THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Science (Chemistry)
DEGREE

Chemistry	Chemistry
FIELD	**DEPARTMENT**

TITLE: Improving Thermal Property of cis-1,4-polyisoprene Using Natural Fillers

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THESIS

IMPROVING THERMAL PROPERTY OF CIS-1,4-POLYISOPRENE USING NATURAL FILLERS

PIRONGRONG PRASERTPONG

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Science (Chemistry)
Graduate School, Kasetsart University
2011

Pirongrong Prasertpong 2011: Improving Thermal Property of cis-1,4-polyisoprene Using Natural Fillers. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Assistant Professor Wirunya Keawwattana, Ph.D. 116 pages.

The objective of this research was to study properties of thermal insulation products from natural rubber filled with natural fillers including perlite, fly ash, rice husk ash, and cellulose fiber from water hyacinth. Properties studied in this work were hardness, compression set, tear strength, modulus, elongation at break and thermal conductivity of the filled natural rubber vulcanizates. The properties of NR vulcanizates were investigated at two different formulations i.e. NR vulcanizates filled with different content of silica from natural resource i.e. perlite, fly ash, rice husk ash (0-60 phr) and NR vulcanizates filled with different content of water hyacinth fiber (0-7 phr). From experimental results, it was found that NR vulcanizates filled with 20 phr of silica and 5 phr of water hyacinth exhibited little improvement in mechanical properties especially tear strength. Therefore, The recommended dosage of silica from natural resource and water hyacinth fiber for using as filler in NR vulcanizates for producing thermal insulation was 20 phr and 5 phr, respectively. The thermal insulation samples of filled NR vulcanizates are molded for testing the thermal properties followed the ASTM C177 standard. From the result, it was found that the thermal insulation of NR vulcanizates filled with natural fillers had thermal conductivity ranging from 0.072 to 0.078 W/m.K. The success of this work proclaims a high feasibility of producing thermal insulation from natural rubber filled with natural fillers.

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Student's signature	Thesis Advisor's signature	

ACKNOWLEDGEMENTS

Firstly, I would like to grateful thank and deeply indebted to my advisor, Assist. Prof. Dr. Wirunya Keawwattana for her advice, encouragement and valuable suggestion for completely writing of thesis. I am also grateful to Assist. Prof. Dr. Duanghathai Pentrakoon, Faculty of Science, Chulalongkorn University for her technical assistance and useful comments and suggestion on my work.

I am sincerely grateful to the Department of Chemistry, Faculty of Science, Kasetsart University, Kasetsart University, The National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials (NCE-PPAM) and Energy Policy and Planning Office, Ministry of Energy, Thailand for funding and making this research program possible.

Finally, I am especially appreciated my parents, my relatives and my friends, who have given me support and encouragement throughout my graduate career. Their love and companionship have been an essential source of strength to me during this course.

Pirongrong Prasertpong

April 2011

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LIST OF ABBREVIATIONS

ASTM	=	American Society of Testing and Materials
BET	=	Brunauer-Emmett-Teller
CBS	=	N-cyclohexyl-2-Benzothiazole Sulphenamide
CV	=	Conventional vulcanization
EV	=	Efficient vulcanization
FA	=	Fly Ash
IPPD	=	N-isopropyl-N'-phenyl-p-phenylene diamine
MDR	=	Moving-Die Rheometer
MPa	=	Mega Pascal
NR	=	Natural rubber
ODR	=	Oscillating Disk Rheometer
PEG	=	Polyethylene glycol
phr	=	parts per hundred of rubber
rpm	=	rounds per minute
RHA	=	Rice Husk Ash
SEM	=	Scanning Electron Microscope
Si-89	=	Bis-[3-(triethoxysilyl)-propyl] tetrasulfide
STR	=	Standard Thai Rubber
TMQ	=	2,2,4-trimethyl-1,2-dihydroquinoline
XRF	=	X-ray fluorescence
ZnO	=	Zinc Oxide

IMPROVING THERMAL PROPERTY OF CIS-1,4-POLYISOPRENE USING NATURAL FILLERS

INTRODUCTION

At the present day, Thailand concerns with the problem of excessive consumption of the energy. Then the policy for saving the energy must be issued and encourage the using of the renewable energy. Using of the excellent of thermal insulation is one of the suitable ways for saving the energy. Then the trend of conservative energy for buildings is proliferated. This can be observed from increasing of using thermal insulation in many office, residential, commercial, and industrial buildings because it can prevent large amount of the heat from outside of the buildings.

Thermal insulation is a material or combination of materials, that, when properly applied, retard the rate of heat flow by conduction, convection, and radiation. It retards heat flow into or out of a building due to its high thermal resistance (Al-homoud, 2005).

There are many benefits for using thermal insulation in buildings, which can be summarized as follows:

1. A matter of principle: Using thermal insulation in buildings helps in reducing the reliance on mechanical/electrical systems to operate buildings comfortably and, therefore, conserves energy and the associated natural resources. This matter of conserving natural resources is a common principle in all religions and human values.

2. Economic benefits: An energy cost is an operating cost, and great energy savings can be achieved by using thermal insulation with little capital expenditure (only about 5% of the building construction cost).

3. Environmental benefits: The use of thermal insulation not only saves energy operating cost, but also results in environmental benefits as reliance upon mechanical means with the associated emitted pollutants are reduced.

4. Customer content and national good: Increased use of thermal insulation in buildings will result in energy savings which will lead to:

- Making energy available to others.
- Decreased customer costs.
- Fewer interruptions of energy services (better service).
- Reduction in the cost of installing new power generating plants required in meeting increased demands of electricity.
- An extension of the life of finite energy resources.
- Conservation of resources for future generations.

5. Thermally comfortable buildings: The use of thermal insulation in buildings does not only reduce the reliance upon mechanical air-conditioning systems but also extends the periods of indoor thermal comfort especially in between seasons.

6. Reduced noise levels: The use of thermal insulation can reduce disturbing noise from neighboring spaces or from outside. This will enhance the acoustical comfort of insulated buildings.

7. Building structural integrity: High temperature changes may cause undesirable thermal movements, which could damage building structure and contents. Keeping buildings with minimum temperature fluctuations helps in preserving the integrity of building structures and contents. This can be achieved through the use of proper thermal insulation, which also helps in increasing the lifetime of building structures.

8. Vapor condensation prevention: Proper design and installation of thermal insulation helps in preventing vapor condensation on building surfaces. However, care

must be given to avoid adverse effects of damaging building structure, which can result from improper insulation material installation and/or poor design. Vapor barriers are usually used to prevent moisture penetration into low-temperature insulation.

9. Fire protection: If the suitable insulation material is selected and properly installed, it can help in retarding heat and preventing flame immigration into building in case of fire.

Many types of building thermal insulation are available which fall under the following basic materials and composites:

Inorganic Materials

- Fibrous materials such as glass, rock, and slag wool.
- Cellular materials such as calcium silicate, bonded perlite, vermiculite, and ceramic products.

Organic Materials

- Fibrous materials such as cellulose, cotton, wood, pulp, cane, or synthetic fibers.
- Cellular materials such as cork, foamed rubber, polystyrene, poly ethylene, polyurethane, polyisocyanurate and other polymers.
- Metallic or metalized reflective membranes. These must face an air-filled, gas-filled, or evacuated space to be effective.

Accordingly, insulating materials are produced in different forms as follows:

- Mineral fiber blankets: batts and rolls (fiberglass and rock wool).
- Loose fill that can be blown-in (fiberglass, rock wool), poured-in, or mixed with concrete (cellulose, perlite, vermiculite).
- Rigid boards (polystyrene, polyurethane, polyisocyanurate, and fiberglass).

- Foamed or sprayed in-place (polyurethane and polyisocyanurate).
- Boards or blocks (perlite and vermiculite).
- Insulated concrete blocks.
- Insulated concrete form.
- Reflective materials (aluminum foil, ceramic coatings).

Thailand has area of planting natural rubber trees around 2.72 million hectares and nearly 90% of Thailand's natural rubber production is for export. More than 2.7 million tons or US$4.26 billion worth of natural rubber was exported in 2009. The top five destinations for Thailand's rubber products in terms of export value that year were China, Malaysia, Japan, the European Union and the United States. According to projections by the Office of Industrial Economics, the country's rubber product exports could reach US$6.6 billion in 2012. By previous reason, the government encourages the planting of natural rubber trees in north-east area of the country. Although, natural rubber has high rate of price but natural rubber is the primary product that can be replaced by the other products (i.e. synthetic rubber) then there is an occasion for reducing of price in the near future. Since natural rubber has the properties of high flexibility and excellent thermal insulation, then the study of natural rubber for construction materials that have property of insulation is initiated.

The recycling of by-products and wastes represents an increasingly urgent problem for the immediate future of human kind. Currently, only a small percentage of these fillers are utilized, the remaining is being directly discharged into landfill, which is unsatisfactory solution both from ecological and economic point of view. Therefore, there is continuing interest in establishing suitable processes in which they can be efficiently reused. Many researchers have been attempts to use silica from natural resources, in addition to fly ash, rice husk ash and perlite. The major constituents of these fillers are SiO_2, Al_2O_3 and Fe_2O_3 with some minor constituents such as CaO, MgO and other oxides. Therefore, these oxides have been mainly considered as a low cost material resource for the rubber industry.

Cellulose fiber, like water hyacinth (*Eichhorinia Crassipes*) is a waste cellulosic product. Water hyacinth fiber has a specific properties, low cost, light weight, renewable, high specific strength and modulus, and excellent thermal insulation. Recently, many researchers have studied thermal insulation materials from lignocellulosic fibers. Wang, (2008) presented the materials with the thermal conductivity less than 0.25 W/m.K are generally seen as thermal insulations. Khedari *et al*., (2004) developed a new low cost particleboard from durian peel and coconut coir mixture with a low thermal conductivity, varying between 0.0728 and 0.1342 W/m.K which was effective for energy saving when used as ceiling and wall insulating material.

Application of natural fillers (i.e. perlite, fly ash, and rice husk ash, water hyacinth fiber) filled in natural rubber for producing thermal insulation materials is well considered great advantages of utilization of natural resources for conserving energy and environment as well as economical benefits. This present work studies on the production, the mechanical properties including tensile modulus, tear strength, hardness, compression set and thermal properties of thermal insulation produced from natural rubber filled with natural fillers.

OBJECTIVES

To study the influence of natural fillers (i.e. perlite, fly ash, rice husk ash, and water hyacinth fiber) on the thermal, physical, and mechanical properties of vulcanized rubbers.

LITERATURE REVIEW

1. Natural Rubber (NR)

1.1 Introduction of natural rubber

Natural rubber (NR) is an unsaturated hydrocarbon consisting solely of carbon and hydrogen with an empirical formula of C_5H_8. Isoprene is the repeating unit of natural rubber where one double bond unit existed for each C_5H_8 group. Natural rubber has a high average molecular weight. It is a straight chain polymer structure which almost all (90-95%) the isoprene have the cis-1,4 configuration in which 1,4 structure means that carbon atoms 1 and 4 are joined in forming the chain as shown in Figure 1.

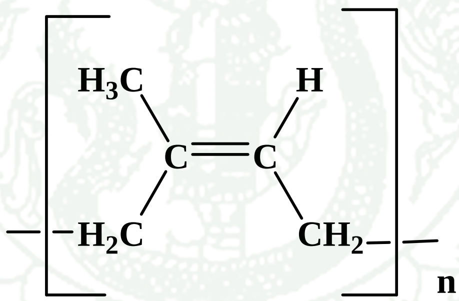


Figure 1 Chemical structure of cis-1,4-polyisoprene.

Natural rubber latex is the form in which rubber is exuded from the *Hevea brasiliensis* tree as an aqueous emulsion. The rubber particles range in size from about 50 Å to about 30,000 Å (3 μm). Exceptionally particles up to 5 or 6 μm in diameter are found. The molecular weight (MW) is normally in the range of 10^4-10^7 g/mol, depending on the age of the rubber tree, weather, method of rubber isolation and other factors. The polydispersity of MW is usually in the region of 2.5-10 (Bhowmick and Stephens, 2001). The rubber collected from the latex in the series of steps involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending. Because of its natural derivation, it is sold in a variety grades based on purity (color and presence of extraneous matter), viscosity, viscosity stability, oxidation resistance, and rate of cure.

The advantages of natural rubber over other synthetic rubbers are its outstanding green strengths and excellent natural tack properties. Apart from that, natural rubber also has good mechanical properties, such as tensile strength and extensibility, elasticity and low hysteresis in the important low strain region of the stress-strain curve, hence low heat build up and good creep properties. The excellent mechanical strength can be attributed to the ability of natural rubber to undergo strain-induced crystallization in which realignment of the polymer chains takes place at high strain.

1.2 Properties of natural rubber (Morton, 1987)

Strength

Natural rubber is well-known for the strength properties of its vulcanizates. The tensile strength of gum vulcanizates range from 17 to 24 MPa while those of black filled vulcanizates range from 24 to 32 MPa. Strength can also be characterized as tear resistance, in both of which natural rubber is excellent. This high strength of natural rubber is certainly due to its ability to undergo strain-induced crystallization. The strength drops rapidly with increase in temperature but is still better than in other elastomers.

Elongation at break

The ultimate elongation depends, naturally, very much on the nature and amount of fillers in the compound, and on the degree of vulcanization. In general, it is about 500 to 1000%, or even greater.

Abrasion and wear

Natural rubber has excellent abrasion resistance, especially under mild abrasive conditions. Below about 35°C, natural rubber shows better wear than styrene butadiene rubber (SBR), while above 35°C, SBR is better.

Dynamic properties

Natural rubber has high resilience, with values exceeding 90% in well-cured gum vulcanizates. At large strain, the fatigue life of natural rubber is superior to that of styrene butadiene rubber, the reverse is true for small strains. Good resistance to flexing and fatigue together with high resilience makes natural rubber useful in applications where cyclic stressing is involved.

Compression set

At ambient and slightly elevated temperature, the compression set of natural rubber vulcanizates is relatively low. At lower temperatures the compression set appear to be poor. Heat resistance of the natural rubber vulcanizate has a detrimental effect on the compression set.

Ageing resistance

Natural rubber vulcanizates can be given adequate heat-aging resistance by a suitable choice of vulcanization system and by use of amine or phenolic antioxidants. The heat-aging resistance of natural rubber vulcanizates is insufficient for many technical applications.

Weather and ozone resistance

Even after vulcanization, the natural rubber has double bonds in the polymer chain. Therefore, it has an insufficient weather and ozone resistance, particularly in light-colored vulcanizates.

2. Vulcanization of natural rubber

Vulcanization was discovered in 1841 accidentally by Charles Goodyear who heated natural rubber that contained sulfur. One year later, Thomas Hancock used the same process in England. Vulcanization, crosslinking, and cure are basically referred to the same process. During vulcanization, the free rubber chains are crosslinked together to form a large three dimensional elastic network via polysulfide bonds, as shown in Figure 2 (Coran, 1978).

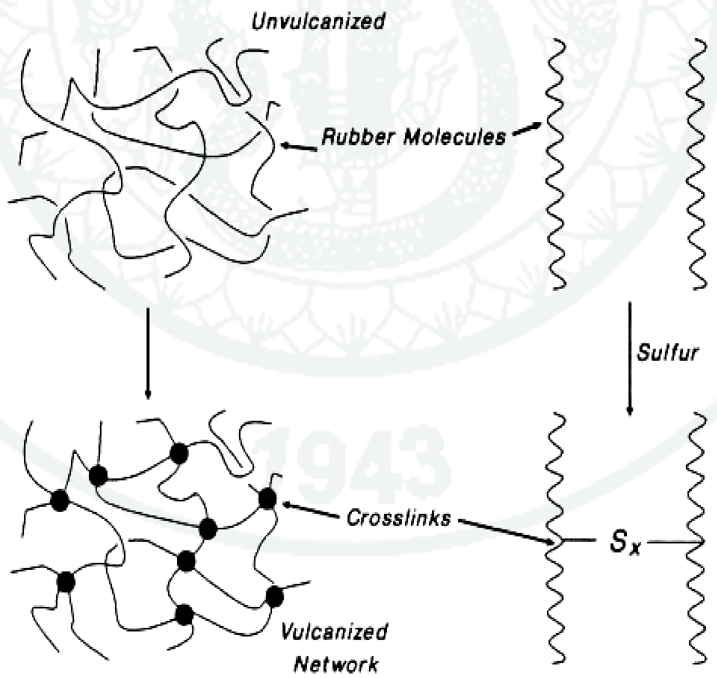


Figure 2 The vulcanization process in rubber.

Vulcanization is a process by which the long chains of the rubber molecules become crosslinked by reactions with the vulcanization agent to form three dimensional structures. The three dimensional structure produced restricts the free mobility of the molecules and transforms the soft and weak plastic-like material into strong elastic product. This vulcanization process also give a product having reduced tendency to crystalline, improved elasticity, better resistivity toward solvent and substantially constant modulus and hardness characteristics over a wide temperature range. The major effects of vulcanization on properties of vulcanized rubber are summarized in Figure 3 (Coran, 1978).

From the Figure 3 it is noted that the vulcanizate properties (tensile strength, modulus etc.) are increased as the number of crosslinks is increased. However, with further increase in crosslink density resulted in decrease of most of the vulcanizate properties. This process is called reversion. Reversion is a term applied to the loss of network structures by nonoxidative thermal aging. The compounder must recognize this dynamic nature of the cure system and optimize the choice of ingredients to produce a stable vulcanizate. However it should be noted that the properties in Figure 3 are not functions of crosslink density only. They are also affected by the type of crosslink, the nature of polymer, the type and amount of filler.

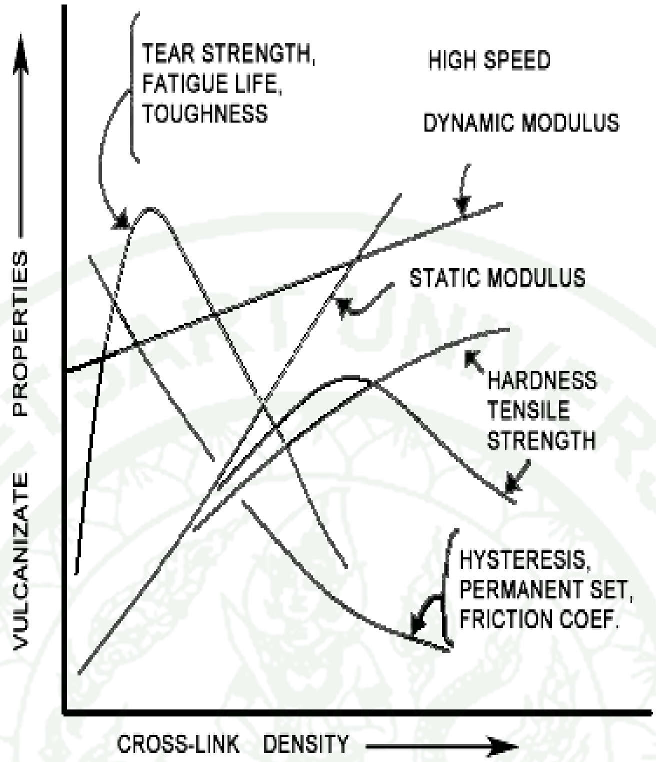


Figure 3 The effects of vulcanization on properties of vulcanized rubber.

After the rubber compound has been processed and formed, it is ulcanized. This process involves three stages: induction, curing, and reversion or overcure. The induction period is the time at vulcanization temperature during which no measurable crosslinking occurs. It determines the safety margin of the compound against “scorch” during the processing steps proceeding crosslinking. Scorch is premature vulcanization that can occur due to the effects of heat and time. Because these effects are cumulative, the time until scorch will slowly decrease with each processing step. Scorching results in a tough and unworkable batch, which must be scraped. The time to scorch is dictated by the processing and the additives used, so that a well designed compound will have a scorch time slightly longer than the equivalent of its maximum anticipated cumulative heat history. The amount of time the compound must be cured, the cure time, is determined in part by the “rate of cure”. This is the rate at which crosslinking and the consequent development of stiffness (modulus) occurs. Cure time is also a function of the desired “state of cure”. As vulcanization (crosslinking) proceeds, the various properties developed by vulcanization are not optimized simultaneously. At any given time during vulcanization, the state of cure is a measure of the development of these properties. Cure time is the time required for the compound to reach a state of cure where the desired balance of properties has been attained. When a compound is cured beyond the point where its balance of properties has been optimized it become overcured. For most elastomers, over cure means the compound becomes harder, weaker and less elastic. With other elastomers, particularly most natural rubber compounds, overcure results in reversion. The compound softens, becoming less elastic and more plastic.

2.1 Cure time

The oscillating disk rheometer (ODR) measures the complete curing characteristics of elastomer compound. The rubber is enclosed in a heated cavity (Figure 4).

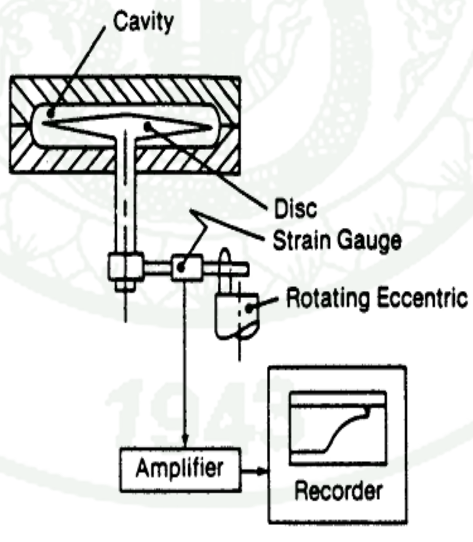


Figure 4 Oscillating disk rheometer.

Embedded in the rubber is a metal disk which oscillates sinusoidally in it plane about its axis. Vulcanization is measured by the increase in the torque required to maintain given amplitude (e.g. degree of arc) of oscillation at a given temperature.

The torque is proportional to a low strain modulus of elasticity. Since this torque is measured at the elevated temperature of vulcanization, the portion of it due to viscous effects is minimal.

New versions of the curemeter have been introduced. The cavity is much smaller and there is no rotor. In this type of curemeter, one-half of the die (e.g., the upper half) is stationary and the other half oscillates. These instruments are called moving die rheometers (MDR). The sample is much smaller and heat transfer is faster. Also, because there is no rotor, the temperature of the cavity and sample can be changed more rapidly.

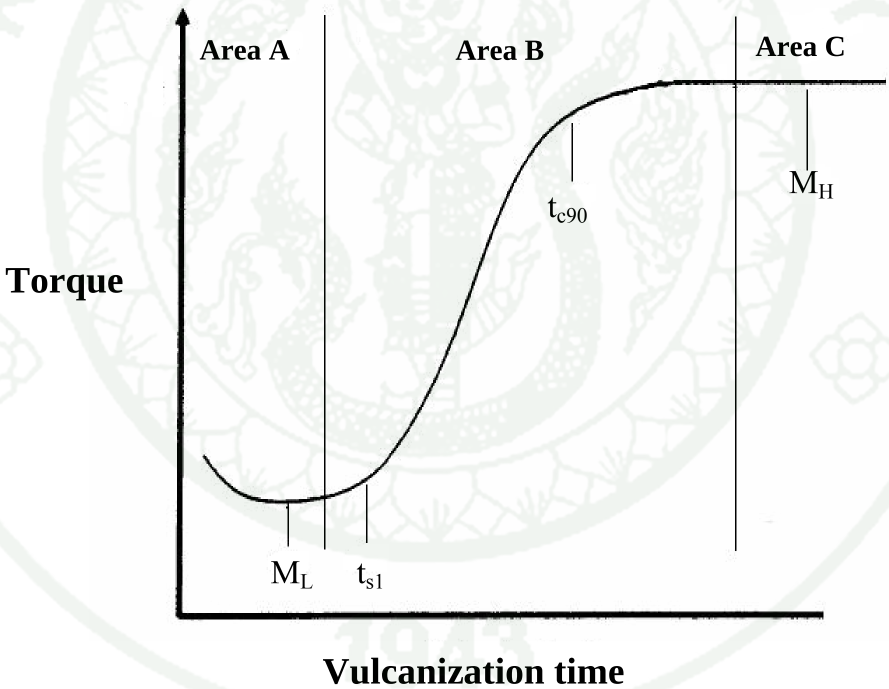


Figure 5 Rheometer cure curve.

The measurements which can be made from this curve and the term used to describe them are:

Area A - This gives an indication of compound viscosity.

Area B - This indicates the rate of cure of the compound.

Area C - This indicates the state of cure of the vulcanizate.

M_L, Minimum torque - A measure of the viscosity of the uncured compound

M_H, Maximum torque - A measure of cure state, with some compound, maximum torque can be related to vulcanizate modulus and hardness.

t_{s1} - Time for torque to increase 1 dn.m (0.1 N.m) or 1 lb_f-in above M_L - a measure of scorch time or processing safety, some laboratories use t_{s2} (i.e., time for torque to increase 2 dN.m or 2 lb_f-in above M_L) instead of t_{s1}.

t_{c50}, t_{c90} - Time for torque to reach $M_L + 0.5\ (M_H\text{-}M_L)$ or $M_L + 0.9\ (M_H\text{-}M_L)$

2.2 Vulcanization systems

Nowadays, the type of curatives for vulcanization depends primarily on the type of rubbers: unsaturated or saturated. For unsaturated rubbers, such as natural rubber, styrene butadiene rubber, and butadiene rubber, sulfur is commonly used. Saturated rubbers such as fluorocarbon rubber and silicon rubber cannot be vulcanized by sulfur. The most common curatives for saturated rubbers are peroxides, quinonedioximes, metal oxides, amines, and isocyanates (Hofmann, 1989).

2.2.1 Sulfur vulcanization

Various mechanisms have been studied to explain the process of the sulfur vulcanization without accelerators. One of the proposed mechanisms, free radical mechanism, is illustrated in Figure 6 (Coran, 1978). Sulfur is in a ring (S_8) structure. During the vulcanization, sulfur rings firstly generate radical polysulfides at a high temperature.

$$S_8 \longrightarrow \bullet S_x \bullet$$

One radical polysulfide removes hydrogen from an allylic site and gives a chain radical. Another polysulfide reacts with the chain radical and forms a new pendent polysulfide radical. This radical can react with another free polymer chain to form a crosslink. The propagation takes place as the radical reaction happens between rubber chains via proton transfer, and then a giant rubber network is formed with polysulfides as bridges.

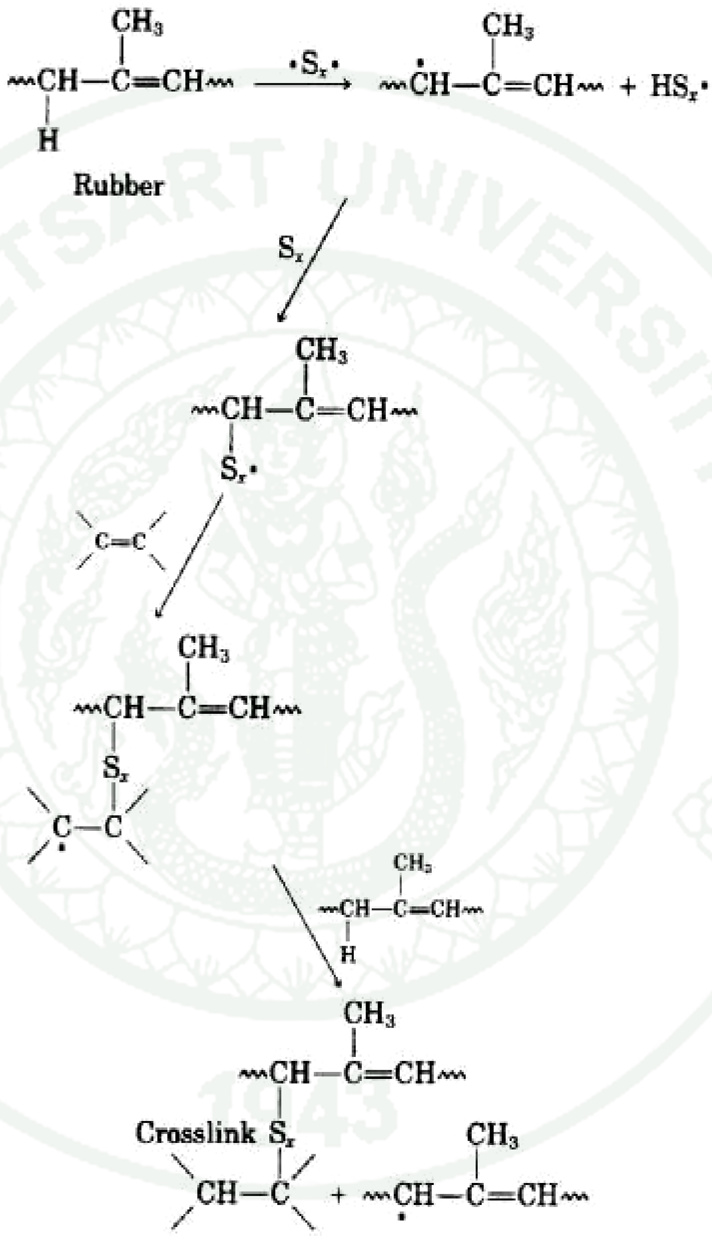
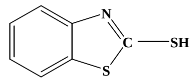
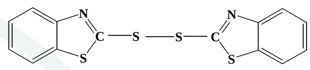
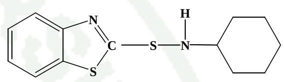
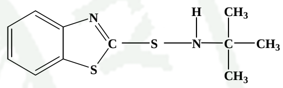
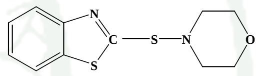
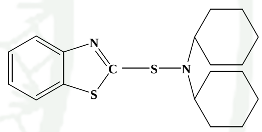
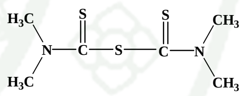
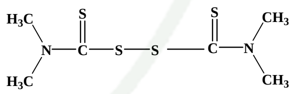
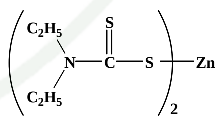
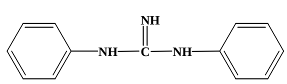
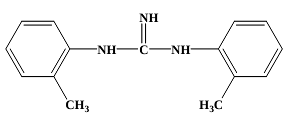


Figure 6 The schematic for free radical mechanism of sulfur vulcanization without accelerators.

Accelerators

The function of an accelerator is to increase the rate of vulcanization. Accelerators can cut the vulcanization time from hours to minutes or seconds at high temperatures; and at lower temperatures the vulcanization time may be reduced from months to hours or minutes. This reduction is of a great importance as this result in very high production rates and reduction in capital investment. The main reason for using accelerators is to aid controlling the time and/or temperature required for vulcanization and thus improves properties of the vulcanizate. Presently there are wide ranges of accelerator system available for elastomers, providing a range of cure rate, scorch times and final properties. The several common accelerators are shown in Table 1. In most of cases the curatives include two accelerators because they can be activated by each other, thus increasing the cure rate.

Table 1 Several common accelerators used in sulfur vulcanization.

Compound	Abbreviation	Structure
Benzothiazoles		
2-Mercaptobenzothiazole	MBT	
2-2'-Dithiobisbenzothiazole	MBTS	
Benzothiazolesulfenamides		
N-Cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-t-Butylbenzothiazole-2-sulfenamide	TBBS	
2-Morpholinothiobenzothiazole	MBS	
N-Dicyclohexabenzothiazole-2-sulfenamide	DCBS	
Dithiocarbamates		
Tetramethylthiuram monosulfide	TMTM	
Tetramethylthiuram disulfide	TMTD	
Zinc diethyldithiocarbamate	ZDEC	
Amines		
Diphenylguanidine	DPG	
Di-o-tolylguanidine	DOTG	

Source: Jame *et.al.* (1994)

The general reaction mechanism of sulfur vulcanization with an accelerator is illustrated as follows, using 2-mercaptobenzo-thiazole (MBT) accelerator as an example (Figure 7). First, the accelerator reacts with polysulfides (S_x) to form MBT-S_x-MBT structure by an initiator. Second, these polysulfides can react with rubber to form rubber-S_x-MBT structure. Finally, rubber polysulfides react either directly or through an intermediate to form rubber-S_x-rubber networks (Coran, 1978).

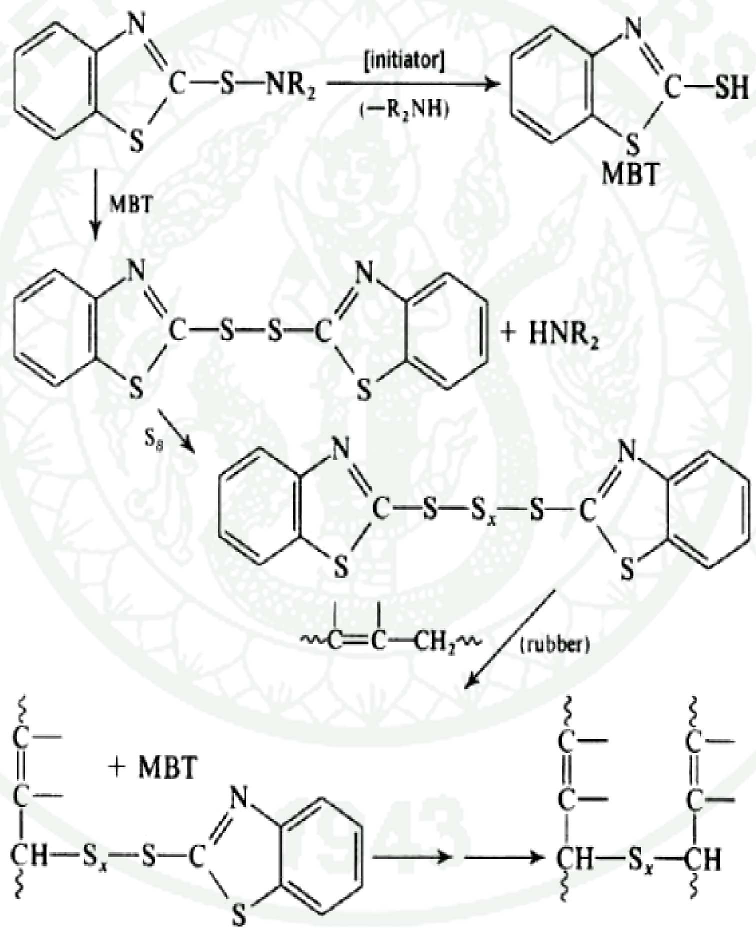


Figure 7 The mechanism of sulfur vulcanization with accelerators.

Sulfur reacts chemically with the raw rubber forming crosslinks between the rubber chains. The crosslinks of rubber and sulfur in the vulcanization network can be in many ways as monosulfide, disulfide or polysulfide as shown in Figure 8.

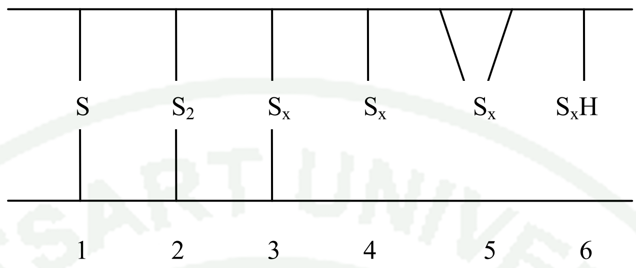


Figure 8 Different crosslink structures: (1) monosulfidic, (2) disulfidic, (3) polysulfidic, when $x \geq 3$, (4) sulfur chain, (5) cyclic sulfur structures, (6) thiol groups.

Activators

These components are used to increase the vulcanization rate by activating accelerators so that it performs more effectively. It is believed that they react in some manner to form intermediate complexes with the accelerators. The complex thus formed is more effective in activating the sulfur present in the mixture, thus increasing the cure rate. Accelerators are grouped as follows:

- Inorganic compounds (mainly metal oxides): zinc oxide, red lead, white lead, magnesium oxide, alkali carbonate, etc. Zinc oxide is the most common and it is often used in combination with a fatty acid to form a rubber-soluble soap in the rubber matrix.

- Organic acids: are normally used in combination with metal oxides; they are generally high molecular weight monobasic acids or mixtures of the following types: stearic, oleic, lauric, palmitic, etc.

- Alkaline substances will increase the pH of a rubber compound and in most instance increase the cure rate. As a rule of thumb, in the majority of recipes, any material which makes the compound more basic will increase the cure rate since acidic materials tend to retard the effect of accelerators.

Almost all organic accelerators require the simultaneous use of inorganic and organic activators to develop their full effectiveness. The main purpose of activator in rubber composites is to support the vulcanization, especially in the sulfur curing systems. The inorganic activators include zinc oxide and magnesium oxide; the organic ones include stearic, palmitic, lauric acid, and their zinc salts. The efficiency of the polysulfide cross-links during vulcanization can be controlled by the complex formed by activators (zinc and carboxylic acid), sulfur, and accelerators. A typical vulcanization system includes, sulfur (0.5-4 phr), diphenyl guanidine (DPG) & N-cyclohexyl-2-benzothiazole sulfenamide (CBS) (0.5-2 phr), zinc oxide (2-10 phr), and stearic acid (1-4 phr).

Antioxidants

Antioxidants design to inhibit oxidative and ozone-caused deterioration, but ultraviolet light protectors and antiflex agents are included as well. The results of oxidative attack depend on the polymer, like NR become soft and sticky. Ozone attack is manifested by cracking at the surface perpendicular to the stress. In the selection of antioxidant, the following factors must be considered: type of protection desired, chemical activity, discoloration, staining and cost. N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD) is one of the most popular antioxidant being used in compounding; the chemical structure is shown in Figure 9.

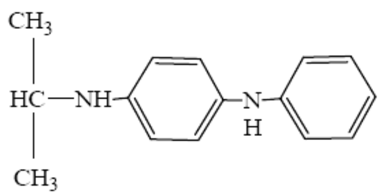


Figure 9 The structure of N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD).

Processing Aids

Processing aids are the ingredient added to a rubber compound to facilitate processing operation, such as mixing, calendering, extrusion and moulding. These materials react chemically to breakdown natural rubber and high Mooney viscosity synthetic elastomers chain and soften the rubber for easier processing or increasing the building tack after mixing. Examples of processing aid are fatty acids, metal salts of fatty acid and other fatty acid derivative, low molecular weight polymers and hydrocarbon oils and peptizer. Among the fatty acid, normally used is stearic acid which acts as a plasticizer and aid in dispersion of carbon black and other fillers. It also minimizes the tendency of rubber compound stick to the mill roll. Zinc laureate, stearate and lead oleate have also been used to soften rubber and improve its processing characteristic. Peptizers such as pentachloro-thiophenol and phenyl-hydrazine which serve as either oxidation catalysts or radical acceptors are essential in removal of free radicals formed during the initial mixing of the elastomer. This is very important as it prevents the polymer from recombining and allowing a consequent drop in polymer molecular weight, and thus the reduction in compound viscosity.

The sulfur vulcanization system can be classified into three types:

Conventional vulcanization (CV)

Most frequently used systems, conventional cure systems which feature a high sulfur level and low accelerator concentration show poor heat and oxidation resistance because the polysulfidic crosslinks are thermally unstable and readily oxidized. But conventional system gives vulcanizates which poses excellent initial properties like strength, resilience and resistance to fatigue and abrasion.

Efficient vulcanization (EV)

Efficient vulcanization systems which feature a low sulfur level, and a high acceleration level show good heat stability and oxidation resistance, however, have a poor resistance to fatigue because of the presence of predominantly monosulfidic and disulfidic crosslinks.

Semi-efficient vulcanization (semi-EV)

Semi-EV cure systems, which are intermediate between EV and conventional systems, are comprised between resistance to oxidation and required product fatigue performance because of the presence of predominantly disulfidic crosslinks.

The level of sulfur and accelerator of such sulfur vulcanization systems are shown in Table 2.

Table 2 The level of sulfur and the ratio of accelerator to sulfur.

Vulcanization system	Sulfur (S,phr)	Accelerator (A,phr)	A/S ratio
Conventional vulcanization (CV)	2.0-3.5	1.2-0.4	0.1-0.6
Semi-efficient vulcanization (semi-EV)	1.0-1.7	2.5-1.2	0.7-2.5
Efficient vulcanization (EV)	0.4-0.8	5.0-2.0	2.5-1.2

Source: Akiba and Hashim (1997)

3. Fillers

3.1 Definition of reinforcement and classifications of filler

Reinforcement is defined as the ability of fillers to increase the stiffness of unvulcanized compounds and to improve a variety of vulcanizate properties, e.g.

tensile strength, abrasion resistance and tear resistance. At the same time the stress values and the hardness are generally increased and as a rule other properties such as elongation at break and rebound and other properties depending on these lowered. The reinforcement's effect of filler shows up especially in its ability to change the viscosity of a compound and also the vulcanizate properties with increase in the amount of filler loading. Those fillers which only lead to small increase in the viscosity of the compound and otherwise to a worsening of the mechanical properties of the vulcanizate, are not reinforcing; they are called non-reinforcing or inert fillers such as talcum, calcium carbonate ($CaCO_3$), and clay. In contrast, reinforcing or also active fillers such as carbon black and silica lead to dramatic increase in viscosity of the compound as well as to maxima of the tensile and the tear strength and the abrasion resistance with increasing amounts of filler loading. Inert fillers are added to the rubber to increase the bulk and reduce costs. In contrast, reinforcing fillers such as carbon black and silica are incorporated in the rubber to enhance the mechanical properties, to change the electrical conductivity, to improve the barrier properties or to increase the resistance to fire and ignition.

Factors affecting filler reinforcement

The characteristics which determine the properties of filler and will impart to a rubber compound are particle size, surface area, structure, and surface activity.

Particle size

One of the most important parameters is the average particle size, as shown in Figure 10. Particles larger than 10^3 nm do not have reinforcing capabilities (at best) or have a detrimental action, and generally increase viscosity by a mere hydrodynamic effect. Reinforcement is readily obtained with sizes smaller than 100 nm but particle structure appears as a more decisive factor. Two classes of minerals have been found to offer significant reinforcing capabilities are carbon black and silica.

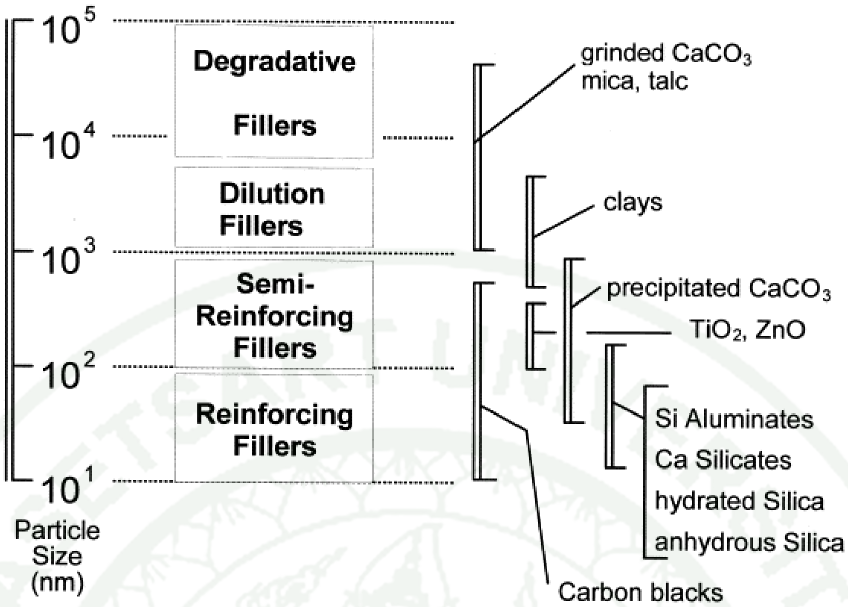


Figure 10 Classification of fillers according to average particle size.

Surface area

Particle size is generally the inverse of surface area. Fillers must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains.

Structure

The shape of an individual particle of reinforcing filler (e.g. carbon black or precipitated silica) is of less importance than the filler's effective shape once dispersed in elastomer. The blacks and precipitated inorganics used for reinforcement have generally round primary particles but function as anisometric acicular aggregates. The round particles clump together into chains or bundles that can be very dense or open and latticelike. These aggregate properties (shape, density, size) define their structure. High structure filler has aggregates favoring high particle count, with those particles jointed in chain-like clusters from which random branching of additional particle chains may occur. The more an aggregate deviates from a solid spherical shape and the larger its size, the higher is its structure. The higher its structure, in turn, the greater its reinforce potential. For reinforcing fillers which exist as aggregates rather than discreet particles, a certain amount of structure that existed at manufacture is lost after compounding. The high shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates. The structure that exists in the rubber compound, the persistent structure, is what affects processability and properties.

Surface activity

A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonpolar; polar fillers work best in polar elastomer. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites on the filler surfaces.

Filler effects

The principal characteristics of rubber fillers (particle size, surface area, structure, and surface activity) are inter dependent in improving rubber properties. In considering fillers of adequately small particle size, reinforcement potential can be qualitatively considered as the product of surface area, surface activity, and persistent structure or anisometry (planar or acicular nature). The general influence of each of these three filler characteristics above on rubber properties can be summarized as follows:

1. Increasing surface area (decreasing particle size) gives lower resilience and higher mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis.

2. Increasing surface activity gives higher abrasion resistance, chemical adsorption or reaction, modulus (at elongation > 300%), and hysteresis.

3. Increasing persistent structure/anisometry gives higher mooney viscosity, modulus (at elongation < 300%), and hysteresis, lower extrusion shrinkage, tear resistance, and resilience, and longer incorporation time.

3.2. Main fillers in rubber vulcanizates

The importance of fillers in the rubber compounds is well known. Fillers are widely used to enhance the performance of rubbers and other polymeric materials. Filler characteristics such as size and shape of particles and aggregates, chemical nature and porosity of surface, dispersibility and tendency to agglomerate and form secondary filler networks determine its effect on rubber compounds.

Fillers can be classified into black and non-black. Soon after carbon black was discovered to be an active filler in rubber, at the beginning of this century, it became one of the most important components in the manufacture of rubber products, with a consumption second only to rubber itself.

3.2.1 Carbon black

Carbon black is the most widely used reinforcing filler in the rubber industry. Carbon black is prepared by incomplete combustion or by thermal cracking of hydrocarbons. Carbon black from incomplete burning of natural gas is acidic on the surface. Carbon blacks can also be produced by thermal cracking of hydrocarbons in the absence of oxygen and have relatively low specific surface area (6-15 m^2/g) (Studebaker, 1965).

Carbon black particles typically have their size ranging from 20 to 300 nm (Studebaker, 1965). There are three morphological forms of carbon black existing in rubber composites: particle, aggregate, and agglomerate (Figure 11). The sizes of these morphological forms has the following order: particle < aggregate < agglomerate. Single carbon black particles are the fewest in rubber composites. Aggregates have their sizes ranging from 100 to 500 nm measured by an electron microscopy (Byers, 1987). They do not break during rubber compounding. Agglomerate consists of a group of aggregates. It requires a tremendous amount of energy to break down the agglomerate during rubber compounding because of the high cohesive forces among carbon black particles.

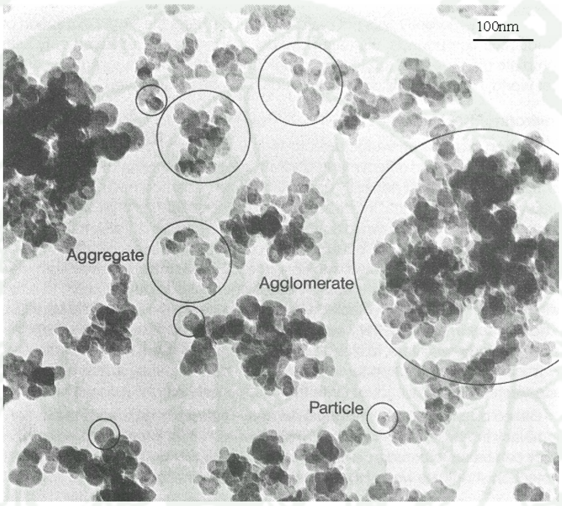


Figure 11 Morphology of carbon black.

Source: Norman, (1990)

Reinforcement of rubber by carbon black depends on many variables: surface area, structure, surface activity, dispersion, and loading. Surface area and surface activity of carbon black play an important role in its interaction with rubber chains. The high surface area means the small size of the carbon black particles in the same weight unit it is also known that the higher the surface area the harder the even dispersion of carbon black into the rubber matrix. The surface area is usually measured by different methods such as Brunauer-Emmett-Teller (BET) N_2 adsorption, liquid cetyltrimethyl ammonium bromide (CTAB) adsorption, and iodine number (Jansen and Kraus, 1971). The interactions between rubber and carbon black can be through either physical adsorption or chemical bonding. Researchers used to believe there was a chemical bonding between carbon black and rubber (Bueche, 1960). New studies showed carbon black particles with these functional groups did not give significant improvement in reinforcement (Le Bras and Papirer, 1978). Physical adsorption seemed to be a more important factor in reinforcement than the chemical bonding.

3.2.2 Non-black Fillers

Non-black fillers are classified as

a) Fillers used mainly to reduce cost
b) Semi-reinforcing fillers
c) Reinforcing fillers used to achieve high performance in non-black products.

Silica is another important reinforcing filler in the rubber industry. There are two types of silica: precipitated silica and fumed silica with different manufacturing methods. Precipitated silica is manufactured by a controlled precipitation from the reactions of sodium silicate with acid or alkaline earth metal salts. It has a size ranging from 10 to 100 nm (Kraus, 1965). The reaction is:

$$nSiO_2 \bullet Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + nSiO_2 \bullet H_2O$$

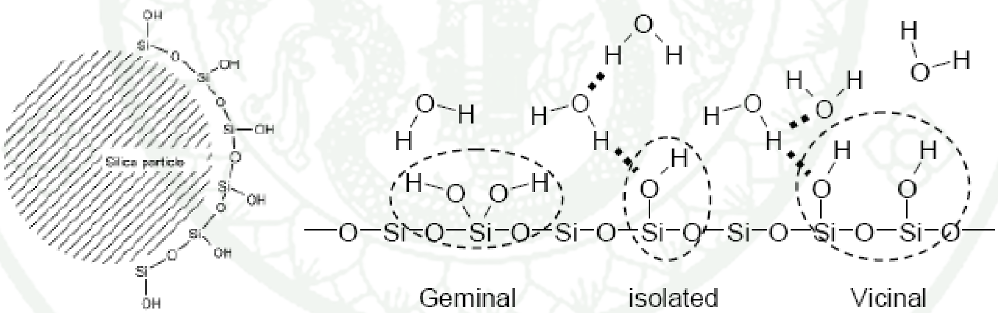
Fumed silica with its size of 7-15 nm is produced at a high temperature by a reaction of silicon tetrachloride with water vapor (Garrett, 1992). The reactions are:

$$2H_2 + O_2 \longrightarrow 2H_2O$$
$$2H_2O + SiCl_4 \longrightarrow SiO_2 + 4HCl$$

The silica surface is composed of siloxane and silanol groups. The chemical characteristics of the silica surface are mainly determined by the amount of silanol groups, the degree of hydration, the amount of adsorbed water and the surface acidity. Figure 12 shows the three types of surface silanol hydroxyls.

Isolated - a single hydroxyl group on a silicon atom
Vicinal - two hydroxyl groups on adjacent silicon atoms
Geminal - two hydroxyl groups on the same silicon atom

The silica surface is highly polar and hydrophilic and contains adsorbed water as shown in Figure 12. The surface hydroxyl groups are acidic and tend to retard cure rate. The reactivity of the surface causes foreign substances to be adsorbed on the filler surfaces till they are saturated. The behavior of the filler and its effect on the rubber may be strongly influenced by that process.



(a) (b)

Figure 12 (a) chemical function on silica surface, and (b) type of silanol groups.

Hydroxyl groups on the surface of silica cause strong filler-filler interactions and water adsorption via hydrogen bonding (Ou *et al.*, 1994), thus silica usually exists as aggregates and agglomerates (Figure 13). The strong hydrogen bonding in aggregates and agglomerates causes a serious problem in rubber composites, e.g., poor dispersion. The problem could be solved by adding silane coupling agents into rubber composites. The details are elaborated in the section of silane coupling agents for silica-filled-rubber composites.

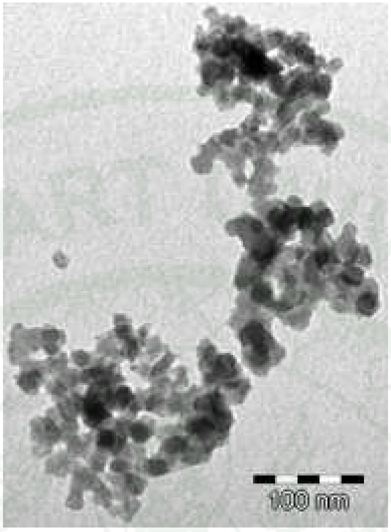


Figure 13 Morphology of silica.

Source: Norman, (1990).

3.3. Fillers from renewable sources

3.3.1 Silica from natural resources

In rubber industry, the silica is widely used as reinforcing filler due to its fine particle size (high specific surface area) and its performance in improving the mechanical properties of the vulcanizates, i.e., tensile strength, tear strength, abrasion resistance and hardness. The silica is available from precipitation of an aqueous sodium silicate solution: precipitate silica, the pyrogenic process: fumed silica, and natural resources e.g. rice husk ash, fly ash and volcanic rock or perlite. Nowaday, many attempts have been made to use silica from natural resources as alternative reinforcing filler in natural rubber because of cost savings, good mechanical properties, better dimensional stability and environmental issue (Thongsang, 2005).

Fly ash (FA)

Fly ash is one of the most plentiful and industrial by-products. It is generated in vast quantities as a by-product of burning coal at electric power plants (Senol *et al.*, 2006). Electric utility companies in many parts of the world generate electricity by burning coal which generate an amount of fly and bottom ash. Fly ash generated by coal combustion based power plants typically fall within the ASTM fly ash classes C and F (Reyes and Pando, 2007). Fly ash consists of inorganic matter present in the coal that has been fused during coal combustion. This material is solidified while suspended in the exhaust gases and is collected from the exhaust gases by electrostatic precipitators. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape. Those fly ash particles collected in electrostatic precipitators usually have a size ranging from 0.005-0.074 mm. As a general problem, the ash particles generated at thermal power plant station need to be disposed outside the plant premises. The disposal of fly ash is become more expensive each year because of large land needed for its disposal. The best way to solve the disposal problem of fly ash is to make productive use of fly ash particle, one of which being to utilize the fly ash as a filler in polymeric materials. This is possible since the fly ash contains nearly 40-50% silica by weight of the total fly ash and the price is relatively low (Sombatsompop, 2007).

Sombatsompop *et al*. (2004) introduced untreated fly ash particles into natural rubber vulcanizates and found that the mechanical properties of fly ash filled natural rubber vulcanizates appeared to be very similar to those of commercial silica-filled vulcanizates at silica contents of 0–30 phr. Above these concentrations, the properties of the fly ash filled compounds remained unchanged, the fly ash particles being used as an extender. The properties of the fly ash filled NR compounds were found to improve with the addition of bis(3-triethoxysilylpropyl) tetrasulfane (Si69) coupling agent at 2.0–4.0 wt %.

Thongsang and Sombatsompop (2005) studied the effect of filler surface treatment on properties of fly ash as reinforcing filler in natural rubber compound with varying bis(3-triethoxysilylpropyl)tetrasulfane (Si69) coupling agent contents. It was found that the scorch and cure times of the natural rubber/fly ash vulcanizates slightly increased with a decrease in crosslink density when increasing Si69 contents. The decrease in crosslink density was compensated by chemical bonding between the rubber and the fly ash particles as a result of Si69. Bis(3-triethoxysilylpropyl)tetrasulfane (Si69) coupling agent was recommended for the improvement of the tensile modulus and tear strength of the NR/FA composites. However, the tensile strength did not change with Si69 content.

Sombatsompop *et al.* (2007) explored the possibility of using silica from fly ash particles as reinforcement in natural rubber/styrene butadiene rubber (NR/SBR) vulcanizates. The addition of silica from fly ash in the NR/SBR vulcanizates was found to improve the elastic behavior, including compression set and resilience, as compared with that of commercial precipitated silica. Taking mechanical properties into account, the recommended dosage for the fly ash silica (FASi) content was 20 phr. For more effective reinforcement, the silica from fly ash particles had to be chemically treated with 2.0 wt % Si69. It was convincing that silica from fly ash particles could be used to replace commercial silica as reinforcement in natural rubber/styrene butadiene rubber vulcanizates for cost saving and environment benefits.

Rice Husk Ash (RHA)

Rice husk ash is produced by incinerating the husks of rice paddy. Rice husk is a by-product of rice milling industry. Controlled incineration of rice husks between 500°C and 800°C produces non-crystalline amorphous RHA (Mehta and Monteiro, 1993, Malhotra, 1993). Rice husk ash is whitish or black in color. The particles of RHA occur in cellular structure with a very high surface fineness. They have 90% to 95% amorphous silica (Mehta, 1992). Due to high silica content, rice husk ash possesses excellent reinforcement in natural rubber.

The physical properties of RHA largely depend on burning conditions. Particularly, the period and temperature of burning affect the micro-structure and characteristics of RHA (Nagataki, 1994). The partial burning of rice husks produces black rice husk ash whereas the complete burning results in either white or black rice husk ash (Ismail and Waliuddin, 1996).

The rice husk ash particles are mostly in the size range of 4-75 μm. The majority of the particles pass 45 μm (No. 325) sieve. The median particle diameter typically ranges from 6 to 38 μm (Mehta 2002), which is larger than that of silica fume. However, unlike silica fume, the rice husk ash particles are porous and possess a honeycomb microstructure (Zhang and Malhotra, 1996). Therefore, the specific surface area of rice husk ash is extremely high. The specific surface area of silica fume is typically 20 m^2/g whereas that of non-crystalline RHA can be in the range of 50 to 100 m^2/g (Mehta 1992). The silica content (SiO_2) of RHA ranges between 90 to 95%, which is similar to that of silica fume (Mehta, 1992, Zhang *et al*., 1996). The typical chemical composition of RHA is given in Table 3.

Nowadays, RHA is used in plastic, rubber, and thermoplastic elastomers because of various advantages, such as ease of processing, easy availability, economic considerations, environmental preservation, and an increased emphasis on the use of renewable resources. Sae-oui *et al*. (2002) investigated the effects of filler loading on the properties of RHA filled NR materials when compared with commercial fillers. They found that both grades of RHA, low and high carbon contents, resulted in inferior mechanical properties (tensile strength, modulus, hardness, abrasion resistance, and tear strength) in comparison with reinforcing fillers such as silica and carbon black. Arayapranee *et al*. (2005) reported that RHA-filled vulcanizates with 20 phr, gave the best results, providing physical properties slightly inferior to unfilled compounds.

Table 3 Typical chemical composition of rice husk ash.

Component	Mass content (%)
Silicon dioxide (SiO_2)	94.34
Aluminium oxide (Al_2O_3)	0.06
Iron oxide (Fe_2O_3)	0.04
Calcium oxide (CaO)	0.48
Magnesium oxide (MgO)	0.13
Sodium oxide (Na_2O)	0.08
Potassium oxide (K_2O)	1.97
Phosphorus oxide (P_2O_5)	1.19
Titanium oxide (TiO_2)	0.02
Sulfur trioxide (SO_3)	0.01
Igneous loss	1.18

Source: Mehta *et.al.* (2002)

Ismail *et al.* (1999) studied the potential of using white rice husk ash (WRHA) as filler for natural rubber compounds. The results showed that tensile and tear strengths increased with increasing white rice husk ash loading to a maximum level (10 phr of filler loading), after which there is a deterioration in both properties. However the tensile modulus (M100 and M300) and hardness increased with increasing white rice husk ash loading.

Ismail *et al.* (1999) studied the effects of multifunctional additive (MFA), silane coupling agent, Si69 and combination of MFA/Si69 on the properties of white rice husk ash (WRHA) filled SMR-L compounds. The incorporation of MFA, Si69 and combination of MFA/Si69 at 10 phr of WRHA could enhance the cure rate and mechanical properties of WRHA filled SMR-L compounds.

Ismail and Chung (1998) studied the effects of bonding agent (resorcinol formaldehyde and hexamethylenetetramine) on the partial replacement of silica by white rice husk ash in natural rubber compounds. The results showed that the optimum weight ratio of white rice husk ash/silica to obtain maximum enhancement of tensile and tear strength was 20/30 (phr/phr). Increasing the white rice husk ash in weight ratio of white rice husk ash/silica decreased the cure time, t_{90}, scorch time, t_2, hardness and elongation at break but increased the resilience of the vulcanizates. For similar vulcanizates, the incorporation of bonding agents enhanced the tensile strength, tear strength, hardness, rubber-filler interaction and resilience, whereas, the elongation at break decreased. The incorporation of bonding agents also increased the cure time and scorch time.

Perlite

Perlite is a volcanic glassy rock with a characteristic texture and an amorphous structure, usually gray, white and almost black in color, but contains two to six percent combined water. Therefore, when heated to a suitable point in its softening range, it expands from four to twenty times its original volume. This expansion is due to the presence of two to six percent combined water in the crude perlite rock. The temperature at which expansion takes place ranges from 760 °C-1100 °C, the crude rock pops in a manner similar to popcorn as the combined water vaporizes. It becomes light weight perlite which is called expanded perlite. Perlite has many benefits and applications. When perlite is expanded it has a high porosity so it can be used to hold water and to provide air for roots of plants. Perlite is an essential element for plant growing such as Fe_2O_3, MgO, CaO, Na_2O, K_2O, MnO and P_2O_5 so we can use it in horticultural applications, for example, as fertilizer, to adjust the pH of soil and to adsorb chemicals in pesticides, in hydroponic growing and green houses. Because it is light in weight; has high heat resistance, and it reduces noise transmission, it is used in the construction industries in materials such as gypsum board, wall boards and swimming pool bases.

Cellulose fiber from water hyacinth

Cellulose fiber, like water hyacinth (*Eichhorinia Crassipes*) is a cellulosic product. Over the past decade there has been growing interesting the use of this fiber as reinforcing elements in polymer matrix. Water hyacinth fiber has a specific properties, low cost, light weight, renewable, high specific strength and modulus, and excellent thermal insulation. The main problem in cellulose fibers filled in natural rubber is incompatability of hydrophilic cellulose fibers and hydrophobic rubber matrix (Abdelmouleh, 2007). Several strategies of surface modifications aim to improve the compatibility between fiber and rubber. The chemical modification using coupling agents bearing two reactive groups, one of which being likely to react with the -OH function at the fiber surface, whereas the other one is left to copolymerize with the matrix, constitutes a highly interesting way allowing the establishment of covalent bonding between fibers and matrix, thus leading to materials with high mechanical properties. Silane coupling chemicals present three main advantages

(i) they are commercially available in a large scale

(ii) at one end, they bear alkoxysilane groups capable of reacting with OH-rich surface

(iii) at the second end, they have a large number of functional groups which can be tailored as a function of the matrix to be used

Anthoine *et al*. (1975) proposed that cellulose short fiber could be used as a filler in natural rubber compounds. Its anisotropic characteristics increase the tensile strength and modulus of the natural rubber product but decrease elongation at break. It was also reported that, in order to maintain the elasticity characteristic of the product, the amount of short fiber should not exceed 10 phr.

Potiyaraj *et al.* (2001) explored the possibility of using water hyacinth fiber as filler in natural rubber compounds. Natural rubber (STR20) was mixed with ground fiber and various chemicals. Effects of the amount and the particle size of the fiber on mechanical properties were investigated. It was found that the hardness and modulus of the products with water hyacinth fiber were higher than those without the fiber. As the amount and the particle size of the fiber were increased, the hardness and the modulus (500%) of the products would increase whereas the tensile strength would decrease. However, the abrasion resistance of the products was lower than that in the compounds without the fiber and the resistance would decrease as the amount and the particle size of the fiber were increased. Better mechanical properties of the products could be obtained by using a suitable coupling agent which would enhance the adhesion between water hyacinth fiber and natural rubber.

Abdelmouleh *et al.* (2007) studied the composites materials based on cellulose fibers (raw or chemically modified) as reinforcing elements and thermoplastic matrices were prepared and characterized, in terms of mechanical performances, thermal properties and water absorbance behavior. Cellulose fibers were incorporated into the matrices, as such or after chemical surface modification involving three silane coupling agents, namely γ-methacryloxypropyltrimethoxy (MPS), γ-mercaptoproyltrimethoxy (MRPS) and hexadecyltrimethoxysilanes (HDS). As expected, the mechanical properties of the composites increased with increasing the average fiber length and the composite materials prepared using both matrices and cellulose fibers treated with MPS and MRPS displayed good mechanical performances. On the other hand with HDS bearing merely aliphatic chain only a modest enhancement on composite properties is observed which was imputed to the incapacity of HDS to bring about covalent bonding with matrix.

4. Filler dispersion

4.1 Adhesion between fillers and rubber matrix

Silica contains a large number of silanol groups on its surface, it is considered as a highly polar filler and, thus, it is less compatible to non-polar rubbers such as natural rubber (NR), styrene butadiene rubber (SBR), etc. The poor rubber-filler interaction would lead to impaired mechanical properties of the rubber vulcanizates. In addition, the silanol groups have the tendency to form hydrogen bonding between each other resulting in strong filler-filler interaction. Silica is, therefore, difficult to distribute and disperse throughout the rubber matrix. Also, when silica is added into rubber at high concentration, it tends to form a secondary network, alternatively called "filler-filler network". This would cause an increase in compound viscosity giving rise to difficulty in processing (Sae-oui *et al*., 2004).

Cellulose fibers contain many hydroxyl groups on its surface, the usually polar fibers have inherently low compatibility with non-polar polymer matrices, especially hydrocarbon matrices such as natural rubber (NR). The incompatibility may cause problems in the composite processing and material properties. Hydrogen bonds may form between the hydrophilic fibers, and thus the fibers tend to agglomerate into bundles and unevenly distribute throughout the non-polar polymer matrix during compounding processing. There is also insufficient wetting of fibers by the non-polar polymer matrices, resulting in weak interfacial adhesion (Xie *et al*., 2010).

Chemical compatibility between fillers and rubber matrix can be expected to play an important role in the dispersion of the fillers in the matrix and in the strong adhesion between the two phases. Different fillers and rubbers require different coupling agents. In general, polyethylene glycol and silane coupling such as bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) is used in order to improve the filler dispersion. The details are discussed in the following sections.

4.2 Polyethylene glycol for silica filled rubber composites

Polyethylene glycol, PEG, $HO-(CH_2CH_2O)_n-H$, is used to prevent the adsorption of curatives on the silica surface. Since PEG has many ether linkages, -CH_2-O-CH_2-, it makes hydrogen bonds with silanols of the silica surface. This results in formation of PEG barrier on the silica surface so that the filler-filler interaction is reduced and adsorption of the curatives on the surface is also prevented. Since fatty acids have a carboxyl group, $-CO_2H$ they also can make hydrogen bonds with the silica. The barrier of the fatty acid will reduce the filler-filler interaction of silica and prevent the adsorption of curatives.

4.3 Silane coupling agents for silica filled rubber composites

Silane coupling agent is a bifunctional compound developed commercially to improve the reinforcing efficiency of silica. It is composed of two functionally active end groups, i.e., the readily hydrolysable alkoxy group and the organo-functional group. The former can react chemically with the silanol groups on silica surface to form stable siloxane linkages whereas the latter, which is relatively non-polar, is more compatible with rubbers and also can participate in the sulfur vulcanization to form chemical linkages with rubbers. As a consequence, silane coupling agent could act as a bridge between silica and rubber to enhance the rubber-filler interaction and, thus, give a significant improvement in properties of silica-filled compounds. For example, (bis(triethoxysilylpropyl)tetrasulfide (TESPT), one functional group being able to form covalent bonding with silica and another being able to form covalent bonding with rubber. Most commonly used silane coupling agents have a general formula of $(R'O)_3SiRY$ where the $(R'O)_3Si$ group reacts with hydroxyl groups of the silica filler to form a siloxane bond (Si-O-Si) and the R group (typically -SH or polysulfide) reacts with rubber to form covalent sulfide bonds.

4.4 Silane coupling agents for lignocellulosic materials filled rubber composites

Lignocellulosic fibers as reinforcing elements in polymeric matrix, it is well known that different surface properties between the fiber and the matrix, i.e. the former is highly polar and hydrophilic while the latter is, generally, non-polar and relatively hydrophobic, impose the surface modification of the fibers surface, in order to improve the fiber/polymer compatibility and their interfacial adhesion. Several strategies of surface modifications aiming at improving the compatibility between cellulose fibers and polymer matrices were recently reviewed. The chemical modification using coupling agents bearing two reactive groups, one of which being likely to react with the OH function at the fiber surface, whereas the other one is left to copolymerize with the matrix, constitutes a highly interesting way allowing the establishment of covalent bonding between fibers and matrix, thus leading to materials with high mechanical properties (Abdelmouleh *et al*., 2007).

5. Thermal conductivity

The insulating materials for construction can reduce energy consumption in building and contribute to reducing carbon dioxide emissions. One of the insulating materials is cellular material that is classified into two main groups including organic cellular material and inorganic cellular material. The well-known of organic cellular materials are expanded polystyrene foam (EPS), extruded polystyrene foam (XPS) and polyurethane foam. The inorganic cellular materials are produced from natural and synthetic such as expanded perlite, expanded clay, ceramic microsphere, glass hollow sphere (Pfundstein *et al*., 2008). Thermal conductivities of various materials were shown in Table 4. These materials contain high porosity or high volume of voids so they are very low thermal conductivity and low density.

Thermal conductivity (W/m.K) is a measure of a materials ability to transfer heat through conduction. The equation relating this property is given by:

$$Q_x = -kA\, dT/d_x \qquad (1)$$

where Q_x is the rate of heat flow in the positive x direction, through area A normal to the x direction. The proportionality constant k, called the thermal conductivity, is a property of the material.

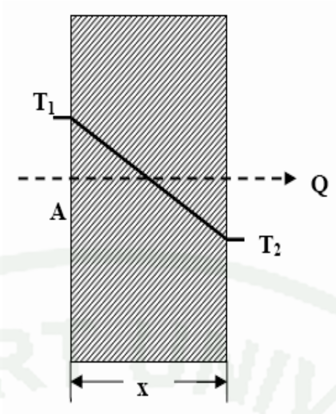


Figure 14 Schematic of thermal conduction.

Table 4 Thermal conductivities of various materials.

Materials	Density (Kg/m^3)	Thermal conductivity (W/m K)
Binderless cotton stalk fiberboard	150–450	0.0585–0.0815
Low-density wheat straw board	150–250	0.0481–0.0521
Particleboard from mixture of durian peel and coconut coir	311–611	0.0728–0.1117
Kenaf binderless board	150–200	0.051–0.058
Wood (pine, lauan)	450–630	0.151
Fiberglass	24–120	0.034–0.047
Rockwool	80–200	0.025–0.035
Extruded polystyrene	24–42	0.026–0.035
Polystyrene (closed cell foam)	16–35	0.034–0.038
Expanded perlite	78–224	0.0477–0.0616
Vermiculite	80–200	0.047–0.07

Source : Zhou *et al.* (2010)

Balo *et al.* (2010) studied the effect of coal fly ash (FA), clay (C), perlite (P) and epoxidized linseed oil (ELO) on the thermal and mechanical properties of insulation materials. The properties examined include density, thermal conductivity coefficient, compressive strength and tensile strength. The results showed that the addition of FA and ELO into insulation material composition decreases the compressive-tensile strength and thermal conductivity coefficient values. The lowest value of thermal conductivity is measured for the sample processed at 200°C. The highest values of compressive and tensile strength are obtained for the samples processed at 160°C. Results of this investigation suggest that class C fly ash, ELO, clay and perlite could be conveniently used in insulation material.

Many researchers have studied thermal insulation materials from lignocellulosic fibers. Khedari *et al.* (2004) developed a new low cost particleboard from durian peel and coconut coir mixture with a lower thermal conductivity, which was effective for energy saving when used as ceiling and wall insulating material. Xu *et al.* (2004) presented a low-density binderless particleboard from kenaf core using steam-injection pressing, with a thermal conductivity similar to those of insulation material (i.e., rock wool). A new composite board with low-thermal conductivity made from a mixture of solid wastes from tissue paper manufacturing and corn peel was reported by Lertsutthiwong *et al.* (2008).

MATERIALS AND METHODS

Materials

1. Natural rubber (NR); STR5L, S.M.P. RUBBER, Thailand

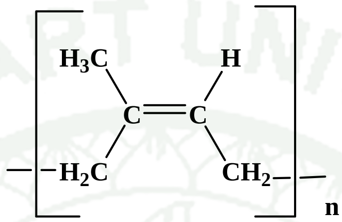


Figure 15 The structure of natural rubber.

2. Reagent
   - ZnO, an activator, Global Chemical, Thailand.
   - Stearic acid, an activator, Imperial Industrial Chemicals, Thailand.
   - N-cyclohexyl-2-benzothiazole sulphenamide (CBS), an accelerator, Flexsys, Germany

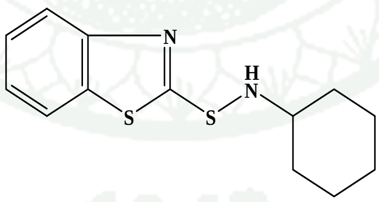


Figure 16 The structure of N-cyclohexyl-2-benzothiazole sulphenamide (CBS).

- 2,2,4-Trimethyl-1,2-dihydroquinoline polymer (TMQ), an antioxidant, Eliokem, USA.

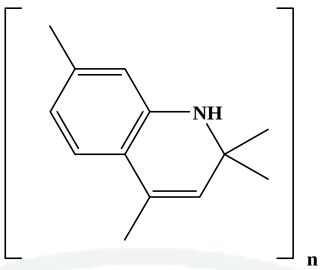


Figure 17 The structure of 2,2,4-trimethyl-1,2-dihydroquinoline polymer (TMQ).

- Rubber oil, a processing aid, PSP Specialties, Thailand.
- Polyethylene glycol, (PEG), an accelerator

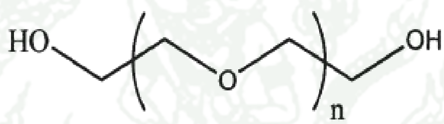


Figure 18 The structure of polyethylene glycol, (PEG).

- Bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (Si-89), a silane coupling agent, Bayer, Germany.

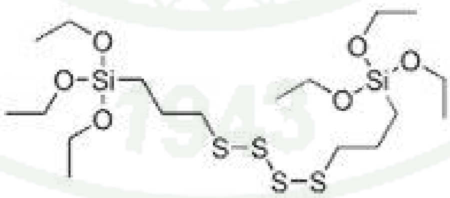


Figure 19 The structure of bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (Si-89).

- Sulfur, a crosslink agent, Sahapaisal Industry, Thailand.

3. Fillers

- Rice husk ash, Pathum rice mill Co.Ltd., Thailand.
- Fly ash, Gold Fly Ash Co.Ltd., Thailand.
- Perlite, Department of Mineral Resource, Kasetsart University, Thailand.
- Water hyacinth fiber, Living museum of Thai farmers, Ban Lan Laem, Nakornchaisri-Don Toom Road. Nakhon Pathom, Thailand.

4. Equipments

- Two-roll-mill, model YFCR 6, Chor.Sri-Anan Co., Ltd.
- Moving Die Rheometer (MDR), Tech PRO
- Compression molding, G30H-15-CX, Wabash, USA
- Scanning Electron Microscope, model JSM-5410LV, JEOL
- X-ray fluorescence spectrometer, Philips model PW2400
- Universal Testing Machine by Instron, USA
- Hardness, Cogenix, Wallace
- Oven, Binder
- Guarded hot plate instruments, model UNITHERM ™ 6000, Anter Corporation

Methods

1. Filler characterization

The surface area was estimated by the Brunauer-Emmett-Teller (BET) on Autosorb-1 method. The pore volume and pore size were determined by using the nitrogen adsorption/desorption method. Each run was performed with 0.02-1.00 g of fillers which was pretreated at 300°C under vacuum. Particle size analyzer (wet sieve) was used to measure the particle size of the fillers.

The chemical composition and morphology of the fillers were measured by X-ray fluorescence and Scanning electron microscope (SEM), respectively.

2. Mixing and vulcanization procedures

Formulations are given in Table 5. The rubber compounds were made in two steps for property evaluations: mastication and compounding. In the mastication step, the rubber was masticated on a two-roll mill at temperature of 50^{o}C, and 40 rpm for 5 min and was then mixed with a specified content of filler for another 15 min. In the compounding step, the rubber and filler were compounded with prepared vulcanization chemicals on the two-roll mill for another 10 min, then, the mixes were sheeted out and kept at room temperature for 24 hr before testing.

Prior to vulcanize the mixes, cure characteristic was evaluated using a Moving Die Rheometer (MDR) according to ASTM D 224. Samples (~4 g) of the respective compounds were tested at the vulcanization temperature (160°C). The mixes were compression molded using a hydraulic hot press at 160°C under pressure of 15 MPa and cut into the standard size for mechanical testing.

Table 5 Formulation of the rubber compounds.

Ingredients	Amounts (phr)			
Formula	1	2	3	4
NR	100	100	100	100
ZnO	5	5	5	5
Stearic acid	2	2	2	2
CBS	0.5	0.5	0.5	0.5
TMQ	0.12	0.12	0.12	0.12
Rubber oil	5	5	5	5
PEG	0.2	0.2	0.2	-
Si-89	-	-	-	3
RHA	0, 20,40, 60	-	-	-
FA	-	0, 20,40, 60	-	-
Perlite	-	-	0, 20,40, 60	-
Cellulose fiber	-	-	-	0, 3,5, 7
Sulfur	3	3	3	3

Note: phr refers to parts per hundred of rubber.

3. Mechanical properties

Tensile properties

The vulcanized rubbers were cut into tensile specimens using the punching machine. The cutting die punched the sample into dumbbell shape (Figure 20). Testing was carried out on the Universal Testing Machine in accordance with ASTM D 412-98.

Figure 20 Universal testing machine.

The testing crosshead speed of 500 mm/min was used with a full scale load cell at 1 kN. At least 5 specimens were used for each measurement. The following tensile properties were measured: 100% Modulus and elongation at break.

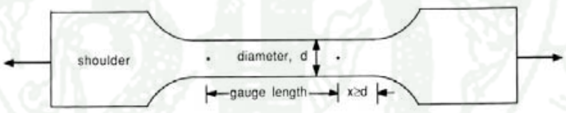


Figure 21 Tensile test specimen.

Calculation

Modulus was calculated from the formula,

$$\sigma = F/A \qquad (2)$$

where

σ = stress (MPa)

F = observed force (N)

A = cross-sectional area of unstretched specimen (mm^2)

The percentage of elongation at break was calculated from the equation below

$$\text{Percentage of elongation} = (l - l_0)/l_0 \times 100 \qquad (3)$$

where

l = observed distance between the grips extensometer on the stretched specimen (mm)

l_0 = original distance between the extensometer (mm)

Hardness

Shore A hardness of the specimens was measured using hardness tester in accordance with ASTM D 2240-97. The specimens about 6 mm in thickness were placed on test platform. The durometer was held in a vertical position with point of the indenter at least 12 mm from any edge of the specimens. Five measurements were made at different position on the test piece at least 6 mm apart. An average of the five measurements was taken as the hardness value of the test sample.

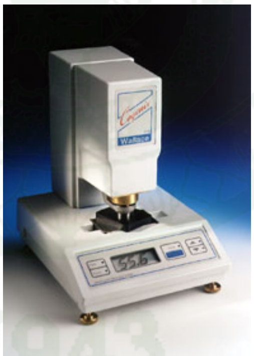


Figure 22 Hardness tester.

Compression set

The original thickness of the specimens was measured. The test specimens were placed between the plates of the compression device with the spacers on each side, allowing sufficient clearance for the bulging of the rubber when compressed at 70^{o}C for 22 hours according to ASTM D 395-01.

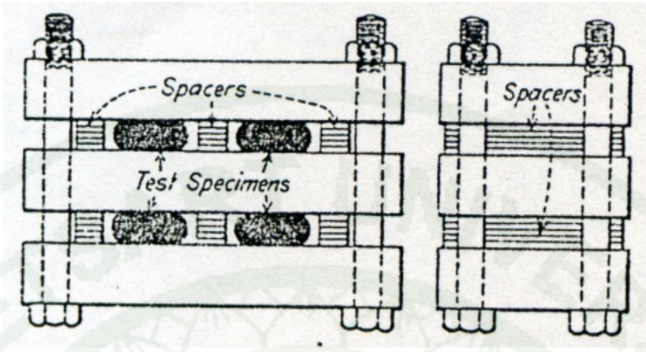


Figure 23 Device for compression set test under constant deflection.

The specimens then rested on poor thermally conducting surface, such as wood, for 30 min before making the measurement of the final thickness.

The expression for the calculation of the compression set:

$$C_B = [(t_o-t_i)/(t_o-t_n)] \times 100 \quad (4)$$

where

C_B = compression set expressed as percentage of the original deflection

t_o = original thickness of specimen

t_i = final thickness of specimen

t_n = thickness of the spacer bar used (4.5 mm)

Tear strength

The vulcanizates were cut into tear specimens by using the punching machine. Testing was carried out on Universal Testing Machine in accordance with ASTM D 624-00.

Figure 24 Tear test specimen cutting dies type C.

The crosshead speed of 500 mm/min was used with a full scale load cell at 1 kN. At least 5 specimens were used for each measurement.

Calculation

Tear strength (T_s) was calculated from the formula,

$$T_s = F/d \qquad (5)$$

where

F = the maximum force (N)

d = the median thickness of each test piece (mm)

Thermal ageing

Accelerated thermal-oxidative ageing testing was followed in the present investigation. The thermal aging experiment was performed in an oven at temperature of 100^{o}C for 22 hours according to ASTM D 573-99.

After the thermal exposure, the specimens were evaluated by mechanical properties. The results were compared with the specimens before testing.

Scanning Electron Microscope (SEM)

Figure 25 scanning electron microscope.

The phase morphology of the vulcanizates was studied by using scanning electron microscope. The samples of the vulcanizates were broken in liquid nitrogen to avoid any possible deformation of phases. The samples were further dried. Then, the dried surfaces of the samples were gold coated and then examined by SEM.

Thermal conductivity

Testing was carried out on the guarded hot plate instruments in accordance with ASTM C 177. The material specimen size of 300 mm^2 and 10 mm thick to be tested is placed on a flat plate heater assembly consisting of an electrically heated inner plate (main heater) surrounded by a guard heater. The guard heater is carefully controlled to maintain the same temperature on both sides of the gap separating the main and the guard heaters.

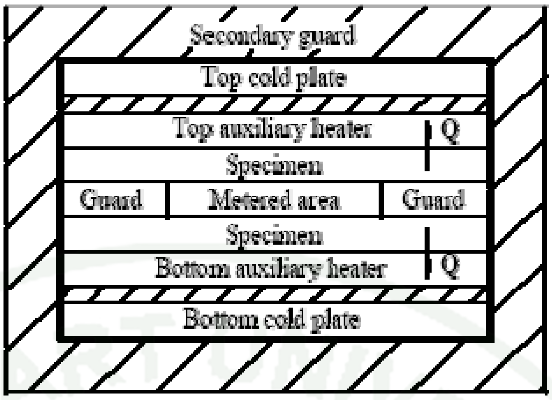


Figure 26 Schematic of the guarded hot plate method for determining thermal conductivity.

This prevents lateral heat flow from the main heater and ensures that all heat energy flows in the direction of the specimen. The opposite side of the specimen is additional flat plate heaters (the "cold" plate) that are controlled at a fixed temperature selected by the operator. For a given heat input to the main heater, the hot plate assembly rises in temperature until the system reaches equilibrium. The final hot plate temperature depends on the electrical power input, the thermal resistance of the specimen, and the temperature of the cold plate. The average thermal conductivity, k, of the specimen is determined from the equation:

$$K = P / [t \times (T_m - T_a)] \quad (6)$$

where

P = power supplied to the main heater

t = the total specimen thickness (twice the single specimen thickness)

T_m = the temperature of the main heater

T_a = the temperature of the auxiliary heater

RESULTS AND DISCUSSION

1. Fillers Characterization

In this part the characteristics of fillers from natural resource including perlite, fly ash (FA), rice husk ash (RHA) and water hyacinth fiber were studied. The chemical compositions (measured by X-ray fluorescence) and physical properties (determined by BET and particle size analyzer) of perlite, fly ash (FA), rice husk ash (RHA) are listed in Table 6 and 7, respectively. The proximate chemical analysis, physical properties, and some surface characteristics of water hyacinth fiber are presented in Table 8.

Table 6 Chemical compositions of fillers.

Chemical compositions	Content (%)		
	RHA	Perlite	Fly ash
SiO_2	93.97	72.70	51.77
Al_2O_3	0.15	12.23	28.47
Na_2O	0.14	2.54	0.62
MgO	0.45	0.17	0.74
K_2O	2.59	9.30	0.81
CaO	1.21	0.94	0.02
TiO_2	0.97	0.43	3.01
Fe_2O_3	0.52	1.54	7.41

Table 6 represents the chemical composition of fillers from natural resources (perlite, fly ash, and rice husk ash) had metal oxide (e.g., Al_2O_3, CaO and MgO), it was found that the major component of fillers was silica (SiO_2) in perlite, fly ash, rice husk ash. However, RHA filler shows the highest silica content. It has been well known that silica is widely used as nonblack reinforcing filler widely used in rubber compounds, perlite, fly ash, and rice husk ash containing mainly silica could show the ability to improve mechanical properties of the vulcanized rubbers, particularly tensile strength, tear resistance, abrasion resistance and hardness (Sae-oui *et al*., 2004). Therefore, it is our interest to study the possibility of using perlite, fly ash, and rice husk ash as alternative filler on rubber compounds.

Table 7 Physical properties of fillers.

Fillers	Mean particle size (μm)	Surface area (m^2/g)	Pore volume (cc/g)
Fly ash	75	2.44	0.0088
RHA	65	16.19	0.0049
Perlite	30	4.62	0.0055

The physical properties of fillers are presented in Table 7. It was found that the mean agglomerate particle sizes of fly ash are greater than those of rice husk ash and perlite, whereas perlite was found to have the smallest particle size. The BET surface area of RHA was greater than that of fly ash and perlite, respectively. The pore volume of RHA and perlite are not significantly different, while fly ash is found to have the highest pore volume.

The proximate chemical analysis showed that the water hyacinth fiber contained holocellulose, hemicellulose, and lignin. The properties of water hyacinth fiber, physical properties, and some surface characteristics are presented in the Table 8. The proximate analyses showed a low amount of moisture, ash, and dry matter, indicating that the particle density is relatively small.

Table 8 Properties of water hyacinth fiber.

Chemical compositions	Content (%)
Ash	4.14
Moisture content	8.44
Lignin	6.70
Holocellulose	54.80
Hemicellulose	21.00
Dry matter	6.2
Physical properties	
Diameter, (mm)	0.80-1.20
Specific gravity (ASTM845-83)	0.428
Water absorption, (%)	388
Particle density, (g cm^{-3})	1.12
Average pore diameter,(Å)	$1.85x10^2$
Pore volume, (cm^3 g^{-1})	0.99427
Surface area, (m^2 g^{-1})	2.44

Morphologies of fillers particles

The morphological characteristics of the filler particles were examined using Scanning Electron Microscope (SEM). Figure 27 shows the SEM images of perlite, fly ash, rice husk ash particles at 500x magnification and water hyacinth fiber at100x magnification. It can be seen that the fly ash particles (27(a)) have round shape with relatively smooth surfaces. Whereas, the structure of rice husk ash (27(b)), perlite (27(c)) and water hyacinth fiber (27(d)) are high porosity with rough surfaces.

In this study, the possibility of using natural fillers (including perlite, fly ash (FA), rice husk ash (RHA) and cellulose fiber from water hyacinth) as filler in natural rubber for producing thermal insulation was investigated. The experiment has been determined based on the effect of type and fillers loading on cure characteristic and mechanical properties including modulus at 100% elongation, elongation at break, tear resistance, hardness, compression set and thermal properties of thermal insulation produced from natural rubber filled with natural fillers.

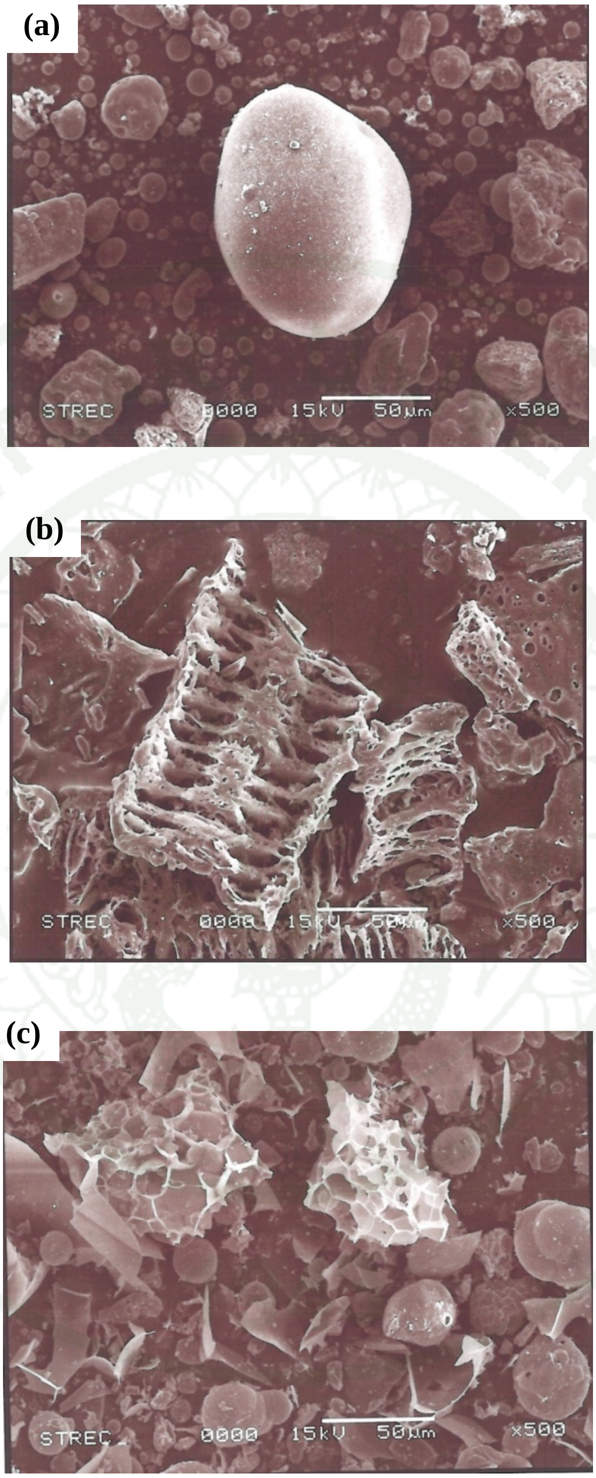


Figure 27 SEM images of (a) fly ash (b) RHA (c) perlite at 500x magnification and (d) water hyacinth fiber at 100x magnification.

(d)

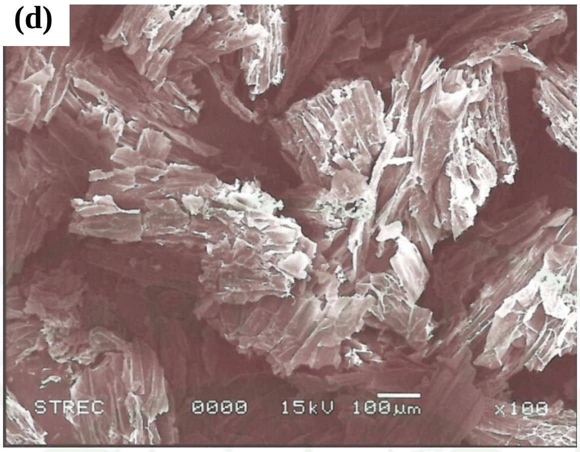


Figure 27 (Continued)

2. Effect of silica content from natural resources

The first part, the influence of silica content from natural resources (perlite, RHA and fly ash) on cure characteristics, mechanical properties, and thermal aging of the filled natural rubber vulcanizates was studied. The experimental results in this work was to seek a suitable filler content for producing thermal insulation.

Charles (1987) and Hofmann (1989) found that the term filler refers to solid additives that are incorporated into the plastic matrix. They are generally inorganic materials and can be classified according to their effect on the mechanical properties or the resulting mixture. Inert or extender fillers are added mainly to reduce the cost of the compound, while reinforcing fillers are added to improve certain mechanical properties such as modulus or tensile strength. Although termed inert, inert filler can nonetheless affect other properties of the compound besides cost. In particular, they may increase the density of the compound, reduce the shrinkage, increase the hardness, and increase the heat deflection temperature.

2.1 Cure characteristics

The vulcanization characteristics of the prepared rubber compounds were determined by using the Moving Die Rheometer (MDR). The data of rubber compounds are shown in term of the scorch time (t_{s2}), the time taken for the minimum torque to increase by 2 units, the optimum cure time (t_{c90}), time for vulcanization where t_{c90} denotes 90% of maximum torque, the minimum torque (M_L), considered to be a measure of the extent of mastication that value indicated the easy or difficult processability of polymer blends and the maximum torque (M_H), an index of the cross-linking density. All the cure characteristics data are presented in Table 9 which summarizes the cure characteristics of rubber compounds with different contents of fillers.

Table 9 shows the cure characteristics of natural rubber compounds filled with various type of silica from natural resources including perlite, rice husk ash and fly ash at content of 0-60 phr**.** It has been known that M_L and M_H indicated a significant dependence on the processability and crosslink density of rubber compounds, respectively. All filled NR compounds showed that the minimum torque (M_L) of rubber compounds decreased with an increase in filler contents. Since M_L is a torque of rubber compounds before an occurrence of crosslink, it can be a measure of viscosity under shearing deformation and therefore can correlate to Mooney viscosity. The decreased in M_L value when filler loading increased indicates that the incorporation of filler into rubber matrix has slightly increased the processability of the rubber compounds due to the addition of filler particles into rubber causes the reduction of mobility of the rubber chain resulting in the decrease in viscosity of rubber compounds. This indicates that the processability of the rubber compounds become easy with increasing the filler content.

Table 9 Cure characteristics of rubber compounds filled with various amount and type of fillers.

Type of filler	**Amount of filler** (phr)	**Cure Characteristics**				
		M_L (lb-in)	**M_H** (lb-in)	**ΔM** (M_H-M_L)	**t_{s2}** (min)	**t_{c90}** (min)
Gum	0	0.25	3.33	3.08	3.19	5.54
Perlite	20	0.30	4.93	4.63	1.54	5.04
	40	0.28	6.62	6.34	1.37	5.09
	60	0.19	7.30	7.11	1.47	5.17
Fly ash	20	0.58	6.67	6.09	1.65	5.28
	40	0.56	7.80	7.24	1.35	5.05
	60	0.37	9.09	8.72	1.25	5.29
Rice Husk Ash	20	0.25	4.72	4.47	2.03	5.02
	40	0.38	6.51	6.13	1.30	4.46
	60	0.28	8.33	8.05	1.21	5.00

For all type of fillers, the results show that increasing the filler content in natural rubber compounds increases of maximum torque (M_H). This indicates that the presence of filler in the rubber compounds has reduced the mobility of the macromolecular chains of the rubber and may be due to the better rubber-filler interaction or higher degree of cross-linking.

As a result of a decrease in M_L value and increase in M_H value when filler loading increased led to a marked increase in the torque (ΔM). It can be noted that delta torque (ΔM) value are comparable with M_L and M_H, which depended mainly on the amount of free curative in the rubber compounds. It has been known that the higher the ΔM, the greater the crosslink formation.

In general, silica had an effect on the cure time, the cure time progressively increasing with silica loading. The change at silica content was caused by reasons:

First reason, filler-filler interactions: because silica has a number of hydroxyl groups on its surface, which result in strong filler-filler interactions due to hydrogen bonding, the added silica particles became aggregated and formed a coherent gel in the rubber matrix. This aggregation physically prevented the rubber from being readily vulcanized and, thus increased cure time.

The second reason is the adsorption of acceleration on the silica surface. The cure accelerator used was absorbed by hydrogen bonds on the silanol groups on the silica surface, and this led to the increase in the cure time.

The third reason is the reduction of zinc-complex formation. This involved the reactivity of the metal oxide (in this case, ZnO) for zinc complex formation in the vulcanization process that was reduced by the presence of silica as a result of interaction between the silica and zinc oxide. This delayed the vulcanization reaction (Sombatsompop *et al*., 2004).

The scorch time (t_{s2}) and optimum cure time (t_{c90}) of rubber compounds filled with silica from natural resources in this present study are also shown in Table 9. In general, as discussed earlier silica had an effect on the cure time, in which the cure time progressively increased with silica loading. However the results in this study showed that all kinds of fillers (perlite, RHA, fly ash) had no significant effect on cure time and scorch time of rubber compounds. This was because fillers had excessive metal oxide (e.g. Al_2O_3, CaO and MgO) presented in the fillers chemical composition as listed in Table 6, the metal oxides acted as activators and accelerator of the curing process, leading to the promotion of the vulcanization process.

2.2 Mechanical properties

The influence of type and amounts of silica from natural resources (perlite, RHA, fly ash) on the mechanical properties, i.e., hardness, compression set, tear strength, modulus, and elongation at break of the filled natural rubber vulcanizates was investigated. The mentioned mechanical properties of perlite, RHA, and fly ash-filled NR vulcanizates are shown in Figures 28-32.

Modulus at 100% elongation of the natural rubber vulcanizates filled with various filler content is shown in Figure 28, it was found that the modulus at 100% elongation of NR vulcanizates filled with all kinds of fillers increased with the increase in filler content. The addition of rigid and stiff particulate filler increased the modulus of the rubber compounds due to the introduction of restrictions to the molecular mobility of the rubber. Moreover, the modulus at 100% elongation of perlite-filled natural rubber was greater than that of RHA and fly ash, respectively. The inferior modulus of RHA- and fly ash-filled rubber vulcanizates may be explained by the fact in Table 7 that RHA and fly ash have larger particle size and therefore, smaller surface areas for rubber-filler interactions.

Elongation at break of the NR vulcanizates filled with various filler content is shown in Figure 29. The elongation at break of NR vulcanizates filled with all kinds of fillers decreased with increasing filler contents because the addition of filler particles into rubber causes the reduction of elasticity in the rubber chain resulting in the decrease in percentage elongation at break. In other words, the vulcanizates became more rigid, so the vulcanizates break at lower elongation. The elongation at break of perlite filled rubber compounds was greater than that of RHA and fly ash because of size effect as mentioned earlier. This was back up by the hardness results as shown in Figure 30. It was observed that hardness increased with increasing filler content. This result is expected due to the higher incorporating of filler particles, lower the elasticity of the rubber chains, resulting in more rigid vulcanizates.

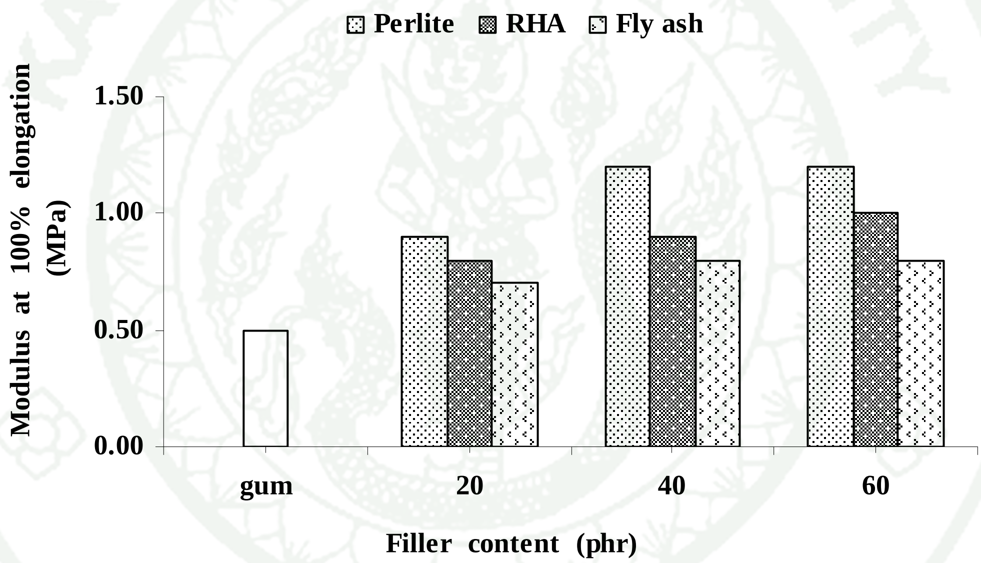


Figure 28 Modulus at 100% elongation of the NR vulcanizates filled with various filler content.

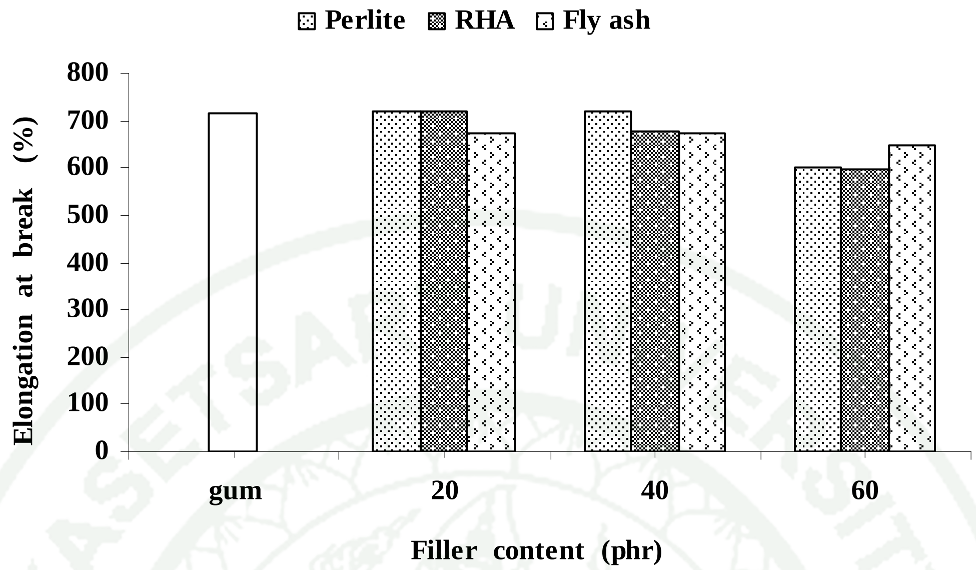


Figure 29 Elongation at break of the NR vulcanizates filled with various filler content.

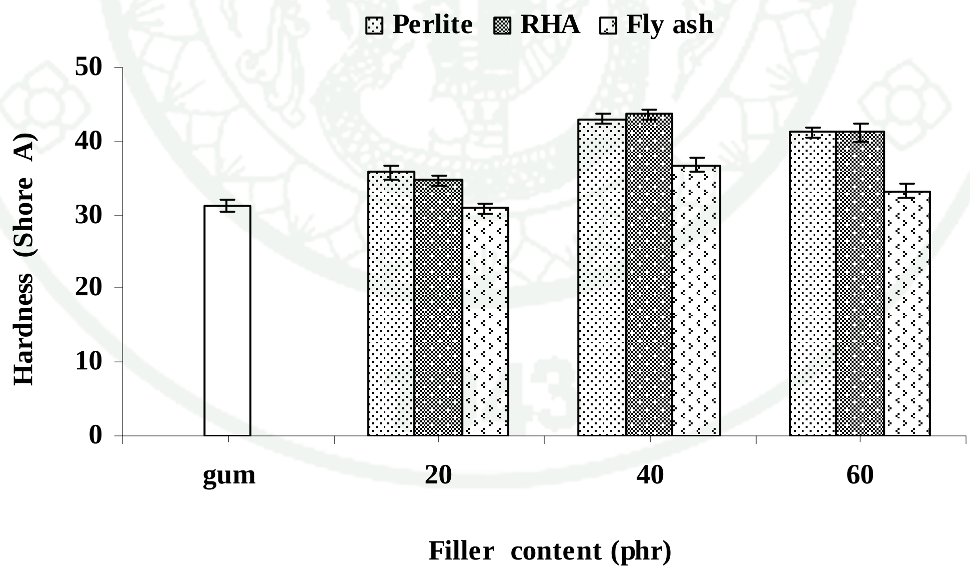


Figure 30 Hardness of the NR vulcanizates filled with various filler content.

Figure 31 shows the influence of filler content on the tear strength of filled NR vulcanizates. It was found that the tear strength of the vulcanizates filled with all kinds of fillers slightly increased to a maximum around 20 phr and then started to decrease at further loading. The increase in tear strength at low filler content (20 phr) is usually discussed in terms of continuity and phase interaction between filler and rubber molecule. At higher filler content, the decrease in tear strength was due to the poor interface interaction between filler particles and the rubber phase (Sombatsompop *et al.*, 2004). It can be seen that the fly ash filled NR vulcanizates at content 20 phr had more continuous rubber-fly ash interphase than RHA and perlite filled NR vulcanizates, leading to the highest tear strength at particular filler loading. The view can be substantiated via SEM micrographs in Figures 33-36.

The ability of the NR vulcanizates to recover after mechanically loaded was evaluated through compression set as shown in Figure 32. Generally, a decrease in compression set indicates good elastic properties of the rubber. In this work, it was suggested that for all types of fillers the elasticity of the filled NR vulcanizates decreased with addition of filler. It can be explained that the more filler particles are introduced into rubber the elasticity of rubber chain is reduced.

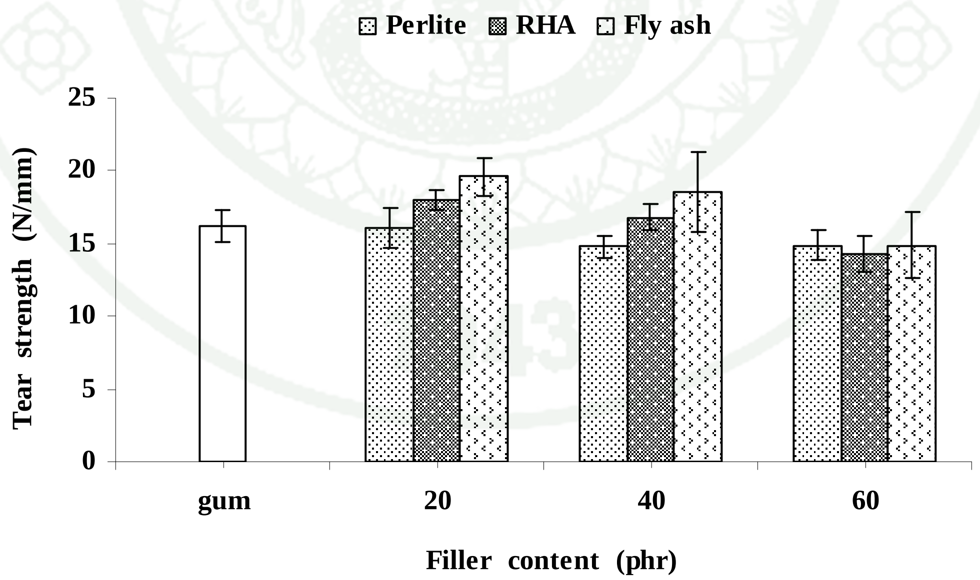


Figure 31 Tear strength of the NR vulcanizates filled with various filler content.

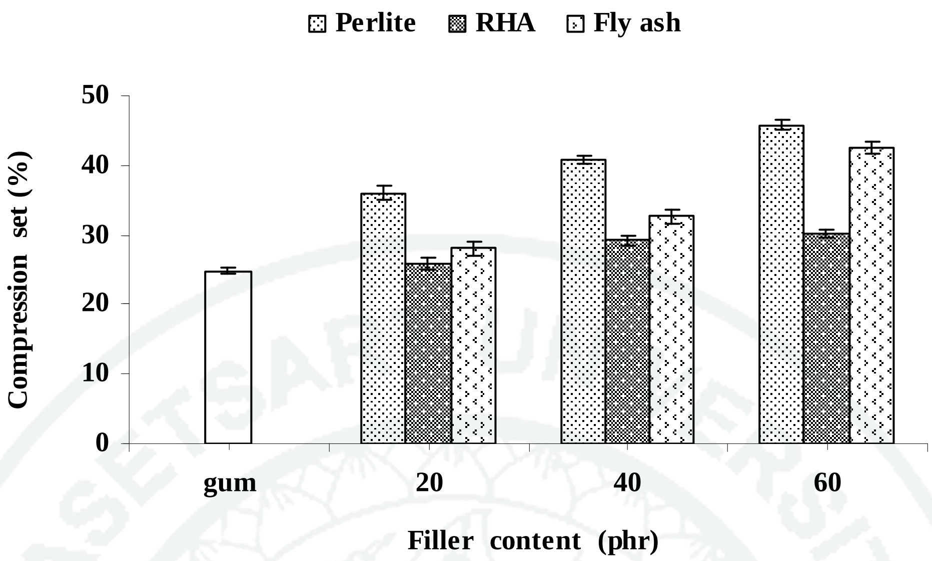


Figure 32 Compression set of the NR vulcanizates filled with various filler content.

The importance of achieving good filler dispersion in rubber compounding is well known. Poor dispersion of fillers gives rise to certain detrimental effects such as reduced product life, poor performance in service, poor product appearance, poor processing characteristics etc. (Ismail *et al*., 1999) These inadequacies are generally the result of undispersed agglomerates which act as failure-initiating flaws and lead to poor mechanical properties. SEM micrographs of perlite, RHA, fly ash-filled NR vulcanizates at 20 phr, 40 phr, and 60 phr content of filler are shown in Figures 33-36. Compounds with 40 phr and 60 phr of fillers showed rough surface with many clumps of filler particles (poor dispersion). Undispersed agglomerates of filler can easily be seen in Figures 34 (b), 34 (c), 35 (b), 35 (c), and 36 (b), 36 (c). However compounds with 20 phr of filler shown in Figures 34 (a), 35 (a), and 36 (a), displayed better filler dispersion with less-clump or undispersed agglomerates. This micrographs explain why the tear strengths decreased with increasing filler content after 20 phr loading of filler.

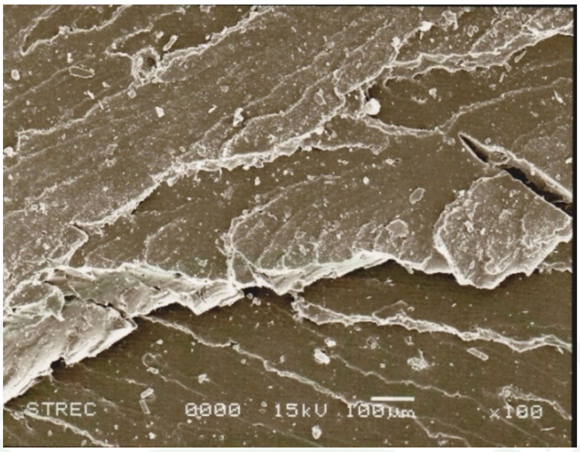


Figure 33 SEM micrographs of vulcanizates without filler (gum) at 100x magnification.

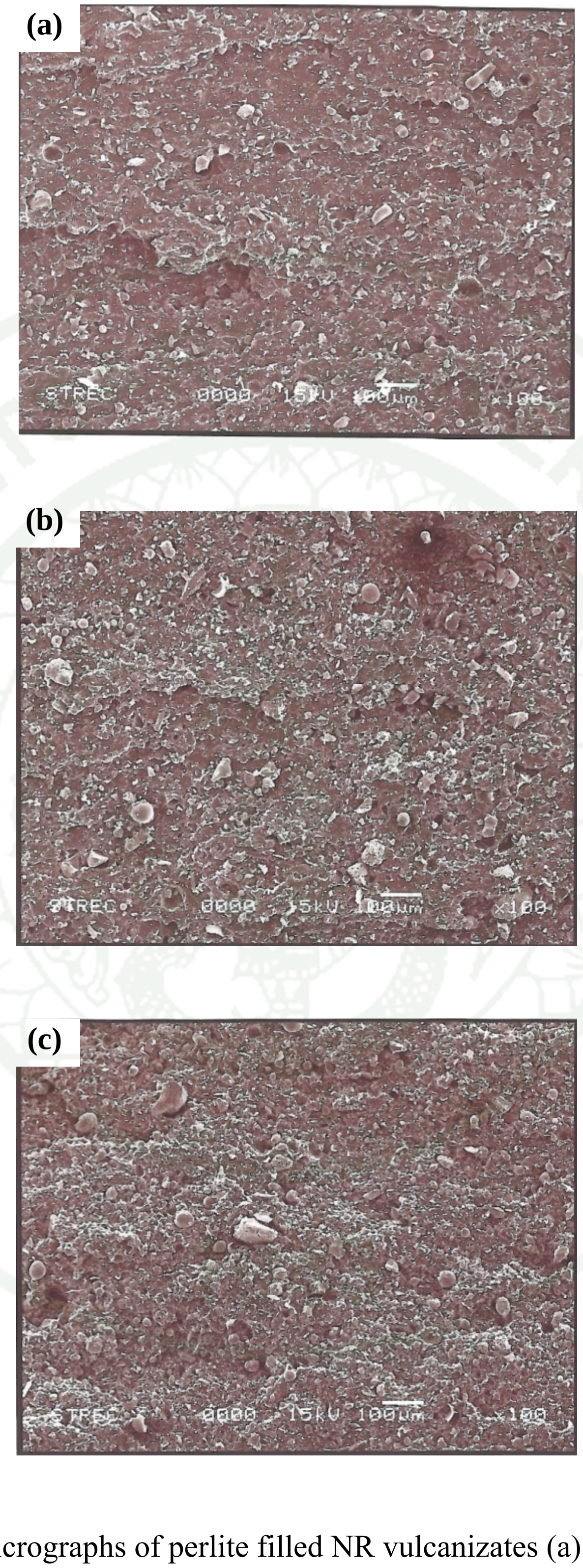


Figure 34 SEM micrographs of perlite filled NR vulcanizates (a) 20 phr, (b) 40 phr, (c) 60 phr of perlite at 100x magnification.

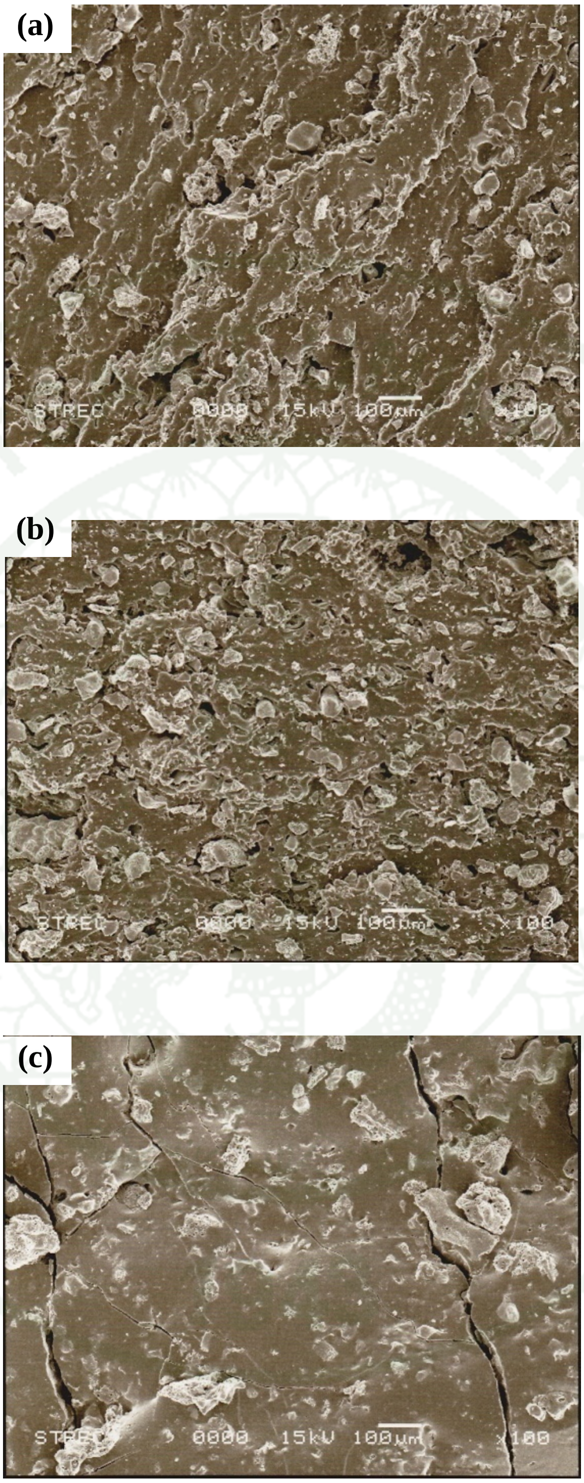


Figure 35 SEM micrographs of RHA filled NR vulcanizates. (a) 20 phr, (b) 40 phr, (c) 60 phr of RHA at 100x magnification.

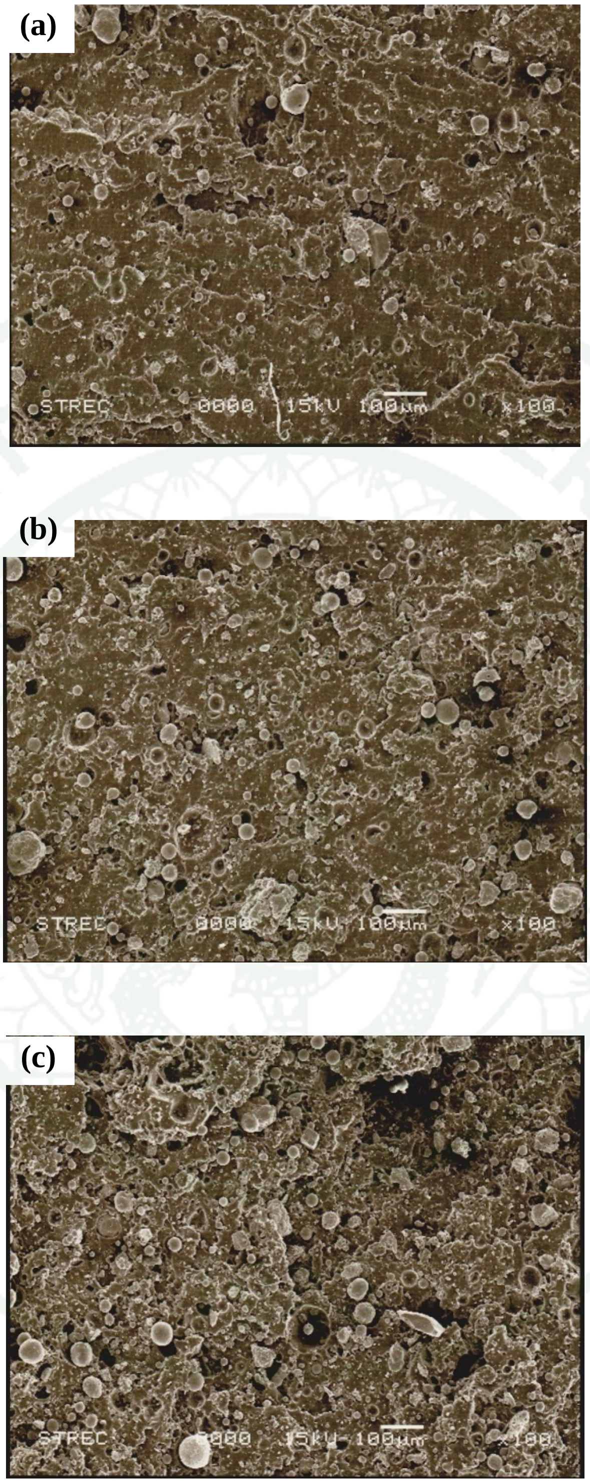


Figure 36 SEM micrographs of fly ash filled NR vulcanizates (a) 20 phr, (b) 40 phr, (c) 60 phr of fly ash at 100x magnification.

The overall mechanical properties of NR vulcanizates filled with silica from natural resources are summarized in Table 10. From the results, it can be seen that silica from natural resources exhibited little reinforcement filler in natural rubber compounds at the content up to 20 phr and then started to decrease at further loading. The increase in mechanical properties at low filler content (20 phr) is usually discussed in terms of continuity and phase interaction between filler and rubber molecule. It can be expected that NR vulcanizates filled with silica from natural resources at the content up to 20 phr tended to produce more continuous phases as a result of chemical bounding between the rubber and the filler particles. At higher filler content, the decrease in mechanical properties was due to the poor interface interaction between filler particles and the rubber phase (Sombatsompop *et al.,* 2004). The mechanical properties are influenced by nature of the filler such as particle size, surface area, and surface properties. The improvement in mechanical properties of filled-vulcanizates can be obtained by increasing surface area and surface activity of filler, filler dispersion and filler-rubber interaction (Egwaikhide *et al.*,2007).

Table 10 Mechanical properties of the natural rubber vulcanizates filled with various filler content.

Filler content (phr)		Mechanical properties				
		Modulus at 100% (MPa)	Elongation at break (%)	Hardness (Shore A)	Tear Strength (N/mm)	Compression set (%)
Gum		0.5	707	31.30±0.76	16.20±1.12	24.82±0.53
Perlite	20	0.9	720	35.80±0.91	16.10±1.36	36.00±0.96
	40	1.2	720	41.30±0.91	14.80±0.76	40.84±0.59
	60	1.2	626	42.90±0.55	14.90±1.08	45.81±0.60
RHA	20	0.8	771	34.70±0.76	18.00±0.73	25.89±0.76
	40	0.9	677	41.20±1.25	16.80±0.91	29.19±0.76
	60	1.0	598	43.70±0.67	14.30±1.26	30.16±0.53
Fly ash	20	0.7	675	30.90±0.65	19.60±1.27	28.05±0.98
	40	0.8	671	33.20±0.97	18.60±2.74	32.68±0.94
	60	0.8	747	36.80±0.91	14.90±2.27	42.52±0.95

2.3 Thermal ageing

The products of interest in this thesis are rubber compounds for producing thermal insulation, therefore prolonged exposure (air, thermal, oil etc.), resulting in the change in elastomer molecule, can not be avoided. These changes are accelerated by oxidation from ozone and oxygen in the atmosphere, ultraviolet rays, temperature variations, and other environmental factors. Nevertheless, the effect of thermo-oxidative degradation on mechanical properties was determined in this study at the specific temperature and time (100^{o}C for 22 hours).

The effect of thermal ageing on the mechanical properties including modulus at 100% elongation, elongation at break and tear strength of the NR vulcanizate filled with various amount and type of fillers including perlite, RHA and fly ash was also investigated. The results are shown as the percentage change of the specimens after thermal aging.

In general, degradation of elastomers is accelerated by a number of factors including heat, humidity, light, ozone, radiation etc.

In rubber compounds, temperature causes two competing reactions namely crosslink formation and scission of chains.

1. Crosslinking: A predominantly di- or polysulfidic crosslink network break down into monosulfidic crosslinks. The hardness increases, fatigue resistance decreases, and the compound become much stiffer.

2. Chain scission: The polymer chain breaks, causing a softening of the compound and decreased abrasion resistance. Natural rubber tends to show such degradation (James *et al*., 1989).

The mechanical properties of NR vulcanizates filled with various filler content before and after thermal ageing are summarized in Table 11. It was found that the NR vulcanizates filled with all kinds of fillers used in this study (perlite, RHA, fly ash) showed lower modulus at 100% elongation, elongation at break and tear strength after thermal aging than those without ageing. This was probably due to the predominant chain scission induced by the thermal oxidative reaction (degradation of crosslinks). The percentage change of the specimens in modulus at 100% elongation, elongation at break and tear strength after thermal aging are shown in Figure 37, Figure 38, and Figure 39 respectively. It was found that the vulcanizates filled with perlite showed lower percentage change in mechanical properties, in other word, the greater heat stability than RHA- and fly ash-filled vulcanizates. This is possibly due to the fact that perlite has larger amount of metal oxide such as Al_2O_3, CaO, MgO than RHA and fly ash, leading to the smaller percentage change in mechanical properties including modulus at 100% elongation, elongation at break and tear strength.

Table 11 Mechanical properties of the natural rubber vulcanizates filled with various filler content before and after thermal ageing.

Mechanical properties	gum	Perlite (phr)			RHA (phr)			Fly ash (phr)		
		20	40	60	20	40	60	20	40	60
Modulus at 100% (MPa)	0.5 * **0.4** ** (20.00%)	0.9* **0.8**** (11.11%)	1.2* **1.0**** (16.67%)	1.2* **1.1**** (8.33%)	0.8* **0.7**** (12.50%)	0.9* **0.8**** (11.11%)	1.0* **0.9**** (10.00%)	0.7* **0.6**** (14.29%)	0.8* **0.6**** (25.00%)	0.8* **0.6**** (25.00%)
Elongation at break (%)	717* **265**** (63.04%)	720* **378**** (47.50%)	720* **437**** (39.31%)	600* **377**** (37.17%)	721* **265**** (63.25%)	677* **289**** (57.31%)	598* **257**** (57.02%)	675* **315**** (53.33%)	671* **379**** (43.52%)	647* **389**** (39.88%)
Tear strength (N/mm)	16.2* **5.3**** (67.28%)	16.1* **8.3**** (48.45%)	14.8* **9.3**** (37.16%)	14.9* **8.4**** (43.62%)	18.0* **5.5**** (69.44%)	16.8* **5.9**** (64.88%)	14.3* **5.8**** (59.44%)	19.6* **5.7**** (70.92%)	18.6* **5.6**** (69.89%)	14.9* **5.4**** (63.76%)

Note: * Before thermal ageing

** **After thermal ageing**

( ) represents the percentage change of the specimens after thermal ageing

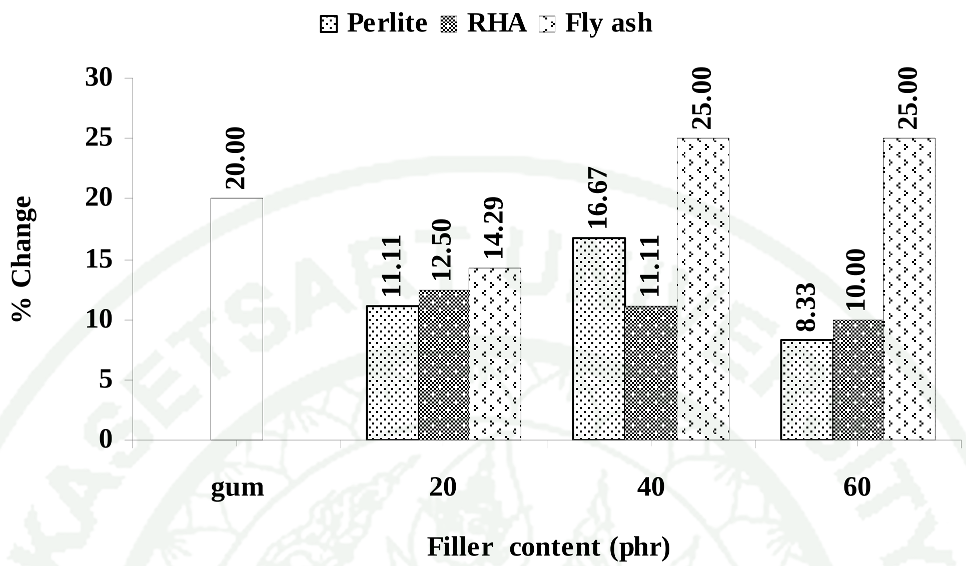


Figure 37 Percentage change in modulus at 100% elongation of the NR vulcanizates filled with various filler content after thermal ageing.

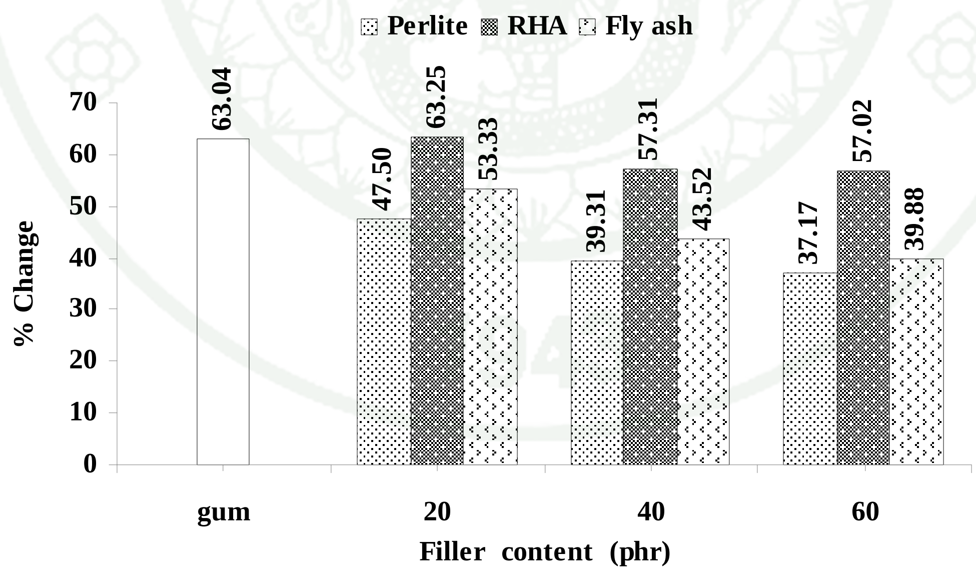


Figure 38 Percentage change in elongation at break of the NR vulcanizates filled with various filler content after thermal ageing.

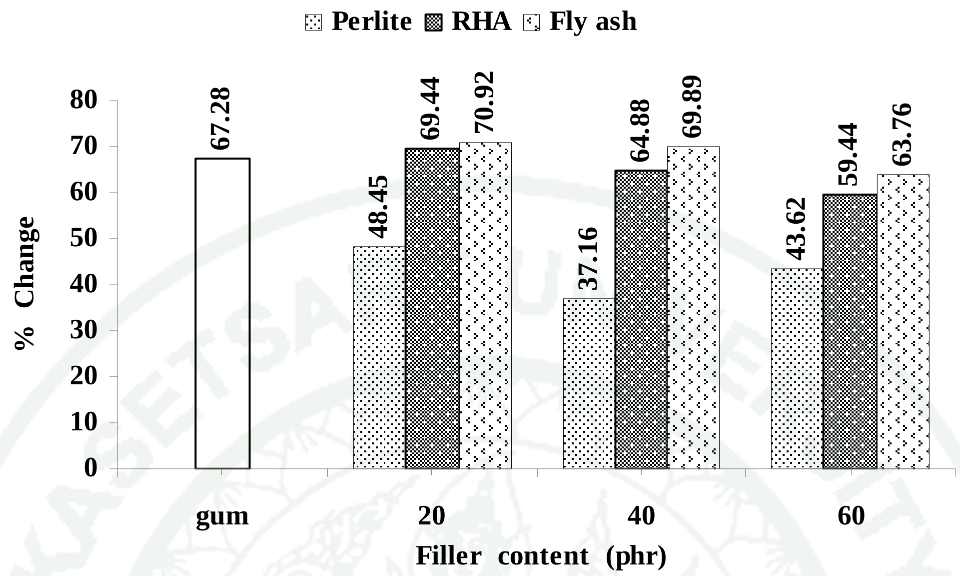


Figure 39 Percentage change in tear strength of the NR vulcanizates filled with various filler content after thermal ageing.

The experimental results in this work suggested that the use of silica from natural resources could be beneficial for improved mechanical properties of the NR vulcanizates. Taking overall mechanical properties into account, the recommended dosage of the silica from natural resources for using as filler in NR vulcanizates for producing thermal insulation was 20 phr.

3. Effect of cellulose fiber from water hyacinth content

In the second part, the influence of cellulose fiber from water hyacinth content on cure characteristics, mechanical properties, and thermal aging of the natural rubber vulcanizates was studied. The experimental study in this work was to seek a suitable content of cellulose fiber from water hyacinth for producing thermal insulation.

3.1 Cure characteristic

The effect of the addition of cellulose fiber from water hyacinth at content of 0-7 phr on cure characteristics of natural rubber compounds, including maximum torque (M_H), minimum torque (M_L), optimum cure time (t_{c90}) and that scorch time (t_{s2}) is shown in Table 12. It is obvious from the table that the maximum torque (M_H), and minimum torque (M_L) slightly increased with increasing cellulose fiber loading. The trend might be due to adhesion between the fiber and the rubber matrix being enhanced and more energy needed to incorporate the fibers due to increased viscosity, while the values of t_{s2} and t_{c90} slightly decreased as the cellulose fiber content increased. This result is expected due to the longer time the rubber compounds remain on the mill during mixing. According to Geethamma *et al.* (1995), as the fiber loading increases, the incorporation time of filler into the rubber matrix also increased and consequently generated more heat due to additional friction. The scorch time also showed similar trend.

The other reason might be due to the improvement in filler dispersion in a rubber matrix by a silane coupling agent (Dannenberg *et al*., 1981). Wagner (1975) reported that the mercaptosilane generally reduced the cure and scorch time to certain degree depending on the types of accelerate system and elastomer. Poh and Ng (1998) found that scorch time decreased with increasing concentration of γ-mercapto propyltrimethoxy silane (A-189). The presene of a thiol group in A-189 is known to exert a catalytic effect on accelerating the curing process of natural rubber compounds.

Table 12 Cure characteristics of rubber compounds filled with various amount of cellulose fiber.

Type of filler	**Amount of filler** (phr)	**Cure Characteristics**				
		M_L (lb-in)	**M_H** (lb-in)	**ΔM** (M_H-M_L)	**t_{s2}** (min)	**t_{c90}** (min)
gum	0	0.33	3.78	3.45	3.25	6.08
	3	0.38	3.81	3.43	3.22	6.07
Cellulose fiber	5	0.46	3.98	3.52	3.06	5.45
	7	0.47	4.01	3.57	3.01	5.34

The slightly increment in maximum (M_H) and minimum torque (M_L) values with increasing fiber loadings indicated that as more fiber gets into the rubber matrix, the mobility of the macromolecular chains of the rubber reduces resulting in more rigid vulcanizates. This behavior will be confirmed when mechanical properties are analyzed.

3.2 Mechanical properties

The influence of cellulose fiber from water hyacinth content on the mechanical properties, i.e., modulus at 100% elongation, elongation at break, hardness, tear strength, and compression set of the natural rubber vulcanizates was investigated. The mentioned mechanical properties of cellulose fiber-filled natural rubber vulcanizates are shown in Figures 40-44.

Figures 40 and 41 show the results of modulus at 100% elongation and hardness of the natural rubber vulcanizates, respectively. It was found that the modulus at 100% elongation and hardness of NR vulcanizates increased with increasing cellulose fiber content. It was observed that the incorporation of cellulose fibers into the rubber matrix can improve the stiffness of the compound. This was supported by the hardness results as shown in Figure 41. According to Krysztafkiewicz and Domka, (1986) the use of silane permits within a shorter vulcanization time an increase in rubber-bound sulfur,the filler surface can be transformed into a hydrophobic with ability to bind active groups of the polymer. Chemical bonds are formed between hydroxyl and silanol group of the filler and alkoxyl group of coupling agents. Consequently, rubber exhibits increased hardness and strength.

Elongation at break indicates the mobility and flexibility of the vulcanizates. Figure 42 shows the influence of fiber content on the elongation at break of the NR vulcanizates. From the results, it was found that elongation at break did not change significantly.

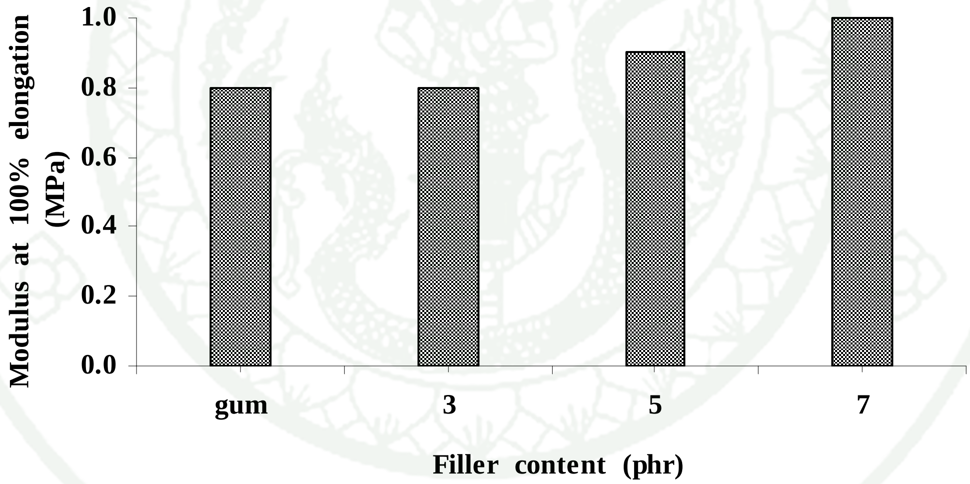


Figure 40 Modulus at 100% elongation of the NR vulcanizates filled with various cellulose fiber content.

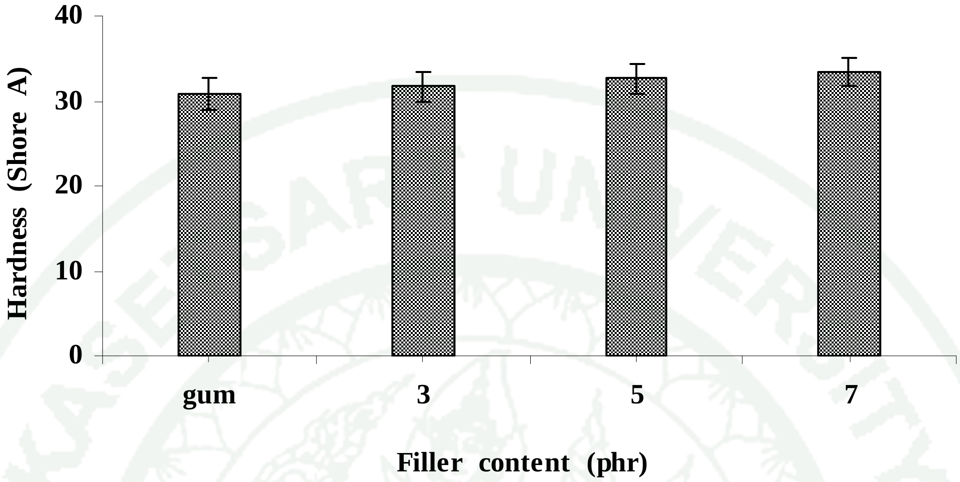


Figure 41 Hardness of the NR vulcanizates filled with various cellulose fiber content.

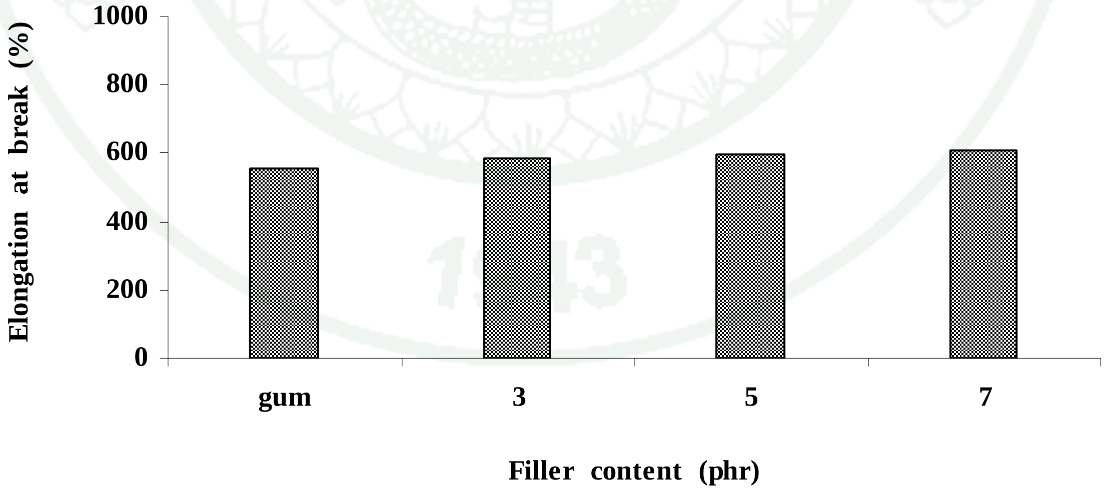


Figure 42 Elongation at break of the NR vulcanizates filled with various cellulose fiber content.

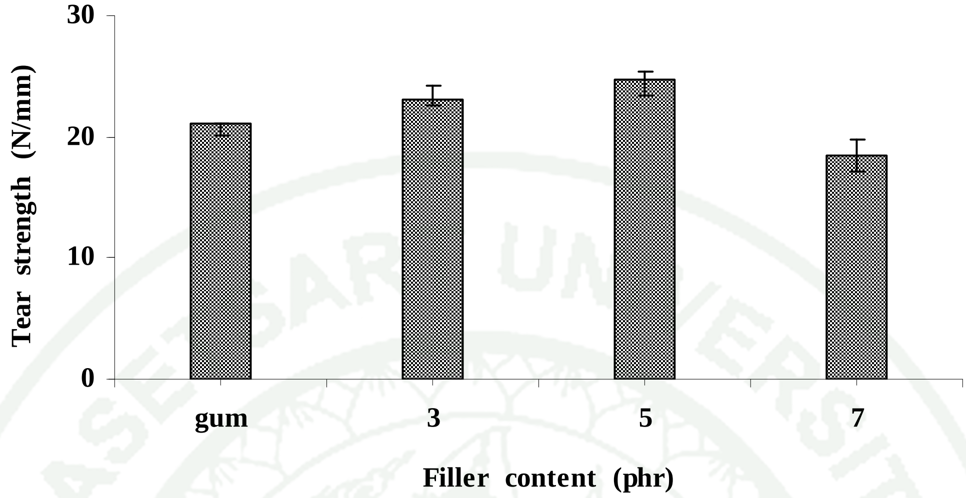


Figure 43 Tear strength of the NR vulcanizates filled with various cellulose fiber content.

Figure 43 shows the influence of fiber content on the tear strength of NR vulcanizates. It was found that the tear strength of the NR vulcanizates filled with various cellulose fiber content increased to a maximum around 5 phr and then started to decrease at further loading. The reason why tear strength of filled vulcanizates increased compared with that of gum compound is probably because the increase in strain between closely packed fibers decreased tearing and increased the tear strength. At the content up to 5 phr, the fiber surface is transformed into a more reactive one with the ability to bind active groups with the rubber matrix. Therefore rubber/fiber chemisorptions increases leading to greater tear strength. At higher cellulose fiber content (7 phr), the decrease in tear strength was due to the poor interface interaction between fiber and the rubber phase. The view can be substantiated via SEM micrographs in Figure 44.

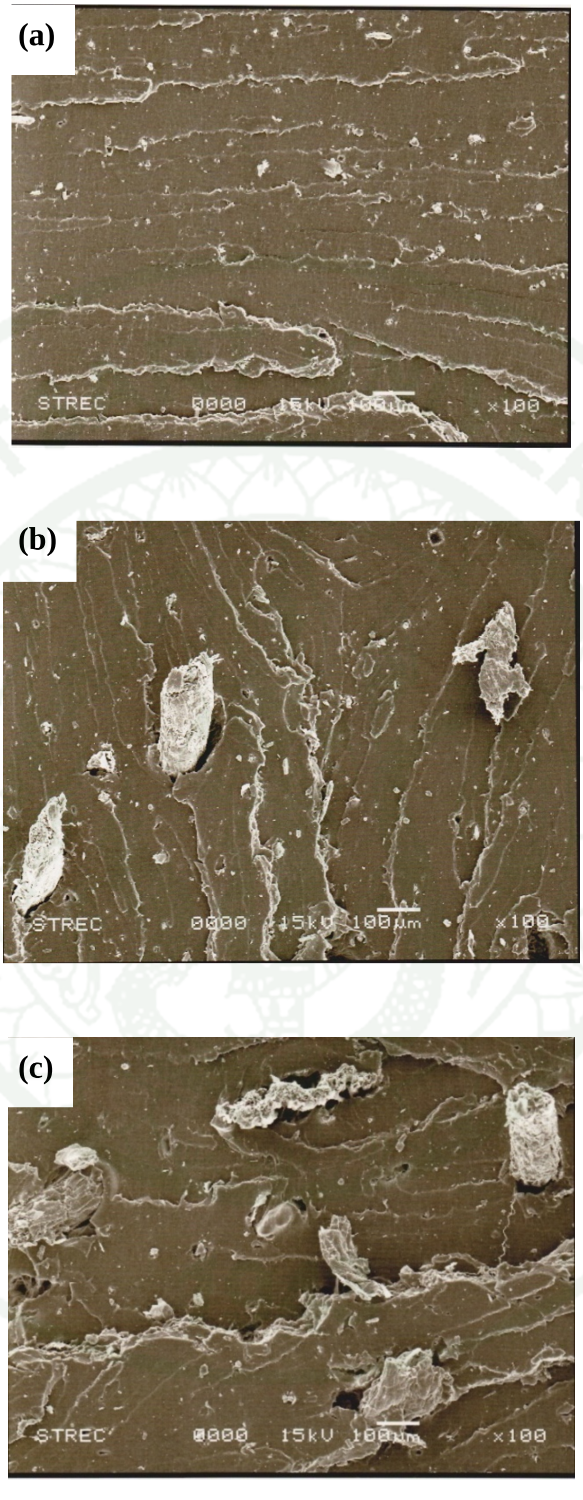


Figure 44 SEM micrographs of NR vulcanizates filled with various amont of cellulose fiber at: (a) gum, (b) 3 phr, (c) 5 phr, (d) 7 phr at 100x magnification.

(d)

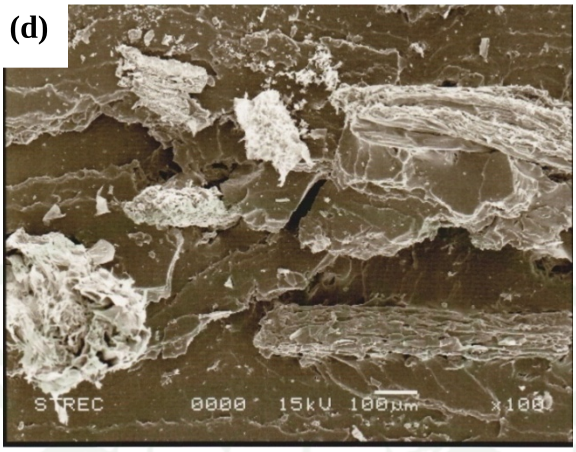


Figure 44 (Continued)

Figure 44 (a), (b), (c) and (d) show fractured surface of NR vulcanizates filled with cellulose fiber at 0 phr or gum, 3 phr, 5 phr and 7 phr, respectively. At high level of fiber loading, Figure 44 (d), the vulcanizates indicates a rough surface with many agglomerates due to the tendency of filler-filler interaction and this indicates that the level of adhesion between the fiber and matrix is poor and when stress is applied it causes the fibers to be pulled-out from the rubber easily leaving behind gaping hole. This observation supports the low tear strength of NR vulcanizates. Compounds with 3 phr and 5 phr filler loading (Figure 44 (b) and (C)) show better filler dispersion with less undispersion agglomerates, leading to the reduction in fiber pull-out. This may promote the good mechanical properties of cellulose fiber filled-NR vulcanizates at low level of fiber loading (3 phr and 5 phr).

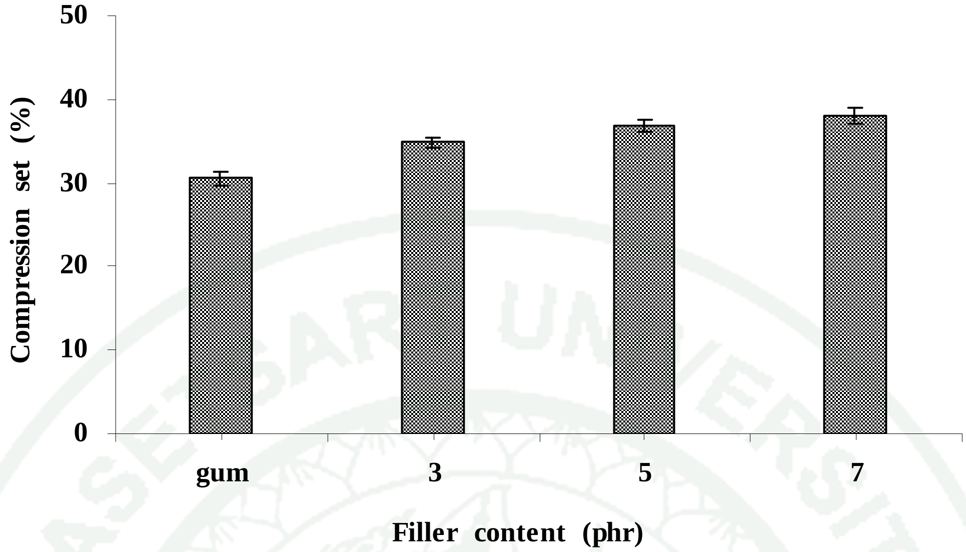


Figure 45 Compression set of the NR vulcanizates filled with various cellulose fiber content.

The effect of cellulose fiber content on compression set of the natural rubber vulcanizates is shown in Figure 45**.** In this work, it was suggested that compression set of the vulcanizates increase with increasing cellulose fiber loading. It can be explained that the more cellulose fiber particles are introduced into rubber, the elasticity of rubber chain is reduced.

The overall mechanical properties of NR vulcanizates filled with various cellulose fiber content are summarized in Table 13. From the results, it can be seen cellulose fiber exhibited little reinforcement filler in natural rubber compounds at the content up to 5 phr and then started to decrease at further loading as can be seen from tear strength results. The increase in mechanical properties at low filler content is usually discussed in terms of continuity and phase interaction between fiber and rubber molecule. At higher filler content, the decrease in mechanical properties was due to the poor interface interaction between cellulose fiber and the rubber matrix.

Table 13 Mechanical properties of the natural rubber vulcanizates filled with various cellulose fiber content.

Filler content (phr)		Mechanical properties				
		Modulus at 100% (MPa)	Elongation at break (%)	Hardness (Shore A)	Tear Strength (N/mm)	Compression set (%)
	gum	0.8	556	30.80±1.86	21.13±1.10	30.51±0.92
cellulose fiber	3	0.8	582	31.70±1.79	23.11±0.60	34.87±0.65
	5	0.9	598	32.60±1.71	24.77±1.33	36.85±0.78
	7	1.0	606	33.40±1.56	18.46±1.35	38.09±0.92

3.3 Thermal ageing

The effect of thermal ageing on the mechanical properties including elongation at break and tear strength of the NR vulcanizate filled with cellulose fiber from water hyacinth was also investigated. The results are shown as the percentage change of the specimens after thermal aging in an oven at temperature of 100^{o}C for 22 hours as illustrated in Figures 46-47.

The mechanical properties of NR vulcanizates filled with various fiber content before and after thermal ageing are summarized in Table 14.

Table 14 Mechanical properties of the natural rubber vulcanizates filled with various fiber content before and after thermal ageing.

Mechanical properties	**Gum**	**Cellulose fiber (phr)**		
		3	**5**	**7**
Elongation at break (%)	556*	582*	598*	606*
	238**	**185****	**165****	**169****
	(57.19%)	(68.21%)	(72.41%)	(72.11%)
Tear strength (N/mm)	21.13*	23.11*	24.77*	18.46*
	5.12**	**5.28****	**5.49****	**6.28****
	(75.77%)	(77.15%)	(77.84%)	(65.98%)

Note: * Before thermal ageing

** **After thermal ageing**

( ) represents the percentage change of the specimens after thermal ageing

It was found that the NR vulcanizates filled with cellulose fiber from water hyacinth showed lower elongation at break and tear strength after thermal aging than those without ageing. This was probably due to the predominant chain scission induced by the thermal oxidative reaction (degradation of crosslinks).

The percentage changes of the specimens after thermal aging are shown in Figures 46-47. It was found that percentage change of elongation at break and tear strength after thermal aging of the NR vulcanizates filled with cellulose fiber increased with increasing cellulose fiber loading, in other word, the lower heat stability at high level of fiber loading. This was due to the fiber deteriorating with thermal ageing, resulting in weak adhesion at the matrix/fiber interface.

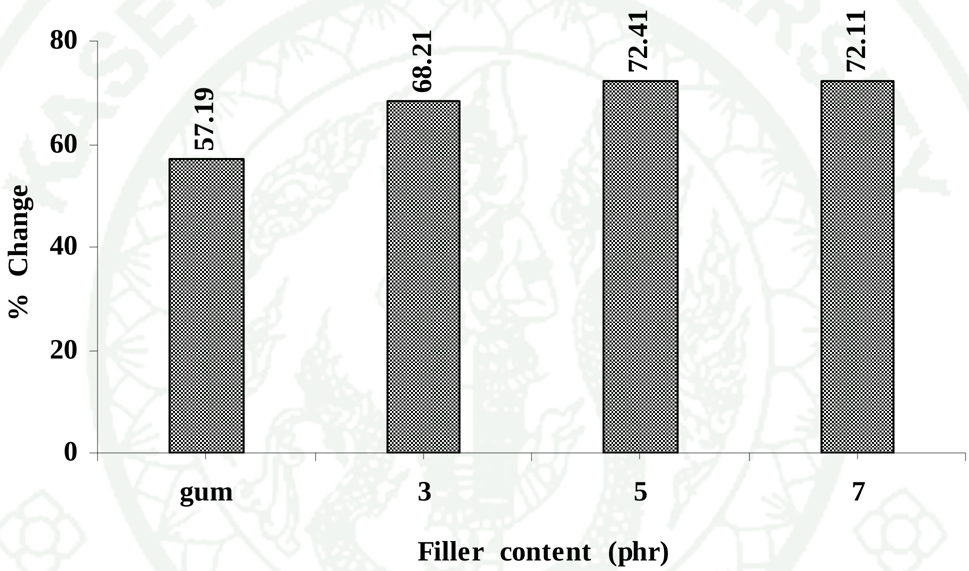


Figure 46 Percentage change in elongation at break of the NR vulcanizates filled with various fiber content after thermal ageing.

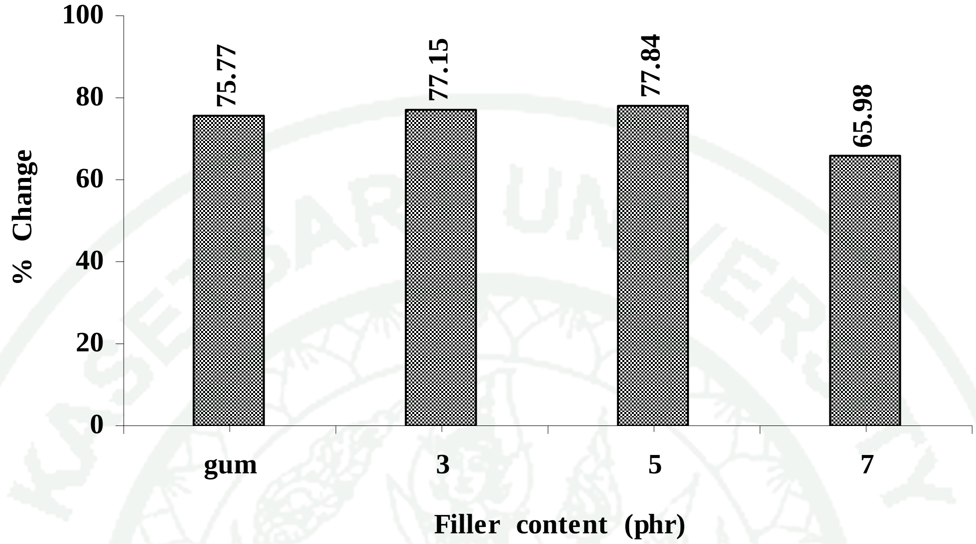


Figure 47 Percentage change in tear strength of the NR vulcanizates filled with various fiber content after thermal ageing.

The experimental results in this part suggested that the use of cellulose fiber from water hyacinth could be beneficial for improved mechanical properties of the NR vulcanizates. Taking overall mechanical properties into account, the cellulose fiber exhibited little reinforcement filler in natural rubber compounds especially in tear strength at the content up to 5 phr and then started to decrease at further loading. At higher filler content, the decrease in tear strength was due to the poor interface interaction between fiber and the rubber phase, the recommended dosage of the cellulose fiber from water hyacinth for using as filler in NR vulcanizates for producing thermal insulation was 5 phr. This was due to better filler dispersion and good adhesion between the filler and the matrix.

4. Thermal conductivity

Thermal conductivity is the time rate of steady state heat flow (W) through a unit area of 1 m thick homogeneous material in a direction perpendicular to isothermal planes, induced by a unit (1K) temperature difference across the sample. Thermal conductivity, k-value, is a measure of the effectiveness of a material in conducting heat. Hence, knowledge of the thermal conductivity values allows quantitative comparison to be made between the effectiveness of different thermal insulation materials (Al-homoud, 2005).

The rate of heat flow through a material, per unit thickness, per degree of temperature difference across the thickness of the specimen is performed using ASTM C 177. Testing is performed using a guarded hot plate apparatus. Two identical samples are placed on opposite sides of the main heater. The main heater and guard heaters are kept at the same temperature. Both auxiliary heaters are maintained a lower temperature. The guard heaters minimize the amount of lateral heat transfer from the main heater. Temperatures are monitored at each surface of thermocouples. The heat transferred through the specimens is equal to the power supplied to the main heater. Thermal equilibrium is established when temperature and voltage readings are steady.

Table 15 Thermal conductivity of materials.

Materials	Thermal conductivity (W/m K)	Source
Natural rubber (vulcanized)	0.15	www.electronics-cooling.com
Rice Husk Ash	0.062	www.knowledgebank .irri.org
Cellulose fiber	0.040	www.cee-environmental.com
Expanded perlite	0.0477-0.0616	Zhou *et al.,* 2010
Fly ash	0.070-0.350	Rohatgi and Guo, 1998

Table 15 compares the thermal conductivity of thermal insulation materials (perlite, RHA, fly ash and water hyacinth fiber) and natural rubber. It is evident that the thermal conductivity of thermal insulation materials is lower than that of natural rubber. Note that materials with the thermal conductivity less than 0.25 (W/m K) are generally considered as thermal insulations (Wang, 2008). This property makes perlite, RHA, fly ash and water hyacinth fiber an ideal material for thermal insulation.

In this part, the thermal conductivity of thermal insulation products were investigated at two different formulations i.e. NR vulcanizates filled with silica from natural resource i.e. perlite, fly ash, rice husk ash and NR vulcanizates filled with water hyacinth fiber. The optimum amount of silica from natural resources (perlite, RHA, fly ash) and water hyacinth fiber for using as filler in NR vulcanizates for producing thermal insulation was 20 phr and 5 phr, respectively.

Figures 48 and 49 show the results for thermal conductivity of thermal insulation products filled with silica from natural resources and filled with water hyacinth fiber, respectively. It was found that the thermal conductivity of all filled natural rubber insulation products has slightly higher than unfilled natural rubber insulation products (gum-1 and gum-2). The range of thermal conductivity for all filled natural rubber insulation products evaluated is between 0.072-0.078 W/m.K. According to Wang, (2008) materials with the thermal conductivity less than 0.25 (W/m K) are generally considered as thermal insulations. Therefore, it can be concluded that perlite, fly ash, rice husk ash, and water hyacinth fiber are excellent insulating materials for producing thermal insulation.

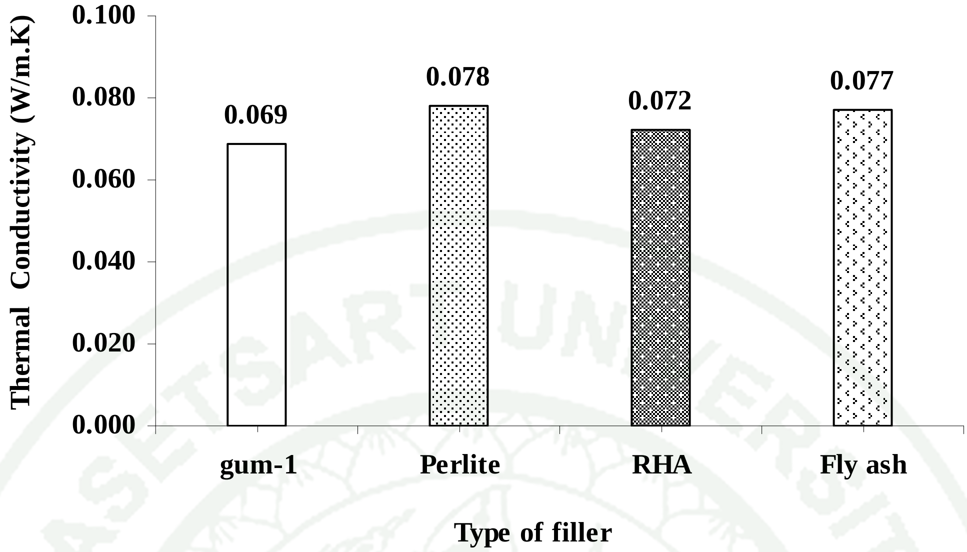


Figure 48 The thermal conductivity of thermal insulation products filled with silica from natural resources.

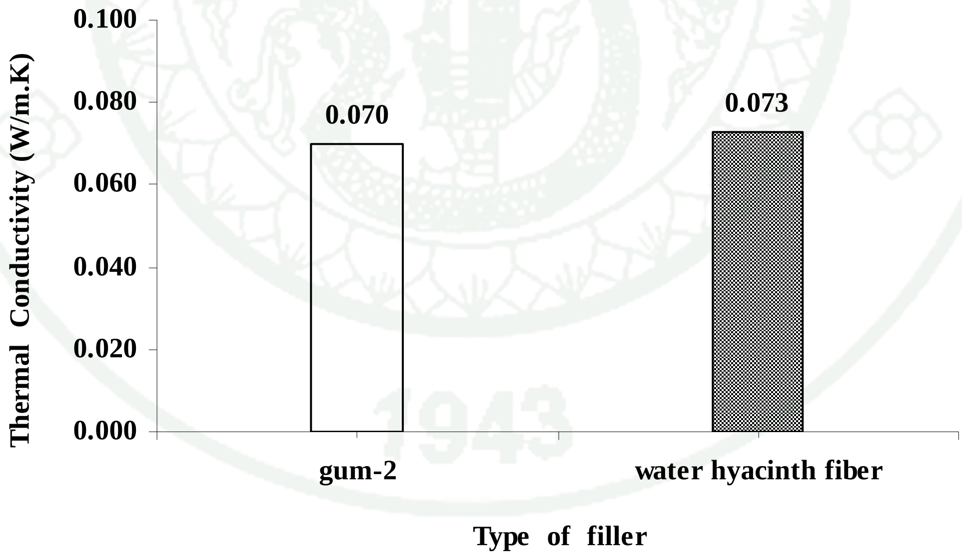


Figure 49 The thermal conductivity of thermal insulation products filled with cellulose fiber from water hyacinth.

In general, natural rubber are popular for their rubber-like elasticity, high flexibility, thermal insulating properties and abrasion resistance, but their applications are confined due to the low strength and stiffness. For compensating these drawbacks, natural rubber can be improved by the addition of various types of fillers. Particulate fillers are added to rubber either to extend and cheapen the rubber compound, or to add desirable qualities to the final compound. Nowaday, application of filler derived from wastes has attracted interest due to their low cost, renewable and environment friendly nature. In this research, it was found that the agricultural wastes improved the mechanical properties of the vulcanizates, i.e., tear resistance, and hardness. From experimental results in this part it can also be concluded that the agricultural wastes had good effect on the thermal properties of NR vulcanizate.

CONCLUSION

This study demonstrated that it is possible to utilize perlite, rice husk ash, fly ash and water hyacinth fiber as alternative natural fillers for the production of the thermal insulation. The conclusion can be divided into three parts.

The first and second parts were studied the influence of amount and type of fillers on the mechanical properties of natural rubber vulcanizates. The properties of NR vulcanizates were investigated at two different formulations i.e. NR vulcanizates filled with different content of silica from natural resource i.e. perlite, fly ash, rice husk ash (0-60 phr) and NR vulcanizates filled with different content of water hyacinth fiber (0-7 phr). The experimental results in this work was to seek a suitable filler content for producing thermal insulation.

The first part, taking overall mechanical properties into account, it was found that the use of silica from natural resources (perlite, rice husk ash, fly ash) could be beneficial for improved mechanical properties of the NR vulcanizates. It was discovered that all kinds of silica from natural resources can be considered as reinforcement filler in natural rubber compounds at the content up to 20 phr and then started to decrease at further loading. Therefore, all kinds of silica from natural resources for using as filler in NR vulcanizates for producing thermal insulation was 20 phr.

The second part, According to the overall mechanical properties, it should be noted that the water hyacinth fiber to be considered as little reinforcement filler in natural rubber compounds at the content up to 5 phr. Therefore, the recommended dosage of the cellulose fiber from water hyacinth for using as filler in NR vulcanizates for producing thermal insulation was 5 phr.

The final part was to study the thermal conductivity of thermal insulation products from natural rubber filled with natural fillers (perlite, rice husk ash, fly ash and water hyacinth fiber) compared with unfilled NR vulcanizates. The thermal insulation samples are molded for testing the thermal properties followed the ASTM C177 standard. From the result, it was found that the range of thermal conductivity for all filled natural rubber insulation products evaluated is between 0.072-0.078 W/m.K. This property makes perlite, RHA, fly ash and water hyacinth fiber an ideal material for thermal insulation, which can help to reduce temperature fluctuations in the buildings that accompany the temperature changes outside. And hence, it can reduce the energy requirements of air-conditioning. As the shortage of energy supply is intensifying, the energy-saving abilities of materials are more and more valued.

LITERATURE CITED

Abdelmouleh, M., S. Boufi, M.N. Belgacem and A. Dufresne. 2007. Short natural fiber reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibers loading. **Composites science and technology**. 67: 1627-1639.

Akiba, M. and A. S. Hashim. 1997. Vulcanization and crosslinking in elastomers. **Progress in Polymer Science**. 22: 475-521.

Al-homoud, M.S. 2005. Performance characteristics and practical applications of common building thermal insulation materials. **Building and Environment.** 40 : 353–366

Anthoine, G., R. Arnold, K. Boustany and J. Campbell. 1975. **European Rubber Journal**. July, 28.

Arayapranee, W., N. Na-Ranong and G. L. Rempel. 2005. Application of rice husk ash as fillers in the natural rubber industry. **Journal of Applied Polymer Science**. 98: 34-41.

Balo, F., A. Ucar and H. L. Yücel. 2010. Development of the insulation material from coal fly ash, perlite, clay and linseed oil. **Ceramics.** 54 (2): 182-191

Bhowmick, A.K. and H.L. Stephens. 2001. **Handbook of elastomers.** 2nd ed. Marcel Dekker, New York.

Bueche, F. 1960. Molecular basis for the mullins effect**. Journal of Applied Polymer Science**. 4: 107-114.

Byers, J. 1987. Fillers Part I: Carbon Black, pp 38-47. *In* M. Morton, eds. **Rubber Technology**. Van Nostrand Reinhold, New York.

Charles, A. Harper. 1987. **Handbook of plastics, elastomers and composites**, Mcgraw-hill, New York.

Coran, A.Y. 1978. Vulcanization, pp 292-329. *In* F.R. Eirich, eds. **The Science and Technology of Rubber.** Academic Press, San Diego.

Dannenberg E.M. 1981. Filler choices in the rubber industry the incumbents and some new candidates. **Elastomeric**. 113: 30-35.

Egwaikhide, P.A., E.E. Akporhonor and F.E. Okiemen. 2007. An Investication on the Potential of Palm Karnel Husk as Fillers in Rubber Reinforcement. **Middle-East Journal of Scientific Research.** 2 (1): 28-32.

Electronic cooling. 2001. **The thermal conductivity of rubber/elastomers**. Available Source: http://www.electronics-cooling.com/2001/11/the-thermal-conductivity-of-rubbers-elastomers, March 26, 2011.

Ferguson, G. 1993. Use of self-cementing fly ashes as a soil stabilization agent, pp 1–14. *In* **Fly ash for soil improvement**. Geotechnical Special Publication, New York.

Geethamma, VG., J. Reethamma and S. Thomas. 1995. Short coir fiber reinforced natural rubber composites. **Journal of Applied Polymer Science.** 55: 583-594

Hamed, G.R., and B.H. Park. 1999. The mechanism of carbon black reinforcement of SBR and NR vulcanizates. **Rubber Chemistry and Technology**. 72: 946-959.

Hofmann, W. 1989. **Rubber technology handbook**. Oxford University Press, New York.

Ismail, H., and F.L.Chung. 1998. Partial replacement of silica by white rice husk ash in natural rubber compounds: The effect of bonding agent. **Iranian Polymer Journal**. 7: 255-261.

Ismail, H., M.N. Nasaruddin and U.S. Ishiaku. 1999. White rice husk ash filled natural rubber compounds: the effect of multifunctional additive and silane coupling agents**. Polymer Testing**. 18: 287–298.

Ismail, H., M.N. Nasaruddin and H.D. Rozman. 1999. The effect of multifunctional additive in white rice husk ash filled natural rubber compounds. **European Polymer Journal**. 35: 1429-1437.

Ismail, M.S., and A.M. Waliuddin. 1996. Effect of rice husk ash on high strength concrete. **Construction and Building Materials**. 10 (7): 521-526.

Jacob, M., S. Thomas, and K.T. Varughese. 2004. Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber compoites. **Composites Science and Technology**. 64: 955–965

Jame, E. M., B. Erman and R. E. Frederick. 1994. **Science and Technology of Rubber**. 2nd ed. Academic Press.

Jame, E. M. 1989. **The science and technology of rubber**. John Wiley & Sons, Inc., United State of America.

Jansen, J., and G. Kraus. 1971. Specific Surface Area Measurements On Carbon Black. **Rubber Chemistry and Technology**. 44: 1287-1296.

Jauberthie, R., F. Rendell, S. Tamba and I. Cisse. Origin of the pozzolanic effect of rice husks. 2000. **Construction and Building Materials**. 14(8): 419-423.

Khedari, J., N. Nankongnab, J. Hirunlabh and S. Teekasap. 2004. New low-cost insulation particleboards from mixture of durian peel and coconut coir. **Building and Environment**. 39 (1): 59–65.

Kraus, G., 1965. Interactions of Elastomers and Reinforcing Fillers. **Rubber Chemistry and Technology**. 38: 1070-1114.

Krysztafkiewicz A. and L. Domka. 1986. Effect of silane coupling in filled rubber Vulcanizates. **Plastic Rubber Process Applied**. 6:197-203.

Le Bras, J., and E. Papirer. 1978. The filler-elastomer chemical link and the reinforcement of rubber. **Journal of Applied Polymer Science.** 22: 525-531.

Lee, S.K. 2007. The surface modification of clay particles by RF plasma technique, pp 5502. In. University of Cincinnati. **Dissertation Abstracts International,** Vol. 68-08, Section: B.

Lertsutthiwong, P., S. Khunthon, K. Siralertmukul, K. Noomun and S. Chandrkrachang. 2008. New insulating particleboards prepared from mixture of solid wastes from tissue paper manufacturing and corn peel. **Bioresource Technology**. 99 (11): 4841–4845.

Makron Engineering. **Cellulose Fibre Technology**. Available Source: http://www.cee-environmental.com/public/data/companyCatalogue 1232309558, March 26, 2011.

Malhotra, V.M. 1993. Fly ash, slag, silica fume, and rice-husk ash in concrete: a review. **Concrete International**. 15(4): 23-28.

Mehta, P.K., and P.J.M. Monteiro. 1993. **Concrete: Microstructure, Properties, and Materials.** 2nd ed. McGraw-Hill Companies, Inc., New York.

Mehta, P.K. 1992. Rice husk ash- a unique supplementary cementing material, pp.407-430. *In* V.M. Malhotra, ed. **Proceedings of the CANMET/ACI International Symposium on Advances in Concrete Technology**. Athens, Greece.

Mehta, P.K. 2002. **Method for Producing a Blended Cementitious Composition**, United States Patent, No. US 6451104 B2. pp13.

Morton, M. 1987. **Rubber Technology**. 3rd ed. Van Nostrand Reinhold, New York.

Nagataki, S. 1994. Mineral admixtures in concrete: state of the art and trends, pp.447-482. *In* P.K. Mehta, ed. **Proceedings of V. Mohan Malhotra Symposium on Concrete Technology: Past, Present, and Future.** American Concrete Institute, Farmington Hills, Michigan, USA.

Norman, D.T. 1990. Rubber Grade Carbon Blacks. p.397. In: Ohm, R.F. Ohm, eds. **The Vanderbilt Rubber Handbook.** R. T. Vanderbilt Company, Inc, Connecticut.

O'Brien, J., E. Cashall, E.G. Wardell and W.J. McBrierty. 1977. An NMR investigation of the interaction between carbon black and cis-polybutadiene. **Rubber Chemistry and Technology**. 50: 747-764.

Ou, Y., Z. Yu, A. Vidal and J. Donnet. 1994. Effects of Alkylation of Silica Filler on Rubber Reinforcement. **Rubber Chemistry and Technology**. 67: 834-844.

Pfundstein, M., R. Gellert, M.H. Spitzner and A. Rudolphi. 2008. **Detail practice insulating materials: Principles, Materials, Applications**. 1st ed. Aumüller Druck, Regensburg.

Poh, B.T., and C.C. Ng. 1998. Effect of Silane Coupling Agents on the Mooney Scorch Time of Silica-Filled Natural Rubber Compound. **European Polymer Journal.** 34: 975-979.

Potiyaraj, P., P. Panchaipech and S. Chuayjuljt. 2001. Using Water-Hyacinth Fiber as a Filler in Natural Rubber. **J. Sci. Res.** Chula. Univ; 26: 11-19.

Reyes, A. and M. Pando. 2007. Evaluation of CFBC fly ash for Improvement of Soft Clays. **World of Coal Ash (WOCA).** Covington, Kentucky, USA.

Rice Knowledge Bank. 2009. **Husk and straw properties**. Available Source: http://www.knowledgebank.irri.org/rkb/index.php/rice-milling/contributions-and-references-milling, March 26, 2011.

Rohatgi, P.K. and R.Q. Guo. 1998. Opportunities of using fly ash particles for synthesis of composites. **Fuel and Energy Abstracts.** 39(1): 28.

Sae-oui, P., C. Sirisinha, U. Thepsuwan and K. Hatthapanit. 2004. Comparison of Reinforcing Efficiency between Si-69 and Si-264 in a Conventional Vulcanization System. **Polymer Testing**. 23: 871-879

Sae-oui, P., C. Rakdee and P. Thanmathorn. 2002. Use of Rice Husk Ash as Filler in Natural Rubber Vulcanizates: In comparison with Other Commercial Fillers. **Journal of Applied Polymer Science**. 83: 2485-2493.

Senol, A., T.C. Edil, Md. Sazzad Bin Shafique, A.A. Hector and C.H. Benson. 2000. Soft Subgrades Stabilization by Using Various Fly Ashes. **Conservation and Recycling**. 46 (4); 365 – 376.

Serizawa, H., T. Nakamura, M. Ito, K. Tanaka and A. Nomura. 1983. Effects of Oxidation of Carbon Black Surface on the Properties of Carbon Black–Natural Rubber Systems. **Polymer Journal**. 15: 201-206.

Sombatsompop, N., S. Thongsang, T. Markpin, and E. Wimolmala. 2004. Fly ash and precipitated silica as filler in rubber. I. Untreated fillers in natural rubber and stryrene-butadiene rubber compound. **Journal of Applied Polymer Science**. 93: 2119-2130.

Sombatsompop, N., E. Wimolmala and T. Markpin. 2007. Fly Ash Particles and Precipitated Silica as Fillers in Rubbers. II. Effects of Silica Content and Si69 Treatment in Natural Rubber/Styrene Butadiene Rubber Vulcanizates. **Journal of Applied Polymer Science**. 104: 3396–3405.

Studebaker, M. 1965. Compounding with carbon black. *In* G. Kraus, ed. **Reinforcement of Elastomers**. Interscience Pulishers,New York.

Thailand Board Of Investment. 2010. **Thailand: World's Top Supplier of Natural Rubber**. Available Source:www.boi.go.th/english/why/rubber_2010, March 26, 2011.

Thongsang, S., and N. Sombatsompop. 2005. Effect of filler surface treatment on properties of fly ash/NR blends. pp 3282-3278. **SPE ANTEC Technical Papers**, Boston, USA. 1-5 May 2005.

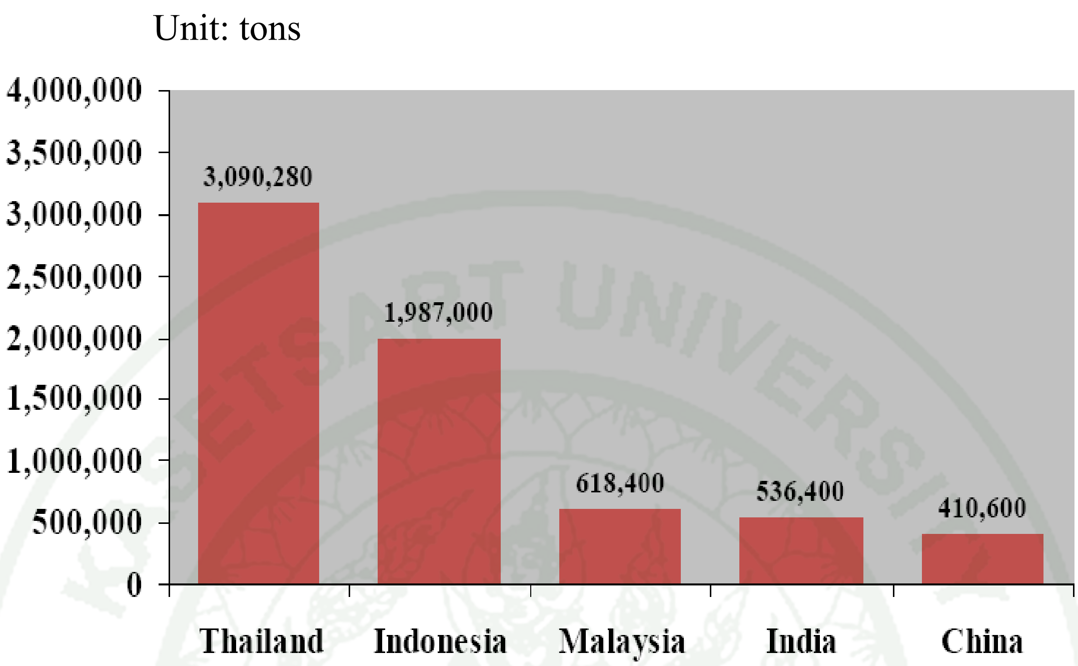
Wang, S.H. 1998. **Construction Materials Science**. China Construction Industry Publisher, Beijing.

Xu, J.Y., R. Sugawara, R. Widyorini, G.P. Han and S. Kawai. 2004. Manufacture and properties of low-density binderless particleboard from kenaf core. **Journal of Wood Science**. 50: 62–67.

Zhang, M.-H., and V.M. Malhotra. 1996. High-performance concrete incorporating rice husk ash as a supplementary cementing material. **ACI Materials Journal**. 93(6): 629-636.

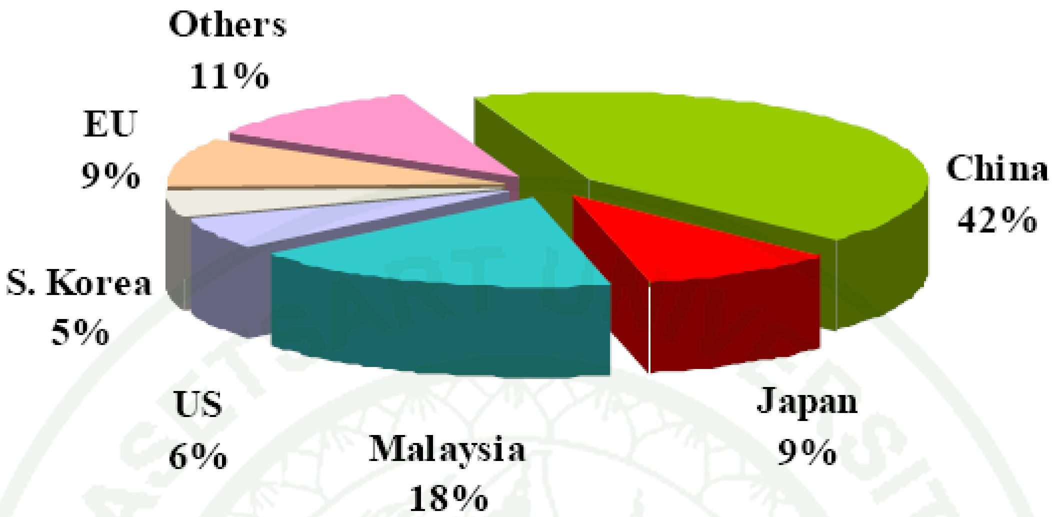
Zhou, X.Y., F. Zheng, H.G. Li and C.L. Lu. 2010. An environment-friendly thermal insulation material from cotton stalk fibers. **Energy and Buildings**. 42: 1070–1074

APPENDIX



Appendix Figure 1 World's Top 5 Producers of Natural Rubber in 2009

Source : Thai Rubber Association. (2009)



Appendix Figure 2 Thailand's Natural Rubber Export Markets 2009

Source: Rubber Research Institute of Thailand. (2009)

แบบ วศ.7

TEST REPORT

Sample's name	**Mark / Brand**	**Laboratory No.**
Rubber vulcanizates gum-1	-	L54/01617.1

Test Result

Thermal Conductivity, W/m.K	0.069

Customer's name	Wirunya Kaewwattana
Customer's address	Faculty of science, Kasetsart university
Sample's description	Rubber sheet size: 1x1 ft, two sheets.
Test date	25 February 2011
Test method	ASTM C177-97

Approved by

(Mr. Sun Jhitkraikroun)

Scientist, Senior Professional Level

Reported by

(Mr. Puckanai Thongthiumporn)

Scientist, Senior Professional Level

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Appendix Figure 3 Report on thermal conductivity of vulcanizates without filler (gum-1).

แบบ วศ.7

TEST REPORT

Sample's name	**Mark / Brand**	**Laboratory No.**
Rubber vulcanizates P,20	-	L54/01617.5

Test Result

Thermal Conductivity, W/m.K 0.078

Customer's name	Wirunya Kaewwattana
Customer's address	Faculty of science, Kasetsart university
Sample's description	Rubber sheet size: 1x1 ft, two sheets.
Test date	3 March 2011
Test method	ASTM C177-97

Approved by

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Appendix Figure 4 Report on thermal conductivity of vulcanizates filled with perlite at 20 phr.

แบบ วศ.7

TEST REPORT

Sample's name	Mark / Brand	Laboratory No.
Rubber vulcanizates Fa,20	-	L54/01617.3

Test Result

Thermal Conductivity, W/m.K	0.077

Customer's name	Wirunya Kaewwattana
Customer's address	Faculty of science, Kasetsart university
Sample's description	Rubber sheet size: 1x1 ft, two sheets.
Test date	1 March 2011
Test method	ASTM C177-97

Approved by	Reported by
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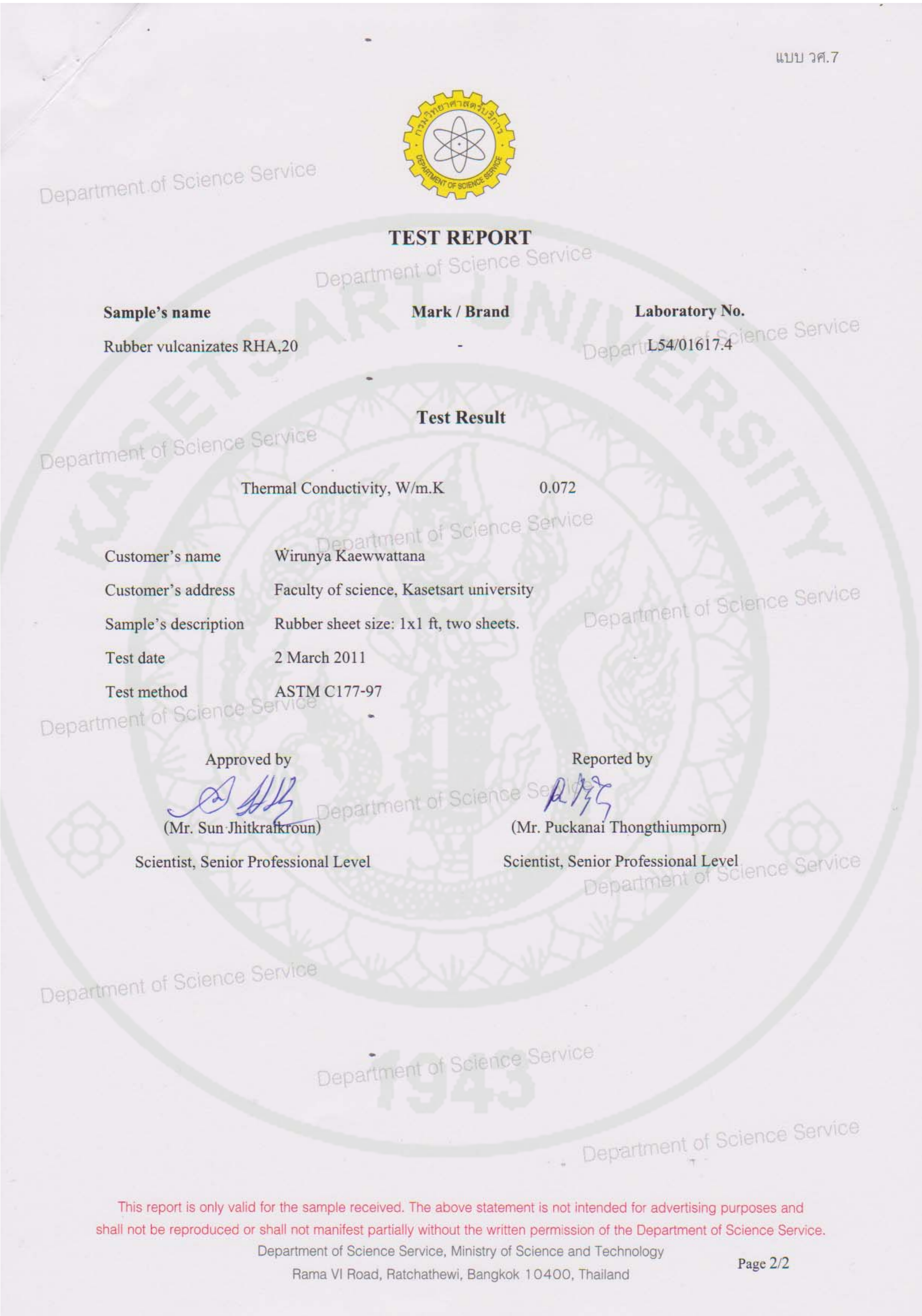
Appendix Figure 5 Report on thermal conductivity of vulcanizates filled with fly ash at 20 phr.



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TEST REPORT

Sample's name	Mark / Brand	Laboratory No.
Rubber vulcanizates RHA,20	-	L54/01617.4

Test Result

Thermal Conductivity, W/m.K 0.072

Customer's name	Wirunya Kaewwattana
Customer's address	Faculty of science, Kasetsart university
Sample's description	Rubber sheet size: 1x1 ft, two sheets.
Test date	2 March 2011
Test method	ASTM C177-97

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Appendix Figure 6 Report on thermal conductivity of vulcanizates filled with rice husk ash at 20 phr.

แบบ วศ.7

TEST REPORT

Sample's name	**Mark / Brand**	**Laboratory No.**
Rubber vulcanizates gum-2	-	L54/01617.2

Test Result

Thermal Conductivity, W/m.K	0.070

Customer's name	Wirunya Kaewwattana
Customer's address	Faculty of science, Kasetsart university
Sample's description	Rubber sheet size: 1x1 ft, two sheets.
Test date	28 February 2011
Test method	ASTM C177-97

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Appendix Figure 7 Report on thermal conductivity of vulcanizates without filler (gum-2).

แบบ วศ.7

TEST REPORT

Sample's name	Mark / Brand	Laboratory No.
Rubber vulcanizates FB,5M	-	L54/01617.6

Test Result

Thermal Conductivity, W/m.K	0.073

Customer's name	Wirunya Kaewwattana
Customer's address	Faculty of science, Kasetsart university
Sample's description	Rubber sheet size: 1x1 ft, two sheets.
Test date	4 March 2011
Test method	ASTM C177-97

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Appendix Figure 8 Report on thermal conductivity of vulcanizates filled with cellulose fiber at 5 phr.

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