

**EFFECT OF ADDITIVES ON THE MECHANICAL, SOLVENT  
TRANSPORT AND HEAT AGEING PROPERTIES OF RUBBER  
VULCANIZATES**

**by**

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## LIST OF ABBREVIATIONS

6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
CaO	Calcium Oxide
CB	Carbon Black
CBS	N-cyclohexyl 2-benzothiazole sulfenamide
CPPD	N-cyclohexyl-N'-phenyl-p-phenylenediamine
CV	Conventional Vulcanization System
DBP	Dibutylphthalate
DCBS	Benzothiazyl-2-cyclo-hexyl sulfenamide
DOTG	Diotolylguanidine
DPG	Diphenylguanidine
DPPD	N-N'-Diphenyl-p-phenylenediamine
EB	Elongation at break
ENB	Ethylene Norbonene
EPDM	Ethylene Propylene Diene Terpolymer
EV	Efficient Vulcanization System
FTIR	Fourier Transform Infrared
HNTs	Halloysite Nanotubes
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
K <sub>2</sub> O	Potassium Oxide
MBS	2-(morpholiniothio)benzothiazole
MBT	2-mercaptobenzothiazole
MgO	Magnesium Oxide
Na <sub>2</sub> O	Sodium Oxide
NR	Natural Rubber

PA	Palm Ash
phr	part per hundred rubber
PPD	p-phenylenediamine
S <sub>8</sub>	Sulfur
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
Semi-EV	Semi Efficient Vulcanization System
Si-264	$\gamma$ -Thiocyanatopropyltriethoxysilane
Si-69	Bis (3-triethoxysilylpropyl-) tetrasulfide
SiO <sub>2</sub>	Silicone Dioxide
SMR-L	Standard Malaysian Rubber
TEOS	Tetraethylorthosilicate
TETD	Tetraethyl Thiuram Disulfide
TGA	Thermogravimetry Analysis
TMOS	Trimethoxyoctylsilane
TMTD	Tetramethyl Thiuram Disulfide
TMTM	Tetramethyl Thiuram Monosulfide
ZDEC	Zinc Diethyl Dithiocarbamate
ZDMC	Zinc Diethyl Monothiocarbamate
ZMBT	Zinc 2-mercaptobenzothiazole



## LIST OF SYMBOLS

$^{\circ}\text{C}$	Celsius
%	Percentage
$\eta$	Viscosity (kg/ms)
$\emptyset$	Volume fraction of filler
$G_f$	Shear modulus of filled rubber (MPa)
$G_{\text{gum}}$	Shear modulus of unfilled rubber (MPa)
$\emptyset_{\text{eff}}$	Efficient volume fraction of filler
$J$	Flux
$\partial c/\partial x$	Concentration gradients
$D$	Diffusion coefficient ( $\text{mm}^2/\text{min}$ )
$d$	Thickness (mm)
$C_0$	Concentration of diffusant at time zero (M)
$C$	Concentration of diffusant (M)
$t$	Time
$x$	Distance (mm)
$Q_t$	Moles percent uptake at time (%)
$Q_{\infty}$	Moles percent uptake at equilibrium swelling (%)
$\theta$	Slope of the initial portion of the plot of $Q_t$ versus $t^{1/2}$
mm	millimeter
$M_s$	Mass of solvent at equilibrium (g)
$M_m$	Molar mass of solvent (g/mole)
$M_p$	Dry mass of samples (g)
S	Solubility
P	Permeation coefficient ( $\text{mm}^2/\text{min}$ )

$M_H$	Maximum torque (dNm)
$M_L$	Minimum torque (dNm)
$t_{s2}$	Scorch time (min)
$t_{90}$	Cure time at 90% crosslinking (min)
nm	nanometer
g	gram
mg	milligram
$V_r$	Volume fraction of rubber
$W_A$	Weight of unswollen rubber (g)
$W_B$	Weight of swollen rubber (g)
$\chi$	Interaction parameter
$\rho_r$	Density of rubber ( $\text{g}/\text{cm}^3$ )
$\rho_s$	Density of toluene ( $\text{g}/\text{cm}^3$ )
mL	milliliter

## **LIST OF APPENDICES**

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**KESAN ADITIF – ADITIF KE ATAS SIFAT – SIFAT MEKANIKAL,  
ANGKUTAN PELARUT DAN PENUAAN HABA BAGI VULKANIZAT -  
VULKANIZAT GETAH**

**ABSTRAK**

Pengaruh aditif – aditif iaitu nisbah pencepat kepada sulfur, antioksidan, dan pengisi ke atas sifat – sifat vulkanizat getah asli (GA) telah disiasat dalam kajian ini. Sifat – sifat mekanikal dan angkutan pelarut sebelum dan selepas penuaan selama 2, 4, 6, 9, dan 12 hari pada 100°C telah dijalankan. Keputusan menunjukkan bahawa vulkanizat GA mempunyai kebolehprosesan dan sifat- sifat mekanikal yang lebih baik daripada getah sintetik (SBR and EPDM). Vulkanizat GA menunjukkan rintangan penuaan haba dan pelarut yang lemah disebabkan oleh kehadiran ketidaktepuan struktur tulang belakang yang tinggi. Vulkanizat dengan sistem pemvulkanan lazim (CV) menunjukkan sifat – sifat mekanikal dan rintangan angkutan pelarut yang lebih baik tetapi mempunyai sifat – sifat terma yang lemah berbanding vulkanizat dengan sistem pemvulkanan cekap (EV) disebabkan oleh kandungan ketidakstabilan terma sambung silang polisulfida yang tinggi. Selepas penuaan selama empat hari pada suhu 100 °C, vulkanizat GA yang dimatangkan secara lazim telah kehilangan kebolehan untuk terikan teraruh penghabluran. Penambahan 2 bsg IPPD sebagai antioksidan telah memperbaiki kekuatan cabikan, rintangan angkutan pelarut dan sifat – sifat terma bagi vulkanizat GA. Penggunaan maerogel dalam vulkanizat GA telah meningkatkan sifat – sifat mekanikal dan kestabilan terma terutama sekali pada pembebanan 3 bsg maerogel bagi sistem pengisi tunggal dan 17/3 pembebanan hitam karbon/maerogel bagi sistem pengisi hibrid. Penggunaan 17/3 bsg dalam vulkanizat pengisi hibrid telah memperbaiki rintangan angkutan pelarut berbanding vulkanizat dengan pengisi tunggal. Penambahan 0.5 bsg agen pengkupel Si-69 dalam vulkanizat GA menunjukkan peningkatan bagi sifat –sifat mekanikal dan rintangan angkutan pelarut.

# **EFFECT OF ADDITIVES ON MECHANICAL, SOLVENT TRANSPORT, AND HEAT AGEING PROPERTIES OF RUBBER VULCANIZATES**

## **ABSTRACT**

The influence of additives which are the ratio of accelerator to sulfur, antioxidant, and fillers on the properties natural rubber (NR) vulcanizates were investigated in this study. The mechanical and solvent transport properties of rubber vulcanizates before and after ageing for 2, 4, 6, 9, and 12 days at 100°C were carried out. Results indicated that the NR vulcanizates have better processability and mechanical properties than synthetic rubbers (SBR and EPDM). However, NR vulcanizates showed poor heat ageing and solvent resistance due to the present of highly unsaturated backbone structure. Vulcanizates cured with conventional vulcanization (CV) system exhibited better mechanical properties and solvent transport resistance but poorer thermal properties compared with vulcanizates with efficient vulcanization (EV) system due to high content of thermally unstable polysulfidic crosslinks. After aged for four days at 100 °C, the NR vulcanizates cured with CV system loss the ability to strain induced crystallization. The utilization of 2 phr IPPD as antioxidant has improved the tear strength, solvent transport resistance, and thermal properties of NR vulcanizates. The incorporation of maerogel in NR vulcanizates increased the mechanical properties and thermal stability especially at 3 phr of maerogel loading for single filler systems and 17/3 phr of carbon black/maerogel loading for hybrid filler system. The utilization of 17/3 phr in hybrid filler vulcanizates improved the solvent transport resistance compared with single filler vulcanizates. The addition of 0.5 phr Si-69 coupling agent in NR vulcanizates showed the enhancement of mechanical properties and solvent transport resistance.

# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Synthetic rubbers have give competition to the natural rubber and its share of total world market since World War I. However, the total production of natural rubber has been able to maintain its position as a highly profitable crop despite the substantial resources of the synthetic rubber industry. Fluctuating oil prices, the main ingredient in production of synthetic rubber, has contribute to the ability of natural rubber to maintain its market share. As the price of oil increases, natural rubber becomes more attractive substitute (Wellhausen & Mukunda, 2009). Natural rubber (NR) is chemically based on cis-1,4-polyisoprene which characterized by good elastic properties, good resilience, and damping behavior but poor chemical resistance and processability. The unique mechanical properties of NR are results from highly stereo-regular microstructure with high molecular weight which contributes to the strain induced crystallization behavior (Vijayalakshmi & Jobish, 2008). However, the resistance to heat, oxygen, and ozone is poor due to the presence of high double bond content in the chemical structure (Alex & Bluma, 2002; Varghese et al., 1994). Therefore, it is important to understand the degradation of natural rubber.

Degradation of natural rubber is caused by a variety of environmental factors, such as elevated temperature, humidity, impurities, mechanical load, irradiation and chemicals. In the presence of atmospheric oxygen, the useful lifetime of many polymer products are limited by the oxidative reactions (Azura & Thomas, 2006).

The radical attack of the polymer chain causes chain scission, crosslink formation and crosslink breakage. The changes in properties of polymers on ageing depend on the extent of such reactions (Stephen et al., 2006). The changing of crosslink density by thermal ageing usually has been discussed generally for sulfur vulcanization system which contributes from sulfidic linkages. Sulfur linkages, especially polysulfides, are easily dissociated by heating and this brings about the reduction of the crosslink density. However, the curatives remaining in a rubber vulcanizates also formed new crosslinks and causes an enhancement of crosslink density (Azura & Thomas, 2006; Sung-Seen et al., 2007).

Natural rubber also widely used in general purposes, industrial, and engineering applications which include hoses, seals, sealant, o-rings, safety boots, tires, bushing, and mountings materials. A variety of liquids such as water, oil, and organic solvent are conducted through the natural rubber products. Therefore, the products should not only be excellent in term of mechanical properties, but also need to have good solvents resistance (Yoshikawa et al., 1995). A comprehensive understanding of the phenomena of molecular transport into rubber vulcanizates is very essential to determine their practical application. Transport parameters such as diffusion, sorption or solubility and permeation are strongly depending on the chemical structure, the type of crosslinking, the nature of additives, and the size of penetrant. The diffusion process is a kinetic parameter related to the free volume within the material, segmental mobility of polymer chains and the size of the penetrant molecule. Solubility is related to the limit of the solvent's amount that depends on the interaction energy of the polymer for the absorbing molecule which related to the free volume available for absorption and external concentration that

can be absorbed under any particular conditions. The process of permeation of chemicals through polymers is a combination of two interrelated mechanisms, namely, solubility and diffusion through the polymer (Lagaron et al., 2001; Pomerantsev, 2005; Stephen, 2006).

Since the natural rubber has several limitations on thermal and solvent degradations behavior due to its unsaturated backbones, many alternatives have been undertaken to overcome this problem. The utilization of suitable amounts of chemical ingredients or so called additives such as antioxidant, antiozonant and fillers in rubber compounding can give significant effect on its heat ageing properties (Dohi et al., 1976). The very high ratio of accelerator to sulfur will increase the mono- and di-sulfidic linkages percentages during vulcanization process. Thus the thermal stability of both types of crosslinks is assumed to increase the heat ageing resistance as well as solvent resistance. It is well known that the addition of antioxidant in rubber materials will inhibit the degradation by oxygen and ozone (Esposito, 1998).

The reinforcement is clarified on the most desired properties needed in rubber industry, therefore many studies on the effects of filler on the rubber properties have been reported. Reinforcing fillers such as carbon black and silica are generally give significant effect in improvement of tensile strength, modulus, abrasion resistance, tear and flexural properties. Besides the influences of filler's particle size and surface area, the filler's surface activities are also one of the critical factors in reinforcement where the enhancement of rubber – filler interactions can increase the mechanical and thermal ageing resistance (Badawy, 2000; Mostafa et al., 2009). George and



Thomas (2000) studied the effect of rubber – filler interaction between SBR and carbon black vulcanizates on transport properties and observed the strongly bonded rubber-filler interface restricts the solvent uptake. Carbon black has chemically active surface that formed by various chemical groups such as carboxyl, quinone, phenol and lactone groups. The presence of these chemical groups enhanced the filler – filler and rubber – filler interactions (Fröhlich et al., 2005). Aerogel has been invented since 1931, but due to high cost has limited its application. The new process to produce maerogel has reduced 80% cost, making it so affordable that it can become a common material for wider applications. Being an inert, non-toxic and environmentally friendly amorphous material, maerogel possesses established physicochemical properties which can be modified for specific applications. Maerogel contains pores, has a very light weight, and very low thermal conductivity. Since the maerogel is produced from rice husk, its chemical structure generally formed by silicone dioxide, SiO<sub>2</sub> (Halimatun, 2005; Jais & Abd Mukhtar, 2007). It has been expected that the incorporation of maerogel give influence on mechanical and transport properties upon heat ageing of NR vulcanizates.

## **1.2 Problem Statements**

Natural rubber usually suffer heat and oxidation degradation during processing, service, and storage due to highly content of double bond can be permanently deformed especially when they are exposed to high temperature for a long time (Ciullo, 1996). During degradation process, oxidation agents especially oxygen will react with the rubber chains resulted in oxidation reaction to produce crosslinking, chain scission, extended crosslinking and combination of molecular chains in rubber products (Rottach et al., 2007). Since the solvent transport properties

generally depending on the crosslink density and free volume of the rubber vulcanizates, the changes in crosslink density after ageing are critical. The addition of polar fillers resulting in strong filler–filler interaction giving rise to high tendency for filler agglomeration in the non-polar rubber matrix and, thus, increase solvent uptake due to low rubber – filler interaction in the vulcanizates (Sae-Oui et al., 2007). The incorporation of reinforcing fillers in natural rubber vulcanizates basically improved the mechanical and solvent transport properties. However, the addition of carbon black as filler has accelerates the oxygen uptake of sulfur-cured rubber and the reaction is accompanied by a rapid degradation of rubber (Hamza, 1998; Mostafa et al., 2009).

The utilization of very high ratio of accelerator to sulfur up to 10 in this research is expected to increase the heat ageing resistance due to less formation of polysulfidic linkages. The addition amide type of antioxidant, IPPD is to optimize the resistance on thermal degradation; thereby the changes of crosslink densities upon ageing can be reduced. In order to reduce agglomeration and to improve the interaction between maerogel and natural rubber matrix, the silane coupling agent, Si-69 has been utilized in this research. The partial replacement of carbon black by maerogel in natural rubber vulcanizates is to reduce the amount of carbon black as catalysts and decreased the rate of oxidation process.

### **1.3 Objectives of the Research**

The main aim of this study is to investigate the capability of the additives as the agents to improve mechanical and solvent uptake resistance during heat ageing

degradations of natural rubber vulcanizates. The objectives of this research are as follows:

1. To investigate the degradation behavior of NR, SBR and EPDM vulcanizates cured with different type of vulcanization systems as control samples.
2. To understand the effect of antioxidant (IPPD) on the degradation behavior of NR vulcanizates.
3. To investigate the influence of maerogel as a filler and Si-69 as coupling agent on the properties of natural rubber vulcanizates upon heat ageing process.
4. To study the effect of partial replacement of carbon black by maerogel on the thermal degradation properties of hybrid filler vulcanizates and to incorporate the Si-69 as coupling agent to improve the maerogel and rubber interaction.

In this research, the effect of additives, basically antioxidant and fillers on tensile, tear, crosslink densities and transport properties of natural rubber vulcanizates cured with efficient vulcanization systems before and after ageing for 2, 4, 6, 9, and 12 days at 100 °C were carried out. Fourier transform infrared (FTIR) characterization, morphology studies, thermogravimetry analysis as well as dynamic mechanical analysis also had been investigated.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Elastomers

Elastomers have many useful applications in engineering due to their special properties. Nowadays, many important products with high requirements are made from elastomers such as tires, seals, vibration mounts, bearing for bridges, and for seismic isolation. Elastomer is defined as a material that can be stretched repeatedly to at least twice its original length and upon immediate release of the stretch will return with force to approximately original length at room temperature (Burtscher et al., 1998; Harper, 2002). Elastomers can be divided into two categories which are natural and synthetic rubbers. The utilization of additives such as vulcanization agents, antioxidants and processing aids in rubber vulcanizates are important to optimize the properties of the product.

##### 2.1.1 Natural Rubber (NR)

Natural rubber is produced from the latex of the *Hevea brasiliensis* tree. Before coagulation, the latex was stabilized with preservatives, for examples, ammonia, formaldehyde, sodium sulfite and hydroxylamine are added to produce technically-specified, constant viscosity grades of natural rubber. Natural rubber contains 93 to 95% of cis-1, 4 polyisoprene as shown in Figure 2.1. Naturally, the great length molecular chains composed of hydrogen and carbon are flexible and independent of each other. In its raw state, natural rubber is a tough material which deforms partly by viscous flow and partly elastic. It becomes soft and sticky when warms, thereby, the practical uses as raw state are limited. Natural rubber has high



resistance. However, like other unsaturated rubbers, it is highly susceptible to degradation, due to the presence of double bonds in the main chain. Degradation of SBR is accelerated by heat, humidity, light, ozone and radiation (Ciullo, 1996; Radhakrishnan et al., 2006). Some properties of SBR such as wear resistance, heat ageing and curing properties are better than natural rubber due to the presence of styrene group in its backbone. SBR was the first major synthetic rubber to be produced commercially (Pocius et al., 2002; Sunggyu & Lee, 2005).

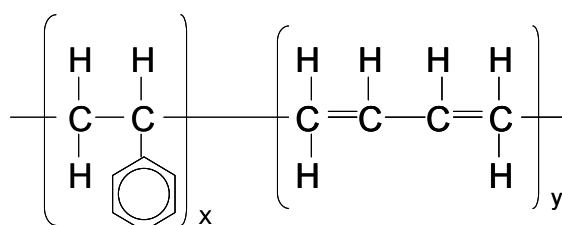


Figure 2.2: Chemical structure of styrene butadiene rubber (Pocius et al., 2002).

### 2.1.2 (b) Ethylene Propylene Diene Terpolymer (EPDM)

In the past, ethylene propylene diene terpolymer (EPDM) elastomers have been manufactured using vanadium based Ziegler-Natta catalyst system. This system has limitation in production and processing of EPDM. One of the limitations is the ability to produce high crystalline products. Typically, the highest level of ethylene achievable is around 80% by weight. Recently, metallocene catalyst based technology has been used with vanadium based Ziegler-Natta catalyst systems to produce desired ethylene levels of EPDM products (Rajan et al., 2003). Comparing with major synthetic elastomers and natural rubber, EPDM is difficult to crosslink because of its fewer double bonds. EPDM is a non-crystallize polymer, and this dominates its low stretching strength. The raw elastomer is seldom used solely because of this disadvantage. EPDM is used in a diverse range of electrical

applications because of its combinations of superior electrical properties, its flexibility over a wide temperature range, and its resistance to moisture and weather. The saturated polymer backbone of EPDM is the key to its oxidative stability and excellent weathering resistance. Proper selection of the ingredients in each category requires that consideration be given to the desired physical, electrical, and environmental properties, as well as cost, ease of mixing, chemical stability, and ease of processing. EPDM also preferred in dynamic applications due to its ageing resistance retains initial product design over time and environmental exposure. EPDM also has high demand in the industry due to its high resilience properties, good resistance to salt solutions, oxygenated solvents and synthetic hydraulic fluids (Barra et al., 1999; Harper, 2002; Lee & Kim, 2000; Zhang et al., 2007). Figure 2.3 shows the chemical structure of EPDM with ethylene norbonene (ENB) has been added as diene to produce the unsaturated site in the backbones.

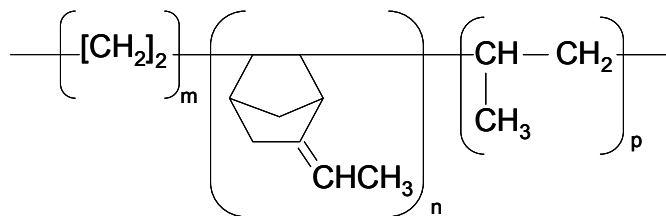


Figure 2.3: Chemical structure of ethylene propylene diene terpolymer (Barra et al., 1999).

## 2.2 Ingredients

Additives such as vulcanization agents, accelerator, activator, fillers, processing aid and others are selected depending on the technical needs and economy. Raw rubber is mixed with the additives by particular processing machine generally two roll-mills and internal mixer.

### **2.2.1 Curing Agents**

Curing agents are utilized to induce chemical reaction in crosslinks formation between rubber molecule chains. Sulfur is commonly used due to low cost (Long, 1985).

#### **2.2.1 (a) Sulfur**

Sulfur reacts chemically with the raw gum elastomer to form crosslinks between the polymer chains, resulting in more dimensionally stable and less heat-sensitive product. The cost is relatively low but its function is essential. There are two types of sulfur possibly used in vulcanization which are soluble (rhombic crystal of S<sub>8</sub> rings) and insoluble (amorphous, polymeric sulfur). As the sulfur level in a compound is increased, some of it can slowly bloom to the surface. Blooming occurs if an additive dissolves totally in the polymer at the processing temperature but is only partially soluble at ambient temperature. In this situation some of the additive precipitates out of solution on cooling, can be collected on the surface of the polymer mass, that caused a bloom. Bloomed sulfur reduced the “tackiness” of rubber vulcanizate. Therefore, the insoluble sulfur is generally selected to prevent sulfur migrate on the surface of vulcanizate (Ciesielski, 1999; Hamed, 1992).

#### **2.2.1 (b) Peroxide**

Saturated backbone rubbers are unable to be crosslinked with sulfur vulcanization system. Organic peroxides are preferred to cure these types of rubber. Peroxide vulcanization takes place via a free-radical mechanism and leads to carbon-carbon (C–C) crosslinks which are quite stable. This will lead to the good ageing resistance as well as improving compression set and creep properties of rubber products. There are some disadvantages where peroxides are rather hazardous



chemicals and require more attention to safe storage and handling procedures than others curing ingredients. Certain types of peroxides produce unpleasant odors in vulcanization and in the vulcanizates. They react more readily with other ingredients than conventional sulfur vulcanization systems, for example, antioxidant which restricted its efficiency. Peroxides are not suitable for vulcanization during the presence of oxygen, such as hot air cures due to radical transfer from the peroxide to the polymer chain can be oxidized. This means that a hydroperoxide can form readily, and when this is thermally decomposed it leads to polymer degradation (Barlow, 1993; Morton, 1973).

### **2.2.2 Accelerators**

The finding of organic accelerator by Oenslager in 1906 that enhance the vulcanization rate and at the same time increase the productivity. The utilization of accelerator also can be vary the vulcanization systems, methods and temperature of processing. The important function of accelerator is to reduce the cure time by accelerate the rate of crosslinks formation. Most of accelerators used contain nitrogen and sulfur (Esposito, 1998; Long, 1985).

The advantages of accelerator are as given belows:

- Cost effective.
- Produce the final products with good physical properties.
- Improve appearance and avoid blooming on the products.
- Enhanced the resistance of degradation.
- Allow vulcanization process to occur at high or low temperature.

There are several types of accelerators generally used in rubber industry such as guanidines (DPG, DOTG), tiazoles (MBT, ZMBT), sulfenamides (CBS, MBS, DCBS), thiurams (TMTD, TETD) and dithiocarbamates (ZDC). Table 2.1 shows the type of accelerators can be used for vulcanization process of rubbers (Blow, 1971; Datta, 2001; Esposito, 1998) and Figure 2.4 showed the chemical structure of 2-Benzothiazolesulfenamide,N-cyclohexyl (CBS).

### 2.2.3 Activators

Generally, the reaction of most organic accelerators will be reached to the optimum with the present of activator. There are two types of activator which are metal oxides and organic acids. Zinc oxide is a metal oxide commonly used in vulcanization of rubber as an activator. For organic acids such as stearic acid, oleic acid and lauric acid are usually chosen for vulcanization process of rubber. The combination of zinc oxide and stearic acid, together with sulfur and accelerator, constitute the vulcanization system for the formulation. Zinc oxide reacts with stearic acid to form zinc stearate and along with the accelerator, the rate of sulfur vulcanization will increases (Ciesielski, 1999; Esposito, 1998).

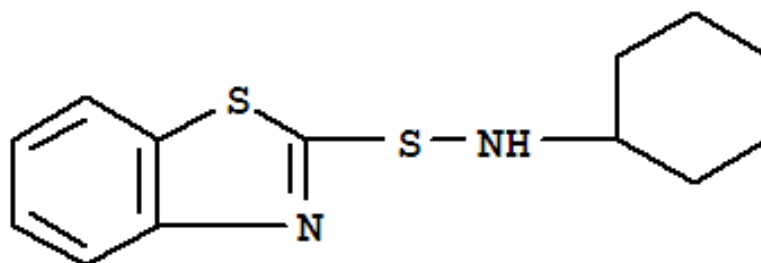


Figure 2.4: Chemical structure of N-cyclohexyl 2-benzothiazole sulfenamide, CBS (Datta, 2000).

Table 2.1: Technical effects of organic accelerators in natural rubber vulcanizates (Blow, 1971).

<b>Range of Speed/Temperature</b>	<b>Type of accelerator</b>	<b>Suggested amount of accelerator(phr)</b>	<b>Amount of sulfur (phr)</b>
Intermediate/ Low (140 – 180 °C)	Guanidines (DPG, DOTG)	1.0 – 1.2	3.0 – 5.0
Semi-fast (130 – 160 °C)	Tiazoles (MBT, MBTS)	0.7 – 1.0	2.5 – 3.5
Fast (130-160 °C)	Sulfenamides (CBS, MBS)	0.5 – 1.5	1.0 – 2.5
Very fast (110 – 130 °C)	Thiurams (TMTD, TETD, TMTM)	0.5 – 2.0	0.5 – 2.0
Over fast (70-110 °C)	Dithiocarbamates (ZDMC, ZDEC)	0.3 – 0.5	0.5 – 1.5

#### 2.2.4 Antioxidants

The most common antioxidants are derivatives of aromatic amines and phenols. In most rubber systems, amines are more effective in preventing long-term oxidative degradation. However, amine antioxidants usually discolor with ageing and may not be the system of choice for light and brightly colored rubber articles where color retention is important. Phenolic antioxidants, in contrast to amine antioxidants, no discolor on ageing but are generally less effective in preventing long-term oxidative degradation. Thus, a compromise may be necessary in the formulation of light or brightly colored rubber vulcanizates. The various antioxidants used in the industry are low-molecular weight vulcanizates, but they will lose their effectiveness over time. They are lost by evaporation, extraction, and migration. Sometimes, they bleed out of the system due to low compatibility (Johnson, 1975; Pospisil et al., 2003; Zaharescu et al., 1995).

p-Phenylenediamine (PPD) is used as an antioxidant and antiozonant for natural and synthetic elastomers and as an antiflex agent for the protection against catalytic degradation by copper and other heavy metals. PPD is chosen because it imparts high temperature stability, high strength, and chemical and electrical resistance. Examples of the most widely used antioxidants or antiozonants derived from p-phenylenediamine are N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), N,N'-Diphenyl-p-phenylenediamine (DPPD), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), and N-Cyclohexyl-N'-phenyl-p-phenylenediamine (CPPD). These derivatives are added to rubber products to retard the degradation by oxygen and ozone (Malshe et al., 2006; Ismail et al., 1997). Figure 2.5 showed the chemical structure of IPPD.

### 2.3 Vulcanization Process of Elastomers

The main reason of vulcanization process is to modify the raw rubber into elastic material with stable dimension. Rubber molecular chains with unsaturated backbones can be vulcanized by accelerated sulfur vulcanization system where the sulfur can attack the double bonds, whereas, for rubber with saturated backbones, it can be vulcanized by peroxide curing system ( Hamed, 1992; Hoffman, 1989; Ivany, 1995). Table 2.2 showed the bond energies of different crosslink types.

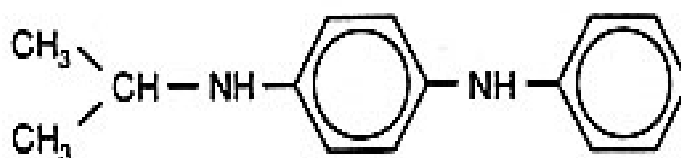


Figure 2.5: Chemical structure of N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) (Ismail et al., 1997).

Table 2.2: Bond energies of different crosslink types (Ivany, 1995).

<b>Types of linkages in rubber network</b>	<b>Bond energies, kJ(mole<sup>-1</sup>)</b>
-C – S <sub>x</sub> – C – (x > 2)	< 268
- C – S <sub>2</sub> – C –	268
- C – S – C –	285
- C – C –	352

### 2.3.1 Accelerated Sulfur Vulcanization System

The accelerated sulfur vulcanization system is the most popular method to produce rubber products. In general, the rubber compound with an accelerated sulfur vulcanization system contains elemental sulfur (S<sub>8</sub>), accelerators and activators. Crosslink network types and crosslink density are known to significantly influence the mechanical and ageing properties of rubber vulcanizates. In general, accelerated sulfur vulcanization system contains predominantly mono- and di-sulfidic networks, and polysulfidic networks along with sulfidic pendant groups and mono- and di-sulfide cyclic groups as shown in Figure 2.6, respectively. The presence of those types of crosslinks will determine the final properties of rubber vulcanizates (Blow, 1971; Rahiman et al., 2005).

The mixtures used for sulfur vulcanization are usually classified into three systems namely conventional (CV), semi-efficient (semi-EV), and efficient (EV) vulcanization systems. The distinction between the three classes are based on the accelerator to sulfur ratios which are 0.1 to 0.6 for conventional, 0.7 to 2.5 for semi-efficient and 2.5 to 12 for efficient (Aprem et al., 2003). Figure 2.7 shows the schematic representation of accelerated sulfur vulcanization process of natural rubber.

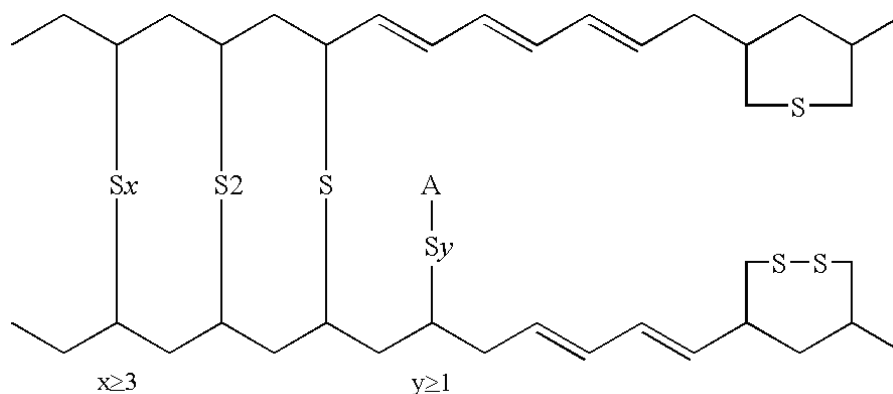


Figure 2.6: Type of sulfidic linkages (Rahiman et al., 2004).

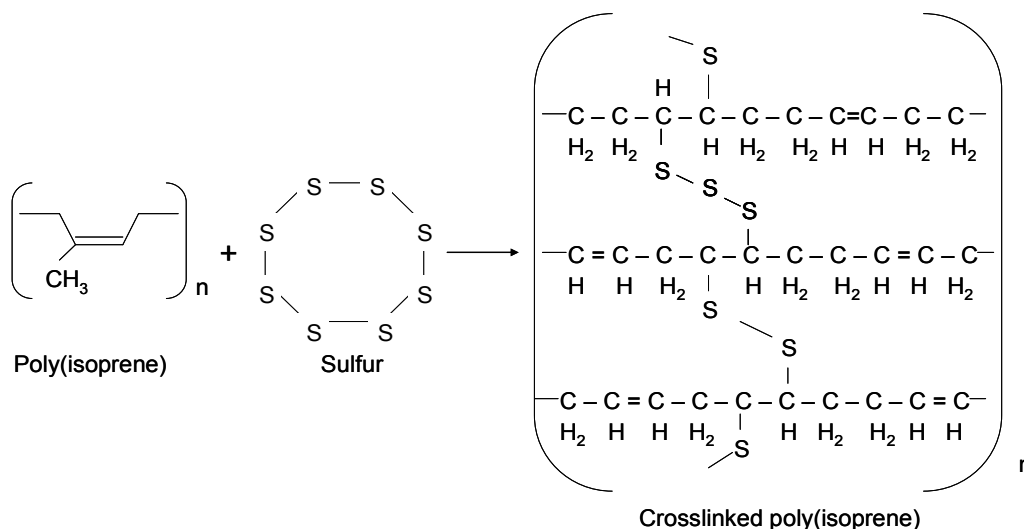


Figure 2.7: Schematic representation of accelerated sulfur vulcanization process of natural rubber (Aprem et al., 2003).

The increased in accelerator to sulfur ratio is believed to reduce main chain modifications, reduce formation of cyclic structures, reduce the rank of sulfur crosslinks, and improve vulcanization efficiency. These changes in structure has been correlated with improved mechanical and ageing properties. At the early stage of vulcanization, the network formation is not depending on the type of formulation or vulcanization system and the initial network contains dominantly polysulfidic linkages. With longer curing time, EV system is tend to form the network structure

of monosulfidic linkages and pendant groups. Whereas CV system which contains higher amount of sulfur with lower accelerator concentration compare to EV system, is tend to form polysulfidic linkages. For semi – EV, the percentages of mono-, di-, and polysulfidic crosslinks formation are similar. The types of vulcanization systems are the major factor to influence the curing rate, crosslink density in rubber network and the properties of final product (Ehabe & Farid, 2000; Dick & Annicelli, 2001). Table 2.3 shows the comparison of final product properties cured with different types of accelerated sulfur vulcanization system.

Table 2.3: Type of accelerated sulfur vulcanization system and their final product properties (Dick & Annicelli, 2001).

<b>Type of accelerated sulfur vulcanization system</b>	<b>CV</b>	<b>Semi - EV</b>	<b>EV</b>
Di- and poly-sulfidic linkages, %	95	50	20
Monosulfide linkages, %	5	50	80
Cyclic sulfidic concentration	High	Medium	Low
Ageing resistance	Low	Medium	High
Reversion resistance	Low	Medium	High
Compression set, % (22 hours at 70 °C)	30	20	10

### 2.3.2 Peroxide Curing System

Peroxides generate free radicals that are capable of crosslinking a wide variety of saturated and unsaturated polymers, respectively. Peroxides create strong carbon-carbon type crosslink bonds which allow the finished product manufacturer to better utilize the full potential engineering of the elastomers. The vulcanizates crosslinked with peroxides have better thermal heat ageing properties, lower

compression set, and good low temperature flexibility (George et al., 1999; Patterson & Keonig, 1984). Figure 2.8 shows the schematic of peroxide curing process of natural rubber.

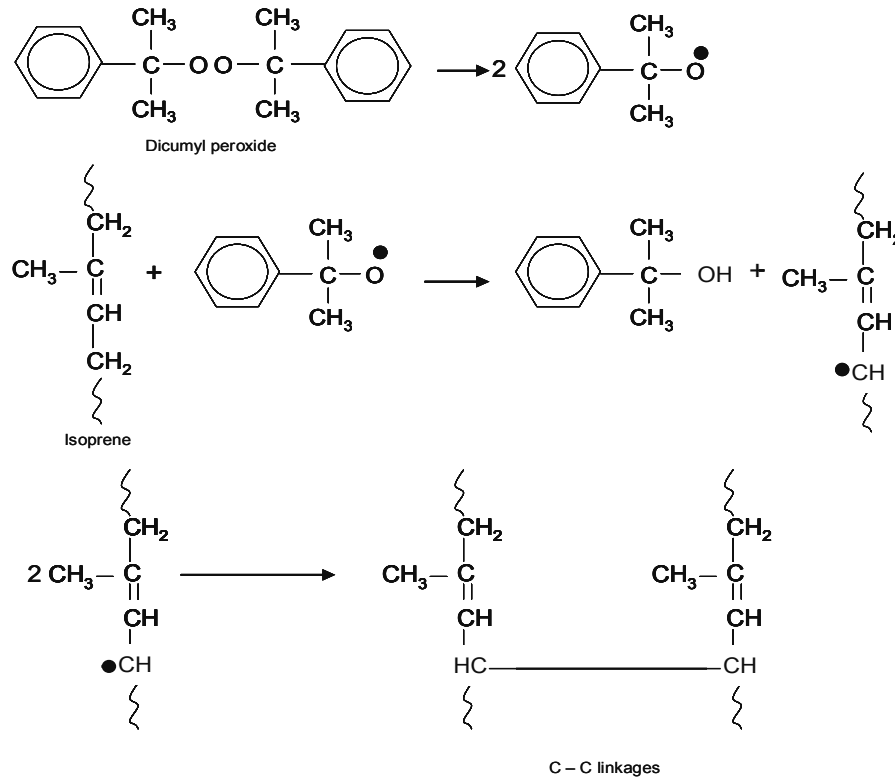


Figure 2.8: Schematic of peroxide curing process of natural rubber (Patterson & Keonig, 1984).

## 2.4 Type of Fillers

For decades, fillers have been widely used in the rubber industry. They are incorporated into rubber compound for many purposes, for example, to improve processability, to reduce cost, and also to modify the physical properties of the vulcanizates (Arayaprane et al., 2005; Sae-Oui et al., 2009; Taha et al., 2010). Generally, fillers can be classified into three main groups, which are reinforcing fillers, semi-reinforcing fillers, and non-reinforcing fillers. Among commercial fillers, carbon black and precipitated silica is the most important reinforcing fillers



and these are extensively used when high strength is essential. Reinforcing fillers such as carbon black and silica are generally give significant effect in improvement of tensile strength, modulus, abrasion resistance, tear and flexural properties. However, for some applications where cost and processability are the greatest concern, the use of non- or semi-reinforcing fillers such as clay, talc, and calcium carbonate is highly recommended. These types of fillers give advantages in the enhancement of stiffness and reduce the tackiness of unvulcanized vulcanizates. Non-reinforcing fillers also play role in the increment of hardness and the decrement of tensile strength, resilience, resistance to abrasion and tear properties. Normally, this type of filler is used to reduce the cost of final product (Esposito, 1998; Sae-Oui et al., 2009).

#### **2.4.1 Carbon Black**

Carbon black is generally used as filler in rubber production to modify the mechanical properties of the tire. Carbon black is produced from incomplete combustion or thermal cracking of a hydrocarbon raw material as shown in Figure 2.9. Nowadays almost all carbon black is manufactured by the oil furnace process where a highly aromatic feedstock is partially burned by atomization into a hot flame made of natural gas and preheated air with the reactor temperature reaching more than 1500°C. At the end of the process, powder (“fluffy”) or palletized carbon black is collected (Crump, 2000).

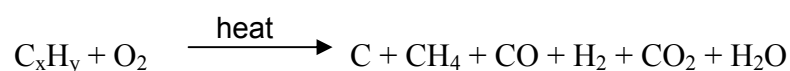


Figure 2.9: Partial oxidation of aromatic hydrocarbons (Crump, 2000).

Carbon black is a particulate form of industrial carbon which exhibits a “quasi-graphitic” microstructure. During the nucleation process as illustrated in Figure 2.10, three to four layers form crystallites are combined to form primary particles and grow into aggregates. The aggregates are then to form agglomerate due to the small distances between them and the presence of strong van der Waals forces (Accorsi, 1999).

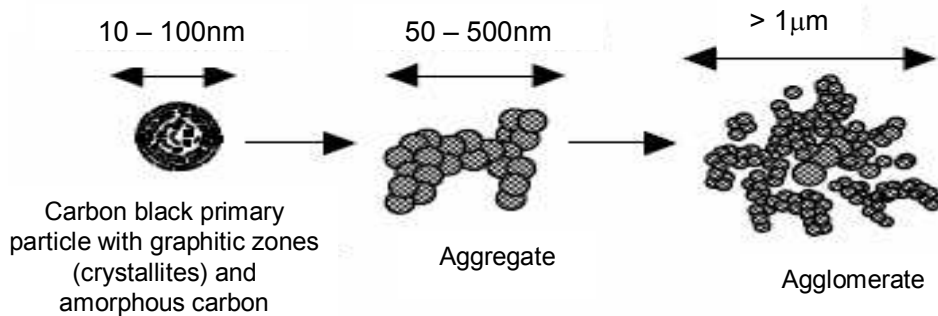


Figure 2.10: Aggregates and agglomerates formation of carbon black primary particles (Accorsi, 1999).

The carbon black reinforcement depended on the nature of the carbon black, including the primary particle size, the structure of the filler particle, and the surface activity. The particle size of carbon black is one of the important characteristics to determine the properties of final product. As particle size becomes smaller, the surface area increases, providing more available contact between the rubber molecule and the filler particle. Small particle can be defined as reinforcing filler due to its potential to increase the mechanical properties such as tensile strength, fatigue and tear resistance. On the other hand, the large particle size will enhance the resilience properties and reduce permanent set. As is well known, high structure blacks exhibit a high number of primary particles per aggregate, which is called a strong aggregation, whereas low structure blacks show only a weak aggregation. These

aggregates may form loose agglomerates linked by van der Waals interactions. The empty space (void volume) within the aggregates and agglomerates, usually expressed as the volume of dibutylphthalate (DBP) absorbed by a given amount of carbon black are refer as structure of carbon black. The larger the DBP value, the higher the carbon black structure (Dick, 2004; Edward, 1990; Li et al., 2008; Long, 1985; Tricás et al., 2002).

Carbon black has chemically active surface that formed by various chemical groups (Figure 2.11) such as carboxyl, quinone, phenol and lactone groups. The interaction between rubber and filler generally is related to the formation of strong covalent bonding especially in unsaturated rubber and as a result, carbon black can be a good reinforcing agent in rubber vulcanizate (Fröhlich et al., 2005). The physical surface of carbon black such as porosity will increase the surface activities. One of the significant effects in increment of carbon black's reactivity is bound rubber (Kohls & Beaucage, 2002; Rothon, 2003). Table 2.4 shows the effect of particle size and structure of carbon black on properties of final product.

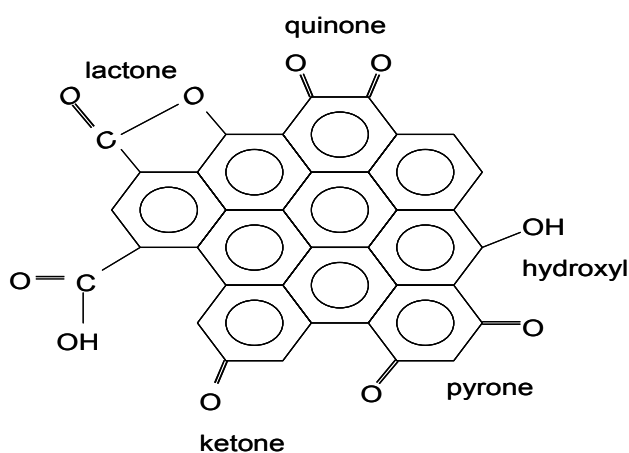


Figure 2.11: Chemical groups on the surface of carbon black (Kohls and Beaucage, 2002).

Table 2.4: Effect of particle size and structure of carbon black on rubber vulcanizate properties (Long, 1985).

<b>Rubber Properties</b>	<b>Reduction of particle size</b>	<b>Increment of structure</b>
Hardness	Increase	Increase
Tensile strength	Increase	Vary
Modulus	Not a major factor	Increase
Elongation at break	Not a major factor	Decrease
Resilience	Decrease	Not a major factor
Dimension stability	Not a major factor	Decrease
Compression set	Increase	Increase
Fatigue resistance	Increase	Increase

#### 2.4.2 Silica

Silica is the name given to a group of minerals composed from one atom of silicon and two atoms of oxygen which the chemical formula is  $\text{SiO}_2$ . The most common form of naturally occurring crystalline silica is quartz, sand and flint. The micro-crystalline silica can be obtained by, for example, crushing, pulverizing and purifying quartzite. The inertness and purify of this crushed vulcanizate, make it a useful reinforcing filler for elastomers (Whelan, 1994).

Synthetic silica can be broadly divided into two categories of stable materials which are vitreous silica or glass and micro-amorphous silica. Vitreous silica or glass is made by fusing quartz at temperatures greater than  $1700^\circ\text{C}$ . Micro-amorphous silica includes silica gels, powders, and porous glasses. Amorphous silica consist a silicon atom covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form either a siloxane (-Si-O-Si-) or a silanol (-Si-O-H) functionally. As opposed to carbon black, which has a lot of different functional groups but in small quantities,

silica has few different chemical groups but in large amounts. Silica has a high-energy surface, because of the siloxane and silanol groups. Silanols can be single or paired. Paired silanols are close enough to each other to develop such interactions as hydrogen bonds. They are either bonded by the same silicon atom and said to be geminal, or bonded by two adjacent silicon atoms and called vicinal as shown in Figure 2.12 (da Costa et al., 2000; Jacqueline & Mary, 1999; Waddell & Evans, 1996).

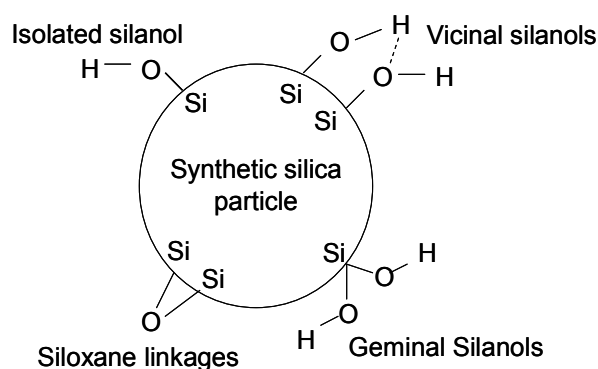


Figure 2.12: Silica surface groups which are siloxane linkages, isolated, vicinal and geminal silanols (Waddell & Evans, 1996).

Silica provides a unique combination of tear strength, abrasion resistance, age resistance, and adhesion properties to rubbers. As silica is highly polar filler, the filler–filler interaction is quite strong giving rise to high tendency for filler agglomeration in the non-polar matrix and, thus, the difficulty in processing. In addition, the presence of silica has negative effects on cure and elasticity of rubber because the silanol groups on silica surface can adsorb the cure activator necessary for sulfur vulcanization (Hexiang et al., 2007; Sae-Oui et al., 2007).

### 2.4.3 Aerogels

Aerogels can be defined as materials in which the typical pore structure and network are largely maintained when the pore liquid of a gel is replaced by air are called aerogels (Nicola & Ulrich, 2005). Aerogels are the lightest of all solid substances. Aerogels consist of nano-meter sized particles are 1 to 10 nm in diameter, which stick together and form chains. These particles have so many points of contact that established a stable three-dimensional network (Figure 2.13) with the distance between the chains is typically 10 to 100 nm (Faez et al., 2005; Levy, 2004). Aerogels are inert, non-toxic, environmental friendly, insulation materials, and have superior performance (Creasey, 1999). The classification for porous materials where pores of less than 2 nm in diameter are called "microporosity", those with diameters between 2 and 50 nm are called "mesoporosity", and those are greater than 50 nm in diameter are called "macroporosity". Aerogel possess pores of all three sizes. However, the majority of the pores fall in the mesoporosity regime, with relatively a few of microporosity as shown in Figure 2.14 (Rolison & Dunn, 2001). The aerogel has many commercial applications such as catalysts, windows, particle detectors, super-capacitors, insulation for heat storage in automobiles, and electrodes for capacitive deionization which depends on physical and chemical properties of aerogels (Hrubesh, 1998).

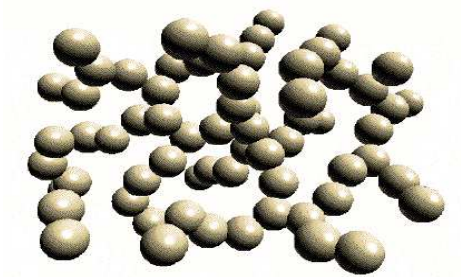


Figure 2.13: Three dimensional network of aerogel (Creasey, 1999).