EFFECT OF RICE HUSK POWDER ON PROPERTIES OF NATURAL RUBBER LATEX FOAM

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EFFECT OF RICE HUSK POWDER ON PROPERTIES OF NATURAL RUBBER LATEX FOAM

By

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DECLARATION

I declare that the content presented in this dissertation is my own work which was done at Universiti Sains Malaysia unless informed otherwise. This dissertation has not been previously submitted for any other degree.

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam disertasi ini adalah hasil kerja saya dan dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Disertasi ini juga tidak pernah disertakan untuk ijazah yang lain sebelumnya.

Signature:

Candidate's Name: Shamala Ramasamy

Date:

Witness:

Signature:

Supervisor's Name: Prof. Hanafi Ismail

Date:

DEDICATION

This research work is especially dedicated to the world best parents and siblings for their everlasting and unconditional love.

My Family

RAMASAMY, KOBI,

VIMAL RAJ, KAVITHA, SURESH

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LIST OF ABBREVIATION

RH	Rice Husk
RHP	Rice Husk Powder
NR	Natural Rubber
NRL	Natural Rubber Latex
NRLF	Natural Rubber Latex Foam
SBR	Styrene Butadiene Rubber
ASTM	American Society for Testing and Materials
ISO	International Standards Organization
FTIR	Fourier Transform Infrared Spectrometry
SEM	Scanning Electron Microscopy
TM 3000	Tabletop Scanning Electron Microscopy 3000
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetric Analysis
phr	Part per hundred of rubber
drc	Dry Rubber Content
PP	Polypropylene
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
HDPE	High-density polyethylene
HA	High Ammonia Preserved Latex
LATZ	Low Ammonia Tetramethylthiuramdisulfide Zinc oxide Preserved Latex.
LA SPP	Low Ammonia Sodium Pentachlorphenate
LA BA	Low Ammonia Boric Acid

ZDEC	Zinc diethyldithiocarbamate
ZMBT	Zinc 2-mercaptobenzhiozolate
S	Sulphur
ZnO	Zinc oxide
SSF	Sodium silicofluoride
DPG	Diphenylguanidine
NaOH	Natrium Hydroxide
NH_4OH	Ammonia
OH	Hydroxide
KOH	Potassium Hydroxide
KOL	Potassium Oleate
H_2O_2	Hydrogen Peroxide

LIST OF SYMBOLS

M100	Stress at 100 % elongation
E_b	Elongation at break
Q_f	Weight of filled vulcanizates
Q_g	Weight of gum vulcanizates
kX	Thousand times magnification
Ct	Constant Deflection Compression Set
Tg	Glass Transition Temperature
Tm	Melting Temperature
rpm	Rotation per minute
Ton	Tonnes
MPa	Mega Pacsal
GPa	Giga pascal
g	Gram
Kg	Kilogram
cm	Centimeter
%	Percentage
wt%	Weight Percentage
+	Plus
°	Degree
°C	Degree Celsius
µm	Micrometer
mm	Millimeter
hrs	hours
min	minute

LIST OF PUBLICATIONS

International Peer Review Journal

1. Shamala Ramasamy, Hanafi Ismail, Yamuna Munusamy. (2012). Tensile and Morphological Properties of Rice Husk Powder Filled Natural Rubber Latex Foam. *Polymer-Plastics Technology and Engineering, 51:15*, p.1524-1529.

2. Shamala Ramasamy, Hanafi Ismail, Yamuna Munusamy. (2013). Effect of rice husk powder on compression behavior and thermal stability of natural rubber latex foam. *BioResources, 8:3*, p. 4258-4269.

3. Shamala Ramasamy, Hanafi Ismail, Yamuna Munusamy. (2013). Preparation and Characterization of Rice Husk Powder Incorporated Natural Rubber Latex Foam. *Advanced Materials Research, 626*, p.523-529

4. Shamala Ramasamy,Hanafi Ismail,Yamuna Munusamy. (2013). Aqueous Dispersion of Rice Husk Powder as a Compatible Filler for Natural Rubber Latex Foam. *Advanced Materials Research, 626* p.530-536

5. Shamala Ramasamy, Hanafi Ismail, Yamuna Munusamy. (2013). Soil Burial, Tensile Properties, Morphology and Biodegradability of Rice Husk Powder Filled Natural Rubber Latex Foam. *Journal of Vinyl Additivies and Technology*, Accepted In Press.

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KESAN SERBUK SEKAM PADI KE ATAS SIFAT BUSA LATEKS GETAH ASLI

ABSTRAK

Serbuk sekam padi (RHP), sisa pertanian telah digabungkan dengan lateks getah asli (NRL) untuk menghasilkan busa lateks getah asli (NRLF) melalui kaedah Dunlop. Sifat-sifat tensil, mekanikal, rintangan haba, pencirian struktur mikro dan kajian degradasi NRLF terisi RHP telah dikaji dan dibandingkan dengan NRLF (tanpa kandungan RHP). Dalam siri pertama, kesan peningkatan kandungan RHP dalam julat 0 hingga 10 phr kepada sifat-sifat NRLFs telah dikaji. Dalam siri kedua, pengaruh pengurangan saiz RHP telah dikaji. Kesan penggantian separa atau lengkap RHP dengan sagu telah dikaji dalam siri ketiga. Nisbah RHP / Sagu telah ditetapkan hingga 10 phr. Dalam siri keempat, RHP terubahsuai digunakan. Kesan kajian 'soil burial' dan 'natural weathering' busa NRLF selama tiga bulan telah diterokai, masing-masing mengikut ASTM D 5247 and ISO 877.2. Hasil kajian menunjukkan kekuatan tensil, tensil modulus, kekerasan, dan kestabilan terma menaik dengan peningkatan pembebanan pengisi, manakala pemanjangan pada takat putus dan peratusan pemulihan busa berkurangan. Dalam siri kedua, pengurangan saiz pengisi menunjukkan peningkatan dalam ciri-ciri NRLF disebabkan peningkatan interaksi RHP-matriks dalam NRLFs. Dalam siri ketiga, penggantian sagu menunjukkan perosotan sifat-sifat mekanikal dan kestabilan terma NRLFs. Pengubahsuaian RHP mengurangkan kandungan lignin dan silika, menyebabkan perosotan sifat-sifat NRLFs. Walau bagaimanapun, pengubahsuaian ini mempercepatkan perosotan NRLFS terisi RHP. Kemerosotan dalam sifat-sifat busa lateks getah asli telah diperhatikan dalam kajian penanaman di dalam tanah dan pencuacaan semulajadi.

EFFECT OF RICE HUSK POWDER ON PROPERTIES OF NATURAL RUBBER LATEX FOAM

ABSTRACT

Rice husk powder (RHP), an agricultural by-product incorporated into natural rubber latex (NRL) compound and foamed to produce natural rubber latex foam (NRLF) via the Dunlop method in this work. The tensile, mechanical, thermal resistance, micro structural characterization and degradation studies of RHP filled NRLF were investigated and compared with the controlled NRLF (zero RHP loading). In the first series, the effect of RHP loading from 0 to 10 phr on the properties of NRLFs was studied. In the second series, the influence of RHP size reduction was studied. The effect of partial or complete replacement of RHP with sago starch was investigated in the third series. The RHP/Sago Starch ratio was fixed to 10 phr. In the fourth series, modified RHP was used. The effects of soil burial test and exposure to natural weathering on all these samples were explored for three months in accordance to ASTM D 5247 and ISO 877.2, respectively. Result showed tensile strength, modulus at break, hardness and thermal stability increases with increasing filler loading while elongation at break and recovery percentage decreased. In second series, reduction of RHP filler size showed an improvement in the properties examined due to the enhanced RHP-matrix interaction in the NRLFS. In third series, the substitution of sago starch showed poor mechanical properties and greater thermal stability of the NRLFs. Modification of RHP reduces the lignin and silca content, thus resulting in reduced properties of NRLFs. However, these modification accelerated the degradation of RHP filled NRLFS. Deterioration in the properties of NRLFs was observed through soil burial and natural weathering test.

CHAPTER 1

INTRODUCTION

1.1 Background

Biodegradation takes place through the action of enzymes and/or chemical deterioration associated with living organisms. This event occurs in two steps. The first one is the fragmentation of the polymers into lower molecular mass species by means of either abiotic reactions, i.e. oxidation, photodegradation or hydrolysis (Goswami et al., 1998), or biotic reactions, i.e. degradations by microorganisms. This is followed by bioassimilation of the polymer fragments by microorganisms and their mineralisation. Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degrading conditions. Mechanisms and estimation techniques of polymer biodegradation have been reviewed. The mechanical behaviour of biodegradable materials depends on their chemical composition, the production, the storage and processing characteristics, the ageing and the application conditions (Vroman and Tighzert, 2009).

Living in an environment with increasing landfill pollution increases the interest of researches to develop biodegradable products. The principal of sustainability and environmental impacts are becoming the factors to be considered in the process of creating future materials and products, alongside with the cost and technical performance (Kim et al., 2006); (Nikolic et al., 2003). With developing environmental ecological awareness, biodegradable polymers are proposed as one of many strategies to alleviate the environmental impact of polymers and are gaining public interest (Koning and Witholt, 1996); (Nakayama et al., 2012). Most of the conventional polymers are non-degradable and no naturally occurring microorganisms can break them down (Phua et al., 2012). The massive increase in the usage of polymer products such as plastics leads to significant environmental impact (Kim et al., 2000).

Latex also contributes in water and landfill pollution in the form of paint, mattresses, cushioning seats for vehicles and furniture, gloves, condoms and etc. Therefore, the substitution of these conventional non degradable latex products with biodegradable ones is of great interest to the society. Natural rubber latex (NRL), a renewable polymeric material displaying excellent physical properties, is widely used in the manufacture of thin film and foam products (Sanguansap et al., 2005). NRL is the form in which rubber is exuded from the *Hevea brasiliensis* tree as an aqueous dispersion with high molecular weight (Okieimen and Akinlabi, 2002), and an appreciable widely varying gel content. The excellent physical properties of NR include resilience, strength and fatigue resistance, and these, together with the fact that it is a renewable resource, means that it is a very important elastomeric material. In efforts to extend its use, there have been various methods developed in order to modify its properties. These modifications have not only been directed towards the enhancement of certain properties characteristic of NR, but also to introduce totally new properties not usually associated with NR. Reactions that have been utilized in this way include substitution, simple addition (Samir et al., 2013), cyclo addition and electro cyclic reactions (Lehrle et al., 1997).

Biodegradable polymers must be cost-effective and have to show similar performance to non degradable polymers. In order to achieve the above-mentioned characteristics, in recent years biodegradable polymers have been combined with natural fibers to produce environmentally sound biopolymers. The use of biodegradable materials based on renewable resources can help reduce the percentage of polymers in industrial and household wastes. These fillers can be categorized into many aspects according to their applications, such as inorganic and organic. Recently, investigations into the use of fillers derived from agricultural-based materials such as hemp, jute, bamboo, and rice husk (RH) as alternatives to inorganic fillers in thermoplastics had been widely reported (Lifang et al., 2009).

Rice husk (RH), a by-product of rice milling industry, among several cellulose products, is biodegradable, inexpensive, low density, abundant, lightweight, and exhibit competitive specific mechanical properties (Ciannamea et al., 2010); (Nurain et al., 2012). Rice husk (RH), lignocellulosic material which has received a great attention as a new type of filler in polymer composites due to its advantages compared to traditional fillers (i.e., carbon black and silica) such as lower density, greater deformability, less abrasiveness to equipments, lower cost of the production and renewable resource (Mohd et al., 2006). However, rice husk disposal is an alarming issue to the environment through open burning and illegal dumping. Abundantly disposed rice husk causes landfill limitation. Thus, since last two decades, the study on utilization of the rice husk powder (RHP) as reinforcing filler has been widely investigated (Yang et al., 2004). The RHP has been incorporated into various kinds of polymer matrix such as high-density polyethylene, low-density polyethylene, polypropylene, styrene butadiene rubber linear low-density polyethylene blends and polyurethane (Attharangsan et al., 2012). Be that as it may, no attempt had been taken to incorporate natural fibers in natural rubber latex foam.

The natural rubber latex foam industry saw the beginning of its true development in the late 1920's was no accident but in many ways a fulfillment. Development of the Dunlop process have formed the basis of what became one time the most important process for the manufacture of latex rubber (Blackley, 1966). The Dunlop process is particularly well adapted to the manufacture of molded latex foam products of thick section such as pillows, cushions, mattresses and upholstery foam (Roslim et al., 2012). Morosely, very few research works have been done on natural rubber latex foam.

However to best of our knowledge, there are no published reports on attempts to incorporate rice husk powder into natural rubber latex foam. Therefore this study is focused on the development of environmental friendly rice husk filled natural rubber latex foam.

1.2 Problem Statement

Contribution of latex to the landfill polluted environment leads to an eye opening research interest in biodegradable latex products. Latex products such as gloves, condoms, cushioning for vehicles and mattresses with a short useful life becomes an issue when they are consumed and discarded into the environment as their utilization ceases. Hence, contributes significantly to the shortage of landfill availability. Latex products degrades slowly in the environment (Blackley, 1966). This growing problem related to finding available landfill areas for the final disposal of non-recyclable polymers gives rise to the development of biodegradable polymers which able to fulfill the new environmental requirements regarding the effective management of post-consumer waste.

For this research study, the use of rice husk powder obtained from rice husk as filler in natural rubber latex foam has been explored to promote biodegradation of latex foam. Concomitant with the rigorous development of the rice milling industries, rice husks, the fibrous, hard, outermost covering of a grain of rice, is generated at 158 million tonnes per year, accounting for about 30% of the annual gross rice production throughout the world. Hitherto, rice husk becomes a burden to the environment through open burning and illegal dumping (http://www.statista.com/statistics/271969/world-rice-husk-2013/). With properties such as annual renewability, large quantity, low cost, lightweight, competitive specific mechanical properties, and environmental friendliness, rice husk has spurred an interest for use as filler in natural rubber latex foam. It is believed that the incorporation of bio fillers such as rice husk powder could enhance the biodegradability of natural rubber latex foam. And, this is an alternative way to solve the waste disposal problem by converting rice milling waste products into raw material of another product. This not only help to create a more environmentally friendly surrounding but also reduces disposal cost and increases income of the milling industry.

1.3 Research Objectives

The aim of this research is concerned with biodegradability of rice husk powder filled natural rubber latex foam.The primarily objectives for this research work are:

i. To study the effect of reduction of rice husk powder and its loading on the tensile properties, compression properties, hardness, thermal properties, foam density, and biodegradability of rice husk filled natural rubber latex foam under different environmental conditions.

ii. To study the effect of partial or complete replacement of rice husk powder by sago starch in natural rubber latex foam, on its tensile properties, compression properties, hardness, thermal properties, foam density, and biodegradability under different environmental conditions.

iii. To study the effect of rice husk modification on its tensile properties, compression properties, hardness, thermal properties, foam density, and biodegradability under different environmental conditions.

1.4 Organization of Thesis

There are five chapters in this thesis and each chapter gives information related to the research interest as follows:

• **Chapter 1** describes the introduction of the project. It covers brief introduction about research background, problem statement, and research objectives.

• **Chapter 2** shows current problem and generation of latex waste, introduction of environmental degradable polymer and benefit of such polymers. It also covers the brief explanation regarding to the natural rubber latex foam, rice husk powder, and other materials used in this project.

• **Chapter 3** contains the information about the materials and equipments specification, and experimental procedure used in this study.

• **Chapter 4** presents the results and discussion of this research. The effect of various loading, sizes and modification of rice husk powder on the natural rubber latex foam will be discussed. Rice husk powder with commercial filler hybrids will also be discussed in term of its tensile properties, compression properties, hardness, thermal properties, foam density, Fourier transform infra-red, and biodegradability under different environmental conditions.

• **Chapter 5** concludes the findings of the research based on results and discussion in Chapter 4 with suggestions for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Fiber

2.1.1 Classification of Natural Fiber

The vast agricultural industry produces many waste streams that are rich in ligno-cellulosic fibers (Sreekala et al., 2011). Natural fibers are known to be renewable and sustainable, but they are in fact, neither. Natural fibers are taken from living plants which are renewable and sustainable, not the fiber themselves. Natural fibers are also subdivided based on their origins, coming from plants, animals or minerals. Generally, plant or vegetable fibers are used to reinforce plastics due to its light weight and low density (Bledzki and Gassan, 1999). Living plants can be classified as primary and secondary depending on their utilization and contribution of natural fibers. Living plants that are grown mainly for their fiber content are considered as primary plants. Whereas, living plants with fibers as a by product are known to be secondary plants or fiber. Sisal, kenaf, hemp and jute are some of the primary plants. Examples of secondary plants are pineapple, rice, oil palm and coir (Omar et al., 2012). Natural fibers can also be grouped in six types. There are leaf fibers (abaca, sisal and pineapple), core fibers (kenaf, hemp and jute), bast fibers (flax, and ramie), reed fibers (wheat, corn and rice), seed fibers (coir, cotton and kapok), and other types (wood and roots) (Omar et al., 2012). Table 2.1 shows the important sources of natural fibers used commercially from all over the world.

Table 2.1: Commercially available fiber sources (Omar et al., 2012).

Fiber source	World production (10^3 ton)
Bamboo	30,000
Jute	2300
Kenaf	970
Flax	830
Sisal	378
Hemp	214
Coir	100
Ramie	100
Abaca	70
Sugar cane bagasse	75,000
Grass	700

Uniformity of natural fiber to be used as filler is a common problem. Age, digestion process and climatic conditions influence not only the structure of natural fibers but also the chemical composition. Compositions of a few natural fibers are shown in Table 2.2.

Table 2.2: Composition of a few natural fibers (Omar et al., 2012).

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Waxes (wt%)
Bagasse	55.2	16.8	25.3	–
Bamboo	26–43	30	21–31	–
Flax	71	18.6–20.6	2.2	1.5
Kenaf	72	20.3	9	–
Jute	61–71	14–20	12–13	0.5
Hemp	68	15	10	0.8
Ramie	68.6–76.2	13–16	0.6–0.7	0.3
Abaca	56–63	20–25	7–9	3
Sisal	65	12	9.9	2
Coir	32–43	0.15–0.25	40–45	–
Oil palm	65	–	29	–
Pineapple	81	–	12.7	–
Curaua	73.6	9.9	7.5	–
Wheat straw	38–45	15–31	12–20	–
Rice husk	35–45	19–25	20	14–17
Rice straw	41–57	33	8–19	8–38

With the exception of cotton, the components of natural fibers are cellulose, hemi-cellulose, lignin, pectin, waxes and water soluble substances, with cellulose, hemi-cellulose and lignin as the basic components with regard to the physical properties of the fibers. Cellulose is the essential component of all plant natural fibers (Omar et al., 2012).

2.1.2 Natural Fiber as Reinforcing Filler

Environmental awareness has an eye on natural fibers as potential alternatives reinforcement to the synthetic fillers due to its unique advantages such as non-toxic, non- irritation of the skin, eyes, or respiratory system, non-corrosive properties (Shalwan and Yousif, 2012). Beyond the environmental benefits, technical aspects also provoke the interest for the natural fibers as a replacement or supplement for common fillers (e.g., glass fibers) in polymer composites (Fei et al., 2008). Additionally for several more technical orientated applications, the fibers have to be specially prepared or modified regarding (Bledzki and Gassan, 1999):

- homogenization of the fiber’s properties;
- degrees of elementarization and degumming;
- degrees of polymerization and crystallization;
- good adhesion between fibre and matrix;
- moisture repellence; and
- flame retardant properties.

Natural fibers attract parties from numerous applications such as automobiles as natural fiber shows superior advantages over synthetic fibers in term of relatively low cost, low weight, less damage to processing equipment, improved surface finish of molded parts composite, good relative mechanical properties, abundant, ease of chemical and mechanical modification, relative high strength, stiffness, low density and renewable resources. Table 2.3 shows mechanical properties of commercially major natural fibers (Ismail et al., 2002; P. Methacanon et al., 2010).

Table 2.3: Mechanical properties of a few common natural fibers.

Fibre	**Density (g/cm3)**	**Elongation (%)**	**Tensile strength (MPa)**	**Young's modulus (GPa)**
Cotton	1.5–1.6	7.0–8.0	287–597	5.5–12.6
Jute	1.3	1.5–1.8	393–773	26.5
Flax	1.5	2.7–3.2	345–1035	27.6
Hemp	-	1.6	690	
Ramie	-	3.6–3.8	400–938	61.4–128
Sisal	1.5	2.0–2.5	511–635	9.4–22.0
Coir	1.2	30	175	4.0–6.0
Viscose (cord)	-	11.4	593	11
Soft wood kraft	1.5	-	1000	40

Natural fibers are much lighter, cheaper and provide much higher strength than most inorganic fillers (Fei et al., 2008; Bledzki and Gassan, 1999). It's a global interest to investigate and study the potential of using natural fibers in various applications under varying loading conditions (Shalwan and Yousif, 2012). Natural fibers especially lignocellulose-based natural fibres have great properties as compared to glass fiber which sparked the interest of researchers from all over the world. Intrinsically, these fibres have a number of interesting mechanical and physical properties as shown in Table 2.4 (Paul et al., 2003).

Table 2.4: Comparison between natural and glass fibres.

	Natural fibers	**Glass fibers**
Density	Low	Twice that of natural fibers
Cost	Low	Low but higher than natural fibers
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO2 neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not biodegradable

2.1.3 Rice Husk

Rice is the largest crop grown in the world that is crucially important as a principal staple food and nourishment provider for the world's population. Rice is grown and cultivated on every continent and is very much related to cultures and multiple rituals. Rice covers about 60 to 70% of the total calorie uptake on average for more than 2000 million people in Asia. Consumption and production of rice in increasing in Latin America and Africa, as the second most consumed food grain in low income and food deficit countries. Rice now covers about 1% of earth surface. The global rice consumption for 2006 was 417 million tonnes which increased to 526 million tonnes on 2013 due to the obvious demand from population growth, social civilization, industrial and technology development. It is expected that by the year 2040, global rice consumption will hike up to 556 million tones (Foo and Hameed, 2009;

http://www.statista.com/statistics/271969/world-rice-husk-2013/). Table 2.5 shows the major world rice production for year 1990, 2000 and 2010.

Table 2.5: Major world rice production (http://www.geohive.com/charts/ag_rice.aspx)

Rice Producing Countries	1990 (Million Tonnes)	2000 (Million Tonnes)	2010 (Million Tonnes)
China	192	189	197
India	112	127	121
Indonesia	45	52	66
Thailand	17	26	32
Myanmar	14	21	33
Philippines	10	12	16
Japan	13	12	11
Sri Lanka	2.6	2.8	4.3
Laos	1.5	2.2	3
Malaysia	1.9	2.1	2.6
Australia	0.92	1.1	2

Concomitant with the accelerating global rice production, world production for rice husk (RH) is about 158 million tonnes, which is about 30% of the annual gross rice production in the world (http://www.statista.com/statistics/271969/world-rice-husk-2013/). Rice husk is an important agricultural waste that can be easily found in some states of Malaysia. Huge amount of rice husks are generated in rice milling industry during the paddy milling process from the fields (Nurain et al., 2012). Removed during the refining of rice, though utilized in multiple ways, were still raising issues due to abundant availability that leads to cost of disposal (Yalcin, N. and Sevinc, 2001). To add on, the amount of rice husk available is far in excess of any local uses and thus has posed disposal problems.

RH, the hard, fibrous, woody, protective shell of the grain, accounts for 20–25% of a rice grain's weight. Figure 2.3 shows the real image of raw rice grains still covered with rice husks while Figure 2.4 is the typical cross section diagrammatic representation of rice grain and rice husk.

Figure 2.1: Real image of raw rice grains still covered with rice husks (http://www.chinapictures.org/photo/china/chinese-food/50516165941296/)

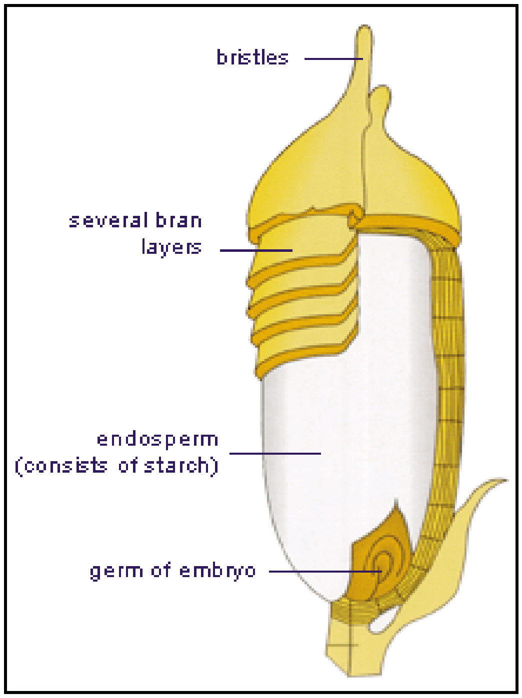

Figure 2.2: Cross section diagrammatic representation of rice grain and rice husk. (http://freespace.virgin.net/robmar.tin/rice/rice.htm)

RH exhibits potential advantages, renewable source, low price, biodegradability, abundant, and causes no damage due to abrasion to the processing machinery (Qiang et al., 2009; Mohd et al., 2006; Khalf and Ward, 2010). Differing from other lignocellulosic materials, RH has a more complex composition. The constituents of rice husk vary with the climate and geographic location of growth. In addition to the main constituents, including cellulose, hemicellulose and lignin, RH also contains a significant content of an inorganic component which is silica (Qiang et al., 2009; Yalcin, N. and Sevinc, 2001). RH has the same basic components as wood but in different proportions as shown in Table 2.6 Khalf and Ward, 2010).

Table 2.6: Basic components of rice husk (Khalf and Ward , 2010).

Components of Rice Husk	(%) by Weight
Cellulose	35
Hemicelluloses	25
Lignin	20
Amorphous silica	15.98
Other soluble substances	1.02

The exterior of rice husk are made of dentate rectangular elements which are mostly silica coated with a thick cuticle and surface hairs, while the mid region and inner epidermis are usually containing smaller amount of silica. The outer surface of RH which contains high amounts of silica is relatively rougher than the inner surface that houses the rice grain. Silica exists on the outer surface of RHs in the form of silicon cellulose membrane that forms a natural protective layer against termites and other micro-organisms attack on the paddy. This component has been alleged to be responsible for insufficient adhesion between accessible functional groups on RH surfaces and various matrix binders. Removal of silica and other surface impurities can be expected to improve the adhesion properties of rice husks to binders and ultimately improve the properties of the composite drastically. The inner surface of rice husk is smooth and may contain wax and natural fats that provide good shelter for the grain (Ndazi et al., 2007).

2.1.4 Utilization of Rice Husk in Polymer Materials.

Despite the increasing trend of the rice husk surplus, proper methods of disposal or utilization of rice husks have yet to be developed. Up to now, alternative applications of RH are limited, and most of the surplus rice husk is disposed of by direct burning in open heaps or thrown in landfill causing land pollution. Lately, rice husk was used to generate electric power through thermal degradation but this method released a large number of green house gases, and the emission of rice husk ash into the ecosystem has attracted huge criticisms and complaints. Due to RH's persistent, carcinogenic and bio-accumulative effects, multiple health issues such as silicosis syndrome, fatigue, shortness of breath, loss of appetite and respiratory failure problem aroused (Ying, 2011); (Qiang, 2009). Open burning of RH is also often the disposal method of rice millers.This leads to environmental concerns and becomes a great environmental threat causing damage to the land and the surrounding area in which it was dumped. Different methods for husk disposal, including finding a commercial use for the waste have been suggested (Nurain, 2012). If we are not able to exploit RH accordingly, a massive harzardous environment pollution will be faced (Ying, 2011). However, in the last decade, many countries imposed new regulations to restrict field burning of rice husk primarily for environmental reasons (Mansaray and Ghaly, 1998)

Utilization of rice husks has been significantly widened for the past few years, serving as an ideal source of pet food fiber, building and insulating materials for reinforcing the tensile strength as fertilizers through vermin-composting techniques, as microbial nutrients for single-cell protein production ,for reducing sugar production and as raw products in the manufacturing of ethanol (Foo, 2009).

Due to RH's fibrous nature, it has been used as filler for making lightweight polymer composites which provides an effective means for proper and optimum utilization of a large quantity of rice husk produced every year (Khalf and Ward, 2010). Research efforts are in progress to incorporate rice husk in polymers so that they can enhance the physical, mechanical and tribological properties of the latter (Navin et al., 2010). Multiple research efforts were taken by incorporating RH into various kinds of polymer matrix such as high-density polyethylene, low-density polyethylene, polypropylene, styrene butadiene rubber and polyurethane. It was known through these studies that RH not only improves the tensile modulus and flexural modulus but also flame retardancy. (Ismail et al., 2012)

RH has been used as a resource for chemical feedstocks or as reinforcement (Samir et al., 2011). Rice husk, a cellulose-based fiber, has also been utilized in the manufacture of composite panels (Ndazi et al., 2007). One of the current applications of RH is its incorporation into polymer matrices such as for the fabrication of RH-filled ecocomposites. The addition of RH can promote the biodegradation process of the polymer matrix, and also make the final materials to be economically more competitive (Qiang et al., 2009; Ismail et al., 2012).

2.2 Natural Rubber

2.2.1 Background and Properties of Natural Rubber

Natural rubber (NR) can be defined as polyisoprene extracted form *Hevea Braziliensis* (Lee et al., 2011). Originally, South America, but in present day, countries such as Malaysia, Indonesia, Sri Lanka, and Nigeria are also major contributors of natural rubber. A slit is made into the bark of *Hevea Braziliensis* (also known as rubber tree) to allow the flow of a milky sap called latex. This is described in Figure 2.3.

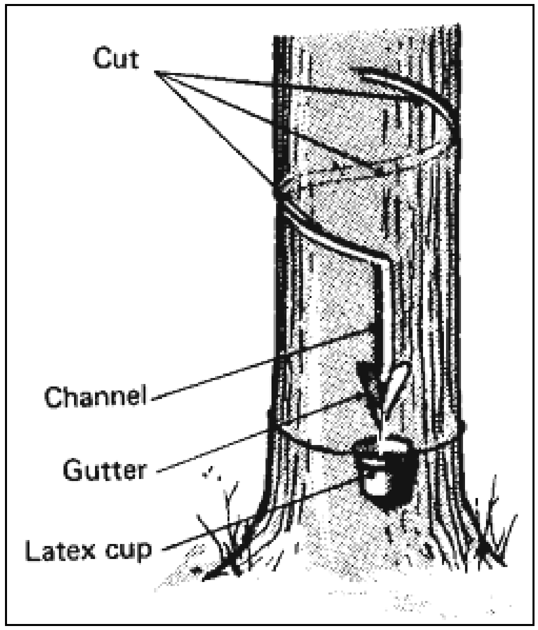

Figure 2.3: Tapping latex from a rubber tree.
(http://www.fao.org/docrep/006/ad221e/ad221e06.htm)

Latex is a mixture of polyisoprene, water and small amount of other ingredients such as proteins, carbohydrates and impurities. Collected latex undergoes multiple processing stages involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending before becoming ‘dry rubber’ (Ciesielski, 1999); (Ciullo and Hewitt, 1999). NR has a very unique ability, to crystallize upon stretching, a phenomenon known as ‘‘strain induced crystallization”. This characteristic is due to NR’s uniform microstructure (Ismail et al., 2011). Processing of NR requires high power input and heavy equipments. Thus, arising the need of rubber to be available in physical form that is friendly to be handled in liquids, fluids, and solids (Okieimen and Akinlabi, 2002). Still, NR is one of the most important elastomers widely used in industrial, technological and engineering fields due to its superior and unique mechanical properties that make it an important and irreplaceable material in certain applications, such as in tires, mountings, gaskets and seals (Okieimen and Akinlabi, 2002).

Composition of latex and dry rubber is similar but varies in its amount. The typical composition of latex and dry rubber is shown in Table 2.7 (Ciesielski, 1999); (Ciullo and Hewitt, 1999); (Morton, 1987).

Table 2.7: Composition of Fresh Latex and Dry Rubber (Morton, 1987)

Constituents	**Dry Rubber (%)**	**Fresh Latex (%)**
Rubber hydrocarbon	93.7	36
Protein	2.2	1.4
Neutral lipids	2.4	1
Carbohydrate	0.4	1.6
Inorganic constituents	0.2	0.5
Water	-	58.5
Glycolipids + Phospholipids	1	0.6
Others	0.1	0.4

NR is composed of both Gel phase, which is the insoluble part in toluene and Sol phase that is the soluble part in toluene. The term ‘‘Gel’’ means a three-dimensional network that is insoluble in solvents. Hence, the Gel phase in NR is not a true Gel since it is soluble to certain solvents and also soluble at high temperatures. Amount of Gel varies with the clones of Hevea tree, ages of tree, and periods of storage, storage conditions and processing conditions.

NR is recently been proposed to be composed of linear poly-isoprene with two terminal groups. These terminal groups are active and can react with natural impurities such as proteins and phospholipids. These reactions can lead to extensions of two linear poly-isoprene segments, connections of three or more linear segments (so-called branches or star), forming a network of different chain connections. As a result, NR has been considered as a mixture of connected linear poly-isoprene segments with different connectivity. This connected mixture is named as the ‘‘naturally occurring network’’. Therefore, the gel phase in NR is composed of the naturally occurring connected network, and the sol phase is composed of extensions and branches of linear chains. The naturally occurring network is thought to be responsible for the elastomeric behavior of NR (Shigeyuki Toki et al., 2009). NR also has high molecular weight compound and weak thermal properties low heat diffusivity and conductivity (Okieimen and Akinlabi, 2002).

2.2.2 Application and Research Development of Natural Rubber

Current trend is to add fillers into NR to gain appropriate properties for specific applications. A wide variety of fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs, and improvements in processing (Ismail et al., 2011; Larissa et al., 2011; Okieimen and Akinlabi, 2002; Nittaya and Sarawut, 2012). For example in automotive engine industry, it is required to improve the thermo-mechanical performance of the current NR, which is commonly used as an anti-vibration system inside the engine compartment. NR composite materials are very much in demand to reduce the cost and increase the life-time durability while maintaining excellent performance under harsh operating conditions (Lee et al., 2011).

Ergo, world wide researchers have attempted to enhance the properties of NR by multiple ways in varying fields and industries. Recently, natural rubber nanocomposites with carbon black and organoclay was prepared by incorporating nanofillers into solid rubber using a conventional two-roll mill (Larissa et al., 2011). Attemps was made to enhance the properties of china clay-filled NR vulcanizates by partially substituting clay with reinforcing fillers. Currently, an interesting work claims that the best balance of heat build-up and abrasion resistance for a heavy-duty truck tire tread is achieved when china clay and silica filled NR compound is used (Nittaya and Sarawut, 2012). NRs are now prepared from the combinations of natural rubber with various conventional plastics, such as polypropylene (PP), low-density polyethylene (LDPE) , linear low-density polyethylene (LLDPE) as well as high density polyethylene (HDPE) (Pongdhorn Sae-Oui et al., 2010).

However, there is also growing environmental awareness regarding the disposal of these materials at the end of their useful life (Ismail et al.,2011). Scrap rubbers, leftover rubber from manufacturing activities and also old and defective rubber products are waste and usually discharged. The discarded scrap rubber does not degrade rapidly enough and this causes environmental pollution. (Ismail et al., 2002).

2.3 Natural Rubber Latex (NRL)

2.3.1 Background and Properties of Natural Rubber Latex (NRL)

Though many plants are capable of producing latex, only the latex from Hevea brasiliensis trees has been exploited over the 100 years.This tree species which grow in the hot humid intertropical regions, is exploited by tapping bark. Natural rubber latex (NRL) is found in latex vessels localized in the cortex, especially in the layer 2 to 3 mm thick nearest to the cambium. NRL is the fluid, milky in appearance, which flows from these plants after the slightest wound. Like all plant materials, latex contains growth-related substances such as carbohydrates, proteins, and other organic and inorganic constituents. The rubber hydrocarbon particles (the elastic components sought in all natural rubber products) comprises 25% to 45% of the latex system.The variation is due to factors such as the clone of the tree, the tapping system, the soil condition and the season. The non rubber substances constitute only a small percentage of the latex system (Sansatsadeekul et al., 2011)

Latex is, in general, an aqueous system in which polymer particles are homogeneously distributed as a colloidal dispersion. It is a two phase system, made of aqueous and solid polymer particles and, therefore, the surface interaction phases are: water to polymer particles and, aqueous to air. The interaction between the aqueous phase and the particles has a certain effect on the latex stability. Improper interaction causes the coagulation of particles to create larger particles. It was found that as the particle size increases the interfacial energy decreases. Therefore, latex may be considered as thermodynamically unstable (Berrin Yilmaz, 2010). NRL, which is usually obtained by the partial depolymerization of NR, was previously found to have most of the natural components that produce the color, appearance, and performance of NR. Not only this, NRL has the same monomer as the rubber 1,4-isoprene unit. Natural rubber Latex (NRL) is an aqueous dispersion of polyisoprene latex particles and non rubber particles in an aqueous serum phase. Apart from the rubber hydrocarbon, a large number of non rubber constituents (mainly carbohydrates, lipids, and proteins) are also present in relatively small amounts in the aqueous phase. Some are associated with the rubber particles themselves (Okieimen and Akinlabi, 2002). When subjected to ultracentrifugation at approximately 59,000*g*, latex can be separated into 3 main fractions3 (Figure 2.6): (1) top rubber hydrocarbon particle phase; (2) ambient C serum in which all latex particles are suspended; and (3) denser bottom fraction of nonrubber particles, particularly lutoids, which contain yet another serum (B-serum).

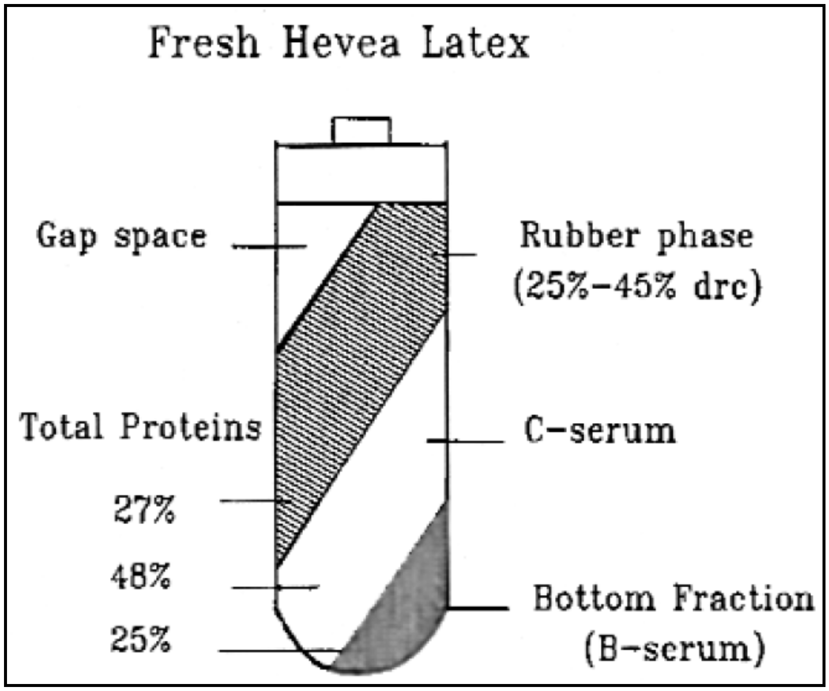

Figure 2.4: Freshly collected *Hevea brasiliensis* latex separated into its 3 main fractions on ultracentrifugation at 59,000*g*. (Esah and Paul, 2002)

When it is required to preserve NRL, chemicals such as formalin, sodium sulphate and ammonia at desired dosages are added in. Ammonia has been recognized as the most effective and desired preservative. However, this chemical has certain drawbacks as well. Higher dosage is required for an effective longer preservation period. High amount of ammonia leads to atmospheric pollution. Thus, preservation systems comprising low levels of ammonia in combination with other chemicals were introduced. However, these systems had issues such as high toxicity, lower mechanical, storage and chemical stability. A composite preservation system consisting tetramethylthiuram disulphide, zinc oxide and ammonia, popular known as LA-TZ system was introduced during 1975 and subsequently commercialized till today (Ho et