-3-15 (7.092 Pas), and O-3-20 (6.682 Pas) were however higher than O-1-10 (6.246 Pas), O-1-15 (6.191 Pas), and O-1-20 (6.446 Pas). SBt values were similarly higher. This may be explained as to the formation of short linear molecular chains on thermal degradation which probably were able to reassociate forming retrograded starch. Pressure steaming resulted in gradual yet extensive drop in the PV as was also evident in some earlier works.[50,51] This drop is similar to that of acid thinned starch used in paper and textile industries.[52] This was accompanied by very low BD with higher CPV. Severe processing causes thermal degradation of starch polymer structure.[53] Increase in the final slurry viscosity, hence may be attributed to leaching of the degraded simpler chains causing rise in slurry

densities. The almost continuous rise in the slurry viscosity with minor BD throughout the RVA cycle indicated the thickening property of the pressure steamed samples, suggesting its suitability for specific uses.

5.3.10. Wide angle x-ray scattering

The native A-type diffraction pattern of LK(N) with characteristic peaks near 15.1, 17.1, 18.3 and 23.2 remained unaltered on hot soaking (Fig 5.4a). While both open and pressure steamed samples from LK1 and only open steamed samples from LK3 conditions gave a mixed pattern with peaks corresponding to all A(2θ = 15.1°, 23.2°), B(2θ = 17.3°) and V-types (2θ = 20°), the high pressure processed LK(3) samples exhibited almost amorphous diffractographs with feeble peaks indicating mixed pattern of B (2θ = 17.3° and 24.1°) and V-types (2θ = 20°).[19,54] Crystallinity was maximum in raw rice. Hot soaking reduced crystallinity. In both 1 min and 3 min series of processed samples, open steaming showed gradual increase in % Crystallinity, while for pressure steamed samples, the % Crystallinity was less in 15 min steaming time than 10 min and 20 min steaming. Such changes in crystallinity were also reported by Yu et al. (2010) and Manful et al. (2008).[1,55] Probably, the new polymorphic forms (B and V type) had increased the % crystallinity (Fig 5.4b).

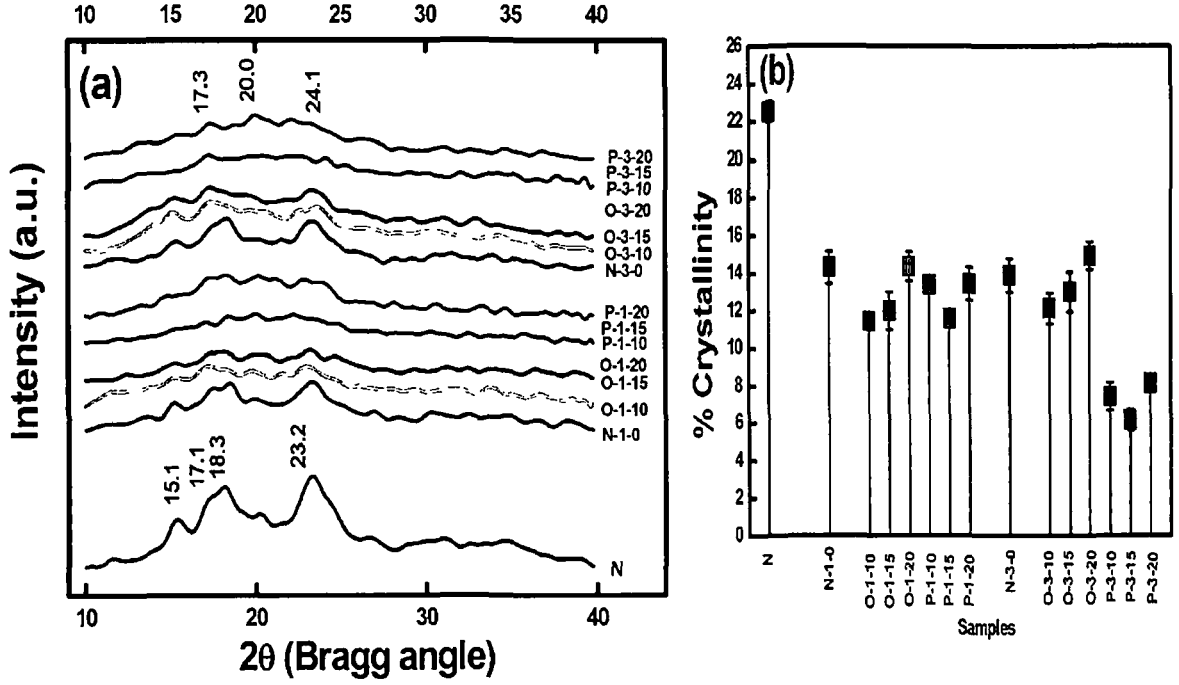

Fig. 5.4. (a) The XRD patterns of raw and processed flour samples with peaks indicated and (b) % Crystallinity of the samples with processing.

5.3.11. Thermal Properties

The DSC thermographs of the samples are shown in Fig 5.5 and the thermal parameter values presented in Table 5.3. Hot soaked sample with no steaming showed marked decrease in melting enthalpy of the rice flour.[55] However, mildly parboiled samples showed higher transition enthalpies with a shift of the melting peak towards higher temperatures.[56] Further higher treatment lowered the enthalpy values with a shift of the peak towards lower temperature again as was also evident in the RVA patterns of the samples.[50] This indicates differences in the thermal properties of the different polymorphs formed depending upon the type and extent of processing. Thermal stability was found to lower with processing severity.[49] Further, hot soaked LK1(N) and LK3(N) with mildly processed LK1-0-10 and the pressure steamed LK1-15-15, LK1-15-20, LK3-15-10, LK3-15-15 and LK3-15-20 did not exhibit any endotherm for amylose-lipid complex melting. The endotherms were observed primarily in the moderately processed samples and all were of type I (melting temperature < 100°C) as reported by Biliaderis and Galloway (1989).[57]

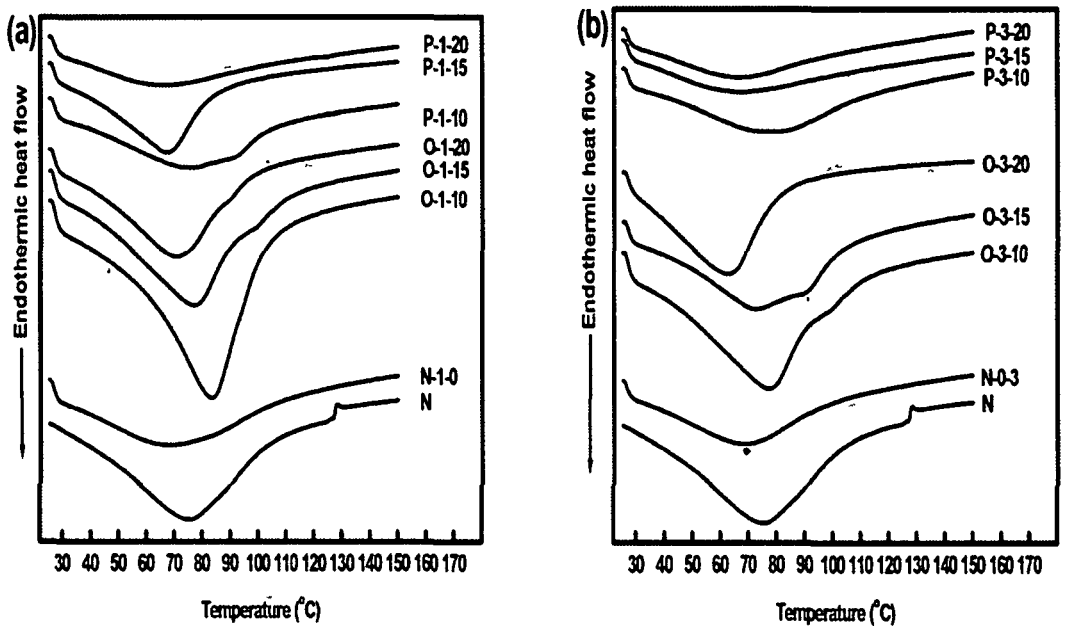

Fig. 5.5. DSC thermographs of parboiled samples hot soaked for (a) 1 min and (b) 3 min.

Table 5.3. DSC thermal parameter values of the raw and processed rice flour samples.*

Sample	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)
N	63.4±1.2^{m}	75.1±0.8^{k}	82.3±1.2^{i}	10.6±^{i}
N-1-0	50.0±2.1^{c}	68.6±1.9^{e}	75.2±2.1^{d}	8.6±1.4^{f}
O-1-10	68.1±1.4^{n}	83.1±1.4^{o}	90.1±1.4^{m}	45.4±1.3^{o}
O-1-15	69.2±1.3^{o}	78.9±2.2^{m}	83.3±1.4^{j}	20.4±1.3^{m}
O-1-20	59.8±1.2^{j}	70.6±1.2^{h}	80.0±1.3^{f}	12.8±1.6^{j}
P-1-10	61.1±2.3^{l}	72.0±2.1^{j}	80.0±2.2^{f}	9.4±1.4^{h}
P-1-15	57.8±1.4^{g}	69.4±1.2^{f}	74.9±1.2^{b}	8.2±1.1^{e}
P-1-20	53.3±2.1^{f}	67.8±1.3^{d}	76.2±2.3^{e}	7.2±0.8^{d}
N-3-0	50.1±1.2^{d}	69.8±1.2^{g}	84.2±1.0^{k}	9.2±1.1^{g}
O-3-10	60.0±2.1^{k}	78.2±0.4^{l}	89.2±2.1^{l}	26.8±0.7^{n}
O-3-15	59.3±1.2^{i}	71.9±1.1^{i}	80.2±1.2^{g}	17.2±0.9^{l}
O-3-20	51.8±2.3^{e}	62.0±2.1^{a}	70.1±1.3^{a}	17.2±1.3^{k}
P-3-10	58.3±1.4^{h}	79.9±2.0^{n}	95.2±2.2^{n}	7.1±1.2^{c}
P-3-15	47.7±2.2^{a}	66.3±1.6^{c}	75.0±1.1^{c}	6.3±1.6^{a}
P-3-20	49.1±1.2^{b}	66.2±1.3^{b}	82.2±1.2^{h}	6.3±0.6^{b}

*To is onset temperature, Tp is peak temperature, Tc is conclusion temperature and ΔH is enthalpy of the crystallite melting endotherm . The means followed by a common letter are not significantly different by Duncan's Multiple Range Test at $p<0.05$

5.3.12. Starch digestibility

Starch digestibility rapidly increased till 90 min of incubation for all flour samples (Fig 5.6), thereafter remained almost constant till 180 min. The raw rice flour showed comparatively lower hydrolysis rate than the rest (69.3 % after 180 min). Hot soaked samples did not differ in starch digestibility from raw. Mild open steaming gave higher digestibility than moderate and severe steaming indicating formation of newer indigestible fractions on retrogradation of gelatinized starch as also was observed by previous workers.[22] Increasing severity of open steaming hence might result in the formation of newer enzyme resistant fractions. The trend was however reversed in pressure steamed samples after 1 and 3 min hot soaking times. Steaming severity increased the digestibility markedly and was highest (93.8 % after 180 min) for LK3-15-20, also observed by Takahashi et al (1994) and Niba (2003).[58,59] Hence, the results were indicative of clear differences in starch digestibility between the products of the two processes.

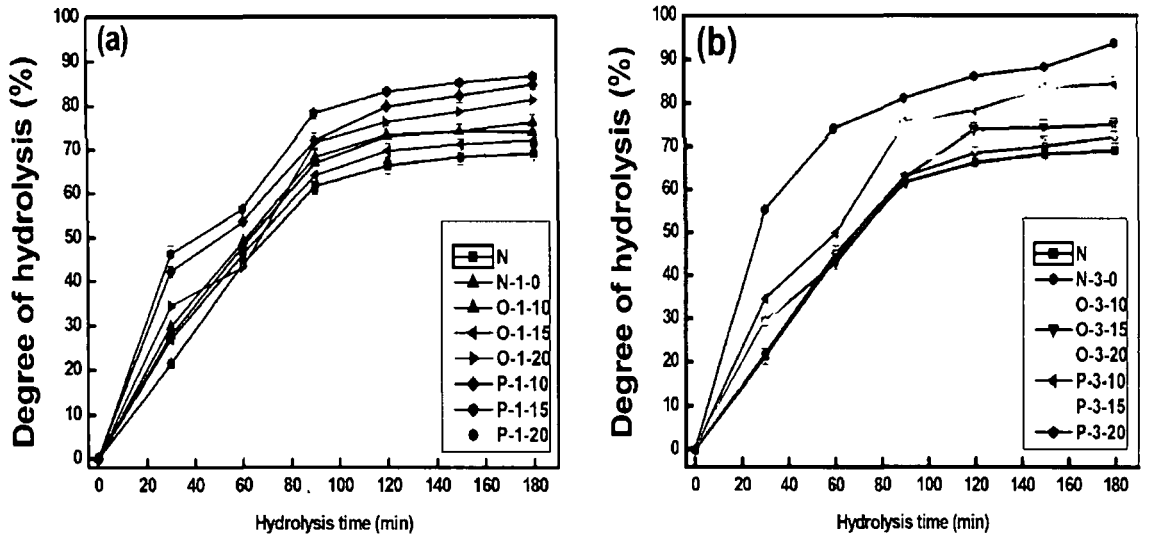

Fig. 5.6. Starch hydrolysis rate of flours of parboiled samples hot soaked for (a) 1 min and (b) 3 min.

5.3.13. Ready to eat *komal chaul*

Komal chaul making process in the traditional way includes simple steps of soaking, steaming, drying and milling. However, traditional process requires longer time of soaking to get the desirable cooking and eating quality. The optimum cooking and eating quality of *komal chaul* is that the *chaul* must soften on soaking in water at RT for 30-40 min. The laboratory developed process in this study has shortened the soaking period. In order to hasten the water absorption by the kernels, the paddy was given a hot soaking treatment that involves cooking the *chokua* paddy in water for 1-3 min and then allowing the paddy to hydrate overnight in that water at RT. The soaked paddy was then steamed. Pressure steaming gives better quality of *komal chaul* as judged by the texture of the soaked *chaul* in water. The textural properties of such pressure steamed rice gives soft textured rice kernels on soaking in water for 20 min at 50°C.

5.4. Conclusions

The pressure steaming of *chokua* paddy after hot soaking treatment gave *komal chaul* similar in texture to cooked rice. Such parboiled rice had different physicochemical properties than those obtained from open steaming technique. The changes in properties can be attributed to the effect of gelatinisation and thermal degradation of starch which may explain their higher rate of starch digestibility. Thus, pressure steaming of hot soaked *chokua* paddy gives ready to eat rice product. On the other hand, *komal chaul*

processed by open steaming of hot soaked paddy gave enzyme resistant starch. Such samples also recorded high pasting and cooling viscosities. These specific properties can be exploited for specific end uses.

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Chapter 6

CHARACTERIZATION OF READY-TO-EAT *BHOJA CHAUL* PROCESSED BY A LABORATORY-SCALE DRY HEAT PARBOILING METHOD

6.1. Introduction

Rice (*Oryza sativa* L.) is parboiled to bring about desirable properties and be consumed as staple food. Parboiling often involves soaking of paddy in water followed by steaming, drying, and milling. Bhattacharya (1985) however has specifically termed this as the conventional parboiling process while a process where steaming is carried out under elevated pressure has been termed as pressure parboiling.[1] A third technique, called dry heat parboiling has been defined to involve conduction heating of moistened paddy at higher temperature for shorter durations. This method with variations in the processing conditions is generally used for making certain speciality rice products.[2-4] While steam parboiling causes starch gelatinization during steaming followed by retrogradation during prolonged drying, dry heat parboiling results in starch gelatinization with no retrogradation due to the simultaneous rapid loss of water from the paddy during conduction heating.[4,5] This results in development of certain peculiar properties in parboiled rice.

Assam, a state in India, produces rice varieties with wide range of apparent amylose content.[6] While the high and intermediate amylose varieties are consumed in staple diet throughout Assam, the low amylose and waxy varieties are often processed into speciality products.[3] Ready-to-eat (RTE) rice products have gained much popularity in the last few decades due to the ease of cooking and fuel economy. *Bhoja chaul* is a popular RTE product of Assam. The traditional product is conventionally processed by soaking low amylose or waxy paddy in water at room temperature for 3-4 days for maximum hydration followed by roasting in iron vessel over wood fire with constant

stirring. The roasting temperature is controlled by the intensity of the wood fire and is stopped when the grains sufficiently dry up. The roasted paddy is then spread over mud floor to cool before milling in *dheki* (a foot pounding machine) to get the product. The prepared *Bhoja chaul* is soaked in water at room temperature prior to consumption to let it hydrate sufficiently to a softer and somewhat sticky texture. After draining the water, the *chaul* is eaten with milk, cream, curd and jaggery. The roasted aroma, colour, and sticky as well as chewy texture of *Bhoja chaul* are considered to be its desirable characteristics by the rural household processors. There is no cooking involved. As per the traditional food processors, extensive hydration of the soaked paddy followed by extensive roasting without allowing puffing yields high quality *Bhoja chaul*. This peculiar edible nature of dry heat parboiled low amylose and waxy varieties has never been discussed before.[7]

Modern analytical tools like Rapid Viscosity Analysis (RVA), X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Texture Profile Analysis (TPA), have been extensively used for understanding the molecular and functional properties of starch and starchy flours. RVA is important for analysing the cooking behaviour that primarily decides their targeted use in processed food systems.[8] XRD and DSC give the idea of molecular structures and their arrangements in a complex polymeric food material.[9] TPA is used as a mechanical tool to assess the human sensory attributes of cooked rice.[10]

Digestibility is one of the primary factors for determining the nutritional status of the starchy foods.[11-13] Mujoo et al (1998) opined that rice roasting results in gelatinization of starch that is more susceptible to enzymatic digestion.[14] Contrary to this, Chitra et al (2010) worked on *in vitro* starch digestibility of three sand roasted rice products and reported the formation of resistant starch which passed the human digestive tract unhydrolyzed.[15] The present study aimed at using an improvised laboratory-scale process for making RTE *Bhoja chaul*, essentially a dry heat parboiled rice product, from a low amylose and a waxy variety of rice and characterizing the product for its physical, physicochemical and nutritional properties.

6.2. Materials and methods

Kola chokua and *Aghoni bora* varieties of paddy from the recent harvest of 2012 were purchased from local farmers of Jorhat district, Assam. The rice varieties fell under low amylose and waxy types with 12.6 % and 1.15% (db) apparent amylose contents, respectively as reported in chapter 3 (section 3.3.1). The samples were kept at room temperature for 24 h and then stored at 4°C until processing. Enzymes and D-glucose standards were procured from Sigma-Aldrich (U.S.A.).

6.2.1. Processing and coding of samples

As the normal process of dry heat parboiling mentioned by Bhattacharya (1985)[(1)] gave *Bhoja chaul* that had raw rice texture while eating (revealed during preliminary studies) due to low moisture absorption on soaking, an improvised method was developed in the laboratory. Briefly, 200g paddy was brought to room temperature and kept for 5 h. The paddy was then added to 3 L of water at 100°C in a vessel kept over flame with continuous stirring for 1 and 3 min. Such hot soaking results in higher absorption of water by the paddy within shorter soaking duration and thereby allows for extensive starch gelatinisation in the kernel. The vessel was then removed from the flame, immediately covered with a thick gunny bag to prevent rapid cooling and kept at room temperature (25±2 C) for 18 h. *Kola chokua* and *Aghoni bora* attained moisture content above 36% (wb) against ~30% moisture that would have been attained without the 1min or 3 min boiling steps as revealed by trials in our laboratory. The excess water was then decanted and the hydrated paddy was roasted with hot sand in a drum type roaster (1:3 paddy to sand). The sand particles (less than 3 mm in diameter) were preheated to temperatures of 220°C which came down to 140°C after addition of the paddy (determined from repeated trials) and was controlled as such throughout the roasting time by wrapping the drum of the roaster with a moistened piece of gunny bag. The roaster had an internal rotatable shaft which was operated at 110-120 rpm for maximum heat distribution throughout the paddy mass. The paddy samples were roasted for 11, 13 and 15 min. The roasted paddy had moisture content between 11-12 % (wb) as was determined immediately after roasting. The roasted samples were then cooled at room temperature for 6 h and milled (8-10% milling, w/w) in a Satake dehusker and a polisher (Satake, Japan). A portion of each sample was ground into flour in a laboratory grain mill (Fritsch Pulverisette 14,

Germany) and passed through a 100 μm sieve. All The samples were stored in polypropylene bags at 4°C until further analyses were carried out. For ease of identification, the rice varieties were coded as LK meaning low amylose *Kola chokua* and WA meaning waxy *Aghoni bora.* LK and WA suffixed with (N) indicated raw rice. Processed sample code indicated variety code suffixed with time of boiling prior to overnight soaking and time of roasting. Thus, LK-1-11 indicated low amylose *Kola chokua* boiled for 1 min prior to overnight soaking followed by roasting at 140°C for 11 min.

6.2.2. Colour measurement

The colour values of all flour samples were obtained by a colour measurement spectrophotometer (Hunter Colour-Lab Ultrascan Vis, US). The results for L (lightness), a (red-green), and b (yellow-blue) values were used to calculate the corresponding hue angle (H) and chroma (C) values.[16]

$$H = \tan\text{-}1\ (b/a) \qquad \textbf{Eq. 6.1}$$

$$C = [(a^2 + b^2]^{1/2} \qquad \textbf{Eq. 6.2}$$

6.2.3. L/B ratio, kernel hardness (H) and head rice yield (HRY)

The length (L) and breadth at the midpoint (B) of the polished kernels were determined using a Seed dial calliper (Baker, India) and the L/B ratio was calculated. H was tested in a Texture Analyzer (TA.HD.plus, Stable Micro Systems, UK) with a 25 kg load cell by using a single compression test with a 2 cm diameter stainless steel probe along the kernel thickness at a speed of 0.5 mm/min followed by return to its original position. The test was repeated for 20 kernels from each sample and the mean was calculated. The maximum force (in Newton) indicated by the force-time curve generated by the inbuilt software (Exponent Lite) was taken as H. HRY was determined as the percentage weight of intact kernels obtained after milling to that of total milled rice.

6.2.4. Porosity (ε)

For ε (%) determination, bulk density (ρb), and true density (ρt) were first determined. For ρb determination, polished grains were allowed to fall into a measuring cylinder from

a constant height up to a known volume. The top level was adjusted by gentle tapping. The weight of the filled grains was determined and ρb was calculated.

ρb (g/cm^3)= mass of grain / volume occupied **Eq. 6.3**

ρt was determined by the solvent displacement method. Polished kernels of known weight were immersed in a known volume of kerosene taken in a measuring cylinder. The cylinder was gently agitated to release any possible air gap. The volume of kerosene displaced by the kernels was then recorded and the ρt was calculated.

ρt (g/cm^3) = mass of grain / volume of kerosene displaced **Eq. 6.4**

The porosity (ε) was determined from Eqs 6.3 and 6.4

ε (%) = [(ρt - ρb) / ρt] x 100 **Eq. 6.5**

6.2.5. Equilibrium moisture content on soaking at room temperature (EMC-S)

Polished rice kernels were soaked at room temperature for 4 h. The excess water was decanted and the surface moisture from the kernels was removed with a piece of blotting paper. The moisture content was then estimated (AOAC, 2000). EMC-S was calculated from the following equation

EMC-S (%, db) = [Moisture content (g) / Dried weight of kernels (g)] x 100 **Eq. 6.6**

6.2.6. Sediment volume (SV)

The test for sediment volume (SV, mL) gives an indirect indication of the degree of gelatinization of pregelatinized rice flour.[1] Briefly, 1 g each of the flour samples was taken in a measuring cylinder and 15 ml of 0.05 N hydrochloric acid was added to it with agitation after each 5 min for 1 h. The level of the flour sediment was observed after 4 h and was reported as the SV of the sample.

6.2.7. Cooking time of raw rice

The objective method of Juliano (1982) was used to determine the cooking time (in min) of the raw rice samples.[17] Sample weighing 20 g was cooked in 200 ml water at 98°C on

a hot plate. After 10 min of cooking, ten kernels were brought out from the middle of the cooked mass and pressed between two clean glass slides. The number of translucent kernels were counted and recorded. The pressing test was repeated after each minute and the time at which 90% of the kernels were translucent was considered as the cooking time of that rice.

6.2.8. Pasting properties

Flour sample (12 % moisture content w/w; 28 g total weight) was added to 25 mL water and allowed for saturation for 5 min. The slurry was then held at 50°C for 1 min, heated from 50°C to 95°C in 3.45 min, held at 95°C for 2.40 min followed by cooling to 50°C in 3.45 min and finally holding at 50°C for 1 min in a Rapid Viscosity Analyser (RVA Starchmaster2, Newport Scientific Instruments, US). The pasting curves obtained were compared and the pasting parameters, namely PV (maximum viscosity during heating phase); HPV (minimum viscosity at 95°C); CPV (final viscosity at 50°C); BD (PV-HPV) and SB (CPV-HPV) were recorded.

6.2.9. Wide angle X-ray scattering (WAXS)

An X-ray diffractometer (Rigaku Miniflex, Japan) with a λ value of 1.54 A°, operating at an acceleration potential of 30 kV with 15 mA current and a copper target was used to obtain wide angle X-ray diffractograms (XRD) of the flour samples. The scanning range was 10–40° of 2θ values in steps of 0.05°. The total area under the curve and the area under each prominent peak were determined and the percentage crystallinity was calculated.[18]

% crystallinity = (area under peaks / total area under the curve) x 100 **Eq. 6.7**

Gaussian fit curves of the diffractograms were obtained using Origin 8 software (OriginLab Corporation, UK) to study any notable change in the overall diffraction patterns of the flour samples.

6.2.10. Thermal properties

Flours of raw rice and 1 min and 3 min hot soaked samples roasted for 15 min were analysed for their thermal profiles. Saturated flour slurries were prepared by mixing 4 mg

each of sample and deionized water (1:2 flour to moisture ratio, db) in aluminium pans and keeping for 1 h at 4°C. The pans were then hermetically sealed and heated in a Differential Scanning Calorimeter (DSC, model DSC-60; Shimadzu, Tokyo, Japan) against an empty reference pan from 30°C to 130°C at a heating rate of 5°C/min under N_2 atmosphere. The onset (To), peak (Tp), and conclusion (Tc) temperatures and enthalpy of gelatinization and/or crystallite melting (ΔH, J/g) were obtained from the thermograms using the inbuilt TA-60WS software.

6.2.11. Starch digestibility

The *in vitro* starch hydrolysis rate of each sample was estimated by the method of Goni et al (1996).[12] A solution containing 1g of pepsin in 10 mL of HCl-KCl buffer (pH 1.5) was prepared and 0.2 mL of this solution was mixed with 50 mg of flour sample and kept for deproteinisation in a shaking water bath at 40°C for 60 min. The volume was then made up to 25 ml with Tris-maleate buffer (pH 6.9) and 5 ml of a Tris-maleate buffer solution containing 2.6 IU pancreatic α-amylase was added before incubating at 37°C for 180 min. One milliliter aliquot was taken out after each 30 min, boiled to inactivate the enzymes and stored under refrigeration. Three millilitres of 0.4 M sodium acetate buffer (pH 4.75) containing 60 μL of amyloglucosidase (Sigma Aldrich) was then added and further incubated at 60°C for 45 min. The glucose liberated was estimated using a D-glucose oxidase-peroxidase assay kit (Robonik, India) and a previously prepared glucose standard curve. The value was converted to starch by multiplying by a factor of 0.9. The total starch content of each sample was calculated by the standard protocol of AOAC (2000) and the degree of hydrolysis (%, db) was calculated as the percentage of starch degraded from each sample after each time interval.

Degree of hydrolysis (%) = (Starch hydrolyzed / Total starch content) x 100 **Eq. 6.8**

Resistant starch (RS) present in the flour samples was measured by a method modified from Englyst et al (1992).[11] Briefly, 100 mg flour was first added to 7 ml acetate buffer (pH 5.2) and incubated at 37°C for 20 min in a shaking water bath (Voltam, India). Then, 3 ml of an enzyme mixture composed of invertase (220 U/ml), pancreatic α-amylase (3000 U/ml) and amyloglucosidase (15 U/ml) were added and incubated further. Aliquots were taken out after 20 min and 120 min and measured for rapidly released and slowly released glucose (G20 and G120) respectively using the glucose assay kit and

standard curve. Rapidly digestible starch (RDS) and slowly digestible starch (SDS) expressed as a percentage of dry matter were evaluated by the following formulae

$$RDS\ (\%) = [(G20 \times 0.9) / TS] \times 100 \qquad \textbf{Eq. 6.9}$$

$$SDS\ (\%) = [(G120 - G20) \times 0.9] \times 100 \qquad \textbf{Eq. 6.10}$$

As mentioned by Patindol et al (2010), the difference between total starch (TS) and the starch digested during the incubation period was calculated as resistant starch (RS) and expressed as percentage of dry matter.[19]

$$RS\ (\%) = [TS - (RDS + SDS)] \times 100 \qquad \textbf{Eq. 6.11}$$

6.2.12. Texture comparison of cooked rice and the RTE product

The raw LK and WA rice samples were cooked at 100°C for 18 and 16 min respectively, their cooking time determined previously and reported in section 6.2.7. Processed samples were soaked in water at room temperature for 20 min as generally practiced in households for *Bhoja chaul*. Excess water from both was decanted and surface water was removed with a blotting paper. The samples were then subjected to texture profile analysis (TPA). For this, a Texture Analyzer (TA.HD.plus, Stable Micro Systems, UK) with a 5-kg load cell fitted with a cylindrical probe of 2 cm diameter was used. The two-cycle compression test involved compressing single kernels collected from the middle of each sample mass to 70% at 0.5 mm/s (Suzuki, 1979).[20] The time between two chews was 3 s. All the TPA parameters, namely hardness, adhesiveness, springiness, and chewiness were determined by the inbuilt software (Exponent Lite). Twenty kernels from each sample were tested separately and average values were taken.

6.2.13. Statistical analysis

All the experiments were carried out in multiple replicates and the means are reported. Significant differences between the means were analysed by Duncan's multiple range test at a significance level of 0.05 using SPSS 11.5 (SPSS Inc., USA).

6.3. Results and discussion

6.3.1. Colour measurement

None of the processed samples exhibited while belly indicating complete gelatinization of starch. Colour values of rice flour samples are presented in Table 6.1. The decreased L value with simultaneous increase in H and C values was indicative of extensive gelatinization of starch, Maillard browning and uniform distribution of the colour compound.[21] Although inward migration of pigments from husk and bran layers into the kernel was proposed by Bhattacharya (1985)[1] and Lamberts et al (2006)[21], it was nullified by the work of Lamberts and Delcour (2008)[22] who found that the carotenoids present in the epidermal layers got reduced to trace levels after steam parboiling and hence do not contribute to the final colour of parboiled rice. The extent of colour change after dry heat parboiling that involved higher temperature of conduction heating was greater than the colour development in steam parboiled rice as was reported in chapter 3 (section 3.3.3). Hence, the colour development in the dry heat parboiled samples may be principally attributed to Maillard browning which accelerated due to formation of reducing sugars by thermal breakdown of starch.

6.3.2. L/B ratio, kernel hardness and head rice yield

Values for L/B, H and HRY (%) are given in Table 6.1. Notable reduction in length with minor yet simultaneous increase in breadth resulted in reduction of L/B ratio. The *Bhoja chaul* samples were hence bolder in shape than the raw rice kernels. This was however contradictory to the findings of Sowbhagya et al (1993) who observed increase in length of kernels after dry heat parboiling.[23] Varietal difference plays an important role in determining raw and parboiled rice properties. Difference in the gap between the raw kernel and the husk and the shape and size of the kernel and swelling tendency of starch can definitely be considered as major determining factors for the shape of the kernel after processing as no splitting of husk layers was observed. Adding to it, conduction heat from the sand probably caused higher tension to develop along the horizontal axis of the kernel which was more exposed to the heating sand. The L/B ratio and H values were indicative of the fact that no puffing occurred during the dry heat parboiling process. Processed kernels were markedly harder than the raw rice. With increased H, the HRY also

increased indicating development of kernel integrity upon processing. Almost all the kernels were intact in the severely dry heat parboiled samples. This indicates suitability of the laboratory-scale process for developing into a commercial parboiling method.

6.3.3. Porosity

Porosity is directly related to the L/B ratio of the kernels.[24] Increase in bulk density upon processing resulted in decreased porosity (Table 6.1) suggesting better packing property of the product than the raw rice, an attribute important for product handling and transportation. This change was comparatively more prominent in the processed WA samples which again may be attributed to difference in paddy structure and higher swelling on gelatinization as amylopectin is the chief factor for deciding starch swelling.[25]

6.3.4. Equilibrium moisture content on soaking at room temperature

The improved dry heat parboiling process followed to make *Bhoja chaul* increased the water uptake capacity of the rice kernels.[7] Processed LK samples showed lower values of EMC-S than WA samples processed under similar conditions. Unnikrishnan and Bhattacharya (1987) also observed a negative correlation amongst amylose content and EMC-S of parboiled rice.[26] EMC-S increased with process severity indicating progressively developed water uptake capacity (Fig 6.1a). The values were hence highest for the WA-1-15 and WA-3-15 samples (174.6 % and 189.4 % respectively). Additionally considering our findings from previous chapters, it can be said that waxy varieties attained higher water absorption property following any method of parboiling.

6.3.5. Sediment volume

Water absorption in dry heat parboiled rice is enhanced due to gelatinized starch.[1] LK(N) and WA(N) exhibited SV values of 2.5 mL and 2.6 mL, respectively which increased with process severity (Fig 6.1b). The extent of gelatinization, similar to EMC-S, was hence highest for the severely processed WA-3-15 samples with SV of 6.4 mL. Samples with boiling time of 3 min gave higher SV than the 1 min boiled samples for both the varieties. This was in accordance with the EMC-S and reflected more

extensive gelatinisation of starch in these samples.[15] Comparison of the values with steam parboiled samples (reported in chapter 3 and 5) showed that the dry heat parboiled rice flour did not swell as much as steam parboiled samples from the same varieties. This was however contradictory to the findings of Bhattacharya and Ali (1976) who opined that the high SV value in dry heat parboiled products is due to lower amounts of retrograded starch in them.[5] Our results indicate that the starch might have got dextrinised due to the high conduction heating which might not have added to the SV of the processed samples and thereby gave lower values.

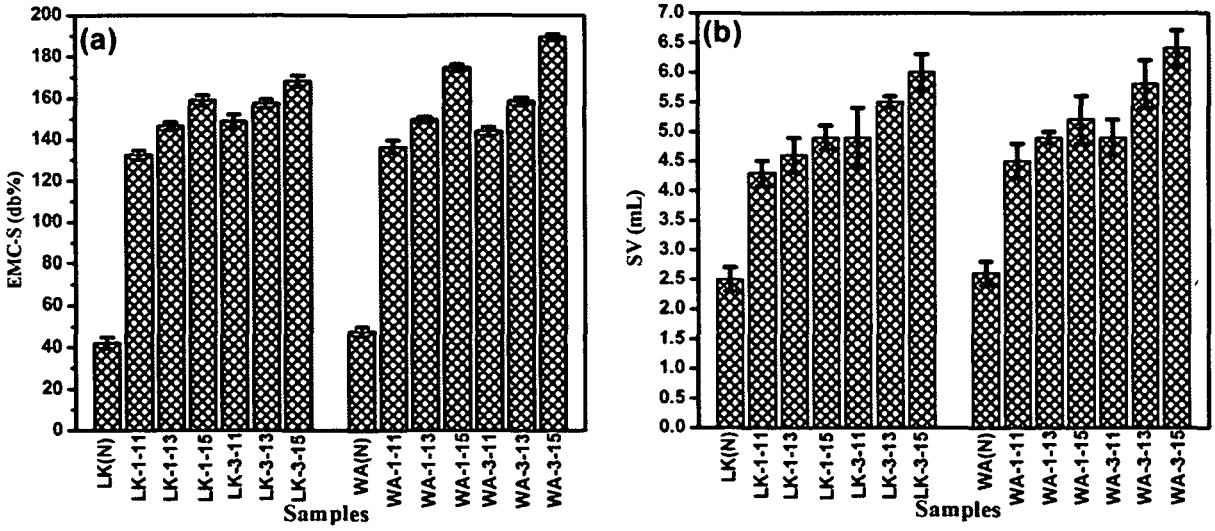

Fig. 6.1. (a) EMC-S of raw and processed rice kernels and (b) SV of raw and processed rice flour.

6.3.6. Pasting properties

The pasting curves indicative of extensive change in starch structures upon roasting are given in Fig 6.2 (a and b) and the values of the pasting parameters are given in Table 6.2. Varavinit et al (2003) suggested that the starch granules in waxy rice flour disrupt more easily on cooking and show a lower tendency towards retrogradation due to lower amylose reassociation.[27] Processing for 11 and 13 min resulted in increased PV for LK variety. For WA, the rise was only for the samples roasted for 11 min. Processed WA samples were seen to be more resistant to swelling on cooking as was evident from the shift of PV to higher time periods.[28] Processed LK samples showed patterns opposite to

Table 6.1. Colour values and physical properties of raw and processed samples.

Samples	Colour readings					Physical properties						
	L	a	b	H	C	L (mm)	L/B	H (N)	HRY %	ρb (g/cm^3)	ρt (g/cm^3)	ε (%)
LK(N)	57.5±0.34^{k}	2.3±0.04^{a}	10.5±0.38^{a}	12.8±0.98^{b}	10.7±0.12^{a}	6.7±0.16^{l}	2.8±0.28^{c}	68.8±0.82^{b}	72.1±1.89^{a}	0.7±0.31^{b}	1.4±0.26^{a}	50.0±0.32
LK-1-11	31.0±1.21^{h}	2.7±0.07^{d}	10.7±0.19^{bc}	14.7±1.12^{d}	11.0±0.17^{b}	6.5±0.22^{h}	2.5±0.04^{b}	83.9±1.11^{d}	92.0±1.19^{c}	0.8±0.04^{c}	1.4±0.17^{a}	42.8±5714
LK-1-13	25.3±0.83^{c}	3.0±0.17^{gh}	10.7±0.74^{bc}	15.9±0.83^{gh}	11.1±0.15^{bc}	6.4±0.07^{fg}	2.4±0.31^{a}	85.4±0.98^{g}	98.0±0.21^{f}	0.8±0.04^{c}	1.4±0.22^{a}	42.8±0.14
LK-1-15	21.1±0.29^{b}	3.2±0.35ij	10.8±0.13^{ab}	16.9±1.25^{k}	11.3±0.19^{d}	6.4±0.15^{f}	2.4±0.14^{a}	89.3±0.56^{jk}	100.0±0.00^{h}	0.9±0.18^{d}	1.5±0.29^{bc}	40.1±0.15
LK-3-11	29.8±1.44^{f}	2.5±0.29c	10.8±0.05^{bc}	13.7±2.11^{c}	11.0±0.11^{b}	6.5±0.28^{h}	2.4±0.17^{a}	84.1±0.39^{d}	91.2±0.12^{c}	0.8±0.13^{c}	1.4±0.37^{a}	42.8±0.57
LK-3-13	24.8±0.99^{c}	2.8±0.41^{ef}	10.8±0.49^{c}	15.1±1.36^{ef}	11.1±0.16^{bc}	6.4±0.19^{f}	2.4±0.16^{a}	84.9±0.18^{f}	96.6±0.67^{e}	0.9±0.14^{d}	1.5±0.19^{b}	40.4±0.17
LK-3-15	20.3±0.39^{a}	2.9±0.03^{fg}	10.9±0.35^{c}	15.6±0.69^{fg}	11.3±0.14^{d}	6.4±0.11^{f}	2.4±0.13^{a}	89.5±1.12^{l}	100.0±0.00^{h}	0.9±0.13^{d}	1.5±0.17^{b}	39.9±0.21
WA(N)	66.7±0.22^{l}	2.2±0.04^{b}	11.2±0.31^{d}	11.2±1.21^{a}	11.4±0.14^{cd}	6.4±0.23^{g}	2.9±0.18^{d}	59.8±0.17^{a}	73.8±1.29^{b}	0.6±0.07^{a}	1.4±0.26^{a}	57.1±0.33
WA-1-11	33.3±1.02^{j}	2.8±0.11^{fg}	11.4±0.77^{e}	14.1±1.48^{c}	11.7±0.17^{e}	6.3±0.26^{e}	2.5±0.33^{b}	83.3±0.19^{c}	94.6±0.39^{d}	0.7±0.06^{b}	1.4±0.31^{a}	50.0±0.28
WA-1-13	30.91±0.69^{h}	3.0±0.18^{gh}	11.5±0.37^{e}	15.1±1.55^{ef}	11.8±0.09^{fg}	6.2±0.17^{cd}	2.4±0.27^{a}	84.1±1.42^{e}	99.0±0.32^{g}	0.8±0.22^{c}	1.5±0.15^{b}	46.6±0.39
WA-1-15	28.1±1.12^{e}	3.3±0.38^{jk}	11.5±0.76^{e}	16.4±1.29^{hi}	11.9±0.22^{gh}	6.2±0.16^{bc}	2.4±0.19^{a}	87.8±0.87^{h}	100.0±0.00^{h}	0.8±0.18^{c}	1.5±0.07^{b}	46.6±0.43
WA-3-11	32.2±0.92^{i}	2.8±0.71^{ef}	11.4±0.99^{e}	14.1±1.37^{c}	11.7±0.16^{e}	6.3±0.26^{e}	2.4±0.26^{a}	83.5±0.97^{c}	94.1±0.45^{d}	0.8±0.17^{c}	1.5±0.24^{bc}	46.6±0.28
WA-3-13	30.1±0.12^{gh}	3.1±0.24^{hi}	11.5±0.51^{e}	15.6±1.92^{fg}	11.9±0.14^{gh}	6.3±0.12^{de}	2.4±0.22^{a}	88.7±0.29^{i}	100.0±0.00^{h}	0.8±0.15^{c}	1.6±0.29^{c}	50.1±0.31
WA-3-15	27.5±0.34^{d}	3.4±0.22^{k}	11.6±0.37^{e}	16.9±1.67^{j}	12.0±0.16^{i}	6.2±0.05^{a}	2.4±0.28^{a}	89.1±0.15^{j}	100±0.00^{h}	0.9±0.14^{d}	1.6±0.18^{c}	43.7±0.14

*The means in each row followed by a common letter are not significantly different by Duncan's Multiple Range Test at $p < 0.05$.

it. Similar observations were also earlier reported for open steam parboiling of LK sample (chapter 3, section 3.3.6). This was hence indicative that the starch chains developed property of higher swelling on cooking thereby exhibiting an increased PV. This was followed by distinct BD and SB like those exhibited by raw samples. This peculiar change in pasting property of parboiled low amylose and waxy rice hence requires further research involving molecular weight characterization.[29,30] Other factors like amylose-lipid complexes (Derycke et al. 2005)[31] and protein (Gelders, 2006)[32] also may affect the pasting properties which need further investigation. Resistance to viscosity loss on hydrothermal processing by low amylose and waxy rice varieties was earlier reported by Biswas and Juliano (1988).[33] Severe processing caused drop in the PV and loss of BD like steam parboiled high amylose rice but peculiarly increased SB for both varieties giving an almost continuously rising pasting curve.[34] This may be attributed to excessive breakdown of amylopectin during the high temperature roasting; forming irreversible simpler leachable fractions that continuously got released into the slurry, making it increasingly thicker and viscous.[35] This property of becoming thick on cooling may prove to be useful for the prepared *Bhoja chaul* powder to be used as thickening agent in cooked food systems.

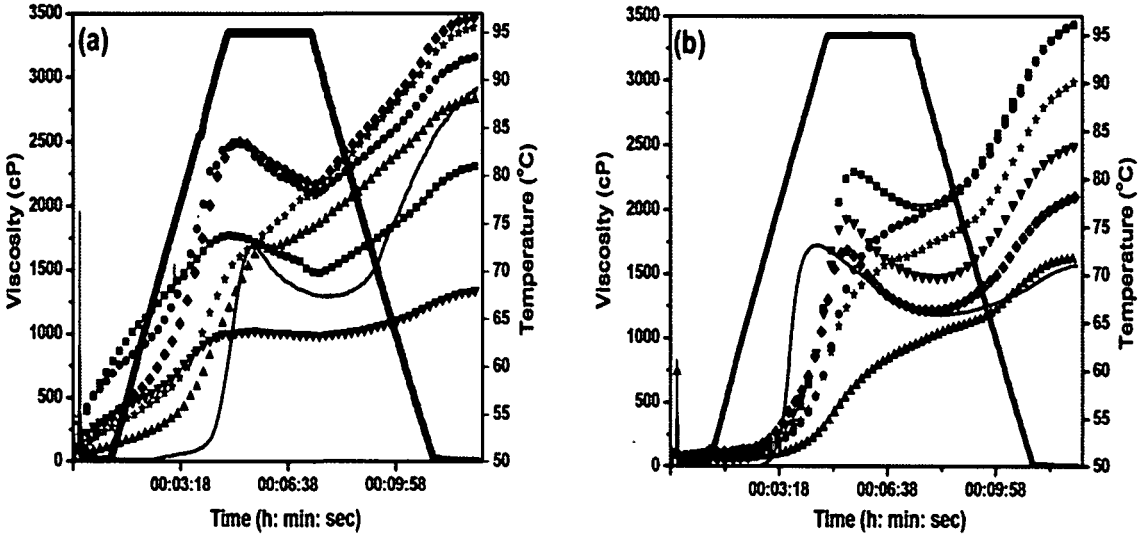

Fig. 6.2. RVA pasting curves of raw and processed (a) LK and (b) WA samples. The representations of the symbolic curves are as follows: Native (——), 1-11 (■), 1-13 (●), 1-15 (▲), 3-11 (▼), 3-13 (◆), 3-15 (✱).

Table 6.2. RVA pasting parameters of raw and processed samples.

Samples	PV (cP)	HPV (cP)	CPV (cP)	BD (cP)	SB (cP)
LK (N)	1687±3.44^{f}	1305±1.09^{d}	2880±1.45^{h}	382±2.12^{j}	1575±1.93^{m}
LK- 1-11	1771±2.98^{i}	1487±2.11^{e}	2291±2.15^{e}	284±1.00^{h}	804±2.19^{d}
LK- 1-13	2495±2.13^{m}	2100±1.56^{i}	3141±3.25^{j}	395±2.64^{k}	1041±3.21^{h}
LK- 1-15	1664±2.34^{e}	1835±4.21^{f}	2811±4.12^{g}	-171±2.69^{e}	976±2.54^{f}
LK- 3-11	1002±1.26^{b}	991±2.45^{a}	1337±2.56^{a}	11±3.94^{f}	346±3.12^{a}
LK- 3-13	2490±1.54^{l}	2155±3.22^{j}	3462±2.64^{m}	335±1.69^{i}	1307±1.08^{k}
LK- 3-15	1528±2.43^{d}	2079±3.11^{i}	3385±2.35^{k}	-551±2.64^{a}	1306±2.10^{k}
WA (N)	1720±3.92^{h}	1179±3.24^{c}	1557±1.68^{b}	541±2.18^{n}	378±3.45^{b}
WA-1-11	2273±2.43^{k}	2018±3.21^{h}	3426±2.02^{l}	255±0.34^{g}	1408±4.12^{l}
WA-1-13	1701±3.21^{g}	2192±2.12^{k}	3436±3.00^{m}	-491±1.32^{b}	1244±1.21^{j}
WA-1-15	803±3.69^{a}	1146±2.67^{b}	1610±2.22^{c}	-343±1.38^{d}	464±1.45^{c}
WA-3-11	1909±2.47^{j}	1472±3.42^{e}	2495±3.13^{f}	437±2.32^{l}	1023±2.22^{g}
WA-3-13	1674±1.69^{e}	1198±2.47^{c}	2092±3.21^{d}	476±1.89^{m}	894±3.16^{e}

*The means in each row followed by a common letter are not significantly different by Duncan's Multiple Range Test at $p < 0.05$.

6.3.7. X-Ray diffraction

XRD of raw rice samples exhibited A-type starch crystalline pattern with strong peaks at 2θ = 15.2, 17.4, 18.1 and 23.3 (Fig 6.3a,b). Feeble peaks at 2θ positions near 20.0 and 22 indicating V-type and B-type starch polymorphs were observed in the diffractograms of processed samples. While the amylose-lipid complex giving V-type diffraction pattern forms during heat processing, the B-type polymorphic structures are retrograded starch.[36,37] Formation of retrograded starch despite of insufficient water is however contradictory to the statement of Bhattacharya (1985).[1] Minor initiation of formation of these structures during cooling and storage of the roasted rice may however be considered responsible for the feeble peaks. In addition to that, a minor peak retained at 2θ value of 18.1 was representative of the native A-type crystalline structure suggesting of either incomplete gelatinization or partial recrystallization into the native structure. These native starch fractions in the processed samples may be related to the distinct PV shown in the RVA pasting curves. Superimposition of the diffractograms of the three basic starch

crystalline structures was earlier reported by Mahanta et al (1989)[39] and was also observed by us in XRD of steam parboiled rice (chapter 3, section 3.3.8). Gaussian fitting of the diffractograms of the processed samples (Fig 6.3 a and b 'insets') indicated that the crystalline peak regions of the curves shifted towards lower values of 2θ. In LK samples, it shifted from 20.2 (LK-1-11) to 18.4 (LK-1-15) and 18.1 (LK-3-15) and in WA samples the shift was from 20.3 (WA-1-11) to 18.8 (WA-1-15) and 19.0 (WA-3-15). This indicated progressive reduction in the average inter-planar space (d) of the crystalline lamellae of starch with process severity[39] as calculated from the Bragg's equation

$$\lambda = 2d \sin\theta \qquad \textbf{Eq. 6.12}$$

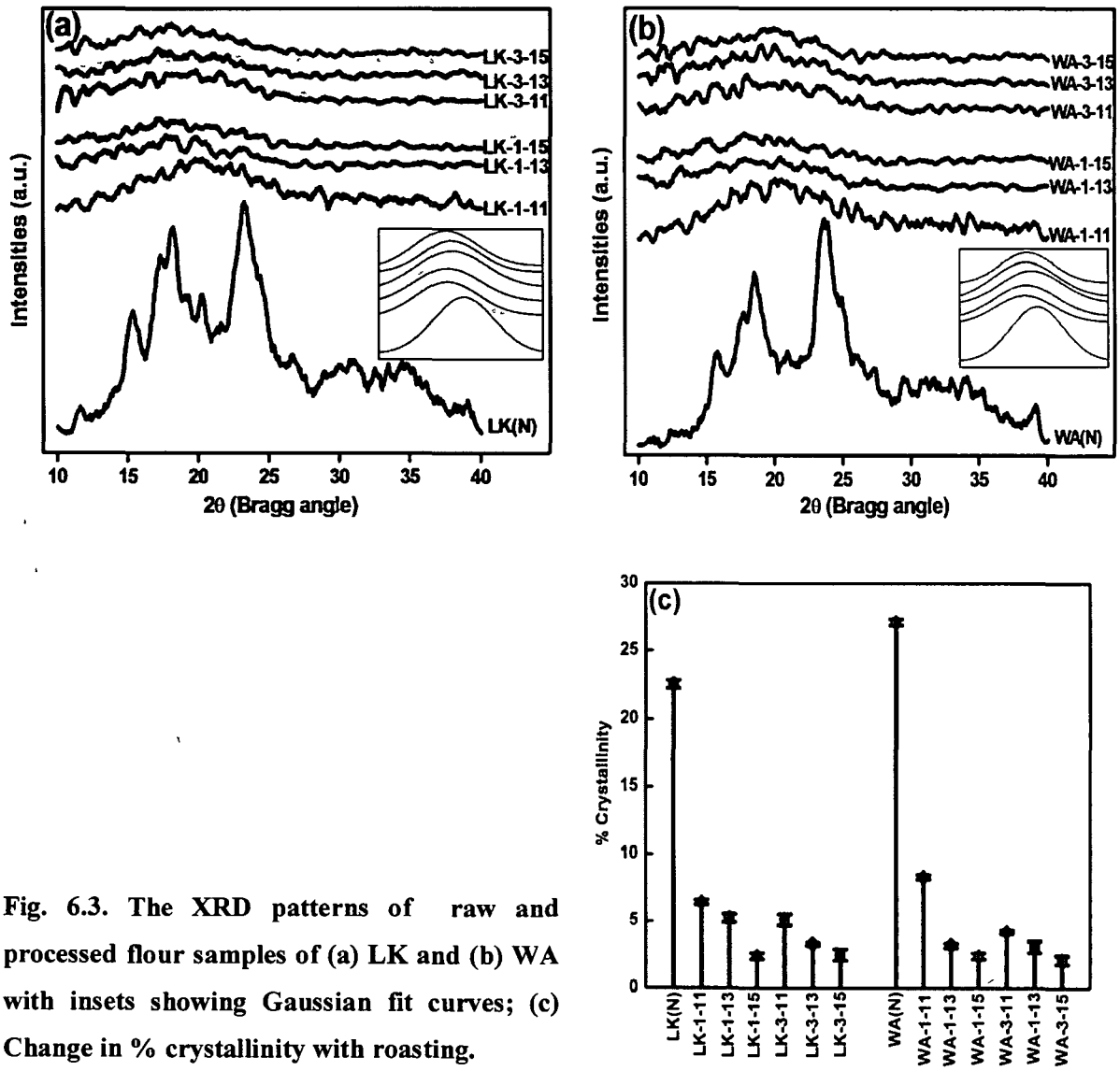

Fig. 6.3. The XRD patterns of raw and processed flour samples of (a) LK and (b) WA with insets showing Gaussian fit curves; (c) Change in % crystallinity with roasting.

Moisture acts as a principal factor for inter-chain interaction of starch.[40] Excessive reduction in moisture from the processed kernels may be considered as the probable reason behind the development of weaker lamellae in dry heat parboiled rice. This may also be related to the significant loss in % crystallinity of both the rice varieties after processing (Fig 6.3c). The loss was marginally greater in processed WA samples as they attained higher degree of starch gelatinization.

6.3.8. Thermal properties

DSC thermograms of the raw and processed samples are presented in Fig 6.4 (a and b). While the gelatinization temperature (Tp) of LK(N) was 79.2 C, WA(N) exhibited a lower Tp of 71.4°C. LK-1-15 and LK-3-15 however showed minor peaks at temperatures of about 79°C indicating melting of native starch fractions in the samples as was also suggested by their pasting curves and XRD spectra. Processed WA samples however did not show this peak indicating higher loss in native crystallinity as shown in Fig 6.3(c). Processed samples of both the varieties exhibited major peaks at 100±10°C for melting of amylose-lipid complexes. Processed LK samples exhibited notably higher values of ΔH for amylose-lipid complex melting (57.3 J/g and 56.3 J/g for LK-1-15 and LK-3-15, respectively) than the processed WA samples (52.2 J/g and 50.0 J/g for WA-1-15 and WA-3-15, respectively). Higher apparent amylose content in LK may be attributed for this significant difference in crystallite formation. Interestingly, formation of such complexes in samples despite of very little amylose indicated that there is scope for further research on this aspect of the product. Murugesan and Bhattacharya (1989) reported significant formation of the complexes when popped rice was hydrated upto 30% moisture content as was also done here during sample preparation prior to the DSC analysis.[2] Iturriaga, Lopez and Anon (2004) also observed formation of such compounds in waxy rice samples.[41] It may be proposed that occurrence of long B-chains in the amylopectin and probable debranching of the same during thermal treatment led to generation of glycosidic chains capable of starch-lipid complex formation. The present study hence suggests that gelatinized starch may form amylose- lipid complex when in excess of water. No distinct peaks for melting of retrograded starch[42] were however observed which indicates that the B-type crystalline polymorph indicated by minor peaks in XRD spectra of the samples were either not detected by the DSC conditions used or

were temporary lamellae that became amorphous once water was added for DSC sample preparation.

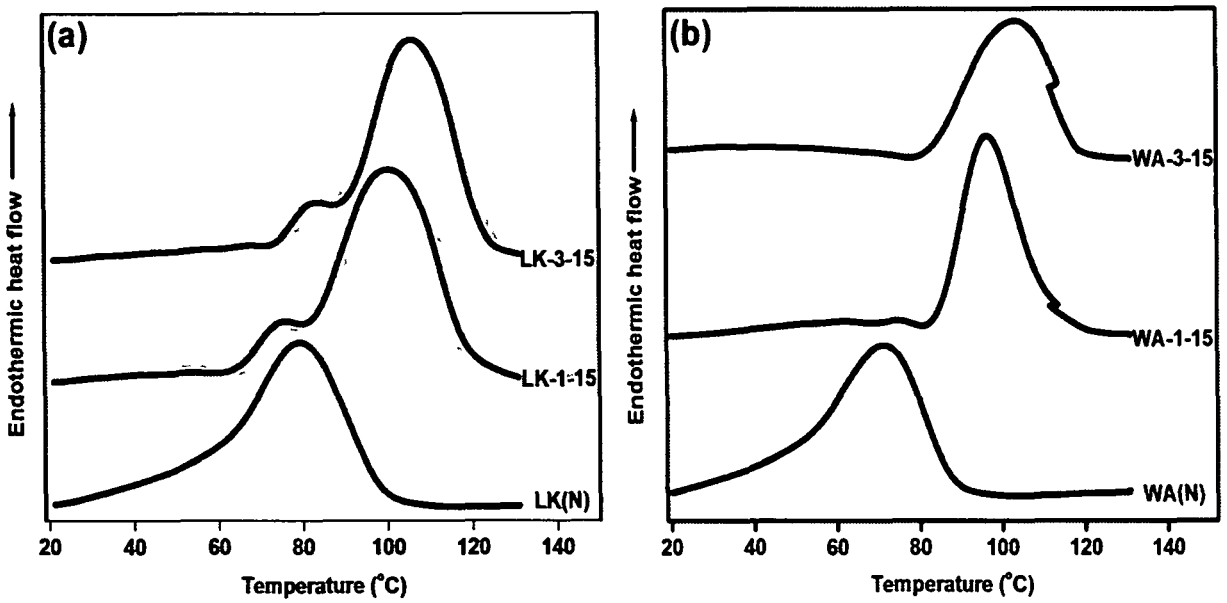

Fig. 6.4. DSC thermographs of pastes of raw and dry heat parboiled (roasted for 15 min after hot soaking for 1 and 3 min) (a) LK and (b) WA samples.

6.3.9. Starch digestibility

While starch in waxy WA(N) flour got digested up to 24.3% and 71.2% in 30 min and 180 min respectively, starch in low amylose LK(N) flour was digested up to 21.2% and 63.7% respectively (Fig 6.5a,b). This was in accordance with the findings of Zhu et al (2011).[30] For both the varieties, hydrolysis rates increased markedly after roasting. While more than 30% of the starch in the processed samples were hydrolysed within 30 min, the moderate and severely processed samples of both the varieties, namely -1-13, -1-15, -3-13 and -3-15 were hydrolysed up to more than 85% (db) after 180 min of incubation. Mujoo et al (1998) suggested that rice roasting resulting in gelatinization causes exposure of starch component to enzymatic digestion.[14] Increased digestibility was related to damage to amylopectin structures by Jaiboon et al (2011).[43] Gunaratne and Hoover (2013) reported upto 50% reduction of RS in one rice variety after parboiling.[28] The increase in hydrolytic rate was higher for the processed WA samples. Increased digestibility was also reflected by the amounts of RDS, SDS and RS contents in the samples (Fig 6.5c,d,e). RDS increased from 67.1% to 95% (db) for raw and processed

LK and from 66.6% to 95% for WA samples. SDS was low for all the processed samples (5.7% to 9.2%, db). Severely processed samples did not contain any RS. The results indicated that gelatinization, uncoiling and thermal degradation on dry heat parboiling exposed starch to the enzymes used and thereby significantly enhanced the hydrolysis rate.[14] *Bhoja chaul* produced by roasting at 140°C for 15 min can hence be well targeted for people with poor state of digestion who require rapid and non-residual digestion.

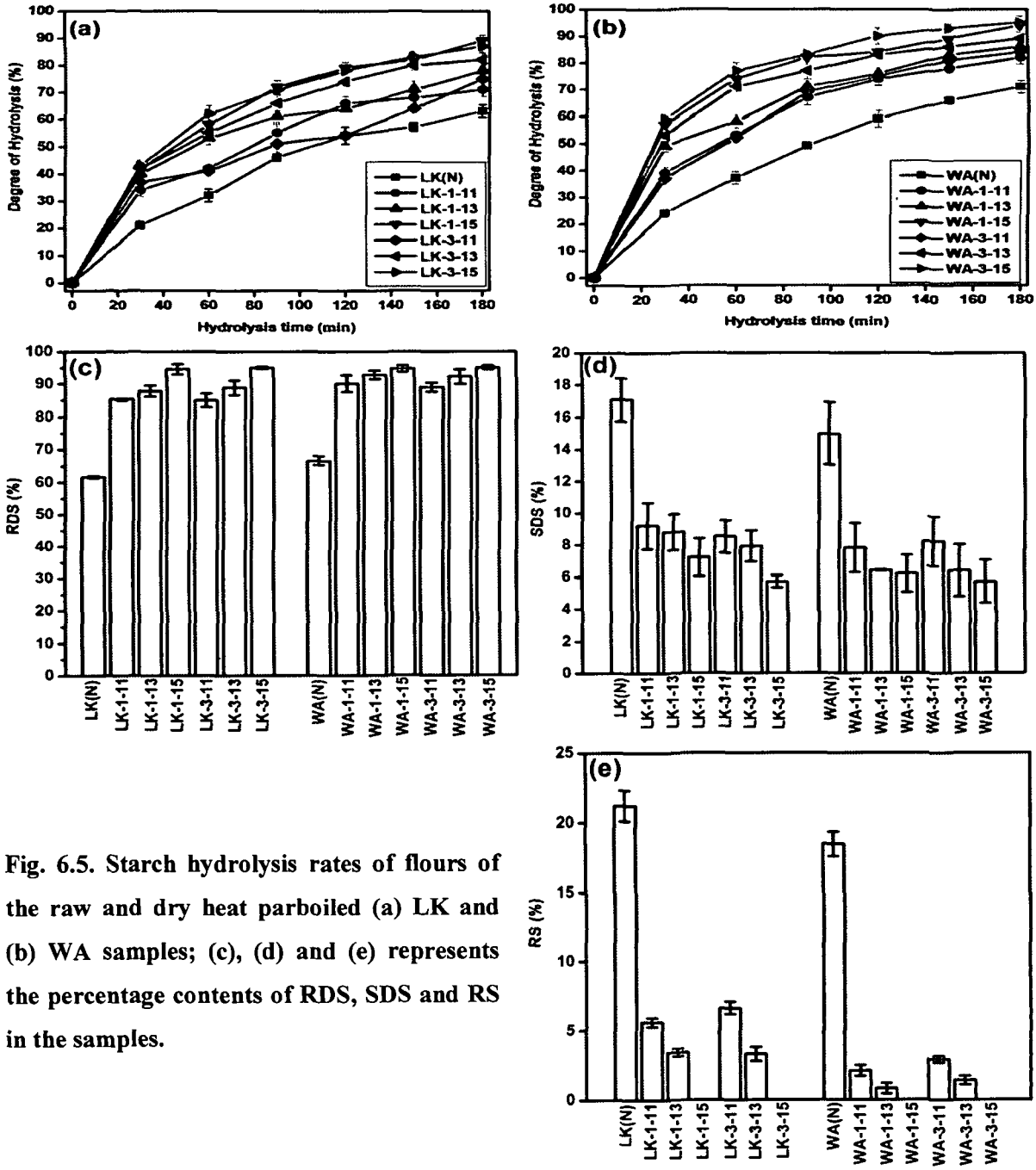

Fig. 6.5. Starch hydrolysis rates of flours of the raw and dry heat parboiled (a) LK and (b) WA samples; (c), (d) and (e) represents the percentage contents of RDS, SDS and RS in the samples.

6.3.10. Texture comparison of cooked rice and the RTE product

Values for the TPA parameters are plotted in Fig 6.6. Hardness of the soaked *Bhoja chaul* samples were higher than cooked rice.[44] Process severity however resulted in marginal lowering of hardness values (Fig 6.6a) in samples from both the rice varieties probably because of thermally degraded starch. Cooked rice was markedly adhesive as compared to the soaked *Bhoja chaul* samples (Fig 6.6b) because of complete gelatinisation of starch that occurred during cooking.[45] Breakdown of amylopectin to shorter fragments also resulted in progressive increase in adhesiveness of the processed samples.[46]

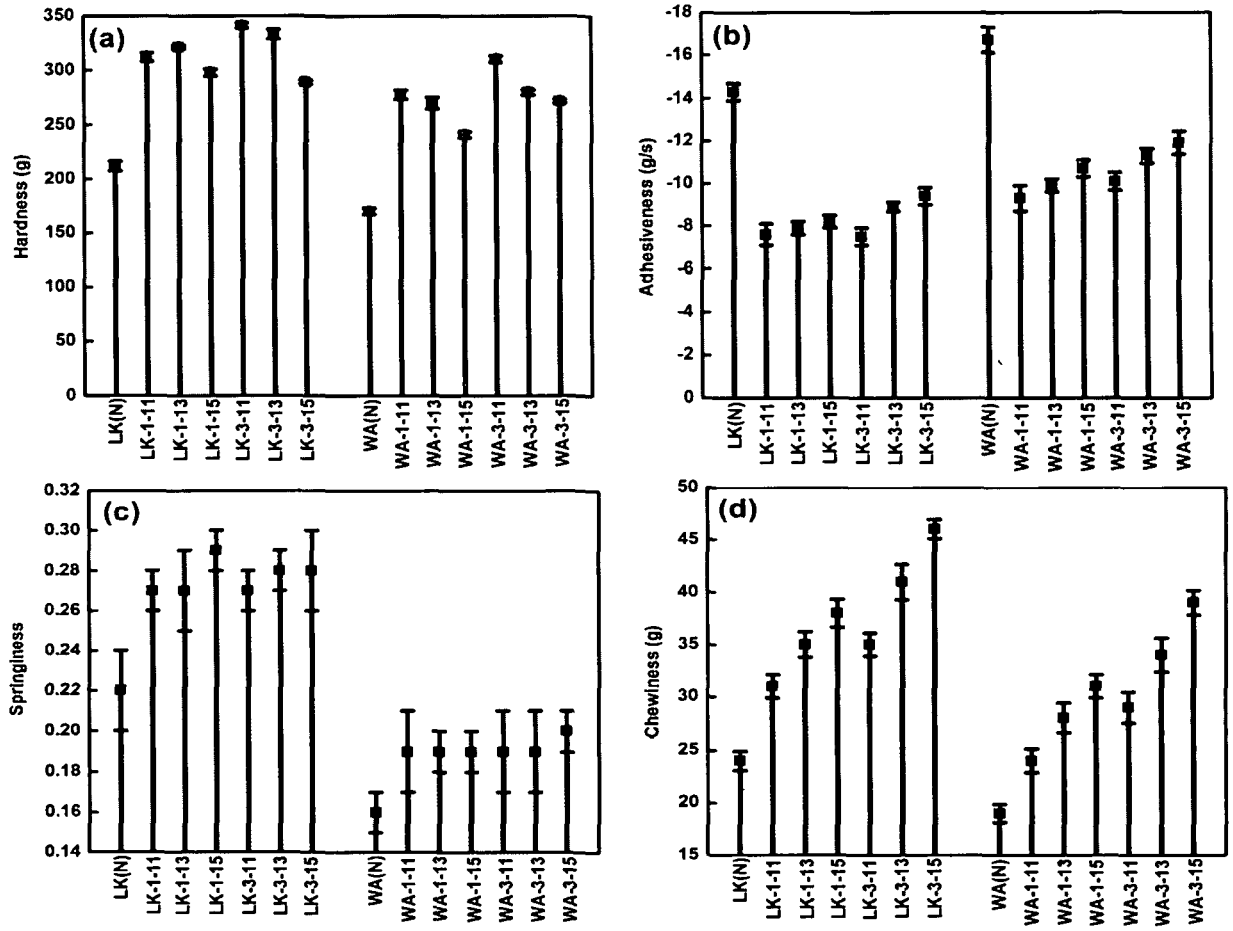

Fig. 6.6. TPA parameters of raw and dry heat parboiled samples.

Significantly lower values of springiness (Fig 6.6c) in both raw and processed WA samples were due to the higher adhesiveness and lower hardness values than LK samples. LK samples exhibited lower adhesiveness and marginally higher springiness. Chewiness

increased progressively with process severity for the RTE samples attributing to the uniformity in kernel texture developed during dry heat parboiling (Fig 6.6d). Chewiness is a positive quality attribute for *Bhoja chaul* acceptability. Cooked rice samples exhibited the lowest chewiness value.

6.3.11. The ready to eat product

As no significant difference was observed among the samples boiled for 1 min and 3 min in water before overnight hydration, hot soaking for 1 min can be considered sufficient for the laboratory process used for making *Bhoja chaul*. It was observed that severe sand roasting of *Kola chokua* paddy at 140°C for 13 to 15 min gave superior RTE product. *Aghoni bora* samples showed higher adhesive property and such sticky texture is liked by some sections of the consumers. Roasted aroma, another quality parameter of the product could be sensed in all the processed samples. Industrial processes for making the product may further be developed based on the present findings.

6.4. Conclusions

Bhoja chaul obtained from the laboratory-scale method was harder in texture than raw rice. The product obtained was uniformly darker in colour due to pigment migration and Maillard browning during processing. The process resulted in marked development in kernel hardness that gave high head rice yield. Better packing property of the product was indicated by the decreased porosity. The peculiar hygroscopicity of the product was due to gelatinized starch as no endothermic peak for retrogradation was observed in DSC. However, peak for amylose-lipid complex melting was evident in the severely processed samples which created scope for further research. Dry heat parboiling led to significant loss in crystallinity with minor reformation of each type of starch crystalline polymorphs during cooling and storage. Progressive increase in inter-planar spaces of the lamellae could be observed from the shift in the crystalline region of the diffractograms. The product was highly digestible with very high amount of rapidly digestible starch and almost no resistant starch in the severely processed samples. This creates scope for the product to be used for children and patients with poor digestive conditions. A general observation was that roasting of the low amylose *Kola chokua* variety for 13 and 15 min at 140°C gave RTE product with better texture than waxy *Aghoni bora*.

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Chapter 7

CHANGES IN PHYTOCHEMICAL CONTENT AND ANTIOXIDANT ACTIVITIES OF THE MILLING FRACTIONS OF PIGMENTED *KOLA CHOKUA* PADDY ON PROCESSING INTO READY-TO-EAT *KOMAL CHAUL* PRODUCT

7.1. Introduction

Pigmented rice varieties have attained much scientific attention due their phytochemical content and antioxidant property.[1] The bioactive compounds in pigmented rice are primarily located in the surface and bran layers of the kernels that are removed during milling (polishing). The pigment compounds quantitatively drop in quantity from the surface of the brown rice to the middle of the endosperm.[2] The milling fractions of rice have attained commercial uses in food, feed and cosmetic industries due to their nutritive values and non-nutritive bioactive compositions.[3,4] The bioactive phenolic compounds in rice include ferulic acid and diferulates, anthocyanins, anthocyanidins and polymeric proanthocyanidins.[5] They act both as reducing agents and singlet oxygen quencher, thereby protect the cells against oxidative carcinogenic affect.[1,5]

Paddy is often parboiled while in the husk and cooked after milling prior to consumption and both the processes involve high temperature conditions. Thermal treatments cause depletion of natural bioactive compounds in foods (Pascual et al., 2013).[6] Two varieties of 6% polished pigmented aromatic rice on cooking at 100°C for 10 min resulted in variable drop in total phenolic content (TPC), total flavonoid content (TFC) and 2, 2-diphenyl-1-picrylhydrazyl (DPPH) scavenging antioxidant potentials.[5] Leaching of the pigments into the cooking water or deeper into the starchy endosperm may result in the drop of the values (Lamberts, 2007).[2] Pigment migration from the husk

and bran layers into the kernel have also been suggested by different authors.[7,8] Parboiling involves very high processing temperature and sufficient processing time for occurrence of non-enzymatic Maillard browning which contributes to the amber colour of kernels.[8,9] Amongst numerous number of Maillard reaction products, the melanoidins are reported to have scavenging hydroxyl radical, superoxide and hydrogen peroxide antioxidant capacities combined with metal chelation activity.[10-12] Four rice varieties when subjected to three stages of steaming showed reduction of carotenoids to trace levels.[13] The authors hence nullified the contribution of pigments to the final colour of the parboiled rice samples.

The state of Assam in India is a hub of rice germplasm.[14] Traditionally cultivated pigmented *Kola chokua* paddy was found to be suitable for processing into traditional ready-to-eat *komal chaùl* product by a developed laboratory-scale steam parboiling method. *Kola chokua* falls under the low amylose class of rice with apparent amylose content (w.b.) of 12.6%.[14] The peculiarity of *komal chaul* is that it attains texture comparable to cooked rice on soaking in lukewarm water for a few minutes.[15]. The developed process uses controlled single-stage steaming of the pigmented paddy followed by drying and milling. This work involved an investigation on the changes in the phytochemical content and antioxidant properties of the milling fractions of *Kola chokua* rice on processing into *komal chaul* product.

7.2. Materials and methods

Kola chokua paddy from the harvest of 2014 was purchased from farmers of Jorhat district of Assam. The paddy was kept for 24 h at room temperature (RT, 27±2°C) before storing at 4°C till processing. Chemicals were purchased from Merck (India) and Sigma (US). Acidified methanol was prepared by mixing 1.0 mL hydrochloric acid in 9.0 mL water.

7.2.1. Parboiling and coding

Four hundred grams of paddy was brought out, kept at RT for 6h and then soaked in water at 100°C for 1 min as described by Dutta and Mahanta.[15] The vessel containing the soaked paddy was then covered with a thick gunny bag and kept at RT for 18h allowing the paddy to hydrate. The excess water was then decanted and the moistened paddy was immediately steamed in an autoclave fitted with a pressure gauze (Equitron

7407ST, India) for 15 min at 103.42 kPa and 121°C. This was followed by drying at RT for 48 h. The paddy was then milled to obtain *komal chaul*. The milling fractions of raw rice were coded with N followed by the degree of milling and those of parboiled rice were coded with P followed by the degree of milling.

7.2.2. Milling

The rough rice was dehusked using a huller (Satake, Japan). The brown rice was then milled under manual control in an abrasive polisher (Satake, Japan). After repeated polishing trials, powdered fractions representing 3%, 6%, 9% and 12% (w.b.) of the brown rice weight were obtained. The samples were sieved through 100μm sieves and stored at 4°C in sealed polypropylene pouches.

7.2.3. Colour analysis

Colour of milled parboiled rice is considered as an indicative parameter of the extent of parboiling (Bhattacharya, 1996).[7] A color measurement spectrophotometer (Hunter Color-Lab, Ultrascan Vis, US) was used to measure the values for L (lightness), a (red-green), and b (yellow-blue) values. Each sample was analysed in triplicates and the mean value was taken. The hue (H) and chroma (C) values were determined from the following formulae:

$$H = \tan^{-1}(b/a) \qquad \textbf{Eq. 7.1}$$

$$C = (a^2+b^2)^{1/2} \qquad \textbf{Eq. 7.2}$$

7.2.4. Sample extraction

One gram each of the samples was treated with 10 mL of a 10% acidified methanol solution (90:10, methanol: acidified water, v/v). The mixture was shaken in water bath at 25°C for 180 min followed by centrifugation at 3000 rpm for 15 min (Hettich centrifuge, EBA21, Germany). The supernatant was stored at -20°C until further analysis of total phenolics, flavonoids, anthocyanins and antioxidant activities.

7.2.5. Total phenolic content (TPC)

TPC in the bran extracts was assessed using a method modified from the Folin–Ciocalteu assay.[16] Gallic acid was used as the standard. An aqueous gallic acid solution (500 mg/L) was diluted with deionized water to give appropriate concentrations for a standard curve. For the analysis, 20μL each of extract, gallic acid standard or blank were taken in separate test tubes and to each 1.58 mL of distilled water was added, followed by 100μL of Folin–Ciocalteu reagent and mixed thoroughly. Three hundred microliters of sodium carbonate was added after 5 min and vortexed immediately before incubating the tubes in the dark for 30 min at 40°C. The absorbance was measured at 765 nm in a UV-Vis spectrophotometer (Cecil, Aquarius 7400, UK). The results were expressed in mg of gallic acid equivalent (mgGAE) per 100g of sample.

7.2.6. Total flavonoid content (TFC)

The aluminium trichloride method of Chang et al (2002) was used.[17] Briefly, 0.5 mL of the extract was mixed with 1.5 mL of 95% ethanol, 0.1mL of 10% aluminum trichloride, 0.1 mL of 1M potassium acetate, and 2.8 mL of deionised water. After incubation at RT for 40 min, the absorbance of reaction mixture was measured at 415 nm against deionised water taken as blank in the UV-Vis spectrophotometer. TFC was expressed as quercetin equivalent (mgQE) per 100g of sample.

7.2.7. Ferric reducing antioxidant potential (FRAP)

FRAP of the acidified methanolic extract was measured by the method of Benzie and Strain (1996).[18] FRAP solution was freshly prepared by mixing 2.5 mL of a 10 mM 2,4,6-TPTZ [2,4,6-tri(2-pyridyl)-1,3,5-triazine] solution in 40mM hydrochloric acid with 2.5 mL of 20 mM ferric chloride and 25 mL of 0.3M acetate buffer (pH 3.6). The solution was pre warmed at 37°C. Sample extract (40μL) was mixed with 3.0mL of FRAP solution and incubated at 37°C for 4 min and the absorbance was determined at 593 nm in the UV-Vis spectrophotometer against a blank that was prepared using distilled water. A calibration curve was prepared, using an aqueous solution of ferrous sulfate (1-10 mM). FRAP value was expressed as μM of ferrous equivalent Fe (II) per 100g of sample.

7.2.8. DPPH radical scavenging activity

2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity of the extract was measured by determining the inhibition rate of the radical.[19,20] Briefly, 100 µL of extract was added to 1.4 mL of 10^{-4} M DPPH radical prepared in methanolic solution. After 30 min, the absorbance at 517 nm was measured against a blank containing a mixture of 100 µL methanol and 1.4 mL of DPPH radical solution. The results were expressed in terms of radical scavenging activity.

Radical scavenging acitivity % = [(Ao-As)/ Ao] × 100 **Eq. 7.3**

Where, Ao was the absorbance of blank and As was the absorbance of sample extract.

7.2.9. Metal chelating capacity (MCC)

Metal chelating capacity was determined by the method of Dinis et al (1994).[21] For this, 1.0 mL of 0.125 mM ferrous sulphate and 1.0 mL of 0.3125 mM Ferrozine were mixed with 0.2 mL of extract. The mixture was allowed to equilibrate for 10 min at room temperature and the absorbance was read at 562 nm. The control contained all the reagents other than the extract. Decreased absorbance of the reaction mixture indicated increased activity and MCC was determined.

MCC % = [(Ao-As)/ Ao] × 100

Eq. 7.4 Where, Ao was the absorbance of control blank, and As was the absorbance of sample extract.

7.2.10. Statistical analysis

All the experiments were carried out in triplicates. Tests of significant differences between means of colour values were determined by Duncan's multiple range tests at a significance level of 0.05 using statistical package for the social sciences SPSS 11.5 (SPSS Inc., Chicago, IL, USA). Pearson correlation coefficient among TPC, TFC, FRAP, DPPH scavenging activity, MCC and L, a, b colour values of the milling fractions were also analyzed.

7.3. Results and discussion

7.3.1 Effect of parboiling on the colour of different milling fractions

The colour values of the various milling fractions of the raw and parboiled rice are given in Table 7.1. The colour difference observed in the milling fractions of raw rice as observed from the L values became subdued on parboiling. In other words, milling fractions of raw rice were lighter in colour than parboiled rice. This indicated that migration of the pigments to the inner layers had occurred during parboiling. The a value of the milling fractions of raw rice ranged between 7.4 and 7.6 and of parboiled rice ranged between 4.2 and 4.7. The a values in the milling fractions of both raw and parboiled rice however did not correlate with changes observed for L. This indicated that the redness of the pigments in raw rice had reduced to some extent on parboiling treatment even though the pigment colour became darker.

The increase in yellowness, as indicated by the b values, with milling of raw rice may be due to higher concentration of carotenoid pigments in the inner layers of the raw rice kernels. [13] The b values dropped extensively after parboiling and showed irregular pattern indicating destruction or non-uniform migration of the pigments in the gelatinized kernel during parboiling. Hue was stronger for raw rice fractions than parboiled rice and both fractions showed drop in hue with increase in the degree of milling. On the other hand, C values were similar for raw rice fractions but decreased in parboiled rice fractions with increase in degree of milling. This indicated that the colour compounds were irregularly distributed in the milling fractions of the *komal chaul* .[22]

Table 7.1. Colour values of milling fractions of raw and parboiled *Kola chokua* rice.

Sample	L	a	b	H	C
N3%	37.0 ± 0.1^{d}	7.6 ± 0.2^{f}	7.9 ± 0.3^{d}	55.64 ± 0.2^{d}	11.0 ± 0.3^{d}
N6%	37.6 ± 0.2^{e}	7.5 ± 0.3^{e}	8.1 ± 0.1^{e}	53.00 ± 0.2^{c}	11.1 ± 0.4^{d}
N9%	38.6 ± 0.1^{f}	7.4 ± 0.2^{d}	8.2 ± 0.4^{e}	52.06 ± 0.3^{ab}	11.1 ± 0.2^{d}
N12%	43.6 ± 0.4^{g}	7.4 ± 0.1^{d}	8.4 ± 0.2^{f}	50.13 ± 0.2^{a}	11.2 ± 0.6^{d}
P3%	35.0 ± 0.3^{ab}	4.7 ± 0.3^{c}	5.4 ± 0.4^{c}	50.22 ± 0.3^{a}	7.2 ± 0.3^{c}
P6%	34.8 ± 0.2^{a}	4.7 ± 0.2^{c}	4.9 ± 0.1^{b}	55.55 ± 0.2^{d}	6.8 ± 0.4^{b}
P9%	35.8 ± 0.3^{b}	4.6 ± 0.2^{bc}	5.0 ± 0.5^{b}	52.43 ± 0.4^{b}	6.8 ± 0.1^{b}
P12%	36.6 ± 0.1^{c}	4.2 ± 0.3^{a}	4.8 ± 0.2^{a}	49.97 ± 0.1^{a}	6.4 ± 0.4^{a}

*The means in each row followed by a common letter are not significantly different by Duncan's Multiple Range Test at $p < 0.05$.

7.3.2 Effect of parboiling on phytochemical content and antioxidant properties of different milling fractions

N3% showed the highest TPC, TFC and FRAP values of 1942.0 mg GAE/100g, 201.0 mgQE/100 g and 7239.6 mM/ 100g respectively (Fig 1a,b,c). The second milling fraction, N6% was also found to possess appreciable amount of phenolic compounds. Higher composition of phenolic compounds in the outer bran layers of rice have also been reported by Tian et al (2004).[23] The values of TPC and TFC of milling fractions of *Kola chokua* paddy of Assam was markedly higher than pigmented rice varieties of China and Thailand.[24] Parboiling resulted in lowering of TPC and TFC as compared to the native samples, however the rate of decrease was lesser than the native rice milling fractions. This may be attributed to the non uniform temperature attained by the different layers of the rice kernels during steaming.

The results hence indicated that the FRAP activity of the raw rice fractions were basically attributed to the phenolic content. The higher milling fractions, namely N6%, N9% and N12% gave lower values of FRAP probably due to the higher starch content in these fractions.[2] Parboiling resulted in partial destruction of the phenolic compounds as exhibited by significant drop in their values. Thermal processing results in structural rearrangement and degradation of native phenolic compounds as well as formation of newer non-phenolic compounds.[25] Changes in the composition and structures of bioactive compound on processing of different grains have been reported by Archana et al (1998) and Saleh et al (2013).[26, 27] The marginal decrease in FRAP values as compared to TPC and TFC values hence may be due possible formation of compounds with higher ferric ion reducing properties. Further, reduction in these values with degree of milling was also observed for the milling fractions of the parboiled rice indicating higher concentration of these new compounds in the outermost layers of the parboiled samples.

DPPH radical scavenging activity and metal chelating properties however did not show significant fall after parboiling as in raw samples (Fig 7.1d & e). Both the parameters showed increased values in milling fractions of parboiled rice as compared to raw rice. The results therefore suggested that phenolic compounds did not have significant influence on the antioxidant activity of the parboiled milling fractions and newer non-phenolic bioactive compounds were formed on processing.

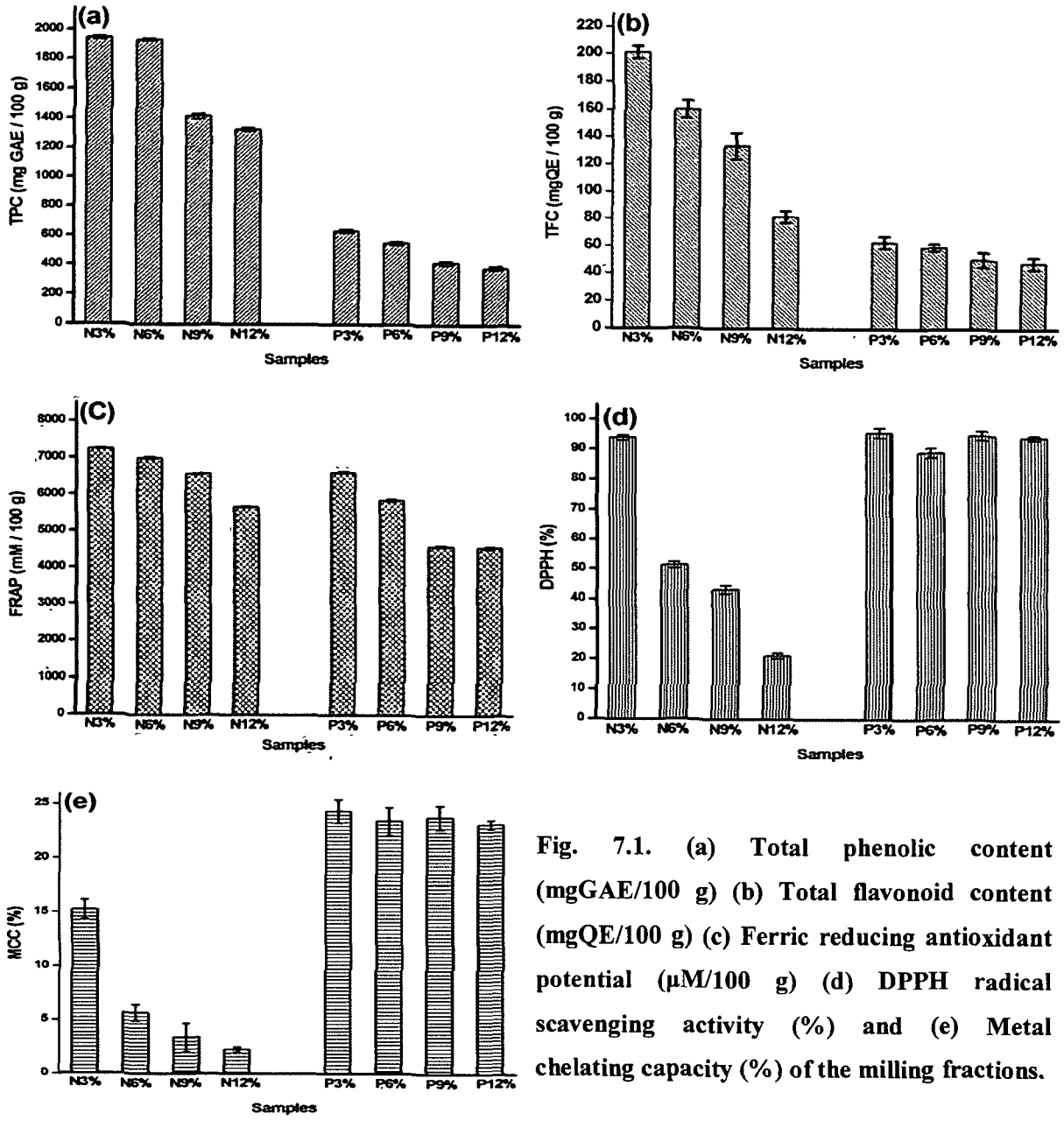

Fig. 7.1. (a) Total phenolic content (mgGAE/100 g) (b) Total flavonoid content (mgQE/100 g) (c) Ferric reducing antioxidant potential (μM/100 g) (d) DPPH radical scavenging activity (%) and (e) Metal chelating capacity (%) of the milling fractions.

High temperature processing reportedly produces Maillard compounds and causes destruction of the natural carotenoids.[13] Probable melanoidin formation in the rice kernel might have resulted in the notable increase in values of MCC and DPPH.[28] DPPH scavenging activity was highest (95.85%) for the 3% milled fraction. Melanoidin compounds form due to reaction of intact protein with the maltodextrin produced by breakdown of starch due to the high heat processing, also popularly known as Strecker degradation reaction.[30] These simpler polysaccharides may have moved out from the endosperm as occurs during cooking but could not release out from the kernel due to the husk and firmer bran layers and hence got accumulated in the surface layers and

simultaneously took part in the Maillard reaction. The bran layers containing higher lipid content are known to act as an effective barrier against starch leaching during rice cooking.[31] Notably higher concentration of these compounds was also seen in the 6% and 12% milled fractions, which also indicates possible inward migration of peptides into the endosperm and formation of melanoidin compounds.[32] Melanoidin compounds also have antimicrobial activity which is related to their metal chelating activity on cations like ferrous, zinc and cuprous, etc.[32]

7.3.3 Correlation between the different parameters studied

Table 7.2 presents the Pearson correlation coefficient values for relation between changes in different parameters of the milling fractions studied. There was strong positive correlation between TPC and TFC. MCC of the milling fractions of the parboiled sample showed significant positive correlation with the DPPH scavenging activity and negative correlation with *b* value.

7.4. Conclusion

Migration of pigments and bioactive compounds and their destruction occur during parboiling that alters the native composition of the milling fractions of rice. A non-uniform distribution of colour in the different milling layers was observed. Pressure parboiling

Table 7.2. Pearson correlation coefficient values for relation between changes in different quality parameters of the milling fractions.

	TFC	FRAP	DPPH	MCC	L	a	b
TPC	0.943*	0.792*	-0.522	-0.765*	0.447	0.954**	0.917**
TFC		-0.881*	-0.245	-0.559	0.186	0.843**	0.774*
FRAP			-0.214	-0.436	0.032	0.686	0.641
DPPH				0.936**	-0.882*	-0.713*	-0.784*
MCC					-0.816*	-0.898**	-0.938**
L						0.650	0.726*
a							0.989**

technique that was followed to make *komal chaul* from pigmented rice caused destruction of natural bioactive compounds as revealed from the TPC and TFC values. The marginal decrease in FRAP of parboiled samples was attributed to formation of newer ferric ion reducing compounds. This was further supported by the DPPH and MCC results that probably indicated the formation of Maillard compounds with reducing properties in the milling fractions of *komal chaul*. Further studies on chromatographic isolation and identification of these compounds may provide more insight into the bioactive composition of *komal chaul* and other numerous pigmented rice and rice products of Assam.

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Chapter 8

CONCLUSIONS AND FUTURE SCOPE OF WORK

8.1. Conclusions

The present work deals with studies on the effects of different parboiling procedures and conditions on Assamese rice varieties widely differing in apparent amylose content. Two traditional rice products, namely *komal chaul* and *bhoja chaul* were also characterized after processing by laboratory-scale parboiling techniques. *Kola chokua*, a pigmented low amylose rice variety was processed by the developed technique followed by necessary milling operations to produce *komal chaul*. The different milling fractions were collected and analysed for their phytochemical content and antioxidant activities. The experimental works and results of the same are detailed from Chapter 3 to Chapter 7 of this thesis. The major conclusions drawn from the present work are enumerated below.

8.1.1. Chapter 3

This chapter included a study on the effect of mild, moderate and severe steam parboiling at open and under steam pressures on four rice varieties, namely *Ranjit*, *Kola chokua*, *Aghoni bora* and *Bhogali bora* with 27.2%, 12.6%, 1.1% and 1.1% apparent amylose content, respectively.

1. Degree of gelatinization in all the four varieties was higher on pressure parboiling than open steam parboiling.
2. Marked increase in water uptake properties indicated altered cooking properties attained by the low amylose and waxy rices after parboiling.
3. Pressure parboiled waxy samples showed extensive drop in gelatinization temperature and increased hydration at lower temperatures as revealed by RVA.

Formation of short amylopectin fine structures in these samples was indicated by sediment volume test and viscosity patterns.

4. Development of retrograded crystallinity in the samples was found to be related to stretching vibration patterns of C-H bonds as revealed from FTIR analysis. Crystallinity, measured by XRD, however could not be related to that measured by FTIR. XRD can, therefore, be considered as a more suitable tool than FTIR for crystallinity study.
5. XRD of raw samples showed peaks at 2θ values near 20 which indicated 'in situ' points for amorphous amylose complex formation. A, B and V-type polymorphs were seen in pressure parboiled samples and only A and V-type polymorphs were observed in open steamed samples.
6. The existence of V-type crystalline pattern was noted even in waxy parboiled rice.
7. Loss in crystallinity with simultaneous increase in water uptake can be attributed to the amorphous fractions in parboiled rice. Waxy varieties are more susceptible to loss of crystallinity than the high amylose variety. Higher crystallinity observed in the most severely parboiled samples than the moderately parboiled samples may be related to higher retrogradation.
8. Low amylose parboiled rice samples of both processing conditions showed higher content of resistant starch and can be commercially exploited.

8.1.2. Chapter 4

This chapter presented a study on the effect of dry heat parboiling at two different temperatures and three different time periods at each temperature (11, 13 15 min at 140°C and 3, 4, 5 min at 200°C) on physical and physicochemical properties of *Ranjit*, *Kola chokua* and *Aghoni bora* varieties of Assam rice.

1. Dry heat parboiling at 140°C resulted in notable improvement in head rice yield. All the samples showed almost 100% head rice yield which could be attributed to the increase in kernel hardness. The laboratory dry heat parboiling can hence be further studied as a replacement of commercially used steam parboiling process.
2. The lower hardness and head rice yield of the high temperature treated samples was attributed to the development of a cavity in the center of the rice kernels. This

cavity was formed as a result of rapid dislocation of the gelatinized starch of the endosperm towards the outer surface of the paddy and simultaneous dehydration as a result of high conduction heating. This also explained the reason for the reported splitting of dry heat parboiled rice on alkali spreading test.

3. The dry heat parboiled kernels of *Kola chokua* and *Aghoni bora* became bolder in shape than raw rice kernels. Length to breadth ratio of *Ranjit* rice however remained almost unaltered indicating varietal differences in the arrangement of kernel material after parboiling.
4. The kernels and flours of dry heat parboiled samples were highly hygroscopic.
5. In low amylose and waxy varieties, milder parboiling caused increased peak viscosity on cooking whereas severe parboiling caused drop in viscosity. The high amylose variety exhibited gradual fall in viscosity parameters with process severity.
6. XRD and DSC curves suggested formation of additional B-type retrograded starch in the high amylose HR variety. Although peaks for amylose-lipid complex formation were feeble in the curves of HR, peaks for melting of starch-lipid complex in processed LK and WA samples were clearly evident from DSC curves.
7. Dry heat parboiled samples were highly digestible as compared to raw rice. The extensive gelatinization and molecular breakdown led to the development of peculiar physicochemical characteristics.

8.1.3. Chapter 5

This chapter deals with processing and characterization of *komal chaul,* a ready-to-eat whole rice product processed from low amylose *Kola chokua* paddy and which requires no cooking. The product was processed by a developed laboratory-scale method and was characterized for different physical and physicochemical parameters.

1. The pressure steaming of *chokua* paddy after hot soaking treatment gave *komal chaul* similar in texture to cooked rice. The textural properties of such pressure steamed rice gives soft textured rice kernels on soaking in water for 20 min at 50°C.

2. Soaking in boiling water results in increased water uptake and altered properties indicating partial gelatinization of the starch. Surface gelatinization of the endosperm prohibits pigment migration on steaming.
3. While the kernel lengths remained almost unchanged on open steaming, pressure steaming caused marked increase. This was accompanied by simultaneous decrease in the breadths, indicating elastic stress development in the kernels during steaming and subsequent drying.
4. Increase in water absorption and thereby lowering of cooking time with severity of steaming was prominent.
5. Severe processing caused thermal degradation of starch polymer structure as revealed by the other physicochemical properties. Increase in the final slurry viscosity, hence may be attributed to leaching of the degraded simpler chains causing rise in slurry densities. The almost continuous rise in the slurry viscosity throughout the RVA cycle with minor breakdown indicated the thickening property of the pressure steamed samples, suggesting its suitability for specific uses.
6. The changes in properties can be attributed to the effect of gelatinisation and thermal degradation of starch which may explain the high rate of starch digestibility of the pressure parboiled samples. On the other hand, *komal chaul* processed by open steaming of hot soaked paddy gave enzyme resistant starch.
7. The laboratory scale method can be further used for analytical studies on *komal chaul* and can further be modified into a larger-scale method.

8.1.4. Chapter 6

This chapter includes a study on characterization of *Bhoja chaul*, another traditional ready-to-eat rice product of Assam. The product was processed by an improvised laboratory-scale dry heat parboiling method using *Kola chokua* and *Aghoni bora* varieties. The paddy soaked in boiling water for 1 and 3 min followed by hydration in the cook water for 18 h was roasted at 140°C for 13, 14 and 15 min.

1. High head rice yield was obtained by the laboratory-scale process. Decreased porosity indicated better packing properties of the product than the raw rice.

2. No endothermic peak for retrogardation was observed in DSC meaning that the product did not retrograde after gelatinization due to absence of necessary moisture for retrogradation to occur.
3. However, peak for amylose-lipid complex melting was evident in the severely processed samples. Longer chains of amylopectin may be able to bind lipid molecules.
4. Dry heat parboiling led to significant loss in crystallinity with minor reformation of each type of starch crystalline polymorphs during cooling and storage. Progressive increase in inter-planar spaces of the lamellae could be observed from the shift in the crystalline region of the diffractograms.
5. The product was highly digestible with very high amount of rapidly digestible starch and almost no resistant starch in the severely processed samples.
6. A general observation was that roasting of the low amylose *Kola chokua* variety for 13 and 15 min at 140°C gave RTE product with better texture on soaking in water at room temperature than cooked rice or processed *Aghoni bora* samples.

8.1.5. Chapter 7

This chapter included a study on the phytochemical content and antioxidant activity of milling fractions of pigmented *Kola chokua* rice before and after processing into *komal chaul* by the developed laboratory-scale method involving pressure steaming.

1. Migration of pigments and bioactive compounds occur during parboiling, thereby altering the native compositional structures of the milling fractions of rice.
2. Pressure parboiling caused destruction of natural bioactive compounds with formation of Maillard browning compounds which showed developed DPPH scavenging and metal chelating properties and colour development in milling fractions of *komal chaul*.
3. While ferric reducing antioxidant potentials of the milling fractions were related to phenoloics and flavonoid compounds, DPPH scavenging activity and metal chelation factors were interrelated.

8.2. Future scopes

From the observations and findings from the present work, the following scopes for future research were enumerated.

1. Ratio of FTIR bands used for measuring crystallinity was found to be related to ratio of FTIR bands responsible for symmetric and asymmetric vibration of H-C-H. Retrogradation may be further analysed with a perspective of involvement of molecular energy.
2. Milder parboiling resulted in development of peak viscosity in the low amylose and waxy samples. Change in molecular structures or nature leading to increased hydration and swelling capacities in these samples may be further analyzed using tools like gel permeation chromatography or high performance size exclusion chromatography.
3. Amylopectin-lipid complexes probably occurred after parboiling. Dry heat parboiling can be further studied as a process for newer starch polymorph formation.
4. The laboratory parboiling techniques used for processing *komal chaul* and *bhoja chaul* may be further developed into industrial processes. Dry heat parboiling with high head rice yield created scope for replacing steam parboiling technique.
5. Based on viscosity and starch digestibility patterns, targeted use of the parboiled rice products to consumer groups with special dietetic needs can be explored.
6. The preliminary investigation on bioactive potential of the bran layers of *Kola chokua* paddy created future scope for a detailed study involving identification and chromatographic isolation of specific bioactive compounds in it and other pigmented rice varieties.

List of publication

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