

**TEXTURAL AND RHEOLOGICAL PROPERTIES OF  
GELATIN OR GELLAN IN MAIZE STARCH – EGG  
WHITE COMPOSITE GELS**

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**TEXTURAL AND RHEOLOGICAL PROPERTIES OF  
GELATIN OR GELLAN IN MAIZE STARCH – EGG  
WHITE COMPOSITE GELS**

**by**

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## TABLE OF CONTENTS

	<b>Page</b>
<b>ACKNOWLEDGEMENTS</b>	ii
<b>TABLE OF CONTENTS</b>	iii
<b>LIST OF TABLES</b>	viii
<b>LIST OF FIGURES</b>	ix
<b>LIST OF PLATES</b>	xv
<b>LIST OF SYMBOLS/ABBREVIATIONS</b>	xvi
<b>LIST OF APPENDICES</b>	xviii
<b>ABSTRAK</b>	xix
<b>ABSTRACT</b>	xxi
<b>CHAPTER 1 INTRODUCTION</b>	<b>1</b>
1.1 BACKGROUND	1
1.2 RATIONALE OF THE STUDY	6
1.3 HYPOTHESIS AND RESEARCH QUESTIONS	6
1.4 OBJECTIVES	9
1.5 THESIS OUTLINE	10

<b>CHAPTER 2</b>	<b>LITERATURE REVIEW</b>	<b>12</b>
2.1	DESCRIPTION OF THE GEL SYSTEMS STUDIED	12
2.2	GELATIN	12
2.2.1	Gelling mechanism of gelatin	13
2.3	GELLAN	15
2.3.1	Gelling mechanism of gellan	17
2.4	MAIZE STARCH	18
2.4.1	Gelling mechanism of maize starch	20
2.5	EGG WHITE	21
2.5.1	Gelling mechanism of egg white	22
2.6	FOOD GELS	23
2.6.1	Single component gels	23
2.6.2	Composite gels	24
2.7	FOOD TEXTURE	26
2.8	RHEOLOGY	27
2.8.1	Deformation of gels	28
2.9	MIXTURE DESIGN EXPERIMENTS	29
<b>CHAPTER 3</b>	<b>MATERIALS AND METHODS</b>	<b>31</b>
3.1	TEXTURAL AND STRUCTURAL BREAKDOWN PROPERTIES OF GELATIN AND GELLAN SIMPLE GELS	31

3.1.1	Materials	31
3.1.2	Gel preparation	32
3.1.3	Texture profile analysis	33
3.1.4	Multiple extrusion cell analysis	33
3.1.5	Statistical analysis	34
3.2	TEXTURAL AND RHEOLOGICAL PROPERTIES OF GELATIN AND GELLAN IN MAIZE STARCH – EGG WHITE COMPOSITE GELS	35
3.2.1	Materials	35
3.2.2	Gel preparation	35
3.2.3	Design of experiment	39
3.2.4	Texture profile analysis	40
3.2.5	Stress relaxation test	40
3.2.6	Uniaxial compression test	41
3.2.7	Mixture regression and statistical analysis	43
3.3	DYNAMIC OSCILLATORY MEASUREMENTS ON NETWORK FORMATION AND MECHANICAL SPECTRA OF GELS	44
3.3.1	Biopolymer stock preparation	44
3.3.2	Dynamic oscillatory test	44
3.4	pH AND MICROSTRUCTURE OF GELS	46
3.4.1	Gel preparation for pH measurement	46
3.4.2	Field emission scanning electron microscope	46
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>		<b>48</b>

4.1	TEXTURAL AND STRUCTURAL BREAKDOWN PROPERTIES OF GELATINA AND GELLAN SIMPLE GELS	48
4.1.1	Texture profile analysis of gelatin and gellan simple gels	49
4.1.2	Multiple extrusion cell analysis of gelatin and gellan simple gels	52
4.1.3	Relating texture profile analysis and multiple extrusion cell analysis	58
4.1.4	Chapter conclusion	59
4.2	TEXTURAL PROPERTIES OF GELATIN AND GELLAN IN MAIZE STARCH – EGG WHITE COMPOSITE GEL SYSTEEMS	61
4.2.1	Textural properties of single component gels	65
4.2.2	Textural properties of binary composite gels	67
4.2.3	Textural properties of ternary composite gels	74
4.2.4	Chapter conclusion	80
4.3	RHEOLOGICAL PROPERTIES OF GELATIN AND GELLAN IN MAIZE STARCH – EGG WHITE COMPOSITE GEL SYSTEMS	81
4.3.1	Small deformation – Stress relaxation	81
4.3.1.1	Stress relaxation behaviour of single component gels	83
4.3.1.2	Stress relaxation behaviour of binary composite gels	87
4.3.1.3	Stress relaxation behaviour of ternary composite gels	93
4.3.2	Large deformation – Fracture properties	99
4.3.2.1	Fracture properties of single component gels and binary composite gels	100
4.3.2.2	Fracture properties of ternary composite gels	105
4.3.3	Chapter conclusion	106
4.4	DYNAMIC OSCILLATORY MEASUREMENTS ON NETWORK DEVELOPMENT AND MECHANICAL SPECTRA OF GELS	110
4.4.1	Network development of gels	111

4.4.2	Mechanical spectra of gels	128
4.4.3	Chapter conclusion	134
4.5	GELLING PROPERTIES IN RELATION TO NETWORK FORMATION OF GELATIN AND GELLAN COMPOSITE GELS	135
4.5.1	Gelatin – Single component gel	140
4.5.2	Gellan – Single component gel	143
4.5.3	Maize starch – Single component gel	145
4.5.4	Egg white – Single component gel	147
4.5.5	Maize starch : Egg white – Binary composite gels	149
4.5.6	Maize starch : Gelatin – Binary composite gels	151
4.5.7	Maize starch : Gellan – Binary composite gels	153
4.5.8	Egg white : Gelatin – Binary composite gels	155
4.5.9	Egg white : Gellan – Binary composite gels	157
4.5.10	Gelatin – Ternary composite gels	159
4.5.11	Gellan – Ternary composite gels	161
4.5.12	Comparison between gelatin and gellan composite gels	163
<b>CHAPTER 5</b>	<b>OVERALL CONCLUSIONS AND RECOMMENDATIONS</b>	<b>166</b>
	<b>REFERENCES</b>	<b>168</b>
	<b>APPENDICES</b>	<b>179</b>
	<b>LIST OF PUBLICATIONS</b>	<b>180</b>



## LIST OF TABLES

		<b>Page</b>
Table 1.1	The applications of gelatin on selected food applications and the technical constraints of the current alternatives.	5
Table 3.1.1	Concentrations of biopolymers for gel preparation.	32
Table 3.2.1	Combinations of composite gels formulated with maize starch, egg white and gelatin or gellan in the augmented simplex centroid design.	37
Table 4.1.1	Texture profile analysis parameters of gelatin and gellan simple gels.	51
Table 4.1.2	Multiple extrusion cell analysis parameters of gelatin and gellan simple gels.	57
Table 4.2.1	Textural parameters of the single component gels studied.	66
Table 4.3.1	Stress relaxation parameters of single component gels.	85
Table 4.4.1	Storage modulus ( $G'$ ), loss modulus ( $G''$ ) and loss tangent ( $\tan \delta$ ) of gels studied.	130
Table 4.5.1	Summary of gelling properties of single component gels.	136
Table 4.5.2	Summary of gelling properties of binary composite gels – [Maize starch : Egg white], [Maize starch : Gelatin] and [Maize starch : Gellan].	137
Table 4.5.3	Summary of gelling properties of binary composite gels – [Egg white : Gelatin] and [Egg white : Gellan].	138
Table 4.5.4	Summary of gelling properties of gelatin and gellan ternary composite gels.	139

## LIST OF FIGURES

		<b>Page</b>
Figure 1.1	The overall research protocol.	8
Figure 2.1	The sol-gel transition in gelatin system.	14
Figure 2.2	The chemical structures of gellan gum: (a) native form (high acyl) and (b) deacylated form (low acyl).	16
Figure 2.3	The sol-gel transition of gellan gum.	17
Figure 2.4	The chemical structures of: (a) amylose and (b) amylopectin.	19
Figure 2.5	The mechanism of starch gelatinisation and retrogradation: a) starch granules; b) swelling of granules in water upon heating; c) leaching of amylose; and d) formation of starch gel matrix.	21
Figure 2.6	Networks of composite gels: a) swollen network; b) interpenetrating network; c) phase separated network and d) coupled network.	26
Figure 2.7	Rheological responses of viscoelastic specimens during deformation.	29
Figure 3.2.1	Preparation of biopolymer stock solutions and gels.	38
Figure 3.2.2	An augmented simplex-centroid mixture design with candidature points for both gelatin (System I) and gellan (System II) composite gels.	40
Figure 4.1.1	Texture profiles of (a) soft and (b) hard gelatin and gellan simple gels.	50
Figure 4.1.2	Multiple extrusion cell curves of hard gellan gel. (a) Representative curve of force as a function of time during breakdown at the rate of 5mm/s for 20 cycles. (b) Same set of data but zoomed in for the first two and a half extrusion cycles.	54
Figure 4.1.3	Breakdown patterns of (a) soft and (b) hard gelatin and gellan simple gels.	56
Figure 4.2.1	Classification of gels studied and their designations.	62

Figure 4.2.2	Modulus of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations (n = 3). Different letters on each symbol indicates significant difference (P < 0.05) among samples of different proportions for each type of binary composite gel.	71
Figure 4.2.3	Hardness of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Egg white], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations (n = 3). Different letters on each symbol indicates significant difference (P < 0.05) among samples of different proportions for each type of binary composite gel.	72
Figure 4.2.4	Cohesiveness of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations (n = 3). Different letters on each symbol indicates significant difference (P < 0.05) among samples of different proportions for each type of binary composite gel.	73
Figure 4.2.5 a	Surface and contour plots of modulus for gelatin-ternary composite gels.	77
Figure 4.2.5 b	Surface and contour plots of modulus for gellan-ternary composite gels.	77
Figure 4.2.6 a	Surface and contour plots of hardness for gelatin-ternary composite gels.	78
Figure 4.2.6 b	Surface and contour plots of hardness for gellan-ternary composite gels.	78
Figure 4.2.7 a	Surface and contour plots of cohesiveness for gelatin-ternary composite gels.	79
Figure 4.2.7 b	Surface and contour plots of cohesiveness for gellan-ternary composite gels.	79
Figure 4.3.1	Stress relaxation curves of four types of single component gel.	84

Figure 4.3.2	Stress relaxation curves of binary composite gels: a) [Maize starch : Egg white], b) [Maize starch : Gelatin], c) [Maize starch : Gellan], d) [Egg white : Gelatin] and e) [Egg white : Gellan].	89
Figure 4.3.3	$F_{max}$ of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations ( $n = 3$ ). Different letters on each symbol indicates significant difference ( $P < 0.05$ ) among samples of different proportions for each type of binary composite gel.	90
Figure 4.3.4	$k_1$ of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations ( $n = 3$ ). Different letters on each symbol indicates significant difference ( $P < 0.05$ ) among samples of different proportions for each type of binary composite gel.	91
Figure 4.3.5	$k_2$ of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations ( $n = 3$ ). Different letters on each symbol indicates significant difference ( $P < 0.05$ ) among samples of different proportions for each type of binary composite gel.	92
Figure 4.3.6 a	Surface and contour plots of $F_{max}$ for gelatin-ternary composite gels.	96
Figure 4.3.6 b	Surface and contour plots of $F_{max}$ for gellan-ternary composite gels.	96
Figure 4.3.7 a	Surface and contour plots of $k_1$ for gelatin-ternary composite gels.	97
Figure 4.3.7 b	Surface and contour plots of $k_1$ for gellan-ternary composite gels.	97
Figure 4.3.8 a	Surface and contour plots of $k_2$ for gelatin-ternary composite gels.	98

Figure 4.3.8 b	Surface and contour plots of $k_2$ for gellan-ternary composite gels.	98
Figure 4.3.9	Fracture properties of single component gels and binary composite gels.	101
Figure 4.3.10	Fracture stress of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations ( $n = 3$ ). Different letters on each symbol indicates significant difference ( $P < 0.05$ ) among samples of different proportions for each type of binary composite gel.	102
Figure 4.3.11	Fracture strain of binary composite gels: i) [Maize starch : Egg white], ii) [Maize starch : Gelatin], iii) [Maize starch : Gellan], iv) [Egg white : Gelatin] and v) [Egg white : Gellan]. Data points are means $\pm$ standard deviations ( $n = 3$ ). Different letters on each symbol indicates significant difference ( $P < 0.05$ ) among samples of different proportions for each type of binary composite gel.	103
Figure 4.3.12 a	Fracture properties of gelatin-ternary composite gels.	107
Figure 4.3.12 b	Fracture properties of gellan-ternary composite gels.	107
Figure 4.3.13 a	Surface and contour plots of fracture stress for gelatin-ternary composite gels.	108
Figure 4.3.13 b	Surface and contour plots of fracture stress for gellan-ternary composite gels.	108
Figure 4.3.14 a	Surface and contour plots of fracture strain for gelatin-ternary composite gels.	109
Figure 4.3.14 b	Surface and contour plots of fracture strain for gellan-ternary composite gels.	109
Figure 4.4.1	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures for each type of single component gel: a) gelatin, b) gellan, c) maize starch and d) egg white. The + line shows the time-temperature profile.	115

Figure 4.4.2	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures of [Maize starch : Egg white]-binary composite gel. The + line shows the time-temperature profile.	117
Figure 4.4.3	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures of [Maize starch : Gelatin]-binary composite gel. The + line shows the time-temperature profile.	119
Figure 4.4.4	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures of [Maize starch : Gellan]-binary composite gel. The + line shows the time-temperature profile.	121
Figure 4.4.5	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures of [Egg white : Gelatin]-binary composite gel. The + line shows the time-temperature profile.	123
Figure 4.4.6	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures of [Egg white : Gellan]-binary composite gel. The + line shows the time-temperature profile.	125
Figure 4.4.7	Evolution of $G'$ ( $\circ$ ) and $G''$ ( $\bullet$ ) during gel preparation procedures of a) gelatin-ternary composite gels and b) gellan-ternary composite gels. The + line shows the time-temperature profile. Each component was at equal ratios for both ternary composite gel systems.	127
Figure 4.4.8	Mechanical spectra of: a) single component gels, b) [Maize starch : Egg white]-binary composite gel, c) [Maize starch : Gelatin]-binary composite gel, d) [Maize starch : Gellan]-binary composite gel, e) [Egg white : Gelatin]-binary composite gel and f) [Egg white : Gellan]-binary composite gel. All samples were tested under 0.1% of strain at 15 °C.	131
Figure 4.4.9	Mechanical spectra as a function of oscillatory frequency of gelatin-ternary composite gels and gellan-ternary composite gels. All samples were tested under 0.1% of strain at 15 °C.	133
Figure 4.5.1	Proposed sol-gel transition mechanism and scanning electron micrographs of gelatin-single component gel at magnifications: (i) 40 $\times$ , (ii) 100 $\times$ and (iii) 1000 $\times$ .	142
Figure 4.5.2	Proposed sol-gel transition mechanism and scanning electron micrographs of gellan-single component gel at magnifications: (i) 40 $\times$ , (ii) 100 $\times$ and (iii) 1000 $\times$ .	144

Figure 4.5.3	Proposed sol-gel transition mechanism and scanning electron micrographs of maize starch-single component gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	146
Figure 4.5.4	Proposed sol-gel transition mechanism and scanning electron micrographs of egg white-single component gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	148
Figure 4.5.5	Proposed sol-gel transition mechanism and scanning electron micrographs of [Maize starch : Egg white]-binary composite gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	150
Figure 4.5.6	Proposed sol-gel transition mechanism and scanning electron micrographs of [Maize starch : Gelatin]-binary composite gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	152
Figure 4.5.7	Proposed sol-gel transition mechanism and scanning electron micrographs of [Maize starch : Gellan]-binary composite gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	154
Figure 4.5.8	Proposed sol-gel transition mechanism and scanning electron micrographs of [Egg white : Gelatin]-binary composite gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	156
Figure 4.5.9	Proposed sol-gel transition mechanism and scanning electron micrographs of [Egg white : Gellan]-binary composite gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	158
Figure 4.5.10	Proposed sol-gel transition mechanism and scanning electron micrographs of gelatin-ternary composite gel at magnifications: (i) 40 ×, (ii) 100 × and (iii) 1000 ×.	160
Figure 4.5.11	Proposed sol-gel transition of gellan-ternary composite gel during gel preparation.	162

## LIST OF PLATES

		<b>Page</b>
Plate 4.2.1	Appearance of single component gels: A) 11% gelatin, B) 2.5% gellan, C) 13% maize starch and D) 9% egg white.	63
Plate 4.2.2	Appearance of single component gels after two cycle compression during texture profile analysis measurement: A) 11% gelatin, B) 2.5% gellan, C) 13% maize starch and D) 9% egg white.	67
Plate 4.2.3	Appearance for each group of binary composite gel at the proportions of: a) [33:67], b) [50:50] and c) [67:33].	68
Plate 4.2.4	Appearance of gelatin-ternary composite gels prepared by [Maize starch : Egg white : Gelatin] in the proportions of: a) [17:17:67], b) [17:42:42], c) [17:67:17], d) [33:33:33], e) [42:17:42], f) [42:42:17], g) [67:17:17].	76
Plate 4.2.5	Appearance of gellan-ternary composite gels prepared by [Maize starch : Egg white : Gellan] in the proportions of: a) [17:17:67], b) [17:42:42], c) [17:67:17], d) [33:33:33], e) [42:17:42], f) [42:42:17], g) [67:17:17].	76



## LIST OF SYMBOLS/ABBREVIATIONS

Symbol/Abbreviation	Caption
Glt	Gelatin
Gll	Gellan
MS	Maize starch
EW	Egg white
SCG	Single component gel
BCG	Binary composite gel
TCG	Ternary composite gel
TPA	Texture profile analysis
MEC	Multiple extrusion cell
ANOVA	One-way analysis of variance
$Y_t$	Decaying parameter
$F_0$	Initial force
$F_t$	Momentary force at time $t$
$F_{max}$	Maximum force of stress relaxation at 20% strain
$k_1$	Initial rate of relaxation
$k_2$	Stress relaxation constant
$t$	time
$\sigma_{true}$	True (Hencky's) stress
$\varepsilon_{true}$	True (Hencky's) strain
$H_0$	Initial height
$H_t$	Height at time $t$
$R_0$	Initial radius
FESEM	Field emission scanning electron microscope

$w(n)$	Work of each extrusion cycle
$w_1$	Loss of energy per extrusion cycle
$n_1$	Decay rate of work per extrusion
$w_{inf}$	Amount of work remained after infinite number of extrusion
$G'$	Storage modulus
$G''$	Loss modulus
$\tan \delta$	Loss tangent

## LIST OF APPENDICES

<b>Appendix</b>	<b>Page</b>
Appendix A    The pH values of gels studied.	180

# **CIRI-CIRI TEKSTUR DAN REOLOGI GELLAN ATAU GELLAN DALAM GEL KOMPOSIT KANJI JAGUNG – PUTIH TELUR**

## **ABSTRAK**

Gellan (GII) telah dicadangkan sebagai salah satu daripada gantian gelatin (GII) kerana gel GII dapat member persepsi deria ‘lebur-dalam-mulut’ seperti gel GII. Walau bagaimanapun, penggunaan GII sebagai gantian GII dalam sistem komposit belum dijelajahi secukupnya. Tujuan kajian ini adalah untuk menjelaskan kesan-kesan peredaran ramuan terhadap sifat tekstur, reologi dan struktur gel komposit yang mengandungi GII atau GII dengan kanji jagung (MS) dan putih telur (EW). Ramuan utama untuk menghasilkan gel adalah dipilih berdasarkan kepada kepentingan pratikal dalam industri makanan. Kajian yang melibatkan rekabentuk campuran telah digunakan untuk menerokai kesan-kesan interaksi yang disebabkan oleh peredaran komponen yang berbeza. Ciri tekstur dan cara kepecahan gel komponen tunggal telah dikaji masing-masing dengan menggunakan analisis profil tekstur (TPA) dan analisis sel penyemperitan berbilang (MEC). Sifat-sifat reologi gel komposit di bawah mampatan telah ditentukan dengan ujian santeian tekanan (perubahan bentuk linear) dan kajian pemecahan. Ciri-ciri struktur gel telah ditentukan melalui proses pembinaan gel dengan menggunakan ‘rheometer’. Morfologi untul gel yang terpilih telah diterokai selanjutnya daripada imej-imej mikroskop pengimbasan elektron. Hubungan berkaitan dengan struktur, reologi dan tekstur gel telah dinilai dan dibanding antara sistem GII dan sistem GII. Daripada keputusan TPA, gel GII adalah kuat dan elastik manakala gel GII adalah lemah dan rapuh. Walau bagaimanapun, gel GII dan gel GII menunjuk corak dan kadar peruputan yang serupa dalam kajian MEC. Ini buat sementara waktu menyokong

cadangan bahawa GII boleh digunakan sebagai gantian Glt dalam produk makanan. Daripada kajian rekabentuk campuran, Glt dan GII menghasilkan gel komposit yang berbeza daripada ciri-ciri tekstur dan reologi. Untuk kedua-dua sistem Glt dan GII, semua komposit binari dan ternari menunjuk kesan-kesan negatif di mana gel komposit adalah lebih lembut dan lemah berbanding dengan gel komponen tunggal. GII mendorong kesan lelemak dalam tekstur gel komposit. Jalur-jalur rangkaian Glt yang berserabut dan fleksibel mengakibatkan sifat elastik. Manakala, gel GII adalah terbina daripada jalur-jalur rangkaian yang nipis dan lemah, jadi gel tersebut mempunyai keupayaan menyimpan tenaga yang rendah. Kedua-dua gel komposit binari Glt dan GII yang mengandungi MS menunjuk struktur rangkaian saling-tembus yang serupa. Struktur gel komposit binari EW dengan Glt terdiri daripada rangkaian gandingan. Manakala, gel komposit binari EW dengan GII terdiri daripada rangkaian fasa terpisah yang mengandungi fasa EW dan fasa GII. Daripada ujian pemecahan, gel komposit yang mengandungi Glt dikategori sebagai gel yang kuat dan elastik, manakala gel komposit yang mengandungi GII adalah lemah dan rapuh. Nisbah komponen mempengaruhi peralihan sol-gel dalam gel komposit. Selain daripada itu, kelakuan gel komposit adalah terutamanya bergantung kepada jenis dan nisbah komponen. Struktur rangkaian yang tidak seragam menjelas selanjutnya bahawa gel komposit menunjukkan ciri-ciri mekanikal yang lemah. Kesimpulannya, GII berupaya menghasilkan gel komposit yang pecah dengan pantas dan dapat meniru persepsi deria 'lebur-dalam-mulut' tetapi pertimbangan terperinci diperlukan untuk menghasilkan gel komposit dengan tekstur yang disasarkan. Pengetahuan asas yang diperolehi daripada kajian ini dapat memudahkan penggunaan GII sebagai gantian Glt dalam sistem komposit.

## **TEXTURAL AND RHEOLOGICAL PROPERTIES OF GELATIN OR GELLAN IN MAIZE STARCH – EGG WHITE COMPOSITE GELS**

### **ABSTRACT**

Gellan (Gll) has been suggested as one of the gelatin (Glt) alternatives as the Gll gels could provide ‘melt-in-mouth’ sensory perception that is similar to Glt gels. However, the application of Gll as a Glt replacer in composite systems has not been sufficiently explored. The purpose of this study was to elucidate the effects of ingredient proportions on the texture, rheology and structural properties of Glt or Gll composite gels consisted of maize starch (MS) and egg white (EW). These main ingredients were chosen to yield gels based on their practical importance in the food industry. Mixture design experiment was applied as a tool in exploring the interaction effects of different proportions of the components. Textural properties and breakdown behaviour of single component gels were determined by using texture profile analysis (TPA) and multiple extrusion cell analysis (MEC), respectively. Rheological properties of composite gels under compression were determined by using stress relaxation test (linear deformation) and fracture analysis. The structural properties of gels were revealed through the gel formations that were determined by using rheometer. The morphologies of selected gels obtained from scanning electron microscopy images further revealed the structures of gels. The relationships of structure, rheology and texture of the gels were then assessed and compared between Glt and Gll systems. From TPA results, Glt gel was strong and elastic while Gll gel was weak and brittle. However, Glt and Gll gels showed similar decay patterns and rates in MEC test. This tentatively supports the notion of Gll as a Glt replacer in food products. From mixture design experiments, Glt and Gll yielded

composite gels that were remarkably different in terms of texture and rheological behaviours. For both Glt and Gll composite systems, all binary and ternary blends showed antagonistic effects in which the composite gels were softer and weaker as compared to the single component gels. Glt composite gels were comparatively stronger than Gll composite gel for both binary and ternary systems. Gll induced a shortening effect on the texture of the composite gels formed. The network strands of Glt gel were fibrous and flexible resulted in elastic behaviour. Whereas, Gll gel composed of tenuous and weak network strands thus the gel had little capability in storing energy. Both Glt and Gll binary composite gels containing MS showed a similar type of gel structure that consisted of interpenetrating networks. The gel structure of EW binary gel with Glt was composed of coupling networks. While EW binary gel contained Gll consisted of phase separated networks with EW rich and Gll rich domains. From fracture test, composite gels contained Glt were categorised as strong and elastic gels whereas Gll composite gels were weak and brittle. The proportions of components in composite gel systems influenced the sol-gel transition process. Besides, the mechanical behaviour of the composite gels was mainly dependent on the types and proportions of the components. The heterogeneity of network structures of composite gel further explained the weaker mechanical properties of composite gels. In conclusion, Gll might be able to yield composite gels that could break down rapidly and mimic the ‘melt-in-mouth’ sensation but careful selection of component blends was required in order to achieve the targeted texture. The fundamental knowledge obtained from this study could facilitate the application of Gll as a Glt replacer in composite systems.

## CHAPTER 1 INTRODUCTION

### 1.1 BACKGROUND

Gelatin (Glt) has long been used in the food industry to serve as a multi-functional ingredient owing to its unique characteristics. However, the sources of Glt become a main drawback in the food applications. Up to the present, the sources of commercial Glt are mainly produced from pig skin, cattle skins and bones. The issue of Glt replacement arose in the 1980s within Europe with the emergence of bovine spongiform encephalopathy disease (Morrison *et al.*, 1999). In addition, the emerging of Halal, Kosher and vegetarian food markets further elevate the demand for suitable gelatin alternatives (Karim and Bhat, 2008). On the other hand, the low-setting and low-melting characteristic for Glt gels is another disadvantage in formulating food products that are not refrigerated especially in hotter climates (Morrison *et al.*, 1999).

Consequently, researchers and food industry have been trying to develop Glt alternatives since the past decade. The ideal alternatives should possess most of the desired Glt characteristics; namely elasticity, clarity, feasibility in applications and excellent mouthfeel (complete and rapid flavour release). Table 1.1 summarises the possible Glt alternatives in specific food applications as well as their technical constraints for each proposed alternative (Morrison *et al.*, 1999). The details and



problems associated with the proposed Glt alternatives were thoroughly reviewed by Karim and Bhat (2008).

Gellan (Gll) has been proposed as one of the Glt alternatives in food applications (Morrison *et al.*, 1999). Most of the studies on Glt replacers relied on the blends of different types of hydrocolloids in order to achieve certain targeted properties. Thus, a wide range of hydrocolloid blends has been proposed (Table 1.1). Besides, various studies have been carried out to show the versatility of Gll as Glt replacer such as manipulating the ratio of high-acyl and low-acyl Gll blends as well as the modification of the chemical structure of Gll in order to yield gels that give similar characteristics as Glt (Morrison *et al.*, 1999, Chantranukul *et al.*, 2009).

Glt and Gll are both helix-forming hydrocolloids and form gels upon cooling. Glt gels are elastic and thermoreversible that melt at body temperature; while, low-acyl Gll gels are brittle and non-thermoreversible (Williams and Philips, 2003). Compared to Glt, Gll has higher gelation and melting temperatures, however, Gll is able to form gels in a short setting time with only a low level of biopolymer concentration as low as 0.05% (Sworn, 2000). The strength and texture of Gll gels are dependent on ionic strength, while those of Glt gels depend more on the concentration of Glt than ionic strength and pH (Lee *et al.*, 2003).

However, the approach to replace Glt with Gll should be application and process specific. It is unlikely that a universal ingredient, or a system of polysaccharide gums, can replace Glt in every food application (Morrison *et al.*, 1999). On top of that, the successful application of Gll as a gelling agent to provide the desired textural properties in foods depends on a thorough understanding of the relationships between the mechanical properties and interactions amongst gel-forming constituents at the molecular level (Yamamoto and Cunha, 2007).

In food industry, a convenient approach to produce novel food products with the desired functional properties is by manipulating the combinations of different biopolymers. A broad range of characteristics would be expected owing to the diversity and complexity of food ingredients available. Therefore, it is critical to understand the interactions of various components within the system in order to achieve the targeted properties (Elgadir *et al.*, 2012).

On the other hand, the combinations of starch – hydrocolloid and protein – hydrocolloid have long been used in the food industry to overcome certain complications. One of the main limitations is the native starch do not generally meet the ideal properties in food preparations. Besides, the application of protein – hydrocolloid combinations serves the same purpose, where hydrocolloids are usually incorporated to improve or provide the desired properties (BeMiller, 2011).

In food industries, starch and protein are common ingredients that have long been used to improve textural properties of food products. In this study, maize starch (MS) and egg white (EW) were selected as the main components in composite gel systems. On the other hand, composite gels could be regarded as models of real food structures that could also provide fundamental knowledge in product development. The main focus of this research was on the characterisation of textural and rheological aspect of GIt or GIll in composite gel systems composed of MS and/or EW.

Table 1.1: The applications of gelatin on selected food applications and the technical constraints of the current alternatives (adapted from Morrison *et al.*, 1999).

Food application	Desired gelatin properties	Current alternatives	Technical constraints of alternative
Desert gels ( <b>Ready To Eat</b> )	Clarity, elastic texture, melt in mouth	Algin, gellan and carrageenan systems	Hot viscosity, higher set temperature
High-solids confectionery	Elastic texture, clarity, low hot viscosity, low set temperature	Gellan gum blends, carrageenan systems, thinned-starch systems	Set temperature and hot viscosity, texture-elasticity gels
Foamed confectionery – marshmallows	Whipping/aeration agent, foam stabiliser, elastic texture	Gellan/starch/emulsifier blends, modified starch/emulsifiers	Textural constraints – low elasticity and/or high set temperature
Low-fat spreads	Elastic gel texture, fatlike melt mouthfeel, emulsion stabilisation	Sodium alginate/gellan/inulin/simplesse/maltodextrin/gum blends	Cost competitive, but good application for alternatives
Stirred yogurt	Creamy mouthfeel, gelled network prevents separation or syneresis	Gellan/modified starch/xanthan/LBG/pectin/modified starch	High viscosity and high set temperature in culture/production process
Desserts – Mousses	Whipping agent, creamy consistency, low set temperature	Alginate/starch blends	Current production process, stored prior to aeration chilling
Sour cream	Smooth texture, creamy mouthfeel	Gellan gum with modified starch	High set temperature during processing

## **1.2 RATIONALE OF THE STUDY**

In food texture research, one of the ultimate goals is to formulate food products with specific texture and desired sensory attributes. However, a fundamental understanding of the food structure formation and its corresponding texture is required. This study was performed to provide insights on the interactions among selected biopolymers in composite gel systems and the relations between network structures and gel properties in term of textural and rheological aspects.

In order to ease the manipulation of Glt and Gll in food applications, basic knowledge on the functional properties of these ingredients is necessary. Thus, the valuable knowledge generated through this project will contribute to more extensive applications of Glt and Gll in food product development.

## **1.3 HYPOTHESIS AND RESEARCH QUESTIONS**

The overview of research protocol for the current project is summarised in Figure 1.1 based on the notion of Gll could yield gels that mimic the unique ‘melt-in-mouth’ characteristic of Glt gels (Koliandris *et al.*, 2008). It was hypothesised that Gll would reveal the same gelling effects as Glt in composite gel systems as Gll and Glt are both helix-forming biopolymers that form gels on cooling. However, there is a lack of studies to comparatively assess between Gll and Glt in composite gel systems.

The specific hypothesis was that composite gels with similar textural and rheological properties could be yielded by manipulating the proportions of Glt or Gll with MS and EW. This study addressed a number of issues in relation to the interactions of Glt or Gll with other biopolymers and the specific research questions in revealing these issues include:

1. How are Glt and Gll simple gels similar or different from in term of texture and breakdown behaviour?
2. Whether Gll can yield similar texture and rheological properties as Glt in composite gel systems?
3. How are texture, rheology and structure of model gels influenced by the ingredient proportions in composite gel systems?

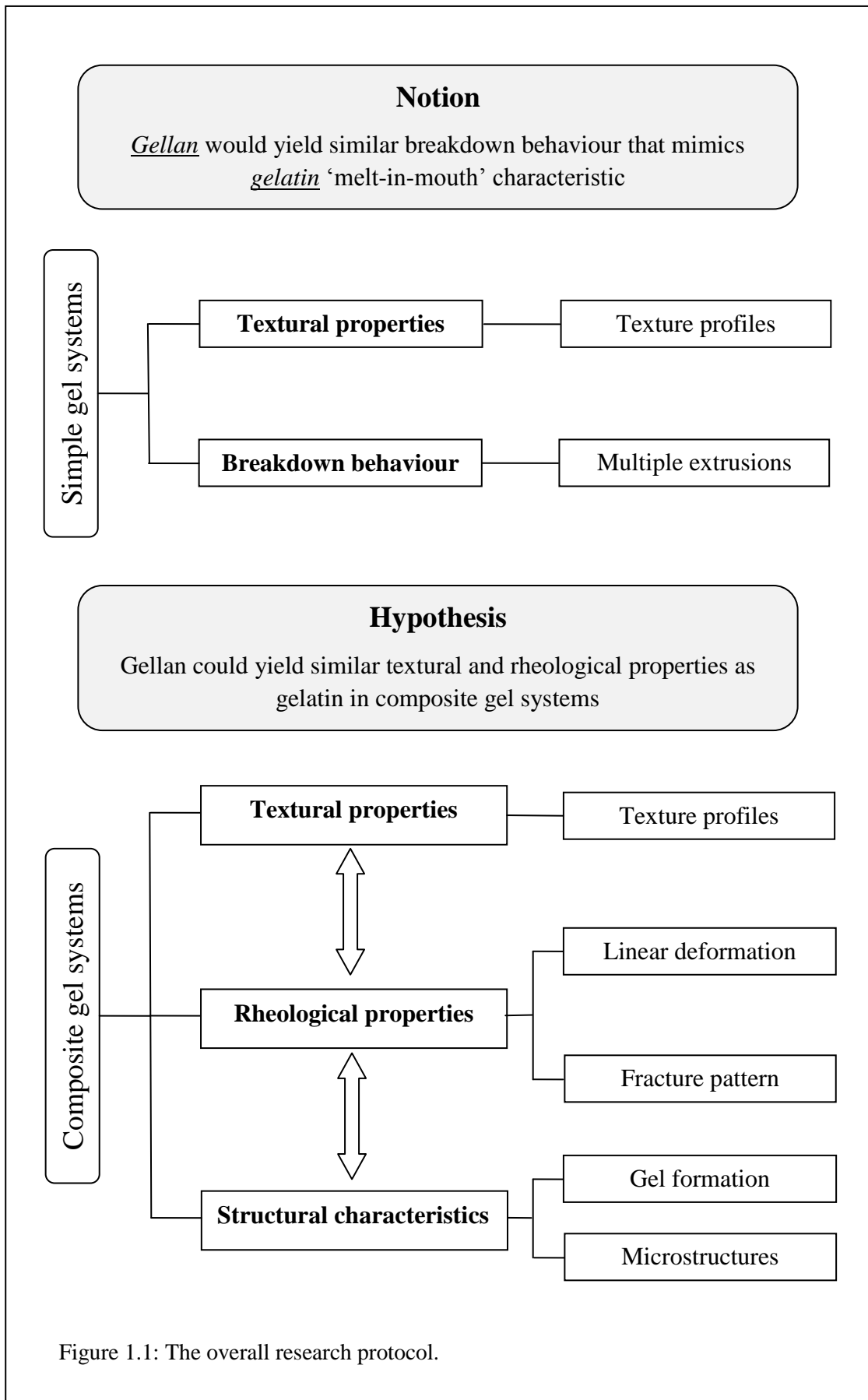


Figure 1.1: The overall research protocol.

## 1.4 OBJECTIVES

The main objective of this research was to understand the interactions among different biopolymers in Glt or Gll composite gel systems containing of MS or/and EW. Subsequently, the textural, rheological and structural properties of these composite gel systems were comparatively assessed. In order to achieve the main objective, the specific objectives were drawn:

- To investigate the texture and breakdown behaviour of Glt and Gll in simple gel systems.
- To characterise and compare the influence of ingredient proportions on textural properties of Glt and Gll composite gel systems containing MS or/and EW.
- To comparatively study the influence of ingredient proportions on the rheological properties (small deformation, large deformation and fracture) of Glt and Gll in composite gel systems containing MS or/and EW.
- To reveal the formation of gel networks and the relationships between structure and textural properties of the gels.



## **1.5 THESIS OUTLINE**

The textural, rheological and structural characteristics of Glt and Gll in composite gels containing MS or/and EW on is presented in this thesis. The main body of this thesis consists of a general introduction and background, literature reviews, material and methods, results and discussions, overall conclusion as well as recommendations for future studies.

Chapter ONE is a general introduction on the background of this study regarding the issues of Glt replacement encountered in the food industry. The proposed alternatives and challenges in the applications are briefly discussed. Besides, the rationales of this study are presented. Finally, the hypothesis and objectives are stated together with a series of research questions.

Chapter TWO is a general literature review of the biopolymers used in this study regarding their structure, functions and gelling mechanisms.

Chapter THREE listed down the materials, design of experiment as well as the methodology for every single assay conducted for the whole study.

The experimental results and discussions are depicted in Chapter FOUR. Generally, the experimental results are divided into five sub-sections. The first section reveals the texture profiles and structural breakdown properties of Glt and Gll in simple gel systems. The finding of this study was used as a preliminary basis to proceed with further studies. In the following two sections (Section 4.2 and 4.3), mixture design experiment was applied to investigate the influence of gelling

component proportions on textural and rheological properties. The former section characterises and compares the textural properties of gels yielded according to the designated blends, while the latter section shows the rheological properties through linear deformation (stress relaxation) and fracture behaviours of the gels. Section 4.4 discusses the processes of network formation and mechanical spectra through dynamic oscillatory measurements. While, the last section (Section 4.5) discloses the gel formation mechanism and the microstructural information through gel morphologies from SEM micrographs. Each subsection is summarised to evaluate the proposed research questions and hypothesis established in Chapter One.

The last chapter (Chapter FIVE) provides the overall conclusion for the whole study and recommendation for future studies.

## **CHAPTER 2 LITERATURE REVIEW**

### **2.1 DESCRIPTION OF THE GEL SYSTEMS STUDIED**

Globular proteins and polysaccharides are two major components that occurred naturally or added into food systems to control structure, texture and stability of the products (Foegeding, 2007). The gel systems selected in this study were aimed to resemble real food products. All the ingredients were chosen for the practical importance as food ingredients that are mainly used to contribute to the food structure.

### **2.2 GELATIN**

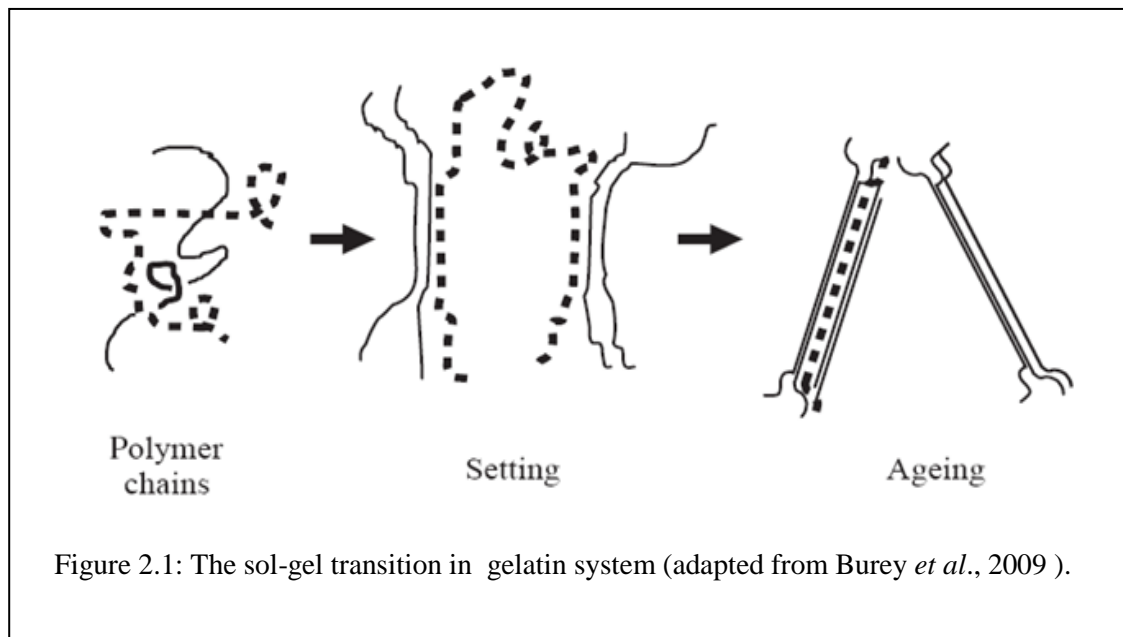
Gelatin (Glt) is widely used in the food industry as a gelling, thickening, texturising, water-binding, emulsifying or/and stabilising agent. Glt is derived from hydrolytic degradation of collagens through either acid or alkaline treatment; producing Type A Glt and Type B Glt, respectively. The typical isoelectric point range for Type A Glt and Type B Glt is 7.5 – 9.0 and 4.6 – 5.2, respectively. During extraction of Glt, most of the asparagin and glutamine would be hydrolysed to aspartic acid and glutamic acid, respectively. The extent of hydrolysis is more pronounce under alkaline condition and therefore resulting in lower isoelectric point for Type B Glt (Harrington and Morris, 2009). Glt is not a nutritionally complete protein and consists mainly of glycine, proline and hydroxyproline. The backbone of

Glt is composed of three main groups of amino acids: ~ 13% positively charged (lysine and arginine), ~ 12% negatively charged (glutamic and aspartic acid) and ~ 11% hydrophobic (leucine, isoleucine, methionine and valine) (Chatterjee and Bohidar, 2006). The composition and sequence of the amino acids vary depending on the collagen source and treatment (Poppe, 1992). Structurally, Glt molecules are extended polypeptide chains, which are associated laterally at various sites to form bundles. These bundles together form crystalline regions. The typical molecular weight of a random coil individual molecule is approximately of 20 kDa (Glicksman, 1969a).

### **2.2.1 Gelling mechanism of gelatin**

Glt is not soluble in cold water but swells and forms large visible particles known as 'fish eyes' (Glicksman, 1969a). When heated to above 40 °C, the hydrated particles dissolve due to the rupture of molecular aggregates and form flexible single random coils (Picout and Ross-Murphy, 2002). Upon cooling, the polypeptide chains form a triple-helical structure through entanglements of molecular chains via junction zone formations (Ledward, 2000). These junction zones are formed with two of participating strands from the same Glt molecule and the third from another molecule (Mao *et al.*, 2001). Glt gel is highly elastic due to the junction zones that are formed by the flexible interconnected peptide chains (Karim and Bhat, 2008). The three-dimensional Glt network is held together by primary bonds, as well as localised and non-localised secondary forces at certain points on the molecules (Glicksman, 1969a). This Glt gel network is weakly held by intermolecular hydrogen

bonds, thus the sol-gel transition is reversible and the gel will melt when it is heated to 35-40 °C (Ledward, 2000). The sol-gel transition of Glt involves two important steps term as setting and ageing as shown in Figure 2.1. The irregular regions of the Glt triple helices link together during setting to form a network throughout the solution. During ageing, the Glt gel is strengthened through continuous adjustment of the molecular network. Consequently, the network thickens and becomes more fibrillar (Burey *et al.*, 2009).



In general, Glt gels are elastic and transparent owing to the flexible and fine-stranded network. The unique characteristic of Glt is its ability to form thermoreversible gels that ‘melt-in-mouth’ to provide excellent mouthfeel and flavour perception (Ledward, 2000, Bayarri *et al.*, 2003). As Glt chains have positive

and negative sites, the electrostatic interactions play an important role in the process of gel stabilisation. Therefore, the gel strength depends greatly on the environmental factors, i.e., pH and ionic conditions (Chatterjee and Bohidar, 2006). At low pH, acidic amino acids become uncharged thus the polymer has significant net positive charge. In contrast, Glt molecule becomes net negative charged as the pH increases. When the surrounding pH approaches the isoelectric point, the positive and negative charges almost cancel off and the molecule becomes virtually uncharged (Harrington and Morris, 2009). On the other hand, the presence of strong electrolytes effectively screens the electrostatic interactions between the charged sites allowing the triple helical molecules to reorganise freely and thus results in weaker gels (Chatterjee and Bohidar, 2006).

### **2.3 GELLAN**

Gellan (Gll) is approved by the Food and Drug Administration (FDA) in 1992 for food applications and it is mainly used as a gelling and texturing agent in confectionery and dairy products (Evageliou *et al.*, 2010). Gll is an extracellular anionic heteropolysaccharide produced from aerobic fermentation of bacterium *Sphingomonas elodea* (formerly known as *Pseudomonas elodea*). This biopolymer is a tetrasaccharide repeated unit comprises 1,3- $\beta$ -D-glucose, 1,4- $\beta$ -D-glucuronic acid, 1,4- $\beta$ -D-glucose and 1,4- $\alpha$ -L-rhamnose. These saccharides are linked together to form a linear primary structure with a molecular weight of ~ 500 kDa (Nussinovitch, 1997, Urayama *et al.*, 2008). Two types of Gll biopolymers are commercially available, i.e., high-acyl Gll and low-acyl Gll. The chemical structures for both Gll molecules

are depicted in Figure 2.2. High-acyl GII is the native form of polymer that contains O-5-acetyl and O-2-glyceryl groups on the (1→3)-linked glucose residue. The low-acyl GII is obtained through high temperature alkaline treatments where both acyl groups are hydrolysed. However, deacylation does not alter the helical structure but improves the intermolecular association and crystallinity of the biopolymer (Mao *et al.*, 2000). For low-acyl GII, each tetrasaccharide unit contains a negatively charged carboxylate group that helps to stabilise the double helix conformation and strengthen the junction zones in the gel network (Tang *et al.*, 1996). Throughout the whole project, the term ‘gellan (GII)’ was used to refer to the low-acyl GII.

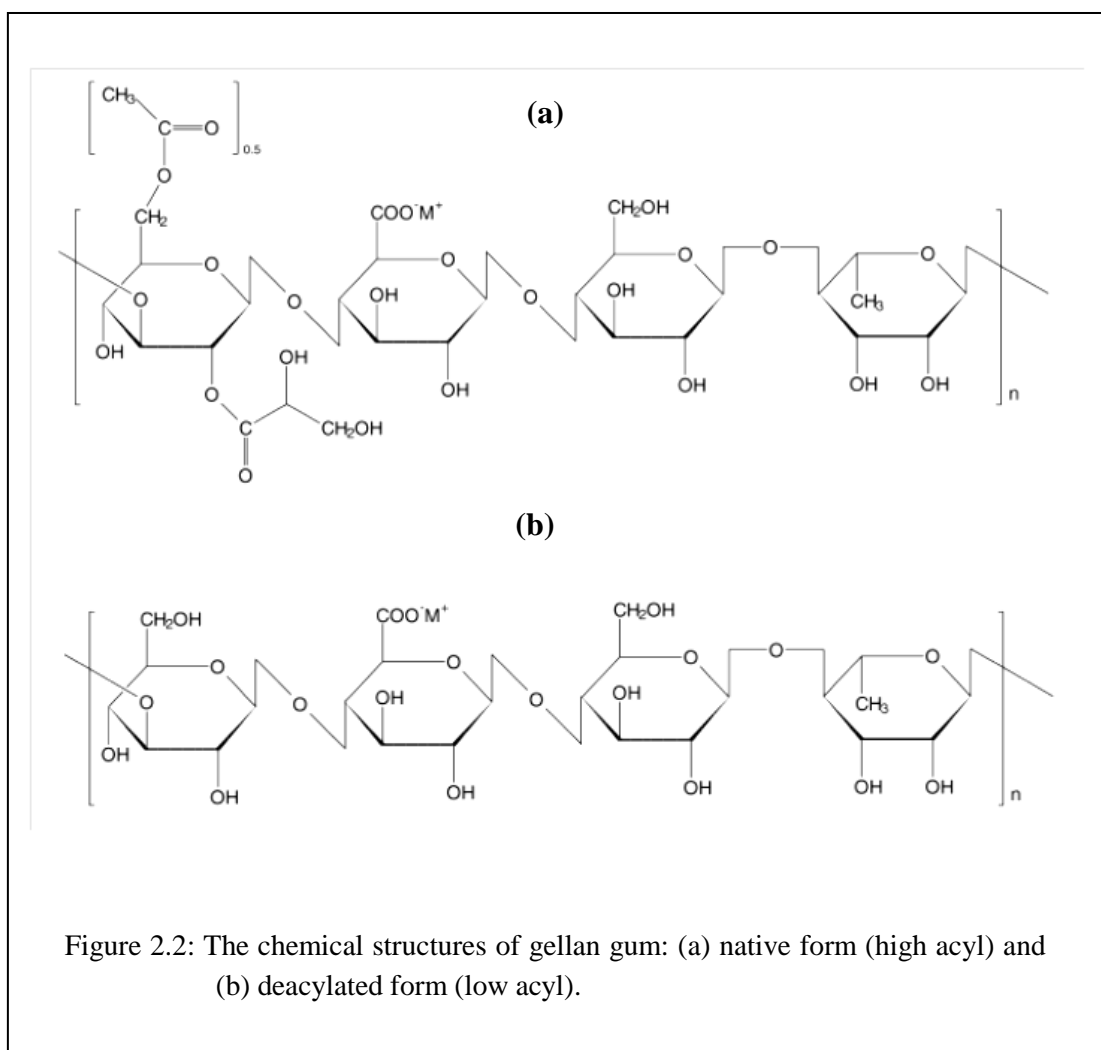


Figure 2.2: The chemical structures of gellan gum: (a) native form (high acyl) and (b) deacylated form (low acyl).

### 2.3.1 Gelling mechanism of gellan

The linear anionic GII biopolymer can only hydrate partially in cold deionised water, it is necessary to heat the dispersion to at least 70 °C in order to achieve complete hydration (Gibson, 1992). The gelling mechanism of GII gum is illustrated in Figure 2.3. In hot aqueous solutions, GII chains appear in disordered random single coils. Upon cooling, GII chains form threefold left-handed double helices that are stabilised by internal hydrogen bonds. The coil-helix transition occurs in the temperature range from 30 to 50 °C. Above the critical gelling concentration, the helices tend to self-associate and form a transparent gel (Sworn, 2000). The GII double helices can further associate in the presence of cations and lead to the formation of an interconnected three-dimensional gel network (Yamamoto and Cunha, 2007).

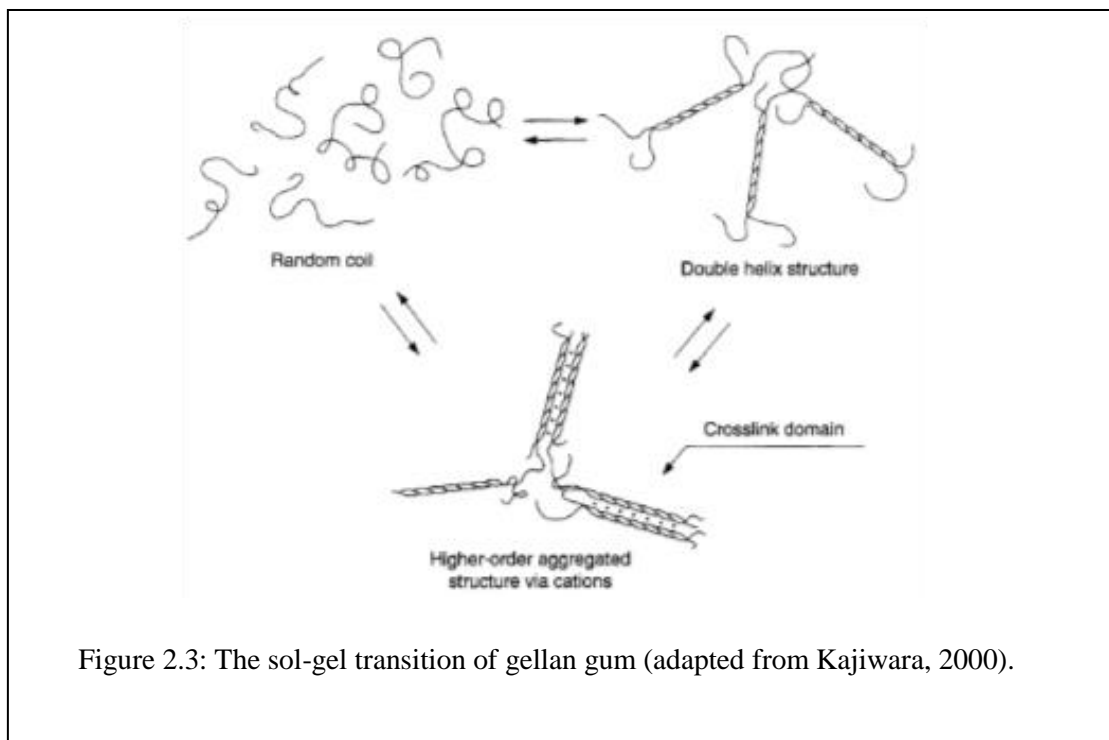


Figure 2.3: The sol-gel transition of gellan gum (adapted from Kajiwara, 2000).



The high-acyl GII produces soft, elastic and thermoreversible gels; while the low-acyl GII gels are firm to touch, brittle and usually non-thermoreversible (Huang *et al.*, 2007). Gels formed by GII are characterised by sparkling clarity (highly transparent), excellent flavour release, no flavour-masking, rapid setting behaviour and low gelling concentrations (Saha and Bhattacharya, 2010). Low-acyl GII is capable of forming self-supporting gels at concentrations as low as 0.05% w/w gum (Sworn, 2000). The texture of GII gels depends on several factors including gum concentration, pH, temperature and the presence of cations, acids and co-solute (e.g., sugars) (Kawai *et al.*, 2007). Carboxyl groups in GII chains are weakly acidic and the degree of dissociation in aqueous systems is dominated by the dissociation constant. At lower pH levels, the fraction of dissociated carboxyl groups is smaller resulting in less anionic chains that aggregate more easily owe to lower electrostatic repulsion. Thus, the strength of GII gel increases with lowering the pH (Yamamoto and Cunha, 2007).

## **2.4 MAIZE STARCH**

Starch is a major food ingredient that presents naturally or is added in food formulations to build up structure, texture and physical properties of many food products (Sui, 2007). For gelled food products, starch is mainly used as support functions, i.e., to improve mouthfeel, to increase nutritional values and to reduce the amount of primary gelling agents (Williams *et al.*, 2004). Raw starch exists in a white granule form and shows birefringence. The biopolymer is held together by an extended micellar network of molecules bound by hydrogen bondings. Chemically,

starch is composed of two different types of  $\alpha$ -glucan polymers, i.e., amylose and amylopectin. Maize (corn) is the largest commercial source of starch that is widely used in food products as a thickening, gelling, and water-retention agent. Normal maize starch (MS) consists of about 25%wt amylose and about 75%wt amylopectin (Sandhu and Singh, 2007). As exhibited in Figure 2.4, amylose has a linear or slightly branched structure exclusively consisting of  $\alpha$ -1,4-linked glucose residues. Whereas, amylopectin is highly branched with a cluster model description consisting of short linear chains of  $\alpha$ -1,4-linked glucose residues and  $\alpha$ -1,6-linked branched points (Glicksman, 1969a).

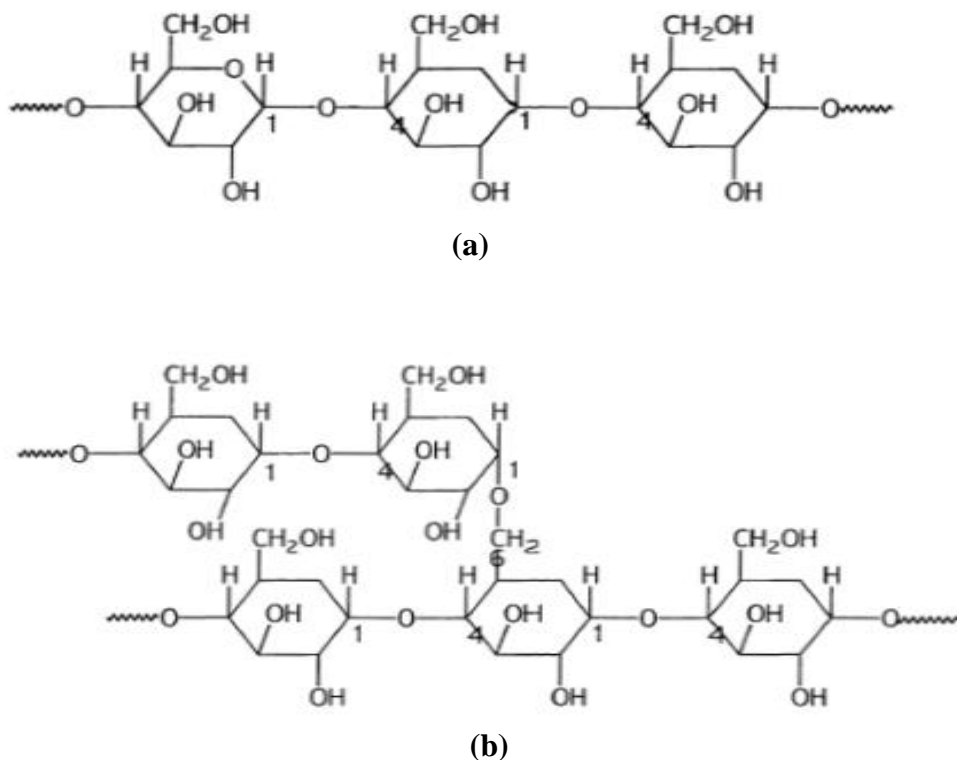


Figure 2.4: The chemical structures of: (a) amylose and (b) amylopectin.

### 2.4.1 Gelling mechanism of maize starch

The gelling mechanism of starch involves two stages, i.e., gelatinisation and retrogradation, as depicted in Figure 2.5. Starch granules can only disperse in cold water to form slurries. When the slurry is heated above the gelatinisation temperature, hydrogen bonds in amorphous regions are disrupted and water molecules become attached to the liberated hydroxyl groups. Consequently, starch granules start to hydrate and swell resulting in leach out of soluble components (mainly amylose) (BeMiller, 2011). Upon cooling, retrogradation occurs where the linear amylose chains orient in a parallel alignment. Thus, a large number of hydroxyl groups along the amylose chains are in close proximity to those of the adjacent chains forming insoluble aggregates that further arrange to form a three-dimensional network (Glicksman, 1969b).

Starch gels are commonly regarded as composite systems consist of swollen particles embedded in an interpenetrating amylose matrix. While, the dispersed phase of the network consists of amylopectin and granule remnants (BeMiller, 2011). The structure of starch gel depends greatly on starch concentrations, amount of leached-out components, configuration of swollen granules and the ratio of amylose/amylopectin as well as their interactions (Kapri and Bhattacharya, 2008). However, the characteristics of starch gel are mainly governed by the volume fraction of the dispersed granular particles, the degree of swelling, rigidity and surface interactions (Burey *et al.*, 2009).

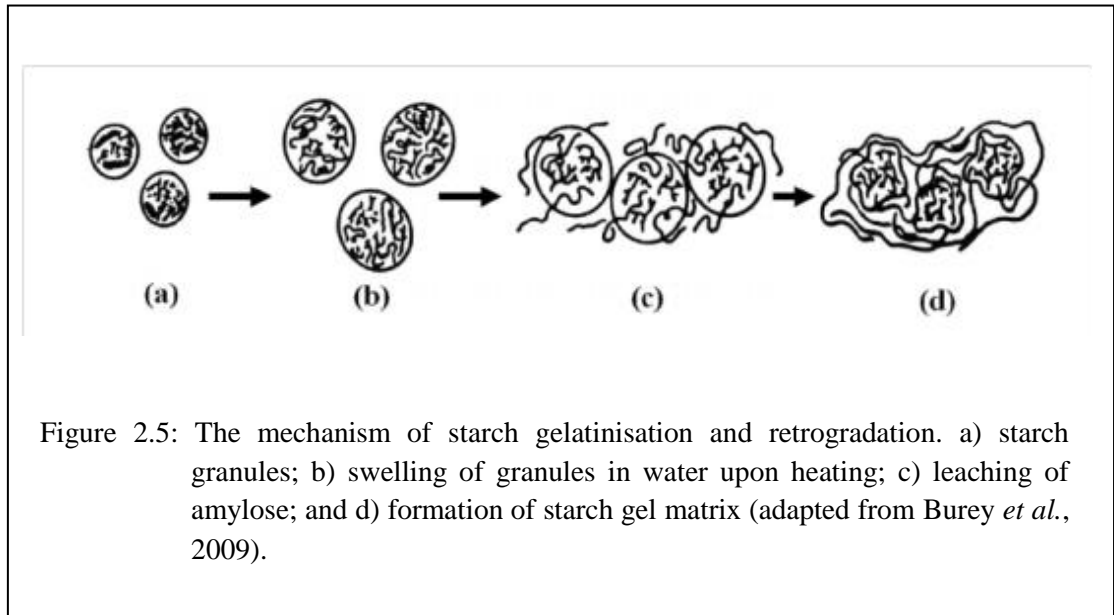


Figure 2.5: The mechanism of starch gelatinisation and retrogradation. a) starch granules; b) swelling of granules in water upon heating; c) leaching of amylose; and d) formation of starch gel matrix (adapted from Burey *et al.*, 2009).

## 2.5 EGG WHITE

Egg albumen or egg white (EW) provides excellent functional and nutritional properties in food applications. It has been extensively used in many foods such as bakery, dairy and meat products to increase protein content and to provide desired functional properties (Wongsasulak *et al.*, 2007). The native EW solution consists approximately of 13 globular proteins while the EW powder contains ~ 95.5% of proteins on dry basis (Christ *et al.*, 2005). The major proteins of EW are ovalbumin (~ 54%), ovotransferrin (~ 12%), ovomucoid (~ 11%), ovomucin (~ 3.5%), and lysozyme (~ 3.4%). The range of isoelectric point for most EW proteins is from 4 to 5 (Weijers *et al.*, 2006).

### 2.5.1 Gelling mechanism of egg white

Heat-induced gelation of EW is one of its important functional properties with respect to the application in food products. Gel formation of globular proteins is a complex process, which often involves several reactions such as denaturation, dissociation-association, and aggregation. The gelling mechanism of EW is considered to be similar to other globular proteins and can be performed in three steps. During the early stage of heating, the native structures of EW proteins are disrupted where the protein chains are partially unfolded and expose the reactive sites (i.e., sulfhydryl groups or hydrophobic groups).

The initial phase of gelation involves hydrophobic interactions between proteins followed by the aggregation of proteins through sulfhydryl–disulfide interchange and sulfhydryl oxidation within the aggregates to form a gel network. This occurs when the attractive forces between the molecules are sufficiently strong to overcome the repulsive forces. The third step is the occurrence of multiple hydrogen bondings that takes place upon cooling (Christ *et al.*, 2005, Donato *et al.*, 2005a, Dranca and Vyazovkin, 2009). Above the critical concentration, protein molecules aggregate and lead to the formation of three-dimensional gel network. Protein aggregation and subsequent network formation is a complex process that depends on several factors such as protein concentration, ionic strength, pH and salts (Raikos *et al.*, 2007).

Generally, gelation of globular protein forms two types of networks: stranded and particulate gels. The translucent fine-stranded protein gels are formed at either a low or high pH range. The gels formed at low pH are weak and brittle, while those

formed at high pH are strong and elastic (Foegeding, 2005). Whereas, the opaque particulate gels are formed under conditions with minimal repulsive forces (i.e., at a pH range closes to pI or at high ionic strength). However, an intermediate structure between stranded and particulate mixed network might exist (Li *et al.*, 1999).

## **2.6 FOOD GELS**

Food gels are of tremendous commercial importance, since the ability to control texture of foods is crucial for appealing to consumers. Food gels can vary from strong and highly integrated gels (i.e., meat chunks, hard-boiled egg, jelly pudding, custard and tofu) to weak and thickening gels (i.e., gravies and sauces). Generally, food gels are often viscoelastic, which means the gels behave like a solid in a short time-scale, but more like a fluid at a long time-scale (Renkema, 2001). In food products, gels mainly contribute to structure and stability. Therefore, gels have been served as model systems in texture studies to provide good descriptions of rheological and mechanical behaviours of real food products (Jones *et al.*, 2003, Li Yuet Hee *et al.*, 2008).

### **2.6.1 Single component gels**

Single component gels (SCG) are the simplest molecular network that could serve as ideal models for studying simple food systems in terms of gelling mechanisms, rheological and mechanical characteristics. Such gels represent the first

step towards a description of more complex composite gels (Brownsey and Morris, 1988).

### **2.6.2 Composite gels**

Gels composed of two or more different biopolymers are known as ‘multicomponent’, ‘mixed’ or ‘composite’ gels. In this study, two types of composite gels were classified, i.e., binary composite gel (BCG) and ternary composite gel (TCG) that consisted of two- and three-biopolymers, respectively.

In composite systems, the knowledge of chemical and physical interactions among the components is a fundamental requirement to develop the target gelled products. The effects of individual component in a mixture system should also be elucidated. These composite systems are ideal for texture studies as a wide range of texture could be generated by manipulating the types and proportions of components, as well as the processing conditions (Aguilera and Stanley, 1999, Foegeding, 2007).

Upon mixing of different biopolymers, two kinds of intermolecular interactions can occur: ‘association’ and ‘segregation’, depending on the thermodynamic compatibility (Morris, 2009). The thermodynamic compatible biopolymers will mix together and associate between each other. On the contrary, the thermodynamic incompatible biopolymers are not miscible, but segregate into regions where the molecules will bind with similar molecules resulting in phase separations (Tolstoguzov, 1996). In most cases, mixing of two or more biopolymers will lead to