EFFECT OF HYDROCOLLOIDS ON PHYSICAL AND RHEOLOGICAL PROPERTIES OF RICE STARCH

JETNAPA TECHAWIPHARAT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
(BIOTECHNOLOGY)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2007

Thesis
Entitled

EFFECT OF HYDROCOLLOIDS ON PHYSICAL AND RHEOLOGICAL PROPERTIES OF RICE STARCH

…………………………………...
Miss Jetnapa Techawipharat
Candidate

…………………………………...
Assoc. Prof. Manop Suphantharika,
Ph.D. (Biochemical Engineering)
Major-Advisor

…………………………………...
Assoc. Prof. Saiyavit Varavinit,
Dr. Ing (Chemical Engineering)
Co-Advisor

…………………………………...
Lect. Pairoj Luangpituksa,
D. Agr. Chem.
(Food and Nutritional Chemistry)
Co-Advisor

…………………………………...
Asst. Prof. Sittiwat Lertsiri,
Ph.D. (Agricultural Science)
Co-Advisor

…………………………………...
Prof. Banchong Mahaisavariya, M.D.
Dean
Faculty of Graduate Studies

…………………………………...
Asst. Prof. Chuenchit Boonchird,
Ph.D. (Molecular Biology)
Chair
Doctor of Philosophy Programme
in Biotechnology
Faculty of Science

Thesis

Entitled

EFFECT OF HYDROCOLLOIDS ON PHYSICAL AND RHEOLOGICAL PROPERTIES OF RICE STARCH

was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Doctor of Philosophy (Biotechnology)
on
December 4, 2007

…………………………………...
Miss Jetnapa Techawipharat
Candidate

…………………………………...
Lect. Attawut Impoolsup,
Ph.D. (Biotechnology)
Chair

…………………………………...
Asst. Prof. Sittiwat Lertsiri,
Ph.D. (Agricultural Science)
Member

…………………………………...
Assoc. Prof. Manop Suphantharika,
Ph.D. (Biochemical engineering)
Member

…………………………………...
Lect. Pairoj Luangpituksa,
D. Agr. Chem.
(Food and Nutritional Technology)
Member

…………………………………...
Assoc. Prof. Saiyavit Varavinit,
Dr. Ing (Chemical engineering)
Member

…………………………………...
Asst. Prof. Jirarat Tattiyakul,
Ph.D. (Food Science and Technology)
Member

…………………………………...
Prof. Skorn Mongkolsuk,
Ph.D.
Dean
Faculty of Science
Mahidol University

…………………………………...
Prof. Banchong Mahaisavariya, M.D.
Dean
Faculty of Graduate Studies
Mahidol University

ACKNOWLEDGEMENTS

I would like to acknowledgement the supervision of my advisor, Assoc. Prof. Manop Suphantharika for his helpful guidance, comments and suggestions throughout of my study. Moreover, I am thankful to him to encourage and allow me to do a research at Purdue University for 14 months. He does not only teach me how to do the research, but he also gives me a great chance to learn how to be a researcher.

My sincerely gratitude is also given to all members of the advisory committee, Assoc. Prof. Saiyavit Varavinit, Asst. Prof. Sittiwat Lertsiri and Lect. Pairoj Luangpituksa for their valuable suggestions, expert comments, generosity in contributing time and criticisms with kindness about the work of my thesis. Moreover, I am thankful for Prof. James N. BeMiller for allowing me to do the research in his laboratory at Department of Food Science, Purdue University and for his helpful comments and suggestions on this study.

I am thankful to Choheng Rice Vermicelli Factory Company, Nakornpathom, Thailand for kindly supporting of rice starch samples. I am also grateful to technician staffs at Mettler Toledo, Bangkok, Thailand for allowing me to use Differential scanning calorimetry (DSC).

I am particularly grateful to all members of the room BT 204, BT 210 and BT 208 for their helps, friendship and also to m all fellows in the Department of Biotechnology, Faculty of Science, Mahidol University.

Finally, I would like to special express my gratitude to my parents, grandmother and brother for their understanding, patience and encouragement during this study.

This work was financial supported from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

Jetnapa Techawipharat

EFFECT OF HYDROCOLLOIDS ON PHYSICAL AND RHEOLOGICAL PROPERTIES OF RICE STARCH

JETNAPA TECHAWIPHARAT 4737321 SCBT/D

Ph.D. (BIOTECHNOLOGY)

THESIS ADVISORS: MANOP SUPHANTHARIKA, Ph.D., SAIYAVIT VARAVINIT, Dr. Ing., SITTIWAT LERTSIRI, Ph.D., PAIROJ LUANGPITUKSA, Dr. Agr. Chem.

ABSTRACT

Rice starch is a very useful additive for blending into many kinds of food products because it has small granule size and soft gel formation. However, it also exhibits negative properties such as gel syneresis, retrogradation and weak-bodies. Blending hydrocolloids into the starch may be an alternative method to chemical modification. Two preparation techniques, a blend of rice starch and hydrocolloids (guar and xanthan gums) prior to dispersed in water (dry mixing) and a blend of gum solutions and starch powders (wet mixing) were used for both normal (NRS) and waxy (WRS) types of starch. This experiment showed that samples from these two techniques did not significantly affect the Rapid-Visco Analyzer (RVA) results. However, the viscosities increased in both starches when hydrocolloid was added. Differential scanning calorimetry (DSC) data demonstrated a decrease of the gelatinization enthalpy (ΔH) and the wet mixing-prepared samples decreased ΔH and enhanced gelatinization temperatures. The wet mixing prepared samples also showed a significant increase in hardness and adhesiveness for both NRS- and WRS-hydrocolloid gels by texture profile analysis.

Moreover, various kinds of hydrocolloids were studied for their effect on the pasting and rheological properties of NRS and WRS. Addition of tested hydrocolloids significantly increased viscosities and pasting temperatures, except for hydroxypropylmethylcellulose (HPMC). The methylcellulose (MC) addition resulted in the most pronounced increase in peak viscosity. Furthermore, locust bean gum and λ-carrageenan increased final viscosity in NRS and WRS, respectively. The hydrocolloid addition to NRS and WRS promoted a decrease in ΔH. The gelatinization temperatures did not differ significantly among the starch samples with different hydrocolloids. Nevertheless, the addition of gums increased swelling power and the solubility index of NRS, but did not significantly affect those of WRS.

Dynamic rheological measurement revealed no effect of the hydrocolloids, except for κ-carrageenan, on G', G'' or η^* in both NRS and WRS. The $\tan\delta$ values of NRS pastes were increased, whereas those of WRS pastes were unaffected by the addition of hydrocolloids. Steady shear tests exhibited an increase in $\eta_{a,100}$ and K values when tested hydrocolloids were added. All samples, including the controls, showed shear-thinning behavior for which $n<1$. Guar gum, xanthan gum and low-methoxyl pectin were chosen to observe the effect on rheological properties in native and cooked starch pastes of both NRS and WRS. Xanthan gum showed the highest increase in G', G'' and η^* in both native and cooked starch pastes. The cooked starch pastes also showed shear-thinning behavior as the native starch pastes. However, the addition of these three gums did not affect $\eta_{a,100}$ and K values in the cooked starch pastes. The increase of hardness and adhesiveness was promoted with the addition of hydrocolloids, especially gellan, κ-carrageenan or ί-carrageenan, in NRS. A similar result was observed in WRS pastes, except for low- and high-methoxyl pectins additions. The photographs of NRS- and WRS-hydrocolloid mixtures showed phase-separated microstructures in which, starch-rich domains were dispersed in a continuous hydrocolloid matrix. Moreover, the addition of ί-carrageenan did not promote the amylopectin aggregation.

KEY WORDS: RICE STARCH/ HYDROCOLLOID/ PASTING/ RHEOLOGY/ MICROSTRUCTURE

p.135

ผลของไฮโดรคอลลอยด์ต่อคุณสมบัติทางกายภาพและรีโอโลยีของแป้งข้าว
(EFFECT OF HYDROCOLLOIDS ON PHYSICAL AND RHEOLOGICAL PROPERTIES OF RICE STARCH)

เจษฎ์นภา เตชวิภารัตน์ 4737321 SCBT/D

ปรด. (เทคโนโลยีชีวภาพ)

คณะกรรมการควบคุมวิทยานิพนธ์: มานพ สุพรรณธริกา, Ph.D., ไสยวิชญ์ วรวินิต, Dr. Ing, สิทธิวัฒน์ เลิศศิริ, Ph.D., ไพโรจน์ หลวงพิทักษ์, Dr. Agr. Chem.

บทคัดย่อ

แป้งข้าวใช้เป็นส่วนผสมในอาหารหลากหลายชนิดเพราะมีขนาดของเม็ดแป้งเล็กและให้เจลที่อ่อนนุ่ม แต่แป้งข้าวมีข้อเสียคือปัญหาการแยกตัวของน้ำออกจากผลิตภัณฑ์อาหารซึ่งมีแป้งเป็นองค์ประกอบ ส่งผลให้โครงสร้างของแป้งข้าวอ่อนแอลง การผสมไฮโดรคอลลอยด์ลงในแป้งข้าวช่วยปรับปรุงคุณภาพของแป้งข้าวซึ่งเป็นอีกทางเลือกหนึ่งนอกเหนือจากการใช้สารเคมีเพื่อปรับปรุงคุณสมบัติของแป้ง ของผสมระหว่างแป้งข้าว(ข้าวเจ้าและข้าวเหนียว)และไฮโดรคอลลอยด์(กัวกัมและแซนแทนกัม)แบบผงแห้ง(ผสมแห้ง)และของผสมระหว่างสารละลายกัมและแป้งแบบผงแห้ง(ผสมเปียก)ถูกนำมาศึกษาถึงความแตกต่างของการเตรียมตัวอย่าง ของผสมจากทั้งสองวิธีไม่ให้ผลที่แตกต่างกันอย่างมีนัยสำคัญจาก Rapid-Visco Analyzer (RVA) แต่ความหนืดของแป้งทั้งสองชนิดเพิ่มขึ้นเมื่อเพิ่มความเข้มข้นของไฮโดรคอลลอยด์ ผลจาก Differential scanning calorimetry (DSC) แสดงการลดลงของค่าพลังงานความร้อนขณะหลอมละลายและของผสมจากการผสมแบบเปียกแสดงค่าการลดลงของค่าพลังงานความร้อนขณะหลอมละลายและเพิ่มอุณหภูมิของการเกิดเจล รวมทั้งยังเพิ่มค่าความแข็งแรงและความเหนียวในแป้งข้าวทั้งสองชนิดเมื่อทำการวัดลักษณะเนื้อสัมผัส

ไฮโดรคอลลอยด์ชนิดอื่นๆได้นำมาศึกษาผลต่อการเกิดเจลและรีโอโลยีในแป้งข้าว การเติมไฮโดรคอลลอยด์ช่วยเพิ่มความหนืดและอุณหภูมิขณะเกิดเจลในแป้งข้าว ยกเว้นการเติม HPMC การเติม MC ช่วยเพิ่มค่าความหนืดขณะเกิดเจลได้สูงสุด นอกจากนี้การเติม locust bean gum และคาราจีแนนชนิดแลมดาช่วยเพิ่มความหนืดขณะลดอุณหภูมิของเจลในแป้งข้าวเจ้าและแป้งข้าวเหนียวตามลำดับ นอกจากนี้การเติมไฮโดรคอลลอยด์ให้ผลในการลดค่าพลังงานความร้อนขณะหลอมละลายของผสม แต่ไม่เกิดความแตกต่างระหว่างไฮโดรคอลลอยด์แต่ละชนิด ไฮโดรคอลลอยด์ช่วยเพิ่มการบวมของเม็ดแป้งและการละลายออกมาของสารประกอบในเม็ดแป้ง ซึ่งการละลายออกมาพบมากในของผสมของแป้งข้าวเจ้า ส่วนแป้งข้าวเหนียวไม่พบความแตกต่างระหว่างของผสมและตัวควบคุม

การเติมไฮโดรคอลลอยด์ไม่ส่งผลกระทบต่อคุณสมบัติการเป็นของกึ่งแข็งกึ่งเหลวในของผสมระหว่างแป้งข้าวและกัม ยกเว้นการเติมคาราจีแนนชนิดคัปปาช่วยในการเพิ่มค่า G', G'' หรือ $\eta*$ ของแป้งข้าวให้สูงขึ้น และการเติมกัมในแป้งข้าวเจ้าช่วยเพิ่มค่า $\tan\delta$ โดยผลลักษณะนี้ไม่พบในแป้งข้าวเหนียว จากคุณสมบัติการไหลของของผสมแสดงให้เห็นว่าการาเติมไฮโดรคอลลอยด์ในแป้งข้าวทั้งสองชนิดและแป้งที่ไม่มีการเติมไฮโดรคอลลอยด์มีพฤติกรรมการไหลแบบ shear-thinning รวมทั้งยังเพิ่มค่า $\eta_{a,100}$ และ K ด้วย กัวกัม แซนแทนกัม และเพคตินชนิด low-methoxyl ได้นำมาเติมในแป้งข้าวต้มสุก พบว่าแซนแทนกัมช่วยเพิ่ม G', G'' และ $\eta*$ ทั้งในแป้งปกติและแป้งต้มสุก การเติมกัวกัม แซนแทนกัมและเพคตินชนิด low-methoxyl ในแป้งข้าวต้มสุกแสดงพฤติกรรมการไหลแบบ shear-thinning เช่นเดียวกับในแป้งข้าวแบบปกติและไม่ส่งผลกระทบต่อค่า $\eta_{a,100}$ และ K การเติมเจลแลน คาราจีแนนชนิดคัปปาและไอออตาในแป้งข้าวช่วยเพิ่มความแข็งแรงและความเหนียวของเจลแป้งข้าว ยกเว้นการเติมเพคตินทั้งสองชนิดที่ลดค่าความแข็งแรงของเจลในแป้งข้าวเหนียวลง การเติมไฮโดรคอลลอยด์ทำให้เกิดการแยกตัวของแป้งในสารละลายไฮโดรคอลลอยด์ขณะเกิดเจลและการเติมคาราจีแนนชนิดไอออตาไม่ทำให้เกิดการจับตัวกันของ amylopectin

135 หน้า

CONTENTS

Page

ACKNOWLEDGEMENTS iii

ABSTRACT (ENGLISH) iv

ABSTRACT (THAI) v

LIST OF TABLES x

LIST OF FIGURES xiii

LIST OF ABBREVIATIONS xvi

CHAPTER

- **I INTRODUCTION** 1
- **II LITERATURE REVIEW** 5
  - 1. Starch 5
    - 1.1 Starch structure and composition 5
    - 1.2 Rice starch 9
      - 1.2.1 Constituents of rice starch 10
      - 1.2.2 Structure and functionality of rice starch 10
      - 1.2.3 Swelling power and solubility 12
      - 1.2.4 Gelatinization of rice starch 13
      - 1.2.5 Retrogradation of rice starch 19
  - 2. Hydrocolloids 20
    - 2.1 Galactomannans 23
    - 2.2 Xanthan gum 28
    - 2.3 Gellan gum 31
    - 2.4 Pectin 37
    - 2.5 Alginates 40
    - 2.6 Carrageenans 43
    - 2.7 Cellulosics 50
  - 3. Interaction of starch and hydrocolloids 56

CONTENTS

(continued)

Page

3.1 Gelatinizations 56

3.2 Rheological properties 58

3.3 Phase separation 61

III MATERIALS AND METHODS 63

1. Materials 63

1.1 Starches 63

1.2 Hydrocolloids 63

2. Methods 64

2.1 Preparation of starch-hydrocolloid dispersions 64

2.1.1 Samples for studying effect of preparation method on pasting, thermal and textural characteristics of normal and waxy rice starches 64

2.1.2 Samples for studying gelatinization (thermal and pasting properties), rheological and textural characteristics, and microscopic observation of normal and waxy rice starches 64

2.1.3 Samples for studying rheological property of cooked starch 64

2.2 Determination of pasting properties 65

2.3 Differential scanning calorimetry (DSC) 65

2.4 Determination of swelling power and solubility index 65

2.5 Rheological measurements 66

2.6 Texture profile analysis 67

2.7 Microscopic examination 67

CONTENTS

(continued)

Page

2.8 Statistical analysis 67

IV RESULTS 69

4.1 Effect of preparation method on pasting, thermal and textural characteristics of normal and waxy rice starches 69

4.1.1 Pasting properties 68

4.1.2 Thermal properties 72

4.1.3 Textural characteristics 75

4.2 Effect of various hydrocolloids on gelatinization (pasting and thermal characteristics and swelling power and solubility index) of normal and waxy rice starches 78

4.2.1 Pasting characteristics 78

4.2.2 Thermal characteristics 81

4.2.3 Swelling power and solubility index 84

4.3 Effect of various hydrocolloids on paste characteristics and microscopic examination of normal and waxy rice starches 86

4.3.1 Dynamic rheological properties 86

4.3.2 Steady shear rheological properties 90

4.3.3 Comparison of dynamic rheological properties between native and cooked starches 93

4.3.4 Comparison of steady shear rheological properties between native and cooked starches 96

4.3.5 Textural properties 99

4.3.6 Microscopic examination 101

CONTENTS

(continued)

Page

V DISCUSSION 104

1. Sample preparation 104
2. Pasting properties 106
3. Thermal characteristics 108
4. Swelling power and solubility index 109
5. Dynamic rheological properties 111
6. Steady rheological properties 113
7. Comparison of rheological (dynamic and steady) properties between native and cooked starches 114
   7.1 Dynamic rheological properties 114
   7.2 Steady shear rheological properties 115
8. Textural properties 115
9. Microscopic examination 117

VI CONCLUSION 119

REFERENCES 122

BIOGRAPHY 135

LIST OF TABLES

TABLE **Page**

2.1 Amylose content, swelling power and solubility index of starches from different rice cultivars 14

2.2 Source of commercially important hydrocolloids 21

2.3 Thickening agents and gelling agents 22

2.4 Typical products containing galactomannan 27

2.5 Typical products containing xanthan gum 32

2.6 Comparison of the key properties of low acyl and high acyl gellan gum 36

2.7 Typical products containing a carrageenan 49

2.8 Typical products containing carboxymethylcellulose 55

4.1 Pasting characteristics of 10% (w/w) aqueous suspensions of normal rice starch (NRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations 70

4.2 Pasting characteristics of 10% (w/w) aqueous suspensions of waxy rice starch (WRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations 71

4.3 Thermal properties of 10% (w/w) aqueous suspensions of normal rice starch (NRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations 73

4.4 Thermal properties of 10% (w/w) aqueous suspensions of waxy rice starch (WRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations 74

LIST OF TABLES

(continued)

TABLE **Page**

4.5 Textural properties of 10% (w/w) normal rice starch (NRS) pastes without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations 76

4.6 Textural properties of 10% (w/w) waxy rice starch (WRS) pastes without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations 77

4.7 Pasting properties of normal rice starch (7.2% w/w) in the presence of various hydrocolloids (0.8% w/w) 79

4.8 Pasting properties of waxy rice starch (7.2% w/w) in the presence of various hydrocolloids (0.8% w/w) 80

4.9 Thermal properties of normal rice starch (7.2% w/w) in the presence of various of hydrocolloids (0.8% w/w) 82

4.10 Thermal properties of waxy rice starch (7.2% w/w) in the presence of various of hydrocolloids (0.8% w/w) 83

4.11 Swelling power and solubility index of normal and waxy rice starches (1.125% w/w) in the presence of various hydrocolloids (0.125% w/w) heated at 100°C for 10 min under low shear conditions 85

4.12 Dynamic rheological properties of normal rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain, and 30°C 88

4.13 Dynamic rheological properties of waxy rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain, and 30°C 89

4.14 Steady shear rheological properties of normal rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) measured at 30°C 91

LIST OF TABLES

(continued)

TABLE **Page**

4.15 Steady shear rheological properties of waxy rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) measured at 30°C 92

4.16 Dynamic rheological properties of native and cooked normal rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain, and 30°C 94

4.17 Dynamic rheological properties of native and cooked waxy rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain, and 30°C 95

4.18 Steady shear rheological properties of native and cooked normal rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 30°C 97

4.19 Steady shear rheological properties of native and cooked waxy rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 30°C 98

4.20 Textural properties of normal or waxy rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at room temperature (25°C) 100

LIST OF FIGURES

FIGURE **Page**

2.1 Some common starch granules viewed with a light microscope: A, common corn starch; B, potato starch; C, wheat starch; D, rice starch. All photographs are of the same magnifications 6

2.2 Cross section of a sorghum kernel treated with α-amylase 7

2.3 Amylose and amylopectin models 8

2.4 Scanning electron micrographs (SEM) of rice starch (bar = 10 μm) 11

2.5 Thermal property of rice starch determined by differential scanning calorimetry (DSC). T_o: onset temperature, T_p: peak temperature, T_c: conclusion temperature 15

2.6 Pasting properties of rice starch determined by Rapid-Visco Analyzer (RVA). PV: peak viscosity; HPV: hot paste (through); CPV: cool paste (end) viscosity; BD: breakdown (PV-HPV); SB: setback (CPV-PV); CS: consistency (CPV-HPV) 17

2.7 Temperature sweep data for gelatinization of 25% TCW70 (a), waxy rice and TCS10 (b), normal rice with amylose content of 17.1% rice starches suspensions, and comparison of G' between TCW70 and TCS10 (c). Symbols: G': closed triangle, G'': opened triangle, $\tan\delta$: * 18

2.8 Chemical structures of guar gum and locust bean gum 24

2.9 Schematic galactomannan molecules with a molecule weight of about 68,000 with about 20% (w/w) of galactose with a random distribution 25

2.10 Primary structure of Xanthan gum 29

2.11 Melting temperature of 1.0% xanthan gum solutions as a function of sodium chloride concentration 30

LIST OF FIGURES

(continued)

FIGURE **Page**

2.12 Substituted tetrasaccharide repeating unit of gellan gum 33

2.13 Unsubstituted tetrasaccharide repeating unit of gellan gum 34

2.14 Structure of low ester and high ester pectins 38

2.15 Hypothetical structure of apple pectin showing I xylogalacturonan region, II region with arabinan side chains, III rhamnogalacturonan region making up the hairy region 39

2.16 The rang of commercial non-amidated pectins with some typical applications 41

2.17 Structure characteristics of alginates: (a) alginate monomer, (b) chain conformation, (c) block distribution 42

2.18 Coordination of a calcium ion with hydroxyl and carboxyl groups on adjacent G-block chains 44

2.19 Representation of the proposed formation of a junction between two alginate molecules promoted by calcium ions 45

2.20 Chemical structures of the three types of commercially available carrageenans: κ, ι, and λ 46

2.21 Gelation of kappa and iota carrageenans with cations 48

2.22 Chemical structure of cellulose 51

2.23 Chemical structure of carboxymethylcellulose 52

2.24 Chemical structures of methylcellulose and hydroxypropylmethylcellulose (or methylhydroxypropylcellulose) 53

2.25 Typical viscosity-shear rate profile for a polymer solution above C^* 59

LIST OF FIGURES

(continued)

FIGURE **Page**

4.1 Photographs of normal rice starch (NRS) (7.2% w/w) pastes produced in the presence of different hydrocolloids (0.8% w/w): (a) none (control), (b) guar gum, (c) locust bean gum, (d) xanthan gum, (e) gellan, (f) low-methoxyl pectin, (g) high-methoxyl pectin, (h) sodium alginate, (i) κ-carrageenan, (j) ί-carrageenan, (k) λ-carrageenan, (l) CMC, (m) MC and (n) HPMC. All pastes were stained with iodine and observed at 100× magnification 102

4.2 Photographs of waxy rice starch (WRS) (7.2% w/w) pastes produced in the presence of different hydrocolloids (0.8% w/w): (a) none (control), (b) guar gum, (c) locust bean gum, (d) xanthan gum, (e) gellan, (f) low-methoxyl pectin, (g) high-methoxyl pectin, (h) sodium alginate, (i) κ-carrageenan, (j) ί-carrageenan, (k) λ-carrageenan, (l) CMC, (m) MC and (n) HPMC. All pastes were stained with iodine and observed at 100× magnification 103

LIST OF ABBREVIATIONS

AAC	Apparent amylose content
AACC	American Association of Cereal Chemists
AE	Amylose equivalent
ANOVA	Analysis of variance
CMC	Carboxymethylcellulose
C^*	Critical polymer concentration
°C	Degree Celsius
DE	Degree of esterification
DP	Degree of polymerization
DS	Degree of substitution
DSC	Differential scanning calorimetry
et al.	Et alii (Latin), and others
ed.	Edition
ed. (eds.)	Editor, editors, edited by
g	Gram, gravitation
G	Guluronic acid
GG	Guar gum
GL	Gellan
G'	Storage modulus, Pa
G''	Loss modulus, Pa
HMP	High-methoxyl pectin
HPMC	Hydroxypropylmethylcellulose
Hz	Hertz
ΔH	Enthalpy, J/g
IGT	Incipient gelation temperature, °C
i.e.	Id est (Latin), that is
K	Consistency coefficient, Pa s^n

LIST OF ABBREVIATIONS

(continued)

LBG	Locust bean gum
LMP	Low-methoxyl pectin
M	Mannuronic acid
MC	Methylcellulose
min	Minute
mL	Milliliter
NMR	Nuclear magnetic resonance
NRS	Normal rice starch
n	Flow behavior index, dimensionless
Pa	Pascal
rad	Radian
RVA	Rapid-Visco Analyzer
R^2	Coefficient of determination
s	Second
SA	Sodium alginate
SD	Standard deviation
SOL	Solubility index, %
SP	Swelling power
TPA	Texture profile analysis
T_c	Conclusion gelatinization temperature, °C
T_o	Onset gelatinization temperature, °C
T_p	Peak gelatinization temperature, °C
$\tan\delta$	Loss tangent, dimensionless
WRS	Waxy rice starch
w/w	Weight by weight
XG	Xanthan gum
&	And

LIST OF ABBREVIATIONS

(continued)

α	Alpha
β	Beta
ί	Iota
ίC	Iota carrageenan
%	Percent
κ	Kappa
κC	Kappa carrageenan
λ	Lamda
λC	Lamda carrageenan
$\dot{\gamma}$	Shear rate, 1/s
μm	micrometer
η	Apparent viscosity, Pa s
η^*	Complex viscosity, Pa s
σ	Shear stress, Pa
ω	Frequency, rad/s

CHAPTER I

INTRODUCTION

Rice (*Oryza sativa* L.) is normally consumed as a cooked mill rice, but a small portion is ground into flour or separated into a starch fraction and used to make pharmaceutical, food and animal food products (Bao & Bergman, 2004). Rice starch, as other starches, is composed of amylose and amylopectin. This starch can be classified into 4 groups according to its amylose content: low amylose (12-20%), intermediate amylose (20-25%), high amylose (>25%), and waxy (little to no amylose) rice starches. These starches have many unique attributes that make them some of the interesting starches in the food industry (Bao & Bergman, 2004). However, rice starches, in common with other cereal starches, have negative aspects, such as gel syneresis, retrogradation and tendency to exhibit breakdown, whether from extended cooking, high shear or acid conditions, producing weak-bodied, cohesive, rubbery pastes and undesirable gels (Whistler & BeMiller, 1997). This is usually desirable and can be controlled by chemical modifications (Wurzburg, 1986). An alternative to the expensive chemical modification to overcome these shortcomings is the blending of native starches with polysaccharide hydrocolloids as reviewed by Appelqvist and Debet (1997). These mixtures are increasingly important ingredients in the modern health-conscious food industry.

Hydrocolloids refer to a range of polysaccharides and proteins that are used in a variety of industrial sectors (Williams & Phillips, 2000) in order to modify texture, control moisture and water mobility, maintain overall product quality during storage (Christianson, Hodge, Osborne, & Detroy, 1981; Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997; Shi & BeMiller, 2002;). Combination of the hydrocolloids and starches has been found in bakery and cereal products, fruit fillings, sauces, frozen foods and confectionary products (Wei, Wang, & Wu, 2001; Ward & Andon, 2002).

Hydrocolloid has shown an effect on gelatinization and retrogradation characteristics of starches. Christianson *et al.* (1981) found that xanthan gum, guar gum and carboxymethyl cellulose (CMC) accelerated onset of initial paste viscosity and increased the final viscosity, and these increases were concluded as the interaction between exudates from starch granules (solubilized amylose and low molecular weight amylopectin) and gum. However, synergistic effect causing the increase of paste viscosity has been attributed to various factors. Alloncle, Lefebvre, Llamas, & Doublier (1989) suggested that, when starch gelatinized in gum medium, the volume of the continuous phase accessible to the gum was reduced; yielding the increase in gum concentration within the continuous phase that resulted in a sharp increase in viscosity. An addition of hydrocolloids also increased the effective starch concentration by immobilizing water molecules.

The gelatinization parameters (onset, T_o; peak, T_p; and conclusion, T_c temperatures and enthalpy, ΔH) as determined by differential scanning calorimetry (DSC) are influenced by the presence of hydrocolloids. Water is reduced in the starch-gum system because the hydrocolloid rapidly hydrates and consequently reduces the amount of water available for gelatinization (Ferrero, Martino, & Zaritzky, 1996; Lelievre, 1976). A result of limited water availability in the presence of gum could explain in the term of incomplete gelatinization, representing a decrease in enthalpy and shift in the gelatinization peak to a higher temperature (Eliasson, 1980; Marchant and Blanshard, 1980).

When starch dispersions are heated, starch granules are swollen and solubilized starches are leached out, affecting the properties of continuous and dispersed phases. The granule swelling is increased by enhancing the temperature during heating (Li and Yeh, 2001). However, the swelling of granules can be affected by hydrocolloid addition, indicating that swelling is enhanced in their presence (Rojas, Rosell, & Benedito de Barber, 1999; Tecante and Doublier, 1999). The addition of hydrocolloids can increase the shear forces applied on the granules as regards with the forces applied in starch-water suspensions. This fact affects significantly the breakdown of granules and the amount of material exuded into the continuous phase (Christianson, 1982; Christianson *et al.*, 1981).

Rheological properties of starch containing foods are widely dependent on the nature and the type of molecular arrangement of starch and its chemical structure, conformation and the forces acting between them (Bhandari, Singhal, & Kale, 2002). A small change in molecular conformation and structure of starch can bring about dramatic change in functional and rheological properties of starch (Djakovic & Dokic, 1972). The rheology of starch-hydrocolloid combinations is particular to each mixture (Tecante & Doublier, 1999). It could be attributed as the thickening property of hydrocolloids (Appelqvist & Debet, 1997). Moreover, amylose matrix, rigidity, volume fraction and shape of the amylopectin granules and probable interactions between amylose and amylopectin influence the resultant rheology of the starch gel (Clegg, 1995). The most important examination is steady flow and dynamic viscoelastic behavior. The steady flow tests described the relationship between shear stress and shear rate which can be fitted by several rheological models. The most simple and popular model applied for food rheology is the power law model described by the equation $\sigma = K\dot{\gamma}^n$, where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is the flow behavior index (dimensionless). The apparent viscosity (μ_a) can be calculated at various $\dot{\gamma}$ from this relationship. The n value indicates the extent of shear thinning behavior of the materials. Song, Kwon, Choi, Kim, & Shin (2006) reported that the rice starch in various hydrocolloid mixtures exhibited the shear-thinning behavior with the n in a range of 0.26-0.49 which higher than that of previous reported data (Yoo, Kim, & Yoo, 2005; Kim & Yoo, 2006). In the case of dynamic viscoelastic property, the viscoelasticity was described as storage modulus (G'), loss modulus (G''), and complex viscosity ($\eta * = \sqrt{(G')^2 + (G'')^2} / \omega$). The relationship of moduli was examined as loss tangent $(\tan\delta = G''/G')$ as a function of frequency (ω). This increase of dynamic moduli in the starch-gum mixture system can be attributed to the increase in viscoelastic properties of added gum, due to its thickening properties (Alloncle & Doublier, 1991).

Much less work has been carried out on the effect of sample preparation for starch-gum mixtures (Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Mandala & Bayas, 2004). In addition, there are few reports on the effect of various kinds of hydrocolloids on pasting (Christianson et al., 1981; Bahnassey & Breene, 1994; Rojas et al., 1999; Shi & BeMiller, 2002; Mandala & Bayas, 2004) and rheological properties (Alloncle et al., 1989; Eidam & Kulicke, 1995; Biliaderis & Arvanitoyannis, 1997; Lai, Huang, & Lii, 1999; Mandala, Pologou, & Kostaropoulos, 2002; Tecante & Doublier, 2002; Kruger, Ferrero, & Zaritzky, 2003) of various starches particularly those on rice starches (Kulicke, Eidam, Kath, Kix, & Kull, 1996; Liu, Eskin, & Cui, 2003; Yoo et al., 2005; song et al., 2006; Kim & Yoo, 2006; Huang, Kennedy, Li, Xu, & Xie, 2007).

The objective of this study was to investigate the effects of various hydrocolloids (guar gum, locust bean gum, xanthan gum, gellan, low- and high-methoxyl pectins, sodium alginate, carrageenans [κ-, ί- and λ-carrageenans] and cellulose derivatives [CMC, MC and HPMC]) on pasting and rheological properties of rice starch (normal and waxy rice starches) by Rapid-Visco analysis (RVA), differential scanning calorimetry (DSC), swelling power and solubility index measurements, rheometry (dynamic and steady shear rheological measurements), texture profile analysis (TPA), and microscopic observation.

CHAPTER II
LITERATURE REVIEW

1. Starch

Starch is one of the most important and abundant main food ingredients of staple foods such as bread and noodles (Funami, Kataoka, Omoto, Goto, Asai, & Nishinari, 2005), including adhesion, binding, clouding, dusting, film-formation, foam strengthening, antistaling, gelling, glazing, moisture retention, stabilizing, texturizing and thickening applications (Whistler & BeMiller, 1997). Commercial starches are obtained from seed, particularly corn, waxy corn (waxy maize), high amylose corn, wheat and various rices, and from tuber or roots, particularly potato, sweet potato, and cassava (tapioca starch) (Whistler & BeMiller, 1997). The starch consists primarily of D-glucopyranose polymers linked together by α-1,4 and α-1,6 glycosidic bonds.

1.1 Starch structure and composition

Starch is unique among carbohydrates because it occurs naturally as discrete particles, called granules (Figure 2.1). Starch is packed in starch granules in the form of semicrystalline composed of crystalline areas and amorphous regions. Starch granules treated with α-amylase demonstrated a ringed pattern analogous to the growth rings (Figure 2.2) (Hoseney, 1994). This growth ring structure illustrated the arrangement of amylose and amylopectin in a form of packing that radially oriented. Amylopectin cluster are also believed to be associated with amylose, which is interwoven throughout the crystalline and amorphous areas.

Amylose is considered as a linear polymer composed almost entirely of α-1,4-linked D-glucopyranose (Figure 2.3); many amylose molecules have a few α-1,6-linked D-glucopyranose branches, perhaps 0.3-0.5% (Whistler & BeMiller, 1997). Amylose is actually helical. The interior of the helix contains hydrogen atoms and is therefore hydrophilic, allowing amylose to form a type of clathrate (an inclusion complex wherein a host molecule entraps a second molecular species as the guest)

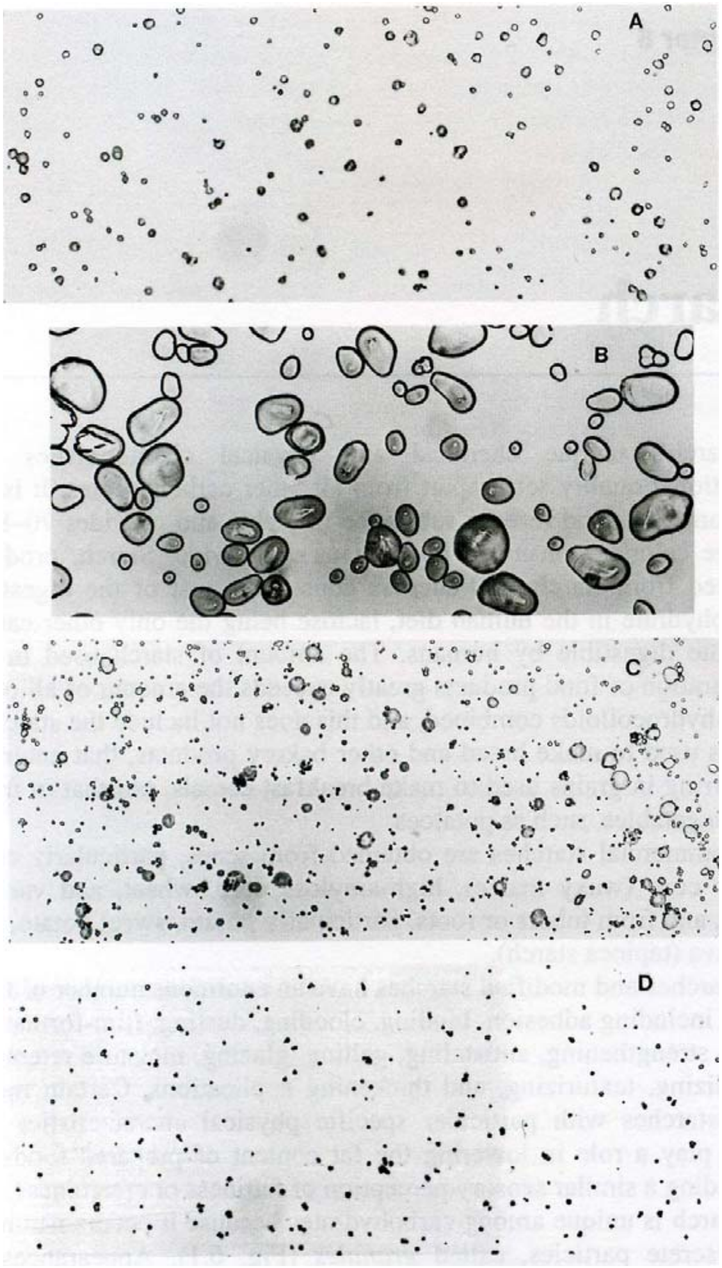


Figure 2.1 Some common starch granules viewed with a light microscope: A, common corn starch; B, potato starch; C, wheat starch; D, rice starch. All photographs are of the same magnification (Whistler & BeMiller, 1997).

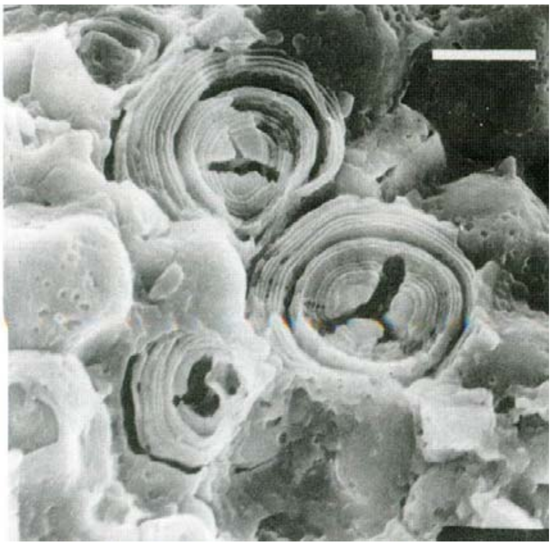


Figure 2.2 Cross section of a sorghum kernel treated with α-amylase (Hoseney, 1994).

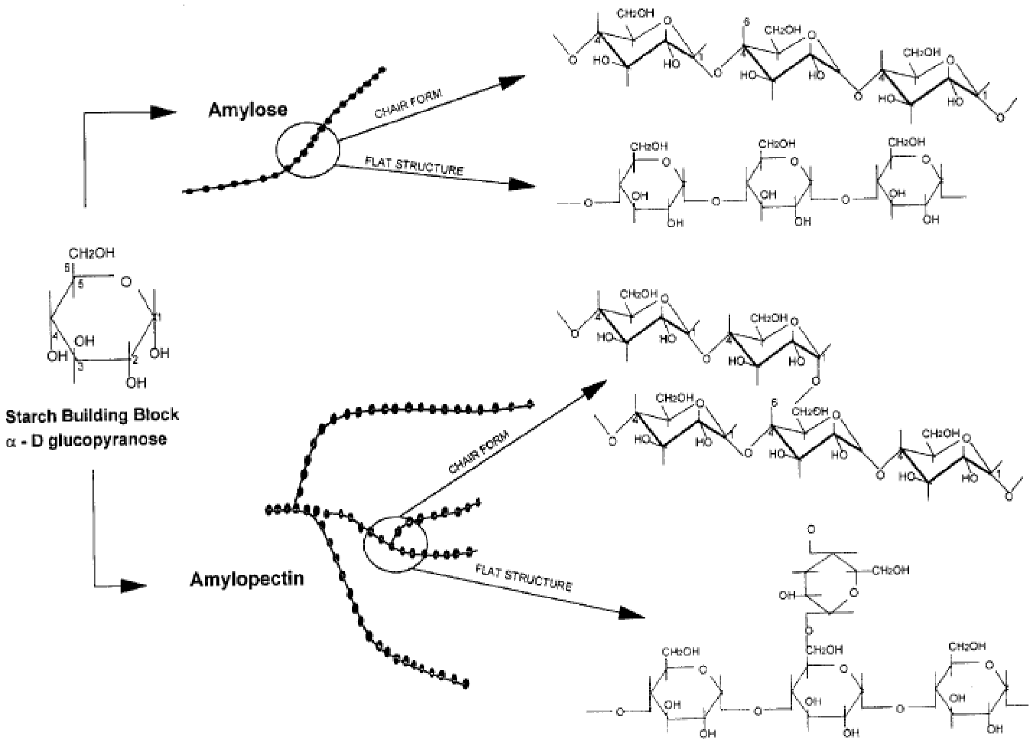


Figure 2.3 Amylose and amylopectin models (Murphy, 2000).

complex with free fatty acids, fatty acid components of glycerides, some alcohol and iodine (Fennema,1985). Amylose has an ability to form a gel after the starch granule has been cooked, i.e., gelatinized and pasted. Gel formation is primarily the result of the reassociation (i.e., retrogradation) of solubilized starch polymers after cooking and can occur quite rapidly with the linear polymer amylose (Thomas & Atwell, 1999).

Amylopectin is composed of α-1,4-linked glucose segments connected by α-1,6-linked branch points (Figure 2.3), estimating about 4-6% of the linkages. This may appear to be a small percentage, but it results in more than 20,000 branches in an average molecule. From this configuration, it contributes to the crystalline nature of amylopectin and an ordered arrangement of amylopectin molecules within the starch granules. Because of highly branched nature of amylopectin, its properties differ from those of amylose. Its retrogradation is slowed and gel formation can either be delayed or prevented. Pastes from starches that contain essentially all amylopectin (waxy starches) are considered to be non-gelling but typically have a cohesive and gummy texture (Thomas & Atwell, 1999). Amylopectin give a reddish-brown color with iodine.

1.2 Rice starch

Rice (*Oryza sativa* L.) is consumed as cooked milled rice, but a small portion if ground into flour or separated into a starch fraction is used to make pharmaceutical, food and animal feed products. Rice starch is hypo-allergenic and bland in flavor, including a small granule size and soft gel formation. From these properties, rice starch have made it desirable as a fat replacer in foods such as flavored milk base beverage, ice cream, yogurt and salad dressing. From being smooth in texture and less filling than fat, rice starch is finding increasing applications in pastry cream. Rice starch is reported to have a rapid hot-set after such processing techniques as extrusion. This characteristic makes it desirable for use in breakfast cereals that need to remain crisp after exposure to milk. It is also used to generate maltodextrins that are incorporated into foods as a filler, flavor carrier, texture modifier or sweetness reducer.

1.2.1 Constituents of rice starch

The difference between rice flour and starch is that most of the native proteins and lipids have been removed from the starch. The protein content of milled rice in the germplasm collection reportedly ranged from 4.5 to 15.9% (Kennedy & Burlingame, 2003). Lipids exist in rice at much lower amounts. Therefore, isolation of starch from rice mainly involves techniques to remove proteins. The majority of the rice protein is alkaline soluble, thus alkaline steeping methods are commonly used in industry and research to produce rice starch with good recovery and low residual protein content (Hogan, 1967; Lumdubwong & Seib, 2000). Besides proteins, other minor constituents, including lipids, phosphorus and trace elements, are commonly found in isolated starch (Champagne, 1996). Non-waxy rice starch contains 0.3-0.4% bound lipids; waxy rice starch reportedly contains less of this fraction (0.03%) (Morrison, Milligan, & Azudin, 1984; Morrison & Azudin, 1987). The composition of the total starch lipids in non-waxy rice starch reportedly has an average of 32% free fatty acids and 68% lysophosphatidyl choline (Morrison et al., 1984). Phosphorus plays an important role in starch functional properties, such as, paste clarity, viscosity consistency and paste stability. Phosphorus in starch is mainly present in two forms; phosphate-monoesters and phospholipids. In non-waxy rice starch, phosphorus is primarily in the form of the phospholipids (0.013%, dry basis of phosphate-monoesters and 0.048% for phospholipids), whereas in waxy rice starch, phosphorus is present as starch phosphate-monoesters (0.003% for phosphate-monoesters and non detectable for phospholipids) (Lim, Kasemsuwan, & Jane, 1994; Jane, Kasemsuwan, & Chen, 1996). Starch phosphate-monoesters in native rice starches are primarily found in amylopectin, and only a trace is found in amylose. About 80-90% phosphate-monoester in waxy rice starch is on the C6 of glucose units (Tabata, Nagata, & Hizukari, 1975; Jane et al., 1996).

1.2.2 Structure and functionality of rice starch

Rice starch granules are the smallest known to exist in cereal grains, with the size reported to range from 3 to 8 μm (Figure 2.4). Rice starch granules have a smooth surface but angular and polygonal shapes. An orientation in the starch granule contains amylose and amylopectin as other starches. Crystallinity is likely

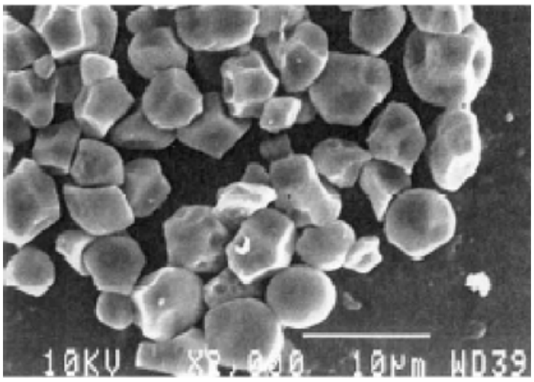


Figure 2.4 Scanning electron micrographs (SEM) of rice starch (bar = 10 μm) (Bao, 2004).

influenced by amylose content and amylopectin structure. In addition, waxy rice starch was more crystalline than non-waxy rice starch (Bao & Berman, 2004).

Amylose essentially consists of long chained α-1,4 linked glucose molecules, but it also may contain a few α-1,6 branch points. The fine structure of rice amylose has not been fully elucidated. In the rice starch studied by Juliano (1998), 40-60% (w/w) of the amylose was linear and 33-60% (w/w) was branched. The affinity of the starch rice flour (defatted and native) for iodine has been used extensively to approximate the amylose content of rice. The name for the fraction which is measured using this phenomenon is amylose equivalent or apparent amylose content (AAC). The AAC value of starch is higher than the absolute amylose content, which can be measured by the iodine affinity of the fractionated and purified amylopectin (Jane, Chen, Lee, McPherson, Wong, Radosavljevic, & Kasemsuwan, 1999) or measured with the soluble amylose equivalent (AE) (Reddy, Ali, & Bhattacharya, 1993). The difference between AAC and true amylose content results from the number of very long branch chains of amylopectin. AAC is reported to vary among rice cultivars, from approximately 0 in waxy rice to nearly 30% in non-waxy genotypes (Chen, Bergman, & Fjellstrom, 2003). Rice amylopectin is a highly branched molecule with the branch points being α-1,6 bonds. It was also affected by the growing environment.

1.2.3 Swelling power and solubility

When starch is heated in excess water, the crystalline structure is disrupted due to the breakage of hydrogen bonds, and water molecules become linked by hydrogen bonding to the exposed hydroxyl group of amylose and amylopectin. This causes an increase in granule swelling and solubility. Swelling power and solubility provide evidence of the magnitude of interaction between starch chains within the amorphous and crystalline domains. The extent of this interaction is thought to be influenced by a sample’s amylose content, amylose and amylopectin structure, degree of granulation and other factors. For example, amylose-lipid complexes have been shown to restrict swelling and solubilization. According to Tester and Morrison (1990a), the swelling behavior of cereal starch is primarily related to amylopectin structure. Vandeputte, Vemeylen, Greeroms, & Delcour (2003a) reported that swelling of normal rice starch is a two-step event. In the first swelling step, i.e., at temperature between 55 and 85°C, amylose does not influence the swelling of normal rice starches, whereas the relative amounts of short amylopectin chain (DP 6-9) increase swelling at 55 and 65°C. Only in the second swelling step (at temperatures between 95 and 125°C), amylose decreases swelling power. In the first swelling step, granule swelling is influenced by the short amylopectin chains whereas, in the second step, it is influenced by amylose leaching. Lii, Tsai, & Tseng (1996) observed that swelling power was inversely proportional to the rigidity to starch granules, thus higher swelling power suggests a less rigid granule structure exist. Sodhi and Singh (2003) showed that in five rice starches, the one with the lowest amylose content (7.8%) had the highest swelling power and lowest solubility; whereas the sample with greatest amylose content had the lowest swelling power (Table 2.1). Lii, Shao, & Tseng (1995) also reported a higher swelling power for rice starch with lower amylose content.

1.2.4 Gelatinization of rice starch

Gelatinization is the process that takes place when starch is heated in the present of water, resulting in the irreversible disruption of molecular order within a starch granule. Evidence of this loss of order can be seen by irreversible granule swelling, loss of birefringence and loss of crystallinity. For gelatinization to occur, the regions of the amorphous starch must first melt or undergo glass transition (Slade & Levine, 1988). Gelatinization is measured by differential scanning calorimetry (DSC). DSC measures the range in transition temperature required for gelatinization to occur. Thermal properties typically reported using DSC include gelatinization onset (T_o), peak (T_p), and conclusion (T_c) temperatures and enthalpy (ΔH) (Figure 2.5). Currently, there is no clear understanding of the relationship between starch structure and thermal properties. Noda, Takahata, Sato, Ikoma, & Mochida (1996) postulated that DSC parameter (T_o, T_p, T_c, ΔH) are influenced by the molecular architecture of the crystalline region of starch, which corresponds to the distribution of amylopectin short chain (DP 6-11), and not by the proportion of crystalline region which corresponds to the amylose content. Cooke & Gidley (1992) have shown that the ΔH values of gelatinization primarily reflect the loss of double helices order rather than the loss of crystallinity. However, Tester & Morrison (1990a) postulated that ΔH reflects the overall crystallinity (quality and amount of starch crystallites) of amylopectin. Tester

Table 2.1 Amylose content, swelling power and solubility of starches from different rice cultivars (Sodhi and Singh, 2003).

Cultivar	Amylose content (%)	Swelling power (g/g)	Solubility (%)
PR-106	16.1 bc	28.8 bc	0.319 b
PR-114	16.1 b	28.6 b	0.360 d
IR-8	15.6 b	30.1 c	0.307 b
PR-103	7.88 a	33.2 d	0.287 a
PR-113	18.9 d	26.1 a	0.346 c

Values with similar letter in a column do not differ significantly ($P<0.05$)

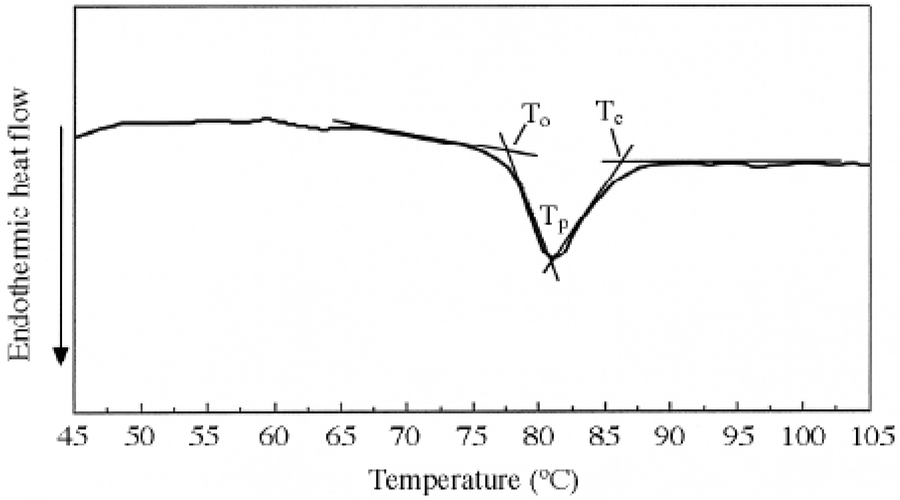


Figure 2.5 Thermal property of rice starch determined by differential scanning calorimetry (DSC). T_o: onset temperature, T_p: peak temperature, T_c: conclusion temperature (Bao & Bergman, 2004).

(1997) suggested that the extent of the crystalline perfection is reflected in the gelatinization temperature. Starch reportedly exhibits lower T_o, T_p and T_c, but higher ΔH compared to the flour prepared from the same sample (Teo, Karim, Cheah, Norziah, & Seow, 2000; Wang, Wang, Shephard, Wang, & Patindol, 2002). This reportedly is due to the heat-moisture treatment during starch preparation.

When the starch granule is heated up to the gelatinization temperature in excess water, heat transfer and moisture transfer phenomena occurs. The granule swells to several times its initial size as a result of the loss of the crystalline order and the absorption of water inside the granule structure. The pasting viscosity during swelling and gelatinization can be recorded using a Brabender Visco Amylograph, a Rapid-Visco Analyzer (RVA) or other viscometers, which record the viscosity continuously as the temperature is increased, held constant for a time and then decreased (Figure 2.6). At the initial step, the viscosity increases rapidly with the increase of temperature as the granule swells. The peak viscosity is reached when granules swelling have been balanced with the granules broken by stirring. With continued stirring, more granules rupture and fragment, causing a further decrease in viscosity. On cooling, some starch molecules partially reassociate to form a precipitate or gels, in which amylose molecules aggregate into a network, embedding remnants of starch granules.

Rheological properties during rice starch gelatinization have been characterized by many researchers using different rheometer (Lii et al., 1995; Lii, Lai, & Tsai, 1996; Sodhi and Singh, 2003). Lii et al. (1996b) reviewed their results and concluded that the starch granular properties are the major factors responsible for starch rheological behavior, followed by the degree of amylose leaching during the gelatinization process, especially in high concentration systems. The change in viscoelastic properties of rice starch suspensions during gelatinization can be placed into three or four transition stages: starch suspension into sol, sol transition to gel, network destruction and network strengthening.

During the early heating of starch granules in water, the increase of storage modulus G' and $\tan\delta$ is relatively small, which indicates that amylose molecules are dissolved and the suspension has been transformed into a sol (Figure 2.7) (Sodhi & Singh, 2003). Then the G' and G'' increase to a maximum in which the

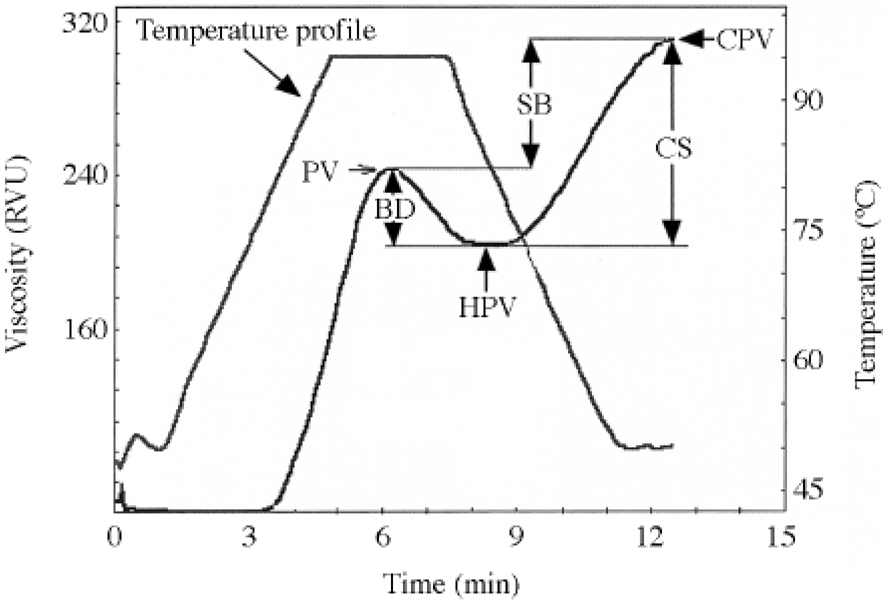


Figure 2.6 Pasting properties of rice starch determined by Rapid-Visco Analyzer (RVA). PV: peak viscosity; HPV: hot paste (through); CPV: cool paste (end) viscosity; BD: breakdown (PV-HPV); SB: setback (CPV-PV); CS: consistency (CPV-HPV) (Bao and Bergman, 2004).

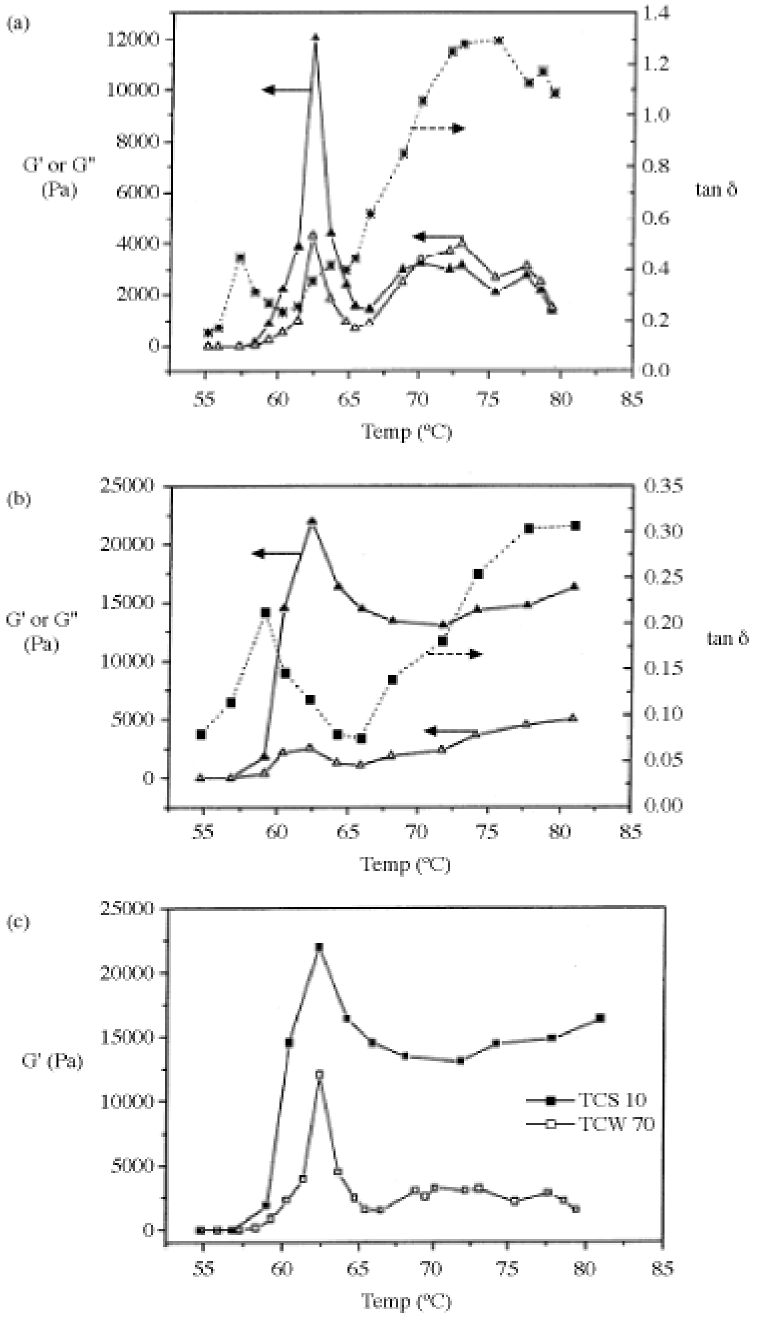


Figure 2.7 Temperature sweep data for gelatinization of 25% TCW70 (a), waxy rice and TCS10 (b), normal rice with amylose content of 17.1% rice starches suspensions, and comparison of G' between TCW70 and TCS10 (c). Symbols: G' : closed triangle, G'' : opened triangle, $\tan\delta$: * (Bao & Bergman, 2004). Note: TCW70 and TCS10 are Taichung waxy 70 and Taichung Sen 10, respectively.

temperature coincides with the onset temperature, which is attributed to the close-packed network of swollen starch granules. Tanδ decreases simultaneously, which indicates that a three-dimensional gel network has been constructed from amylose, reinforced by strong interactions among the swollen starch particles (Lii et al., 1995, 1996b; Sodhi & Singh, 2003). The G' increases during the gelatinization of rice starch are reported to be mainly governed by granule characteristics, which include swollen granule rigidity and the interaction between the close-packed granules (Lii et al., 1996b). In the third stage, continued heating beyond the gelatinization temperature, the G' decreases and tanδ increases, indicating that the gel structure has been destroyed during prolonged heating (Lii et al., 1995, 1996b; Sodhi & Singh, 2003). The destruction is likely due to the melting of the crystalline regions remaining in the swollen starch granule or results from the disentanglement of the amylopectin molecules in the swollen particles, which softens the particles. Another reason for the network collapses may be due to the loss of interaction between particles and the network. The forth stage, G' and G'' are reported to increase and tanδ increase even higher after an inflection point. These authors attributed the G' increase to the leached low molecular weight amylopectin, which interacted with the amylose matrix to strengthen the continuous phase (network). However, a larger tanδ indicated that the dispersed phase (particles) became softer due to continuing dissolution of amylopectin.

1.2.5 Retrogradation of rice starch

Retrogradation describes the process in which a heated starch paste cools to below the melting temperature of starch crystallites, and the amylose and amylopectin reassociate and unite with the swollen starch grains in an ordered structure that results in viscosity increase, gel forming and textural staling of predominantly starch-containing systems. The retrogradation properties can be measured by DSC (Qi, Tester, Snape, & Ansell, 2003; Vandeputte et al., 2003b), rheological properties, starch gel hardness (Vandeputte et al., 2003b) and NMR (Yao, Zhang, & Ding, 2003; Qi et al., 2003). Methods to study retrogradation of starch have been reviewed by Karim, Norziah, & Seow (2000).

This phenomenon is generally regarded as a crystallization or recrystallization (i.e. formation and subsequent aggregation of double helices) process of amylose and amylopectin. The rapid initial rate of retrogradation relates to the loss of networked amylose, the development of amylose aggregates and binding of granule remnants into assemblies by amylose and amylose aggregates. Thus, amylose is responsible for short-term (less than one day) changes during retrogradation (Zhou, Robards, Helliwell, & Blanchard, 2002). Amylopectin forms shorter double helices which can be attributed to restrictions imposed by the branching structure of the amylopectin molecules and the chain lengths of the branches. Because the amount of amylopectin in most starches is greater than amylose, most of the crystallites formed during starch retrogradation are related to the association of amylopectin chains. Thus, amylopectin retrogradation proceeds slowly over several weeks of storage and contributes to the long term rheological and structural changes of starch systems (Lii, Lai, Lu, & Tsai, 1998; Zhou et al., 2002).

2. Hydrocolloids

Hydrocolloids, or gums, are substance consisting of hydrophilic, long-chain, high molecular weight molecules, usually with colloidal properties, that in water-based systems produce gels, i.e., highly viscous suspensions or solutions with low dry-substance content. In addition to their primary purpose of thickening and/or gelation, hydrocolloids often exhibit related secondary functions, such as emulsifying, whipping, suspending and encapsulating. They are generally polysaccharides, but gelatin (a protein) is included because its functionality is very similar to that of the polysaccharide-based gum. The commercially important hydrocolloids and their origin are given in Table 2.2.

Hydrocolloid can be roughly divided into two categories on the basis of their functionality in food systems (Hoefler, 2004): thickening agents and gelling agents (Table 2.3). The thickening agents provide viscosity in a food system, but they are not capable of suspending particulates. They do slow the settling of particulates and of the rising of oil droplets, but they cannot stop the separation from occurring. Gelling agents form links between their molecules, building a three-dimensional lattice in a food system. The result is that particulates or oil droplets become permanently trapped

Table 2.2 Source of commercially important hydrocolloids (Williams & Phillips, 2000).

Botanical	*trees*	cellulose
	tree gum exudates	gum arabic, gum karaya, gum ghatti, gum tragacanth
	plants	starch. Pectin, cellulose
	seeds	guar gum, locust bean gum, tara gum, tamarind gum
	tubers	konjac mannan
Algal	*red seaweeds*	agar, carrageenan
	brown seaweeds	alginate
Microbial		xanthan gum, curdlan, dextran, gellan gum, cellulose
Animal		gelatin, caseinate, whey protein, chitosan

Table 2.3 Thickening agents and gelling agents (Hoefler, 2004).

Thickening/Viscosity agents	Gelling/Yield point agents
Locust bean gum	Agar
Guar gum	Carrageenan
Tara gum	Pectin
Konjac (with acetyl groups)	Konjac (without acetyl groups)
Arabic	Gellan gum
Xanthan gum	Xanthan gum
Tragacanth	Gelatin
Propylene glycol alginate	Sodium alginate
Methylcellulose[a]	Methylcellulose[b]
Hydroxypropylmethylcellulose[a]	Hydroxypropylmethylcellulose[b]
Microcrystalline cellulose	Microcrystalline cellulose
Hydroxypropylcellulose	
Cellulose gum	
Gum karaya	

[a] At 25°C.

[b] At 40-70°C.

in the lattice and do not separate out. Most gelling agent can be used at low concentrations so that the food system pours or flows without separation of oil droplets or ingredients such as strawberries or spices.

When a gum powder is sprinkled onto or poured into slightly stirred water, some will dissolve, but many particles will hydrates quickly on their surface to produce a gelatinous coating (Whistler & BeMiller, 1997). This costing slows the rate of water diffusion through the surface layer, leaving a dry interior. Such gel-coated surfaces are sticky, causing the particles to stick together to form clump called fish eyes that may be large of only barely visible. To prevent this problem and bring about good dissolution of a gum. Finely powdered gum may be sifted slowly into the vortex of rapidly stirred water. The high shear forces ensure that particles become dispersed before significant hydration occurs. The shear forces also tear away partially hydrated molecules and prevent the formation of a microgelatinous layer. Alternatively, the gum may be blended in one part with five parts of sugar or corn syrup solids. This method is particularly useful when the mixing equipment provides very low shear. When this gum-sugar mixture is dispersed into the water, the sugar particles (which do not expand when they become wet) separate the hydrocolloid particles, allowing them to expand without contacting and attaching to a hydrocolloid particle neighbor.

2.1 Galactomannans

Galactomannans are found as cell wall storage polysaccharides of various albuminous or endospermic seeds. Widely used are the seed galactomannans from the carob tree (*Ceratonia siliqua*), named as locust bean gum (LBG) or carob bean gum (CBG), and the guar plant (*Cyamopsis tetragonoloba*), namely guar gum (Wielinga, 2000). Galactomannan consists of a chain (1→4)-linked β-D-mannopyranosyl units with single α-D-galactopyranosyl units connected by (1→6) linkages, on average, to every second main chain unit in the case of guar gum, and every forth main chain unit as in LBG (Figure 2.8). The ratio of D-mannosyl to D-galactosyl units is about 1.8:1 in guar gum and 3.9:1 in LBG. The random distribution of the side units is shown in Figure 2.9.

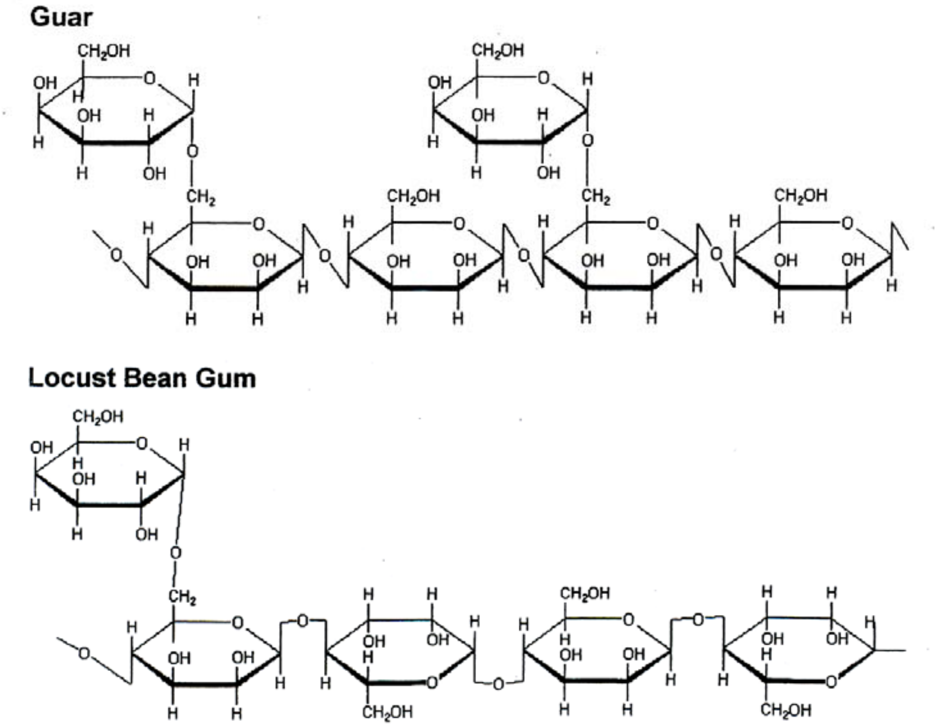


Figure 2.8 Chemical structures of guar gum and locust bean gum (Hoefler, 2004).

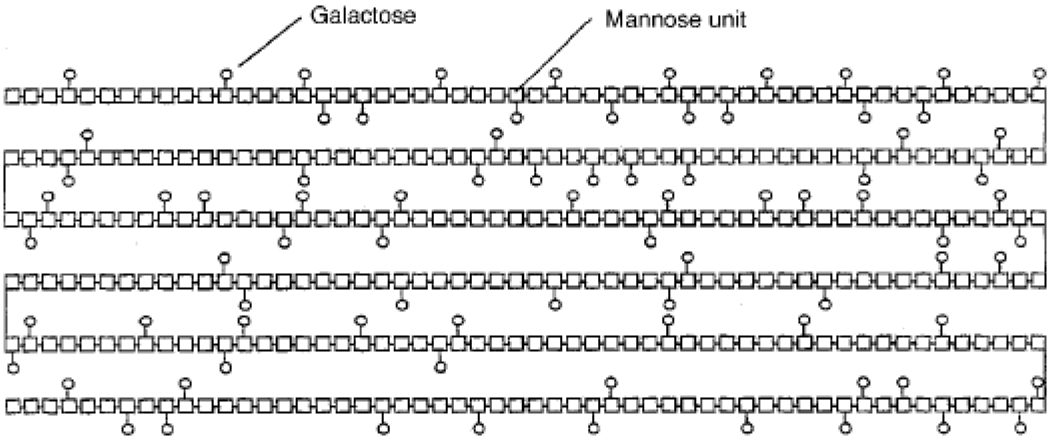


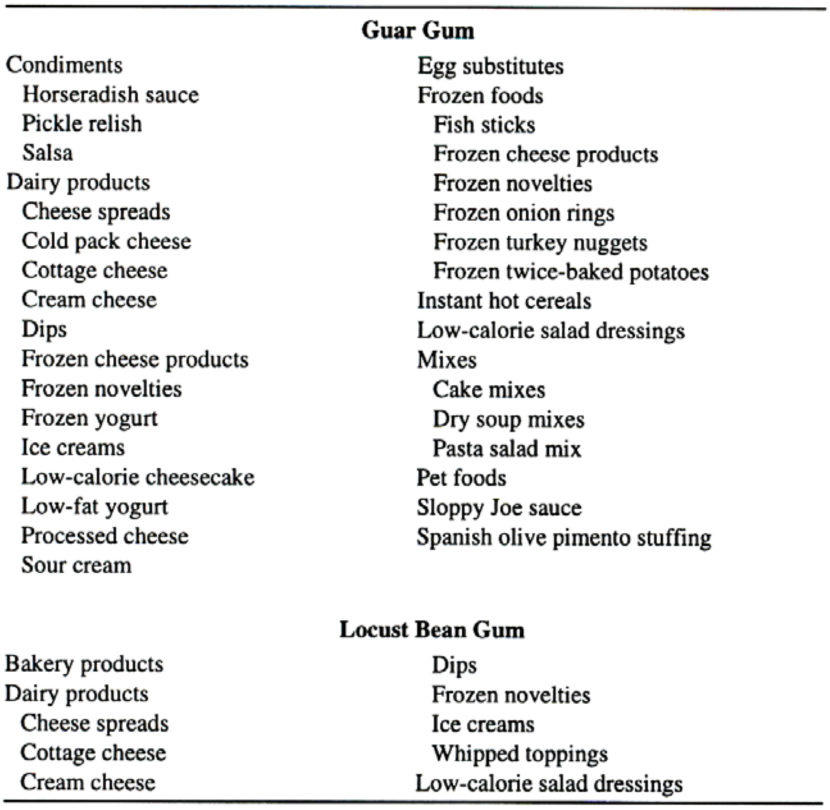
Figure 2.9 Schematic galactomannan molecules with a molecule weight of about 68,000 with about 20% (w/w) of galactose with a random distribution (Wielinga, 2000).

Guar gum containing galactose contents of 33-40% (w/w) is soluble in water of 25°C. The rate of dissolution of guar gum increases with decreasing particle size and with increasing temperature. Hydration rates decrease in the presence of increasing amount of salts and other water-binding agents such as sugar. In the case of LBG, with the larger part containing galactose contents of about 17-21% (w/w), it needs a heat treatment during 10 min at 86-89°C under stirring to dissolve in water. The hydroxyl groups on the long, unsubstituted regions of the LBG molecule form strong hydrogen bonds to their neighbor because they can approach each other so closely. Extra energy, in the form of 86-89°C water, is required to pry the unsubstituted backbone areas apart from each other so they can hydrate. By comparison, the backbones of the guar gum molecules are held apart from each other by the relatively even distribution of the side units. The galactomannans of guar gum and LBG are non-ionic. Therefore, they are susceptible to strong acids, organic acids like citric, acetic and ascorbic acids, alkali in presence of air and strong oxidizing agents, especially at elevated temperatures, and also towards irradiation with γ-rays, so that a depolymerization to different extents may occur. Like most hydrocolloids, both guar gum and LBG shows pseudoplastic, or shear-thinning, behavior in solution. The degree of pseudoplasticity increases with both concentration and molecules weight.

Guar gum provides economical thickening to numerous food products. It is frequently used in combination with other food gums, particularly in dairy products. The prime function of guar gum is to bind water; it also prevents ice crystal growth, improves mouth feel, reduces the chewiness produces by a combination of carrageenan and LBG and slows meltdown. It prevents syneresis in frozen foods and pie filling and controls spreadability in prepared icings.

Locust bean gum is rarely used alone but in combination with other gums such as CMC, carrageenan, xanthan gum and guar gum. In ice cream and related products, it provides excellent heat shock resistance, smooth meltdown and desirable texture and chewiness. LBG can serve as a binder and stabilizing agent in processed comminuted meats, such as sausages. Like guar gum, LBG can be used in barbecue sauces, salad dressings and dry-mix soups and gravies. Typical products containing guar and locust bean gums are given in Table 2.4.

Table 2.4 Typical products containing galactomannan (Whistler & BeMiller, 1997).



Guar Gum

- Condiments
  - Horseradish sauce
  - Pickle relish
  - Salsa
- Dairy products
  - Cheese spreads
  - Cold pack cheese
  - Cottage cheese
  - Cream cheese
  - Dips
  - Frozen cheese products
  - Frozen novelties
  - Frozen yogurt
  - Ice creams
  - Low-calorie cheesecake
  - Low-fat yogurt
  - Processed cheese
  - Sour cream
- Egg substitutes
- Frozen foods
  - Fish sticks
  - Frozen cheese products
  - Frozen novelties
  - Frozen onion rings
  - Frozen turkey nuggets
  - Frozen twice-baked potatoes
- Instant hot cereals
- Low-calorie salad dressings
- Mixes
  - Cake mixes
  - Dry soup mixes
  - Pasta salad mix
- Pet foods
- Sloppy Joe sauce
- Spanish olive pimento stuffing

Locust Bean Gum

- Bakery products
- Dairy products
  - Cheese spreads
  - Cottage cheese
  - Cream cheese
  - Dips
  - Frozen novelties
  - Ice creams
  - Whipped toppings
- Low-calorie salad dressings

2.2 Xanthan gum

Xanthan gum is an extracellular polysaccharide secreted by the microorganism *Xanthomonas campestris*, commonly found on leaves of the cabbage family. The primary structure of xanthan gum, as shown in Figure 2.10., is a linear (1→4) linked β-D-glucose backbone (as in cellulose) with a trisaccharide side chain on every other glucose at C-3, containing a glucuronic acid residue linked (1→4) to a terminal mannose unit and (1→2) to a second mannose that connects to the backbone (Jansson, Kenne, & Lindberg, 1975; Melton, Mindt, Rees, & Sanderson, 1976). Approximately 50% of the terminal mannose residues are pyruvated and the non-terminal residue usually carries an acetyl group at C-6 (Sworn, 2000b). In solution, the side chains wrap around the backbone thereby protecting the labile β-(1→4) linkage from attack. It is thought that this protection is responsible for the stability of the gum under adverse conditions.

Xanthan gum is soluble in cold water and solutions exhibit highly pseudoplastic flow. Its viscosity has excellent stability over a wide pH and temperature ranges. It is also resistant to enzymatic degradation. Xanthan gum solutions at low ionic strength undergo the thermal transition. The transition is thermally reversible with the structure returning to its original state upon cooling. The transition temperature increases with increasing salt concentration as shown in Figure 2.11. Xanthan gum in solution is also able to form intermolecular associations that result in the formation of a complex network of weakly bound molecules (Sworn, 2000b). At use level of 0.15% or higher, xanthan gum reaches its peak viscosity in the presence of 0.02-0.07% sodium chloride. Salt concentrations of greater than 1-2% in the water can slow down the hydration of xanthan gum.

Xanthan gum exhibits a synergistic interaction with the galactomannans, guar gum and LBG. This interaction results in enhanced viscosity or gelation. LBG, which has a mannose to galactose ratio of around 3.9:1, reacts more strongly with xanthan gum than does guar gum, which has a mannose to galactose ratio of slightly less than 1.8:1. Xanthan gum interacts with the unsubstituted smooth regions of the galactomannan. At higher concentrations, soft, elastic gels are formed with LBG. Xanthan gum/LBG gels are thermally reversible setting and melting at approximately

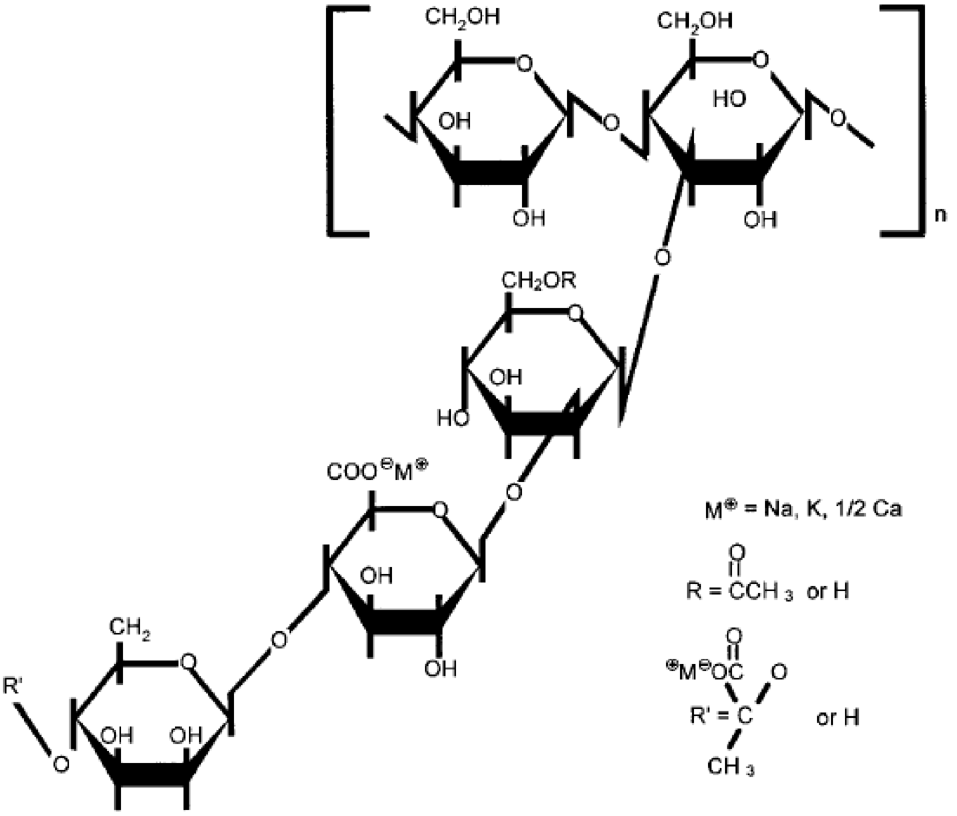


Figure 2.10 Primary structure of xanthan gum (Sworn, 2000b).

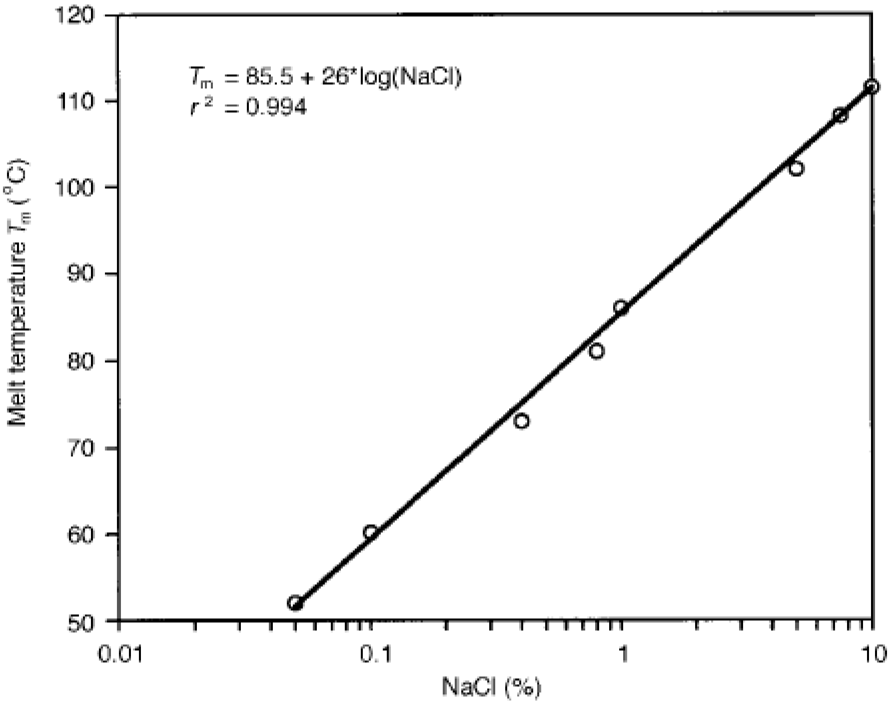


Figure 2.11 Melting temperature of 1.0% xanthan gum solutions as a function of sodium chloride concentration (Sworn, 2000b).

55-60°C. However, heating of the solutions above the transition temperature of the xanthan gum does result in a greater synergistic interaction (Sworn, 2000b).

Xanthan gum is useful as a food gum because of it solubility in hot or cold water, high solution viscosity at low concentrations. However, the viscosity of xanthan gum solutions changes indiscernibly with temperature, that is, its solutions do not thicken upon cooling, make it irreplaceable for thickening and stabilizing such things as pourable salad dressings and chocolate syrup, which need to pour as easily when they are taken from the refrigerators as they do not at room temperature (Whistler & BeMiller, 1997). The products containing xanthan gum are summarized in Table 2.5.

2.3 Gellan gum

Gellan gum is an extracellular polysaccharide secreted by the microorganism *Sphingomonas eloba* (ATCC 31461) previously referred to as *Pseudomonas elodea* (Sworn, 2000a). Gellan gum is a linear, anionic heteropolysaccharide with a molecular weight of around 0.5×10^6 Da (Gibson & Sanderson, 1999). It is composed of tetrasaccharide repeat units (Figure 2.12) comprising 1,3-β-D-glucose, 1,4-β-D- glucuronic acid, 1,4-β-D-glucose and 1,4-α-L-rhamnose. The polymer contains approximately 1.5 acyl substituents per tetrasaccharide repeating unit. These have been identified as a glycerate on C-2 of the 3-linked D-glucose and acetate on C-6 of the same glucose residue (Kuo, Mort, & Dell, 1986). The de-esterified product is a polymer with a well-defined, unsubstituted, tetrasaccharide repeating unit (Figure 2.13). In the solid state the molecule forms a parallel, half-staggered intertwined double helix in which each polysaccharide chain is a left-handed, threefold helix (Chandrasekaran, Millane, Arnott, & Atkins, 1988; Chandrasekaran, Puigjaner, Joyce, & Arnott, 1988). These two types of gellan gum could be considered as low acyl (LA) gellan gum (de-esterified form) and high acyl (HA) gellan gum (native form).

Both terms of gellan gum are insoluble in cold water, although, it will tend to swell in water of low calcium content (Sworn, 2000a). The gum can therefore be readily dispersed in deionized water by stirring and adding the powder slowly to the vortex. As the ion concentration in the water increases, dispersion becomes even easily. By blending the gum with dispersants such as sugar (5-10 times weight of gum)

Table 2.5 Typical products containing xanthan gum (Whistler & BeMiller, 1997).

- Bakery products
  - Cake mixes
  - Danish fillings
  - Pie crust
  - Pie filling mixes
  - Poptarts
  - Refrigerated doughs
- Cereal bars
- Condiments
  - Pickle relish
  - Salsa
- Dairy products
  - Cheesecake
  - Cheese spreads
  - Cottage cheese
  - Cream cheese
  - Frozen cheese
  - Sour cream
  - Whipped toppings
- Egg substitutes
- Frozen foods
  - Frozen cheese
  - Frozen fish florentine
  - Frozen guacamole
  - Frozen lasagna
  - Frozen pizza
  - Frozen rice
- Honey-roasted peanuts
- Meat products
  - Breakfast slices
  - Poultry breast slices
- Mixes
  - Cake mixes
  - Cocktail mixes
  - Fruit drink mixes
  - Gravy mixes
  - Pie filling mixes
  - Pudding mixes
- Salad dressings, etc.
  - Low-calorie pourable salad dressings
  - Pourable salad dressings
  - Reduced-calorie mayonnaise
- Sauces
  - Barbecue sauces
  - Cocktail sauces
  - Mushroom sauce
  - Oriental sauce
  - Pizza sauces
  - Sloppy Joe Sauce
  - Taco sauces
  - Tartar sauce
- Spreads
  - Margarine spreads
  - Sandwich spreads
- Syrups
  - Chocolate syrup
  - Pancake syrup
- Toppings
  - Butterscotch topping
  - Fudge topping
  - Marshmallow creme
  - Whipped toppings

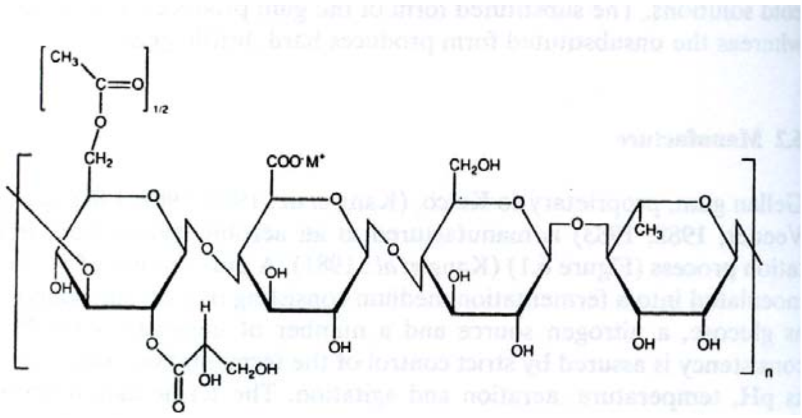


Figure 2.12 Substituted tetrasaccharide repeating unit of gellan gum (Gibson & Sanderson, 1999).

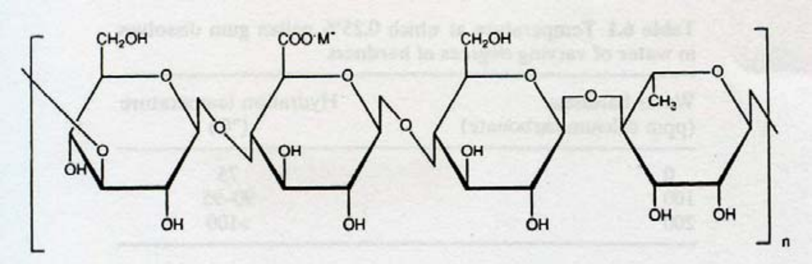


Figure 2.13 Unsubstituted tetrasaccharide repeating unit of gellan gum (Gibson & Sanderson, 1999).

or glycerol, alcohol or oil (3-5 times weight of gum), it is possible to add the gum directly to hot water.The temperature at which LA gellan gum hydrates is dependent on the type and concentration of ions in solution. The presence of ions such as sodium, and in particular calcium, in solution will inhibit the hydration of LA gellan gum. Incomplete hydration will result if the sodium ion concentration exceeds 0.5% (approximately 1.3% sodium chloride). The hydration of HA gellan gum is much less dependent on the concentration of ions in solution than LA gellan gum and generally heating to 85-95°C is sufficient to fully hydrate the gum in both water or milk systems. It swells rapidly at approximately 40-50°C to form a thick, pastry suspension. The suspension loses viscosity suddenly at approximately 80-90°C signifying complete hydration. The LA gellan gum forms a three-dimensional network and the subsequent gels are hard and brittle. The HA gellan gum undergoes a similar disorder to order transition as the solution is cooled, but further aggregation of the helices is limited by the presence of the acetyl group (Morris, Gothard, Hember, Manning, & Robinson, 1996). The subsequent gels are, therefore, soft and elastic. The difference of properties in both LA and HA gellan gums is shown in Table 2.6.

Gellan gum is used in low-calorie jams and jellies because in addition to providing food acid stability, clarity and flavor release, it can be easily incoperated into the manufacturing processes used for these products (Gibson & Sanderson, 1999). It is utilized in a variety of fruit or fruit flavored fillings in bakery products such as doughnuts and pastries. Importantly, gellan gum is not only a tool for making water-based gels, but also an additive for preparing milk gels. Gellan gum forms films and coatings that can be used in breading and batters.

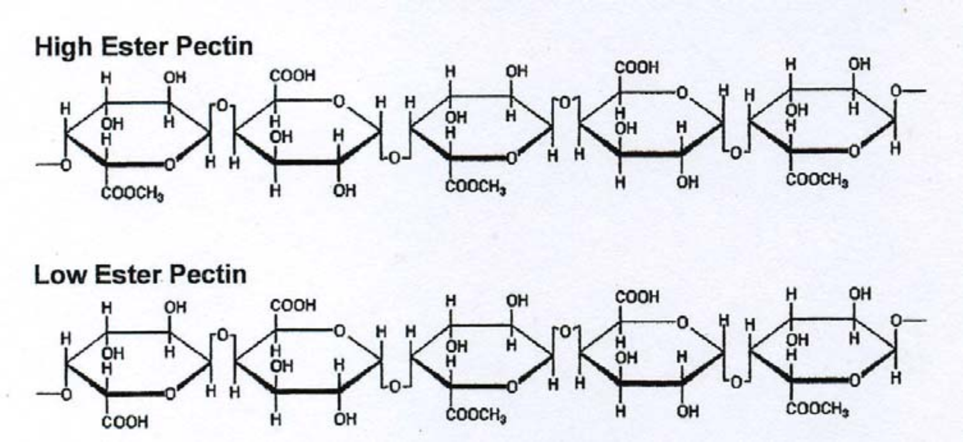
Table 2.6 Comparison of the key properties of low acyl and high acyl gellan gum (Sworn, 2000a).

	Low acyl gellan gum	High acyl gellan gum
Hydration	>80°C	>70°C
Sequestrants	Yes	No
Viscosity	Low	High
Gelling ions	Yes (mono or divalent or acid)	Not required
Setting temperature	10-60°C	70-80°C
Melting	No (except low ionic strength and in milk)	Yes
Clarity	Clear	Opaque
Texture	Firm, brittle	Soft, elastic

2.4 Pectin

Commercial pectins are obtained by acid extraction of citrus peel (20-30% pectin) and apple pomace (10-15% pectin), both by-products of juice manufacturing. That from lemon and lime peels is the highest quality pectin. Pectin consists of a linear chain of galacturonic acid units (Figure 2.14). The acid group may be free (or as a simple salt with sodium, potassium, calcium or ammonium) or naturally esterified with methanol. However, pectins are derived from the breakdown of more complex protopectins which are present in the plant tissue, and also contain a range of neutral sugars, including rhamnose, galactose, arabinose and lesser amounts of other sugars. These sugar units are present in a non-random structure, which consists of blocks of differing character retaining fragments of the original plant cell wall structure. The used of purified enzymes has shown that pectin extracted under very mild conditions contains both linear blocks (smooth regions) consisting of homopolygalacturonic acid, and highly branched blocks (hairy regions) which themselves contains several types of structures (Figure 2.15) (May, 2000). Pectins are subdivided according to their degree of esterification (DE), which is the percentage of carboxyl groups esterified with methanol (Whistler & BeMiller, 1997). Pectins with DE > 50%, that is, with more than one-half of the carboxyl groups in the methyl ester form ($-COOCH_3$), are high-methoxyl (HM) pectins, more properly high methyl-esterified pectins; those with DE < 50% are low-methoxyl (LM) pectins.

Pectin behaves as a gelling agent or protein-stabilizing agent. Pectin can be in the acid or metal salt form. It is water soluble in all forms and can achieve 85% solubility in 21°C water with sufficient shear. For complete hydration, it is necessary to heat a pectin solution to about 60°C. A solution of pectin of the required concentration, which also contains the required concentration of sugar and is at a proper pH value, prepared at a temperature above the gelling temperature and then cooled to decrease the thermal energy of the polymer molecules, will gel because the polymer molecules associate and form junction zones (Whistler & BeMiller, 1997). The temperature at which gelation occurs is the gelling temperature. HM pectins gels are not usually remeltable, and no gel forms at pH values above 3.5 or sugar concentrations below 55%. The setting temperature can be varied from about 35°C to



High Ester Pectin

Low Ester Pectin

Figure 2.14 Structure of low ester and high ester pectins (Hoefler, 2004).

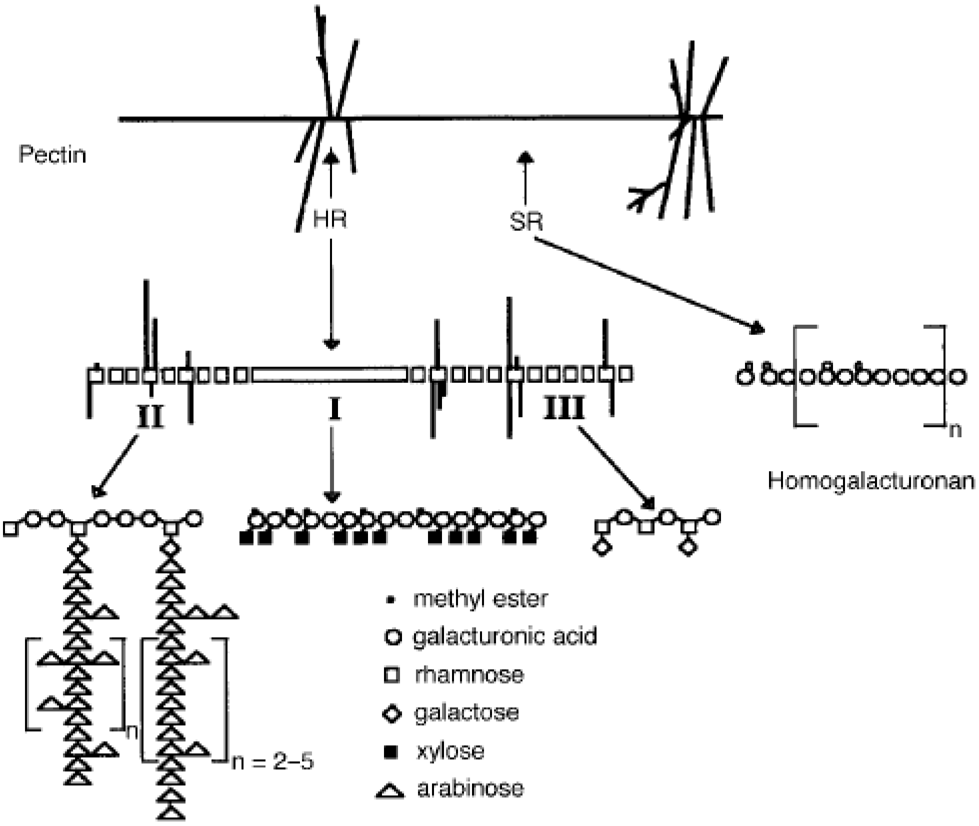


Figure 2.15 Hypothetical structure of apple pectin showing I xylogalacturonan region, II region with arabinan side chains, III rhamnogalacturonan region making up the hairy region (Schols, Ros, Dass, Bakx, & Voragen, 1998).

about 90°C. Gels produced are rigid and hold a cut surface. Syneresis occurs. LM pectin gels can be remelted and reformed repeatedly. The remelt temperature can be as high as 150°C. These gels are spreadable, thixotropic and generally shear reversible. LM pectins will set at pH values of up to about 6.5 (but the usual range is 1-5) and require no sugar for gelation since gel formation is dependent on the presence of Ca ions.

Pectins generally offer a wide range of pectin types for different applications (Figure 2.16). Pectins are used primarily because of their unique ability to form spreadable gels in the presence of sugar and acid or in the presence of calcium ions. Rapid-set pectins are used in canned jams where quick solidification is needed to prevent flotation of fruit and to provide time for bubbles to rise and escape. Milk-fruit drinks can be stabilized by LM pectin during pasteurization because the negatively charged pectin combines with the milk protein, preventing agglomeration and settling.

2.5 Alginates

Alginates are extracted from marine brown algae (*Phaeophycea*) and as capsular polysaccharides in soil bacteria; alginates are quite abundant in nature (Draget, 2000). Alginate is a family of unbranched binary copolymers of (1→4) linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues (Figure 2.17). The distribution of alginate is a true block copolymer composed of homopolymeric regions of M and G, termed M- and G-blocks, respectively, and interspersed with regions of alternating structure (MG-blocks).

Alginates show characteristic ion-binding properties in that their affinity for multivalent cations depends on their composition (Huag, 1964). The characteristic affinities are a property exclusive to polyguluronate; polymannuronate is almost without selectivity. The affinity of alginates for alkaline earth metal increases in the order of Mg<<Ca<Sr<Ba; a property unique for alginates compared to other polyanions. The solutions of alginate are slightly pseudoplastic. Very small amounts of calcium ions will increase viscosity. Slightly more will make alginate solution thixotropic, and more will convert them into permanent gels. Upon addition of calcium ion, cavities formed between two parallel G-block chain regions are filled with

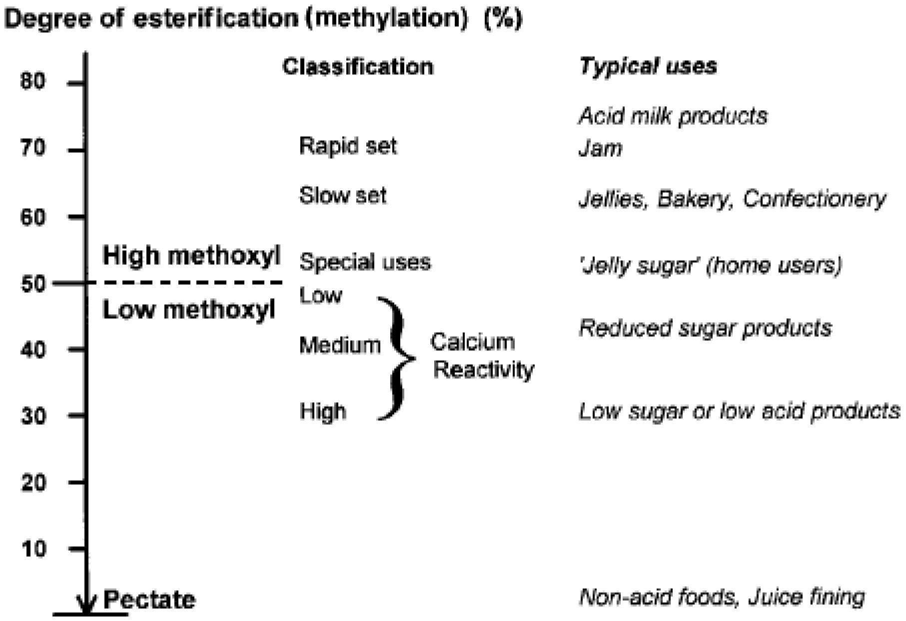


Figure 2.16 The range of commercial non-amidated pectins with some typical applications (May, 2000).

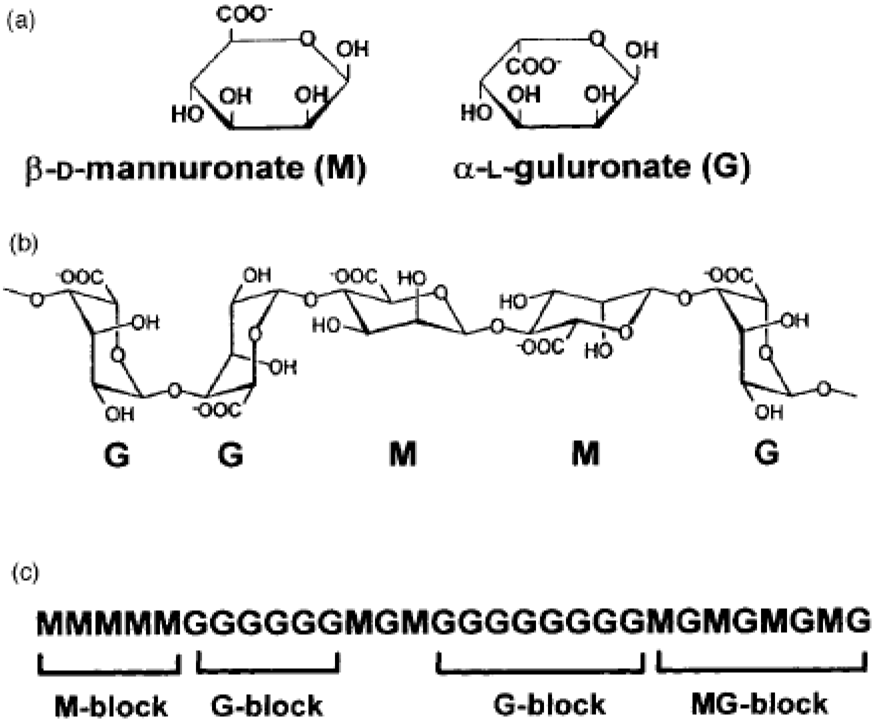


Figure 2.17 Structure characteristics of alginates: (a) alginate monomer, (b) chain conformation, (c) block distribution (Draget, 2000).

calcium ions (Figure 2.18). These cavities contain two carboxylate and two hydroxyl groups, one each from each chain. The result is a junction zone that has been called an egg box arrangement, with the calcium ions being linked to eggs in the pockets of an egg carton (Figure 2.19) (Whistler & BeMiller, 1997). Strength of the gel depends on the content of G-blocks in the alginate used and the concentration of calcium ions. The loss of ionization at low pH values causes the alginate chain to lose their negative charge, giving the molecules more of the characteristics of long neutral molecules, and allows junction zone to develop. As molecular associations increase, the viscosity of solution increases. Finally, when the pH is low enough, alginic acid precipitates from solution because of extensive intermolecular associations.

Alginate is widely used to provide viscosity at low concentrations. Higher viscosity (under low shear conditions) can be achieved by adding a small amount of calcium ions to the gum solution. This characteristic is used to thicken fruit juices and to provide suspension to juice insoluble. Thickening action, and particularly thixotropic behavior brought about by low calcium ion levels, tend to hold the pulp in suspension. Calcium alginate gels are obtained by diffusion setting, internal setting and setting by cooling. Diffusion setting can be used to prepare structured foods. Two examples are structured pimento strips and structured onion rings. Internal setting for fruit mixes, fruit purees and structured fruit (apple, peach, pear and apricot) pieces involves slow release of calcium ions within the mixture. Setting by cooling involves dissolving a calcium salt, a slightly soluble acid and a sequestrant in hot water and allowing the mixture to set on cooling.

2.6 Carrageenans

Carrageenan is extracted from red seaweeds of the family Rhodophyceae. It does not have a single molecular structure; rather it consists of a family of structures, a group of linear galactan polysaccharides that have an ester sulfate content of 15-40% (w/w) and that contain alternating (1→3)- and (1→4)-β-D-glycosidic linkages. The three types of commercially available carrageenans are known as κ, ί and λ (Figure 2.20). These three types are definitions; they do not exist singly in the real world. Commercial carrageenans are either mixtures of three types, with one type

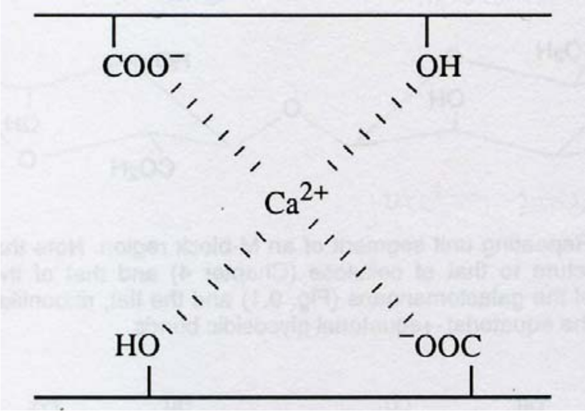


Figure 2.18 Coordination of a calcium ion with hydroxyl and carboxyl groups on adjacent G-block chains (Whistler & BeMiller, 1997).

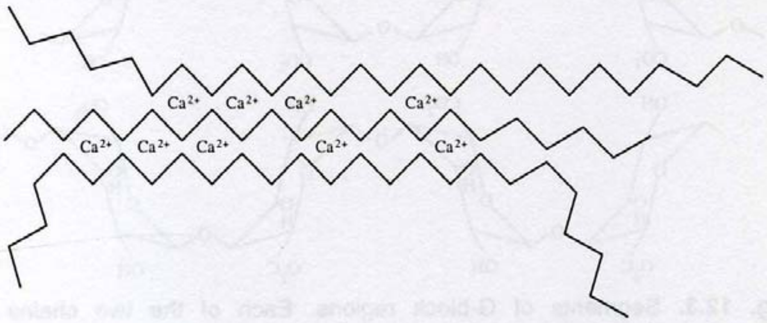


Figure 2.19 Representation of the proposed formation of a junction between two alginate molecules promoted by calcium ions (Whistler & BeMiller, 1997).

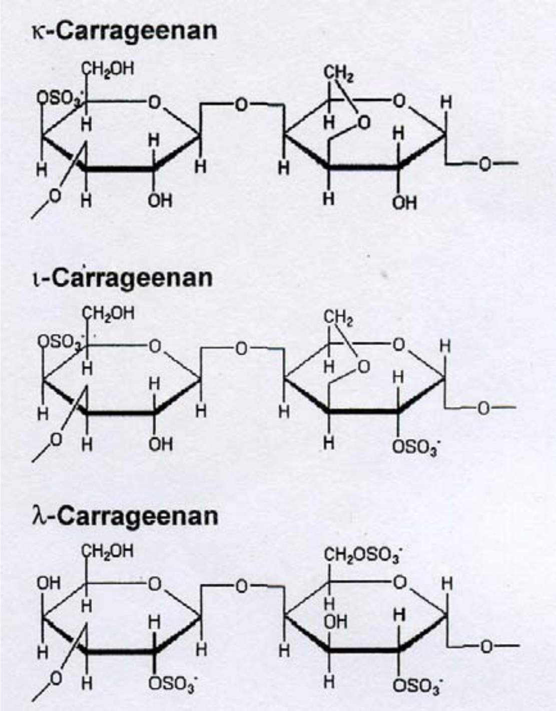


Figure 2.20 Chemical structures of the three types of commercially available carrageenans: κ, ι, and λ (Hoefler, 2004).

predominating, or they are hybrid molecules containing structural components of more than one type. The structure of κ-carrageenan is shown in Figure 2.20. Note that for every two galactose units in the chain, there is one sulfate group. Sulfate groups make the molecule more water soluble by virtue of having more water of hydration associated with them (Hoefler, 2004). There is also one anhydro bridge, which tend to inhibit water solubility because of its hydrocolloids nature. Iota-carrageenan has two sulfate groups for every two galactose units as well as one anhydro bridge. The additional sulfate groups on the ί molecule make it more water soluble than the κ type. The λ molecule has three sulfate groups for every two galactose units and no anhydro bridge, making it the most water soluble of the three carrageenan types. The κ molecule, the least water soluble of the three, is the one most likely to drop halfway out of the solution into what is known as the gelled state. The gelled states are literally half in and half out of solution. They are out of solution at their junction zones (literally crystallized out), while the parts of the molecules that are not involved in junction zones are still fully in solution (hydrated).

All carrageenans are soluble in hot water. However, only λ-carrageenan and the sodium salts of κ- and ί-carrageenans are soluble in cold water (Imeson, 2000). Lambda carrageenan gives viscous solutions which show pseudoplasticity or shear-thinning when pumped or stirred. These solutions are used for thickening, particularly in dairy products, to give a full body with a non-gummy, creamy texture. Hot solutions of κ- and ί-carrageenans set to form a range of gel texture when cooled to between 40 and 60°C depending on the cations present. Carrageenan gels are thermally reversible and exhibit hysteresis or a difference between setting and melting temperature. These gels are stable at room temperature but can be remelted by heating to 5-20°C above the gelling temperature. On cooling the system will re-gel. Kappa carrageenan selects for potassium ions to stabilize the junction zones within the characteristically firm, brittle gel as shown in Figure 2.21a. Iota carrageenan selects for calcium ions to bridge between adjacent chains to give typically soft elastic gels in Figure 2.21b.

Commercial carrageenans can be viscosity builders, gelling agents or stabilizers. Carrageenan products are most often used because of their ability to form gels with milk and water (Table 2.7) (Whistler & BeMiller, 1997). Blending provides

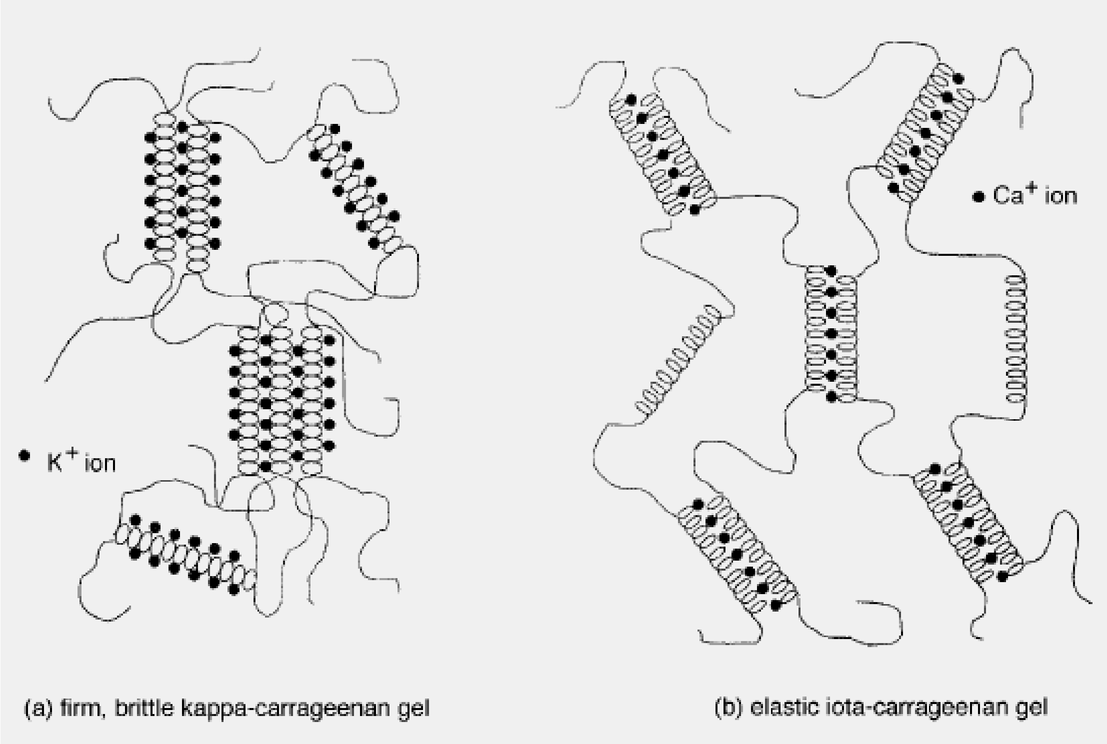
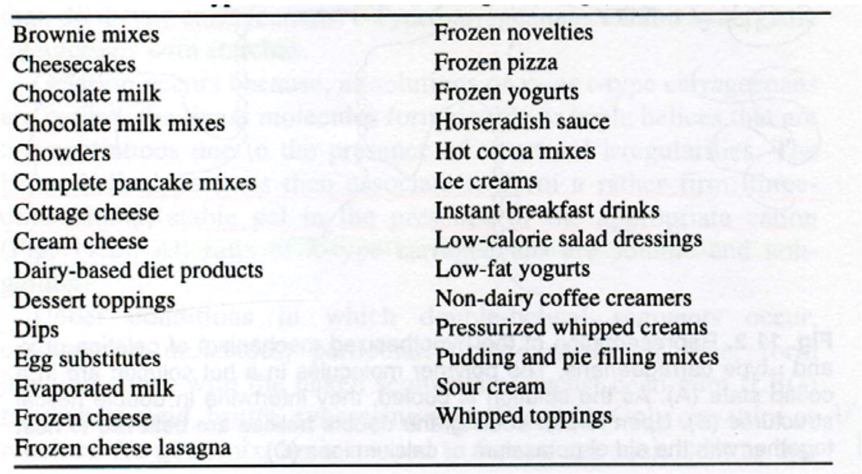


Figure 2.21 Gelation of kappa and iota carrageenans with cations (Imeson, 2000).

Table 2.7 Typical products containing a carrageenan (Whistler & BeMiller, 1997).



Brownie mixes	Frozen novelties
Cheesecakes	Frozen pizza
Chocolate milk	Frozen yogurts
Chocolate milk mixes	Horseradish sauce
Chowders	Hot cocoa mixes
Complete pancake mixes	Ice creams
Cottage cheese	Instant breakfast drinks
Cream cheese	Low-calorie salad dressings
Dairy-based diet products	Low-fat yogurts
Dessert toppings	Non-dairy coffee creamers
Dips	Pressurized whipped creams
Egg substitutes	Pudding and pie filling mixes
Evaporated milk	Sour cream
Frozen cheese	Whipped toppings
Frozen cheese lasagna	

a wide range of products that are standardized with various amounts of sucrose, glucose (dextrose), buffer salts or gelling aids, such as potassium chloride. Iota type carrageenans are more soluble than the κ-types, but with both, only the sodium salt forms are soluble in cold water. While water gels of κ-carrageenans are firm, rigid and characterized by syneresis. Iota carrageenans form elastic, syneresis-free, thermally reversible gels that are stable to repeated freeze-thaw cycling. Lambda type carrageenans are non-gelling gum. They are used as emulsion stabilizers in products such as whipped cream, instant breakfast drinks, initiation coffee creams and milk shakes. A blend of κ- and λ-carrageenan is used in the latter.

2.7 Cellulosics

Cellulose is the principle cell-wall component of higher plants and hence the most abundant organic compound, and the most abundant carbohydrate, on the earth (Whistler & BeMiller, 1997). It is a high-molecular-weight, linear, insoluble homopolymer of repeating β-D-glucopyranosyl unit joined by (1→4) glycosidic linkages (Figure 2.22). Cellulose is insoluble except in few special solvents that can disrupt the intermolecular bonds. However, certain derivatives of cellulose are water soluble and important as food gums.

The cellulose pulp is dispersed in alkali solution to form alkali cellulose and is then treated with appropriated reagents, under tightly controlled conditions, to substitute the anhydroglucose monomers of the cellulose chain (Murray, 2000). The substitution is at the hydroxyl groups. Carboxymethyl cellulose (CMC) is prepared from cotton linters or wood pulps by soaking the raw material in an aqueous sodium hydroxide solution and then introducing monochloroacetic acid. The result is the introduction of carboxymethyl ether groups where there had been hydroxyl groups previously (Figure 2.23). Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) are prepared in a manner similar to that of CMC, except that the reagents used are methyl chloride for MC and a mixture of methyl chloride and propylene oxide for HPMC (Figure 2.24). From Figures 2.23 and 2.24, they illustrated that CMC is anionic (and is sold in the sodium salt form), the other two cellulose-based hydrocolloids (MC and HPMC) are non-ionic. In practical terms, this makes MC and HPMC relatively insensitive to electrolytes, while the viscosity of CMC decreases

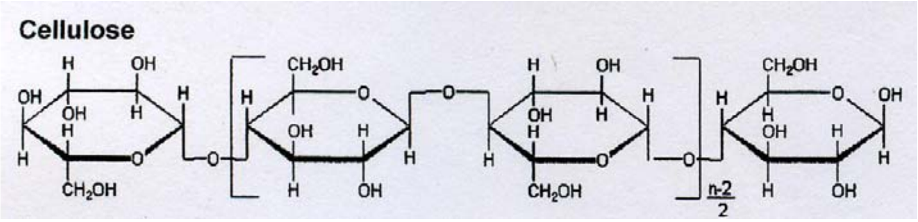


Figure 2.22 Chemical structure of cellulose (Hoefler, 2004).

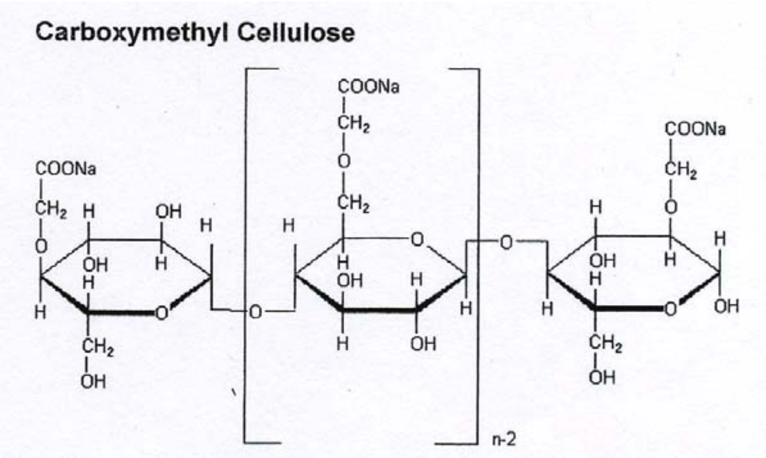


Figure 2.23 Chemical structure of carboxymethylcellulose (Hoefler, 2004).

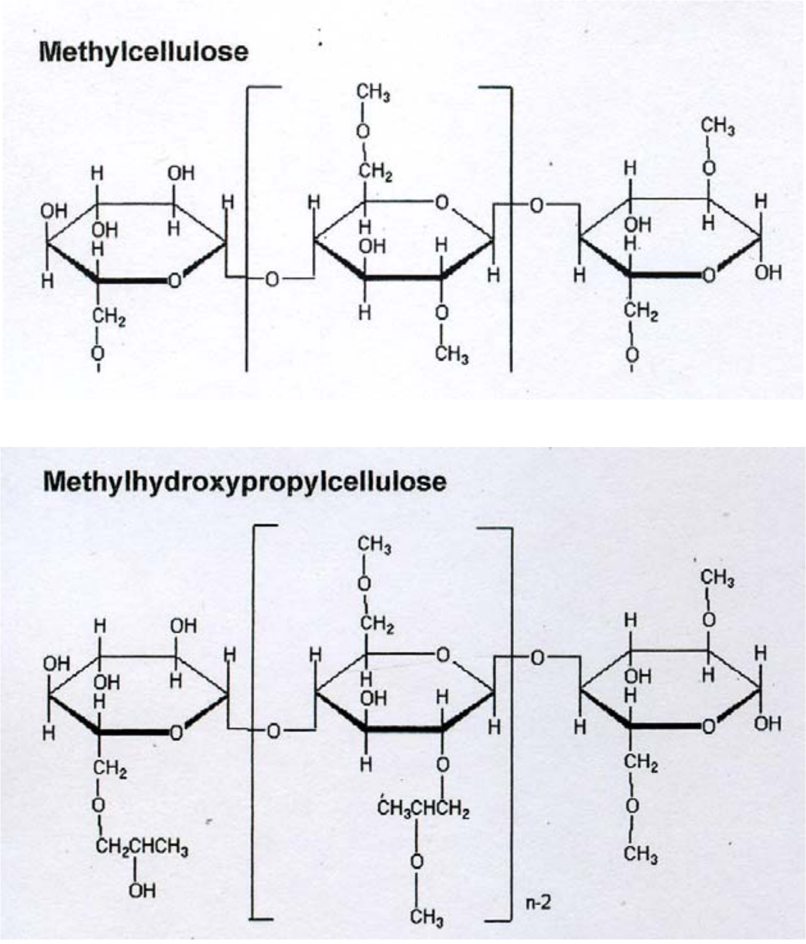


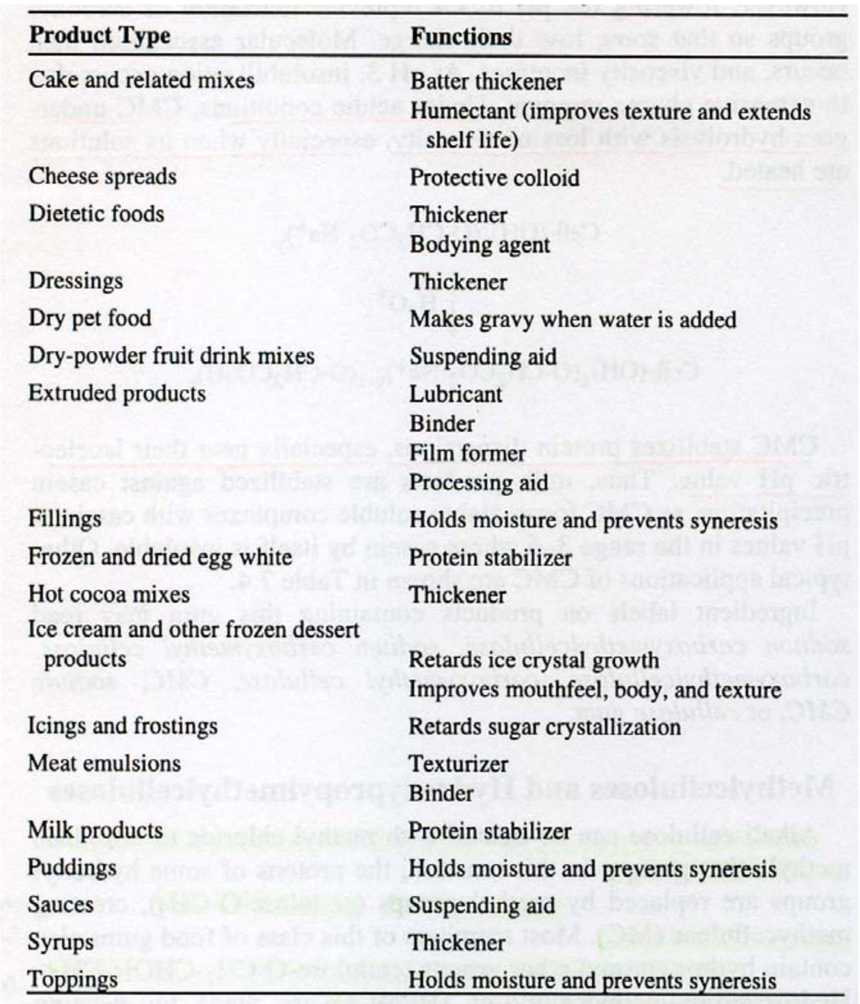
Figure 2.24 Chemical structures of methylcellulose and hydroxypropylmethylcellulose (or methylhydroxypropylcellulose) (Hoefler, 2004).

dramatically if it is not hydrate in water prior to exposure to ionic substances such as salts and acids.

Cellulose derivative hydrocolloids are optically transparent in solution. CMC is soluble in both hot and cold water to give a colorless solution with neutral flavor. The solution viscosity depends on degree of polymerization (DP). The CMC solution shows a reversible reduction of viscosity on heating and thickens again when cooled. Solutions of CMC with low degree of substitution (DS) are thixotropic, whereas higher DS tends to pseudoplasticity. Uniformity of substitution favors pseudoplastic rheology, and solutions of each type give a particular smooth mouthful. For MC and HPMC, they are both soluble in cold water to give solutions with a wide range of viscosity, which is dependent on both DP and DS. The solutions show reasonable viscosity stability over the range of pH 3-11. More important, however, is the behavior of solutions on heating since the solution has been raised above a point known as the incipient gel temperature (IGT). The IGT varies from 52°C for MC, to a range of 63-80°C for HPMC types with increasing degree of hydroxypropyl substitution increasing the IGT. These gels are reversible on cooling, although, there is a pronounced hysteresis between heating and cooling.

CMC will start with applications where viscosity is the major property required. It is normal to use high viscosity grades of CMC. A range of granulometries is available. Although the standard particle size will be suitable in many applications, the coarser particles will be preferred when it is necessary to make up solutions with poor mixing equipment. On the other hand, extra fine powders will be necessary for vending mixes and other instant applications. The typical applications of CMC are shown in Table 2.8. The major applications of MC and HPMC are in the fields of binding and shape retention, film formation and barrier properties, and avoidance of boil-out and bursting at higher temperatures. MC can also be used to reduce the amount of fat in food products through two mechanisms: 1) they impart fat like properties so that the fat content of a product can be reduced and 2) they reduce absorption of fat by products being fried. MC imparts richness (creaminess), provides lubricity (slippery mouthfeel), provides structure and body and generates and stabilizes foams. The major use of HPMC product is in nondairy whipped toppings. At about 0.5% concentration, HPMC stabilizes foams, imparts better whipping

Table 2.8 Typical applications of carboxymethylcellulose (Whistler & BeMiller, 1997).



Product Type	Functions
Cake and related mixes	Batter thickener Humectant (improves texture and extends shelf life)
Cheese spreads	Protective colloid
Dietetic foods	Thickener Bodying agent
Dressings	Thickener
Dry pet food	Makes gravy when water is added
Dry-powder fruit drink mixes	Suspending aid
Extruded products	Lubricant Binder Film former Processing aid
Fillings	Holds moisture and prevents syneresis
Frozen and dried egg white	Protein stabilizer
Hot cocoa mixes	Thickener
Ice cream and other frozen dessert products	Retards ice crystal growth Improves mouthfeel, body, and texture
Icings and frostings	Retards sugar crystallization
Meat emulsions	Texturizer Binder
Milk products	Protein stabilizer
Puddings	Holds moisture and prevents syneresis
Sauces	Suspending aid
Syrups	Thickener
Toppings	Holds moisture and prevents syneresis

characteristics, prevents phase separation through its surface activity and provides freeze-thaw stability by becoming more soluble as the temperature is lowered.

3. Interaction of starch and hydrocolloids

The physical properties of native starches and their colloidal sols limit their usefulness in many commercial applications (Liu, Eskin, & Cui, 2003). Aggregation and crystallization of starch molecules can lead to increase rigidity and syneresis of the starch paste. This phenomenon of retrogradation is further exacerbated during freezing with detrimental effects to the texture, acceptability and digestibility of starch-containing foods (Berry, I'Anson, Miles, Morris, & Russell, 1988). Chemical modification of starch can improve cooking characteristics, decrease retrogradation as well as increase freeze-thaw stability of starch pastes. However, obtaining regulatory approval for new chemical reagents combined with consumer concerns regarding the chemical treatment of foods has led to alternative ways to modify starch such as blending with other hydrocolloids.

3.1 Gelatinization

Heating in water weakens the more crystalline network within the granules by disrupting hydrogen bonds with a concurrent loss of anisotropy (Christianson et al., 1981). In the more amorphous areas, the molecules are not as closely associated, progressive hydration and swelling occur rapidly. Molecules of linear amylose are eventually released into solution and amylopectin remains inside the swollen, partially disrupted granule. The degree of granular collapse is related to heating time, temperature and the type of mechanical treatment applied to the sample (Zobel, 1984). Hydrocolloids interact with the amylose outside the starch granule to produce a more complex matrix of amylose and hydrocolloid surrounding the gelatinized granules (Kruger et al., 2003). According to Abdulmola et al. (1996), starch molecules can interact and a network can be created at concentrations well below close-packing. Xanthan promotes adhesive interactions among the gelatinized granules. It is assumed that it can entrap them keeping them closely. This can enhance the forces applied to them, facilitating water entering (increasing swelling), amylose solubilization and its exudation.

Swelling of the starch granules at and above the gelatinization temperatures and weakens the granule structure, resulting in an increase in the paste viscosity and the susceptibility of the granules to shear damage (Bhandari et al., 2002). The degree of swelling and the granule integrity are directly related to the viscosity of the starch paste (Borwankar, 1992). The increase in starch peak viscosity in the presence of hydrocolloid has been reported previously (Alloncle et al., 1989; Liu & Eskin, 1998; Sasaki, Yasui, & Matsuki, 2000). Christianson et al. (1981) attributed the increase in viscosity to interaction between exudate from the starch granule (solubilized amylose and low-molecular-weight amylopectin) and gums. A second explanation given was that addition of thickening gums enhanced the forces being exerted on the starch granules in the shear field compared to the starch-water suspension with equal starch concentrations. Alloncle et al. (1989) proposed a model to interpret these effects in which the gums were located within the continuous phase of the starch pastes. In this model, the volume of the continuous phase accessible to the gum was reduced, yielding an increase in gum concentration within the continuous phase, which was accompanied by a dramatic increase in viscosity.

The gelatinization process is typically followed using differential scanning calorimetry (DSC) where the terms onset (T_o), peak (T_p), and conclusion (T_c) temperatures and enthalpy (ΔH) can be determined relatively easily (Tester & Sommerville, 2003). Hydrocolloids have been reported to elevate the starch gelatinization temperatures (Kim, Hansen, & Setser, 1986; Kim & Setser, 1992; Kim & Wang, 1999; Tester & Sommerville, 2003). During gelatinization, an increase in T_c as the volume fraction of water is reduced has been explained in terms of delayed starch crystallite dissociation (Dronovan & Mapes, 1980; Ferrero et al., 1996; Sommerville, 1999; Tester & Sommerville, 2003). Yoshimura, Takaya, & Nishinari (1996) proposed that water is imbibed by konjac glucomannan to decrease the amount available for starch gelatinization and increase T_c. Furthermore, limited water availability resulted in a decrease of enthalpy (Eliasson, 1980; Marchant & Blanshard, 1980). Water is reduced in the mixed system because the non-starch polysaccharide readily hydrates and consequently reduces the amount of water available for gelatinization (Ferrero et al., 1996; Lelievre, 1976). The effect that any particular hydrocolloid has on the gelatinization process differs with the type of starch employed

(Gudmundsson, Eliasson, Bengtsson, & Aman, 1991). Rojas et al. (1999) found that alginate, κ-carrageenan, guar gum and xanthan gum decreased the enthalpy of gelatinization in wheat flour, whereas Ferro et al. (1996), in apparent contradiction, reported an increase with increasing concentration of alginate, guar gum, xanthan gum or carboxymethylcellulose. Ghiasi, Heseney, & Varriano-Marston (1982) found that xanthan gum had no effect on starch gelatinization enthalpy at the concentrations they used. Rye arabinoxylan decreases the gelatinization enthalpy for normal potato and maize starches, increase it for wheat starch but has no effect for waxy maize starch (Gudmundson et al., 1991).

3.2 Rheological properties

Rheological properties of starch containing foods are widely dependent on the nature and the type of molecular arrangement of starch and its chemical structure, conformation and the forces acting between them (Bhandari et al., 2002). A small change in molecular conformation and structure of starch can bring about dramatic change in functional and rheological properties of starch (Djakovic & Dokic, 1972). The rheology of starch-hydrocolloid combinations is particular to each mixture and depends on experimental conditions, namely, those involved in paste preparation. Therefore, it is necessary to determine it for each particular case (Tecante & Doublier, 1999). The most important aspects examined are their steady flow and dynamic viscoelastic behaviors.

Hydrocolloids are widely used to thicken food systems. The viscosity of polymer solutions shows a marked increase at a critical polymer concentration, commonly referred to as C^*, corresponding to the transition from the so-called dilute regime, where the polymer molecules are free to move independently in solution without interpenetration to the semi-dilute regime where molecular crowding gives rise to the overlap of polymer coils and interpenetration occurs (Williams & Phillips, 2000). A typical viscosity-shear rate profile for a polymer solution above C^* is given in Figure 2.25 and shows three distinct regions: (a) a low-shear Newtonian plateau; (b) a shear-thinning region and (c) a high-shear Newtonian plateau. At low shear rate, the rate of disruption of entanglement is less than the rate of re-entanglement and hence

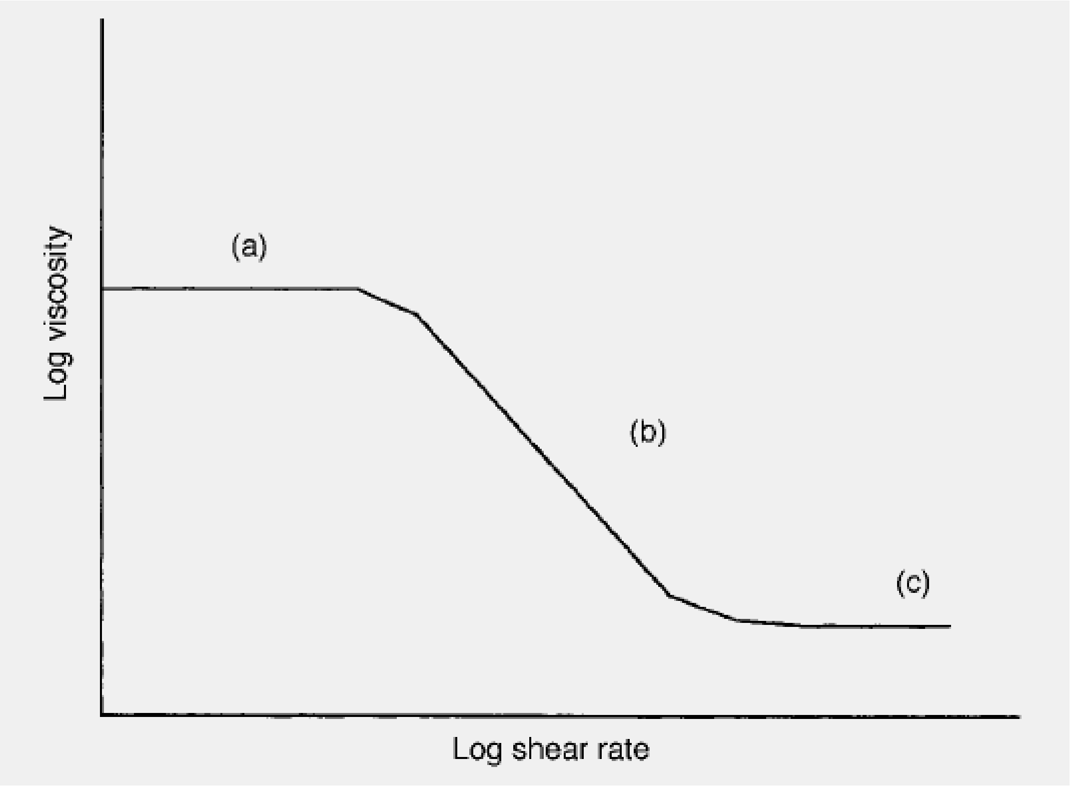


Figure 2.25 typical viscosity-shear rate profile for a polymer solution above C^*.

viscosity is independent of shear. Above a critical shear rate, disentanglement predominates and the viscosity drops to a minimum plateau value at infinite shear rate.

In order to describe the steady-shear rheological properties of starch-hydrocolloid mixtures, it normally fits the data to the well-known power law equation, $\sigma = K\dot{\gamma}^n$, where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index (Pa s^n), n is the flow behavior index (dimensionless). The low concentration of hydrocolloid in solution exhibits Newtonian behavior (as described above). However, the combination of starch and hydrocolloid can cause the increase of concentration of hydrocolloid in continuous phase (Bahnassey & Breene, 1994). It is due to the higher concentration of hydrocolloid phase and the gum solution exhibit pseudoplastic or shear-thinning behavior (Hoefler, 2004). This shear-thinning behavior can be explained by breaking of an entangled polysaccharide molecule network during shearing, as described by Bhandari et al. (2002) and Morris (1999). In an entangled network system, the rate of disruption of existing intermolecular entanglements becomes greater than the rate of reformation of intermolecular entanglement with increasing shear rate, resulting in less resistance to flow and a lower apparent viscosity. Urlacher & Noble (1997) reported that starch-xanthan gum mixtures indicated the shear-thinning behavior that was more pronounced than that of starch dispersion due to the unique property of xanthan gum, showing more shear-thinning than those of other polysaccharides (guar gum, locust bean gum, sodium alginate, cellulose, etc.). The rich starch-galactomannan increased the magnitudes of apparent viscosity, $\eta_{a,100}$, and K indicating a higher synergism between starch-galactomannan interaction (Yoo et al., 2005).

The dynamic shear rheological tests for deformation, in general, have been used to obtained valuable information on the viscoelastic properties of starch-gum mixtures to explain the sample's molecular structure (Gunasekaran & Ak, 2000). The storage modulus G' is a measure of the energy that is stored in the material or recoverable per cycle of deformation, loss modulus G'' is a measure of the energy that is lost as viscous dissipation per cycle of deformation and $\eta *$, complex viscosity, is a measure of the overall resistance to flow. The ratio of G''/G' or loss tangent is for evaluation of the viscoelastic behavior. In starch-gum mixed pastes, the increase of dynamic moduli can be attributed to the increase in viscoelastic properties of added gum, which is concentrated within the continuous phase in the starch-gum mixed systems, dud to its thickening properties, as indicated by Alloncle & Doublier (1991). Further, sometimes partial substitution of starch by a given hydrocolloid even results in lower storage and higher loss modulus than starch alone dispersions of equal total concentration (Eidam et al., 1995).

3.3 Phase separation

Phase separation (demixing) of biopolymer mixtures in aqueous solutions is a fairly common phenomenon due to the limited miscibility of the individual polymeric components, particularly for chemically in compatible macromolecular species and under conditions which favors macromolecular demixing (Biliaderis et al., 1997). This process greatly enhances the concentration of each component in its respective microdomain and thereby brings about a substantial enhancement in the viscosity of the mixed system. The latter has often been described as reflecting a synergistic interaction between the two polymers, but in reality it is rather the thermodynamic incompatibility between the two polymers that forces them to partition in two separate microphases and alters the rheological of the composite network.

In starch dispersion, granules are in an amylose rich phase, which may contain also some amylopectin molecules. In this latter case, a segregative phase separation may occur due to the thermodynamic incompatibility between amylose and amylopectin (Kalichevsky & Ring, 1987). Amylose gelation takes place through association of ordered amylose chains that allows the formation of aggregates, which, at low concentrations, precipitated (Miles, Morris, & Ring, 1984; Ellis & Ring, 1985; Eliasson & Gudmundsson, 1996). Gelation may be followed by turbidity development related to the number, size and compaction of aggregates and by the evolution of the storage modulus depending on the number of junction and on the overall rigidity of the network (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Doublier & Choplin, 1989; Eliasson & Gudmundsson, 1996; Miles et al., 1984; Leloup, Colonna, Ring, Robert, & Wells, 1992). The presence of swollen granules increases the effective concentration of dissolved amylose and amylopectin chains and favors their mutual exclusion, which in turn promotes the aggregation of the highly concentrated amylose located between the starch granules (Conde-Petit & Escher, 1995).

The possible molecular interactions between starch and non-starch polysaccharides include the exclusion effect of swollen granules (Eidam, Kulicke, Kuhn, & Stute, 1995; Liu & Lelievre, 1992). This is due to incompatibility between unlike polymers, amylose and hydrocolloids (Liu et al., 2006). It results in an increase of effective concentration of each component in its microdomain, causing a substantial enhancement in the viscosity of the mixed system with enhanced firmness of the mixed gel. This could be explained as the thermodynamic incompatibility between chemically dissimilar polysaccharide molecules coexisting in the matrices (Alloncle & Doublier, 1991; Kulicke et al., 1996), the interference of ungelling polysaccharide on the association of the coexisting gelling one (Biliaderis et al., 1997), and the coupling action between unlike polysaccharide molecules (Abdulmola, Hember, Richardson, & Morris , 1996; Alloncle & Doublier, 1991; Eidam et al., 1995).

CHAPTER III
MATERIALS AND METHODS

1. Materials

1.1 Starches

Commercial normal (NRS) and waxy (WRS) rice starches obtained from Choheng Rice Vermicelli Factory Company (Nakornpathom, Thailand) had moisture (AACC, 2000, Method 44-19) and amylose (AACC, 2000, Method 61-03) contents of 11.5 and 30.0% w/w, and 10.0 and 0.84% w/w, respectively. The normal and waxy rice starches donated from California Natural Products (Lathrop, CA, USA) and A&B Ingredients (Fairfield, NJ, USA), respectively, had moisture and amylose contents of 10.6 and 11.9% w/w, and 10.7 and 0.92% w/w, respectively.

1.2 Hydrocolloids

Guar gum (GG) (Main Street Ingredients, WI, USA and Shree Ram Gum&Chemicals, Jodhpur, India), locust bean gum (LBG) (Sigma-Aldrich Co., MO, USA), xanthan gum (XG) (KELTROL®, CP Kelco US Inc., IL, USA), gellan (GL) (Gelrite®, CP Kelco US Inc., IL, USA), sodium alginate (SA) (Sigma-Aldrich Co., MO, USA), low-methoxyl pectin (LMP) (Hercules Inc., DE, USA), high-methoxyl pectin (HMP) (Hercules Inc., DE, USA), carboxymethylcellulose (CMC) (Type 7MF, Hercules Inc., DE, USA), methylcellulose (MC) (A4M, Dow Chemical Co., MI, USA), hydroxypropylmethylcellulose (HPMC) (F50LV PREM, Dow Chemical Co., MI, USA), κ-carrageenan (κC) (Type III, Sigma-Aldrich Co., MO, USA), ί-carrageenan (ίC) (Type V, Sigma-Aldrich Co., MO, USA), and λ-carrageenan (λC) (Viscarin® GP 209, FMC Corporation, PA, USA) were commercial samples.

2. Methods

2.1 Preparation of starch-hydrocolloid dispersions

2.1.1 Samples for studying an effect of preparation method on pasting, thermal and textural characteristics of normal and waxy rice starches

Starch-hydrocolloid mixtures with 10% w/w starch and 0.3, 0.6 and 1.0% w/w hydrocolloids (guar or xanthan gum) were prepared with two different methods, (1) starch and gum were dry blended and then dispersed into distilled water with mild stirring for 15 min (dry mixing) and (2) gums were first dissolved in the distilled water, heated at 80°C with mild stirring for 5 min and then, the starch powder was slurried into gum solution at room temperature (wet mixing). The starch without hydrocolloid addition was used as a control.

2.1.2 Samples for studying gelatinization (thermal and pasting properties), rheological and textural characteristics, and microscopic observation of normal and waxy rice starches

Suspensions of starch-hydrocolloid mixtures were prepared as dry blends of starch and hydrocolloid at 7.2 and 0.8% w/w (dry basis), respectively. The well blended powders were dispersed into distilled water with gentle stirring for 1 h at room temperature. The starch alone slurry (8.0% w/w) was used as a control.

2.1.3 Samples for studying rheological property of cooked starch

Starch slurry at 5% w/w (dry basis) was heated to boiling for 30 min. Starch paste was cooled down and then, poured into a freeze-dryer jar and placed into a water bath containing a mixture of dry ice and acetone until frozen. The freeze-dry jar containing frozen paste was moved to a freeze-dryer for freeze-drying the paste. The cooked starch-hydrocolloid mixtures were prepared as describe in Section 2.1.2.

2.2 Determination of pasting properties

Pasting properties of the normal and waxy rice starches were determined in the presence and absence of the hydrocolloids by a Rapid Visco Analyser (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). The slurries (25 g) were poured into aluminum canisters and stirred manually using plastic paddles for 20-30 s before insertion into the RVA. The heating and cooling cycles were programmed following the general pasting method (STD 1). The slurry was held at 50°C for 1 min, heated to 95°C within 3 min 42 s and then held at 95°C for 2 min 30 s. It was subsequently cooled to 50°C within 3 min 48 s and held at 50°C for 2 min, while maintaining a rotation speed of 160 rpm.

2.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC 822^e, Mettler Toledo, Zurich, Switzerland) was used for analyzing the thermal characteristics of starch-hydrocolloid mixtures. Suspension of each starch-gum mixture was prepared as described in Section 2.1.1 and 2.1.2, and the starch without hydrocolloid addition was used as a control. The suspension was placed into 40 μl aluminum pans at 10-15 mg. These aluminum pans were hermetically sealed. The empty pan was used as a reference, and the DSC was calibrated by using indium. The suspensions were heated at a rate of 10°C/min form 25 to 100°C. The transition temperatures, i.e. onset (T_o), peak (T_p) and conclusion (T_c) temperatures, of gelatinization were recorded. Further, an area under the curve was measured as an enthalpy of the gelatinization (ΔH) and expressed in term of J/g on the basis of dry weight of starch.

2.4 Determination of swelling power and solubility index

The concentration of starch used in this experiment was less than the close packing concentration (~ 2.0%) of starch granules (Vandeputte, Derycke, Geeroms, & Delcour, 2003). Swelling power was determined following the method of Sasaki et al. (2000) with slight modification. The starch alone (1.25% w/w) or starch-hydrocolloid (1.125% w/w starch and 0.125% w/w hydrocolloid) suspensions were put into 50-mL centrifuge tubes and heated in a boiling water bath for 10 min with minimum shear conditions. After heating, the centrifuge tubes containing the samples were cooled in an ice bath for 5 min and then centrifuged at 7000 g at 25°C for 15 min. The supernatant was removed for the measurement of solubilized starch by drying to constant weight in a hot air oven at 105°C. Precipitated paste and dried supernatant were weighed. The swelling power (SP) and solubility index (SOL) were calculated based on the assumption that the total amount of gum remained in the supernatant. SP was determined as the ratio in weight of the wet sediment compared to the initial weight of the dry starch. The method of Gibson, Solah, & McCleary (1997) was used to determine total carbohydrates in the recovered supernatant. The SOL is the percentage of dried mass of solubles in the supernatant (after subtraction of the dry weight of gum added) to the dry mass of the whole starch sample.

2.5 Rheological measurements

Dynamic viscoelastic and steady flow properties of the freshly prepared pastes of starch alone and starch-hydrocolloid mixtures obtained from pasting in the RVA were determined after holding at room temperature (~25ºC) for 1 h by using a rheometer (Viscotech DSR, Rheologica Instruments Inc., NJ, USA) with a cone and plate geometry sensor (2° cone angle, 50 mm diameter, and 50 µm gap). The sample was placed into the rheometer which was equilibrated to 30°C. Two dynamic viscoelastic measurements were made: (1) deformation sweeps at a constant frequency (10 Hz) to determine the maximum deformation attainable by a sample in the linear viscoelastic range and (2) frequency sweeps over a range of 1 to 100 Hz at a constant deformation (0.5% strain) within the linear viscoelastic range. The storage modulus (G'), loss modulus (G''), complex viscosity (η^* = $\sqrt{(G')^2 + (G'')^2} / \omega$), and loss tangent ($\tan\delta = G''/G'$) as a function of frequency (ω) were obtained.

Steady flow tests were also performed on the freshly prepared paste samples at 30°C to obtain shear rate versus shear stress data. The rheometer was programmed to increase the shear rate from 1 to 500 s^{-1} (up curve) in 400 s followed immediately by a reduction from 500 to 1 s^{-1} in 400 s (down curve). Data from the down curve of the shear cycle were used to characterize the flow of the paste samples and to estimate the power law parameters by using the equation $\sigma = K\dot{\gamma}^n$, where σ is the shear stress

(Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is the flow behavior index.

2.6 Texture profile analysis

Texture profile analyses of the freshly prepared paste samples (8 wt%) were performed at room temperature (~25°C) using a TA.XT2i Texture Analyzer (Stable Micro Systems Ltd., Surrey, UK) equipped with Texture Expert for Windows version 1 software; a 2 kg load was used for force calibration. Weighed paste samples (~25 g) were poured into cylindrical containers (35 mm internal diameter, 65 mm height) and kept at room temperature (~25°C) for 1 h prior to measurement. One compression cycle was applied using a hemispherical probe (P/0.5HS) at a constant crosshead velocity of 1 mm/s to a sample depth of 15 mm (50% gel height), followed by return to the original position. From the resulting force-time curve, the values for texture attributes, i.e., hardness and adhesiveness, of the paste samples were measured according to the definitions of Pons and Fiszman (1996). Hardness is defined as the peak force observed during the compression cycle. Adhesiveness is the negative force area representing the work necessary to pull the compressing plunger away from the sample.

2.7 Microscopic examination

Freshly prepared paste samples (8% w/w) obtained from the RVA analysis were cooled down and kept at room temperature for 1 h prior to examination. The samples were placed on microscope slides, stained with Lugol's solution (333 mg I_2 + 667 mg KI in 100 mL water), and then covered with cover glasses. The microstructure of the paste samples was examined using a Leitz Laborlux 12 Pol microscope (W. Nuhsbaum, Inc., IL, USA) at 100× magnification.

2.8 Statistical analysis

All measurements were made in triplicate for each sample. Results are expressed as mean ± standard deviations. A one-way analysis of variance (ANOVA) and Tukey's test were used to establish the significance of differences among the mean values at 0.05 level of confidence. The statistical analyses were performed using SPSS version 12.0 for Windows program (SPSS Inc., Chicago, IL, USA).

CHAPTER IV

RESULTS

4.1 Effect of preparation method on pasting, thermal and textural characteristics of normal and waxy rice starches

4.1.1 Pasting properties

The pasting properties of 10% (w/w) normal rice starch (NRS) and waxy rice starch (WRS) in the presence of various concentrations (0-1%) of GG and XG prepared by two different methods are summarized in Tables 4.1 and 4.2, respectively. Starch-gum mixtures of NRS and WRS showed an increase of peak viscosity from both preparation techniques. This value was significantly ($P \leqslant 0.05$) increased when the gum concentration increased. GG exhibited more effective than XG in combination with NRS, and this effect was also more pronounced in breakdown viscosity. However, in WRS-gum mixtures, XG showed higher effect than GG for these parameters. Setback viscosity exhibited a reassociation of solubilized starch during cooling and NRS containing higher amylose had higher tendency to reorder than WRS (with <1% apparent amylose). XG addition significantly ($P \leqslant 0.05$) decreased the setback viscosity in the mixture of NRS. On the contrary, the hydrocolloid additions slightly affected this parameter in the combination of WRS, especially for samples from dry mixing technique. The final viscosities of both starches were increased by the addition of gums and this effect was more pronounced at higher gum concentrations. However, GG exhibited higher effect than XG in NRS suspension. The starch-gum mixtures showed a significant ($P \leqslant 0.05$) increase of pasting temperature when compared to their corresponding controls for both preparation techniques.

Table 4.1

Pasting characteristics of 10% (w/w) aqueous suspensions of normal rice starch (NRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations.

Sample	Gum cencentration (%)	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
Dry mixing						
NRS/water	0.0	229.0±2.3^{e}	43.1±4.5^{d}	300.2±6.9^{c}	114.3±11.6^{ab}	81.3±0.5^{b}
NRS/GG	0.3	359.9±18.0^{c}	88.8±11.6^{c}	387.7±17.3^{ab}	116.6±12.7^{ab}	85.3±8.5^{ab}
NRS/GG	0.6	458.8±13.6^{b}	191.6±11.7^{b}	399.9±22.1^{ab}	132.7±32.1^{a}	92.7±0.1^{a}
NRS/GG	1.0	593.7±14.3^{a}	276.7±7.5^{a}	419.1±25.8^{a}	102.1±21.4^{ab}	95.1±0.0^{a}
NRS/XG	0.3	274.7±12.2^{d}	47.7±4.1^{d}	308.9±11.9^{c}	82.0±3.2^{bc}	89.3±5.1^{ab}
NRS/XG	0.6	337.2±1.6^{c}	50.8±3.3^{d}	361.7±2.5^{b}	75.3±0.9^{bc}	95.0±0.2^{a}
NRS/XG	1.0	368.5±13.6^{c}	20.6±3.1^{e}	394.2±6.7^{ab}	48.6±18.6^{c}	94.8±0.1^{a}
Wet mixing						
NRS/water	0.0	229.0±2.3^{e}	43.1±4.5^{c}	300.2±6.9^{c}	114.3±11.6^{a}	81.3±0.5^{c}
NRS/GG	0.3	357.1±11.6^{cd}	90.8±12.4^{b}	380.0±5.3^{ab}	113.7±6.2^{a}	80.7±0.0^{c}
NRS/GG	0.6	460.6± 9.4^{b}	183.2±7.6^{a}	408.1±3.9^{a}	130.8±11.8^{a}	95.0±0.4^{a}
NRS/GG	1.0	548.2±24.0^{a}	224.4±36.8^{a}	381.4±8.7^{a}	57.6±4.3^{c}	94.6±0.5^{ab}
NRS/XG	0.3	271.6±21.6^{e}	43.4±4.1^{bc}	311.2±25.8^{c}	83.0±3.6^{b}	89.1±5.3^{b}
NRS/XG	0.6	321.0±13.0^{d}	59.5±1.5^{bc}	346.2±14.3^{b}	84.8±3.0^{b}	94.9±0.1^{a}
NRS/XG	1.0	365.6±15.6^{c}	31.7±7.3^{c}	377.5±6.0^{ab}	48.6±18.6^{c}	94.9±0.0^{a}

Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different (*P*≤0.05).

Table 4.2

Pasting characteristics of 10% (w/w) aqueous suspensions of waxy rice starch (WRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations.

Sample	Gum concentration (%)	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
Dry mixing						
WRS/water	0.0	270.3±0.3^{e}	115.1±0.7^{e}	170.2±1.2^{e}	15.1±1.0^{a}	74.4±0.1^{d}
WRS/GG	0.3	302.1±3.5^{d}	144.4±2.3^{d}	183.1±2.0^{cd}	25.5±5.3^{a}	79.4±0.5^{c}
WRS/GG	0.6	334.1±2.8^{c}	156.7±0.7^{bcd}	195.2±2.8^{c}	17.8±1.7^{a}	84.4±1.0^{b}
WRS/GG	1.0	347.2±2.9^{bc}	151.1±5.9^{cd}	222.0±8.5^{b}	25.9±5.6^{a}	85.8±0.5^{b}
WRS/XG	0.3	330.1±5.5^{c}	176.5±1.1^{ab}	178.7±4.2d^{e}	25.1±0.3^{a}	84.6±0.8^{b}
WRS/XG	0.6	359.8±19.4^{b}	171.6±16.1^{ab}	210.4±6.0^{b}	22.2±2.8^{a}	86.3±0.1^{ab}
WRS/XG	1.0	410.5±7.8^{a}	185.9±11.1^{a}	241.2±3.3^{a}	16.5±6.1^{a}	88.0±1.4^{a}
Wet mixing						
WRS/water	0.0	270.3±0.3^{d}	115.1±0.7^{c}	170.2±1.2^{d}	15.1±1.0^{bc}	74.4±0.1^{e}
WRS/GG	0.3	301.1±1.1^{cd}	140.7±8.6^{abc}	182.3±5.8^{d}	21.9±3.6^{ab}	78.8±0.4^{d}
WRS/GG	0.6	332.8±1.4^{abc}	160.3±6.0^{ab}	200.7±4.0^{c}	28.2±3.6^{a}	85.5±0.0^{b}
WRS/GG	1.0	350.6±14.1^{ab}	154.4±8.5^{ab}	222.6±10.4^{ab}	26.4±3.1^{a}	86.6±0.4^{ab}
WRS/XG	0.3	308.0±11.0^{bc}	148.7±8.8^{abc}	179.4±2.8^{d}	20.1±2.3^{ab}	83.9±0.1^{c}
WRS/XG	0.6	353.9±4.6^{a}	165.3±9.3^{a}	213.0±4.3^{bc}	24.2±3.6^{ab}	86.1±0.5^{ab}
WRS/XG	1.0	357.9±36.3^{a}	128.1±29.3^{bc}	240.0±8.9^{a}	10.2±3.9^{c}	87.4±1.3^{a}

Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

4.1.2 Thermal properties

The effect of hydrocolloid addition and preparation method on onset (T_o), peak (T_p), conclusion (T_c) temperatures and gelatinization enthalpy (ΔH) of NRS and WRS determined by DSC is shown in Tables 4.3 and 4.4, respectively. For NRS-gum suspensions, the T_o, T_p and T_c from dry mixing technique were not significantly ($P \leq 0.05$) different when compared to the control (starch alone), however, the opposite results were exhibited in the wet mixing method as the increase of gum concentration resulted in a significant increase in these temperature values. In addition, for the suspensions of WRS-gum, hydrocolloid addition showed little effect on these gelatinization temperatures, except for the T_o values of the dry blended samples and the T_o and T_p values of the wet blended samples which in creased as compared with the controls and seemed to be independent of the gum concentration. A significant ($P \leq 0.05$) decrease in ΔH values was observed in NRS-gum suspensions obtained from both preparation methods. For WRS-gum mixtures, the ΔH values of the dry blended samples were unaffected by gum addition, whereas those of the wet blended samples were significantly decreased and seemed to be independent of gum concentration.

Table 4.3

Thermal properties of 10 % (w/w) aqueous suspensions of normal rice starch (NRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations.

Sample	Gum concentration (%)	T_o(°C)	T_p(°C)	T_c(°C)	Enthalpy (J/g dry starch)
Dry mixing					
NRS/water	0.0	70.8 ± 0.1^{a}	75.1 ± 0.2^{a}	78.4 ± 0.3^{a}	13.7 ± 0.7^{a}
NRS/GG	0.3	70.9 ± 0.1^{a}	74.9 ± 0.1^{a}	78.7 ± 0.2^{a}	8.7 ± 0.6^{b}
NRS/GG	0.6	70.6 ± 0.5^{a}	74.9 ± 0.2^{a}	78.8 ± 0.3^{a}	8.2 ± 0.3^{b}
NRS/GG	1.0	71.2 ± 0.7^{a}	75.4 ± 0.4^{a}	79.2 ± 0.3^{a}	7.4 ± 1.2^{b}
NRS/XG	0.3	71.2 ± 0.1^{a}	75.3 ± 0.2^{a}	79.0 ± 0.3^{a}	8.8 ± 0.5^{b}
NRS/XG	0.6	71.4 ± 0.2^{a}	75.4 ± 0.2^{a}	79.2 ± 0.8^{a}	7.5 ± 0.1^{b}
NRS/XG	1.0	71.5 ± 0.0^{a}	75.4 ± 0.2^{a}	79.4 ± 0.2^{a}	7.2 ± 0.3^{b}
Wet mixing					
NRS/water	0.0	70.8 ± 0.1^{d}	75.1 ± 0.2^{c}	78.4 ± 0.3^{d}	13.7 ± 0.7^{a}
NRS/GG	0.3	71.1 ± 0.2^{cd}	75.1 ± 0.2^{bc}	79.1 ± 0.3^{cd}	7.4 ± 0.2^{b}
NRS/GG	0.6	71.2 ± 0.1^{bc}	75.4 ± 0.2^{abc}	79.3 ± 0.2^{bc}	7.0 ± 0.2^{bc}
NRS/GG	1.0	71.2 ± 0.2^{bc}	75.2 ± 0.3^{bc}	79.2 ± 0.2^{bcd}	6.6 ± 0.2^{bc}
NRS/XG	0.3	71.6 ± 0.3^{ab}	75.7 ± 0.3^{ab}	79.8 ± 0.3^{ab}	7.6 ± 0.4^{b}
NRS/XG	0.6	71.6 ± 0.1^{ab}	75.6 ± 0.2^{abc}	79.7 ± 0.3^{abc}	7.1 ± 0.1^{bc}
NRS/XG	1.0	71.8 ± 0.2^{a}	76.0 ± 0.3^{a}	80.0 ± 0.1^{a}	6.3 ± 0.4^{c}

GG and XG are guar gum and xanthan gum, respectively.

T_o, T_p and T_c are onset temperature, peak temperature and conclusion temperature, respectively.

Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

Table 4.4

Thermal properties of 10 % (w/w) aqueous suspensions of waxy rice starch (WRS) without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations.

Sample	Gum concentration (%)	T_o(°C)	T_p(°C)	T_c(°C)	Enthalpy (J/g dry starch)
Dry mixing					
WRS/water	0.0	59.8±0.3^{b}	66.7±0.1^{b}	73.4±0.2^{a}	11.0±1.2^{a}
WRS/GG	0.3	60.3±0.2^{ab}	67.2±0.1^{a}	72.3±0.1^{b}	11.2±0.5^{a}
WRS/GG	0.6	60.9±0.4^{a}	67.5±0.2^{a}	72.4±0.2^{b}	9.9±1.9^{a}
WRS/GG	1.0	60.2±0.3^{ab}	67.4±0.2^{a}	72.6±0.3^{b}	11.5±1.3^{a}
WRS/XG	0.3	60.6±0.1^{ab}	67.5±0.3^{a}	72.5±0.3^{a}	11.2±0.7^{a}
WRS/XG	0.6	61.1±0.9^{ab}	67.7±0.2^{a}	72.2±1.0^{a}	8.6±3.9^{a}
WRS/XG	1.0	61.4±0.7^{a}	68.0±0.3^{a}	73.0±0.3^{a}	9.5±2.1^{a}
Wet mixing					
WRS/water	0.0	59.8±0.3^{c}	66.7±0.1^{b}	73.4±0.2^{a}	11.0±1.2^{a}
WRS/GG	0.3	60.7±0.1^{bc}	67.4±0.1^{ab}	72.5±0.2^{a}	10.1±0.0^{ab}
WRS/GG	0.6	61.3±0.4^{ab}	67.8±0.6^{a}	72.9±0.8^{a}	9.4±0.4^{b}
WRS/GG	1.0	61.4±0.1^{a}	67.8±0.1^{a}	72.8±0.1^{a}	9.5±0.3^{ab}
WRS/XG	0.3	61.3±0.1^{a}	67.6±0.1^{b}	72.5±0.3^{a}	9.4±0.3^{b}
WRS/XG	0.6	61.5±0.2^{a}	68.0±0.2^{ab}	73.0±0.3^{a}	9.4±0.2^{b}
WRS/XG	1.0	61.7±0.2^{a}	68.1±0.2^{a}	73.0±0.2^{a}	9.0±0.3^{b}

GG and XG are guar gum and xanthan gum, respectively.

T_o, T_p and T_c are onset temperature, peak temperature and conclusion temperature, respectively. Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

4.1.3 Textural characteristics

The textural properties of NRS and WRS pastes with and without hydrocolloid addition from two different preparation methods are shown in Tables 4.5 and 4.6, respectively. Hardness and adhesiveness values were slightly affected by the hydrocolloid addition in NRS suspensions from both preparation techniques, except for the hardness parameter of the NRS-guar gum mixture at the concentrations of 0.6 and 1.0% from wet mixing technique. For WRS-gum mixture, the hardness values of the dry blended samples were unaffected by gum addition, whereas the adhesiveness significantly increased with gum concentration. These parameters were significantly increased by the wet mixing of gum at high levels (0.6-1.0%) as compared with the control.

Table 4.5

Textural properties of 10% (w/w) normal rice starch (NRS) pastes without and with Addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations.

Sample	Gum concentration (%)	Dry mixing		Wet mixing	
		Hardness (g)	Adhesiveness (g.mm)	Hardness (g)	Adhesiveness (g.mm)
NRS/water	0.0	49.1±5.6^{c}	519.8±103.0^{ab}	49.1±5.6^{bc}	519.8±103.0^{ab}
NRS/GG	0.3	50.1±2.7^{c}	498.2±72.3^{ab}	69.6±4.4^{ab}	316.4±47.8^{b}
NRS/GG	0.6	67.6±2.0^{ab}	401.6±86.4^{bc}	79.0±2.5^{a}	367.5±33.8^{b}
NRS/GG	1.0	78.6±3.5^{a}	662.3±64.2^{a}	85.6±17.8^{a}	707.4±264.0^{a}
NRS/XG	0.3	51.0±11.5^{c}	407.1±141.8^{bc}	48.1±12.4^{bc}	425.3±104.6^{ab}
NRS/XG	0.6	53.0±0.5^{bc}	431.6±86.0^{abc}	44.9±3.1^{c}	551.9±87.2^{ab}
NRS/XG	1.0	51.6±3.0^{c}	186.3±19.4^{c}	39.9±2.5^{c}	644.7±31.1^{ab}

Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

Table 4.6

Textural properties of 10% (w/w) waxy rice starch (WRS) pastes without and with addition of guar gum (GG) or xanthan gum (XG) at different concentrations obtained by different preparations.

Sample	Gum concentration (%)	Dry mixing		Wet mixing	
		Hardness (g)	Adhesiveness (g.mm)	Hardness (g)	Adhesiveness (g.mm)
WRS/water	0.0	13.0 ± 2.7^{b}	4.6 ± 0.6^{e}	13.0 ± 2.7^{b}	4.6 ± 0.6^{d}
WRS/GG	0.3	15.8 ± 1.4^{ab}	17.2 ± 2.7^{de}	15.4 ± 1.0^{ab}	13.0 ± 2.6^{cd}
WRS/GG	0.6	15.8 ± 2.7^{ab}	24.0 ± 2.7^{bcd}	17.8 ± 2.4^{a}	29.0 ± 2.1^{c}
WRS/GG	1.0	17.3 ± 1.0^{ab}	35.5 ± 3.5^{bc}	18.0 ± 1.6^{a}	35.5 ± 1.8^{bc}
WRS/XG	0.3	16.7 ± 0.3^{ab}	22.5 ± 2.7^{cd}	17.2 ± 0.0^{ab}	26.5 ± 5.4^{cd}
WRS/XG	0.6	16.3 ± 1.0^{ab}	39.1 ± 13.5^{b}	18.8 ± 0.6^{a}	56.1 ± 5.8^{b}
WRS/XG	1.0	19.4 ± 2.1^{a}	92.0 ± 4.9^{a}	19.8 ± 1.2^{a}	94.6 ± 20.8^{a}

Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

4.2 Effect of various hydrocolloids on gelatinization (pasting, thermal characteristics, swelling power, and solubility index) of normal and waxy rice starches

4.2.1 Pasting characteristics

The pasting and paste characteristics of the normal rice starch (NRS) and waxy rice starch (WRS) in the absence and presence of various hydrocolloids determined by RVA analysis are summarized in Tables 4.7 and 4.8, respectively. The NRS alone exhibited higher peak, breakdown, final and setback viscosities and lower pasting temperature than the WRS alone. Addition of hydrocolloids to both NRS and WRS generally resulted in a significant ($P \leq 0.05$) increase in peak, breakdown, final and setback viscosities and pasting temperatures, with the exception of LM-pectin and HPMC, which did not significantly affect the pasting properties of NRS and both NRS and WRS, respectively. The highest peak and breakdown viscosities were observed when MC was added to both starches. Addition of locust bean gum (LBG) and λ-carrageenan (λC) to NRS and WRS, respectively, exhibited the highest final viscosities of the gels. The greatest setback values were observed with NRS-alginate and WRS-CMC combinations. The pasting temperatures were found to be highest when xanthan gum (XG) was added to both starches.

Table 4.7

Pasting properties of normal rice starch (7.2 % w/w) in the absence and presence of various hydrocolloids (0.8% w/w)[1]

Hydrocolloid	Peak viscosity (mPa s)	Breakdown (mPa s)	Final viscosity (mPa s)	Setback (mPa s)	Pasting temperature (°C)
None (control)[2]	2430±28^{f}	944±19^{d}	1693±19^{fg}	207±10^{cd}	67.0±0.2^{d}
Guar gum	4082±85^{b}	1849±45^{b}	2627±36^{ab}	393±9^{b}	72.3±4.8^{abc}
Locust bean gum	4092±70^{b}	1834±40^{b}	2743±36^{a}	485±15^{ab}	66.8±0.5^{d}
Xanthan gum	3179±10^{cd}	1057±53^{cd}	2271± 38de	150±46^{cd}	75.8±1.6^{a}
Gellan	3191±58^{cd}	1269±49^{c}	2352±114^{cde}	428±107^{ab}	70.2±0.1^{bcd}
LM-pectin	2481±22^{f}	915±20^{d}	1734±4^{f}	168±3^{cd}	68.9±0.5^{cd}
HM-pectin	2757±46^{e}	1049±10^{cd}	1906±25^{f}	198±14^{cd}	68.9±0.5^{cd}
Sodium alginate	3241±13^{cd}	1297±15^{c}	2472±21^{bcd}	528±21^{a}	70.0±0.1^{bcd}
κ-carrageenan	2615±13^{ef}	602±39^{e}	2187±21^{e}	174±9^{cd}	71.6±0.5^{abc}
ί-carrageenan	3096±89^{d}	1132±31^{cd}	2377±37^{cde}	440±21^{ab}	73.5±0.8^{ab}
λ-carrageenan	3991±23^{b}	1948±60^{b}	2509±41^{bc}	465±17^{ab}	74.2±1.6^{ab}
CMC	3382±136^{c}	1313±76^{c}	2517±16^{bc}	448±60^{ab}	70.2±0.1^{bcd}
MC	4351±185^{a}	2378±305^{a}	2221±223^{e}	248±23^{c}	66.5±0.5^{d}
HPMC	2406±90^{f}	1048±60^{cd}	1488±16^{g}	130±35^{d}	68.9±0.5^{cd}

---

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \le 0.05$).

[2] 8% w/w normal rice starch (NRS)

Table 4.8

Pasting properties of waxy rice starch (7.2 % w/w) in the absence and presence of various hydrocolloids (0.8% w/w)[1]

Hydrocolloid	Peak viscosity (mPa s)	Breakdown (mPa s)	Final viscosity (mPa s)	Setback (mPa s)	Pasting temperature (°C)
None (control)[2]	1414±17^{h}	660±11^{j}	895±9^{gh}	141±4^{f}	69.1±0.4^{ef}
Guar gum	2630±46^{c}	1365±30^{bc}	1581±44^{e}	316±24^{c}	76.3±1.2^{ab}
Locust bean gum	2821±19^{b}	1464±4^{b}	1762±23^{bc}	405±7^{ab}	67.2±0.4^{f}
Xanthan gum	2650±9^{c}	1040±16^{fg}	1816±48^{b}	206±25^{e}	78.0± 2.1^{a}
Gellan	2286±78^{e}	1079±49^{ef}	1608±39de	400±16^{b}	71.3±0.4^{de}
LM-Pectin	1734±16^{g}	1075±16^{ef}	797±8^{i}	138±9^{f}	70.4±0.5^{de}
HM-Pectin	1910±32^{f}	1103±25^{ef}	966± 6^{g}	159±6^{f}	70.7±0.5^{de}
Sodium alginate	2461±8^{d}	1186±17de	1686±13^{cd}	411±12^{ab}	71.5±0.4^{de}
κ-carrageenan	1884±27^{f}	806±16^{hi}	1332±15^{f}	154±9^{d}	71.8±0.9^{cd}
ί-carrageenan	2197±29^{e}	925±30^{gh}	1686±17^{cd}	414±9^{ab}	74.3±0.8^{bc}
λ-carrageenan	2759±17^{bc}	1254±40^{cd}	1932±12^{a}	428±20^{ab}	75.4±1.0^{ab}
CMC	2327±41de	1142±27^{def}	1632±14de	447±6^{a}	71.6± 0.5^{de}
MC	3122±128^{a}	1812±143^{a}	1550±60^{e}	239±31de	72.4±0.5^{cd}
HPMC	1513±16^{h}	772±25^{ij}	871±18^{hi}	130±11^{f}	70.6±1.0^{de}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

[2] 8% w/w waxy rice starch (WRS)

4.2.2 Thermal characteristics

The effect of hydrocolloid addition on onset (T_o), peak (T_p), and conclusion (T_c) temperatures and enthalpy (ΔH) of NRS and WRS determined using DSC is summarized in Tables 4.9 and 4.10, respectively. The T_o, T_p, and T_c of NRS-hydrocolloid mixtures were not significantly ($P \leqslant 0.05$) affected by the gum addition. This trend was also observed in WRS-hydrocolloid mixtures, except for T_c that significantly ($P \leqslant 0.05$) decreased when guar gum (GG), LBG, or XG was added to WRS suspension. All NRS-gum suspensions exhibited a significant ($P \leqslant 0.05$) decrease in ΔH values when compared to the control (starch alone), whereas the ΔH values of WRS suspensions were unaffected by addition of most of the gums studied except for LBG, XG, gellan, and λC which significantly decreased the ΔH values of the WRS-gum suspensions.

Table 4.9

Thermal properties of normal rice starch (7.2% w/w) in the absence and presence of various of hydrocolloids (0.8% w/w)[1]

Hydrocolloid	T_o(°C)	T_p(°C)	T_c(°C)	Enthalpy (J/g dry starch)
None (control)[2]	59.2 ± 0.7^{a}	66.8 ± 0.6^{a}	76.8 ± 1.5^{a}	20.5 ± 1.6^{a}
Guar gum	61.1 ± 1.0^{a}	66.8 ± 0.7^{a}	76.8 ± 0.6^{a}	10.8 ± 0.1^{bcd}
Locust bean gum	61.9 ± 0.9^{a}	68.8 ± 1.7^{a}	78.2 ± 1.1^{a}	9.7 ± 0.9^{bcd}
Xanthan gum	61.9 ± 1.4^{a}	67.9 ± 1.2^{a}	77.1 ± 1.2^{a}	9.5 ± 1.8^{bcd}
Gellan	60.5 ± 2.2^{a}	67.7 ± 0.7^{a}	77.2 ± 1.4^{a}	11.8 ± 1.7^{bc}
LM-pectin	62.2 ± 0.5^{a}	68.5 ± 0.7^{a}	77.5 ± 0.1^{a}	10.8 ± 0.1^{bcd}
HM-pectin	61.5 ± 0.1^{a}	66.5 ± 1.2^{a}	77.6 ± 0.6^{a}	12.7 ± 0.2^{b}
Sodium alginate	61.6 ± 0.4^{a}	67.9 ± 0.7^{a}	77.3 ± 1.5^{a}	10.4 ± 1.4^{bcd}
κ-carrageenan	61.9 ± 0.3^{a}	68.5 ± 0.3^{a}	76.2 ± 0.5^{a}	8.1 ± 0.1^{bcd}
ί-carrageenan	61.8 ± 0.4^{a}	68.0 ± 0.6^{a}	76.8 ± 0.6^{a}	8.9 ± 0.5^{cd}
λ-carrageenan	61.5 ± 0.2^{a}	67.7 ± 0.1^{a}	75.9 ± 1.1^{a}	8.0 ± 0.5^{d}
CMC	61.8 ± 0.3^{a}	67.8 ± 1.0^{a}	75.4 ± 0.8^{a}	9.2 ± 0.4^{bcd}
MC	60.9 ± 0.5^{a}	67.0 ± 0.3^{a}	75.1 ± 0.3^{a}	8.9 ± 0.1^{cd}
HPMC	61.7 ± 0.0^{a}	68.8 ± 1.7^{a}	76.5 ± 3.0^{a}	9.8 ± 1.0^{d}

T_o, T_p and T_c are onset temperature, peak temperature and conclusion temperature, respectively.

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

[2] 8% w/w normal rice starch (NRS)

Table 4.10

Thermal properties of waxy rice starch (7.2% w/w) in the absence and presence of various of hydrocolloids (0.8% w/w)[1]

Hydrocolloid	T_o(°C)	T_p(°C)	T_c(°C)	Enthalpy (J/g dry starch)
None (control)[2]	60.6±0.0^{a}	68.1±0.7^{a}	77.9±0.6^{a}	10.4±0.3^{a}
Guar gum	60.0±0.4^{a}	67.4±0.0^{a}	73.8±0.8^{bc}	8.2±0.0^{abcd}
Locust bean gum	60.5±0.3^{a}	67.5±0.1^{a}	74.1±0.4^{bc}	7.4±0.2^{cd}
Xanthan gum	62.6±0.5^{a}	68.7±0.4^{a}	73.3±1.9^{c}	7.2±0.1^{d}
Gellan	64.7±4.6^{a}	68.6±0.7^{a}	75.9±1.4^{abc}	7.9±0.1^{bcd}
LM-pectin	60.8±0.4^{a}	68.6±0.1^{a}	76.6±0.2^{ab}	8.8±0.1^{abcd}
HM-pectin	60.6±0.3^{a}	67.8±0.7^{a}	76.7±1.1^{ab}	9.3±0.3^{abcd}
Sodium alginate	62.1±1.1^{a}	69.9±2.0^{a}	76.8±0.1^{ab}	8.8±0.9^{abcd}
κ-carrageenan	62.1±0.1^{a}	68.9±0.5^{a}	78.0±1.4^{a}	9.6±0.1^{abcd}
ί-carrageenan	61.5±0.4^{a}	68.9±0.0^{a}	76.1±0.0^{abc}	8.4±0.5^{abcd}
λ-carrageenan	60.8±0.1^{a}	68.8±1.1^{a}	76.5±0.4^{ab}	7.7±0.8^{bcd}
CMC	61.0±0.0^{a}	68.7±0.5^{a}	75.3±0.5^{abc}	9.8±1.5^{abc}
MC	61.3±0.6^{a}	68.3±0.1^{a}	76.3±0.1^{abc}	10.5±0.2^{a}
HPMC	61.0±0.5^{a}	67.5±0.4^{a}	75.6±0.2^{abc}	9.9±1.0^{ab}

T_o, $T_{p\text{ and}}$ T_c are onset temperature, peak temperature and conclusion temperature, respectively.

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] 8% w/w waxy rice starch (WRS)

4.2.3 Swelling power and solubility index

The effect of hydrocolloid addition on swelling power (SP) and solubility index (SOL) of NRS and WRS is shown in Table 4.11. The SP and SOL of WRS alone were higher than those of NRS. Addition of tested hydrocolloids to NRS slightly increased SP, and the highest SP value was observed for NRS-XG. Moreover, all hydrocolloids significantly ($P \leqslant 0.05$) promoted the leaching of solubilized starch from NRS at temperatures above the gelatinization temperature particularly for the addition of CMC. However, this effect was not much different among the different hydrocolloids. For the case of WRS, the addition of gum produced a variety of effects on its SP during heating in the presence of different hydrocolloids, it decreased (LBG, GL and MC), increased (XG) or had no effect (GG, LMP, HMP, sodium alginate [SA], κC, ί-carrageenan [ίC], λC, CMC and HPMC), whereas SOL tended to decrease.

Table 4.11

Swelling power and solubility index of normal and waxy rice starches (1.125% w/w) in the absence and presence of various hydrocolloids (0.125% w/w) heated at 100°C for 10 min under low shear condition[1]

Hydrocolloid	Normal rice starch		Waxy rice starch	
	Swelling power (g/g)[2]	Solubility index (%)	Swelling power (g/g)[2]	Solubility index (%)
None (control)[3]	15.5±0.7^{d}	3.9±0.6^{c}	26.9±2.6^{bc}	14.9±2.8^{a}
Guar gum	25.9±0.5^{ab}	11.3±0.2^{b}	31.5±2.3^{bc}	4.1±0.3^{gh}
Locust bean gum	23.0±0.3^{bc}	11.1±0.2^{b}	20.4±1.6^{de}	3.1± 0.8^{h}
Xanthan gum	30.1±0.2^{a}	11.9±0.5^{ab}	43.7±0.8^{a}	5.3±1.5^{fgh}
Gellan	20.7±0.5^{bcd}	12.3±0.1^{ab}	17.8±0.5^{e}	5.9±0.6^{efgh}
LM-pectin	20.4±3.5^{bcd}	12.1±2.0^{ab}	32.2±5.4^{b}	11.6±1.9^{abc}
HM-pectin	18.1±1.5^{cd}	11.0±0.2^{b}	32.6±1.2^{b}	6.7±2.3^{defgh}
Sodium alginate	19.2±0.3^{cd}	12.3±0.3^{ab}	30.1±1.7^{bc}	10.8±0.7^{abcd}
κ-carrageenan	20.6±1.2^{bcd}	13.7±0.2^{a}	28.2±0.7^{bc}	13.1±0.8^{ab}
í-carrageenan	18.7±1.7^{cd}	12.4±0.0^{ab}	31.7±1.3^{bc}	10.0±1.9^{bcde}
λ-carrageenan	21.6±5.1^{bc}	12.6±0.6^{ab}	26.0±0.1^{cd}	8.3±0.5^{cdefg}
CMC	22.7±0.2^{bc}	13.8±0.1^{a}	31.0±1.6^{bc}	12.9±2.2^{ab}
MC	17.4±0.7^{cd}	12.6±0.9^{ab}	19.1±0.4^{e}	9.1±0.5^{bcdef}
HPMC	17.3±2.8^{cd}	12.3±0.4^{ab}	26.3±0.7^{c}	11.2±0.5^{abc}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

[2] Grams of starch gel per gram of its dry weight.

[3] 1.25% (w/w) normal rice starch (NRS) or waxy rice starch (WRS).

4.3 Effect of various hydrocolloids on paste characteristics and microscopic observation of normal and waxy rice starches

4.3.1 Dynamic rheological properties

The dynamic rheological properties of NRS and WRS in the absence and presence of various hydrocolloids are shown in Tables 4.12 and 4.13, respectively. The G' value of the NRS alone paste was 1.7 times greater than that of the WRS alone paste. The G' values of the NRS pastes prepared with added hydrocolloids were 1.1-4.1 times higher than the G' values of the of the WRS pastes prepared with added hydrocolloids, with the exception of κC which increased the G' value of the NRS paste to 12 times that of the NRS alone paste and 8.8 times that of the WRS-κC paste, indicating a much greater elasticity (gel-like character) of the NRS-κC paste via a κC-amylose interaction. In the case of WRS paste, the addition of ίC exhibited the highest G' value when compared to the WRS alone paste. However, this G' value of WRS-ίC was 1.1 times lower than that of the NRS-ίC paste. This can be attributed to an interaction of carrageenan and leached amylose and/or low molecular weight amylopectin.

In the case of tan δ, the value for the WRS alone paste was 4.75 times that for the NRS alone paste. When the hydrocolloids were present, the values for the WRS-hydrocolloid pastes were only slightly greater (1.0-1.4) than those of the NRS-hydrocolloid pastes, with the exception of the pastes containing sodium alginate (SA), MC, LMP and HPMC, in which cases the tan δ values of NRS-hydrocolloid pastes were 1.2, 1.3, 1.8 and 2.6 times greater than those for the WRS-hydrocolloid pastes, respectively.

Addition of all tested hydrocolloids, with the exception of κC and GL, did not significantly affect G', G'' and $\eta*$ values of NRS, whereas tan δ values were slightly increased (Table 4.12). The κC and GL significantly ($P \leq 0.05$) increased G', G'' and $\eta*$ values of NRS pastes. Addition of most of hydrocolloids, except for GG, HMP, κC, ίC, and CMC, significantly ($P \leq 0.05$) increased tan δ values.

Addition of GG, XG, GL, κC, ίC, and λC to WRS exhibited a significant ($P \leqslant 0.05$) increase in G', G'' and $\eta*$ values, whereas the other hydrocolloids did not produce any significant effect on the viscoelastic behavior (Table 4.13). The tan δ value of all the WRS-hydrocolloid pastes did not differ significantly from that of the control.

Table 4.12

Dynamic rheological properties of normal rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain, and 30°C[1,2]

Hydrocolloid	G' (Pa)	G'' (Pa)	η^* (Pa.s)	tan δ
None (control)[3]	128.0 ± 11.4^{c}	4.8 ± 2.1^{c}	2.1 ± 0.3^{c}	0.04 ± 0.01^{e}
Guar gum	192.0 ± 14.7^{c}	31.4 ± 3.5^{c}	3.1 ± 0.2^{c}	0.16 ± 0.03^{cde}
Locust bean gum	230.3 ± 22.7^{c}	51.8 ± 5.9^{c}	3.8 ± 0.4^{c}	0.23 ± 0.01^{abc}
Xanthan gum	285.0 ± 5.3^{bc}	49.4 ± 5.3^{c}	4.6 ± 0.1^{bc}	0.17 ± 0.02^{bcd}
Gellan	527.0 ± 58.7^{b}	136.3 ± 14.6^{b}	8.7 ± 1.0^{b}	0.26 ± 0.01^{ab}
LM-pectin	256.0 ± 6.1^{bc}	53.0 ± 26.5^{c}	3.7 ± 1.0^{c}	0.20 ± 0.10^{abcd}
HM-pectin	157.3 ± 7.2^{c}	12.7 ± 1.2^{c}	2.5 ± 0.1^{c}	0.08 ± 0.00^{de}
Sodium alginate	151.0 ± 9.5^{c}	28.5 ± 2.3^{c}	2.4 ± 0.1^{c}	0.18 ± 0.03^{abcd}
Κ-carrageenan	1513.3 ± 350.2^{a}	241.3 ± 62.1^{a}	24.4 ± 5.7^{a}	0.16 ± 0.01^{cde}
ί-carrageenan	310.0 ± 37.7^{bc}	34.5 ± 2.4^{c}	5.0 ± 0.6^{bc}	0.11 ± 0.01^{cde}
λ-carrageenan	186.3 ± 8.1^{c}	37.0 ± 2.0^{c}	3.0 ± 0.1^{c}	0.20 ± 0.02^{abcd}
CMC	154.0 ± 18.0^{c}	22.0 ± 7.4^{c}	2.5 ± 0.3^{c}	0.14 ± 0.03^{cde}
MC	192.7 ± 17.6^{c}	49.9 ± 3.4^{c}	3.2 ± 0.3^{c}	0.26 ± 0.02^{ab}
HPMC	99.7 ± 31.1^{c}	28.9 ± 4.1^{c}	1.6 ± 0.5^{c}	0.31 ± 0.12^{a}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] G', storage modulus; G'', loss modulus; η^*, complex viscosity; tan δ, loss tangent.

[3] 8% (w/w) normal rice starch (NRS).

Table 4.13

Dynamic rheological properties of waxy rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain, and 30°C[1,2]

Hydrocolloid	G' (Pa)	G'' (Pa)	η^* (Pa.s)	tan δ
None (control)[3]	74.6 ± 15.2^{fgh}	13.9 ± 1.4^{de}	1.2 ± 0.2^{fgh}	0.19 ± 0.03^{abcd}
Guar gum	145.7 ± 36.7^{cde}	32.3 ± 9.8^{bc}	2.4 ± 0.6^{cde}	0.22 ± 0.03^{ab}
Locust bean gum	125.0 ± 25.5^{def}	29.0 ± 12.9^{bcd}	2.0 ± 0.5^{def}	0.23 ± 0.06^{ab}
Xanthan gum	199.3 ± 23.3^{bc}	33.2 ± 2.5^{bc}	3.2 ± 0.4^{bc}	0.17 ± 0.02^{bcd}
Gellan	226.3 ± 25.7^{ab}	62.0 ± 7.2^{a}	3.7 ± 0.4^{ab}	0.27 ± 0.01^{a}
LM-pectin	61.9 ± 6.8^{h}	6.9 ± 3.9^{e}	1.0 ± 0.1^{h}	0.11 ± 0.07^{d}
HM-pectin	67.9 ± 7.0^{fgh}	7.0 ± 3.1^{e}	1.1 ± 0.1^{gh}	0.11 ± 0.4^{cd}
Sodium alginate	97.2 ± 9.0^{efgh}	14.8 ± 1.2^{de}	1.6 ± 0.1^{efgh}	0.15 ± 0.02^{bcd}
Κ-carrageenan	172.0 ± 25.5^{bcd}	35.1 ± 3.3^{b}	2.8 ± 0.4^{cd}	0.20 ± 0.01^{abc}
ί-carrageenan	271.0 ± 4.4^{a}	33.3 ± 0.7^{bc}	4.4 ± 0.1^{a}	0.12 ± 0.01^{cd}
λ-carrageenan	145.7 ± 1.9^{cde}	34.0 ± 0.5^{bc}	2.4 ± 0.2^{cde}	0.23 ± 0.02^{ab}
CMC	109.0 ± 5.0^{efgh}	18.6 ± 3.4^{cde}	1.8 ± 0.1^{efgh}	0.17 ± 0.04^{bcd}
MC	123.0 ± 20.1^{defg}	24.4 ± 7.7^{bcd}	2.0 ± 0.3^{defg}	0.20 ± 0.03^{abcd}
HPMC	66.9 ± 17.4^{gh}	8.1 ± 2.3^{e}	1.1 ± 0.3^{gh}	0.12 ± 0.03^{cd}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] G', storage modulus; G'', loss modulus; η^*, complex viscosity; tan δ, loss tangent.

[3] 8% (w/w) waxy rice starch (WRS).

4.3.2 Steady shear rheological properties

For the range of shear rate used in this study, power law model accurately described the flow behavior of each paste. Shear stress-shear rate data of rice starch-hydrocolloid pastes were tested for various rheological models using the software provided along with the rheometer. Based of standard error data obtained, it was found that the power law model was suitable to predict the flow behavior of the starch-hydrocolloid mixtures. Consistency coefficients (K) and flow behavior indices (n) along with coefficients of determination (R^2) and apparent viscosities at a shear rate of 100 s^{-1} $(\eta_{a,100})$ for the flow curves of NRS and WRS pastes in the absence and presence of the tested hydrocolloids are summarized in Tables 4.14 and 4.15, respectively. All the pastes exhibited pseudoplastic, shear-thinning behavior, for which $n < 1$.

Addition of all tested hydrocolloids except for HPMC, to NRS and WRS exhibited a significant increase in $\eta_{a,100}$ and K values and a slight effect on n values of the pastes. The $\eta_{a,100}$ and K values of both starches were slightly decreased, whereas the n values were significantly increased by HPMC addition as compared to the control pastes without hydrocolloid.

Table 4.14

Steady shear rheological properties of normal rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) measured at 30°C[1,2]

Hydrocolloid	$\eta_{a,100}$ (Pa s)	K (Pa s^n)	n (-)	R^2
None (control)[3]	1.3 ± 0.0^{fg}	14.2 ± 0.4^{gh}	0.48 ± 0.01^{bc}	0.9995
Guar gum	3.0 ± 0.1^{a}	34.9 ± 0.8^{cdef}	0.47 ± 0.01^{bc}	0.9976
Locust bean gum	2.7 ± 0.3^{ab}	30.4 ± 6.6^{defg}	0.48 ± 0.02^{bc}	0.9995
Xanthan gum	2.3 ± 0.0^{abcd}	46.9 ± 0.7^{abcd}	0.36 ± 0.00^{e}	0.9986
Gellan	2.7 ± 0.2^{ab}	53.7 ± 2.9^{ab}	0.37 ± 0.01^{e}	0.9977
LM-pectin	1.6 ± 0.1^{defg}	19.3 ± 1.0^{fgh}	0.46 ± 0.01^{c}	0.9998
HM-pectin	1.9 ± 0.1^{cdef}	22.0 ± 0.9^{efgh}	0.47 ± 0.00^{bc}	0.9998
Sodium alginate	2.9 ± 0.1^{ab}	39.7 ± 1.1^{bcde}	0.43 ± 0.01^{d}	0.9974
Κ-carrageenan	1.5 ± 0.8^{efg}	32.0 ± 19.8^{cdefg}	0.36 ± 0.02^{e}	0.9889
ί-carrageenan	2.6 ± 0.1^{abc}	49.4 ± 4.0^{abc}	0.34 ± 0.01^{ef}	0.9948
λ-carrageenan	2.2 ± 0.1^{bcd}	60.5 ± 3.7^{a}	0.33 ± 0.01^{f}	0.9989
CMC	2.4 ± 0.3^{abc}	33.7 ± 6.6^{cdef}	0.43 ± 0.01^{d}	0.9987
MC	2.1 ± 0.1^{bcde}	22.4 ± 1.2^{efgh}	0.49 ± 0.01^{ab}	0.9996
HPMC	1.0 ± 0.0^{g}	9.9 ± 0.2^{h}	0.51 ± 0.01^{a}	0.9996

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P\leqslant0.05$).

[2] $\eta_{a,100}$, apparent viscosity at $\dot{\gamma}$ = 100 s^{-1}; K, consistency coefficient; n, flow behavior index; R^2, coefficient of determination.

[3] 8% (w/w) normal rice starch (NRS).

Table 4.15

Steady shear rheological properties of waxy rice starch (7.2% w/w) and various hydrocolloids (0.8% w/w) measured at 30°C[1,2]

Hydrocolloid	$\eta_{a,100}$ (Pa s)	K (Pa s^{n})	n (-)	R^2
None (control)[3]	1.1 ± 0.0^{e}	14.3 ± 0.6^{h}	0.45 ± 0.01^{def}	0.9999
Guar gum	2.4 ± 0.2^{ab}	24.7 ± 1.8^{f}	0.50 ± 0.01^{a}	0.9994
Locust bean gum	2.3 ± 0.0^{bc}	24.4 ± 0.2^{f}	0.50 ± 0.01^{ab}	0.9995
Xanthan gum	2.2 ± 0.1^{bc}	43.7 ± 0.4^{c}	0.37 ± 0.01^{h}	0.9980
Gellan	2.6 ± 0.1^{b}	56.8 ± 2.3^{a}	0.35 ± 0.01^{h}	0.9978
LM-pectin	1.4 ± 0.0^{d}	16.6 ± 0.3^{gh}	0.46 ± 0.01^{cde}	0.9995
HM-pectin	1.6 ± 0.1^{d}	18.8 ± 1.3^{g}	0.47 ± 0.01^{cd}	0.9992
Sodium alginate	2.7 ± 0.0^{a}	35.9 ± 0.5^{d}	0.44 ± 0.01^{ef}	0.9978
Κ-carrageenan	2.1 ± 0.0^{c}	31.5 ± 0.7^{e}	0.42 ± 0.01^{g}	0.9989
ί-carrageenan	2.4 ± 0.1^{ab}	50.6 ± 1.3^{b}	0.35 ± 0.01^{h}	0.9927
λ-carrageenan	2.5 ± 0.0^{ab}	50.6 ± 2.7^{b}	0.35 ± 0.01^{h}	0.9988
CMC	2.4 ± 0.1^{ab}	32.9 ± 1.4^{de}	0.43 ± 0.01^{fg}	0.9991
MC	2.1 ± 0.1^{c}	23.1 ± 1.6^{f}	0.48 ± 0.01^{bc}	0.9997
HPMC	0.9 ± 0.0^{e}	9.6 ± 0.3^{i}	0.49 ± 0.01^{ab}	0.9996

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] $\eta_{a,100}$, apparent viscosity at $\dot{\gamma} = 100\ \mathrm{s}^{-1}$; K, consistency coefficient; n, flow behavior index; R^2, coefficient of determination.

[3] 8% (w/w) waxy rice starch (WRS).

4.3.3 Comparison of dynamic rheological properties between native and cooked starches in the presence of hydrocolloids

The dynamic rheological properties of native and cooked starches of NRS and WRS in the absence and presence of hydrocolloids are summarized in Tables 4.16 and 4.17, respectively. In the case of starch alone, the dynamic rheological properties of both starches did not significantly affected by cooking, except for the G' value of cooked NRS which is significantly lower than that of the native NRS. Addition of tested hydrocolloids (GG, XG, and LMP) to native or cooked NRS resulted in a significant ($P \leqslant 0.05$) increase in all dynamic rheological parameters of the mixed pastes as compared with those of the controls. A similar result was also observed in the case of native and cooked WRS-hydrocolloid systems except for those obtained from the LMP addition and the tan δ values of all WRS-hydrocolloid pastes which did not differ significantly from those of the controls.

Table 4.16

Dynamic rheological properties of native and cooked normal rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain and 30°C[1,2]

Starch	Hydrocolloid	G' (Pa)	G'' (Pa)	η^* (Pa.s)	tan δ
Native starch	None (control)[3]	128.0±11.4^{d}	4.8±2.1^{b}	2.1±0.3^{c}	0.04±0.01^{b}
	Guar gum	192.0±14.7^{c}	31.4±3.5^{ab}	3.1±0.2^{bc}	0.16±0.03^{ab}
	Xanthan gum	285.0±5.3^{a}	49.4±5.3^{a}	4.6±0.1^{a}	0.17±0.02^{a}
	LM-pectin	256.0±6.1^{b}	53.0±26.5^{a}	3.7±1.0^{ab}	0.20±0.10^{a}
Cooked starch	None (control)[3]	97.7±10.4^{c}	3.6±1.3^{b}	1.6±0.2^{c}	0.04±0.02^{b}
	Guar gum	132.7±12.7^{bc}	29.8±3.3^{a}	2.2±0.2^{bc}	0.23±0.03^{a}
	Xanthan gum	236.3±4.9^{a}	32.3±0.7^{a}	3.8±0.1^{a}	0.14±0.00^{a}
	LM-pectin	154.0±34.0^{b}	24.6±15.3^{a}	2.5±0.6^{b}	0.15±0.06^{a}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] G', storage modulus; G'', loss modulus; η^*, complex viscosity; tan δ, loss tangent.

[3] 8% (w/w) normal rice starch (NRS).

Table 4.17

Dynamic rheological properties of native and cooked waxy rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 10 Hz, 0.5% strain and 30°C[1,2]

Starch	Hydrocolloid	G' (Pa)	G'' (Pa)	η^* (Pa.s)	tan δ
Native starch	None (control)[3]	74.6±15.2^{b}	13.9±1.4^{b}	1.2±0.2^{b}	0.19±0.03^{ab}
	Guar gum	145.7±36.7^{a}	32.3±9.8^{a}	2.4±0.6^{a}	0.22±0.03^{a}
	Xanthan gum	199.3±23.3^{a}	33.2±2.5^{a}	3.2±0.4^{a}	0.17±0.02^{ab}
	LM-pectin	61.9±6.8^{b}	6.9±3.9^{b}	1.0±0.1^{b}	0.11±0.07^{b}
Cooked starch	None (control)[3]	68.6±20.7^{b}	13.9±1.8^{bc}	1.1±0.3^{b}	0.21±0.05^{a}
	Guar gum	114.7±22.8^{b}	22.2±7.5^{ab}	1.9±0.4^{b}	0.19±0.04^{a}
	Xanthan gum	181.7±1.5^{a}	26.4±4.7^{a}	2.9±0.0^{a}	0.15±0.03^{a}
	LM-pectin	74.7±25.4^{b}	7.3±1.2^{c}	1.2±0.4^{b}	0.11±0.05^{a}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] G', storage modulus; G'', loss modulus; η^*, complex viscosity; tan δ, loss tangent.

[3] 8% (w/w) waxy rice starch (WRS).

4.3.4 Comparison of steady shear rheological properties between native and cooked starches in the presence of hydrocolloids

Consistency coefficients (K) and flow behavior indices (n) along with coefficients of determination (R^2) and apparent viscosities at a shear rate of 100 s^{-1} $(\eta_{a,100})$ for the flow curves of native and cooked NRS and WRS pastes in the absence and presence of hydrocolloids are summarized in Tables 4.18 and 4.19, respectively. All the pastes obtained in this study exhibited pseudoplastic, shear-thinning behavior as $n < 1$.

For the starch alone pastes obtained from both native and cooked NRS and WRS, their steady shear rheological properties were similar. The presence of hydrocolloids in both native and cooked NRS and WRS significantly ($P \leqslant 0.05$) increased $\eta_{a,100}$ and K values, except for the cooked NRS-LMP (Table 4.18) and cooked WRS-LMP (Table 4.19). The $\eta_{a,100}$ and K values for the cooked starch-hydrocolloid pastes were lower than those of their corresponding native starch-hydrocolloid pastes. However, addition of LMP to the cooked starch pastes did not significantly affect the steady shear rheological properties of these pastes as compared to those of the controls. A variety of effects, i.e. increase, decrease, or had no effect, on the n values was observed by the addition of different hydrocolloids to various starches.

Table 4.18

Steady shear rheological properties of native and cooked normal rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 30°C[1,2]

Starch	Hydrocolloid	$\eta_{a,100}$ (Pa s)	K (Pa s^{n})	n (-)	R^2
Native starch	None (control)[3]	1.3±0.0^{d}	14.2±0.4^{d}	0.48±0.01^{a}	0.9995
	Guar gum	3.0±0.1^{a}	34.9±0.8^{b}	0.47±0.01^{ab}	0.9976
	Xanthan gum	2.3±0.0^{b}	46.9±0.7^{a}	0.36±0.00^{c}	0.9986
	LM-pectin	1.6±0.1^{c}	19.3± 1.0^{c}	0.46±0.01^{b}	0.9998
Cooked starch	None (control)[3]	1.3±0.1^{b}	14.5±0.6^{c}	0.48±0.00^{b}	0.9987
	Guar gum	2.0±0.1^{a}	20.7±1.7^{b}	0.50±0.00^{a}	0.9987
	Xanthan gum	1.8±0.0^{a}	35.3±0.3^{a}	0.36±0.00^{c}	0.9981
	LM-pectin	1.2±0.0^{b}	13.3±0.5^{c}	0.48±0.00^{b}	0.9999

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] $\eta_{a,100}$, apparent viscosity at $\dot{\gamma}$ = 100 s^{-1}; K, consistency coefficient; n, flow behavior index; R^2, coefficient of determination.

[3] 8% (w/w) normal rice starch (NRS).

Table 4.19

Steady shear rheological properties of native and cooked waxy rice starches (7.2% w/w) and various hydrocolloids (0.8% w/w) gels measured at 30°C[1,2]

Starch	Hydrocolloid	$\eta_{a,100}$ (Pa s)	K (Pa s^n)	n (-)	R^2
Native starch	None (control)[3]	1.1±0.0^c	14.3±0.6^c	0.45±0.01^b	0.9999
	Guar gum	2.4±0.2^a	24.7±1.8^b	0.50±0.01^a	0.9994
	Xanthan gum	2.2±0.1^a	43.7±0.4^a	0.37±0.01^c	0.9980
	LM-pectin	1.4±0.0^b	16.6±0.3^c	0.46±0.01^b	0.9995
Cooked starch	None (control)[3]	1.1±0.0^b	14.9±0.4^c	0.45±0.0^b	0.9986
	Guar gum	2.0±0.3^a	21.4±3.8^b	0.49±0.01^a	0.9977
	Xanthan gum	1.7±0.0^a	32.6±0.6^a	0.37±0.00^c	0.9970
	LM-pectin	1.0±0.0^b	11.6±1.3^c	0.49±0.00^a	0.9999

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leq 0.05$).

[2] $\eta_{a,100}$, apparent viscosity at $\dot{\gamma} = 100$ s^{-1}; K, consistency coefficient; n, flow behavior index; R^2, coefficient of determination.

[3] 8% (w/w) waxy rice starch (WRS).

4.3.5 Textural properties

Hardness and adhesiveness of NRS and WRS pastes with and without hydrocolloids are presented in Table 4.20. In the case of starch alone pastes, the NRS paste exhibited slightly higher hardness and adhesiveness than the WRS paste. Addition of hydrocolloids at a concentration used in this experiment seemed to have no effect on the textural properties of both NRS and WRS pastes, except for GL, κC, and ίC in the case of NRS and GG, XG, GL, LMP, HMP, ίC, and MC in the case of WRS pastes. Addition of GL, κC, and ίC to NRS significantly ($P \leqslant 0.05$) increased hardness and adhesiveness of the pastes. The hardness of the WRS pastes was significantly increased by GL and ίC additions and decreased by LMP and HPM additions, whereas the adhesiveness was significantly increased by GG, XG, GL, ίC, and MC additions. In general, the highest hardness and adhesiveness values of both NRS and WRS pastes when compared with the other paste samples were obtained by GL addition.

Table 4.20

Textural properties of normal or waxy rice starches (7.2% w/w) pastes in the absence and presence of various hydrocolloids (0.8% w/w) measured at room temperature (25°C)[1]

Hydrocolloid	Normal rice starch		Waxy rice starch	
	Hardness (g)	Adhesiveness (g mm)	Hardness (g)	Adhesiveness (g mm)
None (control)[2]	12.1±0.4^{d}	16.2±1.1^{de}	9.1±0.3^{cd}	7.5±2.0^{fg}
Guar gum	12.5±0.4^{d}	28.4±1.5^{cde}	9.0±0.6^{cd}	19.6±1.2^{cd}
Locust bean gum	12.0±0.4^{d}	30.2±3.7^{cde}	7.9±0.5^{cde}	18.3±0.7^{cdef}
Xanthan gum	12.6±0.4^{d}	45.4±4.0^{bcd}	10.3±0.4^{c}	31.9±2.4^{b}
Gellan	72.8±0.9^{a}	172.7±26.7^{a}	41.6±3.6^{a}	59.0±8.3^{a}
LM-pectin	14.9±0.3^{d}	18.5±1.6^{de}	5.0±0.3^{e}	10.9±2.1^{defg}
HM-pectin	12.6±0.4^{d}	16.4±4.4^{de}	5.5±0.0^{e}	8.3±1.4^{efg}
Sodium alginate	11.9±0.3^{d}	21.7±1.9^{de}	7.2±0.1^{cde}	15.3±0.2^{defg}
κ-carrageenan	47.7±8.0^{b}	70.6±25.3^{b}	6.9±0.8^{de}	12.7±1.1^{defg}
ί-carrageenan	40.1±1.4^{c}	55.5±14.1^{bc}	37.5±1.2^{b}	28.9±10.0^{bc}
λ-carrageenan	11.8±0.3^{d}	27.4±3.0^{cde}	7.7±0.4^{cde}	17.3±2.1^{def}
CMC	11.7±0.3^{d}	25.9±0.8^{cde}	7.3±0.4^{cde}	12.0±0.3^{defg}
MC	13.3±0.1^{d}	28.1±0.9^{cde}	10.5±1.2^{c}	19.3±1.5^{cde}
HPMC	8.6±0.2^{d}	9.4±0.6^{e}	7.8±0.4^{cde}	5.7±0.3^{g}

[1] Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

[2] 8% (w/w) normal rice starch (NRS) or waxy rice starch (WRS).

4.3.6 Microscopic observations

Light micrographs of NRS and WRS gels with and without hydrocolloids stained with iodine are shown in Figures. 4.1 and 4.2, respectively. Generally, the microstructures of these starch-hydrocolloid gels were found upon cooling to phase-separate into a starch-rich disperse phase and a hydrocolloid-rich continuous phase. All pastes contained very few, if any, identifiable granules or granule remnants. Amylose released from the granules appeared as small discrete particles within what is assumed to be a continuous hydrocolloid matrix. The presence of all hydrocolloids, except for ίC, also promoted amylopectin aggregation in the continuous phase so that a three-phase system containing amylose clusters, amylopectin clusters, and a solution of hydrocolloid molecules was formed. Iota-carrageenan did not enhance amylopectin aggregation in either NRS (Fig. 4.1j) or WRS (Fig. 4.2j) gels, possibly due to its association with amylopectin.

In the case of NRS, addition of hydrocolloids resulted in a heterogeneous microstructure with amylose- and amylopectin-rich domains unevenly distributed in a hydrocolloid network matrix (Figure 4.1b-n), whereas a more homogeneous structure in which very small amylose-rich domains uniformly dispersed in the gel matrix was observed in the NRS alone paste (Figure 4.1a). In contrast, the WRS pastes seemed to be unaffected by the addition of hydrocolloids as evidenced by similar microstructures (Figure 4.2a-n).

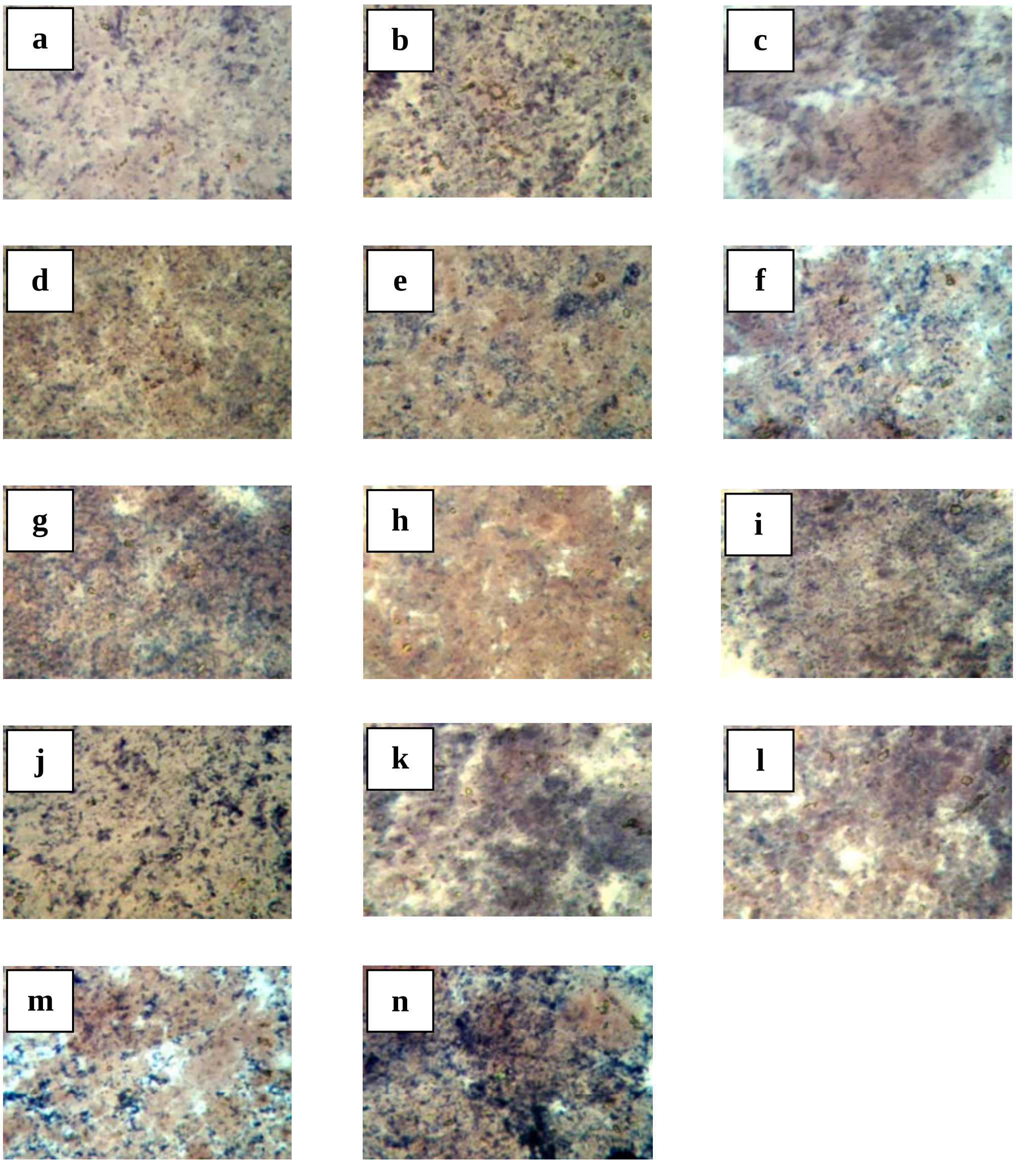


Figure 4.1 Photographs of normal rice starch (NRS) (7.2% w/w) pastes produced in the presence of different hydrocolloids (0.8% w/w): (a) none (control), (b) guar gum, (c) locust bean gum, (d) xanthan gum, (e) gellan, (f) low-methoxyl pectin, (g) high-methoxyl pectin, (h) sodium alginate, (i) κ-carrageenan, (j) ί-carrageenan, (k) λ-carrageenan, (l) CMC, (m) MC and (n) HPMC. All pastes were stained with iodine and observed at 100× magnification .

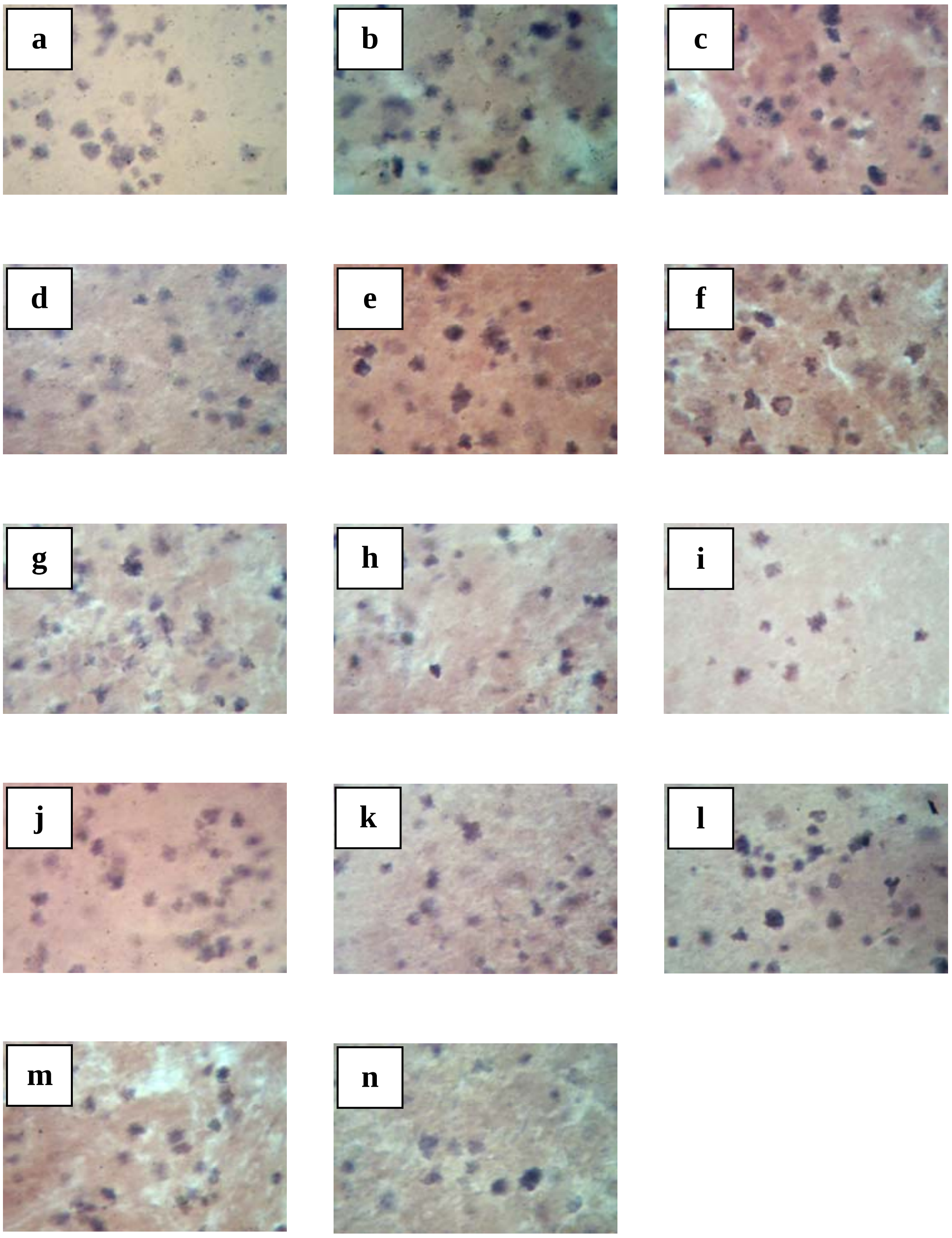


Figure 4.2 Photographs of waxy rice starch (WRS) (7.2% w/w) pastes produced in the presence of different hydrocolloids (0.8% w/w): (a) none (control), (b) guar gum, (c) locust bean gum, (d) xanthan gum, (e) gellan, (f) low-methoxyl pectin, (g) high-methoxyl pectin, (h) sodium alginate, (i) κ-carrageenan, (j) ί-carrageenan, (k) λ-carrageenan, (l) CMC, (m) MC and (n) HPMC. All pastes were stained with iodine and observed at 100× magnification.

CHAPTER V
DISCUSSION

1. Sample preparation

Starch-hydrocolloid mixtures were prepared by two different techniques; (1) blend of starch and gum powders was dispersed into distilled water and stirred at room temperature for 15 min (dry mixing) and (2) the gum was prepared as a solution by heating at 80°C and then was mixed with a starch powder (wet mixing). The difference of sample preparations did not significantly affect pasting properties of both NRS and WRS, as shown in Tables 4.1 and 4.2, respectively. For each starch, an addition of hydrocolloid exhibited higher viscosities than those of the control (starch alone), and the viscosities significantly ($P \leq 0.05$) increased as the gum concentration increased. The starch-gum mixtures show significant ($P \leq 0.05$) increase of pasting temperatures, as increase of the hydrocolloid concentration, when compared to the control. However, the increase of theses temperature was not affected from the difference of sample preparation procedures. A result of the pasting properties in this experiment did not tend to be compatible to the preparation technique of Mandala & Bayas (2004) reporting that the sample prepared as a separation of heating of starch dispersion and xanthan gum solutions, and subsequent mixing had greater viscosity than that prepared as powders mixing, adding water and heating suspensions thereafter.

The addition of GG and XG to NRS prepared by the wet mixing technique showed a significant ($P \leq 0.05$) increase of T_o, T_p and T_c when the gum concentration was increased (Table 4.3). The presence of hydrocolloid seemed to affect an availability of water for starch during gelatinization, similarly to a reduction in water content (Ferrero et al., 1996). From the restriction of water, a destabilizing effect of amorphous regions decreases and only partial melting of crystalline regions occur. Therefore, it is subsequent redistribution of the water around the unmelted crystallites that will assist their melting upon further heating at higher temperatures (Biliaderis et al., 1980). However, the dry mixing samples of NRS-hydrocolloid mixtures exhibited no significant effect of gum addition at a concentration range used in this study on these gelatinization temperatures. It might be proposed that the rate of water absorption during heating of the dry blended samples (dry mixing) differed from that of the wet blended samples (wet mixing). In the wet mixing preparation, the hydrocolloid has already absorbed water by heating prior to gelatinization process, therefore, the water availability for starch gelatinization of the wet mixing samples could be reduced and it caused the increase of the gelatinization temperatures. A similar trend was observed in the case of WRS-gum systems in which the wet mixing method seemed to have a more pronounced effect on the gelatinization temperatures (both T_o and T_p significantly increased at higher gum levels) than the dry mixing technique (only to increased at higher gum level) (Table 4.4). However, the T_c values of all samples, including the control, were lower than the RVA pasting temperatures, indicating that the melting of starch crystallites cooperatively in excess water precedes the first rise in viscosity where the rate of development of viscosity was the greatest (Satrapai & Suphantharika, 2007). The addition of GG and XG also significantly ($P \leq 0.05$) decreased gelatinization enthalpy (ΔH) of starch-gum mixtures, especially in NRS-gum mixtures. This could be explained as the lower ratios of free water to starch due to immobilization of water molecules by gums (Biliaderis et al., 1980; Chungcharoen & Lund, 1987), lower heat transfer rates (Kruger et al., 2003), and mass transfer of water, which could make starch gelatinization more difficult in the presence of gum (Chaisawang & Suphantharika, 2005). These phenomena have been explained in term of incompleted starch gelatinization as a result of limited water availability (Eliasson, 1980; Marchant & Blanshard, 1980).

The textural properties of NRS- and WRS-hydrocolloid mixed gels obtained from two different preparations were determined in the terms of hardness and adhesiveness (Tables 4.5 and 4.6). The hardness and adhesiveness of starch-hydrocolloid gels were slightly affected by the preparation method. However, the NRS-GG gels from both preparation techniques exhibited the significantly ($P \leq 0.05$) highest hardness at the GG concentration of 1.0% (w/w). This effect was more pronounced in the wet mixing prepared gels than that in the dry mixing prepared gels.

This result was opposite to the final viscosity of NRS-GG mixtures obtained from the RVA profile (Table 4.1) because the NRS-GG mixtures containing 1.0% (w/w) GG from the dry mixing preparation technique showed higher final viscosity than that obtained from the wet mixing preparation technique. The addition of hydrocolloids to the WRS showed a significant (*P*≤0.05) increase of the hardness and adhesiveness only at concentration of 0.6 and 1.0% (w/w) for the wet mixing technique. For the dry mixing technique, the hardness of the WRS-gum gels was not significantly different from the control, except for the WRS-XG gel with 1.0% XG, whereas the adhesiveness of the WRS-gum gels was significantly higher than the control. An enhancement of adhesiveness parameters in starch-hydrocolloid systems could be indicated as a cohesion in-between different molecules, solubilized starch molecules and hydrocolloids for this case, in continuous phase and granules (Mandala et al., 2002). The adhesiveness of the NRS-hydrocolloid gels from both preparation techniques increased only at the GG concentration of 1.0% (w/w). The NRS-XG gels obtained from wet mixing technique also showed a similar result. Nevertheless, with the dry mixing technique, the NRS-XG at the highest XG concentration showed a significant (*P*≤0.05) decrease of adhesiveness. Xanthan gum dispersions are considered to contain weakly associated microgel particles or aggregates (Morris, 1995). It might be attributed at to a competition for water between starch and XG in the system. The insufficiency of water in this system gave the incomplete gelatinization (Eliasson, 1980; Marchant & Blanshard, 1980) that could be a cause of inadequate leached out of amylose to interact and cooperate with XG for the cohesion between the molecules. However, the effect of hydrocolloid addition to WRS gels showed a significant (*P*≤0.05) increase of adhesiveness when the gum concentration increased to 0.6 and 1.0% (w/w) from both preparation techniques. This effect was more pronounced by the addition of 1.0% XG for both preparation techniques.

2. Pasting properties

The result showed the NRS alone gel exhibited higher peak, breakdown, final and setback viscosities and lower pasting temperature than the WRS alone gel (Tables 4.7 and 4.8). This could be attributed to the fact that the WRS (with <1% apparent amylose) had a much higher swelling power than the NRS (see Section 4.2.3), leading to a lower rigidity of the starch granular structure (Lii et al., 1996). In a concentrated regime, i.e., one which is higher than an average close packing concentration (2.0% [75-125°C] and 3.0% [95-125°C] for the WRS and NRS, respectively), the viscosities of starch suspensions during pasting are mainly determined by the particle rigidity of the swollen granules (Vandeputte et al., 2003). It can be concluded that the pasting properties of starch depended mainly on interactions among the close-packed granules and their rigidity during the heating process.

In general, the resulted showed a significant increase in peak, breakdown, final and setback viscosities of both NRS and WRS by addition of most of the hydrocolloids used in this study. The increase of viscosity reflects the ability of the starch granules to swell freely before their physical breakdown (Rojas et al., 1999). However, the addition of hydrocolloids affected the starch concentration by immobilizing water molecules (Yoshimura et al., 1996). When the aqueous suspensions of starch-hydrocolloid mixtures were heated, the starch gelatinized in the gum medium, a volume of the continuous phase accessible to the gum was reduced, yielding in an increase in gum concentration within the continuous phase that resulted in a dramatic increase in viscosity (Alloncle et al., 1989). Therefore, a thickening capacity of each tested hydrocolloid could dominate the viscosity of the starch-hydrocolloid pastes. It has also been proposed that the increase in viscosity of starch-hydrocolloid systems is due to interactions between leached amylose and low-molecular-weight amylopectin molecules and hydrocolloids (Bhanassey & Breene, 1994; Christianson et al., 1981; Shi & BeMiller, 2002), and that these are a function of the structure of hydrocolloid so structural and rheological properties of the hydrocolloid are very relevant. Possibly, both of these mechanisms are involved.

The increase in viscosity can make the shear force exerted on the swollen granules in the shear field much larger than those encountered in starch-water suspensions (Christianson et al., 1981). This results in the loss of granule integrity and subsequent disruption leading to a reduction in the paste viscosity, which is defined as breakdown viscosity. This hypothesis is most evident in this study in which the starch-gum gels with higher peak viscosity generally gave higher breakdown viscosity too. The setback correlates to tendency of dispersed starch molecules association or retrogradation when the pastes are cooled, resulting in the increase in viscosity

(Christianson et al., 1981). However, the increase of the setback viscosity in this study for both starches-hydrocolloid mixtures could be concluded as the interactions between starch exudates and hydrocolloid molecules in the continuous phase, incorporating with the reassociation of amylose. Addition of XG, LMP, HMP, κC, MC, and HPMC to NRS and LMP, HMP, and HPMC to WRS did not significantly affect the setback values of the starch gels, indicating that there might be a different interaction between these hydrocolloids and leached starch molecules. Bahnassey & Breene reported that starch gelation takes place upon cooling and is strongly influenced by the gelation of amylose which is modified by the added hydrocolloid. In addition, they also reported that the diffusion of water from the continuous phase into the starch granules increases the gum concentration surrounding them, exhibiting as the increase of viscosity. These explanations given could be attributed to the increase of final viscosity. A significant ($P \leq 0.05$) shift in the gelatinization to a higher temperature in the presence of hydrocolloids could be resulted from the decrease of water availability (Ferrero et al., 1996), which could make starch gelatinization more difficult (Kruger et al., 2003).

3. Thermal characteristics

Water is well established as a plasticizer of the amorphous regions of starch granules and also promotes rupture of hydrogen bonds when heat applied in gelatinization process (Lelievre, 1976; Slade & Levine, 1984; 1987; Tester & Sommerville, 2003). When non-starch polysaccharides are present, they have capacity to hydrate and consequently restrict the mobility of plasticizer and hence delay initiation of the gelatinization process (Tester & Sommerville, 2003). In this study, the interactions between starch and each tested hydrocolloid promoted a delay of the starch gelatinization, showing as a slight increase of T_o in both NRS- and WRS-hydrocolloid mixtures (Tables 4.9 and 4.10), with the exception of WRS-GG, WRS-LBG and WRS-HMP. However, these interactions did not affect the T_p and T_c in both starches. For the effect of different preparation techniques (Section 4.1.2), the T_o, T_p and T_c values of all samples, from both preparation techniques, are lower than the RVA pasting temperatures. Satrapai & Suphantharika (2007) reported that the melting of starch crystallites cooperatively in excess water precedes the first rise in viscosity where the rate of development of viscosity was the greatest. Nevertheless, this study showed a different result in which T_p values were generally comparable to the RVA pasting temperatures, whereas T_c values were significantly higher. The NRS used in this experiment had lower amylose content (11.9%) than the NRS used in the previous work (30.0%). It is known that the NRS granules with higher amylose content were more rigid, less swelling, and not easily ruptured. However, in this case, the low amylose content of NRS could cause the less rigidity of granule and the lower energy used for melting of starch granules as determined by DSC. In the case of WRS, the WRS used in Section 4.1 had comparable amylose content with that used in Section 4.2 (< 1% apparent amylose). Therefore, a total solid content might be involved in the lower T_c values when compared to the RVA pasting temperatures, as shown in Tables 4.10 and 4.8, respectively.

The enthalpy (ΔH) was significantly ($P \leq 0.05$) decreased by addition of gums, especially for NRS-hydrocolloid mixtures. The WRS-hydrocolloid mixtures exhibited a slight decrease of this parameter. This can be explained by the lower ratios of free water to starch due to immobilization of water molecules by gums (Biliaderis et al., 1980; Chungcharoen & Lund, 1987), lower heat transfer rates (Kruer et al., 2003), and mass transfer of water, which could make starch gelatinization more difficult in the presence of the gum (Chaisawang & Suphantharika, 2005). It can be concluded that the presence of hydrocolloid limited the water mobility and reduced water availability to starch influence the gelatinization process by decreasing the ΔH (as shown in Tables 4.9 and 4.10). This phenomenon has been explained in terms of incomplete starch gelatinization as a result of limited water availability (Eliasson, 1980; Marchant & Blanshard, 1980).

4. Swelling power and solubility index

The swelling power (SP) and solubility index (SOL) of WRS alone were, as expected, higher than those of NRS, as the swelling behavior of cereal starch is primarily the property of its amylopectin content and amylose acts as both a diluent and an inhibitor of swelling (Tester & Morrison, 1990a). Maximal swelling might also be related to the molecular weights and the shapes of the amylopectin molecules (Tester & Morrison, 1990b). Lii et al. (1996) observed that WRS granules were less firm and tended to disintegrated easily while swollen and extensively overcrowded. In contrast, NRS granules were more rigid, less swelling, and not easily ruptured. The degree of swelling and the granule integrity are directly related to the viscosity of the starch paste (Borwankar, 1992). Generally, the amount of exudate from NRS granules was small; suggesting that the main component leached from the granules was amylose (Mandala & Bayas, 2004), whereas the amount of exudate from WRS granules was large and consited of amylopectin molecules (Tester & Morrison, 1990a).

Addition of the tested hydrocolloids to NRS slightly increased SP (Table 4.11). According to Christianson et al. (1981), the addition of hydrocolloids can make the shear forces exerted on the swollen granules in the shear field much larger than those encountered in the starch-water suspensions. This can enhance water uptake (increasing swelling), the breakdown of granules and the amount of material exuded into the continuous phase. This effect was not much different among the different hydrocolloids, indicating that SP and SOL of NRS were affected to the same degree by the different tested hydrocolloids. The most pronounced increase of SP was observed with the addition of XG. It was previously reported that SP of starch granules during heating was enhanced by the presence of hydrocolloids (Chaisawang & Suphantharika, 2006; Mandala & Bayas, 2004). Abdulmola et al. (1996), reported that starch molecules can interact and a network can be created at concentrations well below close-packing. It is assumed that hydrocolloid can entrap the starch granules to keep them closely. This can enhance the forces applied to them, facilitating water entering (increasing swelling), amylose solubilization and its exudation. This explanation was compatible to the result of this study that the NRS-hydrocolloid mixtures significantly ($P \leq 0.05$) promoted the leaching of amylose at temperature above the gelatinization temperatures which is consisted with the other report (Mandala & Bayas, 2004).

Addition of hydrocolloids to WRS produced a variety of effects on its SP during heating, i.e., with different tested hydrocolloids, it increased, decreased or had no effect, whereas SOL tended to decrease (Table 4.11). This evidence could be explained by the fact that the swollen WRS granules were less firm and might be more disintegrated, even in the low-shear environment of the experiment, and therefore, addition of hydrocolloids did not increase SOL of the starch-hydrocolloid systems. The different effect of each tested hydrocolloid on SP of WRS demonstrated different interactions of each hydrocolloid and WRS, which in turn depended upon the chemical structure of the added hydrocolloids. The presence of hydrocolloid was found to increase the granule size (swelling) of waxy corn starch and crosslinked waxy corn starch during heating (Achayuthakan, Suphantharika, & Rao, 2006; Tecante & Doublier, 1999).

5. Dynamic rheological properties

The dynamic rheological properties of NRS and WRS pastes with and without hydrocolloid additions are presented in term of storage modulus (G'), loss modulus (G'') and complex viscosity $(\eta *)$ which were measured at 10 Hz, 0.5% strain and 30°C (Tables 4.12 and 4.13), respectively. The G' is a measure of the energy that is stored in the material or recoverable per cycle of deformation, G'' is a measure of the energy that is lost as viscous dissipation per cycle of deformation and $\eta *$ is a measure of the overall resistance to flow (Yoo et al., 2005). In general, all pastes displayed a typical gel behavior (Clark & Ross-Murphy, 1987) where G' is higher than G'' throughout the measured frequency range. The greater G' value of the NRS alone paste as compared to that of WRS alone paste indicated that the more rigid swollen NRS granules created a stronger gel network than that of the softer WRS granules at concentration well above close-packing. The G' values of NRS-hydrocolloid pastes, as expected, were higher than those of WRS-hydrocolloid pastes, evidencing that the stronger gel network was possible formed by the amylose-amylose and/or amylose-hydrocolloid interaction both of which existing in the continuous phase in addition to the more rigid structure of the NRS granules. The most pronounced effect among all the pastes examined was found for NRS-κC paste. This indicated that a greater elasticity (gel-like character) of the NRS-κC paste was due to a κC-amylose interaction. Furthermore, an increase of G' values was also related with the rate of amylose and amylose-gum associations that occurred during cooling (Chaisawang & Suphantharika, 2005). The increase of G' cannot be attributed to the aggregation of amylopectin because amylopectin retrogradation occurs over long time period (Biliaderis & Prokopowich, 1994).

The viscoelastic behavior of the pastes can be evaluated in terms of $\tan\delta$ which is the ratios of G''/G'. A $\tan\delta<1$ indicates predominantly elastic behavior while $\tan\delta>1$ indicates predominantly viscous behavior (Yoo et al., 2005). The result showed that $\tan\delta$ values of all the pastes with and without hydrocolloid addition were less than 1.0, indicating that all the pastes were more elastic than viscous. The WRS alone paste gave much higher $\tan\delta$ value than the NRS alone paste. This can be explained by the fact that the weaker and more highly swollen WRS granules (Table 4.11) produce a less rigid paste, as compared to the more rigid NRS granule, indicating that their overall structure became weaker, less solid-like and rigidity. This was possibly due to preventing amylose retrogradation to the greatest degree; although since their $\tan\delta$ values were even less than those for WRS-hydrocolloid pastes, there may be an additional factor of amylose-amylose association. Additionally, amylose did not seem to interact with hydrocolloids in the continuous phase, and different polymers excluded each other. This finding supports the hypothesis that these systems involve mixtures in which intermolecular interactions between like molecules are favored, which locally at least results in mutual exclusion (Annable et al., 1994). This result was confirmed by microscopic examination of the paste structure (Fig. 4.1) (to be discussed later). According to Eidam, Kulicke, Kuhn, & Stute (1995), in the three-dimensional network the hydrocolloid molecules function as disruptive sites, resulting in network deflects. The number of permanent junction zones in the starch is reduced and the overall elasticity decreases. Therefore, it was concluded that the decrease in junction zones of rice starch molecules with the hydrocolloid additions, resulting in the increase of the viscous properties.

Addition of all tested hydrocolloids, with the exception of κC and GL, did not significantly affect G', G'' and $\eta*$ values of NRS, whereas the addition of κC and GL including GG, XG, ίC, and λC to WRS exhibited a significant ($P\le0.05$) increase in these values. In the case of $\tan\delta$ values, the hydrocolloid additions to NRS did not significantly differ among the different hydrocolloids. The $\tan\delta$ values of WRS-hydrocolloid pastes also exhibited the results in a similar way as NRS-hydrocolloid pastes. In addition, the $\tan\delta$ values of these WRS-hydrocolloid pastes did not significantly differ from that of the control, indicating a similar microstructure of these pastes (Fig. 4.2). Due to an absence of amylose in the WRS paste, short-term retrogradation was absent and therefore, the addition of hydrocolloid could not alter the viscoelastic characteristics of the WRS pastes.

6. Steady rheological properties

The result showed that addition of most of hydrocolloid, except for HPMC, to NRS and WRS caused a significant increase in the $\eta_{a,100}$ and K values and a slight effect on the n values of the pastes (Tables 4.14 and 4.15). All samples exhibited shear-thinning behavior with values of flow behavior index less than one. The shear-thinning behavior can be explained by breaking out of an entangled polysaccharide molecule network during shearing, resulting in overcoming the intermolecular resistance to flow (Bhandari et al., 2002).

Eliasson (1986) observed that more highly swollen (and presumably softer) granules lead to a reduction in a starch paste rigidity. The WRS pastes in the absence and presence of tested hydrocolloids exhibited higher swelling power than those of the NRS. However, in this study, the NRS and WRS pastes with and without tested hydrocolloid additions showed similar steady shear rheological properties. The decrease of paste viscosity for the HPMC addition was consistent with a decrease in $\eta*$ by dynamic rheological measurement (Tables 4.12 and 4.13). A reduction of viscosity by adding HPMC was also due to its property that was consistent to the peak, final and setback viscosities, in which a tendency to reassociate of amylose leach out, in both NRS and WRS (Table 4.7 and 4.8). However, the opposite result was observed for n values of NRS-HPMC and WRS-HPMC pastes. The addition of XG, GL, and carrageenans to NRS and WRS significantly promoted the degree of pseudoplasticity, indicated by a decrease in the n values. The difference of tested hydrocolloids exhibited similar n values for each hydrocolloid when compared between NRS and WRS pastes.

7. Comparison of rheological (dynamic and steady) properties between native and cooked starches in the presence of hydrocolloids.

7.1 Dynamic rheological properties

The native and cooked NRS or WRS pastes with and without GG, XG and LMP additions were determined for the dynamic rheological properties, i.e. storage modulus (G'), loss modulus (G'') and complex viscosity $(\eta *)$. The viscoelastic properties of those pastes were observed as a loss tangent ($\tan\delta = G''/G'$). The native and cooked NRS alone pastes exhibited similar dynamic rheological properties, except for the G' value of native NRS paste which is significantly greater than that of the cooked NRS paste (Table 4.16). This resulted implied that the native NRS granules were not completely disrupted during pasting in the RVA. The presence of the swollen NRS granules embedded in amylose network would strengthen the paste structure. On the contrary, all the dynamic rheological parameters of the native and cooked WRS alone paste did not differ significantly (Table 4.17), indicating that the WRS granules were completely disrupted during the RVA pasting. Addition of tested hydrocolloids to native and cooked NRS pastes significantly increased all rheological parameters, relating to the amylose-amylose and/or amylose-gum associations that occurred during cooling (Chaisawang & Suphantharika, 2005). A similar result was observed for both native and cooked WRS in the presence of hydrocolloids, except for the LMP which did not significantly affect the dynamic rheological properties of these starches. This can be attributed to a specific interaction of LMP and amylose. Therefore, an absence of amylose in the WRS paste, the addition of LMP could not alter the viscoelastic characteristics of the WRS pastes. All the pastes obtained in this study exhibited a weak gel-like behavior. i.e. $G' > G''$, as defined by Clark & Ross-Murphy (1987).

The magnitudes of tan δ were significantly increased by the addition of tested hydrocolloids to both native and cooked NRS. This result indicated that these pastes exhibited less structured and less solid-like when compared to the controls (starch alone), perhaps by preventing amylose retrogradation. On the other hand, the tan δ values of both native and cooked WRS pastes in the presence of hydrocolloids did not significantly differ from those of their controls. This was due to an absence of amylose in the WRS pastes, and short-term retrogradation was absent. Therefore, the addition of hydrocolloids could not alter the viscoelastic characteristics of the WRS pastes.

7.2 Steady shear rheological properties

The steady flow properties were evaluated in terms of consistency coefficients (K) and flow behavior indices (n) along with coefficients of determination (R^2) and apparent viscosities at a shear rate of 100 s^{-1} $(\eta_{a,100})$ for the native and cooked starch pastes with and without hydrocolloid (GG, XG and LMP) additions. All paste samples exhibited pseudoplastic behavior as $n<1$ (Tables 4.18 and 4.19). For the starch alone pastes, a cooking process did not significantly affect the steady shear rheological properties of both NRS and WRS. Addition of XG to all starches resulted in the highest K value and the lowest n value of the mixed pastes when compared among all the pastes tested, indicting that the starch-XG pastes were more pseudoplastic than the other starch-hydrocolloid pastes. This was possibly due to a unique rigid, rod-like conformation and high molecular weight of XG (Urlacher & Noble, 1997). Addition of all tested hydrocolloids, except for LMP, to the native and cooked NRS and WRS starch pastes significantly increase the K and $\eta_{a,100}$ values. This result reflects the overall rheological behavior of the pastes which is influenced not only by the solubilized starch components but also by the swollen granules being dispersed in the continuous phase (Anastasiades, Thanou, Loulis, Stapatoris, & Karapantsios, 2002). However, the K and $\eta_{a,100}$ values of native starch-hydrocolloid pastes were higher than those of cooked starch-hydrocolloid pastes. This could be explained by the fact that the starch granules were completely disrupted during cooking under high shear conditions before pasting by the RVA. The absence of the swollen starch granules in the cooked starch-hydrocolloid pastes could be responsible for the low consistency of the pastes.

8. Textural properties

For texture profile analysis (TPA), samples are usually subjected to large deformation (75-80%) (Mandala et al., 2002). A smaller deformation level, 50% gel height, was chosen in this study. As recommended by Pons & Fiszman (1996), the deformation level between 20% and 50% has been applied on food gel systems. Furthermore, under large deformation, the samples were collapsed and invalid parameters were obtained. Hardness, which is the peak force observed during the compression cycle, and adhesiveness, the negative force area representing the work necessary to pull the compression plunger away from the sample, were observed for NRS and WRS pastes in the absence and presence of tested hydrocolloids (Table 4.20). The NRS alone paste had higher hardness and adhesiveness values than that of the WRS alone paste. This was due to the presence of amylose in the NRS which leached out into the continuous phase during heating, resulting in an amylose reassociation upon cooling (Bahnassey & Breene, 1995; Christianson et al., 1981). This result is consistent with the dynamic rheological data in which the NRS paste exhibited higher G' value and lower tan δ value than the WRS paste (Table 4.12).

Hydrocolloid concentration within the continuous phase around the swollen starch granules increases when starch swells during gelatinization (Sasaki et al., 2000). This is contributed to an increase in gel hardness. However, addition of tested hydrocolloids to NRS and WRS gels did not significantly affect both the hardness and adhesiveness (Table 4.20), except for the addition of GL, κC and ίC to NRS gel and GL and ίC to WRS gel. The hardness of the NRS and WRS gels with GL addition mainly came from the network structure of gellan rather than the rearrangement of amylose. As a hot solution cools in the RVA, gellan undergoes a disorder-order transition (Grazdalen & Smidsrod, 1987). This transition has been attributed to a coil-helix transition, and further aggregation of the helices to thicken gel (Hoefler, 2004). The κC and ίC also showed a similar result as that of gellan. The main reason might be that κC and ίC are both gelling polysaccharides which can form network structures and enhance the textural properties of the pastes. Therefore, it could be also concluded that the hardness of NRS and WRS pastes with carrageenan additions mainly resulted from the network structure of κC and ίC rather than the retrogradation of amylose (Huang et al., 2007). However, the addition of the other carrageenan, λC, did not affect the textural properties of both NRS and WRS gels due to the fact that it is non-gelling. Addition of GL or ίC also significantly increased the adhesiveness of both NRS and WRS. The adhesiveness is more of a surface characteristic and depends on a combined effect of adhesive and cohesive forces, and others include viscosity and viscoelasticity as well (Adhikari, Howes, Bhandari & Troung, 2001). The addition of HPMC slightly decreased the hardness and adhesiveness for both NRS and WRS pastes. This was consistent to the lower G', G'' and $\eta*$ values in NRS and WRS pastes when compared to the controls as represented in Tables 4.12 and 4.13, respectively. In addition, a decrease in hardness of WRS-LMP and WRS-HMP pastes is also consistent to the lower G' values of these pastes as presented in Table 4.13.

9. Microscopic observations

Microstructures of NRS and WRS pastes in the absence and presence of tested hydrocolloids are illustrated in Figures 4.1 and 4.2, respectively. The NRS alone paste exhibited a homogeneous microstructure in which very small amylose-rich domains (blue color) uniformly dispersed in the gel matrix. Addition of hydrocolloids resulted in a heterogeneity of the paste microstructures possibly due to a phase separation of the starch-hydrocolloid mixed pastes. It is known that when different polymers are mixed they tend to become incompatible for thermodynamic reasons, resulting in phase separation (Morris, 1990). This causes a separation of the mixed polymers into two phases in which one component is driven out of another component. The presence of hydrocolloids in the NRS and WRS pastes resulted in a heterogeneous microstructure in which amylose (blue color)- and amylopectin (reddish brown color)-rich domains unevenly distributed in a hydrocolloid network matrix (Figures 4.1 and 4.2, respectively). The amylopectin aggregation in the continuous phase was also promoted by the addition of all hydrocolloids, except for ίC. Iota-carrageenan did not enhance amylopectin aggregation in either the NRS (Fig. 4.1j) or the WRS (Fig. 4.2j) gels, possible due to its association with amylopectin. This result is in good agreement with the texture analysis data (Table 4.20) in which the hardness and adhesiveness of the NRS-ίC and WRS-ίC gels were higher than those of the other gels, except for NRS-κC, NRS-GL and WRS-GL gels. Generally, this result is consistent with the dynamic rheological data. The more homogeneous microstructure of the NRS alone paste reflected the more structured and more solid-like characteristic as evidenced by a lower tan δ value when compared to the NRS-hydrocolloid pastes (Table 4.12). In contrast, the WRS pastes seemed to be unaffected by the addition of hydrocolloids as evidenced by their similar microstructures (Fig. 4.2) and as well as similar tanδ values (Table 4.13).

CHAPTER VI

CONCLUSION

The study clarified that the pasting and rheological properties of the rice starch, normal and waxy rice starches (NRS and WRS, respectively), were largely affected by the addition of various hydrocolloids. The study was divided into three parts to investigate the effect of hydrocolloids on sample preparation method, pasting properties and rheological characteristics of rice starches. In the sample preparation part, the differences of preparation technique (dry and wet mixings) did not affect the pasting properties of NRS- and WRS-hydrocolloid mixtures. However, the increase of gum concentration, both GG and XG, promoted the increase of viscosities and pasting temperatures, but decreased the gelatinization enthalpy (ΔH). In addition, this effect was more pronounced in NRS-hydrocolloid suspensions when compared to WRS-hydrocolloid suspensions, and the wet mixing technique was more influenced to gelatinization temperatures and ΔH, when compared to those of the dry mixing technique. For the texture profile analysis (TPA), the differences in the sample preparation techniques exhibited significant effect on hardness and adhesiveness. The NRS- and WRS-hydrocolloid gels prepared by wet mixing technique showed higher hardness than those prepared by the dry mixing technique. The result was also more pronounced at higher gum concentration. However, the NRS-hydrocolloid pastes showed a similar adhesiveness between the dry and wet mixed samples. The WRS-hydrocolloid gels were also unaffected by these two different techniques, but the increase of hydrocolloid concentration influenced this parameter, resulting in an increase in adhesiveness..

In this study, it was not only GG and XG, but also LBG, GL, SA, LMP, HMP, CMC, MC, HPMC, κC, ίC and λC were used for studying the pasting properties and rheological characteristics of NRS and WRS. The NRS alone had higher peak, breakdown, final and setback viscosities and lower pasting temperature than that the WRS alone. The addition of hydrocolloids to both NRS and WRS increased viscosities and pasting temperatures and the highest effect was observed in starch-MC mixtures. The increase of final viscosity was promoted, especially by the addition of LBG and λC to NRS and WRS, respectively. The HPMC addition decreased setback viscosities of both starches and showed the lowest viscosity when compared to the other starch-hydrocolloid mixtures. The most pronounced increase in pasting temperature was observed with the addition of XG. In the case of thermal properties, the NRS alone showed higher ΔH than the WRS. Addition of the tested hydrocolloids to NRS and WRS exhibited a significant decrease in ΔH, especially in NRS-λC and WRS-XG. The decrease of ΔH could be attributed to the water immobilization of hydrocolloids which reduced water mobility and availability for starch gelatinization. However, the gelatinization temperatures (T_o, T_p and T_c) were not much different among the different hydrocolloids in each starch. In the case of swelling power (SP) and solubility index (SOL), the NRS alone, which was more rigid, less swelling and not easily ruptured, had lower SP and SOL than the WRS alone. The addition of the tested hydrocolloids exhibited an increase in SP and SOL of NRS. However, this effect was not much different among the different hydrocolloids. The SP and SOL of WRS were much less affected by the addition of hydrocolloids.

Dynamic rheological measurements revealed no effect of the hydrocolloids, except for κC, on G', G'' or $\eta*$, but the $\tan\delta$ values of the NRS pastes were increased by the addition of hydrocolloids, indicating that the pastes were less structured and less solid like than the control paste. On the contrary, the hydrocolloids had no effect on the $\tan\delta$ values of WRS pastes, indicating their structures were similar to those of the control. Steady shear rate tests showed that all hydrocolloids, except for HPMC, increased $\eta_{a,100}$ and K values of both starches with trends similar to those found during pasting, whereas the opposite trend was observed for n values. The dynamic and steady rheological tests were also performed to determine rheological characteristics of the native and cooked NRS and WRS pastes. The addition of XG significantly increased G', G'' or $\eta*$ in both native and cooked starch pastes. Furthermore, the addition of hydrocolloids (GG, XG and LMP) reduced the G', G'' or $\eta*$ in the cooked NRS and WRS pastes, except for LMP in WRS, which was not much different between native and cooked starch pastes. Moreover, for the steady shear test, all samples exhibited pseudoplastic behavior, in which $n<1$. The presence of hydrocolloids increased $\eta_{a,100}$ in both native and cooked starch pastes of NRS and WRS, except for LMP addition. However, the addition of hydrocolloids showed less effect on the $\eta_{a,100}$ values of the cooked starch pastes than the native starch pastes. This trend was also observed for the K values. Textural tests demonstrated that the added GL, κC or ίC significantly increased hardness and adhesiveness of the NRS pastes, whereas the other hydrocolloids did not significantly affect these textural properties. A similar result was also observed in the case of WRS, except for LMP and HMP, in which case they significantly decreased the hardness of the paste. Microscopic examination showed a phase-separate microstructure of the starch-hydrocolloid pastes in which starch-rich domains were dispersed in a continuous hydrocolloid matrix. The addition of hydrocolloids promoted amylopectin aggregation in the paste, except for ίC addition. It was possibly due to ίC associated with amylopectin.

REFERENCES

AACC. (2000). *Approved methods of the AACC* (10th ed.). St. Paul, MN, USA: American Association of Cereal Chemists.

Abdulmola, N. A., Hember, M. W. N., Richardson, R. K., & Morris, E. R. (1996). Effect of xanthan on the small-deformation rheology of crosslinked and uncrosslinked waxy maize starch. *Carbohydrate Polymers*, *31*, 65-78.

Achayuthakan, P., Suphantharika, M., & Rao, M. A. (2006). Yield stress components of waxy corn starch-xanthan mixtures: Effect of xanthan concentration and different starches. *Carbohydrate Polymers*, *65*, 469-478.

Adhikari, B., Howes, T., Bhandari, B. R., & Truong, V. (2001). Stickiness in foods: A review of mechanisms and test methods. International Journal of Food Properties, 4, 1-33.

Alloncle, M., & Doublier, J. L. (1991). Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocolloids*, *5*, 455-467.

Alloncle, M., Lefebvre, J., Llamas, G., & Doublier, J. L. (1989). A rheological characterization of cereal starch-galactomannan mixtures. *Cereal Chemistry*, *66*, 90-93.

Anastasiades, A., Thanou, S., Loulis, D., Stapatoris, A., & Karapantsios, T. D. (2002). Rheological and physical characterization of pregelatinized maize starches. *Journal of Food Engineering*, *52*, 57-66.

Annable, P., Fitton, M. G., Harris, B., Phillips, G.O., & Williams, P. A. (1994). Phase behavior and rheology of mixed polymer systems containing starch. *Food Hydrocolloids*, *8*, 351-359.

Appelqvist, I. A. M., & Debet, M. R. M. (1997). Starch-biopolymer interactions-A reviews. *Food Reviews International*, *13*, 163-224.

Bahnassey, Y. A., & Breene, W. M. (1994). Rapid Visco-Analyzer (RVA) pasting profiles of wheat, corn, waxy corn, tapioca and amaranth starches (*A. hypochondriacus* and *A. cruentus*) in the presence of konjac flour, gellan, guar, xanthan and locust bean gums. *Starch/Stärke*, *46*, 134-141.

Bao, J., & Bergman, C. J. (2004). The functionality of rice starch. In A. C. Eliasson (Ed.), *Starch in food: structure, function and applications* (pp.259-294). Boca Raton, FL: Woodhead Publishing Limited and CRC Press LLC.

Berry, C. S., I'Anson, K., Miles, M. J., Morris, V. J., & Russell, P. L. (1988). Physical chemical characterization of resistant starch from wheat. *Journal of Cereal Science*, *8*, 203-206.

Bhandari, P. N., Singhal, R. S., & Kole, D. D. (2002). Effect of succinylation on the rheological profile of starch pastes. *Carbohydrate Polymers*, *47*, 365-371.

Biliaderis, C. G., Arvanitoyannis, I., Izydorczyk, M. S., & Prokopowich, D. J. (1997). Effect of hydrocolloids on gelatinization and structure formation in concentrated waxy maize and wheat starch gels. *Starch/Stärke*, *49*, 278-283.

Biliaderis, C. G., Maurice, T. J., & Vosr, J. R. (1980). Starch gelatinization phenomena studied by differential scanning calorimetry. *Journal of Food Science*, *45*, 1669-1680.

Biliaderis, C. G., & Prokopowich, D. J. (1994). Effect of polyhydroxy compounds on waxy maize starch gels: A colorimetric study. *Carbohydrate Polymers*, *23*, 193-202.

Borwankar, R. P. (1992). Food texture and rheology. In R. P. Borwankar & C. F. Shoemaker (Eds.), *Rheology of Foods* (pp. 1-16). New York: Elsevier.

Chaisawang, M., & Suphantharika, M. (2005). Effects of guar gum and xanthan gum additions on physical and rheological properties of cationic tapioca starch. *Carbohydrate Polymers*, *61*, 288-295.

Chaisawang, M., & Suphantharika, M. (2006). Pasting and rheological properties of native and anionic tapioca starches as modified guar gum and xanthan gum. *Food Hydrocolloids*, *20*, 641-649.

Champagne, E. T. (1996). Rice starch composition and characteristics. *Cereal Foods World*, *41*, 833-838.

Chandrasekran, R., Millane, R. P., Arnott, S., & Atkins, E. D. T. (1988). The crystal structure of gellan. *Carbohydrate Research*, *175*, 1-15.

Chandrasekran, R., Puigjaner, L. C., Joyce, K. L., & Arnott, S. (1988). Cation interactions in gellan: an X-ray study of the potassium salt. *Carbohydrate Research*, *181*, 23-40.

Chen, M. H., Bergman, C. J., & Fjellstrom, R. G. (2003). Genetic variation at the waxy locus associated with amylose content in international rice germplasm. Plant an Animal Genome Conference, San Diego, Ca USA, January 11-15.

Christianson, D. D. (1982). Food carbohydrates. In D. R. Lineback & G. E. Inglett (Eds.), *Hydrocolloid interactions with starches* (pp. 399-419). Westport: AVI Publishing Company.

Christianson, D. D., Hodge, J. E., Osborne, D., & Detroy, R. W. (1981). Gelatinization of wheat starches as modified by xanthan gum, guar gum and cellulose gum. *Cereal Chemistry*, *58*, 513-517.

Chungcharoen, A, & Lund, D. B. (1987). Influence of solutes and water on rice starch gelatinization. *Cereal Chemistry*, *64*, 240-243.

Clark, A. H., Gidley, M. J., Richardson, R. K., & Ross-Murphy, S. B. (1989). Rheological study of amylose gels: the effect of chain length and concentration on gel modulus. *Macromolecules*, *22*, 346-356.

Clark, A. H., & Ross-Murphy, S. B. (1987). Structural and mechanical properties of biopolymer gel. *Advances in Polymer Science*, *83*, 57-192.

Clegg, S. M. (1995). Thickeners gels and gelling. In S. T. Beckett (Ed.), *Physicochemical aspects of food processing* (pp. 117-141). UK: Blackie.

Closs, C. B., Conde-Petit, B., Roberts, I. D., Tolstoguzov, V. B., & Escher, F. (1999). Phase separation and rheology of aqueous starch/galactomannan systems. *Carbohydrate Polymers*, *39*, 67-77.

Conde-Petit, B., & Escher, F. (1995). Complexation induced changes of rheological properties of starch systems at different moisture levels. *Journal of Rheology*, *39*, 1497-1518.

Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinization. Origin of the enthalpic transition. *Carbohydrate Research*, *227*, 103-112.

Djakovic, L. J., & Dokic, P. (1972). Rheological characteristics of starch gels. *Starch/Stärke*, *24*, 195-201.

Donovan, J. W., & Mapes, C. J. (1980). Multiple phase transitions of starches and nageli amylodextrins. *Starch/Stärke*, *32*, 190-193.

Doublier, J. L., & Choplin, L. (1989). A rheological description of amylose gelation. *Carbohydrate Research*, *193*, 215-226.

Draget, K. I. (2000). Alginates. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 137-154). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Eidam, D., Kulicke, W. M., Kuhn, K., & Stute, R. (1995). Formation of maize starch gels selectively regulated by the addition of hydrocolloids. *Starch/Stärke*, *47*, 378-384.

Eliasson, A. C. (1980). Effects of water content on the gelatinization of wheat starch. *Starch/Stärke*, *32*, 270-272.

Eliasson, A. C. (1986). Viscoelastic behavior during the gelatinization of starch I. Comparison of wheat, maize, potato and waxy-barley starches. *Journal of Texture Studies*, *17*, 253-265.

Eliasson, A. C., & Gudnundsson, M. (1996). Starch: physicochemical and function aspects. In A. C. Eliasson (Ed.), *Carbohydrates in food* (pp. 431-502). New York: Marcel Dekker.

Ellis, H. S., & Ring, S. G. (1985). A study of some factors influencing amylose gelation. *Carbohydrate Polymers*, *5*, 201-213.

Evans, I. C., & Haisman, D. R. (1979). Rheology of gelatinized starch suspension. *Journal of Texture Studies*, *10*, 347-370.

Fennema, O. R. (1985). Water and ice. In O. R. Fennema (Ed.), *Food chemistry* (pp. 23-67). New York: Marcel Dekker.

Ferrero, C. Martino, M. N., & Zaritzky, N. E. (1996). Effect of hydrocolloids on starch thermal transitions, as measured by DSC. *Journal of Thermal Analysis*, *47*, 1247-1266.

Funami, T, Kataoka, Y., Omota, T., Goto, Y., Asai, I., & Nishinari, K. (2005). Food hydrocolloids control the gelatinization and retrogradation behavior of starches. 2a. Functions of guar gums with different molecular weights on the gelatinization behavior of corn starch. *Food Hydrocolloids*, *19*, 15-24.

Ghiasi, K., Hosehey, R. C., & Varriano-Marston, E. (1982). Gelatinization of wheat starch. 2. Starch-surfactant interactions. *Cereal Chemistry*, *59*, 81-85.

Gibson, T. S., Solah, V. A., & McCleary, B. V. (1997). A procedure to measure amylose in cereal starches and flours with concanavalin A. *Journal of Cereal Science*, *25*, 111-119.

Gibson, W., & Sanderson, G. R. (1999). Gellan gum. In A. Imeson (Ed.), *Thickening and gelling agents for food* (2nd Ed.) (pp. 119-143). Maryland: Aspen Publishers Inc.

Grazdalen, H., & Smidsrod, O. (1987). Gelation of gellan gum. *Carbohydrate Polymers*, *7*, 371-393.

Gudmundsson, M., Eliasson, A. C., Bengtsson, S., & Aman, P. (1991). The effects of water soluble arabinoxylan on gelatinization and retrogradation of starch. *Starch/Stärke*, *43*, 5-10.

Gunasekaran, S., & Ak, M. M. (2000). Dynamic oscillatory shear testing of foods-selected applications. *Trends in Food Science and Technology*, *11*, 115-127.

Hoefler, A. C. (2004). *Hydrocolloids*. Minnesota: American association of Cereal Chemists.

Hogan, J. T. (1967). The manufacture of rice starch. *Starch Chemical Technology*, *2*, 65-78.

Holdsworth, S. D. (1977). Applicability of rheological models to the interpretation of flow and processing behavior of fluid food products. *Journal of Texture Studies*, *10*, 347-370.

Hoseney, R.C. (1994). *Principles of cereal science and technology* (2nd Ed.). St. Paul, Minnesota: American Association of Cereal Chemists.

Huag, A. (2000). Composition and properties of alginates. *Thesis*, Norwegian Institute of Technology, Trondheim.

Huang, M., Kennedy, J. F., Li, B., Xu, X., & Xie, B. J. (2007). Characters of rice starch gel modified by gellan, carrageenan and glucomannan: A texture profile analysis study. *Carbohydrate Polymers*, *69*, 411-418.

Imeson, A. P. (2000). Carrageenan. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 87-102). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Jane, J., Chen, Y. Y., Lee, L. F., McPherson, A., Wong, K. S., Radosavljevic, M., &

Kasemsuwan, T. (1999). Effect of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. *Cereal Chemistry*, *76*, 629-637.

Jane, J., Kasemsuwan, T., & Chen, L. F. (1996). Phosphorus in rice and other starches. *Cereal Food World*, *41*, 827-832.

Jansson, P. E., Kenne, L., & lindberg, B. (1975). Structure of the exocellular polysaccharide from *Xanthomonas campestris*. *Carbohydrate Research*, *45*, 275-282

Juliano, B. O. (1998). Varietal impact on rice quality. *Cereal Food World*, *43*, 207-222.

Kalichevskym M. T., & Ring, S. G. (1987). Incompatibility of amylose and amylopectin in aqueous solution. *Carbohydrate Research*, *162*, 323-328.

Karim, A. A., Noriziah, M. H., & Seow, C. C. (2000). Methods for the study of starch retrogradation. *Food Chemistry*, *71*, 9-36.

Kennedy, G., & Burlingame, B. (2003). Analysis of food composition data on rice from a plant genetic resources perspective. *Food Chemistry*, *80*, 589-596.

Kim, C., & Yoo, B. (2006). Rheological properties of rice starch-xanthan gum mixtures. *Journal of Food Engineering*, *75*, 120-128.

Kim, K. O., Hanson, L., & Setser, C. S. (1986). Phase transitions of starch-water systems containing polydextrose. *Journal of Food Science*, *51*, 1095-1097.

Kim, Y., & Setser, C. S. (1992). Wheat-starch gelatinization in the presence of polydextrose or barley beta-glucan. *Cereal Chemistry*, *69*, 447-452.

Kim, Y., & Wang, S. S. (1999). Starch cooking with limited water as affected by zein and guar gum. *Journal of Food Science*, *64*, 133-135.

Kruger, A., Ferrero, C., & Zaritzky, N. E. (2003). Modeling corn starch swelling in batch systems: Effect of sucrose and hydrocolloids. *Journal of Food Engineering*, *58*, 125-133.

Kulicke, W. M., Eidam, D., Kath, F., Kix, M., & Kull, A. H. (1996). Hydrocolloids and rheology: Regulation of Visco-elastic characteristics of waxy rice starch in mixtures with galactomannans. *Starch/Stärke*, *48*, 105-114.

Kuo, M. S., Mort, A. J., & Dell, A. (1986). Identification and location of L-glycerate, an unusual acyl substituents in gellan gum. *Carbohydrate Research*, *156*, 173-187.

Lai, V. M. F., Huang, A. L., & Lii, C. Y. (1999). Rheological properties and phase transition of red algal polysaccharide-starch composites. *Food Hydrocolloids*, *13*, 409-418.

Lelievre, J. (1976). Theory of gelatinization in a starch-water solute system. *Polymer*, *17*, 854-858.

Leloup, V. M., Colonna, P., Ring, S. G., Roberts, K., & Wells, B. (1992). Microstructure of amylose gels. *Carbohydrate Polymers*, *18*, 189-197.

Li, J. Y., & Yeh, A. I. (2001). Relationships between thermal, rheological characteristics and swelling power for various starches. *Journal of Food Engineering*, *50*, 141-148.

Lii, C. Y., Lai, V. M. F., Lu, S., & Tsai, M. L. (1998). Correlation between the physical property, eating quality and the molecular structure of rice-starchy systems. *Zywnosc Technologia Jakosc*, *4*, 72-86.

Lii, C. Y., Shao, Y. Y., Tseng, K. H. (1995). Gelation mechanism and rheological properties of rice starch. *Cereal Chemistry*, *72*, 393-400.

Lii, C. Y., Tsai, M. L., & Tseng, K. H. (1996a). Effect of amylose content on the rheological property of rice starch. *Cereal Chemistry*, *73*, 425-420.

Lii, C. Y., Tsai, M. L., & Tseng, K. H. (1996b). Studies on starch gelatinization and retrogradation with dynamic rheometry-the influence of starch granular structure and composition. *Zywnosc Technologia Jakosc*, *2*, 27-53.

Lim, S. T., Kasemsuwan, T., & Jane, J. (1994). Characterization of phosphorus in starch by 31P-nuclear magnetic resonance spectroscopy. *Cereal Chemistry*, *71*, 488.

Liu, H., & Eskin, N. A. M. (1998). Interaction of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatin. *Food Hydrocolloids*, *12*, 37-41.

Liu, H., Eskin, N. A. M., & Cui, S. W. (2003). Interaction of wheat and rice starches with yellow mustard mucilage. *Food Hydrocolloids*, *17*, 863-869.

Liu, H., Eskin, N. A. M., & Cui, S. W. (2006). Effects of yellow mustard mucilage on functional and rheological properties of buckwheat and pea starches. *Food Chemistry*, *95*, 83-93.

Liu, H., & Lelievre, J. (1992). Differential scanning calorimetric and rheological study of the gelatinization of starch granules embedded in a gel matrix. *Cereal Chemistry*, *69*, 597-599.

Lumdubwong, N., & Sieb, P. A. (2000). Rice starch isolation by alkaline protease digestion of wet-milled rice flour. *Journal of Cereal Science*, *31*, 63-74.

Mandala, I. G., & Bayas, E. (2004). Xanthan effect on swelling, solubility and viscosity of wheat starch dispersions. *Food Hydrocolloids*, *18*, 191-201.

Mandala, I. G., Palogou, E. D., & Kostaropoulos, A. E. (2002). Influence of preparation and storage conditions on texture of xanthan-starch mixtures. *Journal of Food Engineering*, *53*, 27-38.

Marchant, J. L., & Blanshard, J. M. V. (1980). Changes in the birefringent characteristics of cereal starch granules at different temperatures and water activities. *Starch/Stärke*, *32*, 223-226.

May, C. D. (2000). Pectins. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 169-188). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Melton, L. D., Mindt, l., Rees, D. A., & Sanderson, G. R. (1976). Covalent structure of the polysaccharide from *Xanthomonas cempestris*: evidence from partial hydrocolysis studies. *Carbohydrate Research*, *45*, 275-282.

Miles, M. J., Morris, V. J., & Ring, s. G. (1984). Some recent observations on the retrogradation of amylose. *Carbohydrate Polymers*, *4*, 73-77.

Morris, E. R. (1989). Polysaccharide solution properties: Origin, rheological characterization and implications for food system. In R. P. Millane, J. N. BeMiller, R. Chandrasekavan (Eds.), *Frontier in carbohydrate research-1: Food applications* (pp. 132-163). London-New York: Elsevier Applied Science Publishers.

Morris, E. R. (1990). Mixed polymer gels in food gels. In P. Harris (Ed.), *Applied food science series* (pp. 291-360). Amsterdam: Elsevier.

Morris, E. R., Gothard, M. G. E., Hember, M. W. N., Manning, C. D., & Robinson, G.

(1996). Conformational and rheological transitions of welan, rhamsan and acetylated gellan. *Carbohydrate Polymers*, *30*, 165-175.

Morris, V. J. (1995). Bacterial polysaccharides. In A. M. Stephen (Ed.), *Food polysaccharides and their application* (pp. 341-374). New York: Marcel Dekker.

Morrison, W. R., & Azudin, M. N. (1987). Variation in the amylose and lipid contents and some physical properties of rice starches. *Journal of Cereal Science*, *5*, 35-39.

Morrison, W. R., Milligan, T. P., & Azudin, M. N. (1984). A relationship between the amylose and lipid contents of starches from lipid cereals. *Journal of Cereal Science*, *2*, 257-260.

Murray, J. C. F. (2000). Cellulosics. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 219-230). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Noda, T., Takahata, Y., Sato, T., Ikoma, H., & Mochida, H. (1996). Physicochemical properties of starches from purple and orange fleshed sweet potato roots at two levels of fertilizer. *Starch/Stärke*, *48*, 395-399.

Pons, M., & Fiszman, S. M. (1996). Instrumental texture profile analysis with particular reference to gelled systems. *Journal of Texture Studies*, *27*, 597-624.

Qi, X., Tester, R. F., Snape, C. E., & Ansell, R. (2003). Molecular basis of the gelatinization and swelling characteristics of waxy rice starches grown in the same location during the same season. *Journal of Cereal Science*, *37*, 363-376.

Reddy, K. R., Ali, S. Z., Bhattacharya, K. R. (1993). The fine structure of rice starch amylopectin and its relation to the texture of cooked rice. *Carbohydrate Polymers*, *22*, 267-275.

Rojas, J. A., Rosell, C. M., & Benedito de Barber, C. (1999). Pasting properties of different wheat flour-hydrocolloid system. *Food Hydrocolloids*, *13*, 27-33.

Sandhya Rani, M. R. & Bhattacharya, K. R. (1989). Rheology of rice flour paste: Effect of variety, concentration, time and temperature of cooking. *Journal of Texture Studies*, *20*, 127-137.

Sasaki, T., Yasui, T., & Matsuki, J. (2000). Influence of non-starch polysaccharides isolated from wheat flour on the gelatinization and gelation of wheat starches. *Food Hydrocolloids*, *14*, 295-303.

Satrapai, S., & Suphantharika, M. (2007). Influence of spent brewer's yeast β-glucan on gelatinization and retrogradation of rice starch. *Carbohydrate Polymers*, *67*, 500-510.

Schols, H. A., Ros, J. M., Dass, P. J. H., Bakx, E. J., & Vorage, A. G. J. (1998). Structural features of native and commercially extracted pectins. In P. A. Williams & G. O. Phillips (Eds.). *Gums and stabilizers for the food industry* (9th Ed.). Wrexham: The Royal Society of Chemistry.

Shi, S., & BeMiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers*, *50*, 7-18.

Slade, L., & Levine, H. (1984). In A. R. McGhie, *Proceedings of the 13th annual NATAS conference* (p. 64). Philadelphia: NATAS.

Slade, L., & Levine, H. (1987). Recent advances in starch retrogradation. In S. S. Stivala, V. Crescenzi, & I. C. M. Dea, *Industrial polysaccharides. The impact of biotechnology and advanced methodologies* (pp. 387-430). New York: Gordon and Breach Science Publishers.

Slade, L., &Levine, H. (1988). Non-equilibrium melting of native granular starch. Part I. Temperature location of the glass transition associated with gelatinization of A-type cereal starches. *Carbohydrate Polymers*, *8*, 183-203.

Sodhi, N. S, & Singh, N. (2003). Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. *Food Chemistry*, *80*, 99-108.

Sommerville, M. D. (1999). The effects of non-starch polysaccharides on the hydrolysis, gelatinization and retrogradation of starch. *Ph.D. Thesis*, Glasgow Caledonian University, Glasgow.

Song, J. Y., Kwon, J. Y., Choi, J., Kim, Y. C., & Shin, M. (2006). Pasting properties of non-waxy rice starch-hydrocolloid mixtures. *Starch/Stärke*, *58*, 223-230.

Sworn, G. (2000a). Gellan gum. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 117-135). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Sworn, G. (2000b). Xanthan gum. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 103-115). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Tabata, S., Nagata, K., & Hizukari, S. (1975). Studies on starch phosphates. Part 3: On the esterified phosphates in some cereal starches. *Starch/Stärke*, *27*, 333.

Tecante, A., & Doublier, J. L. (1999). Steady flow and viscoelastic behavior of crosslinked waxy corn starch-κ-carrageenan pastes and gels. *Carbohydrate Polymers*, *40*, 221-231.

Tecante, A., & Doublier, J. L. (2002). Rheological investigation of the interaction between amylose and κ-carrageenan. *Carbohydrate Polymers*, *49*, 177-183.

Teo, C. H, Karim, a. A., Cheah, P. B., Norziah, M. H., & Seow, C. C. (2000). On the roles of protein and starch in the aging of non-waxy rice flour. *Food Chemistry*, *69*, 229-236.

Tester, R. F. (1997). Starch: the polysachharide fractions. In P. J. Frazier, P. Richmond, & A. M. Donald (Eds.), *Starch: structure and functionality* (pp. 163-171). Wrexham: The Royal Society of Chemistry.

Tester, R. F., & Morrison, W. R. (1990a). Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose and lipids. *Cereal Chemistry*, *67*, 551-557.

Tester, R. F., & Morrison, W. R. (1990b). Swelling and gelatinization of cereal starches. II. Waxy rice starches. *Cereal Chemistry*, *67*, 558-563.

Tester, R. F., & Sommerville, M. D. (2003). The effects of non-starch polysaccharides on the extent of gelatinization, swelling and α-amylase hydrolysis of maize and wheat starches. *Food Hydrocolloids*, *17*, 41-54.

Thomas, D. J., & Atwell, W. A. (1999). *Starches*. Minnesota: American Association and Cereal Chemists.

Urlacher, B., & Noble, O. (1997). Xanthan. In A. Imeson, (Ed.), *Thickening and gelling agents for food* (pp. 284-311). London: Chapman & Hall.

Vandeputte, G. E., Derycke, v., Geeroms, J., & Delcour, J. A. (2003a). Rice starches. II. Structural aspects provide insight in swelling and pasting properties. *Journal of Cereal Science*, *38*, 53-59.

Vandeputte, G. E., Derycke, v., Geeroms, J., & Delcour, J. A. (2003b). Rice starches.

III. Structural aspexts provid insight in amylopectin retrogradation properties and gel texture. *Journal of Cereal Science*, *38*, 61-68.

Wang, Y. J., Wang, L. F., Shephard, D., Wang, F. D., & Parindol, J. (2002). Properties and structures of flours and starches from whole, broken and yellowed rice kernels in a model study. *Cereal Chemistry*, *79*, 383-386.

Ward, F. M., & Andon, S. A. (2002). Hydrocolloids as film formers, adhesives and gelling agents for bakery and cereal products. *Cereal Food World*, *47*, 52-55.

Wei, Y. P., Wang, C. S., & Wu, J. S. B. (2001). Floe properties of fruit fillings. *Food Research International*, *34*, 377-381.

Whistler, R. L., & BeMiller, J. N. (1997). *Carbohydrate chemistry for food scientists*. St Paul, MN: Eagan Press.

Wielinga, W. C. (2000). Galactomannan. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 137-154). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Williams, P. A, & Phillips, G. O. (2000). Introduction of food hydrocolloids. In G. O. Phillips & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 1-19). Boca Raton, Fl: Woodhead Publishing Limited and CRC Press LLC.

Wurzburg, O. B. (1986). Introduction. In O. B. Wurxburg (Ed.), *Modified starches: Properties and uses* (pp. 3-16). Boca Raton, FL: CRC Press.

Yoshimura, M., Takaya, T., & Nishinari, K. (1996). Effects of konjac-glucomannan on the gelatinization and retrogradation of corn starches as determined by rheology and differential scanning calorimetry. *Journal of Agriculture and Food Chemistry*, *44*, 2970-2976.

Yao, Y., Zhang, J. M., & Ding, X. L. (2002). Structure-retrogradation relationship of rice starch in starch purified starches and cooked rice grains: a statistical investigation. *Journal of Agriculture and Food Chemistry*, *50*, 7420-7425.

Yoo, D., Kim, C., & Yoo, B. (2005). Steady and dynamic shear rheology of rice starch-galactomannan mixtures. *Starch/Stärke*, *57*, 310-318.

Zobel, h. (1984). Gelatinization of starch and mechanical properties of starch pastes. In R. L. Whistler (Ed.), *Starch chemistry and technology* (2nd Ed.) (pp. 285-309). London: Academic Press Inc.

Zhou, Z. K., Robards, K., Helliwell, S., & Blanchard, C. (2002). Composition and functional properties of rice. *International Journal of Food Science and Technology*, *37*, 849-868.

BIOGRAPHY

NAME	Miss Jetnapa Techawipharat
DATE OF BIRTH	November 17, 1978
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTIONS ATTEND	Mahidol University, Bangkok, 1997-2001: Bachelor of Science (Biotechnology) Mahidol University, Bangkok, 2001-2003: Master of Science (Biotechnology) Mahidol University, Bangkok, 2004-2007: Doctor of Philosophy (Biotechnology)
STUDY & RESEARCH GRANT	The Royal Golden Jubilee Ph.D. Program
HOME ADDRESS	288/2 Moo 9, Jumpa sub-District, Tharua District, Ayutthaya 13130 Tel. 08-1554-0410, 035-341307 Email: jetnapa@yahoo.com
PRESENTATION	RGJ -Ph.D. Congress 8th, The Thailand Research Fund; 20-22 April 2007. Jomtien Palm Beach Hotel, Pattaya, Chon Buri, Thailand. IFT 2007 Annual Meeting and Food Expo; 28 July-1 August 2007. McCormick Place, Chicago, Illinois, USA.