SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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Comparison of Different Types of Sago Starch Dispersion and on Mechanical Properties of Biodegradable NR Latex Films

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Comparison of Different Types of Sago Starch Dispersions and on Mechanical Properties of Biodegradable NR Latex Films”. I also declare that it has not been previously submitted for award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
AGUs	Anhydroglucose units
CMC	Carboxyl Methyl Cellulose
DRC	Dry Rubber Content
FTIR	Fourier Transform Infrared
H_2SO_4	Sulphuric Acid
MST	Mechanical Stirring Time
NR	Natural Rubber
KOH No.	Potassium Hydroxide Number
SDS	Sodium Dodecylbenzene Sulfonate
TSC	Total Solid Content
VFA No.	Volatile Fatty Acid Number
FTIR	Fourier Transform Infrared
ZDEC	Zinc Diethyldithiocarbamate
ZnO	Zinc Oxide

NOMENCLATURES

m	Mass in grams of the test portion
P_r	density of the NR latex samples
P_s	density of toluene
T_o	Initial tensile strength
T_t	Tensile strength after biodegradation
V	Volume in millilitres of barium hydroxide solution required to neutralize the distillate
V_r	Volume fraction of latex in the swollen network
V_s	Molecular volume of the toluene
W_i	Initial weight of NR latex films in gram
W_b	Weight after soil burial of NR latex films in gram
W_B	Weights of NR latex samples before toluene immersion
W_A	Weights of NR latex samples after toluene immersion
W_i	Initial weight of sample
W_f	Weight of sample after heating
W_{coag}	Weight in gram of dried coagulum
W_i	Initial weight in gram of NR latex
X	Crosslink density

PERBANDINGAN PELBAGAI JENIS AGEN PENYEBARAN KANJI SAGU KEATAS SIFAT-SIFAT MEKANIKAL BIODEGRADASI LATEKS FILEM GETAH ASLI

ABSTRAK

Peningkatan produk lateks getah asli (GA), terutamanya sarung tangan dalam penggunaan global menghasilkan sejumlah besar produk lateks GA yang dibuang dan menyumbang kepada masalah pelupusan sisa pepejal. Biodegradasi lateks GA boleh diperbaiki dengan penambahan penyebaran kanji sagu yang biasanya disediakan dengan menggunakan ankoid sebagai ajen penyebaran. Tujuan kajian ini adalah untuk mengkaji penggunaan agen-agen penyebaran yang berbeza, natrium alginat dan Carboxy Methyl Cellulose (CMC) dalam penyediaan serakan kanji sagu untuk meningkatkan taburan saiz zarah kanji sagu dan penguraian lateks filem GA. Penyebaran kanji sagu ankoid, kanji sagu natrium alginate dan kanji sagu CMC telah disediakan dengan menggunakan kaedah pengilling bebola, masing-masing sebelum ditambah pada 10 phr bahagian ke dalam sebatian lateks GA. Sebatian telah pra-pemvulkanan pada suhu 70°C sehingga bilangan kloroform 2 telah dicapai. Kesan penambahan penyebaran kanji sagu yang berbeza ke atas sifat mekanikal (sifat tegangan dan kekuatan koyak), potensi zeta, bengkak indeks, ketumpatan sambung silang getah asli filem lateks diperolehi. Lateks GA dengan serakan kanji sagu natrium alginat memberikan kestabilan penyebaran dan sifat-sifat mekanikal (sifat tegangan dan kekuatan koyak) yang baik berbanding lateks GA dengan kanji sagu CMC. Index pembengkakan Lateks GA dengan kanji sagu natrium alginate menurun menunjukkan bahawa ketumpatan sambung silang yang lebih tinggi. Pasca pemprosesan (larut lesap, penuaan dan penguraian) Lateks GA dengan serakan kanji sagu yang berbeza telah diperolehi. Berdasarkan keputusan yang diperolehi, penggunaan agen penyebaran natrium alginat dapat digunakan sebagai penganti ejen penyebaran anchoid dalam penyediaan serakan kanji sagu dengan sifat-sifat yang setanding bagi lateks GA terurai.

COMPARISON OF DIFFERENT TYPES OF SAGO STARCH DISPERSION ON MECHANICAL PROPERTIES OF BIODEGRADABLE NR LATEX FILMS

ABSTRACT

The increase in Natural Rubber (NR) latex products, particularly gloves in global consumption results in enormous amounts of discarded NR latex products and contributed to the solid waste disposal problems. The biodegradability of NR latex can be improved by addition of sago starch dispersion which commonly prepared using anchoid as dispersing agent. The purpose of this studies were to investigate the utilisation of different dispersing agents, sodium alginate and Carboxy Methyl Cellulose (CMC) in preparation of sago starch dispersions in order to improve the sago starch particle size distribution and biodegradability of the NR latex films. The sago starch anchoid, sago starch sodium alginate and sago starch CMC dispersions were prepared by using ball milling method, respectively before adding at 10 phr loading into NR latex compounds. The compound was pre-vulcanised at 70°C until chloroform number 2 was achieved. The effect of addition of different types of sago starch dispersions on mechanical properties (tensile properties and tear strength), zeta potential, swelling index, crosslink density of NR latex films were obtained. NR latex with sago starch sodium alginate dispersion give good dispersion stability and better mechanical properties (tensile properties and tear strength) compared to NR latex with sago starch CMC dispersion. The swelling index NR latex with sago starch sodium alginate decreased indicated that higher crosslink density. The post processing (leaching, aging and biodegradation) of the NR latex with different sago starch dispersions were obtained. Based from the results obtained, the utilisation of sodium alginate dispersing agent can be used as replacement of anchoid dispersing agent in preparing the sago starch dispersions which gives comparable properties of biodegradable NR latex films.

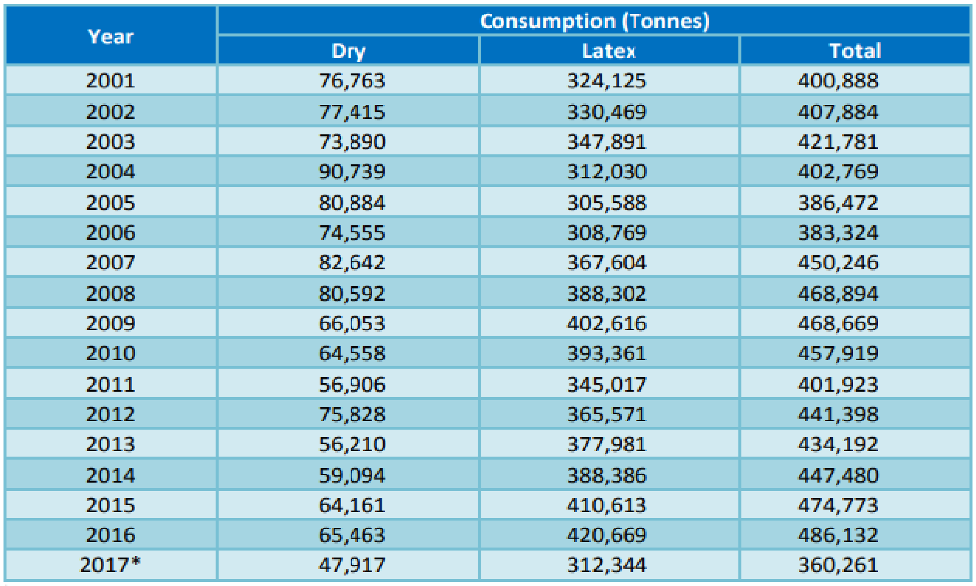
CHAPTER 1

INTRODUCTION

1.1 Research Background

Malaysia was the top five of NR latex production in the world. NR latex was obtained from the tapping process which was harvested mainly in the form of the liquid from the rubber tree known also as Hevea brasiliensis. The latex is then refined and ready for commercial processing into various latex products. Figure 1.1 and Figure 1.2 shown the Malaysian's NR consumption from year 2001 until September of 2017.Based on the Figure 1.1(a) and Figure 1.1(b), the total NR latex consumption shown an increment of 30% from year 2001 to year 2015 in Malaysia (Malaysia Rubber Board,2018). The growing of NR consumption explained that NR latex was still an important raw material for the production of latex gloves in Malaysia.

Figure 1.3 shown the distribution of Malaysian rubber product companies by product sector in year 2017.It shown that the second major production of latex products were mostly gloves which makes about 48.62%, then condom about 9.17% and followed by catheters,4.59% and latex thread, 0.92%.Gloves had the highest production and consumption because it's uses in daily life as single used materials for hand barrier protection equipment which offer excellent protection and performance in a variety of applications and across a broad range of industries such as medical, sanitary and food industry. Both statistical analysis from Figure 1.1 and 1.2 indicates that the demands in NR latex gloves are maintain high every year and thus contribute to the municipal solid waste stream due to NR latex gloves are designed for single application use only.



Year	Consumption (Tonnes)		
	Dry	Latex	Total
2001	76,763	324,125	400,888
2002	77,415	330,469	407,884
2003	73,890	347,891	421,781
2004	90,739	312,030	402,769
2005	80,884	305,588	386,472
2006	74,555	308,769	383,324
2007	82,642	367,604	450,246
2008	80,592	388,302	468,894
2009	66,053	402,616	468,669
2010	64,558	393,361	457,919
2011	56,906	345,017	401,923
2012	75,828	365,571	441,398
2013	56,210	377,981	434,192
2014	59,094	388,386	447,480
2015	64,161	410,613	474,773
2016	65,463	420,669	486,132
2017*	47,917	312,344	360,261

Figure 1.1(a): Malaysia's NR consumption from year 2001 until March of 2017(Malaysian Rubber Board,2018)

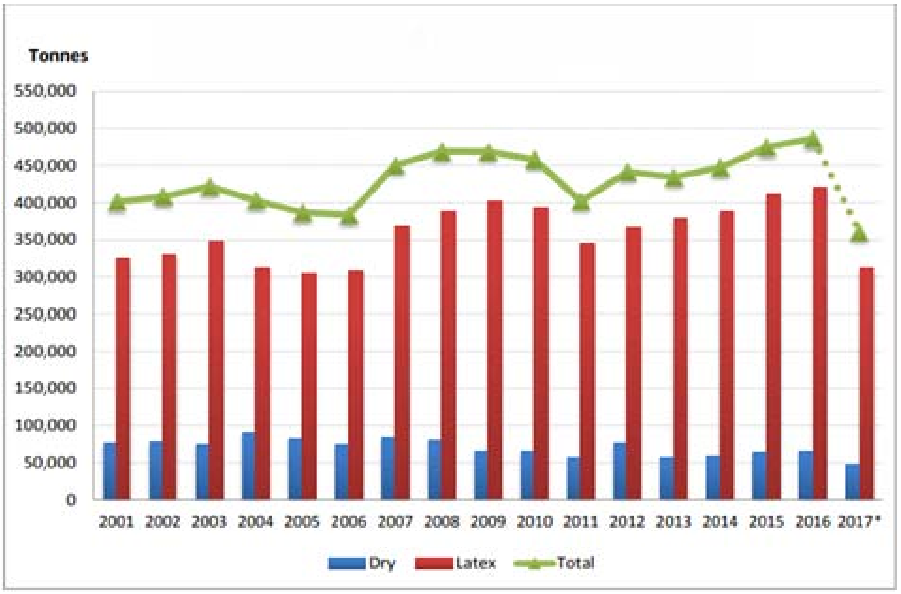


Figure 1.2(b): Malaysia's NR consumption from year 2001 until March of 2017(Malaysian Rubber Board,2018)

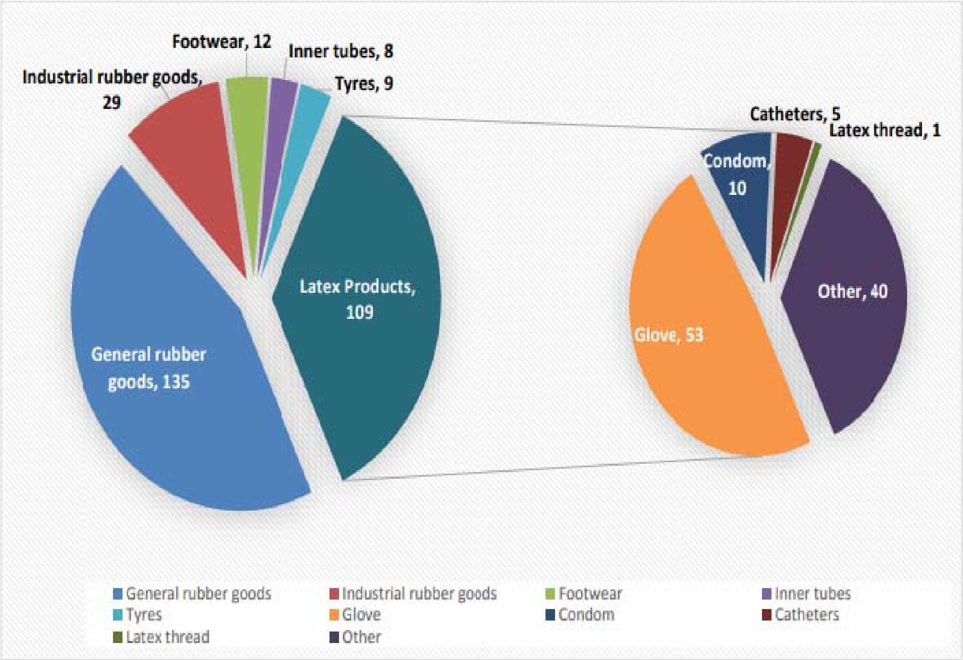


Figure 1.3: Distribution of Malaysia rubber product companies by product sector for year 2017(Malaysian Rubber Board,2018)

Among all the industries, the critical industries that really rely on latex gloves are medical industry which gloves play an important role protecting and acts as a barrier towards harmful pathogens, bacteria and contaminants from spreading. This gives mutual benefit on both sides includes the medical staffs and the patients as the patients gain benefit when the medical staffs wear medical gloves, which prevent potential hazards from entering and spreading to harm their bodies. Latex gloves also offers the benefit of chemical resistance against most of the chemicals. Latex gloves which feature puncture resistance also are mostly been used in food service industry. Latex gloves that are industrial grade are used in industrial applications such as in automotive and manufacturing as it provides optimal benefits of durability, comfort, fit, and dexterity (Mok et al., 1994)

Rubber gloves are one of the highest productions of consumable and disposable commodity worldwide. Analysis in 2014 shows 178.6 billion pieces of rubber gloves produced and predicted to grow at 8% to 10% in 2015. Malaysia currently has known as the largest glove manufacturer share about 62% of global markets. The continuing increased in demands of rubber gloves directly contribute to rubber waste solid disposal problem. This is due to complexity of latex based products to degrade in nature environment hence increased the time for degradation in the landfill which normally occurred after more than 2 years. One of natural fillers which have been extensively study to be incorporated with natural rubber latex is starch base materials. Sago starch (Metroxylon sagu) is a non-toxic biopolymer, natural renewable and low environmental impact which readily biodegradable in soil. Sago starch has multitude uses in both food and non-food industries (Misman et al., 2015).

In order to produce totally biodegradable NR latex products, need to completely change of the raw material (latex). However, to produce partial biodegradable NR latex products is easier and it can be achieved by addition of biodegradable material as one of the components in the NR latex formulation (Misman et al., 2015).In previous study the sago starch and banana stem powder has been studied as a filler in NR latex compound by using similar dispersing agents which is sodium 2-naphthalenesulfonate known as anchoid. The results shown that natural filler can improve the biodegradability of the latex film and enhance the mechanical properties NR latex of films.

Sago Starch is produced in great abundance in South-East Asia and it is a naturally renewable polysaccharide and has been used in NR latex compound which is naturally readily available, low cost, and able to biodegrade (Izmar et al., 2012). However, starch also has disadvantages; large particle size, poor mechanical properties, poor dimensional stability, and hydrophilic in nature. The addition of starch tends to reduce the mechanical properties of NR latex films due to the hydrophilic nature of starch, attributed to abundant hydroxyl groups, decreases the interface compatibility between hydrophilic starch and hydrophobic rubber matrix. The starch presence does not contribute to the reinforcing properties as reinforcing filler as it is a biodegradable filler accelerated the biodegradability of NR latex films.

Generally, the addition of fillers in the NR latex compounding need to be prepared in aqueous –liquid medium prior to mixing in order to improve dispersion and homogeneity. In order to produce starch dispersion, dispersion agents and ball milling method were used. Ball milling is a mechanical method to reduce the crystalline region and to modify the physicochemical properties of starch using friction, shear, impingement, collision or other mechanical actions. This method generally related to the mechanical and physical process in preparation of dispersion. The basic processing parameters include ball milling time and ball rotation speed (Suki et al., 2016).

1.2 Problem Statement

The increase in NR latex products, particularly gloves in global consumption results in enormous amounts of discarded NR latex products generated and contributed to the solid waste disposal problems. Although NR latex products can biodegrade in the soil, the process is slow due to high molecular weight of NR latex macromolecules. The NR latex products normally required vulcanisation process where the polyisoprene molecules are covalently linked by bridges of elemental sulphur. These crosslinked are stable at ambient environment condition which can withstand the soil environment for a very long time (Nayanashree and Thippeswamy, 2013). Other potential factor contributing towards the slow degradation rate is due to the presence of additives such as antioxidant vulcanised NR latex which are assumed to inhibit the microbial growth upon disposal land, hence the awareness about this environmental; issue has led the industries to look for more promising alternatives such as increasing the bio-compatibility of natural dispersing agents with the incorporation of sago starch as biodegradable filler NR latex based .

The addition of polysaccharides such as sago starch in NR has potentially improve the biodegradability (Misman et al.,2015). The dispersion agents used to disperse the sago starch may be the reasons to increase the rate of biodegradation in the NR latex films due to better dispersed of the starch dispersions. Sodium alginate and CMC are considered as amphiphilic materials which predominantly comes from polysaccharides and small molecule surfactant. The presence of the additional polysaccharides group in dispersing agent of the preparation of the sago starch dispersions in NR latex film will enhance the biodegradation rate thus decreasing the time taken for the NR latex films to degrade. Sodium alginate and CMC may be a good dispersing agent as both is known as a good stabilising agent because of their hydrophilicity. Other than that, the effect of both sodium alginate and CMC might lead to gelation behaviour which might increase the viscosity of the NR latex films due to the formation of hydrocolloids(Kralova and Sjöblom, 2009).

NR latex is hydrophobic while sago starch is hydrophilic material. Sago starch which is an aqueous suspension when heated lead to absorption of water which swelled the starch granules and become gelling known as gelatinisation process. This process is called gelatinization. Further heating, contribute to sago starch retrogradation where chains of the sago starch are realigned and become crystal. The gelatinized temperature is where the sago starch molecule re-associates to form gel state. The gelatinisation temperature of sago starch is normally at 70°C(Ahmad *et al.*, 1999).

The crystalline region of starch with the compact arrangements of molecules inhibits or limits water or chemical reagents to penetrate and react with molecules resulting the higher gelatinisation temperature and decreased in chemical reactivity. During gelatinisation, there are three main processes occurs: starch granule swelling, crystal or double helical melting and amylose leaching. The mechanism of starch gelatinisation occurs when the water molecules penetrate into the amorphous region and cause the granule to swell. When heat is applied, a decrease of birefringence, loss of the double helix structure and loss of crystallinity of starch granule occurred. The amylose begins to leach out from the granule including fragments of amylopectin and starch stabilisation occurred. Finally, the starch granules which contain mostly amylopectin are collapsed and held in the matrix of amylose to form a gel network. Thus, the preparation of starch dispersion needs to be carefully carried out in order to avoid gelatinization of starch during the preparation process (Yahya, et al., 2014). The food additives used in dispersion of starch need to be compatible with the starch structure to ensure the repulsion of the starch particles from agglomerate giving the well disperses dispersion disperse in the NR latex. Hence reaction of the starch and the dispersion agents will gives a better starch dispersions without disturbing the colloidal stability of NR latex.

Surfactants have been used in industry as essential to the creation and stabilisation of structures in food. The increasing use of surfactants, the identification of compounds with low toxicity and good surface activity properties is of great interest. Polysaccharides and small molecule surfactants are two of the predominant groups of amphiphilic materials which refers to the chemical compounds that possess both hydrophilic and liphophilic properties, that have been explored for the stabilization of emulsions. Sodium alginate and carboxymethyl cellulose (CMC) are used as a surfactant which are also known as dispersing agents in preparation of sago starch dispersions in the NR latex instead of using anchoid as dispersing agent. Both sodium alginate and CMC modify the ionic surface of a particle in water, rendering the particles to become mutually repellent. This action only promotes deflocculation of the particles. Both do not lower the surface or interfacial tension of the resultant colloidal system, so there is no tendency to form a foam. In addition, polymer-surfactant systems are the ability to control stability and rheology over a wide range of composition, hence both sodium alginate and CMC may control the rheology, compatibility of the sago starch dispersion in NR latex compound thus giving a good dispersion of particles as well as increase the compatibility of the sago starch particles from forming into colloidal state and flocculate in the NR latex (Kralova and Sjöblom, 2009).

1.3 Research Objectives

1. To compare the effect of different types of dispersing agent on the stability of sago starch dispersions

2. To investigate the effect of different sago starch dispersion on the mechanical properties of NR latex films.
3. To study the effect of different sago starch dispersion on post processing (leaching, aging and biodegradation) on the mechanical properties of NR latex films

1.4 Thesis Outline

The main structure of this thesis as below:

Chapter 1 provides an overview of the research background for this 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 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 also included in this chapter.

Chapter 4 discuss about the findings from 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 which is known as natural rubber hydrocarbon in an aqueous serum and as the name implies is of biological origin which is basically in a milky fluid obtained by tapping the bark of Hevea brasiliences trees. Tapping involves the removing of strips of bark from the trees in order to wound the latex in order for the latex to be exude. The latex collected known as field latex which consists of 25% and 40% rubber by weight. Moreover, field latex need to be preserve and concentration process needed before its commercial use (Blackley, 1997).

Microbial attack on latex coagulates it within a few hours of collection unless a preservative is added. The ideal preservative enhances the colloidal stability of latex by increasing the charge on the particles and the zeta-potential at the rubber-water interface. Since the protecting proteins of the NR latex are already on the alkaline side of their isoelectric point when the latex leaves the tree, this means that a preservative should increase the pH of the latex and should be an alkali. A preservative should destroy micro-organisms which cause putrefaction or suppress their activity and growth. It should also deactivate trace metals, particularly heavy metal ions, either by sequestration or by precipitation. This is desirable for two reasons. Firstly, some of these metal ions are necessary for the growth and survival of those micro-organisms which cause spontaneous coagulation. Secondly, some metal ions themselves tend to destabilise the latex, for example magnesium ions. Ammonia fulfils these requirements and is the most widely used preservative. To act as an effective bactericide ammonia must be added at a level of at least 0.1 % of the whole latex. Ammonia interacts with the adsorbed proteins on the latex particles to enhance the zeta-potential at the rubber-serum interface; it also