SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

STUDY THE SYNTHESIS PARAMETERS AND EFFECT OF ADDITION OF ACID HYDROLYZED SAGO STARCH ON MECHANICAL PROPERTIES OF NR AND XNBR LATEX FILMS

By

YAP SOON YOU

Supervisor: Professor Dr. Azura binti A. Rashid

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Study the Synthesis Parameters and Effect of Addition of Acid Hydrolyzed Sago Starch on Mechanical Properties of NR and XNBR Latex Films”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Name of student: Yap Soon You Signature:

Date: 12June 2018

Witnessed by

Supervisor: Professor Dr. Azura Signature:

Date: 12June 2018

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LIST OF ABBREVIATIONS

AHSS	Acid Hydrolysed Sago Starch
ASTM	American Society for Testing and Materials
DRC	Dry Rubber Content
HA-NR	High Ammonia Natural Rubber
H_2SO_4	Sulphuric Acid
ISO	International Standard Organization
SEM	Scanning Electron Microscope
SNC	Starch Nanocrystal
TDI	Toluene Diisocyanate
TSC	Total Solid Content
MST	Mechanical Stability Time
NR	Natural Rubber
NSS	Native Sago Starch
PCL	Polycaprolactone
PEGME	Poly(ethylene glycol) Methyl Ether
PPGBE	Poly(propylene glycol) Monobutyl Ether
PTHF	Poly(tetrahydrofuran)

PVNR	Prevulcanized Natural Rubber
XNBR	Carboxylated Acrylonitrile Butadiene Rubber
XRD	X-Ray Diffraction Analysis
ZDEC	Zinc Diethyldithiocarbamate

LIST OF SYMBOLS

°C	Degree Celsius
%	Percentage
wt%	Weight Percentage
g	Gram
g/mol	Molar Mass Unit
MPa	Mega Pascal
μm	Micrometer
rpm	Rotation per minute
pH	A measure of acidity or basicity of the solution
phr	Part per hundred rubber
nm	Nanometer
min	Minute
M	unit for concentration of solvent

KAJIAN PARAMETER SINTESIS DAN KESAN PENAMBAHAN KANJI SAGU DIHIDROLISIS ACID PADA SIFAT MEKANIKAL FILEM LATEKS (NR DAN XNBR)

ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan kanji sagu yang mempunyai saiz zarah kecil dengan motivasi untuk meningkatkan sifat mekanikal dan biodegradasi filem lateks semasa pelupusan. Tahap 1 penyelidikan mengkaji parameter sintesis yang optima untuk kanji sagu dihidrolisis asid (KSHA). Kanji sagu dihidrolisis dengan keadaan hidrolisis yang berbeza pada suhu, keasidan dan tempoh yang berlainan. Keputusan menunjukkan bahawa parameter sintesis optima untuk penyediaan KSHA (313.10 nm) pada 2.18 M asid sulfuric dalam keadaan tidak panas (27 °C) selama 7 hari. Tahap 2 penyelidikan, mengkaji kesan penambahan KSHA pada sifat mekanikal (sifat-sifat tensil dan kekuatan cabikan), sifat fizikal (pengukuran ketumpatan sambung-silang), morfologi (mikroskop optic dan mikroskop pengimbasan elektron) dan biodegradasi filem lateks (NR dan XNBR) (analisis kehilangan berat). Melalui kajian ini, didapati bahawa KSHA telah meningkatkan sifat mekanikal dan rintangan bengkak filem lateks berbanding dengan kesan kanji sagu asli (KSA) dalam filem lateks NR dan XNBR. Ini disebabkan peningkatan keserasian zarah kanji sagu dengan matriks getah yang dikaitkan dengan saiz zarah relative kecil, kehadiran kumpulan ester sulphate dan penghabluran yang rendah dalam KSHA. Penilaian biodegradasi oleh analisis kehilangan berat menunjukkan filem lateks (NR dan XNBR) yang isikan oleh KSHA mempunyai kadar biodegradasi yang lebih tinggi. Analisis morfologi dengan mikroskop optic mendapati perubahan warna filem, hasilan bintik hitam dan lompang yang dihasilkan daripada pembentukan filem dapat meningkatkan kadar degradasi untuk mikroorganisma.Secara keseluruhan, AHSS telah meningkatkan sifat mekanikal, sifat fizikal dan biodegradability kedua-dua jenis filem lateks (NR dan XNBR) berbanding dengan KSA.

STUDY THE SYNTHESIS PARAMETERS AND EFFECT OF ADDITION OF ACID HYDROLYZED SAGO STARCH ON NR AND XNBR LATEX FILMS

ABSTRACT

The objective of this research was to develop a small particle size sago starch with the motivation to improve mechanical properties and biodegradability of latex films upon disposal. The research's stage 1 investigated the optimum synthesis parameter of the acid hydrolyzed sago starch (AHSS) powder. The native sago starch (NSS) were hydrolyzed with different hydrolysis condition at different temperature, acidity and duration. The results showed that the optimum synthesis parameters of preparation acid hydrolysis sago starch fillers (313.10 nm) was at 2.18 M sulphuric acid under non heated condition (27°C) for 7 days. Stage 2 of work, investigated the effect of addition of AHSS fillers on mechanical properties (tensile properties and tear strength), physical properties (crosslink density measurement), morphological (optical and scanning electron microscopes (SEM)) and biodegradability of NR latex films and XNBR latex films (mass loss analysis). It was found that the AHSS has improved mechanical properties and swelling resistance of latex films as compared to NSS filled NR latex films and NSS filled XNBR latex films. This was contributes by improvement in compatibility of sago starch particles with rubber matrix which attributed from the relative smaller particle size, presence of sulphate ester group and low crystallinity of AHSS. The biodegradation assessment by mass loss analysis indicates AHSS filled NR latex and XNBR filled latex films has higher degree of biodegradation rate. Morphological analyses with optical microscope shows the discoloration of the films and voids resulted from an increased of degradation sites for microorganisms during the biodegradation process. Overall, AHSS has increased the mechanical properties,

physical properties and biodegradability of both type of latex films (NR and XNBR) compared to NSS.

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Malaysia remains the world's largest producer and exporter of rubber gloves which accounts for 63% of global supply followed by Thailand (21%), China (5%) and Indonesia (3%). The top gloves producer included Top Gloves, Hartalega, Kossan and Supermax dominate 50% global supply, giving them an edge when price adjustments for their products are needed. Malaysia’s dominance is difficult to imitate because of the strength in differentiating products even to the nearest rivals Thailand as it focuses more on latex-based products. Other countries also difficult to challenge Malaysia's prominence on the world stage because Malaysia is well known as the world's leading glove manufacturer in terms of world-class quality and therefore significantly influence of price and supply on the world market (Azharuddin, 2018).

Currently, Malaysia is the world's largest nitrile glove manufacturer with medical gloves as the mainstay of glove producers in Malaysia. The higher demand for nitrile gloves mainly from developed countries (US, UK and Western Europe) due to increase in healthcare facilities, pandemic diseases and concern in hygiene standards in developed countries. Nitrile gloves desired for developed countries because it can replace US FDA banned powder latex medical gloves and free of latex allergy issue while providing excellent resistance to punctures and tears. Hence, overall exports of Malaysia’s rubber gloves grew by 11.6%, driven by both growth of nitrile butadiene rubber gloves (+27.3%) and natural latex rubber gloves (+1.7%). Malaysia Rubber Gloves Manufacturers Association (MAGMA) and industry participants estimated that global demand for gloves will continue to increase by 8-10% p.a. over the next 4 years (Azharuddin, 2018).

Recently, although global demand of latex glove has increased but the disposal of latex waste product had become an issue to the environment. Service lifetime of rubber glove is very short because of a single used application commodity and usually disposed after single usage especially for medical gloves. The disposed gloves take more than 2 years to degrade naturally and completely in soil (Afiq and Azura, 2011). Disposal and biodegradation problems can be overcome by incorporation of degradable material into the latex systems (Afiqet.al., 2015; Azura et.al., 2010). The microorganisms in landfill will secrete specific enzymes that can break the rubber molecular chain and consume the nutrients from degradable material. Thiseffects increased rates of biodegradation for latex products upon disposal but the rate is slowed down due to degradation normally occur at the surface of the latex gloves waste (Afiq and Azura, 2014).

Polysaccharide is one of the most widely used groups of organic filler in latex films. Polysaccharide with high biodegradable capability is desired from the viewpoint of biodegradable latex film. Starch is by far the commonly used polysaccharide for biodegradable latex film; here biodegradable properties relies on growth of microorganism due to secretion of extracellular enzyme to degrade the starch particles in latex films consequently formation of voids/ holes on films or fragment of films.

Low molecular weight polysaccharide is a new group of polysaccharides which consist of nanometric scale crystals or particles. The main advantage of nanoscale starch over conventional microscale starch is the larger surface area and greater aspect ratio. Over the past few years, nano starch has attracted increasing attention and have been considered for application in biomedical fields, food processing fields and food packaging fields. Most recently, bio nanocomposites have been developed such that inclusion of nanostarch in polymer blend enable additional reinforcement and barrier properties through nanoscale size effect of starch dispersed in the matrix and the strong interaction between filler and matrix (Saba et.al., 2017).

Acid hydrolysis commonly used to synthesis starch nanocrystal. Formation of such nanoscale structure relies on the mechanism such that acid hydrolyze amorphous region of starch granule without large disruption of the crystalline structure of starch granules (Lin et al., 2011). Strong acids such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) are commonly utilize in acid hydrolysis process. The H_2SO_4 hydrolyzed sample has higher stability, which is due to the presence of sulphate groups (Wei et.al., 2014; Angellier et al., 2004; Hoover, 2000).

Similarly, for all latex films, the properties of starch filled latex films depend not only on the type of latex and filler particles, but also on dispersity of starch and interaction between starch and latex matrix (Senna et al., 2012; Wu et al., 2004). For starch filled biodegradable films has sets a challenge. For other latex films component, the incompatibility of filler and the matrix can lead to poor wettability as well as nonuniformity of filler dispersion leading to the agglomeration. Therefore, it is sensible to modify the surface of sago starch in order to improve ease of interaction with and dispersion within the latex matrix. Surface of starch can be covered with hydroxyl groups, which contribute to its hydrophilic nature and also provides the possibility for chemical modification.

1.2 PROBLEM STATEMENT

Sago starch can be used as filler in latex because it is economic and abundant. Sago starch is organic filler that provide biodegradable properties to NR latex glove or XNBR thin film products upon disposal. There is antagonism effect between biodegradability and mechanical properties of sago filled XNBR latex film. In detail, sago starch is prone to agglomeration (Afiq et.al., 2014) and incompatibility between hydrophobic lattice system and hydrophilic sago starch system eventually reduced the mechanical properties of latex films with sago starch loading (Azura et.al., 2010; Afiq et.al., 2014; Afiq et.al., 2015 (a); Afiq et.al., 2018). Surface of hydrophilic starch is covered with hydroxyl groups which provide possibility for chemical modification to improve compatibility between latex system and sago starch. Therefore, works has carried out to modify the surface of sago starch in order to improve ease of interaction and dispersion within the NR latex matrix (Afiqet.al., 2015 (b)) as well as within XNBR latex matrix (Afiq et.al., 2015 (a)).

Chemical modification of native sago starch can be achieved using a number of approaches; for instance, modification by chemical treatment or physical treatment (Singh et.al., 2007). Among various modification approaches; acid hydrolysis become one of the approach while at the same time capable to reduce particle size of starch. Acid hydrolysis induce formation of sulphate ester group on the surface of starch particle which increase the tendency to form links between rubber matrix and starch (Rohanaet.al., 2015). Although, this type of modification was used but optimization of acid hydrolysis parameter for sago starch and its effect acid hydrolyzed sago starch (AHSS) for used in NR latex. However, the addition of AHSS in XNBR latex has not been extensively investigated. Rohana et.al. (2015) has reported on effect of AHSS on reinforcing effect of sago starch was positive but has poor biodegradability for NR latex films.

In this work, NR latex films and XNBR latex films filled with acid hydrolyzed sago starch (AHSS) were prepared. AHSS with nanoscale structure has large surface area and high aspect ratio classified as high potential and promising filler in latex. Acid hydrolysis modified surface of the sago starch can reduced the starch particle size, transform it into moieties capable of increasing interactions with latex matrix. Therefore, there is potential for improvement of sago starch interaction and latex matrix interaction by using AHSS. It is apparently desiring to obtain biodegradable NR latex films and XNBR latex films with good mechanical properties. Therefore, this research is conducted to assess the potential of AHSS in mechanical properties and biodegradability of XNBR latex films and compared the results with NR latex films.

1.3 RESEARCH OBJECTIVES

The main objective of this study is to develop biodegradable NR and XNBR films with AHSS. The specific objectives include:

I. To obtain the optimum synthesis parameters of preparation acid hydrolysis sago starch fillers.
II. To investigate the effect of addition of AHSS fillers on mechanical properties of NR latex films and XNBR latex films.
III. To determine the biodegradability of NR latex films and XNBR latex films with addition of AHSS fillers.

1.4 THESIS OUTLINE

This thesis is covered all chapters that consist of:

Chapter 1: Consists of background, problem statement and objective of the research.

Chapter 2: Provide literature review of project, review of methods to produce AHSS and testing that conducted to the both AHSS filled latex films.

Chapter 3: State the detail of the raw materials that used in this research, experimental procedures employed, and machine handling that were involved in generating experimental data for this research.

Chapter 4: Data and results obtained as well as charts discussion on optimization of AHSS synthesis parameter, mechanical and morphological properties of rubber latex films would be presented in detail.

Chapter 5: Summary and conclusion on this present work as well as suggestions for the further research.

Chapter 6: List of references that were used in this research.

CHAPTER 2

LITERATURE REVIEW

2.1 NATURAL RUBBER (NR) LATEX

Natural rubber (NR) latex is milky rubber that obtained from tapping the bark of Hevea brasiliensis (Hevea). Hevea trees which originate from Brazil, suitable to grow in tropical country especially in Southeast Asia. Currently, largest natural rubber producers are from Southeast Asia such as Thailand, Vietnam and Indonesia (UN comtrade, 2013).

NR latex (cis-1,4-polyisoprene) with the chemical structure as shown in Figure 2.1 (James, 1995). Commercial NR latex is concentrated to 60% (vol/vol) and preserved with ammonia. NR latex contain protein, carbohydrate, organic and inorganic constituents (Yip.et.al, 2002). Amount of non rubber content is relatively in a small fraction in the whole latex system. The non rubber substances help in stabilize the NR latex (Araham et al., 2012) and contribute to excellent properties of NR latex (Tarachiwin et.al., 2005). The advantages of NR latex films including the outstanding elasticity and flexibility (Peter, 2001). Meanwhile, the drawbacks of NR latex products are allergenic protein (Yip et al., 2002) and waste disposal problems (Ikram, 1999). Besides, carbon-carbon double bond in NR latex structure (Figure 2.1) causes poor resistance to heat, chemical, oxygen and ozone attack. Presence of protein content is also the distinct characteristic of NR latex from synthetic latex. Waste disposal problem of NR latex products can be overcome by incorporation of biodegradable fillers because is cheap, abundant and environment friendly.

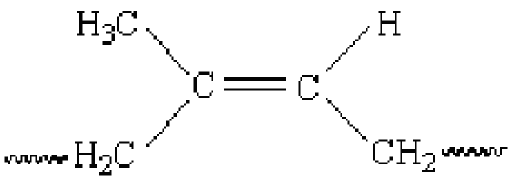
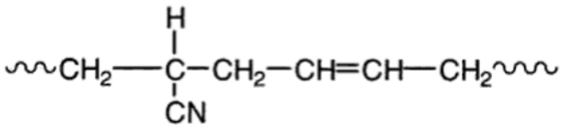


Figure 2. 1: Chemical Structure of NR latex (James, 1995)

2.2 CARBOXYLATED ACRYLONITRILE BUTADIENE RUBBER (XNBR) LATEX

Acrylonitrile butadiene rubbers are copolymers of butadiene and acrylonitrile produce by emulsion polymerization initiated by redox catalyst system. Acrylonitrile is often copolymerized with other monomers rather than used alone in emulsion polymerization due to the highly water-soluble property of monomer and the effect of copolymerization can improved the chemical resistance in automotive and latex glove applications (Christopher and Eric, 2003). Acrylonitrile butadiene copolymer commonly called as nitrile. Nitrile ionomer is terpolymer which comprises not only acrylonitrile and butadiene but also carboxylic acid units and known as carboxylated NBR latex (XNBR). The chemical structure of NBR and XNBR are shown in Figure 2.2 and Figure 2.3 respectively (Rapra Technology Limited, 2004; Foo, 2013).



$$\sim CH_2-\overset{H}{\underset{CN}{C}}-CH_2-CH=CH-CH_2\sim$$

Figure 2. 2: Chemical structure of NBR (Rapra Technology Limited, 2004)

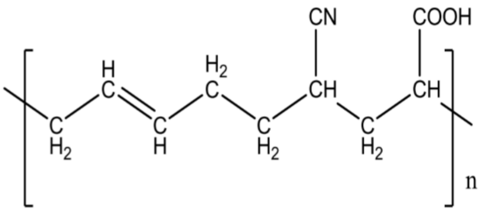


Figure 2. 3: Chemical structure of XNBR (Foo, 2013)

NBR and XNBR are synthetic latex. The main advantage of these synthetic polymers are possess many NR latex characteristics yet free of any latex proteins. Superior properties of nitrile gloves as compared to NR latex gloves are better chemical and biohazard protection, more resistant to puncture, tear and longer shelf life. The drawbacks of nitrile gloves are being non-biodegradable, less elastic and form fitting compared to NR. Another drawback of nitrile is pricing, nitrile is a petroleum based product and the price of nitrile fluctuates with the price of oil. Nitrile has been steadily moving towards becoming more user friendly with improvements in formulations and manufacturing processes. Shen Wei USA, Inc. is one of the first manufacturers able to manufacture a soft nitrile glove that received FDA’s 510k approval (www.shenweiusa.wordpress.com). Indeed, at present, general research in develop biodegradable FDA approved nitrile disposable glove is still in its infancy.

2.3 STARCH

Starch is found in almost all tissues green plants. Only a small number of plants are commercially grown for starch; they include cereal (such as wheat, corn, sorghum, and rice), tuber (mainly potato), root (tapioca and arrowroot), stem (sago), and legume (mainly pea) crops (Ratnayake et.al., 2003). Starch is obtained from of many monosaccharides in plants. Large amount of monosaccharides (thousands) link up to form polysaccharides. Starch also known as homopolysaccharides because contains a single type of monosaccharides. For examples, it only contains glucose molecules that link together. Starch as shown in Figure 2.4 can be found in two form which are branched and unbranched. Unbranched starch contains only a chain of glucose link together by α (1-4) glycosidic bonds. It is refer as amylose. Meanwhile, branched starch contains both α (1-4) glycosidic bonds and α (1-6) glycosidic bonds therefore refer as amylopectin. Starch and glycogen are made up of glucoses and have similar structure which the polysaccharides can be branched or unbranched. Their main difference is starch has branch points occurs every 24-30 glucose residues whereas glycogen has branch points occur every 8-12 glucose residues (Xie et.al., 2013).

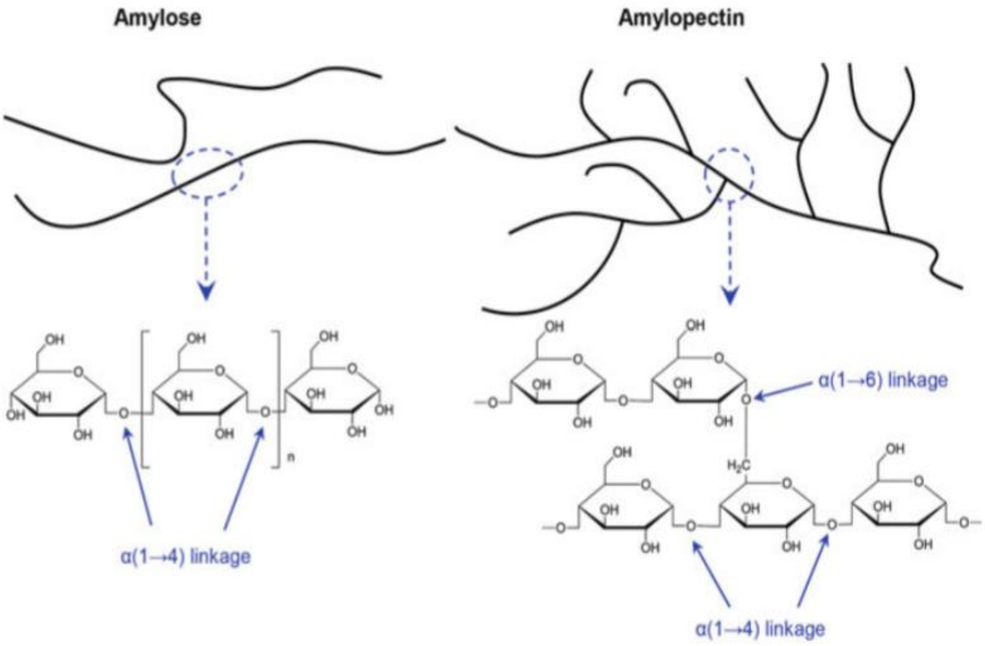


Figure 2. 4: Chemical structure of amylose and amylopectin molecules of starch (Xie et.al., 2013)

2.3.1 Sago Starch

Sago starch is the powdery starch produce from pith inside trunk of Metroxylon Sagu palm trees. It is also well known for abundance in Malaysia’s starch production sector and bring great agricultural revenue that ranks fifth place after pepper, oil palm, cocoa, and rubber (Abd Aziz, 2002).

Overview of starch granule structure is shown in Figure 2.5, which illustrates a concentric three-dimensional architecture from the hilum, with a crystallinity varying from 15 % to 45 % depending on the botanical source (Zobel 1988). At the lowest level of granule organization (upper left), alternating crystalline (hard) and semicrystalline (soft) shells are shown (dark and light colors, respectively). Shells are thinner toward the granule exterior (due to increasing surface area to be added to by constant growth rate) and the hilum is shown off-center. At a higher level of structure, the blocklet structure is shown in association with amorphous radial channels. Blocklet size is smaller in the semicrystalline shells than in the crystalline shells. At the next highest level of structure, one blocklet is shown containing several amorphous crystalline lamellae. In the next diagram, amylopectin is shown in the lamellae. The next image is a reminder of the importance of amylose–lipid (and protein) components in the organization of amylopectin chains. At the highest level of order, crystal structures of the starch polymers are shown (Gallant et.al.,1997; Imberty et.al.,1988).

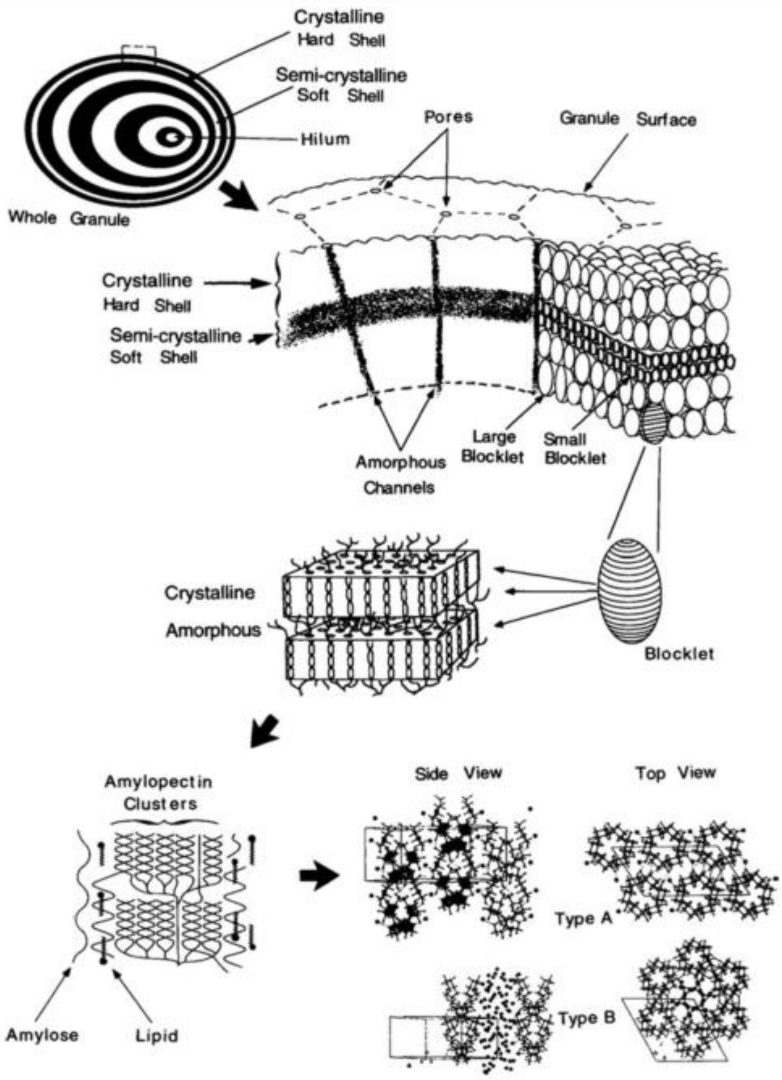


Figure 2. 5: Overview of starch granule structure (Gallant et.al.,1997; Imberty et.al.,1988)

Sago starch made up from composition and starch granules that different from other botanical sources. The basic characteristic and composition of starch granules as shown in Table 2.1 and Table 2.2 respectively. Sago starch granules is cereal type, shape of oval, unimodal distribution and have size in range of 20-40 µm (Tester and Karkalas, 2002). Sago starch composed of two macromolecular, namely linear amylose and branched amylopectin. Sago starch consist of 25.65% amylose and 74.35% amylopectin classified as low amylose content starch (Kristijarti et al., 2012). Amylose is water soluble but readily undergoes aggregation and precipitation, whereas, amylopectin is water insoluble but readily gelatinize when heated with water. The crystalline region contributes by linear amylose while the amorphous region contributes by amylopectin in disorder conformation, whereas the semi-crystalline rings are formed by the lamellar structure of alternating crystalline and amorphous regions.

The glycosidic chains presents spiral shaped single or double helices with rotation on the α (1-4) link and with six glucoses per turn, the arrangement causes hydroxyl groups to be displayed toward the exterior of the helices. Therefore, core of the helix is mainly hydrophobic (Pérez et al. 2009). The distribution of chain length in amylopectin critically influences the inner assembly structure of starch granules and the interaction with the water or solvent (Lin, 2010). Moreover, this unique hierarchical structure of starch makes it possible to extract platelet-like nanoparticles (Bel Haaj et al., 2013).

Table 2. 1: Characteristics of starch granules from different botanical sources (Tester and Karkalas, 2002)

Starch	Type	Shape	Distribution	Size (um)
Barley	Cereal	Lenticular (A-type), spherical (B-type)	Bimodal	15–25, 2–5
Maize (waxy and normal)	Cereal	Spherical/polyhedral	Unimodal	2–30
Amylomaize	Cereal	Irregular	Unimodal	2–30
Millet	Cereal	Polyhedral	Unimodal	4–12
Oat	Cereal	Polyhedral	Unimodal	3–10 (single) 80 (compound)
Pea	Legum	Rentiform (single)	Unimodal	5–10
Potato	Tuber	Lenticular	Unimodal	5–100
Rice	Cereal	Polyhedral	Unimodal	3–8 (single) 150 (compound)
Rye	Cereal	Lenticular (A-type), Spherical (B-type)	Bimodal	10–40, 5-10
Sorghum	Cereal	Spherical	Unimodal	5–20
Tapioca	Root	Spherical/lenticular	Unimodal	5–45
Triticale	Cereal	Spherical	Unimodal	1–30
Sago	Cereal	Oval	Unimodal	20–40
Wheat	Cereal	Lenticular (A-type), Spherical (B-type)	Bimodal	15–35, 2-10

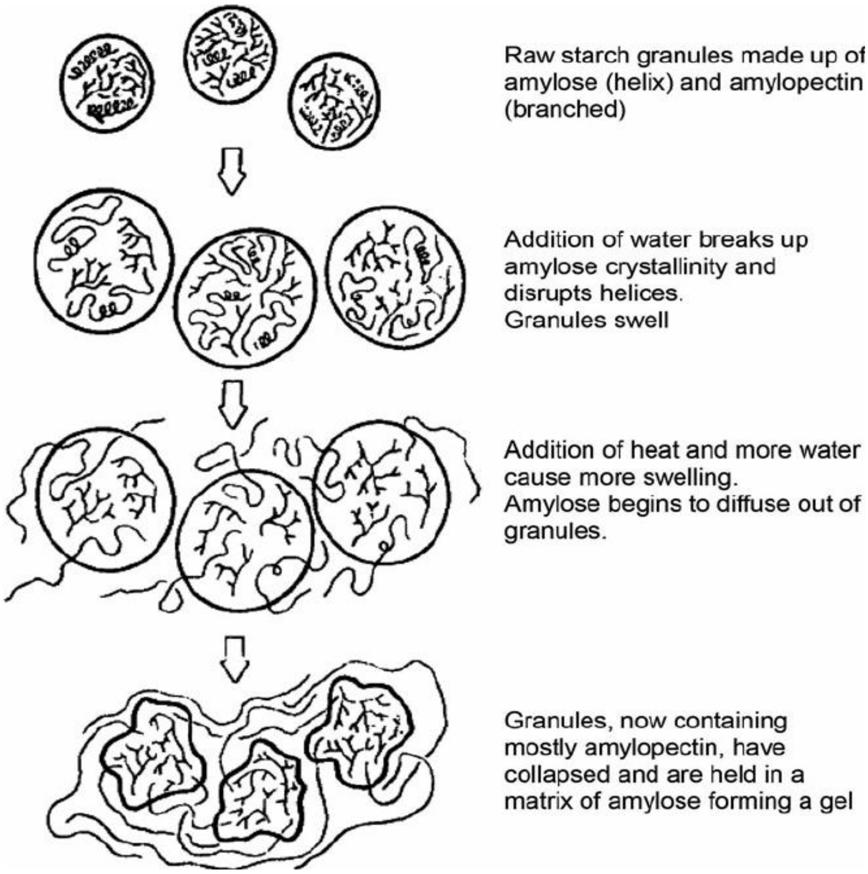
Table 2. 2: Composition of sago starch (Kristijarti et al., 2012)

Contents	Value
Carbohydrates	84.78%
Amylose	25.65%
Amylopectin	74.35%

2.3.2 Sago Starch Gelatinization and Retrogradation

Starch gelatinization occur in the presence of water and heat with the condition that starch-water system heated beyond gelatinization temperature. Gelatinization temperature of sago starch in excess water is about 60-77°C (Ahmad et al., 1998). Gelatinization disrupt structure of starch granules lead to sequence of irreversible changes. Some researchers claim that gelatinization starts when granular birefringence is lost, others believe it is initiated when an increase in viscosity occurs. Generally during gelatinization, starch granule will swell as water diffuse in slowly, however as more water diffuse in via amorphous region, starch granule swell further to a maximum extent cause sudden increase in volume of starch granule which affects starch crystallinity by destruct crystalline or double helix structure.

Next, amylose start to move out from the granules and followed by larger molecular weight polymers such as fragments of amylopectin while some of the starch become solubilized (Ghanbarzadeh and Almasi, 2013; Ratnayake and Jackson, 2007; Palavand Seetharaman, 2006; Shi and and Seib, 1992; Lait and Kokini, 1991). The solubilized starch granules form a gel network in viscous paste (Wang et al., 2017). A schematic representation of starch gelatinization mechanism shown in Figure 2.6 (Remsen and Clark, 1978). Many theories of gelatinization mechanism developed such as semi-cooperative (Marchant and Blanshard, 1978), water availability (Donovan, 1979), crystallite stability (Evans and Haisman, 1982), sequential phase transitions (Nakazawa et.al., 1984) and three-stage phase transition theories (Biliaderis et.al., 1986); but none of them are able to explain starch gelatinization mechanism completely (Ratnayake and Jackson, 2009).



Raw starch granules made up of amylose (helix) and amylopectin (branched)

Addition of water breaks up amylose crystallinity and disrupts helices. Granules swell

Addition of heat and more water cause more swelling. Amylose begins to diffuse out of granules.

Granules, now containing mostly amylopectin, have collapsed and are held in a matrix of amylose forming a gel

Figure 2. 6: Mechanism of starch gelatinization (Remsen and Clark, 1978)

Upon cooling and aging of gelatinized starch at storage, the gelatinized starch undergoes retrogradation (Figure 2.7) which is the phenomena involve rearrangement of both amylose and amylopectin reform crystalline structure (Yu and Christie, 2005). There are two stages of starch retrogradation occurs with instantaneous reaggregates and realignment of amylose then followed by recrystallization of amylopectin.

Retrogradation begins with amylose as amylose rearrange at faster rate than amylopectin at which linear chain of amylose facilitates formation of hydrogen bond to build up single or double helices structure, whereas amylose has branched chain that delay rearrangement of outermost short branches for recrystallization (Sandhu and Singh, 2007; Perera and Hoover, 1999; Bornet, 1993; Kett, 2013). Consequently, duration of retrogradation depend on content of both amylose and amylopectin and closely related to structural arrangement of starch chains before gelatinization. The process of retrogradation causes gelatinized starch become stiffer and harder with the increases of amylose content leads to starch embrittlement (Liu et.al., 2009).

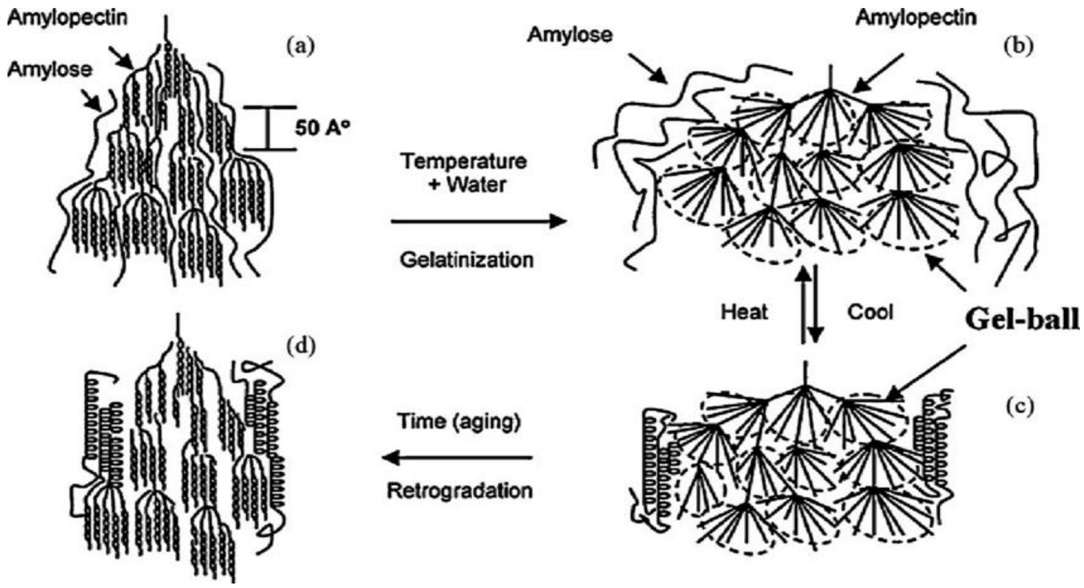


Figure 2. 7: Schematic representations of starch gelatinization and retrogradation (Yu and Christie, 2005)

Gelatinization temperature of sago starch in excess water is about 60-77°C (Ahmad et al., 1998; Hashim et al., 2000). Gelatinization temperature can be influence by electrolyte. In other word, electrolyte affect swelling and gelation of sago starch. Electrolyte is solutions that can conduct electricity due to presence of particles or ions in the solvent by addition of salts, sugars, acids or bases. Salts solution can increase or decrease gelatinization temperature of sago starch (Wooton and Bamunuarachchi, 1980; Evans and Haisman, 1982; Chuncharoen and Lund, 1987; Paredes-Lopez and Hernandez-Lopez, 1991; Jane, 1993) and the influences is very complex depend on type and concentration of salts (Ahmad et al., 1999).

Besides, the other alternative to gelatinize the starch is by alkali treatment. Alkali treatment can gelatinize starch under room temperature and is recommended over the method uses water and heat because will not experience retrogradation of starch (Karim et al., 2006). In previous study, alkali gelatinized starch enhanced the starch dispersion in NR latex and thereby improve the mechanical properties of NR latex films (Wu et.al., 2004; Rohaya et.al., 2014).

2.3.3 Starch Modification

In latex application, sago starch is used as organic filler to accelerate the biodegradation process. However, sago starch is highly hydrophilic and lack of compatibility with latex system. Therefore, sago starch modification which involve alteration of physical and chemical characteristics of native sago starch to improve its hydrophobicity or reduce its size, can be used to tailor the sago starch for specific latex application.

General starch modification can be categories into physical methods and chemical methods. Physical modification applied heat or moisture treatment whereas chemical modification involves derivatization or conversion to introduce functional groups into starch molecules (Singh et al., 2007). Surface modification of starch by chemical grafting was successful for cornstarch to reinforce natural rubber composite (Liu et.al., 2008). Angelier et.al. (2005) reported the study of functionalization of starch nanocrystal (SNC) to broaden the number of possible polymeric matrices by allowing the processing of composite materials from an organic solvent instead of aqueous suspensions. This finding disclosed the potential possibility of surface modification of SNC as there are more modification were studied. For example, stearate grafting, partial grafting, poly(ethylene glycol) methyl ether (PEGME) modification via toluene diisocyanate (TDI), grafting of poly(tetrahydrofuran) (PTHF), poly(propylene glycol) monobutyl ether (PPGBE), and poly(caprolactone) (PCL), and preparation of amphiphilic SNC. Summary of starch modification and preparation techniques are shown in Table 2.3.

Table 2. 3: Types of starch modifications and preparation techniques (Singh et al., 2007)

Modification	Types	Preparation
Physical	Heat/moisture treatment	Heat–moisture treatment—Heating starch at a temperature above its gelatinization point with insufficient moisture to cause gelatinization
		Annealing—Heating a slurry of granular starch at a temperature below its gelatinization point for prolonged periods of time
Conversion	Partial acid hydrolysis	Treatment with hydrochloric acid or ortho-phosphoric acid or sulphuric acid
	Partial enzymatic hydrolysis	Treatment in an aqueous solution at a temperature below the gelatinization point with one or more food-grade amylolytic enzymes
	Alkali treatment	Treatment with sodium hydroxide or potassium hydroxide

	Oxidation/bleaching	Treatment with peracetic acid and/or hydrogen peroxide, or sodium hypochlorite or sodium chlorite, or sulphur dioxide, or potassium permanganate or ammonium persulphate

Table 2.3 (Continued): Types of starch modifications and preparation techniques (Singh et al., 2007)

Modification	Types	Preparation
	Pyroconversion (dextrinization)	Pyrodextrins—Prepared by dry roasting acidified starch
Derivatization	Etherification	Hydroxypropyl starch—Esterification with propylene oxide
	Esterification	Starch acetate—Esterification with acetic anhydride or vinyl acetate
		Acetylated distarch adipate—Esterification with acetic anhydride and adipic anhydride
		Starch sodium octenylsuccinate—Esterification by octenylsuccinic anhydride
	Cross-linking	Monostarch phosphate—Esterification with ortho-phosphoric acid, or sodium or potassium ortho-phosphate, or sodium tripolyphosphate
		Distarch phosphate—Esterification with sodium trimetaphosphate or phosphorus oxychloride
		Phosphated distarch phosphate—Combination of treatments for monostarch phosphate and Distarch phosphate
	Dual	Acetylated distarch phosphate—Esterification by

	modification	sodium trimetaphosphate or phosphorus oxychloride combined with esterification by acetic anhydride or vinyl acetate
		Hydroxypropyl distarch phosphate—Esterification by sodium

Among the starch modification methods, starch size can be reduced through either chemical treatment or physical treatment. Example of several methods, such as acid hydrolysis (Angellier et al., 2005), chemical gelatinization (Jane and Shen 1993; Wang et.al., 2007), starch dissolution (Stevenson et.al., 2007; Syahariza et.al., 2010), nanoprecipitation (Hornig et al. 2009; Chin et al. 2011; Tan et al. 2012), ultrasonic irradiation (Suki et.al., 2016), ball milling (Kerr et.al., 2001; Vertuccio et.al., 2009).

2.3.3 (a)Chemical Treatment – Acid Hydrolysis Sago Starch

The chemical treatment which based on the use of acid hydrolysis to dissolve the amorphous and paracrystalline regions of the starch granules is commonly adopted to produce starch nanocrystals (Angellier et al., 2005). Reaction mechanism of acid hydrolyses starch as shown in Figure 2.8. Initially, hydroxonium ion (H_3O^+) attack the oxygen atom of the α (1-4) glycosidic bond (Figure 2.8 (A)) and then hydrolyzes the linkage. Next, the electrons in one of the carbon–oxygen bonds move onto the oxygen atom (Figure 2.8 (B)) to generate an intermediate (Figure 2.8 (C)). The carbocation intermediate is a Lewis acid, so it subsequently reacts with water (Figure 2.8 (D)), a Lewis base, leading to the regeneration of a hydroxyl group (Figure 2.8 (E)). The acid works on the starch granule surface before enter the inner region of starch (Hoover, 2000)

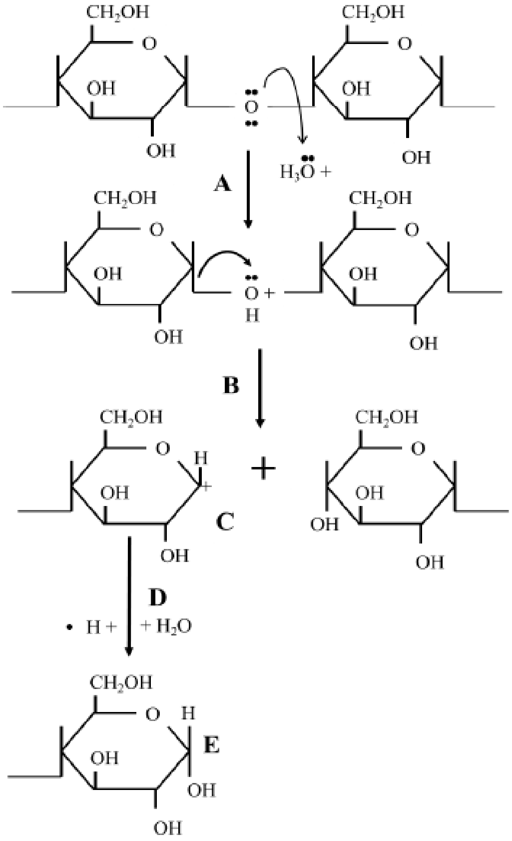


Figure 2. 8: Mechanism of acid hydrolysis on starch (Hoover, 2000)

Dominant reaction of acid hydrolysis involves breakage of α (1-4) and α (1-6) glycosidic bond thus disrupt amylopectin and amylose glucose polymer. This process removes amorphous and semicrystalline layers of the starch until remaining the acid-resistant fraction known as starch nanocrystal (SNC). Hydrolysis will breaks polysaccharides into smaller and smaller molecules until level of monosaccharides such as glucose whereby glucose will further degrade to formic and levulinic acids. These acids then adsorb to the surface of SNC induces negative-charged (Figure 2.9). Meanwhile, esterification reaction occur simultaneously and form sulfate ester groups on the surface of the SNC.

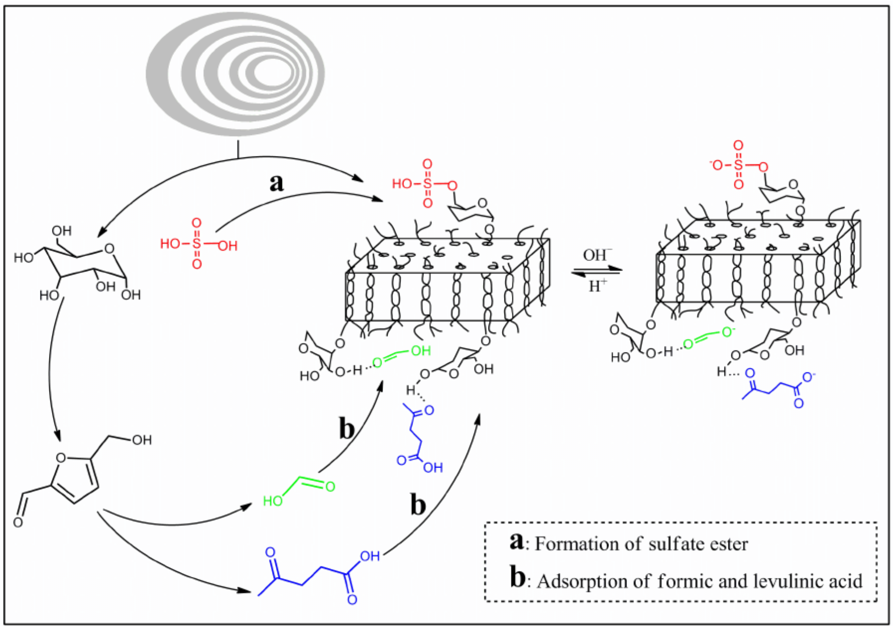


Figure 2. 9: Formation of sulfate esters and adsorption of formic and levulinic acids on the surface of SNC (a: Formation of sulfate ester, b: adsorption of formic and levulinic acids)(Wei et al.,2014)

Effect of acid hydrolysis depends on botanical origin, the ratio of amylose and amylopectin, the crystalline type of starch and the granule morphology, conditions of acid hydrolysis, for examples, types of acid, acidity, temperature and duration of hydrolysis (Angellier et al., 2004; Hoover, 2000).

Research done by Wei et.al. (2014) on surface chemical composition and dispersity of starch nanocrystals (SNC) formed by sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) hydrolysis found out that H_2SO_4 hydrolyzed sample has higher stability and relative small particle distribution of SNC. These cause more stable suspensions due to presence of sulphate group. Besides, in term of starch crystallinity, crystalline region less prone to acid attack due to the dense structure in the crystallite. The presence of glycosidic linkages in the interior of the double helix which are both reasons tend to hinder the penetration of hydrogen ions, regardless of solvation effect (Utrilla-Coello et al., 2014; Jacobs et al., 2008). Furthermore, effect of acid hydrolysis