EFFECT OF BANA[illegible]L BEHAVIOR OF NATURAL RUBBER LATEX FILMS

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ABSTRACT

This study is done to produce latex film with 0 %, 5 %, 10 %, 15 % and 20 % banana skins as filler and to investigate the effect of banana skin on thermal behavior of natural rubber latex films. Banana skin contains a lot of minerals, sugar, starch, protein and so on. The bio-based material such as starch is widely use in latex industries to produce of biodegradable plastic and in the production of latex glove due to its properties. In terms of industrial application, thermal performance of rubber is the key importance since in the production of rubber based products processing temperature are usually high and close to their degradation temperature. Banana skin is dried by using drying cabinet at 40 °C until fully dried and followed by grinding process by using grinder to get banana skin powder. Sieving process is necessary to produce fine banana skin powder before dissolve it into distilled water. Effect of different banana loading on natural rubber latex films are investigated after vulcanization process and dipping process. Thermal properties of the natural rubber latex which filled with banana skin powder are determined by using Mettler Toledo Thermagravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC). It can evaluate the thermal stability such as weight loss, rate of degradation and also heat flow. Finally, observation for microscopic behavior on surface of films will carry out by using Scanning Electron Microscope (SEM). This is to study the dispersion of different banana loading on the natural rubber latex films. There are no significant difference in term of thermal stability of pure natural rubber latex film and natural rubber latex with filler. Therefore by adding banana skin powder into natural rubber latex is potentially to apply in latex based product industry.

ABSTRAK

Penyelidikan ini dilakukan untuk menghasilkan filem lateks dengan menggunakan 0 %, 5 %, 10 %, 15 % dan 20 % kulit pisang sebagai pengisi dan untuk mengetahui kesan kulit pisang terhadap sifat-sifat haba pada filem lateks getah asli. Kulit pisang mengandungi pelbagai mineral, gula, protein, pati dan sebagainya. Bahan yang berdasar biologi seperti pati yang digunakan secara luas dalam industri lateks dapat menghasilkan plastik yang dapat degradasi dan dalam pengeluaran sarung tangan lateks kerana sifat-sifatnya. Dari segi kegunaan industri, prestasi haba adalah paling penting kerana dalam pemprosesan pada pengeluaran produk berasaskan getah adalah bersuhu tinggi dan dekat dengan suhu degradasi. Kulit pisang dikeringkan dengan menggunakan pengeringan kabinet pada suhu 40 °C sehingga kulit pisang kering sepenuhnya dan seterusnya menggisarkan kulit pisang yang kering tersebut dengan menggunakkan pengisar untuk mendapatkan serbuk kulit pisang. Proses penapisan dilaksanakan untuk menghasilkan serbuk kulit pisang yang halus sebelum melarut ke dalam air suling. Kesan daripada pembebanan pisang yang berbeza pada filem lateks getah asli diselidiki selepas proses vulkanisasi dan proses pencelupan. Sifat-sifat haba lateks getah asli yang diisi dengan serbuk kulit pisang ditentukan dengan menggunakan 'Mettler Toledo Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC)'. Alat ini dapat menilai sifat-sifat haba seperti kehilangan jisim, kadar degradasi and aliran haba. Akhirnya, pemerhatian bagi perilaku mikroskopik pada permukaan filem akan melaksanakan dengan menggunakan mikroskop electron (SEM). Ini adalah untuk mengkaji penyebaran beban kulit pisang yang berbeza ke atas filem lateks getah asli. Tiada perbezaan dari segi kestabilan haba bagi kestabilan haba tulen filem lateks getah asli dengan pengisi. Oleh itu, penambahan serbuk kulit pisang ke dalam lateks getah asli berpotensi untuk mengaplikasikan dalam produk lateks dalam industri.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
^oC	Degree Celsius
T_g	Glass Transition Temperature
T_c	Crystallization Temperature
T_m	Melting Temperature
α	Alpha
β	Beta

LIST OF ABBREVIATIONS

Da	Dalton
DRC	Dry Rubber Content
DSC	Differential Scanning Calorimetry
ha	Hectare
kg	Kilogram
KOH	Potassium Hydroxide
µm	Micrometer
mPa	Millipascal
MPa	Megapascal
MT	Million Tonnes
NR	Natural Rubber
NR/DDAMMT	Natural Rubber/Dodecyl Ammonia Chloride and Sodium Montmorillonite
NRL	Natural Rubber Latex
phr	Part Per Hundred
rpm	Revolution per Minute
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
TSC	Total Solid Content
Yr	Year
ZDEC	Zinc-diethyl Carbamate
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Banana, Musa sapientum is an herbaceous plant of the family of Musaceae. It is known to have originated from the tropical region of Southern Asia. It is reported that the plant is cultivated primarily for its fruits and to a lesser extent for the production of fiber and it is also believed to be an ornamental plant. Musa sapientum fruits can prevent anaemia by stimulating the production of hemoglobin in the blood. Its role to regulate blood pressure has been associated with the high content of potassium. Besides that, banana helps in solving the problem of constipation without necessary resorting to laxatives (Anhwange et al., 2009). It can cure heart burns stress, strokes, ulcers and many other ailments. While the peels are useful in making banana charcoal, an alternative source of cooking fuel (Wath and Wijk, 1962). Banana skins contain a lot of minerals such as potassium, calcium, magnesium, and slicic acid. It also contains sugar, starch, proteins fat, tannic acid, colouring agents, and phenyl-alkyl-amines. Besides that, total dietary fiber, protein, polyunsaturated fatty acids especially as linoleic and a-linoleic acids, and amino acids in the form of leucine, lysine, phenylalanine, threonine, and valine. Banana peels are rich in phosphorus and potassium which are important macro-nutrients plants need. It is a natural source of the phosphorous and potassium found in expensive fertilizers (Osma et al., 2006).

Natural rubber latex is produced by over 2,000 plant species, and its main constituent is poly(cis-1,4-isoprene), a highly unsaturated hydrocarbon. The term natural rubber or caoutchouc refers to a coagulated or precipitated product which obtained from latex of rubber plants (*Hevea brasiliensis*), which forms non-linked but partially vulcanizable polymer chains which have molecular masses of about 10^6 Da with elastic properties (Rose and Steinbuchel, 2005). Natural latex with high solids content is used for making molds for casting plaster, cement, wax, low temperature metals, and limited run polyester articles. It has ability to shrink around the object to be reproduced, so that the smallest detail will be reproduced in the cast. Latex is also used to help stabilize desert soils to make them suitable for agricultural uses. Latex is the stable dispersion of polymer micro particles in an aqueous medium and it may be natural or synthetic. NRL is a cloudy white liquid. For the composition of latex sap, it consists of 30 % to 40 % rubber particles, 55 % to 65 % water and small amounts of protein, sterol glycosides, resins, ash, and sugars. Besides that, natural rubber has high elasticity and a polymer molecular structure which consists of a long chain made up of tens of thousands of monomer strung together (Sheppard, 2011).

1.2 PROBLEM STATEMENT

Due to the increased concern over environment pollution caused by non-biodegradable materials, the development of biodegradable materials for wide application is on demand. As starch-based materials have been proven to be good biodegradable sources, banana skins are chosen to be used in developing biodegradable composite with natural rubber latex. Natural rubber latex is used because it is a renewable resource which can be biodegraded and it contains natural stabilizers such as proteins and lipids that could help compatibilization with starch (Rouilly et al., 2004). Some researchers have previously reported on some polymer blends like starch which only enable partial environmental degradability.

The price for natural rubber latex is kept on fluctuating. As natural source is depleting it is expect that price of natural rubber will be kept on increasing. Therefore it is quite expensive for rubber product industry for example production of rubber glove. By adding banana skin into the latex, it is able to decrease the cost of production. Therefore less latex is necessary for production but still able to produced product with good quality. Nevertheless by using banana skin into natural rubber latex also able helps to resolve environmental issue like waste production. As banana skin able to apply into the industry therefore able to reduce solid waste to the environment. Through this value added process, banana skin which is a zero value waste is turn into valuable starting material for rubber industry.

Thermal performance of rubber is very important in application for industrial. Usually the processing temperature are high and near to degradation temperature. By adding filler into latex may affect the thermal performance in the process, therefore this is important to investigate the thermal properties of natural rubber latex film with filler.

1.3 RESEARCH OBJECTIVES

There are three objectives to achieve in this study:

- To produce latex film with banana skins as a filler
- To investigate thermal properties of natural rubber latex with new bio-based organic filler
- To investigate the morphology of latex film with banana skins as a filler

CHAPTER 2

LITERATURE REVIEW

2.1 BACKGROUND OF NATURAL RUBBER LATEX

Natural rubber (NR) which from *Hevea brasiliensis*, is an important source of natural rubber due to its excellent physical properties. NR is composed primarily of cis-polyisoprene. In solid natural rubber contains approximately 94 % of rubber hydrocarbon and 6 % of non-rubber components such as lipids, protein carbohydrates and so on (Eng and Tanaka, 1993). For those non-rubber components play a role in stabilizing latex particles and also contribute to the outstanding natural rubber properties (Tarachiwin et al., 2005). NR generally is an elastic hydrocarbon polymer that was originally derived from latex, a milky colloid produced by rubber tree. NRL is the protective fluid contained in tissue beneath the bark of the rubber tree, *Hevea brasiliensis.* This tree originated from Brazil but by 1890, Britain had introduced rubber plantations in Malaysia and was harvesting latex (Sinaco Pte. Ltd., 2011). NRL is an emulsion of rubber polymer in an aqueous dispersion (Perez, 1993). It is harvested from rubber tree and then flows down along cut segment of rubber tree into small collection cup. After that, latex is collected from the cups and processed into commercial rubber latex (Perrella and Gaspari, 2002). Basically the concentration of the latex is about 30 % after tapping and there is only a small percentage is used directly while the greatest part is processed into harder rubber through a lot of processes including evaporation, hydro extracting, creaming and also electro decanting (INFU, 2003). The collected rubber latex contains a lot of natural substances which include around 33 % of polyisoprene rubber polymer and also proteins which are organic substances that contain carbon, hydrogen, nitrogen, oxygen and sulfur (Perrella and Gaspari, 2002).

The steady growth of natural rubber production from around one million tons in the late 1930s to over 5 million tons last year is due not only to the increased hectarage under rubber, but also to agricultural research. The original plantings of *Hevea brasiliensis* yielded about 250 kg/ha/yr – tree breeding and selection have raised potential yields to well over 3,000 kg/ha/yr. Consumption has grown only slightly since 1970 to almost one million tons in 1987, a decline in terms of market share from 30 % to about 20 %. As well as the obvious growth in Taiwan, South Korea, Hong Kong and Singapore, the natural rubber producing countries are rapidly expanding their domestic rubber consumption. Malaysia, for example, is actively encouraging the growth of resource-based industries, and government policy in this area was laid down in the Industrial Master Plan of 1986 (Davies and Barbara, 1989). Figure 2.1 shows the image of natural rubber latex.

Figure 2.1: Natural rubber latex (NRL)

Source: Davis (1996)

There are certain functions for natural rubber latex. Latex can be removed without affect to the health of *Hevea* tree. However, removal of latex stimulates the tree to the production of large additional quantities of this substance which having the same composition as the latex originally present. Besides that, latex vessels serve as additional channels for the transport of food. It is the storage of food, storage of water, storage of excretory products or a combination of any two or more of the functions. Latex can also against the attacks of insects and other enemies. It undoubtedly serves a protective function (Lock, 1913).

2.2 COMPOSITION OF NATURAL RUBBER LATEX

NRL is derived from milky sap from *Hevea brasiliensis* tree. Basically it can used to make gloves and also used to manufacture a number of products as diverse as tyres, clothing, medical products and toys (Ansell Healthcare Europe N.V., 2011). The composition of latex is not much altered by moderate tapping, but the amount of rubber present may be greatly reduced if the tapping is excessive (Lock, 1913).

Table 2.1 shows the composition of natural rubber latex sap. The constituents contained in natural rubber latex includes rubber particles, also known as cis-1,4-polyisoprene, protein, water, sterol glycosides, resins, ash and also sugars. Water contained in NRL is higher as compared to other constituents, which consist of 55 % to 65 %. About 30 % to 40 % of rubbers particles are contained in the NRL while for the other constituents are small in amount in the NRL. Natural rubber has a high elasticity and it also has a polymer molecular structure which consists of a long chain made up of tens of thousands of monomer strung together (Sheppard, 2011).

Table 2.1: Composition of natural rubber latex sap

Constituent	% Composition
Rubber particles (cis-1,4-polyisoprene)	30-40 %
Protein	2-3 %
Water	55-65 %
Sterol glycosides	0.1-0.5 %
Resins	1.5-3.5 %
Ash	0.5-1.0 %
Sugars	1.0-2.0 %

Source: MEDIDEX (1996)

2.3 STRUCTURE OF NATURAL RUBBER LATEX

Rubber is primarily hydrocarbon in nature. According to English chemist Michael Faraday (1826), the natural rubber is analyzed and the empirical formula for natural rubber is found. It has the empirical formula C_5H_8, along with 2-4 percent protein and 1-4 percent acetone-soluble materials which are resins, fatty acids and sterols. While in 1860, an English chemist Charles Hanson Greville Williams (1829-1910) confirmed Faraday's analysis and in 1862 distilled natural rubber to obtain the pure monomer, which called isoprene (Kauffman, 2011). Natural rubber has the repeating unit in cis configuration, which is essential for elasticity. While if the configuration is trans, the polymer is either a hard plastic naturally occurring gutta-percha, obtained from the leaves of Palaquium, a species of sapotaceous Malaysian and East Indies trees that was used for wire and cable coating (Kauffman, 2011). Figure 2.2 shows the structure for isoprene.

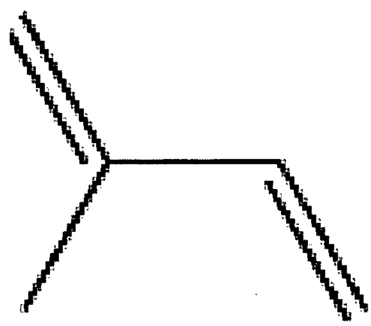

Figure 2.2: Structure for isoprene

2.4 PROPERTIES OF NATURAL RUBBER LATEX

The composition, structure and properties of natural rubber are important for many applications. Natural rubber has outstanding resilience and tensile strength, as well as low heat build-up. NRL has high ability to stick to it and to other materials. This makes it suitable for pressure-sensitive adhesives and excellent water resistance. A drawback is natural rubber moderate environmental resistance to factors such as oxidation and ozone, therefore it scarce resistance to chemicals including gasoline, kerosene, hydraulic fluids, degreasers, synthetic lubricants and also solvents

(UNCTAD secretariat, 2011). As for the storage climate conditions for natural rubber, temperature, humidity or moisture and possibly ventilation conditions are the most important factors. Table 2.2 shows that the favorable and optimum travel temperature for natural rubber (Transport Information Service, 2011).

Table 2.2: Favorable and optimum travel temperature for natural rubber

Term	**Temperature range, °C**
Favorable travel temperature range	5 - 25
Optimum travel temperature	20

Source: Transport Information Service (2011)

Storage temperature that greater than 30 °C and exposed to sunlight for few hours can result in activation of the rot-causing bacteria especially in conjunction with moisture and proteins. Moreover, oxidation and associated molecular breakdown are encouraged causing rubber develops soft patches, stickiness and becomes oxidized rubber (Transport Information Service, 2011).

Crude rubber is a tough and an elastic solid. It will become soft and sticky as the temperature rises. Since natural rubber is an unsaturated elastomer, hence it is readily susceptible to oxidation. This is reflected in the loss in tensile strength with aging at 100 °C for one day (Rodgers et al., 2005). Its specific gravity is 0.915. The most important property of natural rubber is its elasticity. It expands when it stretched and attains its original state, when released. This is due to its coil-like structure. The molecules straighten out when stretched and when released, they coil up again. Therefore applying a stress can easily deform rubber. This is note that when this stress is removed, it retains its original shape. Natural rubber is insoluble in water, alcohol, acetone, dilute acids and alkalis but soluble in ether, carbon disulphide, carbon tetrachloride, petrol and turpentine. Other than that, pure rubber also is a transparent, amorphous solid, which on stretching or prolonged cooling becomes crystalline (Parekh, 2011).

As for the molecular behavior of natural rubber, glass transition temperature is about -70 °C and melting temperature is 25 °C (UNCTAD secretariat, 2011). According to Causin (2009), the glass transition temperature, T_g of natural rubber is located at extremely low an temperature which is about -70 °C and it is not easily measurable with accuracy by common equipment.

2.5 CHARACTERISTICS OF NATURAL RUBBER LATEX

Natural rubber latex (NRL) is a cross-linked polymeric material. It is offering excellent strength and able to stretch many times its original length without destroying it. NRL memory is high and it is allowing the material return to its original shape and along with its elasticity makes it superior to other glove materials in terms of comfort and also fit. Besides that, latex is resistant to punctures and it has the tendency to seal itself if a small hole occurs even though it can be pierced by very sharp objects. As for example natural rubber latex gloves provide a good protection from caustic chemicals and detergents. On the other hands, NRL is a natural, biodegradable product, and do not contain with any petroleum by-products or dioxins. It also enable disposal by land fill and incineration without environmental damage (Ansell Healthcare Europe N.V., 2011).

As for physical properties of natural latex, the concentration with age of fresh, seasonal, tapping systems differ, basically contain only 20 % to 40 % of total solid content. Viscosity of total solid content is about 35 % of fresh latex of its viscosity is about 12 mPa to 15 mPa. It has significantly changed with acquisition period and other factors. The higher total solids content generally high viscosity, but the same total solid content of latex, the method of preservation, storage time, the different particle size, viscosity differences will occur. Large amounts of latex can be reducing surface tension of water surface active substances such as protein and fatty acid which can reduce surface tension of latex (ShenZhen ShiBangXing Rubber Co., Ltd., 2010).

pH value of latex has great effect on its stability. The pH value for fresh latex is slightly alkaline tendencies which are 7 to 7.2. Due to bacteria and enzymes, the pH value of latex will becomes acidic and lead to coagulation after few hours to more than ten hours. Therefore, ammonia or other base is necessary in order to be able to preserve a long time, which pH value is 10 to 10.5 (ShenZhen ShiBangXing Rubber Co., Ltd., 2010). On the others hand, latex-based rubbers are great tensile strength, resilience and elongation. It should be treated with special chemicals and additives due to easily corroded by heat, sunlight and even oxygen. The ideal temperature range for using latex is between 55 °C to 82 °C (Williams, 2010).

2.6 KEY PROPERTIES AND CHARACTERISTIC OF NATURAL RUBBER

Table 2.3 shows the key properties and characteristic of natural rubber from Aslett Rubber Incorporation (1885).

Table 2.3: Key properties and characteristic of natural rubber

Durometer (Shore A)	30-90
Tear Strength	E
Specific Gravity (Polymer)	0.92
Flame Retardent Properties	P
Tensile Strength Max-psi (Mpa)	3500 (24.1)
Weathering Characteristics	P
Low Temperature Brittle Point (°C/°F)	-58/-70
Oxidation Resistance	G
Resilience	E
Ozone Resistance	P
Compression Set	G
Oil Resistance	P
Heat Aging	F
Acid Resistance	F to G
Abrasion Resistance	E
Resistance to Alkali Substances	F to G

Legend: P=Poor; F=Fair; G=Good; E=Excellent

Source: Astlett Rubber Inc. (1885)

The outstanding strength of natural rubber has maintained its position as the preferred material in many engineering applications. It has a long fatigue life and high strength, even without reinforcing fillers. Other than thin sections, it can be used to approximately 100 °C, and sometimes above. Natural rubber can maintain flexibility down to -60 °C if compounded for the purpose. It has good creep and stress relaxation resistance and is low cost. Its chief disadvantage is its poor oil, oxygen and ozone resistance, although these latter disadvantages can be ameliorated by chemical protection (Astlett Rubber Inc., 1885).

2.7 COMPARISON BETWEEN PURE NATURAL LATEX, NATURAL LATEX WITH FILLERS

Table 2.4 shows that the comparison between pure natural latex with synthetic latex and latex with fillers.

Table 2.4: A table comparing pure natural latex with synthetic latex, and latex with fillers

	Pure Natural Latex	**Natural Latex with Fillers**	**Synthetic (SBR) Latex**
Physical Appearance	Creamy white natural latex colour. Extremely fine foam structure. Sweet odour of natural latex when fresh	Colour varies according to the type of filler used. Titanium dioxide for example will give the foam a dull white colour. Kaolin clay produces grey foam. Coarse structure. The sweet fresh natural latex odour is suppressed by fillers.	Artificial White colour. Coarse structure with large pores and thin bubble cell wall.
Structural Properties	Open cell system Extremely fine structure – strong gel strength and excellent support capability.	Open cell system Coarse foam structure - filler reduces gel strength and causes poor support capability.	Open cell system Large pores, poor gel strength and poor support capabilities

Table 2.4: Continued

	Pure Natural Latex	Natural Latex with Fillers	Synthetic (SBR) Latex
Costituent Composition	100 % Pure Natural Latex	70 – 85 % natural latex 15 – 30 % fillers are added to increase hardness and as a cheapener to reduce the cost of production.	70 – 85 % SBR 15 – 30 % fillers may be added to increase hardness and to act as a cheapener.
Dynamic Properties	Excellent, with good resilience, low hysteresis, low permanent set, high elasticity, excellent tensile properties and highest recovery to original shape after deformation. Excellent tear resistance.	Poor. Inorganic fillers reduce tensile properties, particularly elongation at break. They also suppress resilience, promote high permanent set and reduce its ability to recover to the original shape. Filled latex is as good as 'dead' foam.	Very poor as SBR foam does not recover its original shape after compression. It is nowhere close to the resiliency natural latex can provide. SBR foam has poor tensile properties and weak tear strength.
Durability	Natural Latex Foam is durable. According to research a pure Natural Latex Foam without fillers can easily last 25 years.	Natural latex with fillers is not as durable as pure latex. The service life of latex product with fillers is not expected to exceed 5 years.	Synthetic Latex foam loses its strength after a short period of use. It is not as durable as Natural Latex foam in any way.
Environmental Considerations	Natural Latex is derived from pure, super clean, unadulterated natural rubber latex from trees. It is cultivated through new planting and replanting programs from large scale plantations to ensure a sustainable supply of latex.	The environmentally friendly attributes of natural latex are suppressed by the presence of fillers, particularly when fillers such as calcium oxide or titanium dioxide are used.	Synthetic latex can be seen as an environmental hazard - it is a product of the petrochemical industry and it is contributing to the depletion of our non-renewable fossil resources.