

**EFFECTS OF FILLER LOADING AND DIFFERENT PREPARATION  
METHODS ON THE PROPERTIES OF CASSAVA STARCH FILLED  
NATURAL RUBBER COMPOSITES**

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**UNIVERSITI SAINS MALAYSIA  
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NATURAL RUBBER COMPOSITES**

**by**

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## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	i
TABLE OF CONTENTS	ii
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	xiii
LIST OF SYMBOLS	xv
ABSTACK	xvi
ABSTRACT	xvii
CHAPTER 1: INTRODUCTION	1
1.1    Overview	1
1.2    Problem Statement	3
1.3    Research Objectives	4
CHAPTER 2: LITERATURE REVIEW	6
2.1    Natural Rubber	6
2.1.1    Classification of Natural Rubber	7
2.1.2    Natural Rubber Latex	8
2.1.3    Standard Malaysia Rubber	10
2.2    Cassava Starch	12
2.2.1    Cassava Starch	12
2.2.2    Cassava Starch as Filler for Rubber	15
1)    Starch Gelatinization	17

2)	Starch Retrogradation	20
3)	Starch Syneresis	21
2.2.3	Cassava Starch/Natural Rubber Composite.	22
2.2.4	Starch/Rubber Composites Preparation Methods	26
1)	Direct blending method	26
2)	Co-coagulation method	28
3)	Free-drying method	30
2.3	Rubber Compounding	31
2.3.1	Mixing	32
2.3.2	Forming	33
2.3.3	Curing	34
2.4	Vulcanizing Ingredients	35
2.4.1	Accelerators	36
2.4.2	Activators	37
2.4.3	Antioxidants	38
2.4.4	Special-Purpose Ingredients	38
CHAPTER 3 : RESEARCH AND METHODOLOGY		41
3.1	Materials	41
3.2	Equipments	42
3.3	Compounding Process	42
3.3.1	Formulation	42
3.3.2	Compounding Process	43
1)	Direct blending method	43
2)	Co-coagulation method	46

3) Freeze drying method	46
3.4 Curing Characteristics	47
3.5 Sample Preparation	48
3.6 Tensile and Tear Test	49
3.7 Hardness Test	50
3.8 Swelling Test	50
3.9 Thermogravimetric Analysis	51
3.10 X-ray Diffraction Analysis	51
3.11 Scanning Electron Microscopy	52
CHAPTER 4 : RESULTS AND DISCUSSION	53
4.1. The Effects of Filler Loading on the Properties of Cassava Starch/Natural Rubber Composites	53
4.1.1 Introduction	53
4.1.2 Curing Characteristics	53
4.1.3 Mechanical Properties	56
4.1.4 Hardness	60
4.1.5 Swelling Behavior	61
4.1.6 Scanning Electron Microscopy (SEM)	62
4.1.7 X-ray Diffraction (XRD) Analysis	63
4.2. A Comparative Study between the Direct-Blending and Co-coagulation Methods	65
4.2.1 Introduction	65
4.2.2 Curing Characteristics	65
4.2.3 Mechanical Properties	69

4.2.4	Hardness	73
4.2.5	Swelling Behavior	74
4.2.6	Thermogravimetric Analysis (TGA)	75
4.2.7	Scanning Electron Microscopy (SEM)	77
4.2.8	X-ray Diffraction (XRD) Analysis	80
4.3.	The Effects of Freeze-drying Method on The Properties of Cassava Starch/Natural Rubber Composites	82
4.3.1	Introduction	82
4.3.2	Curing Characteristics	82
4.3.3	Mechanical Properties	83
4.3.4	Hardness	86
4.3.5	Thermogravimetric Analysis (TGA)	87
4.3.6	Scanning Electron Microscopy (SEM)	90
4.3.7	X-ray Diffraction (XRD) Analysis	94
CHAPTER 5 : CONCLUSIONS		96
5.1	Conclusions	96
5.1.1	The effects of filler loading on the properties of cassava starch/natural rubber composites.	96
5.1.2	A comparative study between the direct blending and co-coagulation methods for cassava starch/NR composites	97
5.1.3	The effects of freeze-drying method on the properties of cassava starch/NR composites.	98

5.2	Suggestions for Further Studies	99
	REFERENCES	100
	PUBLICATIONS	105



## LIST OF TABLES

		Page
Table 2.1	Composition and Physical Properties of Natural Rubber Latex as Obtained from the Field.	8
Table 2.2	Requirements for specified latex types.	9
Table 2.3	SMR L properties and specifications.	10
Table 2.4	Starch granular size from different plant.	12
Table 2.5	Typical composition of cassava starch.	14
Table 2.6	Mechanical properties of starch/rubber composites with 10 phr starch.	25
Table 2.7	Values of modulus ( $E_1$ %), elongation ( $e_r$ ) and ultimate tensile strength (UTS) determined for the blends conditioned at 53% relative humidity.	25
Table 2.8	A general rubber formulation.	31
Table 3.1	List of materials and functions.	41
Table 3.2	Equipments used in the research.	42
Table 3.3	Formulation CS/NR composites.	43
Table 3.4	Compounding process for gum compounds.	44
Table 3.5	Compounding process for filled composites.	45
Table 4.1	Thermal degradation of NR gum vulcanizate, CS/NR composites with different preparation methods.	77
Table 4.2	Curing characteristics of NR and its composite.	83
Table 4.3	Weight loss (%) and maximum temperature of the rate of thermal decomposition reaction ( $T_{max}$ ) for natural rubber and CS/NR composite.	89

## LIST OF FIGURES

	Page
Figure 2.1	(a) <i>cis</i> -1, 4-polyisoprene, (b) <i>trans</i> -1, 4-polyisoprene. 6
Figure 2.2	General natural rubber types and grades. 7
Figure 2.3	Processing routes by which raw materials are converted into the various grades of Standard Malaysian Rubber. 11
Figure 2.4	SEM images for (a) corn (b) potato (c) cassava (d) rice (e) wheat and (f) sago starches with their respective size indicator. 13
Figure 2.5	The chemical composition of starch. 15
Figure 2.6	Enzymatic reaction of starch. 16
Figure 2.7	Schematic presentation of starch gelatinization. 18
Figure 2.8	Typical starch transition phase diagram. 19
Figure 2.9	Starch gelatinization (A to B) and retrogradation (B to C) process. 20
Figure 2.10	Comparison between sago starch syneresis profiles with other cereal starches. 21
Figure 2.11	Scorch time and cure time of NR-g-PMMA blends at various quantities of cassava starch. 23
Figure 2.12	Variation of mechanical properties of NR/starch composites via starch content. 24
Figure 2.13	Physico-mechanical properties as a function of starch content. 26
Figure 2.14	SEM micrographs of starch particles and the tensile fracture surface of starch/rubber composites: (a) starch particles; (b) starch/SBR composite prepared by direct blending. 27
Figure 2.15	SEM micrographs of starch particles and the tensile fracture surface of starch/rubber composites: (a) starch particles; (b) starch/SBR composite prepared by co-coagulation. 28

Figure 2.16	SEM micrographs of starch powder (A) and freeze-fractured surface of NR/starch composite (B).	29
Figure 2.17	Scanning electron micrographs of vertical sections inside tablets compacted from amorphous waxy maize starches dried under different conditions.	30
Figure 2.18	Flow chart of rubber compounding.	32
Figure 2.19	<i>N</i> -isopropyl- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine (IPPD).	38
Figure 3.1	Cure curves for a maximum torque with reversion.	48
Figure 3.2	Shape and dimension of tear test specimen in trouser type.	50
Figure 4.1	Effect of cassava starch loading on scorch time and cure time of cassava starch filled natural rubber composites.	54
Figure 4.2	Effect of cassava starch loading on cure index of cassava starch filled natural rubber composites.	55
Figure 4.3	Effect of cassava starch loading on maximum torque ( $M_H$ ) of cassava starch filled natural rubber composites.	56
Figure 4.4	Tensile strength of cassava starch filled natural rubber composites at different cassava starch loadings.	57
Figure 4.5	Effect of cassava starch loading on the Elongation at break of cassava/NR composites.	58
Figure 4.6	M100 and M300 of cassava starch filled natural composites rubber at different cassava starch loadings.	69
Figure 4.7	Effect of cassava starch loading on the tear strength of CS/NR composites.	60
Figure 4.8	Hardness of Cassava starch filled NR composites at different cassava starch loading.	61

Figure 4.9	Effect of cassava starch loading on swelling percentage of NR composites.	62
Figure 4.10	SEM micrographs of cassava starch particles and composites: (a) pure CS; (b) CS (10 phr)/NR composite; (c) CS (20 phr)/NR composite; (d) CS (25 phr)/NR composite.	63
Figure 4.11	X-ray diffraction patterns of CS and CS /NR composites: (a) pure CS; (b) pure NR; (c) CS/NR composite.	64
Figure 4.12	Effect of cassava starch loading on scorch time of cassava starch filled natural rubber composites.	66
Figure 4.13	Effect of cassava starch loading on cure time of cassava starch filled natural rubber composites.	67
Figure 4.14	Effect of cassava starch loading on cure index of cassava starch filled natural rubber composites.	67
Figure 4.15	Effect of cassava starch loading on Maximum torque of cassava starch filled natural rubber composite.	68
Figure 4.16	Effect of cassava starch loading on the tensile strength of CS/NR composites prepared by different methods.	70
Figure 4.17	Effect of cassava starch loading on the tensile strength of CS/NR composites prepared by different methods.	70
Figure 4.18	Effect of cassava starch loading on the elongation at break of CS/NR composites.	71
Figure 4.19	Effect of cassava starch loading on the tensile modulus M100 of CS/NR composites prepared by different methods.	72
Figure 4.20	Effect of cassava starch loading on the tensile modulus M300 of CS/NR composites prepared by different methods.	73
Figure 4.21	Effect of cassava starch loading on the hardness of CS/NR composites.	74

Figure 4.22	Effect of cassava starch loading on swelling percentage of CS/NR composites prepared by different methods.	75
Figure 4.23	TG cure of NR and composites (a) NR; (b) CS (10phr)/NR composites prepared by direct blending; (c) CS (10phr)/NR composites prepared by co-coagulation.	76
Figure 4.24	DTG curves of NR and composites. (a) NR; (b) CS (10phr)/NR composites prepared by direct blending; (c) CS (10phr)/NR composites prepared by co-coagulation.	77
Figure 4.25	SEM micrographs of cassava starch particles and composites: (a) pure cassava starch; (b) B-CS/NR (10 phr)/NR composite; (c) B-CS/NR (20 phr)/NR composite; (d) C-CS/NR (10 phr)/NR composite; (e) C-CS/NR (20 phr)/NR composite.	79
Figure 4.26	X-ray diffraction patterns of cassava starch and CS/NR composites: (a) Cassava starch paste; (b) Pure NR; (c) C-CS/NR composites.	81
Figure 4.27	Effect of cassava starch loading on tensile strength of CS/NR composites.	84
Figure 4.28	Effect of cassava starch loading on tensile elongation at break of CS/NR composite.	85
Figure 4.29	Effect of cassava starch loading on modulus (M100, M300) of CS/NR composites.	85
Figure 4.30	Effect of cassava starch loading on hardness of CS/NR composites.	87
Figure 4.31	TG cure of NR and composites (a) NR; (b) CS (10phr)/NR composites; (c) CS (20phr)/NR composites.	88
Figure 4.32	DTG curves of NR and composites. (a) NR; (b) CS (10phr)/NR composites; (c) CS (20phr)/NR composites.	89
Figure 4.33	SEM images of NR gum vulcanizate.	90
Figure 4.34	SEM images of cassava starch filled NR composite at 5 phr of cassava starch.	91

Figure 4.35	SEM images of cassava starch filled NR composite at 20 phr of cassava starch.	92
Figure 4.36	SEM micrographs of cassava starch particles and composites: (a) pure cassava starch; (b) B-CS/NR (10 phr)/NR composite; (c) F-CS/NR (10 phr)/NR composite; (d) C-CS/NR (10 phr)/NR composite.	93
Figure 4.37	Schematic representation of the structure of the CS/NR composites	94
Figure 4.38	X-ray diffraction patterns of cassava starch and CS/NR composites: (a) Cassava starch; (b) 10CS/ NR composite; (c) 20CS/NR composite.	95

## LIST OF ABBREVIATIONS

ASTM	American Standard for Testing and Materials
ADS	Air Dried Sheets
CS	Cassava starch
CH <sub>3</sub>	Methyl group
C <sub>5</sub> H <sub>8</sub>	Cis-1,4-polyisoprenne
CaCl <sub>2</sub>	Calcium chloride
CRI	Cure Rate Index
DPNR	Deproteinized Natural Rubber
DPG	Diphenyl guanidine
DRC	Dry Rubber Content
EB	Elongation at Break
HA	High Ammonia
IDDP	N-isopropyl-N'-phenyl-p-phenylenediamine
MBTS	Dibenzothiazonle Disulfide
MDR	Monsanto Moving Die Rheometer
MST	Chemically Modified Starch Paste
M100	Stress at 100% Elongation
M300	Stress at 300% Elongation
NR	Natural rubber
NRL	Natural Rubber Latex
PBA	Polybutylacrylate
PRI	Plasticity Retention Index
SEM	Scanning Electron Microscope

SMR L	Standard Malaysia Rubber Grade L
SMR CV	Standard Malaysia Rubber Constant Viscosity
TGA	Thermo Gravimetric Analysis
TSR	Technically Specified Rubber
RSS	Ribbed Smoked Sheets
XRD	X-ray Diffraction
ZnO	Zinc oxide



## LIST OF SYMBOLS

dN.m	Deci Newton Meter
d	Interlayer spacing
$M_H$	Maximum Torque
nm	Nanometer
F	Force
phr	Part per Hundred Rubber
Q	Swelling Ratio
$t_{90}$	Cure time
$t_{s2}$	Scorch time
$T_s$	Tear strength
$W_i$	Original mass
$W_f$	Final weight
$W_t$	Swollen mass
	X-ray wavelength
	Angle of diffraction
$\mu\text{m}$	Micrometer

**KESAN – KESAN PEMBEBANAN PENGISI DAN KAEDAH-KAEDAH  
PENYEDIAAN YANG BERBEZA KE ATAS SIFAT – SIFAT KOMPOSIT  
KANJI UBI KAYU TERISI GETAH ASLI**

**ABSTRAK**

Projek ini mengenai dengan kaedah – kaedah penyediaan kanji ubi kayu/getah komposit asli. Pertama, kesan – kesan pembebanan kanji ubi kayu (KUK) yang berbeza ke atas sifat – sifat komposit getah asli (GA) telah dikaji. Komposit KUK/GA pada pembebanan KUK yang berbeza (5 -25 bsg) telah disebatikan dengan menggunakan penggiling bergulung dua pada suhu bilik. Keputusan – keputusan menunjukkan masa skorj dan pematangan komposit KUK/GA hanya berkurang sedikit dengan peningkatan pembebanan KUK. Walaupun begitu, penggunaan KUK telah mengurangkan tork maksimum, kestabilan terma dan sifat – sifat mekanikal komposit KUK/GA. Kekuatan tensil dan kekuatan cabikan pada tahap optimum telah diperolehi pada 10 bsg pembebanan KUK dan berkurang dengan peningkatan pembebanan KUK. Kedua, kesan – kesan pembebanan KUK dan kaedah – kaedah penyediaan ke atas sifat – sifat komposit GA telah dikaji. Tiga jenis kaedah – kaedah penyediaan telah digunakan di dalam projek ini yang dikenali sebagai pencampuran langsung, penggumpalan bersama, dan pengeringan-beku. Komposit KUK/GA disediakan dengan menggunakan kaedah – kaedah penggumpalan bersama dan pengeringan-beku telah menunjukkan sifat – sifat mekanikal dan kestabilan terma yang lebih baik berbanding komposit KUK/GA yang telah disediakan dengan menggunakan kaedah pencampuran langsung. Di dalam semua kaedah yang telah dikaji, kekerasan komposit meningkat dengan peningkatan pembebanan KUK. Kajian morfologi menunjukkan bahawa kaedah pengeringan-beku telah memperbaiki penyebaran KUK di dalam matriks GA berbanding kaedah – kaedah pencampuran langsung dan penggumpalan bersama.

**EFFECTS OF FILLER LOADING AND DIFFERENT PREPARATION  
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**ABSTRACT**

This project is concerned with the preparation methods of cassava starch/natural rubber composite. First, the effects of different cassava starch (CS) loading on the properties of natural rubber (NR) composites were investigated. CS/NR composites at different CS loading (5-25 phr) were compounded using a two-roll mill under room temperature. Results indicated that the scorch time and cure of CS/NR composites slightly reduced with increasing CS loading. However, the addition of CS reduced the maximum torque, thermal stability and mechanical properties of CS/NR composites. The optimum tensile strength and tear strength were obtained at 10 phr of CS and decreased considerably with higher CS loadings. Second, the effects of CS loading and preparation methods on properties of CS/NR composites have been investigated. Three types of preparation methods were used in this project namely; direct blending, co-coagulation, and freeze-drying. The CS/NR composites prepared by co-coagulation and freeze-drying methods exhibit better mechanical properties and thermal stability than CS/NR composites prepared by direct blending method. In all methods studied, the hardness increased with increasing CS loading. Moreover, the morphological study confirmed that the freeze-drying method improved the dispersion of CS in NR matrix than direct blending and co-coagulation methods.

# CHAPTER 1

## INTRODUCTION

### 1.1 Overview

Natural rubber (NR) is produced from the *Hevea brasiliensis* latex tree. Natural rubber is a relatively excellent type of raw material. Due to several climate factors, NR usually found in Southeast Asian region where Thailand, Indonesia, Malaysia and Vietnam as major producer. Accumulated NR production from these regions reaches 70 % of total world supplies (UNCTAD, 2011). Natural rubber possesses excellent comprehensive properties, such as outstanding resilience, high strength and good process-ability. This cumulative property makes NR the most suitable rubber for hoses, conveyor belts, seals, footwear, balloons, toys, etc.

Reinforcement of elastomeric materials is found to be important and primarily related to the enhancement of strength, strength-related properties such as stiffness, modulus, tensile strength, hardness and abrasion resistance. Reinforcing materials such as carbon black, silica, clay minerals and starch are commonly used as filler in elastomeric composites to improve the mechanical and thermal properties as well as to reduce cost and the weight of the rubber compounds (Ismail and Chia, 1998, Arroyo et al., 2003, Ismail and Ramli, 2008, Wang et al., 2009). However, starch was admirably suited as filler materials in rubber composite due to the gradual decreased of petroleum and the higher demand of environmental protection. Starch is

known as natural, cost-effectiveness, abundant and biodegradable material. For decades, many researches on starch/NR composite have been carried out and were found to be valuable (Liu et al., 2008, Carvalho et al., 2003, Khalaf and Sadek, 2011, Nakason et al., 2005, Rouilly et al., 2004, Wang et al., 2009, Wu et al., 2004a, Miren et al., 2011, Mayur and Sonal, 2010).

Starch/rubber composites are prepared by different methods such as direct blending, co-coagulation, etc. Early studies have reported the properties of starch filled rubber composites prepared by direct blending method (Khalaf and Sadek, 2011, Wu et al., 2004a). They found that the interfacial interaction between the blend components was poor, which is reflected in a considerable decrease in mechanical properties of starch/rubber composites. Starch/rubber composites prepared by co-coagulation method shows better mechanical properties compared to the direct blending method (Wu et al., 2004a). Some other research work by Liu et al., (2008), Tang et al., (2006) and Rouilly et al., (2004) reported a great improvement in properties were achieved by fine dispersion of starch into NR, styrene-butadiene-rubber (SBR) and chemical modify NR respectively. Only 10 phr of starch are enough to obtain a similar mechanical behaviour as the composite with 30 phr of carbon black. It can be assumed that the well dispersion of starch into the rubber matrix and improvement of filler-matrix compatibility are important for better mechanical properties of starch/NR composite.

## 1.2 Problem Statement

Natural rubber technology has been developed rapidly and filler become the most important additive as the second largest component following the base polymer in rubber compounding (Blow and Hepburn, 1982). They are incorporated in to rubber compound to improve processability and physic-mechanical properties. Among commercial fillers, carbon black and precipitated silica are the most important reinforcing fillers and extensively used when high strength is required. However, for some applications where cost and processability are great concern, the use of non or semi reinforcing fillers such as clay, talc, and calcium carbonate as well as fillers from renewable resources are important. Starch was used as fillers for rubber, which are low cost, renewable and environment friendly. Starch is not only renewable and biodegradable. It is also inexpensive and abundant. With the declining source of petroleum, much effort has been devoted to develop starch-based polymers.

Even though, many studies have been done on starch/rubber composite but there is no particular study focused on the filler loading and preparation methods. The methods proposed have the advantages and disadvantages. For direct blending method, it was straight forward process where do not required two stage process compared to co-coagulation method. However the resulted composites normally showed poor properties due to inhomogeneous distribution of fillers in the composites. For freeze dying method gives good filler dispersion due to hinder associations of starch chain during the freeze during process. Therefore, this research

was carried out to study the effect of cassava starch loading and different preparation methods on properties of cassava starch-filled natural rubber composites. The different methods applied will give comparative results for better choices on the best methods to produce the good cassava starch/natural rubber composites. The results obtained can be used as research and development of cassava starch as one of the reinforcing fillers for NR composites as well as to reduce the overall compounding cost and reduce environmental effect.

### **1.3 Objectives of The Study**

In this research, the preparation and properties of cassava starch/NR composites were studied using three preparation methods: direct blending, co-coagulation and freeze-drying. The objectives of this research are:

1. To study the effects of filler loading on properties of cassava starch natural rubber composites.
2. To compare the properties of natural rubber latex/cassava starch paste composite prepared by direct blending and co-coagulating method.
3. To understand the freeze-drying method on the properties of cassava starch/natural rubber composite.

For each part of the research, the curing characteristics, mechanical properties (tensile strength, tear strength, elongation at break, tensile modulus at 100 % and tensile modulus at 300%), hardness, swelling behavior and thermogravimetric

analysis (TGA) were carried out. In addition, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were also conducted to characterize the cassava starch/NR composites.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Natural Rubber

Natural rubber (NR) is one type of the elastomers, which is produced from the *Hevea brasiliensis* latex tree. Natural rubber is a relatively excellent type of raw material source. The main component of NR is the rubber hydrocarbon of 93 to 95 percent, polyisoprene with the general formula  $(C_5H_8)_n$  as showed in Figure 2.1 (Billmeyer, 1971). The average molecular weight of natural rubber is between  $0.25 \times 10^6$  and  $2.71 \times 10^6$ , and the content of double bonds in the macromolecule is 95 to 98.5 % of the theoretical value. The glass transition temperature of natural rubber is about  $-70\text{ }^\circ\text{C}$  and its specific gravity is 0.93 at  $20\text{ }^\circ\text{C}$ . Natural rubber shows excellent physical properties. However, the resistance to oxygen, ozone and heat is poor. It is due to the presence of the double bond in its chemical structure (Sirqueira and Soares, 2002).

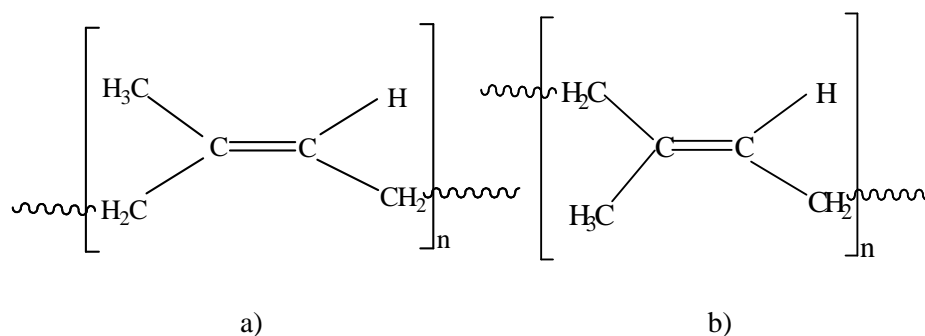


Figure 2.1 (a) *cis*-1, 4-polyisoprene, (b) *trans*-1, 4-polyisoprene

### 2.1.1 Classification of Natural Rubber

Natural rubber can be classified into different grades according to different applications. The natural rubber products such as glove and foam are made from latex, whereas tire is produced from dry rubber. Normally, natural rubber is classified as latex and cuplump (dry rubber) as shown in Figure 2.2 (Heng and Ong, 2001).

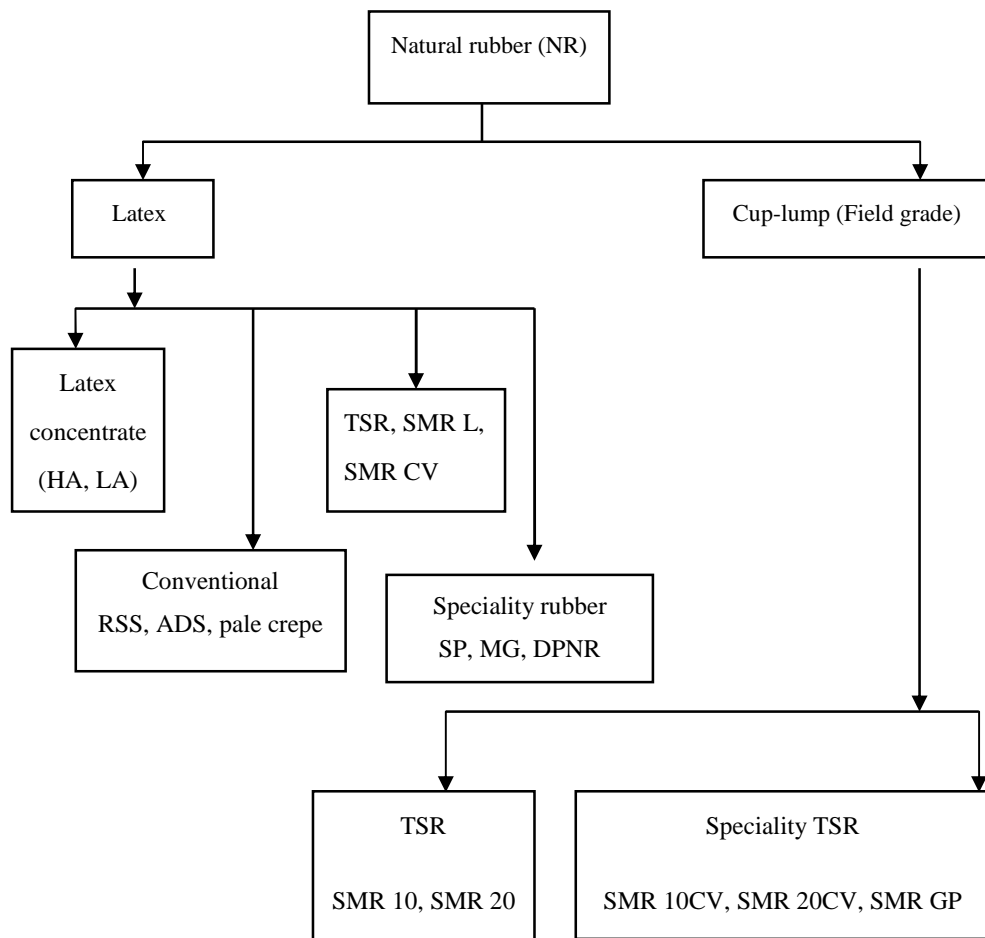


Figure 2.2 General natural rubber types and grades (Heng and Ong, 2001)

### 2.1.2 Natural Rubber Latex

Natural rubber latex (NRL) is milky white liquid obtained from the rubber tree (*Hevea brasiliensis*) by controlled wounding of the rubber tree. Natural rubber latex is a colloid with a specific gravity of 0.96 to 0.98 and a pH in the range of 6.5 to 7.0. The dispersed phase is mainly rubber and the dispersion medium is water. However, in addition to rubber and water, latex contains small quantities of proteins, resins including fats, fatty acids, other lipids, sterol and sterol esters, carbohydrates and mineral matter (Sadhan and Jim, 2001) . The composition of NRL is given in Table 2.1 (Blackley, 1997). The dominant particulate constituent of fresh latex is the rubber hydrocarbon with a size ranging from 0.02 to 3.0  $\mu\text{m}$  and shape mostly spherical and strongly protected in suspension by a film of adsorbed proteins and phospholipids (Archer et al., 1963).

Table 2.1 Composition and physical properties of natural rubber latex as obtained from the field (Blackley, 1997)

Constituent/property	Weight (%)
Rubber hydrocarbon	20-35
Protein	1.0-1.5
Resin	1.0-2.5
Ash	< 1.0
Sugars	0.5-1.0
Water	60-70
Fats	0.5-1.0
Density	975-985 $\text{kgm}^{-3}$
PH	6.5-7.0
Surface energy	0.04-0.045 $\text{Jm}^{-2}$

The low rubber content (20-35 % DRC) and high non-rubber solids found in NR latex has severely limits its usefulness as an industrial raw material. Therefore it is necessary to concentrate the field latex to increase its dry rubber content (DRC). Three concentration methods available are creaming, evaporation and centrifugation. The NRL usually concentrate to 60 % DRC. Natural rubber latex concentrate is marketed to strict technical specifications. The current ASTM specifications for latex concentrates are shown in Table 2.2 (ASTM D1076-97).

Table 2.2 Requirements for specified latex types

	Type1	Type 2	Type 3
Total solids, min, %	61.5	66.0	61.5
Dry rubber content (DRC), min, %	60.0	64.0	60.0
Total solids content minus dry rubber content, max, %	2.0	2.0	2.0
Total alkalinity calculated as ammonia, as % on latex	0.6 min	0.55 min	0.29 max
Sludge content, max, %	0.1	0.1	0.1
Coagulum content, max, %	0.05	0.05	0.05
KOH number, max	0.8	0.8	0.8
Mechanical stability, S, min	650	650	650
Copper content, max, % of total solids	0.008	0.008	0.008
Manganese content, max, % of total solids	0.008	0.008	0.008
Colour on visual inspection	A	A	A
Odour after neutralisation with boric acid	B	B	B

A - No pronounced blue or grey

B - No putrefactive odour

Type 1 - Centrifuged natural latex preserved with ammonia

Type 2 - Creamed natural latex preserved with ammonia

Type 3 - Centrifuged natural latex preserved with low ammonia with secondary preservatives

### 2.1.3 Standard Malaysia Rubber

Standard Malaysia Rubber (SMR) for natural rubber is graded by the technical specified rubber (TSR). SMR is a light-colored rubber produced from high quality latex. It has low ash and dirt content and is packed and presented in Table 2.3 (Fulton and Thorpe, 1996). The advantages of SMR are light color together with its cleanliness and better heat aging resistance. Technologically, SMR presents high tensile strength, modulus, and ultimate elongation at break for both black and nonblack mix. SMR can be used for light-colored and transparent products such as surgical or pressure-sensitive tape, textiles, rubber bands, hot water bottles, surgical and pharmaceutical products, large industrial rollers for the paper printing industry, sportswear, bicycle tubes, chewing gum, cable sheaths, gaskets, adhesive solutions and tapes (Rodgers, 2004).

Table 2.3 SMR L properties and specifications (Fulton and Thorpe, 1996)

<b>Parameters</b>	<b>Value</b>
Dirt retained on 44 $\mu$ aperture (max), % wt	0.02
Ash content (max), % wt	0.50
Nitrogen (max), % wt	0.60
Volatile matter (max), % wt	0.80
Wallace rapid plasticity (P <sub>0</sub> ), min	30
Plasticity Retention Index (PRI), min, %	60
Lovibond color:	
Individual value (max)	6.0
Individual range (max)	2.0

Figure 2.3 shows the SMR scheme with the relationship between source materials and grades (Fulton and Thorpe, 1996).

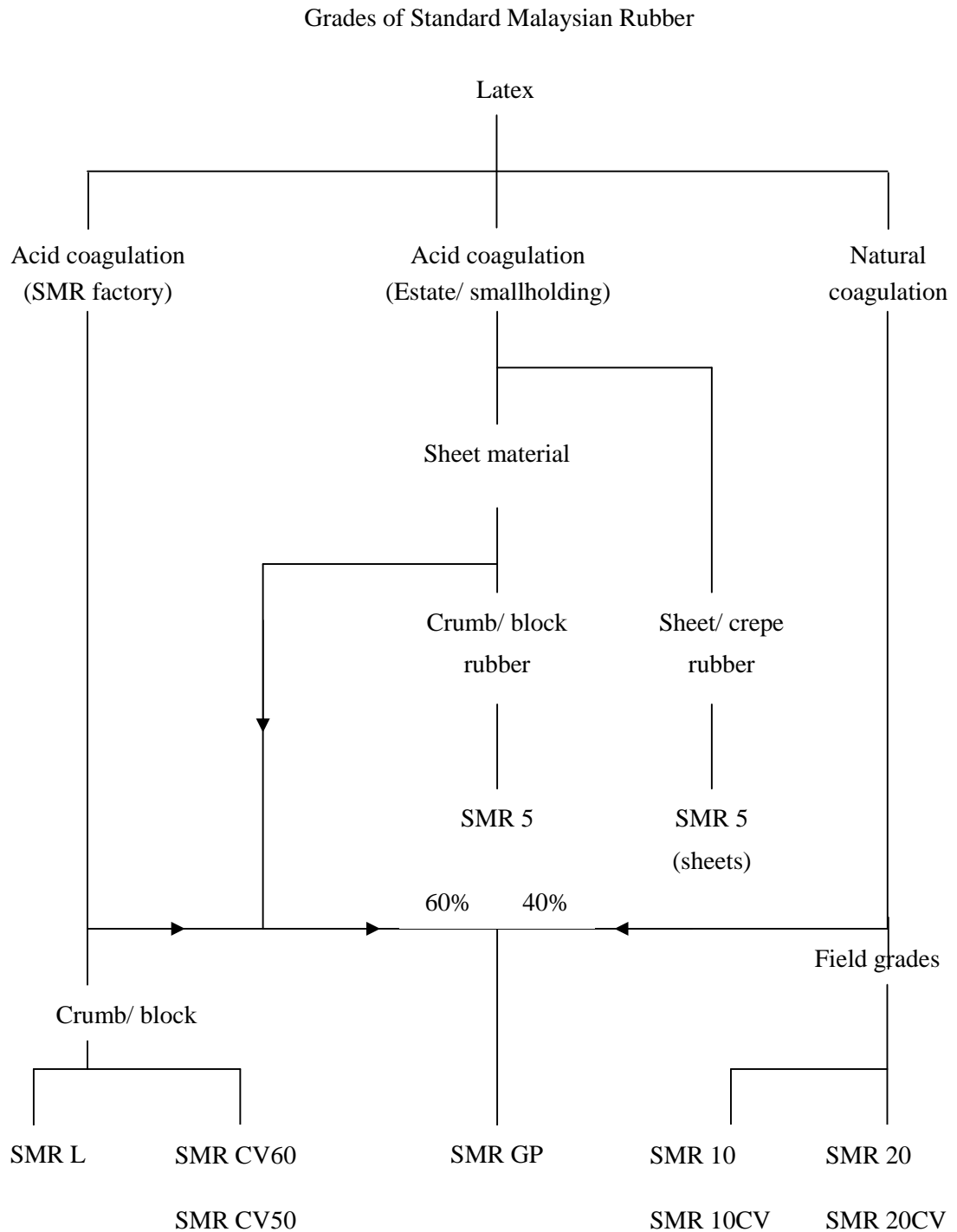


Figure 2.3 Processing routes by which raw materials are converted into the various grades of Standard Malaysian Rubber (Fulton and Thorpe, 1996)

## 2.2 Cassava Starch

### 2.2.1 Cassava Starch

Cassava (*Manihot esculenta*), also called yuca or manioc, is a woody shrub of the *Euphorbiaceae* (spurge family) native to South America. Cassava is extensively cultivated as an annual crop in tropical and subtropical regions for its edible starchy tuberous root, as a major source for carbohydrates. Size of cassava granules starts from 5 to 15 micron with average 10 micron. Table 2.4 shows the comparison of cassava granules with other starch granules from different plant while Figure 2.4 shows their images under SEM analysis (Karim et al., 2008).

Table 2.4 Starch granular size from different plants (Karim et al., 2008)

Granules origin	Size range, $\mu\text{m}$
Sago	10 – 50
Rice	3 – 10
Corn	5 – 20
Wheat	22 – 36
Cassava	5- 25
Potato	15 – 85

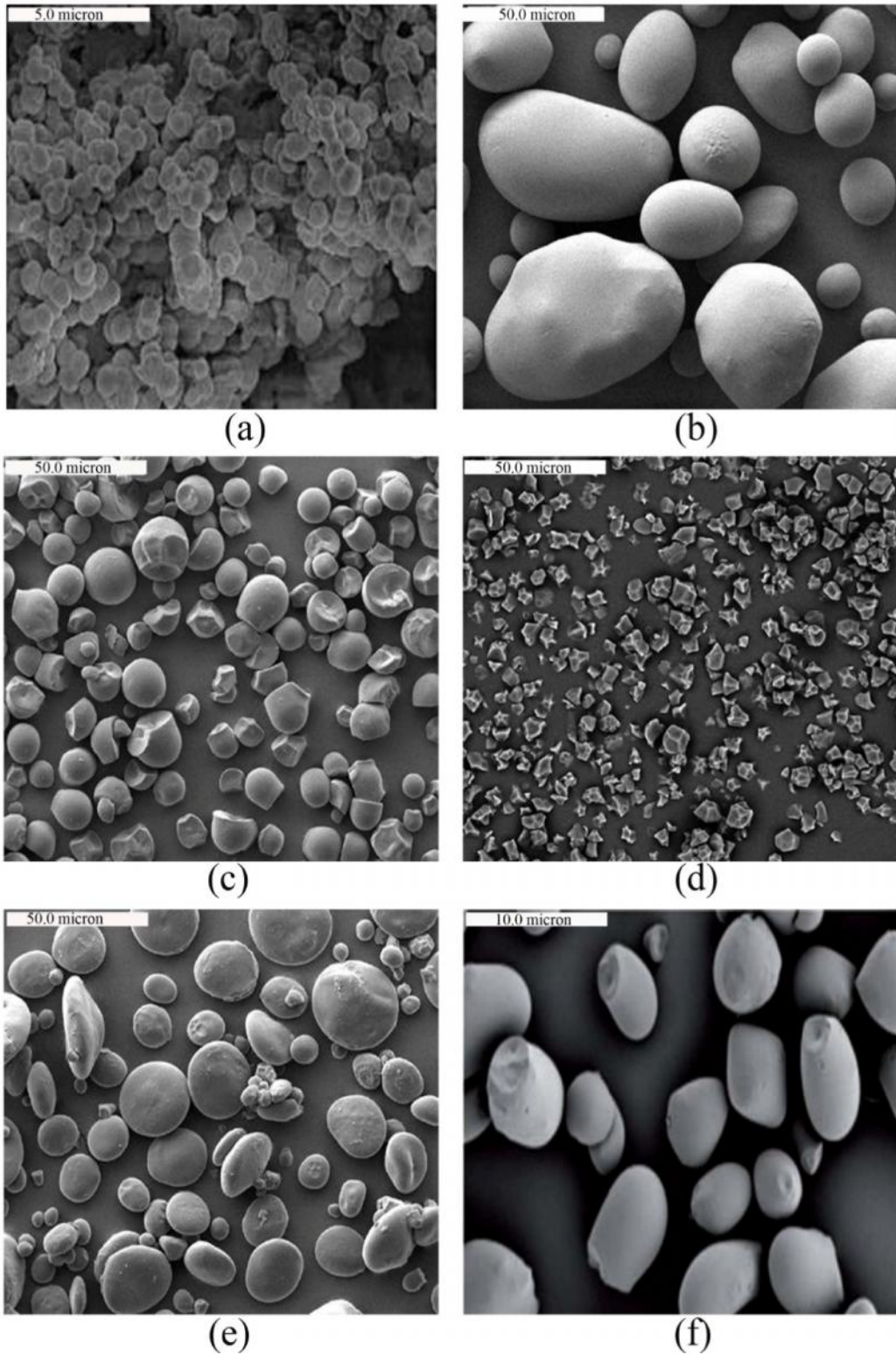


Figure 2.4 SEM images for (a) corn (b) potato (c) cassava (d) rice (e) wheat and (f) sagó starches with their respective size indicator (www.medicinescomplete.com, 2010, www.cassava.vn.refer.org, 2010, www.aacnet.org.net, 2010)



Typical composition of cassava starch as shown in Table 2.5 (Nunfor et al., 1995). Native starches vary widely among sources due to their content of different proportions of amylose (10–20 %) and amylopectin (80–90 %). But more importantly, the ratio of amylose to amylopectin defines the architecture of the regular semicrystalline arrays of amylopectin in the supramolecular complex called the starch granule (Figure 2.5). In chloroplasts and amyoplasts (seed endosperm plastids), amylose and amylopectin are organized in relatively dense spheroidal granules (0.1 to > 50  $\mu\text{m}$  in diameter) that vary in shape and size (Lincoln and Eduardo, 2010).

Table 2.5 Typical composition of cassava starch (Nunfor et al., 1995)

<b>Components</b>	<b>Composition, %</b>
Total carbohydrate (%)	99.44 $\pm$ 0.1
Apparent amylose (%)	19.76 $\pm$ 2.3
Total sugars ( $\mu\text{g/mL}$ )	37.63 $\pm$ 1.9
Cure fibre (%)	0.15 $\pm$ 0.04
Ash (%)	0.19 $\pm$ 0.03
Lipids (%)	0.13 $\pm$ 0.02
Cure protein (%)	0.09 $\pm$ 0.01
Cyanide (mg/kg)	1.14 $\pm$ 0.19
Acidity (g/dL) as acetic acid	0.43 $\pm$ 0.06

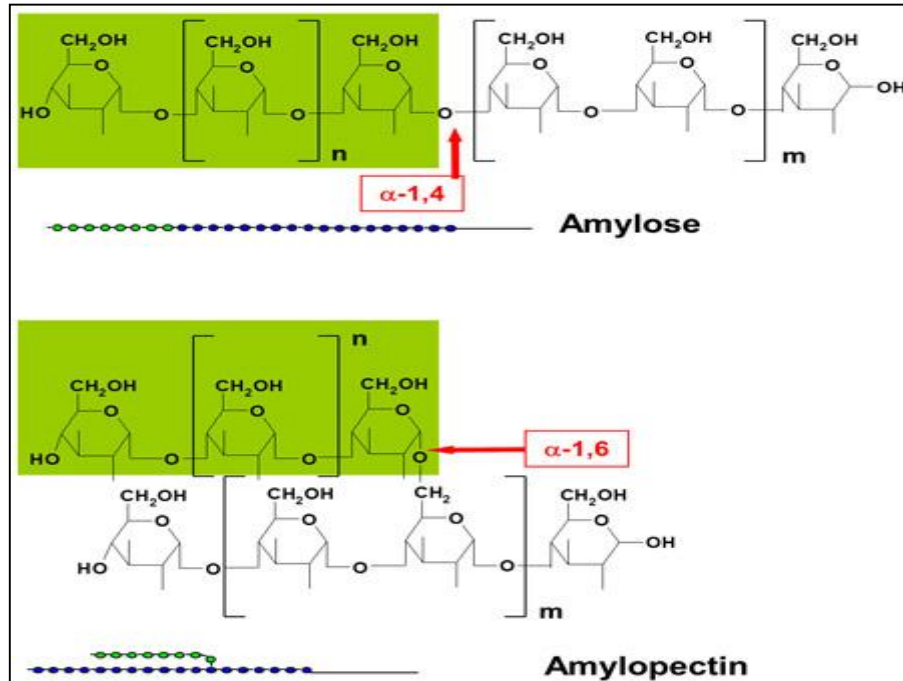


Figure 2.5 The chemical composition of starch (Lincoln and Eduardo, 2010)

### 2.2.2 Starch as Filler for Rubber

In recent years, with the gradual decreased of petroleum and the higher demand of environmental protection, starch as a rubber-reinforcing filler has drawn interest from many researchers. In addition, as a renewable, biodegradable, inexpensive and widely obtainable biopolymer, the application of starch is also attractive due to energy shortage and environmental pollution (Yu et al., 2006). Starches usually in a form of granules consist of linear structure of amylose and branched structure amylopectin (Lincoln and Eduardo, 2010). During application, starch is inserted in its original form, melted or dispersed in a medium. Upon heating in a presence of water, starch granule swell as it absorbs water and coalesces with other starch granules to form gel-like materials. This process is called gelatinization

(Richard and William, 1990). The gelatinization temperature for starch may vary depends on the types of starch sources. If the starch were left cooled or excessive heat were applied, it may lose water and rearrangement of molecular chain occurred leading to irreversible process of retrogradation. During microorganism consumption of carbon chain in polyisoprene chain, the metabolism process of the microbes will produce an enzyme such as amylases and glucosidases (Chandra and Rustgi, 1998). Both of these enzymes will break the amylose and amylopectin structure in a hydrolysis process. The mechanisms of this process are presented in

Figure 2.6

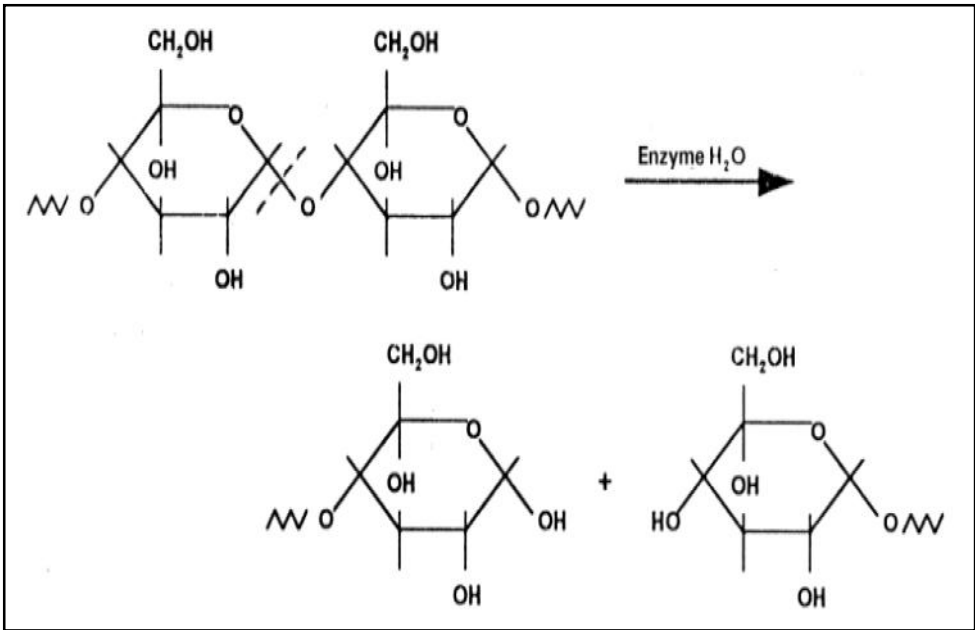


Figure 2.6 Enzymatic reaction of starch (Chandra and Rustgi, 1998)

The properties of starch can be explained in details as:

### **1) Starch Gelatinization Process**

One of the most important characteristic of starch is the ability to gelatinize at high temperature. Gelatinization is the process of breaking the starch granules by means of mechanical shearing or temperature induction in a presence of water. During the process, the starch granule were heated or as mechanical sheared where amylose and amylopectin structure were leached configuration order due to penetration and adsorption of water in starch granules hence resulting in granules swollen. Starch gelatinization process usually affected by its processing environment. Asoka et al., (1985), in their work indicates that, higher gelatinization temperature of starches obtained from starches which are produced in higher origins temperature. The content of randomly coiled amylose also reported to give significant influence on the gelatinization temperature of starch.

Starch gelatinization was studied by Differential Scanning Calorimetry (DSC) where the swelling starts at a temperature corresponding to the onset temperature ( $T_o$ ) of the DSC endothermic transition and continues well above the concluding temperature ( $T_c$ ). Different starches exhibit different swelling behaviours, both in terms of the final gel volumes obtained and in the temperature response (Wajira et al., 2009). Figure 2.7 presents the schematic gelatinization process of starch.

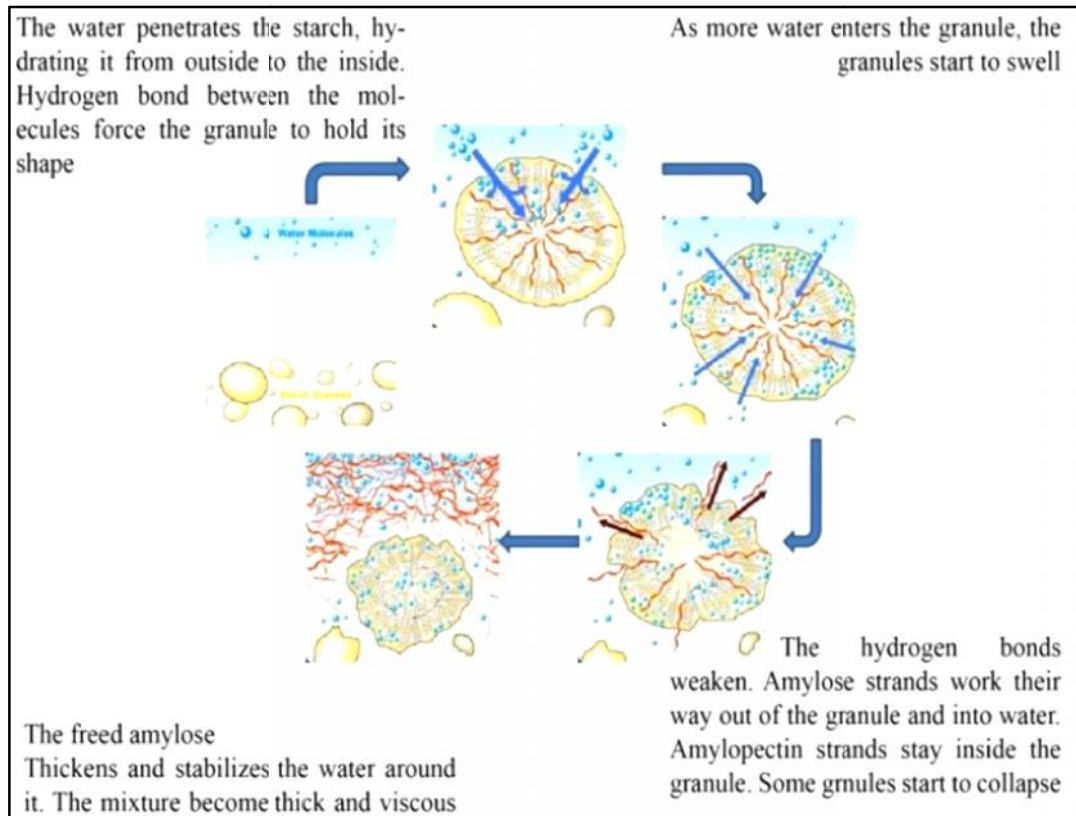


Figure 2.7 Schematic presentation of starch gelatinization (Jansson, 2008)

During gelatinization, starch becomes an amorphous material that can be found in three different states; firstly, at low temperature, the glassy state was present where the starch is hard and brittle. Secondly, the rubbery state where starch is soft and flexible and the lastly, at higher temperature or under pressure, starch behaves as a viscous liquid. The transitions between these states are called glass transition and melting transition respectively. These processes are represented in Figure 2.8, where starch state diagram were established under atmospheric pressure (Tran et al., 2007)

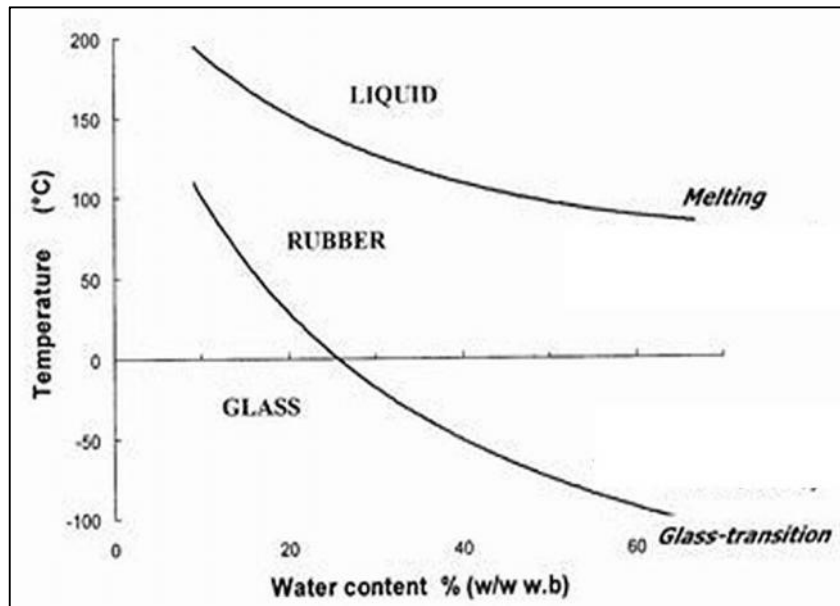


Figure 2.8 Typical starch transition phase diagram (Tran et al., 2007)

At room temperature (25 °C), starch based products with moisture contents below 20 % were classified under glassy state and in a form of hard and brittle materials, while for product with more than 20 %, the products are in rubbery state and having a soft texture. A practical application of the state diagram is to allow plotting the steps of any process involving the heating of starch to visualize what states the materials experiences and to identify the technical difficulties that may arise, such as viscosity changes or undesirable molecular transition.

The glassy, rubbery and liquid states correspond to different levels of starch molecular mobility, the glass and melting transition are characterized by sudden changes in their mechanical properties due to the change in the mobility of starch molecules. The temperature and moisture content are the main factors that

determined the glass and melting transitions. The glass transition also depends on the molecular weight of the starch molecules; a lower molecular weight, resulting from starch degradation during processing will increase molecular mobility and reduced the glass transition temperature ( $T_g$ ). The starch origin has little influence on the glass transition because most starches have a similar range of molecular weights (Tran et al., 2007)

## 2) Starch Retrogradation Process

Starch retrogradation is the process of molecular arrangement of amylose chain due to long cooling. This re-association of amylose structure led into formation of crystal structure. These properties exhibit by amylose and less shown by amylopectin. The process also discards water absorbed during starch swelling or gelatinization which the process refers as syneresis (Mohamed et al., 2008). Figure 2.9 shows the schematic representation of starch gelatinization and retrogradation (<http://www.food-info.net/uk/carbs/starch.htm>)

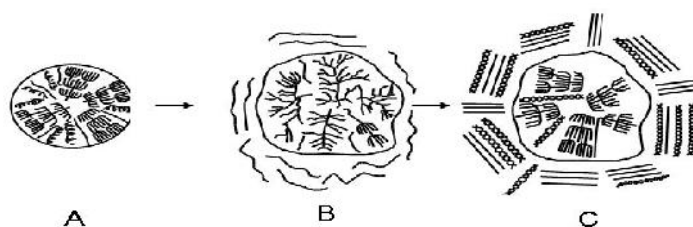


Figure 2.9 Starch gelatinization (A to B) and retrogradation (B to C) process

(<http://www.food-info.net/uk/carbs/starch.htm>)

### 3) Starch Syneresis Process

Syneresis is the process of shrinking of starch granules. This is occurred due to de-association of water within amylose in bulky medium and amylopectin in starch granules which more diffusion of amylose structure and molecular realignment to form a crystalline region. As indicated by Ahmad and Williams, (1998), during the process, amylose and amylopectin aggregations is detected which related with molecular mass of amylose and starch. They also indicate that cassava starch experiences highest syneresis process compared to other cereal starches (Figure 2.10).

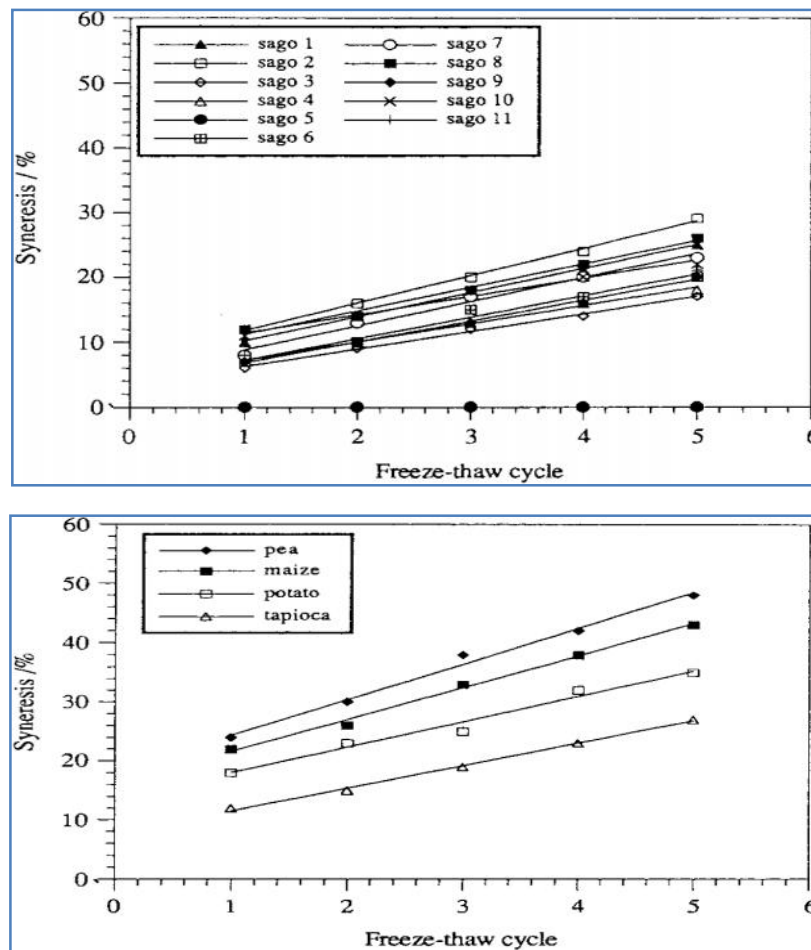


Figure 2.10 Comparison between sago starch syneresis profiles and other cereal starches (Ahmad and Williams, 1998)



### **2.2.3 Cassava Starch /Natural Rubber Composite.**

In recent years, starch/rubber composites have been investigated for a number of rubber matrices. Most of the researches have been focused on some well-known rubbery materials, such as natural rubber (NR), ethylene propylene diene rubber (EPDM), styrene-butadiene rubber (SBR), and nitrile rubber (NBR). However, some other reports also focused on other types of polymer such as polyvinyl alcohol (PVOH), polyvinyl acetate (PVA), low density polyethylene (LDPE) and polybutadiene rubber (BR) (Qi et al., 2006, Chaléat et al., 2012, Yoon et al., 2012, Pedroso and Rosa, 2005).

Rubber composites based on natural rubber (NR) with cassava starch loading have mainly been prepared on two roll mill, followed by a vulcanization process. The vulcanization characteristics of filled natural rubber composites, such as scorch time, optimum cure time were sharply reduced with the addition of cassava starch (Figure 2.11). This behavior resulted from the existence of hydroxyl groups in the cassava starch structure (Nakason et al., 2005).

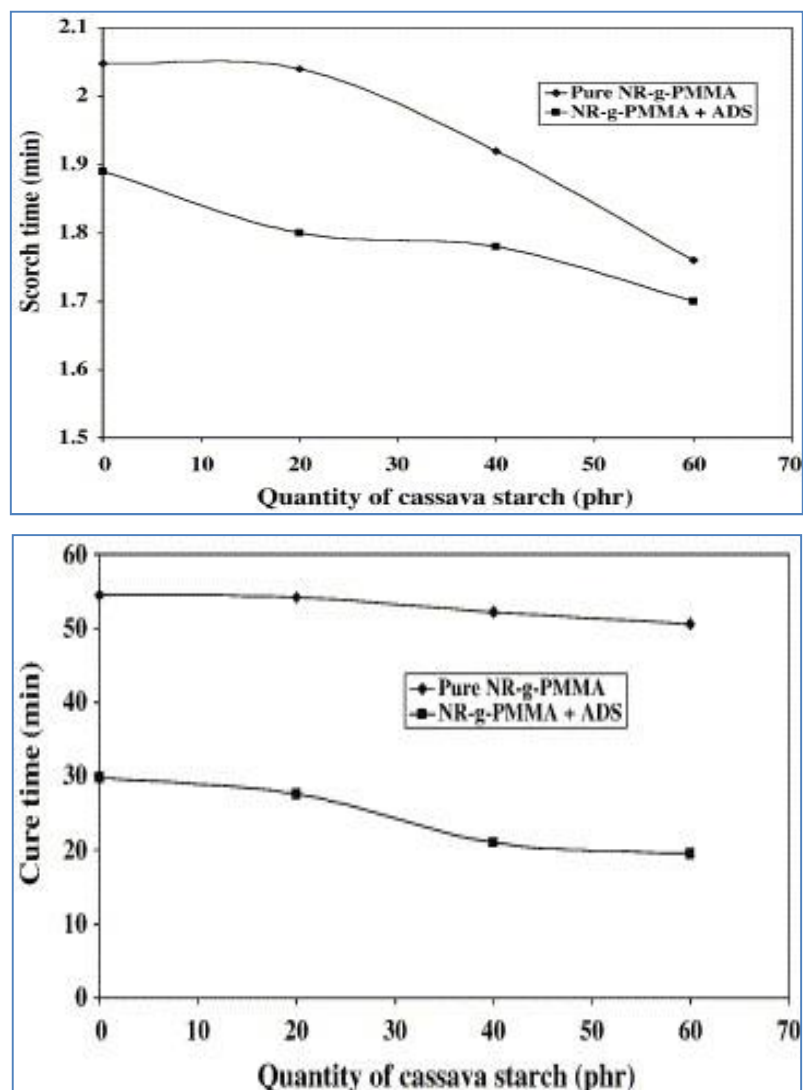


Figure 2.11 Scorch time and cure time of NR-g-PMMA blends at various quantities of cassava starch (Nakason et al., 2005)

Two of the critical factors for rubber reinforcement are starch dispersion and/or improving interfacial strength between starch and rubber. Liu et al. (2008) reported that chemically modified starch paste (MST) with polybutylacrylate (PBA) graft chains can work as reinforcing filler in natural rubber. The results have shown obvious reinforcement effect at optimum MST on NR matrix through increased tensile strength, elongation at break and tear strength besides modulus and hardness (Figure 2.12).

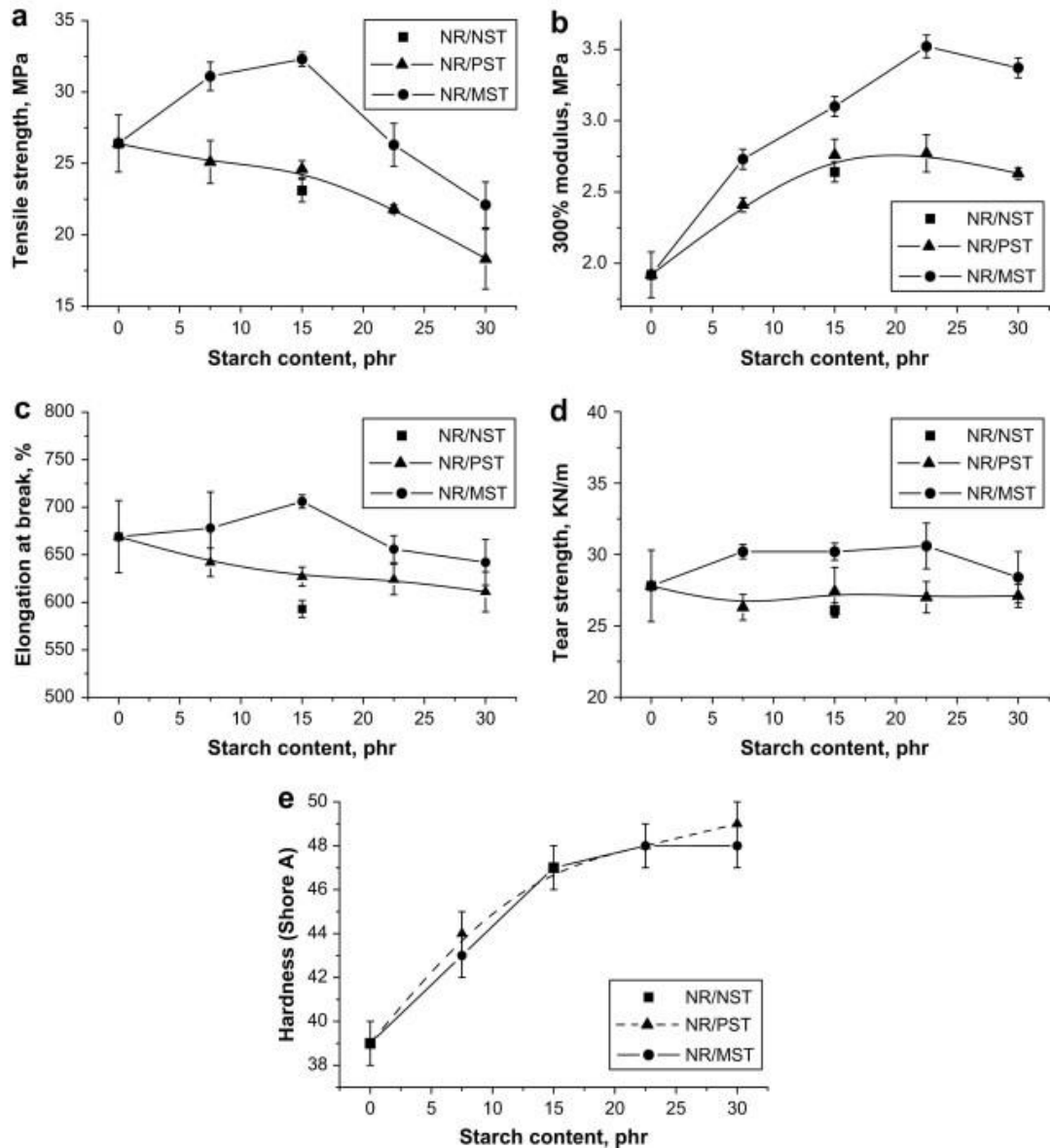


Figure 2.12 Variation of mechanical properties of NR/starch composites via starch content (NST: Natural starch powder; PST: unmodified starch paste; MST: modified starch paste) (Liu et al., 2008).

Wu et al. (2004) were successfully prepared starch/rubber composites through coagulation of cassava starch paste and NR latex. The XRD and SEM results revealed the better dispersion of starch in rubber matrix and the particle size of starch to less than 1000 nm. This caused the increasing of mechanical properties (Table 2.6).