UNIVERSITI PUTRA MALAYSIA

PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF MALAYSIAN RICE FLOURS AND STARCHES

NOR AFIZAH BINTI MUSTAPHA

FSTM 2007 10

PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF MALAYSIAN RICE FLOURS AND STARCHES

By

NOR AFIZAH BINTI MUSTAPHA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

December 2007

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF MALAYSIAN RICE FLOURS AND STARCHES

By

NOR AFIZAH BINTI MUSTAPHA

December 2007

Chairman : Associate Professor Sharifah Kharidah Syed Muhammad, PhD

Faculty : Food Science and Technology

Physicochemical and rheological properties of flours and starches from nine Malaysian rice varieties (seven MR and two MRQ) were investigated. The physicochemical properties determined were swelling power (SP), carbohydrate leaching (CL), gelatinization, pasting, and textural characteristics, whereas the rheological properties studied were steady and dynamic shear. The varieties can be classified into low, intermediate and high amylose (AM) rice and also into intermediate and high-gelatinization temperature (GT). The varieties can be clearly grouped into MR and MRQ varieties based on setback (SB) and final (FV) viscosities and textural analysis. MRQ possessed greater SB, FV and gel hardness but lower gel adhesiveness, whereas, MR varieties showed the opposing results. An increase in AM increased the SB, FV, gel hardness, apparent viscosities(η_a) at and above 8% and 6% for flours and starches, respectively), and, storage modulus (G'), loss modulus (G"), complex modulus (G^*) and complex viscosity (η^*), but decreased the SP, T_o, T_p, T_c, enthalpies (ΔH), peak viscosity

(PV), breakdown (BV), gel adhesiveness, and tan δ. η_a of the flours and starches increased with increasing solid concentrations and the viscosities depended on concentration regimes. Close-packing concentration was observed at concentration ranges of 6.4-8.7% (w/w) and 3.4-4.7% (w/w) in both flour and starch pastes, respectively. Cross-over concentration in the viscosity of the flour (5.6–7.9%, w/w) and starch (2.3–3.4%, w/w) pastes between high (MR) and low (MRQ) swelling varieties was found to occur at around the close-packing concentration. G', G", G* and η* increased whereas tan δ decreased with storage. Dynamic viscoelastic measurements of the starch and flour pastes before and after cooling indicated strong gel characteristics, with MRQ giving stronger and elastic gels. Cox-Merz rule was applicable in the rice starch only at certain concentrations. However, η* could provide a reasonable estimate of η_a. The interplay of starch granular properties and AM contents primarily influence the physicochemical and rheological characteristics of rice flours and starches, whereas the presence of flour components especially proteins significantly influenced the flour properties. MRQ34 exhibited interesting properties that possessed similar characteristics to the high AM variety (MRQ74). Strong correlation observed between the physicochemical (SP, FV, hardness and adhesiveness) and rheological (η_a, G', G", G^* and η^*) characteristics provide a means of predicting of the physicochemical properties via rheological methods and vice versa.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENCIRIAN FIZIKOKIMIA DAN RHEOLOGI TEPUNG BERAS DAN KANJI BERAS

Oleh

NOR AFIZAH BINTI MUSTAPHA

Disember 2007

Pengerusi : Profesor Madya Sharifah Kharidah Syed Muhammad, PhD

Fakulti : Sains dan Teknologi Makanan

Ciri-ciri fizikokimia dan rheologi tepung dan kanji beras dari sembilan variety padi dikaji (tujuh MR dan dua MRQ). Sifat-sifat fizikokimia ditentukan dalam bentuk darjah pembengkakan granul kanji, keterlarutan karbohidrat, gelatinisasi, pempesan dan ciri-ciri tekstur, manakala, sifat-sifat rheologi dikaji dalam bentuk ricihan stabil dan dinamik. Varieti-varieti beras dapat diklasifikasikan kepada varieti yang mengandungi kandungan amilosa (AM) rendah, pertengahan dan tinggi, dan juga dikelaskan sebagai mempunyai suhu gelatinisasi pertengahan dan tinggi. Varieti-varieti tersebut dapat dikelaskan dengan jelas ke dalam dua kumpulan; MR dan MRQ, berdasarkan kelikatan ‘setback’, kelikatan akhir dan analisis tekstur. MRQ mempunyai kelikatan ‘setback’, kelikatan akhir dan kekerasan gel yang lebih tinggi, tetapi kelekitan gel yang rendah, sedangkan variety-varieti MR mempamerkan sifat yang berlawanan. Peningkatan kandungan amilosa meningkatkan kelikatan ‘setback’, kelikatan akhir, kekerasan gel, kelikatan nyata (η_a, masing-masing pada dan melebihi 8% and 6% dalam tepung dan kanji beras)

dan modulus tersimpan (G'), modulus terhilang (G"), modulus kompleks (G*) and kelikatan kompleks (η*), tetapi merendahkan darjah pembengkakan, T_o, T_p, T_c, entalpi, kelikatan puncak, kelikatan 'breakdown', kelekitan gel dan tan δ. Kelikatan nyata tepung dan kanji beras meningkat dengan peningkatan dalam kepekatan bahan pepejal dan kelikatan tersebut adalah bergantung kepada rejim kepekatan. Kepekatan 'close-packing' berlaku pada julat kepekatan 6.4-8.7% (w/w) dan 3.4-4.7% (w/w) dalam kedua-dua pes tepung dan kanji. Kepekatan 'cross-over' kelikatan nyata pes tepung (5.6–7.9%, w/w) dan pes kanji (2.3–3.4%, w/w) di antara varieti yang mempunyai darjah pembengkakan yang tinggi (MR) dan darjah pembengkakan yang rendah (MRQ) didapati berlaku di sekitar kepekatan 'close-packing'. G', G", G* and η* meningkat manakala tan δ berkurang selepas penstoran. Pengukuran viskoelastik secara dynamic yang dilakukan kepada pes kanji dan tepung sebelum dan selepas penyejukan menujukkan pes besifat sebagai gel yang kuat, di mana MRQ bersifat sebagai gel yang lebih kuat dan elastic. Peraturan Cox-Merz dipersetujui hanya pada kepekatan tertentu sahaja. Walau bagaimanapun, η* memberikan satu anggaran yang munasabah bagi penentuan η_a. Pengaruh salingan sifat-sifat granul kanji dan kandungan amilosa adalah faktor utama yang mempengaruhi ciri-ciri fizikokimia dan rheologi tepung dan kanji beras, manakala kehadiran komponen-komponen lain dalam tepung terutamanya protein mempengaruhi ciri-ciri fizikokimia tepung secara signifikan. MRQ34 menujukkan ciri-ciri menarik di mana ia mempunyai sifat-sifat menyamai varieti yang mempunyai kandungan amilosa yang tinggi (MRQ74). Pertalian kuat yang didapati wujud antara sifat-sifat fizikokimia (darjah pembengkakan, kelikatan akhir, kekerasan dan kelekitan gel) dan sifat-sifat rheologi (η_a, G', G", G* and η*) memberikan satu cara untuk menentukan sifat-sifat fizikokimmia melalui kaedah-kaedah rheologi, dan sebaliknya.

ACKNOWLEDGEMENTS

All praise due to Allah, the most gracious and merciful, for giving me the strength, health and determination to complete this research study. I would like to express my deepest appreciation and gratitude to my supervisors, Assoc. Prof Dr. Sharifah Kharidah Syed Muhammad and En Dzulkifly Mat Hashim for their patience, invaluable guidance and suggestions throughout the planning and development of this research. I would like to express my sincere gratitude to Assoc. Prof. Dr Nazamid Saari, Prof. Dr. Hasanah Mohd Ghazali, Dr. Karim Saboo and Dr. Nazimah for the facilities and technical assistance provided. I would also like to thank all my friends especially Wan Zunairah, Husni Hayati, Nor Khaizura and Norhayati for their support and cooperation throughout the period of this study. Appreciation is extended to En. Soib, En Amran, En. Mohd Noh and En. Azman for their assistance in making this project possible. Finally, I would like to express a special note of appreciation to my beloved parents for their constant support throughout the duration of the study.

I certify that an examination Committee has met on 18 December 2007 to conduct the final examination of Nor Afizah Mustapha on her Master of Science thesis entitled "Physicochemical and Rheological Characterization of Malaysian Rice Flours and Starches" in accordance with Universiti Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the Degree of Master of Science.

Members of the Examination Committee were as follows:

Jamilah Bakar, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Chairman)

Hasanah Mohd. Ghazali, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Internal Examiner)

Nazamid Saari, PhD
Associate Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Internal Examiner)

Abd. Karim Alias, PhD
Professor
Pusat Pengajian Teknologi Industri
Universiti Sains Malaysia
(External Examiner)

HASANAH MOHD. GHAZALI, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 1 April 2008

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the Degree of Master of Science. The members of the Supervisory Committee were as follows:

Sharifah Kharidah Syed Muhammad, PhD
Associate Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Chairman)

Dzulkifly Mat Hashim, M.Sc.
Lecturer
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

AINI IDERIS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 10 April 2008

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any degree at Universiti Putra Malaysia or at any other institution.

NOR AFIZAH BINTI MUSTAPHA

Date: 24 March 2008

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Symbols

ΔH	Enthalpy
ΔT	Gelatinization temperature range
η_a	Apparent viscosity
γ	Shear rate
η^*	Complex viscosity
ω	Frequency (rad/s)
f	Frequency (Hz)
$[\eta]$	Intrinsic viscosity

Abbreviations

AM	Amylose
AP	Amylopectin
SP	Swelling power
CL	Carbohydrate leaching
DSC	Differential scanning calorimetry
T_o	Onset temperature
T_p	Peak temperature
T_c	Conclusion temperature
RVA	Rapid Visco Analyzer
cP	Centipoise
PT	Pasting temperature

PV	Peak viscosity
BV	Breakdown
SB	Setback
FV	Final viscosity
K	Consistency index
n	Flow behavior index
G’	Storage modulus
G”	Loss modulus
G*	Complex modulus
GT	Gelatinization temperature
LAM	Lipid-complexed amylose
FAM	Free amylose
ae	Amylose extender

CHAPTER 1

INTRODUCTION

Cultivated rice (*Oryza sativa L.*) is one of the most widely consumed basic foodstuffs in the world. It sustains two-third of the world's population (Zhou *et al*., 2002). Worldwide, there are more than 120000 different varieties (IRRI, 2008), although only small number offers quality acceptable to be grown commercially in Malaysia (Abdullah *et al*., 2005). The rice germplasm collection at the Rice Genebank (Malaysia) stands at 11470 registered accessions. Different climatic conditions, soil characteristics and resistance towards pests and disease have seen around 33 modern varieties being developed and released for commercial planting (Abdullah *et al*., 2005).

There are many varieties of rice including normal white, waxy, aromatic and elongating types. Each type has its own characteristic and therefore, owns its place in rice cooking (Villareal *et al*., 1993). The different varieties produced different cooking and eating quality of cooked rice and rice-based products. Low amylose (18-20%) (AM) rice are favored more than higher AM (20-25%) varieties because when freshly cooked the latter will not be too sticky or too hard when aged (Juliano, 1998). Moreover, rice flours and starches are important ingredients in both traditional and novel foods. They are widely used to manufacture products such as puddings, infant foods and breakfast cereals (Juliano, 1993). Different rice products require different kinds of rice with different starch properties. For example, waxy and low AM rice are preferred for processing cracker and biscuits, whereas high-AM varieties are favored for parboiled rice, rice bread and noodles (Juliano, 1998).

Rice comprises primarily starch (90%) and the rest are non-starch components (protein, lipids) (Juliano, 1985a). Starch consequently plays an important role as a determinant of the quality of rice and rice-based products because most functional attributes of rice can be related to temperature-dependence interaction of starch with water during gelatinization, pasting and gelation (retrogradation) (Atwell *et al*., 1988). Gelatinization occurs during heating of starch in excess water. It includes loss of birefringence, hydration and swelling of the granules several times of their original size, diffusion and solubilization of linear molecules from ruptured granules, increased clarity, marked increase in consistency and formation of a paste-like mass or gel when it is cooled (Olkku and Rha, 1978).

Consequently, there would be a relationship between the cooking and eating quality of rice and the physicochemical properties of its starch. Among the indices used in determining the composition-properties relationship of starch are Brabender viscoamylograph, rapid visco analyzer (RVA) and rotational viscometry that are used extensively for measuring pasting behavior, and paste viscosity, whereas and dynamic rheometer are used for studying the rheological properties of starch pastes/gels (Wiesenborn *et al*., 1994; Lii *et al*., 1995). The pasting behavior is helpful in understanding the textural changes or retrogradation potency of the flours and starches, while, viscosity parameters can be interpreted on the basis of swelling and solubility or granular rigidity (Bagley and Christianson, 1982), soluble matrices and volumetric fraction of granular remnants (Eliasson, 1986). Furthermore, by determining rheological properties, the relationship between pasting properties of starches and the rheology of their respective gels can effectively be investigated (Singh *et al*., 2003).

It is generally accepted that the cooking of rice is strongly influenced by the compositions and physical properties of rice components, where it has long been associated with AM contents. AM correlates directly with volume expansion, water absorption and hardness of cooked rice (Juliano, 1985a). The amylose/amylopectin (AM/AP) ratio among varieties of rice varies, but typically about 25% is AM and 75% is AP (Liu *et al*., 1991). These properties therefore allow a wide functionality of rice. However, increasing cross-breeding activities have generated rice that exhibit different cooking and eating properties although they may possess similar AM contents (Juliano *et al*., 1987), pasting or gelatinization characteristics (Juliano, 1990).

Although present in smaller amounts, proteins and lipids have both received attention due to generation of possible intra- or inter-molecular interactions with starch during cooking (Eliasson and Gudmunsson, 1996). The protein content has been reported by Hamaker *et al*. (1991) to be inversely related to cooked rice stickiness and adhesiveness but Champagne *et al*. (1999) reported that no correlation was observed between the protein content and textural properties. Proteins have also been reported to influence the gelatinization, swelling and viscosity of rice flours (Martin and Fitzgerald, 2002). Lim *et al*. (1999) showed that removal of rice proteins increased peak viscosity but decreased pasting temperature of rice starch. Lipids are known to affect the physicochemical and viscosleastic properties by forming a complex with AM (Biliaderis and Tonogai, 1991) thus altering the swelling and solubility of starch granules (Eliasson and Gudmunsson, 1996). Maningat and Juliano (1980) found that defatting of rice starch reduced the gelatinization temperature (GT) and gel viscosity.

Perez and Juliano (1979) reported that the differences that exist among varieties are related to GT and gel consistency. GT has been shown to be one of the most important determinants in rice cooking quality (Bao *et al*., 2004). Moreover, texture of the cooked rice is affected by the amount and structure of leached out materials (Priestly, 1977; Ong and Blanshard, 1995b). There is an interdependence between physicochemical properties of starch to each other. Swelling and leaching also affect rice starch pastes' viscosity and texture (Ong and Blanshard, 1995b; Li and Yeh, 2001). Leloup *et al*. (1991) reported that rheological properties of the volume fraction of the continuous phase (leached out materials), shape and deformability of dispersed phase (swollen granules) were associated with mechanical properties of starch gels.

The demand for functionality varies for different products and in order to fulfill this demand, the properties of rice flours and their starches need to be characterized. Physicochemical, cooking and textural, thermal and rheological properties of flours and starches of several Indian (Sodhi and Singh, 2003), Argentine (Iturriaga *et al*., 2004), Thai (Varavinit *et al*., 2003), Chinese (Wang *et al*., 1999) and Korean rice (Chun and Yoo, 2004) have been investigated. As the markets for rice are expanding (Oryza Market Report, 2004), it is important to assess the properties of Malaysian varieties and to determine the factors that influence eating quality. Currently, there are only a few studies dealing with the physicochemical properties of Malaysian rice varieties (Teo *et al*., 2000; Nurul Islam and Mohd. Azemi, 2006). In addition, no work has been reported regarding the rheological properties of Malaysian rice.

Thus, the objectives of this study were;

i) To determine the relationship between the various physicochemical properties of rice flours and starches.

ii) To determine the correlation between the physicochemical and rheological properties of rice flours and starches.