CHARACTERIZATION AND PROPERTIES OF ULTRAFINE SILICA AS A FILLER IN NATURAL RUBBER COMPOUNDS

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CHARACTERIZATION AND PROPERTIES OF ULTRAFINE SILICA AS A FILLER IN NATURAL RUBBER COMPOUNDS

by

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LIST OF SYMBOLS

t_2	Scorch time
t_{90}	Cure time
M_L	Minimum torque
M_H	Maximum torque
E_b	Elongation at break
M100	Modulus at 100% elongation
M300	Modulus at 300% elongation
V	Fluid velocity
d_{50}	Mean particle size
d_{90}	90% of particles in the feed reported to underflow
d_{10}	10% of particles in the feed reported to underflow
S_{total}	Total surface area
S	Specific surface area
N	Avogadro's number
s	Adsorption cross section
v_m	Monolayer adsorbed gas quantity
V	Molar volume of adsorbent gas
a	Molar mass of adsorbed species
D_v	volume weighted mean of the crystallite size
D	Crystallite size
B	Half width
FWHM	Full-width at half maximum
2θ	Peak position
θ	the Bragg angle of (*h k l*) reflection
A	Area under peak
$I_{\max}$	Maximum height of the peak

K	Constant close to unity
λ	Wavelength of X-ray
ε	Lattice strain
A_o	Areas under the prominent plane for feed
A	Areas under the prominent plane for classified sample
C	Crystallinity index
P	Perimeter of the silhouette particle
A	Area of the silhouette particle
MWD	Molecular weight distribution

LIST OF ABBREVIATION

DMG	Department of Mineral and Geoscience Malaysia
NMP	National Mineral Policy
NR	Natural rubber
SMR L	Standard Malaysian Rubber - Light
TSR	Technically Specified Rubber
PRI	Plasticity Retention Index
DRC	Dry rubber content
ASTM	American Society of Testing Material
CV	Conventional vulcanization
Semi-EV	Semi-efficient vulcanization
EV	Efficient vulcanization
ENR	Epoxidized natural rubber
MRPRA	Malaysia Rubber Producers Research Association
EVA	Ethylene vinylacetate
EPM	Ethylene propylene copolymer
CM	Chlorinated polyethylene
HDPE	High density polyethylene
CR	Chloroprene rubber
ETU	Ethylene thiourea
IIR	Butyl rubber
CDO	p-Benzoquinonedioxime
MSTS	dibenzothiazole disupfide
SBR	Styrene-butadiene rubber
SiOH	Silanol group
TEST, Si-69	bis [(3-triethoxysilylpropyl) tetra sulfide]

CBS	N-cychlohexyl-benzothiazole-2-sulfenamide
IPPD	N’-phenyl-p-phenylene diamine
PSA	Particle Size Analysis
XRD	X-ray diffraction
SEM	Scanning electron microscope
FESEM	Field Emission Scanning Electron Microscope
UTM	Universal Testing Machine
FTIR	Fourier-transform infrared spectroscopy
EDAX	Energy Dispersive Spectroscopy Using X-Ray

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ABSTRACT

In Malaysia, silica had been selling in crude way and part of it was being exported to overseas to be value added and yet Malaysia is importing the high quality silica for the local manufacturing industry consumption. Besides agglomeration problem, this imported precipitated silica was very expensive. Therefore, upgrading local silica in term of physical and chemical characteristics could be the best solution. In this study, there are two major parts involved, i.e. value adding of silica to become ultrafine silica via air classification and incorporation of ultrafine silica as a filler in SMR L grade natural rubber. Silica from local resources were upgraded by using 50 ATP-forced vortex air classifier. The fineness product obtained was 1.01 µm with span value of 0.83 when it was classified at 12 kg/h, 7000 rpm and 100 m^3/h. The classification process was influenced by all the operational parameters. The degree of crystallinity of the classified product ranged from 68.44% to 87.41%. Three series of work had been carried out to investigate the incorporation of ultrafine silica as filler i.e. comparison of ultrafine silica and commercial silica, comparison of silanized ultrafine silica and untreated ultrafine silica and effect of differences shape of ultrafine silica. The results shows that the improvements in the characteristics of the ultrafine silica had shown better cure characteristics, tensile properties and rubber-filler interaction compared to commercial precipitated silica. The presence of silane coupling agents, bis [(3-triethoxysilylpropyl) tetra sulfide] (TESPT, or Si-69) had improved the adhesion between ultrafine silica and natural rubber matrix, consequently giving better properties compared to untreated ultrafine silica. Having irregular shape of ultrafine silica giving highest tensile properties compared to cubical shape and elongated shape. However, there is no significant trend when varying several of shapes in cure characteristic.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Malaysia is endowed with various types of minerals and these minerals are the main feedstock for the manufacturing and construction industry. Among the mineral resources in Malaysia, non-metallic mineral are the major contributor from mineral industry and silica is one of the important raw materials which is widely used as filler in various manufacturing industries such as ceramics, adhesive, rubber, plastic, paint and coating, electronics and construction (Ciullo, 1996; Johnstone and Johnstone, 1961; Thomas, 1997). Silica is widely found in Perak, Johor, Kedah, Sarawak and Selangor and according to Department of Statistics, Malaysia, its production has increase in average of 75% for the past ten years(1997-2007) (malaysianmineral.com; www.mcom.com.my).

Although the production of silica increased, Malaysian producers are still selling it in a crude manner and part of the local resources is being exported to overseas to be value added and yet Malaysia is importing the high quality silica from Taiwan and Japan for the local manufacturing industry consumption. In fact, these local silica resources has high potential to be upgraded/value added in terms of its physical and chemical properties so that it can be use as filler in various industries. The main factors to value adding process is the availability of the technology and knowledge in terms of research. These factors are concerned but the availability of cheap and practical technology that can produce high quality materials will be the main drive for the industry to invest in the high technology mineral production. Another important factor will be the pricing of the value added product, which should compensate the investment to produce it and its competitiveness of these minerals in the market. In order to achieve competitiveness in the market, the mineral should have special specification compared to the normal product in the market with improved physical and chemical characteristics.

The rapid growth of the Malaysian rubber products industry has enabled Malaysia to become the world's largest consumer of natural rubber latex and the ninth largest consumer of all rubber. This industry is made up more than 510 manufacturers producing rubber products with more than 68,700 workers and contributed RM10.58 billion to the country’s export earnings in 2007 (www.mida.gov.my). In order to obtain useful products that perform under a variety of demanding condition, the rubber matrix can be tailor made by selecting from a broad range of polymers and additives (Forrest, 2001). Fillers are one of the common additives used in rubber and besides providing cost reduction, it also used to enhance the desired properties especially mechanical properties such as tensile strength, tear strength, elongation at break and abrasion resistance (Rothon, 2002; Palaniandy *et al*., 2009; Arroyo *et al*., 2003; Chun *et al*., 2002; Zapata-Massot and Le Bolay, 2007; Bokobza, 2004; Sae-oui *et al*., 2007). In order to obtain the best reinforcement in rubber products, these fillers need to have excellent filler characteristics such as particle size, particle shape, particle dispersion, surface area, surface reactivity, surface of the filler, and the adhesion between the fillers and the rubber matrix (Chun *et al*., 2002; Mohd Ishak *et al*., 1995; Ismail and Hashim, 1998; Ismail, 2000; Ismail *et al*., 2004; Edwards, 1990).

Silica is well known one of the best reinforcement agents beside carbon black. However, currently the imported nano size precipitated silica is used as filler in Malaysia rubber products. Besides being expensive this materials exhibits high degree of agglomeration (Sae-oui *et al*., 2007) and needs costly specific processing technique. The presence of siloxane and silanol groups on precipitated silica surfaces had made the filler acidic and absorbed moisture that have affinity to agglomerate (Ansarifar *et al*., 2007; Sae-oui *et al*., 2007). Moreover, the processing becomes more difficult when a large amount of silica is added, because the viscosity increases significantly (Ostad-Movahed *et al*., 2008). As it is well known, this will reduce the dispersion of the silica particles into rubber matrix, and giving the poor adhesion between the silica particles and the rubber matrix (Valentı´n *et al*., 2007). Therefore, the silane coupling agent such as bis [(3-triethoxysilylpropyl) tetra sulfide] (TESPT, or Si-69) have been introduced for the last three decades to improve the performance of silica by increased the adhesion between the two phases.

The main task of this work are to replace the imported precipitated silica with locally available resources that has been value added in terms of physical and chemical characteristics through ultra fine classifying technique to obtain fines particles with narrow distribution. Importantly these fine particles have less moisture and highly dispersive which will overcome the agglomeration problem in rubber compounds. The air classifying technique was choosen to value add the available silica because to obtain smaller particles size in range of micron to sub-micron size with single particle is impossible since silica tend to agglomerate after prolonged grinding (Palaniandy *et al*., 2007; Palaniandy *et al*., 2008). Beside, Benezed and Benhassaine (1999) also suggested that silica structure could not be modified by grinding process, whilst Kanno (1985) showed that SiO_2 changed to amorphous phase after 120h of grinding in vibrating mill. Therefore, classifying becomes alternative processing technique to obtain fines particles with high degree of crystallinity and less agglomeration.

1.2 Research Objectives

The aim of this research was to investigate the potential of value added silica (later will refer as ultrafine silica) as a filler in SMR L grade natural rubber compounds. Hence, the research was divided in 4 phases:

1. To study the characteristics of ultrafine silica after value added via Hosokawa Alpine 50 ATP turboplex classifier.
2. To compare the properties of ultrafine silica and commercial precipitated silica as filler in SMR L compounds
3. To compare the properties of silanized ultrafine silica and untreated ultrafine silica as filler in SMR L compounds
4. To study the effect of differences shape of ultrafine silica as filler in SMR L compounds

1.3 Scope of Works

The tests involved in part 1 were particle size analysis, x-ray diffraction (XRD) analysis and Scanning Electron Microscope (SEM) analysis. The particle size analyses were done to measure particle size of each product from classification. The XRD analysis was done to characterize the microstructure in terms of defects parameter such as crystallite size, lattice strain and degree of crystallinity. The morphology properties such as silica shapes and filler distribution were investigate using SEM analysis and been used for all parts of research. The testing involved in part 2 to part 4 were cure characteristic, tensile test, swelling test and morphological study. The cure characteristics parameter measured scorch time (t_{s2}), cure time (t_{90}) and maximum torque (MH). The tensile tests include tensile strength, modulus at 100%, modulus at 300%, elongation at break and hardness. Swelling test was conducted by measuring the swelling percentage of the rubber compounds.

CHAPTER 2

LITERATURE REVIEW

2.1 Mineral in Malaysia

Malaysia is endowed with over 33 different mineral types, comprising metallic, non-metallic and energy minerals. The metallic mineral produces minerals such as tin, gold, bauxite, iron-ore, ilmenite and other associated minerals as by-products of tin and gold mining such as zircon, monazite, rutile, struverite and silver. The non-metallic or industrial mineral produces limestone, clays, kaolin, silica, sand and gravel, aggregates, feldspar and mica. The energy minerals include coal, natural gas and crude petroleum (malaysianmineral.com; www.mcom.com.my).

Malaysia's mineral resource industry (excluding energy minerals) remained sluggish despite the continuing good demand and high prices for most metals and minerals in 2007. However, non-metallic sector remained to provide the dominant share in the overall mineral production. This sector registered a production value of RM1.95 billion in 2007. The production value for the metallic and energy mineral sectors in 2007 were RM0.46 billion and RM0.12 billion, respectively (malaysianmineral.com; www.mcom.com.my).

There was generally a lack of exploration, mine development and capacity expansion in the industry. Therefore, the Department of Mineral and Geoscience Malaysia (DMG) has draw out the National Mineral Policy (NMP) to ensure that the mineral industry's contribution to the national economy and its global competitiveness remain strong (Ghiathuddin *et al*.,2003). The NMP has been specifically formulated to focus on the sustainable development and optimum utilization of mineral resources via value adding and promoting the use of local minerals and further development of mineral-based products. The existence and role of the mineral industry towards the nation building cannot be denied. As example, in 1998, the Government began the promotion of the development of silica-based industry, which was to focus on higher value-added processing activities to produce such value added products as silicon wafer, optical fiber, crystal glass, sheet glass, and other glass products.

2.2 Silica

2.2.1 Reserve and Production

Silica-sand resources are found throughout Malaysia comprising largely of natural sand deposits and ex-tin mine tailings. The Department of Mineral and Geoscience Malaysia (DMG) has estimated that the silica-sand reserves are more than 148.4 million tonnes, located in the states of Johor, Perak, Terengganu, Kelantan, Sabah and Sarawak. Table 2.1 shows the production, import, export and value of silica-sand during 2007 compared with the preceding year. The production of silica-sand in 2007 increased to 719,221 tonnes from 512,277 tonnes produced in 2006. Meanwhile, Figure 2.1 shows the production of silica has increased in average of 75% from 1997 to 2007 (Malaysia Silica Production, http://www.mcom.com.my).

Table 2.1 : The production, import and export value of silica-sand.

Year	2006	2007
Production (tonnes)	512,277	719,221
Value (RM million)	22.62	32.06
No of mines	13	24
Import (tonnes)	395,441	19,415
Value (RM million)	9.39	8.37
Export (tonnes)	104,880	128,713
Value (RM million)	5.86	34.87

Sources: Department of Mineral and Geoscience, Malaysia
Department of Statistics, Malaysia

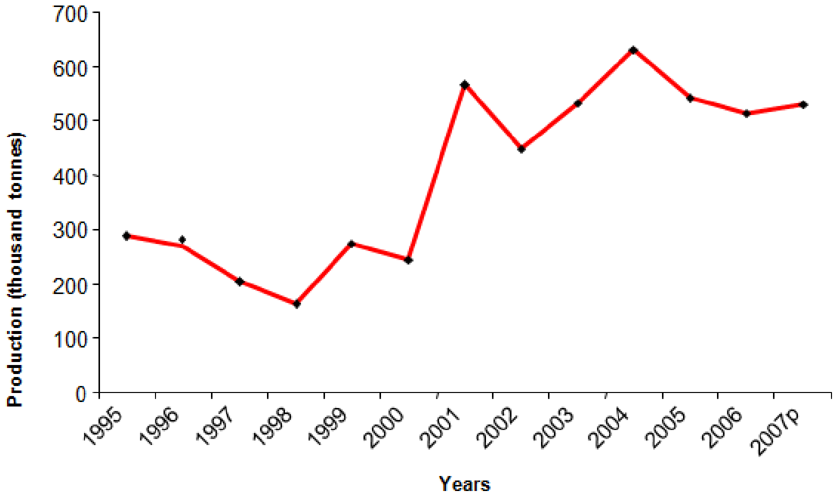

Figure 2.1: Production of silica in Malaysia

2.2.2 Characteristics and properties

There are two types of silica, i.e. natural silica and synthetic silica. Table 2.2 shows some properties of natural silica and synthetic silica. Natural silica products are crystalline and are classified for most of their uses under the term 'sand and gravel'. It is generally characterized as off-white to white and abrasive, with the low surface area, low binder demand and low cost. The examples of natural silica are; ground silica, novaculite, crystobalite, tripoli, flint and silica sand.

Table 2.2 : The properties of natural silica and synthetic silica (Ciullo, 1996)

Properties	Natural silica	Synthetic silica
Chemical formula	SiO_2	SiO_2
Form	Crystalline	Amorphous
Specific gravity	2.65	2 – 2.3
Refractive Index	1.54	1.45
Mohs Hardness	7	5 – 6

The synthetic silica are characterized as amorphous and white, with high purity, a high surface area, high liquid absorption, and ultrafine particle size. It is highly costs as compared to natural silica. These include silica gel and precipitated silica, also known as hydrated silicas, and fumed silica, also known as pyrogenic or anhydrous silica.

2.2.3 Application in Industries

The application of silica can be divided into 2 major categories i.e. ‘industrial sand and gravel’ and quartz crystal. Virtually all quartz crystal used for electronics was cultured rather than natural crystal. Electronic-grade quartz crystal was essential for making filters, frequency controls, and timers in electronic circuits employed for a wide range of products, such as communications equipment, computers, and many consumer goods, such as electronic games and television receivers (USGS, 2009). The uses of industrial sand and gravel can be divided as shown in Figure 2.2 and 8% from it was used as whole-grain filler and building products. In filler application, the silica, either natural silica or synthetic silica can be used in ceramics, adhesive, rubber, plastics, electronics, construction and paint and coating. For polymer systems i.e. rubber and plastics, silica fillers are mainly used for property enhancements and cost reduction. The major improvements imparted by silica include increases in stiffness, strength, temperature resistance, dimensional stability, surface hardness and scratch resistance (Johnstone and Johnstone, 1961; Hofmann, 1989; Ciullo, 1996; Ismail, 2000). In this research, the focus would be silica application as filler in rubber industry.

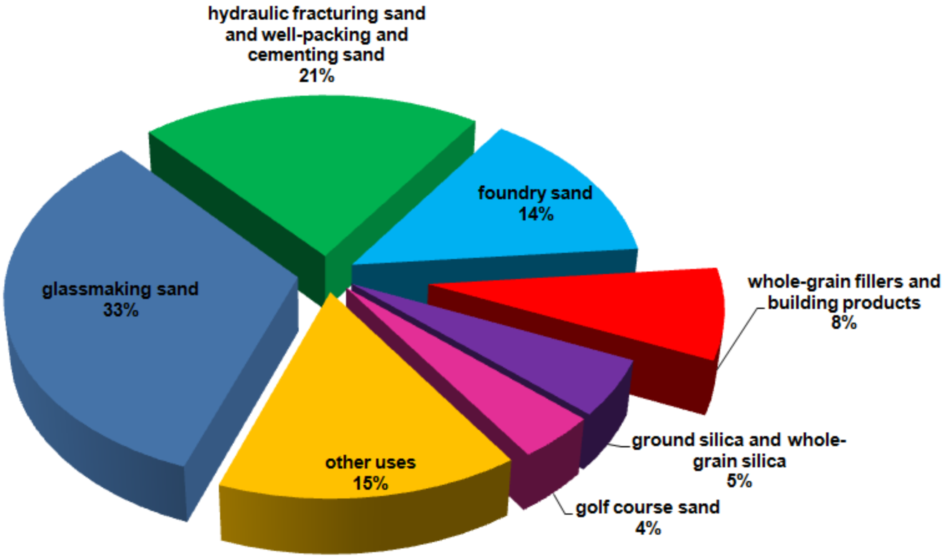

Figure 2.2: Silica consumption (USGS, Mineral Commodity Summaries – January 2009)

2.3 Classification Process

Classification is a method of separating mixtures of minerals into two or more products with different range of particle size on the basic of the velocity with which the grains fall through a fluid medium (Wills, 1979). In mineral processing, the fluid medium usually water for wet classification and air for air classification. Since the velocity of the medium fluid is dependent on not only the size, but also on the specific gravity and shape of the particles, the principles of the classification are important in mineral separations utilising gravity concentrators. In this study, the focus was only on air classification system. The benefits of classifications include the following, all of which enhance the economics of the process:

- ✓ reduced load on the grinding unit
- ✓ better efficiency
- ✓ possible production of many grades of powder from the same feedstock
- ✓ capability of producing finer products with steeper particle size distributions from the same grinding step

2.3.1 Principles of Air Classification

Air classifiers work on the principle that wherever relative motion exists between a particle and a surrounding fluid, the fluid will exert a drag force on the particle. If the individual particle were falling under the influence of gravity in still air, it would accelerate until it reached a constant velocity, which is known as the terminal settling velocity. This occurs when the drag force exerted by the air balances the gravitational force exerted on the particle. If the air rising with this velocity then smaller particles of lower terminal settling velocity would be entrained and carried upwards

Figure 2.3 shows classifier-sorting column (classifier chamber) in which a fluid is rising at a uniform rate. Particles that had introduced into a sorting column either sink or rise according to whether their terminal velocities are greater or less than the upward velocity of the fluid. The sorting column therefore separates the feed into two products – an overflow consisting of particles with terminal velocities less than the velocity of the fluid and an underflow of spigot product of particles with terminal velocities greater than the rising velocity (Wills, 1979).

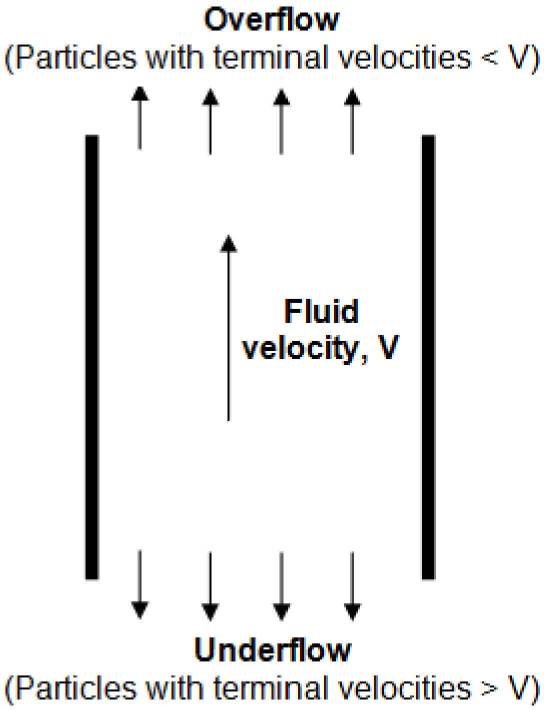

Figure 2.3: Classifier-sorting column (Wills, 1979)

2.3.4 Factors Affecting Classification Efficiency

2.3.4(a) Cutpoint and Particle Size Distribution

Cutpoint and particle size distribution are the most important factors that have to be considered in order to increase the classification efficiency. Figure 2.4 shows the Tromp curve (partition curve) which relates the weight fraction, or percentage, of each particle size in the feed that reports to the underflow or overflow of particle size. Cutpoint briefly describes as the particle that has equal chance of being found in fines (underflow) or in the coarse (overflow) i.e. 50% of particles in the feed reported to underflow (Wills, 1979). This point usually referred as d_{50} size. Some materials have very homogeneous particle size distribution and these will ease the classification performance. However, there also particles like crushed limestone that have unlimited extremes with large quantities of coarse particles and very fines minus 10 µm particles. Larger particles of feed material with wider particles distribution will reduce the classification efficiency resulting more particles reported to coarse products with large d_{50} size.

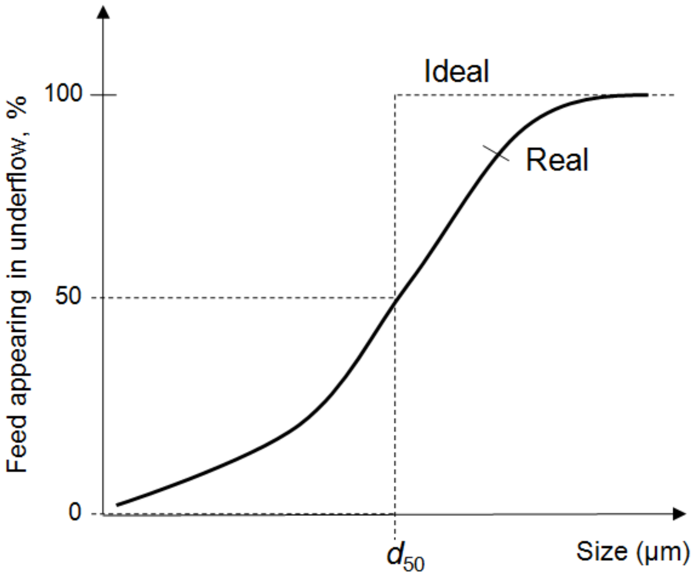

Figure 2.4: Partition or Tromp curve in particle classification system (Wills, 1979)

2.3.4(b) Particle Behavior in an Air Stream

A classifier classifies the particles according to their settling velocities in the air and several factors affect the particles settling velocities such as particle specific gravity and particle shapes.

Specific gravity related to particle mass and therefore, particles with high specific gravity has higher terminal velocity compared to its rising velocities and vice versa. The specific gravity is important in order to classify two different types of samples. For example, a 75 µm particle with specific gravity of 2 g/cm^3 will behave in the same manner as a 54 µm particle with specific gravity of 4 g/cm^3. Besides, the porous or hollow particles such as diatomaceous earth and flyash will have the same affect on their settling velocities as the actual specific gravity of solid particles (Wills, 1979).

The particle shapes affects the classifier performance when deviating from spherical forms due to their changing surface area as the particle tumbles in an air stream producing a variable drag force on it. Particles differing widely from spherical shape are difficult to define size and to measure reliably. For example, a mica flake can have a length and width six times its thickness. If the mean diameter and mass of a particular flake are of a magnitude to have it normally classified as coarse, the particle can still be swept with the fines if the plane in which the flake shows the largest area is perpendicular to the air stream at the moment of its classification.

2.3.4(c) Surface Moisture

Free water content of pulverized material when present on the surface of the particles changes the apparent particle size distribution of the classifier feed by formation of agglomerates. The free water content tolerated by air classifying devices depends entirely on the nature of the material being classified. For example, flour containing approximately 18% of free water; there is no affect on the classification. However, 1% water in fine limestone will seriously affect the efficiency of the classification. (Wills, 1979; Buell, 2008)

2.3.4(d) Viscosity of Gas Stream

Air classifiers may be operated with heated of refrigerated air of gases such as nitrogen, having different viscosities from standard air. As the drag force acting on the particles is directly related to viscosity of the gas stream, the gravitational, inertial or centrifugal force acting on the particle must changed proportionally to retain a set cutpoint (Wills, 1979; Buell, 2008).

2.3.4(e) Electrostatically Charged Particles

These particles will repel each other when they have the same polarity, as is usually the case. The material disperses more readily in an air stream and becomes more difficult to collect by mechanical means. This results in higher classifier cutpoint and lowers the efficiencies (Wills, 1979; Buell, 2008).

2.3.4(f) Flow Characteristics

Free flowing materials disperse readily in an air stream and can be distributed evenly without difficulty. Both factors are important prerequisites to good classification. The opposite is true for materials with poor flow characteristics. In addition, materials that have tendencies to build up on classifier surfaces will create flow disturbances or plug the classifier (Wills, 1979; Buell, 2008).

2.3.4(g) Surface Area

The number of particles per unit volume is an important factor in determining the capacity of any classifying device. The finer the material, the more particles for the given volume unit and the lower the capacity of the classifying device. This results in lower efficiencies as lower capacity of the classifying device will reduce the homogeneous mixture of the particles (Wills, 1979; Buell, 2008).

2.3.4(h) Particles Hardness

Hard particles besides being abrasive have a tendency to bounce and ricochet inside the classifier chamber when handled at medium to high velocities. This results in abnormal amounts of stray coarse particles in the fine product (Wills, 1979; Buell, 2008).

2.4 Rubber

2.4.1 Natural Rubber

Natural rubber (NR) was discovered around 400 years ago. It was found in the sap of some plants such as *Hevea braziliensis*, *Castilloa elastica*, *Landophylia owariensis* and *Ficus elastica*. The basic polymer appears in the sap called polyisoprene. The *Hevea braziliensis*, a member of the spurge family, *Euphorbiaceous* produces 99.99% cis-1,4-polyisoprene and remains the most widely used products nowadays. The typical content of natural rubber is shown in Table 2.3. where the analysis was conducted by using acetone extracting method (Barlow and Fred, 1988). The word ‘rubber’ normally refers to the natural rubber, however, in the mid of 20-century, some chemists had discovered the use of Zieger-Natta catalyst for the production of the synthetic cis-polyisoprene (Bhowmick and Stephen, 2001). Therefore, the application of the one word expanded in common usage to include an ever-growing range of synthetic rubber. However, the synthetic rubber cannot replace the natural rubber due to the toxic waste generated from its industry and this remain the natural rubber becomes most widely used rubber in the world since it is a sustainable raw material.

Table 2.3: Typical content of NR (Barlow and Fred, 1988)

Component	%
Moisture	0.6
Acetone extract	2.9
Protein (Calculated from nitrogen)	2.8
Ash	0.4
Rubber hydrocarbon	93.3

The chemical structure of cis-polyisoprene is shown in Figure 2.5. The average molecular weight of this homopolymer was in ranges from 200,000 to 400,000 with broad molecular weight distribution (MWD). The molecular weight could be broken down to facilitate the processability of rubber by mastication process. The broad MWD resulted in good processing behaviour of NR (Hofmann, 1989). However, the determination of the molecular weight of the natural rubber is difficult because the long chain of the rubber would degrade in gas permeation chromatography unless some parameters such as solvent and interstitial gaps are well maintained (Bhowmick and Stephen, 2001). Thus, light scattering measurement conducted is more effective in determining the molecular weight. The MWD of NR depends on the tapping frequency, the more frequency of tapping the lesser the gel content. The rubber tapped for the first time contains around 80% gel (Bhowmick and Stephen, 2001).

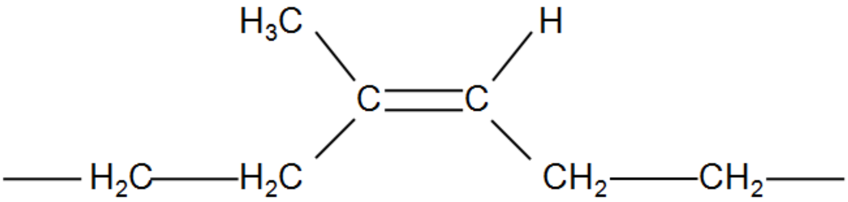

Figure 2.5: Structure of cis 1,4-polyisoprene (Hofmann, 1989)

The double bond of polyisoprene in NR is important for sulphur vulcanization process. However, these double bonds are easily attacked by oxygen or ozone consequently degrading the rubber. Thus, antioxidant is normally added into the rubber compound in order to prevent it from reacting with oxygen. Some of the antioxidant such as lignin (Gregorovà *et al*., 2006) and alkylated phenolic resins (Malshe *et al*., 2006) are quite effective in reducing the degradation of the rubber vulcanizates. The raw NR has less resistance to the organic solvent of liquid such as benzene, toluene, gasoline, vegetable oil and mineral oil. These liquid would swell the unvulcanized rubber to viscous liquid because the breakage of polymer chains. Therefore, the chemical crosslinking in NR is important to reduce the swelling effect of NR. The employment of the filler in NR vulcanizate can also decrease the swelling percentage. Ismail *et al*. (1999) reported that the incorporation of the filler could reduce the swelling effect of diamine salt fatty acid in NR. According to Da Costa *et al*. (2001), the additional of rice husk ash in NR can also decreased the swelling effect of the rubber to organic solvent.

The raw NR has the specific gravity of 0.934 at 20°C. The specific heat of NR is 0.502 at 20°C. The refraction index after acetone extraction ranges between 1.5215 and 1.5238. Besides, the specific resistivity of rubber sheets and crepe is 1 x 10^{15} and 2 x 10^{15} ohm-cm respectively (Hofmann, 1989). The NR can undergo cold crystallization at temperature around -25°C. The rate of the crystallization of the synthetic cis 1,4-polyisoprene containing stearic acid is lower compared to NR (Burfield, 1984). The stereoregularity of the polymer chain of NR can undergo stress-induced crystallization. The phenomenon can be observed from tensile tests of the NR vulcanizate. Several researches indicated that tensile modulus is greatly increased while the stress applied on the vulcanizate. The tensile strength is even higher than semi-reinforcing filler filled vulcanizate (Poh *et al*., 2002; Anantharaman *et al*., 2001; Sam, 2007). NR also has unique thermal effects with the elongation of the rubber, when the rubber is elongated at small extent, the temperature would drop. However, the temperature increased at greater elongation (Stern and Jacob, 1967).

The NR grades plantation rubbers are very hard to process, thus the mastication process is required to break down the molecular weight of the polymer chains for the eased of processing. NR also has excellent extrudability and calendability. The high cure rate of NR is also important for the rubber processability. The double bonds present in the polyisoprene contributed to this property (Hofmann, 1989). In the process of producing rubber products, the rubber undergoes creep, stress relaxation, recovery and flow. These phenomenons could influence the processability of the rubber. For instance, the elastic properties of rubbers could influence the die swell, nerve, green strength, shrinkage, etc. The stress relaxation of the viscoelastic materials always brings the bad impact of the rubber springs in engineering. There are 2 phases of stress relaxation i.e the short-term physical relaxation and long term chemical relaxation. The physical relaxation refers to the molecular rearrangement and orientation whereas the chemical relaxation is the molecular chain scission and reformation.

2.4.2 SMR L

The classification of the standard of the smoked sheet and pale crepe from different plantation is needed because the cure rate and processability can vary. SMR (Standard Malaysia Rubber) is a scheme produced by Malaysia to classify the grades of the rubber for dirt content, ash content, nitrogen content, Plasticity Retention Index (PRI), Mooney viscosity and others related specification. This scheme is widely recognized by some rubber producing countries. This type of Technically Specified Rubber (TSR) is supplied in compact, pressed bales or sheets. The marketing successes of natural rubber graded by SMR bring about grading of other countries such as SIR from Indonesia, SLR from Sri Lanka, TTR from Thailand etc (Hofmann, 1989). The production of the SMR L is focused on its color. The light colored SMR is producing by adding sodium metabisulfite at 0.04% dry rubber content (DRC). Table 2.4 shows the SMR L specification. (Bhowmick and Stephens, 2001)

Table 2.4: Specification of SMR L (Bhowmick and Stephens, 2001)

Parameter	SMR L
Dirt retained on 44μ aperture (max, % wt)	0.03
Ash content (max, % wt)	0.5
Nitrogen content (max, % wt)	0.60
Volatile matter (max, % wt)	0.80
Wallace Rapid Plasticity-minimum initial value (P_0)	30
Plasticity Retention Index, PRI (min, %)	60
Color limit (Lovibond Scale, max)	6.0

2.4.3 Rubber Compounding

2.4.3(a) Definition of Rubber Compounding

In principles, the basic properties of the elastomers or rubber come from its nature. However, the incorporation of other ingredient into the matrix can modify the properties (Hofmann, 1989). The process of the introducing the chemicals or additives into the rubber to modify its properties is called rubber compounding. A good compounding needs to consider many aspects such as environmentally safe, good processability, satisfactory service life and minimum production costs (Barlow, 1988). The different types of additives and chemical contribute to the above factors. Table 2.5 shows some of the ingredients and their function in rubber compounds (Barlow, 1988).

Table 2.5: The rubber ingredients and their function in rubber compounds (Barlow, 1988)

Ingredient	Function
Elastomer	The main characteristics of the rubber compounds
Vulcanizing agent	To produce chemical reaction with rubber matrix to form crosslinking
Accelerators	Materials used in quickening the speed of the vulcanization
Activators	A substance that increase the effect of accelerators
Fillers	It divided into black and non-black filler to reinforce the rubbers
Age resistor	Material used to prolong the service life of the rubber products

2.4.3(b) Rubber Compounding Process

The overall compounding process is shown in Figure 2.6. The early stage of the rubber compounding is the softening process of raw rubber by mastication. Sometimes the peptisers will be added. In rubber industry, the widely used equipment to masticate rubber is two roll mills. The mastication is normally applied to NR rather than synthetic rubber since they are tailored made and can be processed directly. Mastication time of NR is longer than synthetic rubber because the NR is normally has high Mooney viscosity. The mastication process of NR took within 15 minutes whilst the synthetic rubber is just only 2 minutes. Mastication process is prior to produce a homogenous dispersion of filler into the rubber matrix since the filler can only be dispersed well in rubber matrix when certain level of viscosity is archived. The proper viscosity can improve the processability if the rubber compounds.

Basically, there are two categories of mastication process, i.e mastication without peptisers and mastication with peptisers. The mastication without peptisers requires high shear force of two roll mills or internal mixer to break down the polymer chain and thus reduce the molecular weight. Mastication with peptiser more easily as peptisers are used to increase the efficiency of mastication (i.e. to increase the rate of molecular breakdown) so the mixing time of mastication was less. The mastication process depends on the temperature. As the temperature increase, the elastomers become soften and consequently absorb less mechanical energy. The high temperature can cause oxidative attack and increase the rate of chain scissor thus reducing the viscosity. The mechanical degradation will then occur and lead to the excessive softening.

After mastication process, the ingredients will be added in the raw rubber by using two roll mills or internal mixer. A typical recipe and mixing schedule for the reference of rubber compounder in rubber mixing process can be found in standard procedure that had been agreed by worldwide. For example, the mixing procedure of carbon black in NR can be found in ASTM Designation D 3192-82. In the finishing step of compounding, the mass of the compounds need to be checked. If the mass difference of the batch is more than 0.5%, compared to the theoretical mass, the batch has to be rejected (Morton, 1987).

The finishing step of rubber product processing is the shaping of products. During the vulcanization process, the long chain of the rubber molecules forms crosslinks with the reaction of vulcanization agent into three-dimensional (3D) structures. Therefore, the rubber transforms from soft to stronger elastic material. Besides that, the rubber would have better resistance to heat, light and some solvent. The details features and benefit of the vulcanization process will be discussed in next section.

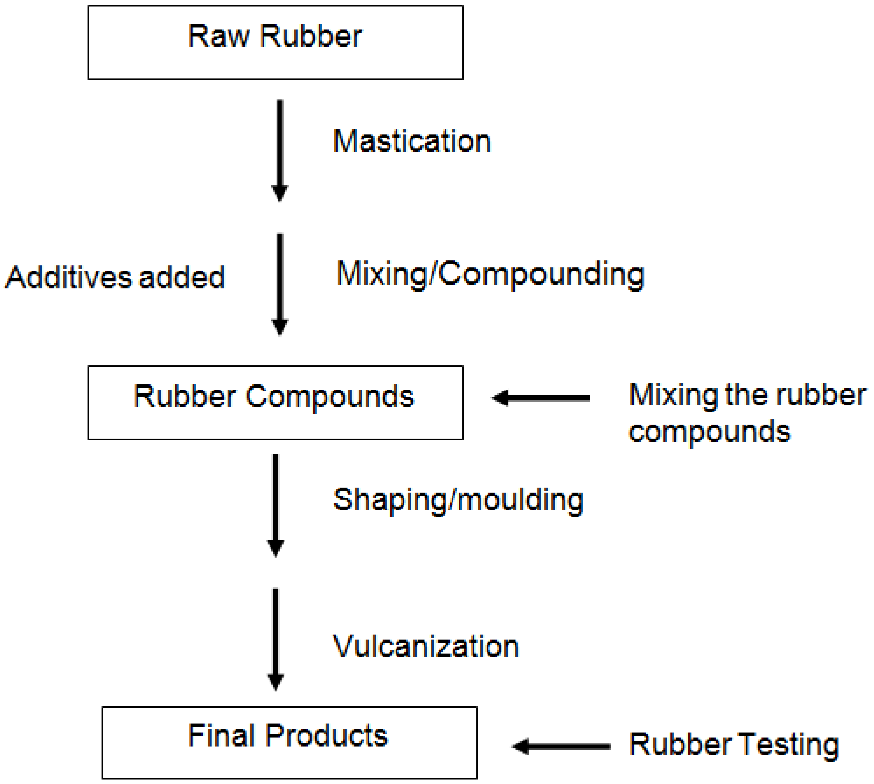

Figure 2.6: Rubber processing steps from raw rubber to final products (Ismail and Hashim, 1998)

2.4.3(c) Vulcanization Systems

(i) Sulfur Crosslinking Agent

Vulcanization is a process that increases the overall elasticity of rubber by locking the chains to each other through chemical crosslinks. The slippage behaviour of the plastic-like material would change to more dimensional stable material (Ciesielski, 1999). The most common use of crosslink agent in rubber is sulfur because it is expensive and plentiful. This crosslinker can link the double bonds of the rubber together. NR is always crosslinked by this type of vulcanization process due to the small amount of sulphur used.

Generally, there are a number of sites, which are attractive to sulfur atoms along the rubber molecules called cure sites. In the vulcanization reaction, the eight-membered ring of sulfur breaks down in smaller parts with varying numbers of sulfur atoms. Figure 2.7 represents the sulfur crosslinking process of polyisoprene. One or more sulfur atoms can attach itself to the double bond, and then the sulfur can grow until it reaches the other cure sites of double bonds. The sulfur bridge can vary from two to ten atoms. The length of the sulfur chain can affect the physical properties of the vulcanizate. The shorter the sulfur crosslink give the better heat resistance to rubber vulcanizate. Thus, the efficient vulcanization (EV) system that has lower polysulfide crosslinks gives better heat and aging resistance. However, the high crosslink in the rubber vulcanizate produce very good dynamic properties, which important in tyre sidewall industry. Good flexing properties can reduce the formation of cracks and consequently minimize the failure if the rubber product (Ciesielski, 1999).

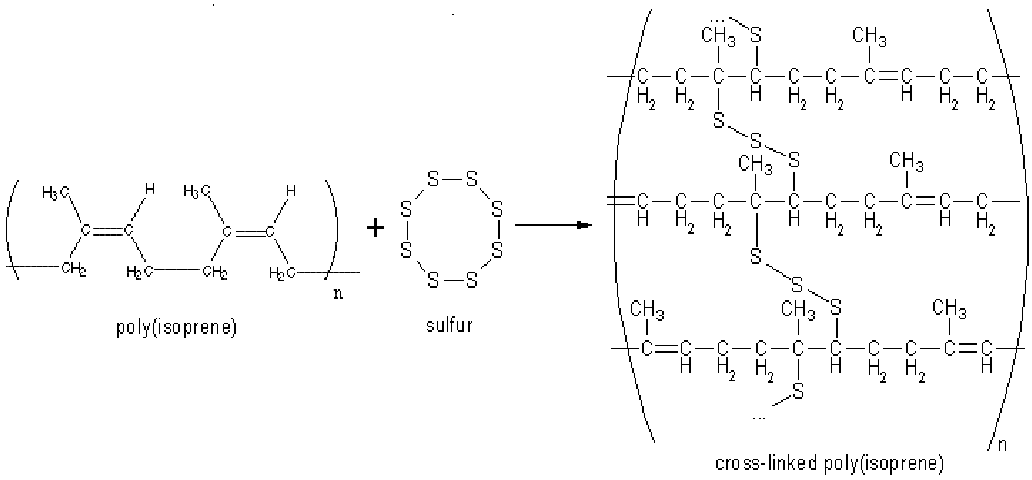

Figure 2.7 : The sulfur crosslinking process of polyisoprene

Three categories of sulfur vulcanization system are used in rubber technology, i.e. conventional vulcanization (CV), semi-efficient vulcanization (semi-

EV) and efficient vulcanization (EV). The difference between these systems is the ratio of sulfur and accelerator added into the rubber compounds which giving different properties. Table 2.6 represents the type of vulcanization system and its characteristics.

Table 2.6 : Type of vulcanization system and its characteristics (Ismail and Hashim, 1998)

Properties	CV	Semi-EV	EV
Sulfur content	2.0 – 3.5	1.0 – 2.0	0.3 – 1.0
Accelerator content	1.0 – 0.5	2.5 – 1.0	6.0 – 2.0
E* value	8 – 25	4 – 8	1.5 – 4
di- and polysulfide crosslinks	98	50	20
Monosulfidic crosslinks	5	50	80
Cyclic sulfidic concentration	High	Medium	Low
Heat aging resistance	Low	Medium	High
Resilience	Low	Medium	High
Compression set (%) at 70°C for 220 hours	30	20	10

The CV system produces multiple sulfurs in the crosslink called polysulfidic crosslinks whilst more monosulfidic crosslinks were produced by using EV system. Semi-EV system is compromise between CV and EV system. The sulfur to accelerator ratio of different vulcanization system represents the different cure rate of the system. As well known, the EV system with highest accelerator to sulfur ratio has highest cure rate. However, as the temperature increased, the effect of the accelerator to sulfur ratio becomes insignificant (Sadequl *et al*., 1998). The heat aging resistance of CV is poorer than semi-EV and EV due to the presence of polysulfidic crosslinks. The sulfur-sulfur bonds are weaker than sulfur-carbon bonds, which eventually leads to the thermally unstable in CV system. Nevertheless, the mechanical properties of the CV vulcanizate were greater than EV system. The type of rubber and additives used would affect the properties of the vulcanization system. Ismail and Chia (1998) reported the effect of multifunctional additive and vulcanization system on silica filled epoxidized natural rubber (ENR). The result showed that the semi-EV system exhibited greater tensile strength and tear strength followed by EV and CV system. There are research indicated that the crosslink density of the CV in ENR was greatest as it showed higher hardness and maximum torque compared to semi-EV and EV system.

(ii) Urethane Crosslinking Agent

Sometimes the sulfur cure system is used in conjunction with urethane crosslinkers. The urethane crosslinker was discovered by Researchers of Malaysia Rubber Producers Research Association (MRPRA) and had been commercialized under the trade name Novor 924. The crosslinker in an adduct of p-nitosophenol and diisocyanate which is called quinine oxime urethane. The rubber vulcanizate formed with this crosslinker would have better heat aging resistance (Barlow, 1988).

(iii) Peroxide Crosslinking Agent

Peroxide crosslinking was discovered in early 1950s. It becomes more important with the development of saturated synthetic rubber such as Ethylene vinylacetate (EVM), Ethylene propylene copolymer (EPM), Chlorinated polyethylene (CM) and silicone rubber. There are several advantages of using peroxide curing system such as scorch free storage of compounds, rapid vulcanization at high temperatures, low compression set, no discoloration and stable at high temperature. Moreover, this curing agent is easy in handling and not hazardous (Hofmann, 1989).

The mechanism of peroxide curing system is shown in Figure 2.8. The curing reaction starts when peroxides start to decompose (Step 1). The decomposition of peroxides is influenced by heat, light, or high-energy radiation and reactions with other materials (Hofmann, 1989). At that time, the hydrogen atom was extracted from polymer chains to become hydrocarbon radicals (Step 2). These hydrocarbons radical then reacts to make stable carbon crosslinks (Step 3). The greater proportion of hydrogen radicals from polymer chains resulting the greater crosslinking efficiency.

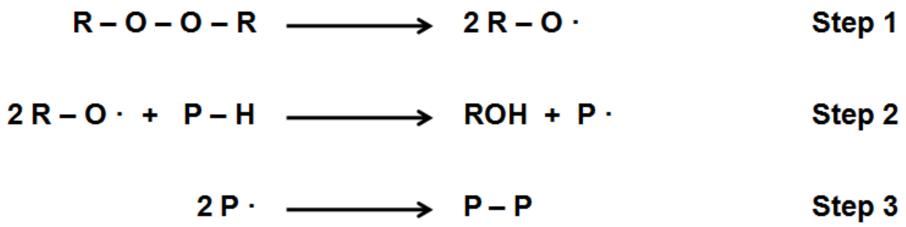

Figure 2.8 : Mechanism of peroxide curing system (Hofmann, 1989)

In term of vulcanizate, the products normally have lower tear resistance, lower elasticity and poorer dynamic properties compared to sulfur vulcanizate. Nakason *et al*. (2006) investigated the effect of curing system on dynamic vulcanization of NR/high density polyethylene (HDPE) blends. They cured the blends through three vulcanization system, i.e. sulfur, peroxide and mixed both systems. The peroxide cured products showed higher tensile strength, tension set and hardness compared to sulfur cured vulcanization. Nevertheless, the elongation at break of peroxide cured products was inferior. This is however depends on the type of rubber or the blends involved in the system. Peroxides cured products generally give lower swelling resistance compared to sulfur cured system, but heat stability and compression set is better than the sulfur system.

(iv) Metallic Oxide Crosslinking Agent

Generally, metallic oxides are used as curing agent for chloroprene rubber (CR). The metal oxides used include zinc oxide, magnesium oxide and lead oxide. The addition of the metallic oxide can improve the water resistance of the vulcanizate and always used to control the scorch time of CR.