SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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PREPARATION AND CHARACTERIZATION OF SUGARCANE BAGASSE AS BIODEGRADABLE FILLERS ON NATURAL RUBBER LATEX FILMS

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “**Preparation and Characterization of Sugarcane Bagasse as Biodegradable Fillers on Natural Rubber 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.

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Date: 21 June 2017

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LIST OF ABBREVIATIONS

ASTM	American Standard for Testing Materials
DRC	Dry Rubber Content
KOH No.	Potassium Hydroxide Number
MST	Mechanical Stability Test
NR	Natural Rubber
TSC	Total Solid Content

LIST OF SYMBOLS

˚C	Degree Celsius
g	Gram
µm	Micro Millimeter
MPa	Mega Pascal
d. nm	Diameter in Nano meter
N/mm	Newton per Millimeter
pphr	Part per Hundred Rubber
cm^{-1}	Per Centimeter
rpm	Revolution per Minutes
w/w	Weight per Weight
%	Percentage

PERSEDIAAN DAN PENCIRIAN SISA TEBU SEBAGAI BIODEGRADASI PENGISI DALAM FILEM LATEKS GETAH ASLI (GA)

ABSTRAK

Kajian ini dijalankan untuk meningkatkan biodegradasi filem lateks getah asli (GA) dengan menambah pengisi yang biodegradasi ke dalam sebatian lateks GA. Keperluan untuk bahan-bahan ekonomi dan mesra alam telah melanjutkan minat dalam mengguna gentian buangan semula jadi, sisa tebu. Sisa tebu adalah banyak dan murah. Oleh itu, pengisi yang biodegradasi yang diguna dalam kajian ini adalah kanji sagu dan sisa tebu. Kanji sagu diperoleh daripada pembekal dan sisa tebu disediakan di dalam bilik makmal. Terdapat dua kaedah untuk menyediakan penyebaran pengisi, iaitu bola pengilangan dengan ejen dan process rawatan dengan menggunakan 2 % natrium hipoklorit yang dirujuk sebagai sisa tebu dirawat. Filem lateks GA dengan kanji sagu menunjukkan sifat-sifat mekanikal yang lebih baik berbanding dengan filem lateks GA denagn sisa tebu. Kekuatan tegangan, pemanjangan dan kekuatan koyakan filem lateks GA dengan sisa tebu yang dirawat menunjukkan sifat-sifat yang lebih baik berbanding filem lateks GA dengan sisa tebu. Ujian kehilangan jisim, filem lateks GA dengan kanji sagu mempunyai biodegradasi yang tertinggi, diikuti filem lateks GA dengan tebu sisa yang dirawat dan kemudian filem lateks GA denagan sisa tebu. Ia membuktikan bahawa penambahan pengisi biodegradasi boleh meningkatkan keupayaan biodegradasi filem lateks GA. Pembebanan optimum sisa tebu yang dirawat dalam filem lateks GA adalah 5 pphr dengan menunjukkan kekuatan tegangan, pemanjangan pada takat putus, modulus tegangan dan kekuatan koyakan yang tinggi. Peningkatan pembebanan kandungan sisa tebu yang dirawat boleh menyebabkan pengisi bergumpul dan menjadi sebagai titik kegagalan dalam filem lateks GA. Sebagai kesimpulan, sisa tebu merupakan pengisi bio yang berpotensi untuk menggantikan kanji sagu di dam filem lateks GA.

PREPARATION AND CHARACTERIZATION OF SUGARCANE BAGASSE AS BIODEGRADABLE FILLERS ON NATURAL RUBBER LATEX FILMS

ABSTRACT

The studied was carried out to improve the biodegradability of Natural Rubber (NR) latex films by adding biodegradable filler in the NR latex compound. The requirement for economic and environmental-friendly materials have extended an interest in using of natural waste fibres, sugarcane bagasse. Sugarcane bagasse was abundant and cheap. Hence, the biodegradable filler used in this studied was sago starch and sugarcane bagasse. Sago starch was obtained from the supplier, while the sugarcane bagasse was prepared in the laboratory. There were two methods use to prepare the filler dispersion, which were ball-milling with dispersing agent and treatment process by using 2 % sodium hypochlorite solution, which referred as treated sugarcane bagasse. NR latex film with sago starch shown better mechanical properties compared to NR latex film with sugarcane bagasse. The tensile strength, elongation at break and tear strength of NR latex film with treated sugarcane bagasse shown better properties compared to NR latex film with sugarcane bagasse. In the mass loss test, NR latex film with sago starch has the highest biodegradability, follow by NR latex film with treated sugarcane bagasse and then NR latex film with sugarcane bagasse. It proved that the addition of biodegradable filler can improved the biodegradability of NR latex film. The optimum loading of NR latex film with treated sugarcane bagasse was obtained at 5 pphr with high tensile strength, elongation at break, tensile modulus and tear strength. At higher loading of treated sugarcane bagasse tends to form agglomerate and act as failure point in NR latex film. To conclude, sugarcane bagasse shown a potential as bio fillers to replace sago starch in NR latex film.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Malaysia was the top five of NR latex production in the world. NR latex was obtained from the taping process of Hevea Brasilienisis plantation and it was use for production of different type of rubbery goods. Figure 1.1 shown the Malaysia's NR consumption from year 2000 until March of 2016. Based on Figure 1.1, the total NR consumption shown an increment of 30 % from year 2000 to year 2015 in Malaysia (Malaysia Rubber Board, 2016). The growing of NR consumption explained that NR was still an important raw material for the production of gloves in Malaysia.

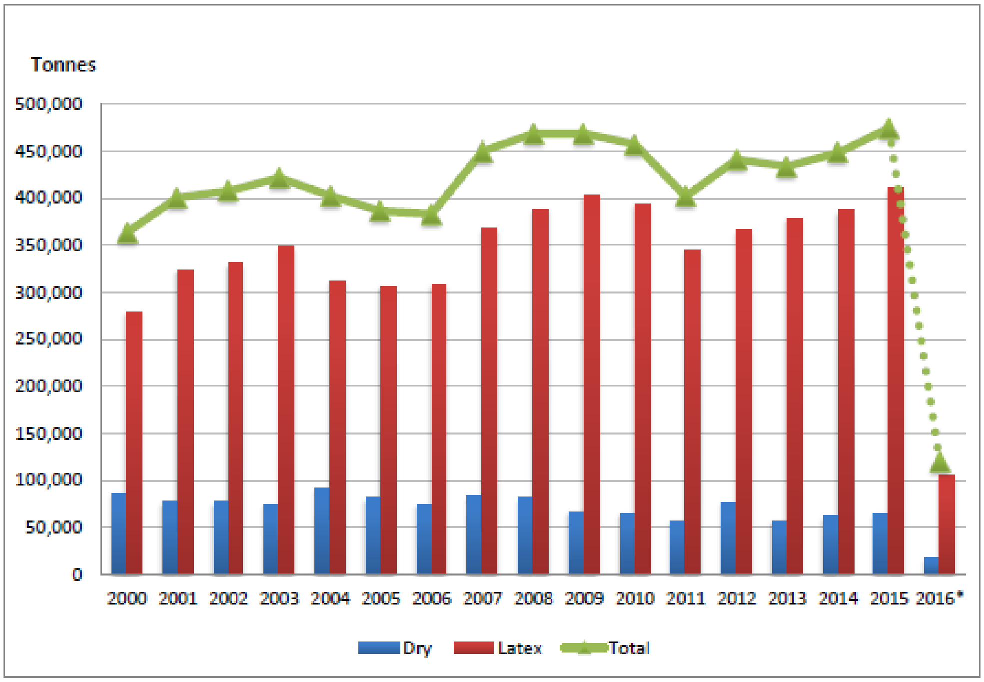

Figure 1.1: Malaysia's NR consumption from year 2000 until March of 2016 (Malaysian Rubber Board, 2016).

NR latex was a preferred raw material for latex end products manufacturers around the world due to ease of processing and the excellent performance of latex end products in critical environments (https://www.vytex.com/blog/deproteinized-natural-rubber-latex/). Figure 1.2 shown the distribution of Malaysian rubber product companies by product sector in year 2015. It shown that the major production of latex products were gloves, condoms, catheters and latex thread. Among all the latex product companies, 49.53 % of them were manufactured glove products (Malaysian Rubber Board, 2016).

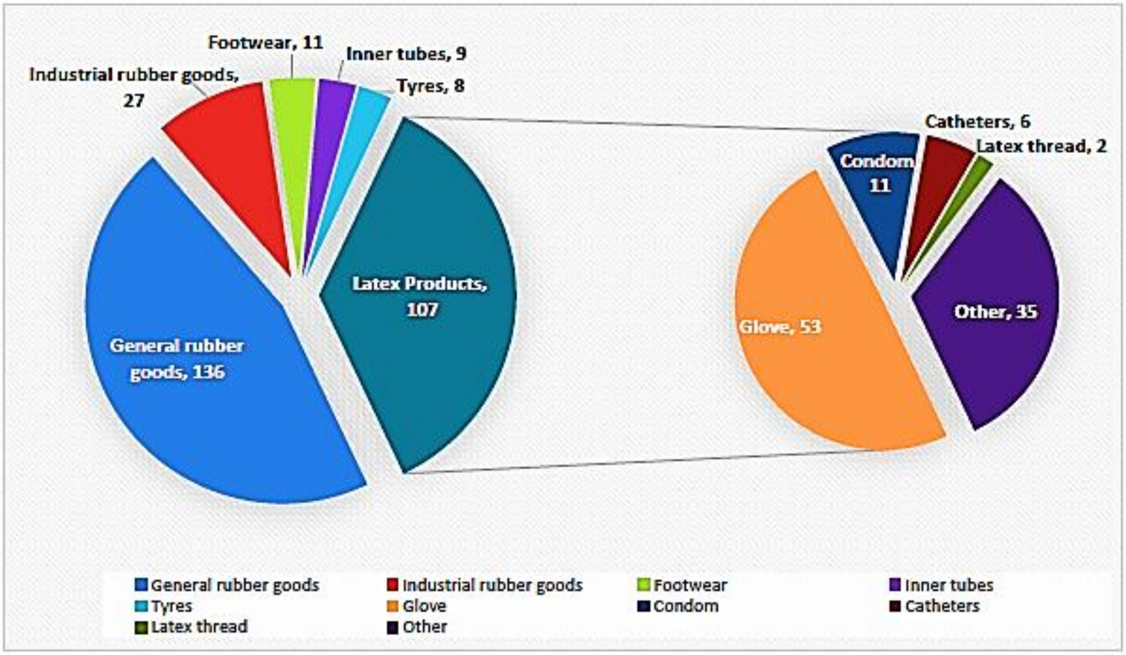

Figure 1.2: Distribution of Malaysia rubber product companies by product sector for year 2015 (Malaysian Rubber Board, 2016).

The huge production of latex glove based on its function as a hand barrier protection equipment which provide a great performance in a broad range of industries such as medical, sanitary and food industry. Among all the industries, latex glove takes a vital role in medical industry. The medical staff need to protect themselves from harmful pathogens and contaminants by wearing medical glove. The patients also gain benefit when the medical staff wearing a medical glove, which prevent potential hazards to harm their bodies (https://www.esafetysupplies.com/Importance-of-Surgical-Gloves.html).

Latex glove was a single use commodity, which was thrown away after usage. In 2012, the production of medical glove alone was already about 140 billion pieces. The industry demand for latex glove was increased every year where the glove product has increased 9 -10 % each year. The increasing of NR latex glove production result in increase of the latex glove solid waste disposal. 24 % of medical total solid wastes come from rubber gloves which in total were 2.1 million pieces or 19.4 tones from total solid waste fraction (Misman and Azura, 2014). In year 2013, Global Development Research Center (2011) reported that 57 – 80 % of rubber solid wastes are disposed in a landfill.

The disposed gloves took more than 2 years to degrade in the natural environment. The prolonged life of disposed latex glove was due to the compounding ingredients especially sulphur and antioxidant. Sulphur was a crosslinking agent which formed the chemical bond to form the three-dimensional network during vulcanization process. These sulphur linkages prevented the latex/rubber products to degrade easily in natural environment (Misman and Azura, 2014).

In order to produce totally biodegradable glove, it was necessary to change it raw material which was NR latex. However, it was easier to produce partially biodegradable glove by using biodegradable fillers as one of the latex compounding ingredients (Siti Nuraya et. al., 2012). Sago starch and banana stem powder has been studied as a filler in NR latex compound. The results shown that the natural filler can improve the biodegradability of the NR latex film and enhance the mechanical properties of the film. (Siti Nuraya et. al., 2012; Afiq and Azura, 2013). In the study, it found out that the NR latex film shown the highest tensile strength (around 18 MPa – 19 MPa) when the loading of sago starch loading was at

10 pphr (Afiq and Azura, 2013). Meanwhile, the NR latex film shown the highest tensile strength (19.67 MPa) when the loading of banana stem powder was at 5 pphr (Siti Nuraya et. al., 2012).

The requirement for economical and environment-friendly materials have extended an interest in using of natural waste fibres. Sugarcane bagasse was a fibrous residue obtained from sugarcane after extraction of sugar juice. It was a residue produced in large quantities by sugar industries. The total plantation area of sugarcane in Malaysia was nearly 34,500 acres and approximately 140 kg of bagasse was generated from each ton of sugarcane after being processed. However, the utilization of sugarcane bagasse was still limited and was mainly used as a fuel to power sugar mill (Aeslina et. al., 2013). Hence, sugarcane bagasse was chosen as potential biodegradable filler in this research work.

1.2 Problem Statement

The largest production of the NR latex end products was the production of gloves. According to the Malaysian Rubber Board (2016), the gloves consumption has shown an increment of 30 % from year 2000 to year 2015. The gloves consumption cannot be reduced and replaced as it has an important role in many industries, especially in medical industry. Gloves were designed as a single used commodity which difficult to degrade due to the compounding ingredients used such as sulphur. Sulphur crosslinks has prevented the latex based products to degrade by means of natural environment or microorganisms facilitation (Misman and Azura, 2013). Hence, the solution to use biodegradable filler with NR latex help to improve the biodegradability of NR latex gloves.

In latex industry, many studies have been done based on the utilization of organic filler, sago starch and banana stem powder in NR latex compound (Siti Nuraya et. al., 2012;

Afiq and Azura, 2013). The studies shown that the biodegradability and mechanical properties of NR latex film with sago starch were improved. However, sago starch was a food grade material and it mainly use in the food industry for the production of bread, crackers, biscuits and many other traditional foods (Adrina, 2004). Food was the main energy sources of human and there are a lot of people were in starvation around the globe. Hence, it was better to utilize the waste to generate the organic filler use in latex compound.

With growing environmental awareness, ecological concerns and new legislations, bio fiber reinforced composite was increase the attention (Singh et. al., 2011). Sugarcane bagasse was a waste fibrous material which was obtained after extraction of sugar from the sugarcane. It has high aspect ratio, cheap and abundant. Thus, it was a potential biodegradable filler to be used in NR latex products.

Besides, it was believed that the fibre treatment process can modify the filler surface to improve the compatibility of the raw material and the filler. Hence, treatment process of sugarcane bagasse was also carried out in this study to determine the ability of the treatment process of sugarcane bagasse in improving the properties of NR latex films.

1.3 Research Objectives

The objectives of this study include:-

I. To compare different types of filler (sago starch and sugarcane bagasse) on the mechanical properties and biodegradability of NR latex film.

II. To compare different preparation methods of sugarcane bagasse dispersion on the mechanical properties and biodegradability of NR latex film.

III. To identify the optimum loading of treated sugarcane bagasse on the mechanical properties of NR latex films.

1.4 Scope of Research Study

In this study, NR latex films with organic fillers, which were sago starch, sugarcane bagasse and treated sugarcane bagasse were prepared. Firstly, preliminary tests were carried out for the raw NR latex to ensure the quality of NR latex meet the standard requirement. The preliminary tests include DRC, TSC, KOH No., MST and alkalinity. Before the NR latex compounding, filler dispersion was prepared. In first method, sago starch and sugarcane bagasse dispersion were prepared by mixing with distilled water, 3 % KOH (w/w) and 5 % anchoid (w/w) and then ball-milled for 24 hours. In the second method, the sugarcane bagasse was bleached with 2 % sodium hypochlorite solution for 24 hours at 40 ˚C. Then, ammonia hydroxide was added until the pH of the treated sugarcane bagasse dispersion maintained at 11 and then ball-milled for 24 hours. The NR latex was compounded after the filler dispersion has been prepared. After compound, the NR latex leave to undergo maturation for 18 hours, and then carried out dipping process, drying process and stripping process. The NR latex films prepared were proceeded for further testing. Different loading (5 pphr, 10 pphr, 15 pphr and 20 pphr) of treated sugarcane bagasse was also compounded with the NR latex to investigate the effect of filler loading on optimum mechanical properties of NR latex films.

1.5 Thesis Structure

The main structure of this thesis as below:

Chapter 1 provides an overview of the research background for this research work. This chapter includes problem statement, research objectives and scope of study.

Chapter 2 provide information and knowledge related to this research work through journals, articles and books.

Chapter 3 provide information about the supplier of the materials, the methodology of the research work and the equipment use to carry out the testing. The flow chart of the overall research work was also included in this chapter.

Chapter 4 discuss about the findings from the experiment.

Chapter 5 conclude all the findings from this research and also provide recommendation for future research work.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber (NR) Latex

NR latex is defined as a stable colloidal dispersion of a polymeric substance in an aqueous medium (Blackley, 1997). NR latex is collected by tapping of the Hevea brasiliensis tree. The typical composition of NR latex is shown in Table 2.1. The composition of the NR latex is varying from source to source as it influences by various factors such as soil conditions, season, clone, fertilizer application techniques and tapping frequencies (Liyanage, 1999).

Tale 2.1: Typical composition of NR latex (Kalyani, 1999).

Composition	% by weight of latex
Dry rubber content	30 – 35
Proteinous substances	1 – 1.5
Lipids	1 – 2.5
Sugars	1
Inorganic Ions	1
Water	60 - 65

The chemical structure of rubber content in the NR latex is identified as linear cis-1,4-polyisoprene as shown in Figure 2.1 (Matador rubber, 2007). Polyisoprene is a polymer having a broad molecular weight distribution with a high structural regularity. Due to this reason, NR tends to crystallize spontaneously at low temperatures or when it is stretched. NR exhibit outstanding tear and tensile strength, resilience and flexibility due to its high molecular weight and chemical nature (Wijesinghe et. al., 2016).

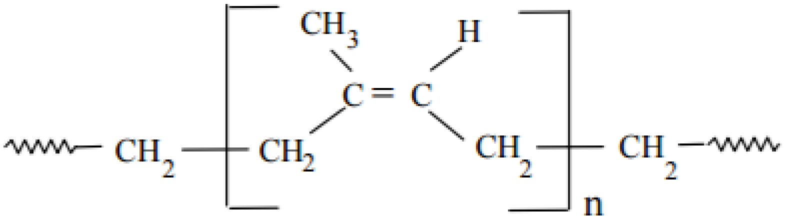

Figure 2.1: Chemical structure of cis-1,4-polyisoprene (Matador rubber, 2007).

2.1.1 Application of Raw NR Latex

There are four main major applications of NR latex which includes dipped goods, latex foam, elastic thread and adhesives. This research work mainly focus on the dipped goods. The example of dipped goods are gloves, medical tubing, condoms, balloons, rubber band and so on (Claramaa, 1997). Among all the dipped goods products, glove has the highest production rate in Malaysia (Malaysian Rubber Board, 2016).

Gloves can be used in wide industries such as medical, food processing and sanitary. The consumption of medical is increase year by year. This is due to the increase in awareness regarding better healthcare services and standards. The medical institutions in Malaysia prefer latex medical gloves compared to synthetic and vinyl gloves. In the medical institutions, the using of only latex medical gloves is about 90 % while the using of both latex and synthetic gloves is about 5 %. The demand of gloves in medical industry is higher during the disease outbreak period (https://www.members.mrepc.com/market2/report/528595443.pdf)

2.2 Latex Compounding Ingredients

Latex compounding is a process of mixing different types of chemicals into latex to attain the required characteristic either for the latex mix or for the dry film. Latex compounding ingredients can be classified into three groups, which are surfactants, liquid phase modifiers and elastomer phase modifiers (Morton, 2013).

2.2.1 Surfactants

Surfactants are molecules which able to form bridge at the interfacial surface. All ingredients need to be converted to water-insoluble solid and water-immiscible liquid compounding materials to water-compatible system without destabilize the latex colloidal stability. Wetting agents and emulsifiers can reduce the surface tension of water. This allowed the compounding materials to mix uniformly into the latex without upsetting the latex colloid stability (Morton, 2013).

2.2.2 Liquid Phase Modifiers

Liquid phase modifiers are used for maintaining the colloidal properties of the latex particles, which prevent the particles undergoes coagulation and consequently affect the quality of the latex. There are few kinds of liquid phase modifiers such as stabilizers, thickeners, wetting agents, coagulants, heat sensitizers and gelling agents (Morton, 2013). Stabilizers added into latex not only modify or maintain the stability of latex, but also act as the pH modifiers to enhance the stability of the latex colloidal system. One of the examples of pH modifiers is potassium hydroxide (Blakley, 1997).

2.2.3 Elastomer Phase Modifiers

Elastomer phase modifiers are important when latex is transformed from liquid phase to elastomer phase. Water-insoluble solid and water-immiscible liquid compounding ingredients used as elastomer phase modifiers must be converted to water-compatible system that can be mixed uniformly into the latex without upsetting the latex colloid stability (Morton, 2013). The examples of elastomer phase modifiers are vulcanizing agent, accelerator, activator, antioxidant and filler.

2.2.3.1 Vulcanizing Agent

The most well-known vulcanizing agent in natural rubber and synthetic rubber is sulfur. The vulcanization process of latex compound can only occur by the presence of vulcanizing agent. Vulcanization is a cross linking process that chemical cross link the molecular chains into a three-dimensional network. In latex compounding, the sulphur used should be easily dispersed in water so the latex film produce has high crosslink density where the mechanical properties of the film can also be enhanced (Babitskii et. al., 1961).

2.2.3.2 Accelerator

The addition of accelerator in latex compound can increase the rate of sulfur vulcanization, which in turn reduce the cure time to minutes. The type of accelerator commonly use in latex compound is dialkyl dithiocarbamates, for example zinc diethyl dithiocarbamate (ZDEC). ZDEC is primary accelerator and ZDEC is intermediate accelerator. Under normal storage conditions, ZDEC can result in gradual thickening of ammonia preserved NR latex because of slow liberation of zinc ions. Most of the accelerators for sulfur cure are nitrogen-bearing. The color of the latex films will turn brown in the presence of dithiocarbamate and copper due to the formation of copper dithiocarbamate (http://www.smithersrapra.com/SmithersRapra/media/Sample-Chapters/Practical-Guide-to-Latex-Technology.pdf).

2.2.3.3 Activator

In latex compounding, the using of sulphur without activator can still able to vulcanize the rubber latexes. However, it might take days to complete the vulcanization process at high temperature. Meanwhile, the oxidation process is occurs in the latex at a prolong time of high temperature and hence affect the NR latex film produce. Thus, activator is required for NR latex compounding as it is able to activate the crosslinking action of the sulfur and decrease the time of vulcanization. Zinc oxide (ZnO) is recognized as the best activator for sulfur vulcanization (Bob, 1990). ZnO is a activator in latex compound where it improve the crosslinking efficiency during the pre-vulcanization of NR latex compound. However, it has been reported that the addition of ZnO reduces the latex stability and film clarity when used above 0.2 pphr (Anand et. al., 2014).

2.2.3.4 Antioxidant

It is the similar method for the oxygen to attack and degrade the latex film and dry rubber products. The ageing resistance of the NR latex products can be enhanced by the addition of antioxidants during compounding process. In NR latex compounding, there are two main types of antioxidants, which are phenolic type and amine type. The phenolic type antioxidant is more prefer than amine type antioxidant. This is due to the amine type antioxidant consist of resinous which has low dispersivity in NR latex and cause discoloration of the latex products after ageing. Hence, phenolic antioxidants are more common to use in

NR latex. Water insoluble antioxidants are incorporated into the latex as an emulsion in water. The emulsified antioxidant droplets are adsorbed on to the rubber particles as the compound matures (http://www.smithersrapra.com/SmithersRapra/media/ Sample-Chapters/Practical-Guide-to-Latex-Technology.pdf).

2.2.3.5 Filler

Blackley (1997) defines filler as a solid material capable of changing the physical and chemical properties of materials by surface interaction. Fillers can be classified into two categories, which are reinforcing and non-reinforcing. The examples of reinforcing filler are carbon black and silica, while the example of non-reinforcing filler is white mineral fillers, such as calcium carbonates, clays and silicates. White mineral fillers are widely used in glove manufacturing industry. The use of non-reinforcing fillers can reduce the cost of production as well as it improves the stiffness and other mechanical properties of gloves up to some extent. Filler can also be classified based on the source. The classification of filler base on source is shown in Figure 2.2 (Omofuma et. al., 2011).

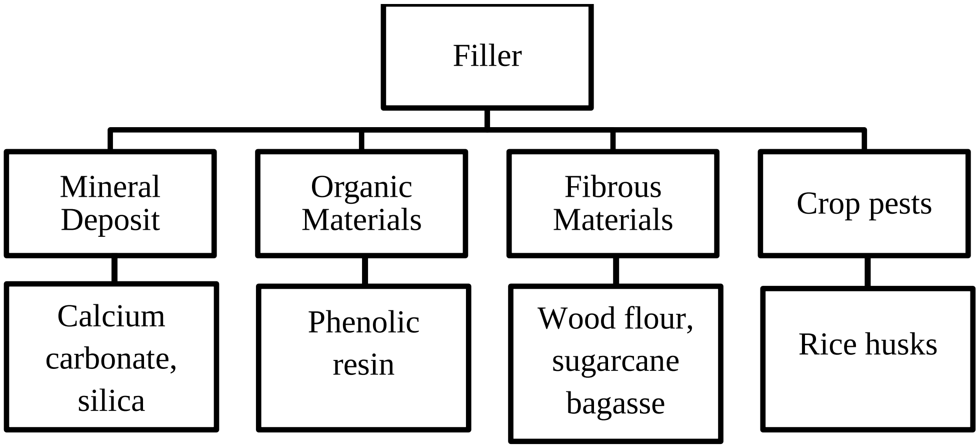

Figure 2.2: Classification of filler base on source (Omofuma et. al., 2011).

Filler has been used for reinforcement purpose in latex technology for many decades. The filler is used to fill the void between the rubber particles, improve the interaction of the latex matrix during processing and also to reduce the production cost. Filler fill the empty spaces between the rubber particles in latex and hence enhance the interphase effects and improve the mechanical properties of the latex films. Reinforcement of latex depends on the efficiency of load transfer from filler to the latex matrix during deformation. The efficiency of load transfer is dependent on the level of filler – filler and filler – matrix interactions, which in turn influenced by the level of filler dispersion and amount of filler used (Syazwani et. al., 2012).

Filler is expected to adhere to the rubber particles as other non-rubber materials when NR latex films are formed. Roslim et. al. (2010) has shown that the tensile strength and tear strength of NR latex films were improved after the addition of filler in latex compound due to the reinforcing effect of the filler on the rubber interphase.

2.3 Biodegradable Filler

The advantages of biodegradable filler as compare to conventional filler is due to their low price, low density and it also a renewable nature. Sago starch is one of the common biodegradable filler use in latex compounding. It is commonly use as its natural availability and it has proven that the addition of sago starch in latex compound can improve the biodegradability of NR latex products (Izmar et. al., 2012).

2.3.1 Sago Starch

Sago starch is derived from the pith of the sago palm, which is distributed throughout South East Asia. Metroxylon sagu and M. rumphii are the two common sago species found in Malaysia. Metroxylon sagu is planted in most of the areas as it can provide higher quality products. Approximately of 100 – 550 kg of sago flour can be produced by a mature palm tree. Hence, it is predicted that 60 million tonnes of sago starch are produced per year in South East Asia (Fasihuddin et. al., 1999).

Starch is a polysaccharide material having random coiled amylose and a branched structure of amylopectin linked by glucosidic linkages. Generally, the ratio of amylose to amylopectin is 20 : 80. However, the ratio of amylose to amylopectin will be varies from the source of the starch. Sago starch also contains a small percentage of lipids and proteins. The granules of sago starch are in oval shape, with diameters of 20 to 40 μm (Kiing et. al., 2010).

Amylose is a chain polymer of α-D-gluco-pyranosyl residues linked 1 → 4. The structure of amylose is shown in Figure 2.3. Amylopectin is a branched glucan with side chains attached in the 6-position of the glucose. The structure of amylopectin is shown in Figure 2.4 (Belitz et. al., 2009).

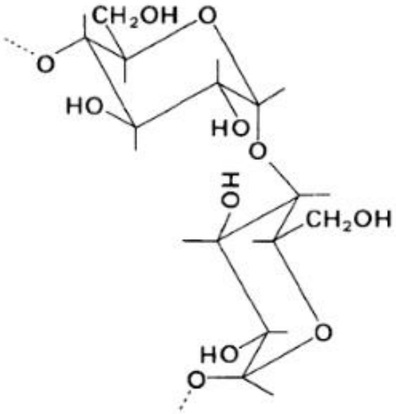

Figure 2.3: The structure of amylose (Belitz et. al., 2009).

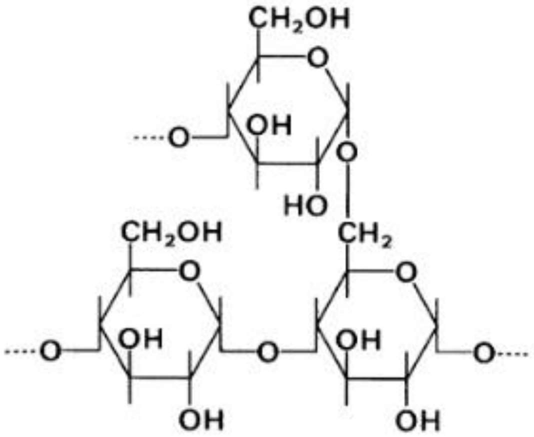

Figure 2.4: The structure of amylopectin (Belitz et. al., 2009).

2.3.1.1 NR Latex with Sago Starch as Filler

The used of sago starch is an attractive alternative in developing cheap degradable materials which are environmental friendly, biodegradable and once degrade, it is compostable. Sago starch can incorporate with the latex molecular structure particles by the formation of chemical bonding (Azura et. al., 2010).

Gelatinization is a process that breaks down the intermolecular bond of starch in the presence of water and heat, allowing the hydrogen bonding sites to engage more water. This process is occurred when the aqueous suspension of starch is heated, the hydrogen bonds weaken, water is absorbed, and the starch granules swell. Sago starch exhibits a 2-stage swelling process in an aqueous medium which occurs at the gelatinization temperature about 70˚C, while the second stage of swelling occurs at about 80˚C (Izmar et. al., 2012).

Cooling of gelatinized starch resulted in the re-association of the leached amylose from gelatinized granules. This process called starch retrogradation, referred as a reaction that takes place in gelatinized starch when the amylose and amylopectin chains realign themselves after being cooled at lower temperature for long enough periods. Consequently, the linear molecules, amylose, and linear parts of amylopectin molecules retrograded and rearranged themselves again to become more crystalline. Amylose is much more susceptible to retrogradation and amylopectin is minimally involved in starch (Izmar et. al., 2012).

2.3.2 Filler from Fibrous Materials

Fibers are class of hair-like materials that are in discrete elongated pieces, it is similar to pieces of thread. Fiber can be classified into two main group, which are man-made fiber and natural fiber (Santini, 2010). The classification of fiber is shown in Figure 2.5.

Natural fiber of vegetable origin includes all forms of fibers from woody plants, fruits, grasses, agriculture crops, palms, leaves, wild plants and water plants. Natural fibers can be used in the form of particulate or filler, short fibres, long fibres, continuous roving, woven fabric and non-woven fabric (Salit, 2014).

In general, the plant based fibers are mainly consist of cellulose and non-cellulose material. The examples of non-cellulose materials are hemicellulose, pectin and lignin. They are also known as lignocellulosic or cellulosic fibers (Salit, 2014). Lignocellulosic fibers have been being used as reinforcing or filling materials for the past 3000 years, in association with polymeric materials. Biofibers are used because of their low cost, ease of separation, lower density, higher toughness and significant biodegradability.

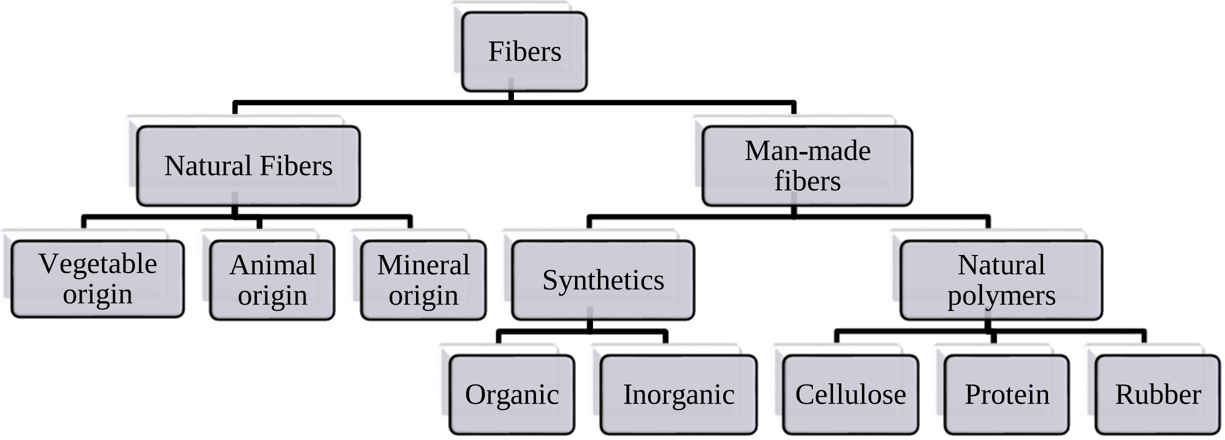

Figure 2.5: Classification of fibers (Santini, 2010).

As compare with the conventional reinforcing fibers, such as glass, carbon and Kevlar, natural fibers exhibit additional advantages, which are environmentally friendly, fully biodegradable, non-toxic, low density, good thermal properties, compostable, reduced tool wear, relatively low cost, free from health hazards (cause no skin irritations) and with acceptable specific strength properties. The disadvantages of natural fibers are poor compatibility with hydrophobic polymer matrix and it will undergo degradation after being stored for a long period. Natural fibers also tend to form aggregates during processing (Salit, 2014).

2.3.2.1 Sugarcane Bagasse

After the sugarcane is pressed to remove sucrose or known as table sugar, the residue is known as sugarcane bagasse which contains highly fibrous residue. Sugarcane, Saccharum spp., is a plant belonging to the family Poaceae and class Monocotyledones. Sugarcane bagasse is an agricultural by-product. In the sugar industry, sugarcane bagasse is more related as the by-product in sugarcane mills (Aeslina et. al., 2013). The total plantation area of sugarcane in Malaysia is nearly 34,500 acres. Approximately 140 kg of bagasse is generated from each ton of sugarcane after being processed.

Plant biomass (lignocellulose) is the fibrous material that forms the structural framework of the plant cell wall. The main component of lignocellulosic biomasses of sugarcane bagasse are cellulose, hemicellulose and lignin. Ash is also present in small amount. Table 2.2 shows the typical composition of sugarcane bagasse (Aeslina et. al., 2013).

Table 2.2: Typical composition of sugarcane bagasse (Aeslina et. al., 2013).

Component	% dry mass
Cellulose	38
Hemicellulose	33
Lignin	22
Ash	3

Cellulose is a homo-polysaccharide composed entirely of β-1,4-glucosidic linked glucose monomers. The degree of polymerization of cellulose is more than 10,000. The simplified structure of cellulose is shown in Figure 2.6. The linear structure of cellulose chain result in the formation of inter- and intramolecular hydrogen bonds. These bonding cause the aggregation of glucose chains to form crystalline fibrils. Therefore, the crystallinity of cellulose is approximate 50 – 90 %. The crystallinity of the cellulose varied from source to source. The linear structure and intermolecular hydrogen bonding of cellulose contribute to the properties of high tensile strength, resistance against microbial attack and also make it insoluble in most solvents (Walford, 2008).

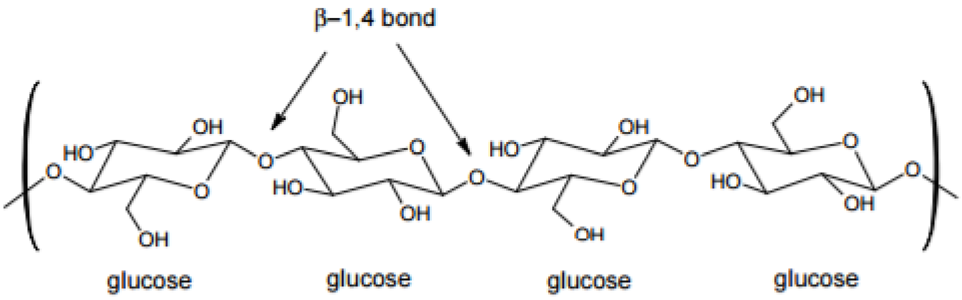

Figure 2.6: Simplified structure of cellulose (Walford, 2008).

Hemicellulose is a heterogeneous polysaccharide composed of D-xylose, D-glucose, D-mannose, D-galactose, L-arabinose, D-glucuronic acid and 4-O-methyl-D-glucuronic acid. The simplified structure of hemicellulose is shown in Figure 2.7. The specific composition of each component is based on the biomass source. Hemicellulose has a low degree of polymerization, often contains side chains and is typically acetylated. Classification is according to the main sugar in the polmer backbone, e.g. xylan (β-1,4-linked xylose) or mannan (β-1,4-linked mannose). Bagasse hemicellulose is composed of a backbone of xylose, branched with glucose and arabinose units (Walford, 2008).

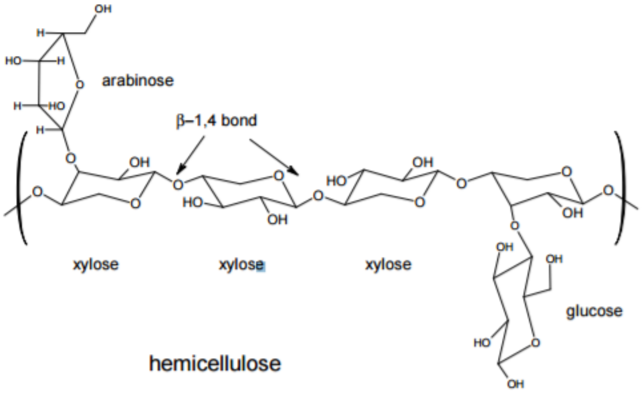

Figure 2.7: Simplified structure of hemicellulose (Walford, 2008).

Lignin is a three-dimensional polymer, which are made up from three different phenyl-propane precursor monomers: *p*-coumaryl, coniferyl and sinapyl alcohols. The structure of phenyl-propane precursor monomers and lignin is shown in Figure 2.8. The monomers are linked together by aryl-aryl, alkyl-aryl and alkyl-alkyl ether bonds. This polymer is imbedded in the cellulose or hemicellulose structure, which act as a 'glue-like' material. Lignin helps impart rigidity and offers further protection to the biomass against microbial and chemical attack (Walford, 2008).

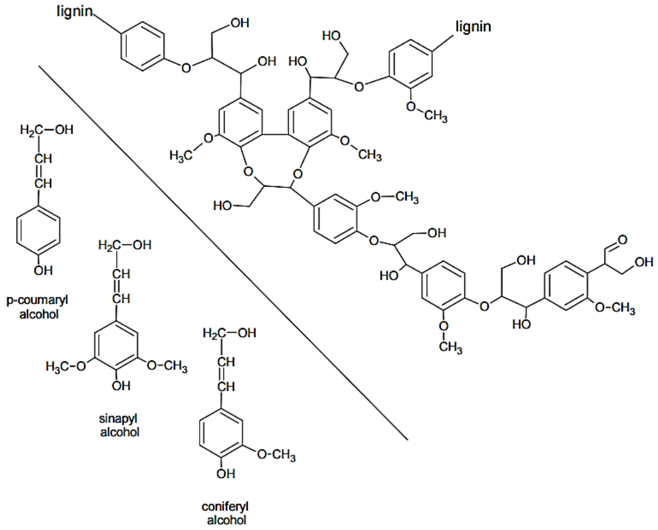

Figure 2.8: Structure of phenyl-propane precursors (left) and a model lignin structure (right) (Walford, 2008).

In lignocellulosic biomasses, the ash components present are all inorganic compounds, for example calcium, potassium, magnesium, manganese, iron and copper. The inorganic compounds present in the lignocellulosic biomass is absorbed directly from the soil (Danila, 2015).

2.4 Preparation of Filler Dispersion

The filler dispersion can be prepared by mixing the filler with water and dispersing agent and then undergoes ball-milling process. Ball-milling is a process that the container is rotated about it cylindrical axis in a horizontal plane at such a speed that the charge is tumbled.

The grinding charge consists of unglazed porcelain or glass balls. The ball used in laboratory is usually about 1.2 – 1.5 cm diameter. The size of the ball is depending on the size of the ball-mill used. The average diameter of the balls needed for large mill is about 2.5 cm diameter. The speed of the ball-mill will affect the dispersion obtained. If the mill rotates too rapidly, centrifugal force will cause the charge to adhere to the container walls and no grinding results. Slower speeds may be used but the time of milling will be extended since the grinding is achieved by a definite number of rotations of the mill (http://www.smithersrapra. com/SmithersRapra/media/Sample-Chapters/Practical-Guide-to-Latex-Technology.pdf).

The chosen and the quantity of dispersing agent to be added during the preparation dispersion is based on the physical properties of the material to be dispersed. The function of dispersing agent is to prevent the particles from aggregate together and also to mix the particles into the solution. The amount of dispersing agent should be maintained at minimum required to produce the desired effect. (http://www.smithersrapra. com/SmithersRapra/media/Sample-Chapters/Practical-Guide-to-Latex-Technology.pdf).

2.4.1 Treatment Process of Fillers Preparation

The reinforcing properties of the fibres can be improve by undergone treatment process. There are various kinds of treatment process such as alkali treatment, graft modification and infiltration. The treatment process is mainly used to improve the interfacial compatibility of the fibre with the matrix component. Alkali treatment is one of the effective modification methods which can increase the interfacial adhesion by removing hemicellulose, lignin and other components from natural fibre, resulting in better purified cellulose and increase the properties of the composites (Zhang et. al., 2015). Sodium hypochlorite is used to treat sugarcane bagasse in this study, which is an alkaline solution.

Sugarcane bagasse dispersion can also be prepared by undergoes treatment process. It is necessary to carry out chemical modification of the filler surface in order to achieved high compatibility between NR latex and filler. These can be done by incorporation of a coupling agent, delignification, bleaching or chlorination (Fasihah et. al., 2016). In this project, the sugarcane bagasse is bleached by using sodium hypochlorite before incorporated into the latex. Sodium hypochlorite is an oxidative bleaching agent.

Sodium hypochlorite is a sodium salt of hypochlorous acid (HOCl). It can be prepared by passing chlorine gas into a tank containing prepared solution of caustic soda, calcium carbonate or mixture of the two at about 27˚C. It is an effective color stripping agent and bacterial control agent. Acid hypochlorite chlorinated the lignin fraction, which then becomes soluble on subsequent alkaline scouring. Bleaching at pH 4 gives higher whiteness, but also causes a higher rise in fluidity than at pH 10.5 (Karmakar, 1999).

Sodium hypochlorite, being a sodium salt of hypochlorous acid, does not require any dissolving arrangement and are ready for immediate use. However, bleaching with sodium hypochlorite produces slight damage to cellulosic fibers. Sodium hypochlorite produces unpleasant odours in working environment (Karmakar, 1999).

2.5 NR Latex Film Processing

2.5.1 Pre-vulcanization Process

During the vulcanization of NR latex, the latex serum together with its natural non-rubber content provides a medium in which some of the vulcanization reactions may occur. The natural non-rubbers in the latex serum are often regarded as secondary activators for vulcanization reactions. Vulcanization of NR latex is carried out either during the latex stage (pre-vulcanization) or after the films have been formed (post-vulcanization). In this project, pre-vulcanization technique is used to vulcanize the NR latex (Amir and Morris, 1999).

Pre-vulcanization is a process whereby the latex together with its vulcanizing ingredients is heated at a temperature of 70˚C. The use of pre-vulcanized latex has advantages, which the wet and dry gel strength of the dipped film is generally improved, compared to latex that is not pre-vulcanized. The total process time is also reduced, since only a limited amount of time is devoted to vulcanizing after dipping and drying (Rapra Technology Limited, 2001).

Chloroform coagulum test is commonly used to assess the degree of vulcanization of pre-vulcanized NR latex. In this method, the latex is stirred with a fixed proportion of chloroform, and the degree of vulcanization judged from the appearance of the coagulum which forms (Blackley, 1997).

Another accurate method to access the degree of vulcanization is toluene swelling test. In the toluene swelling test, a thin film is first cast from the latex. The latex film is then immersed into the toluene solvent. The extent of which the latex film has swollen can be determined by weighing the latex film or measure the diameter of the latex film before and after immersed in the toluene solvent. The swelling index of the latex film is inversely proportional to the degree of vulcanization. The accurate measurement of the degree of vulcanization of latex film can be obtained if the test is carried out with care (Blackley, 1997).

2.6.2 Latex Dipping Process

In latex technology, NR latex is commonly used to manufacture latex dipped articles. There are three different methods of latex dipping, which are straight dipping, coagulant