

**THE EFFECT OF CARBON BLACK AND SILICA
FILLERS ON CURE CHARACTERISTICS AND
MECHANICAL PROPERTIES OF BREAKER
COMPOUNDS**

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UNIVERSITY SCIENCE MALAYSIA

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ON CURE CHARACTERISTICS AND MECHANICAL
PROPERTIES OF BREAKER COMPOUNDS**

by

YAM KOK PENG

**Thesis Submitted in Fulfillment of the
Requirements for the degree
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LIST OF SYMBOLS

M_L	Minimum Torque/Viscosity
M_H	Maximum Torque/Viscosity
$S'@M_L$	Minimum Elastic Torque
$S'@M_H$	Maximum Elastic Torque
t_{s1}	Induction Time
t_{s2}	Scorch Time (time require to raise 2 unit from minimum torque)
t_{s5}	Scorch Time (time require to raise 5 unit from minimum torque)
t_{c90}	Optimum Vulcanization Time
E_B	Elongation at break
M_{300}	Modulus at 300% elongation

LIST OF ABBREVIATION

SBAT	Standard Block Adhesion Test
SMR	Standard Malaysian Rubber
TCR	Technically Classified Rubber
TSR	Technically Specified Rubber
NR	Natural Rubber
SR	Synthetic Rubber
BR	Butadiene Rubber
ASTM	American Society for Testing and Material
IRHD	International Rubber Hardness Degrees
HAF	High Abrasion Furnace
PHR	Part per Hundred Rubber
MDR	Moving Die Rheometer

Kesan pengisi karbon hitam dan silika ke atas ciri-ciri pematangan dan sifat-sifat mekanikal sebatian 'breaker'

ABSTRAK

Ketahanan sistem rantai tayar yang berprestasi tinggi adalah bergantung kepada ikatan yang terhasil antara dawai besi dan campuran getah. Campuran getah yang digunakan dalam penglitup dawai besi merupakan campuran 'breaker'. Campuran getah dengan jumlah silica dan karbon hitam yang berlainan disediakan dengan menggunakan pengisar rol dua, kemudian ujikaji dalam sifat campuran getah tervulkan, sifat mekanikal dan ketahanan terhadap penuaan. Dalam sifat tervulkan, karbon hitam yang tinggi dalam suatu campuran getah akan menurunkan masa pengvulkanan campuran getah dan masa lecur, meningkatkan nilai M_H , M_L dan ketumpatan pematangan. Pengisi silika akan meningkatkan masa lecur, masa pengvulkanan, M_H dan ketumpatan pematangan apabila digunakan. Dalam sifat mekanikal, kekuatan tensil dan kekuatan tarik keluar juga meningkat apabila jumlah kandungan karbon hitam meningkat. Tetapi selepas tahap maksimum, kekuatan tensil dan kekuatan tarik keluar akan menurun jika jumlah karbon hitam masih meningkat. Selain itu, pengantian karbon hitam dengan silika jelas sekali akan meningkat sifat kekuatan tarik keluar dan kekuatan tensil. Walaubagaimanapun, sifat ini akan menurun jika jumlah silika melebihi jumlah optimum. Selepas proses penuaan, ketahanan penuaan terhadap M_{300} and kekerasan meningkat, penurunan nilai dalam E_B and SBAT. Ketahanan penuaan terhadap kekuatan tensil menurun kecuali 15phr silika digunakan.

The effect of carbon black and silica fillers on cure characteristics and mechanical properties of breaker compounds

ABSTRACT

The reliability of a high performance steel belt tyre is significantly dependent on the adhesion of steel reinforcement to rubber compound. Rubber compounds used to coat on the steel belts was known as breaker compound. Rubber compounds which were filled with different dosage of silica and carbon black was prepared by using two roll mills and then were studied on cure characteristics, mechanical properties and aging properties. On cure characteristics, higher loading of carbon black had decreased the cure time and scorch time, higher value of M_H , M_L and crosslink density. Silica fillers have increased scorch time, cure time, $S'@M_H$ and crosslink density when used in the rubber compound. On the mechanical properties, tensile strength and pull out force (SBAT) increased as the amount of carbon black increased until a maximum value, after which the value decreased. When silica added into the rubber compound system, it significantly increased the pull out force but decreased after the optimum value achieved. After aging process, aging retention of M_{300} and hardness increased, lower at E_B and SBAT values. Aging retention of tensile strength decreased except for those using 15phr silica.

OBJECTIVES

Tyre is common thing that we use everyday such as motorcycle tyre, vehicle tyre, bus tyre, commercial tyre, monorail tyre and etc. The important of tyre is no doubt for this century with the improvement of science and technology especially in automotive industries as well for tyre industries. The growth in automotive to produce luxury and sport car where the aspect of tyre safety, performance and durability are highly concern for consumer. Tyre make from many type of rubber compound and fabric. Different compounds pay a different role in tyre. But most tyre fail is due to poor adhesion between fabric to rubber compound and the heat generated during tyre performance. Fabric can be defined as a nylon, polyamide, polyester, woven, carbon and steel wire.

Breaker compound define as a compound where bonding occur between two different materials such as rubber and fabric. Without any bonding, each component can't hold together to give a good adhesion performance. Breaker compound give a very important role in tyre performance because most of tyre fail at these area. Basically breaker consists of rubber compound and steel cord coated with brass. The adhesion of rubber to brass-coated steel cord has been the subject of much research over the last 30 years and it is well known that such adhesion is significant enhanced with the addition of cobalt. When time pass a strong adhesion are required, therefore additional adhesion promoter was added such as hexamethoxymethylmelamine. Nowadays, there are a dramatically increase of price for synthetic and natural rubber. Most of the tyre manufacturer use fillers such as silica and carbon black to reduce the amount of rubber. Different

fillers give a different physical properties to the end product such as adhesion to fabric, heat generated, Mooney viscosity, hardness, scorch, tensile and etc.

A tyre undergoes repeated stress cycling during service causing a temperature rise due to the heat generation in the vulcanizate belt is located beneath the tread undergoing compression and bending. The operating temperature would be as high as 60°C with passenger car tyres. Under this situation, the physical properties of the belt-skim vulcanizate are gradually changed by oxidative aging. The aging properties on belt-skim during service were study by Hiroyuki Kaidou and A. Ahagon, 1990.

A research needs to be conduct to evaluate the effects of carbon black and silica fillers on cure characteristics and mechanical properties of breaker compounds before and after aging process.

The objectives of this project are:

- 1) To study the effect of carbon black and silica on the curing characteristics of breaker compound.
- 2) To study the effect of carbon black and silica on the physical properties of vulcanizate breaker in tyre.
- 3) To study the effect of aging on the characteristics of vulcanizate breaker using different dosage of carbon black and silica.

Chapter One: 1.0 Literature Review

1.1 Natural Rubber

1.1.1 History and Development

Natural rubber also has been called ‘the supreme agricultural colonist of all times’. It is originally indigenous from the Amazon Valley forest, but has been cultivated principally in Southeast Asia, especially for countries like Malaysia and Indonesia. Where more than fourteen million acres of land have been cleared and planted with rubber trees (Myers, 1973).

Priestley, the English chemist, gave the name ‘rubber’ to the raw material in 1770, when he found it would ‘rub off’ pencil marks. In early 1800’s, a Scotsman, Macintosh, patented the first raincoat, consisting of a layer of rubber sandwiched between two thicknesses of cloths. A London, coachman Thomas Hancock, then cut rubber into long strips, and invented the ‘rubber band’ in 1823. In 1839, the tremendous discovery of vulcanization occurred, which ultimately made possible the multibillion dollar industry of today. The combination of sulfur dust and heat added to raw rubber resulted in remarkable resistance of the ‘vulcanized’ rubber to extreme temperature changes has found by Hancock and Charles Goodyear (Myers, 1973).

In 1846, Thomas Hancock made solid rubber tyres for the carriage of Queen Victoria, thereby launching our present vast tyre industry. In 1877, a consignment of 22 seedlings was shipped to Singapore and planted in Economic Gardens. By 1888, about one thousand trees were scattered throughout the Malaya Peninsula. Henry Ridley suggested to plant rubber trees instead of coffee. Ridley anticipated that the newly invented pneumatic tyre,

Although the chemical building block of the polymer is always the same, i.e. polyisoprene. Natural rubber (NR) is available in many grades related to its 'dirt' content (comes from tree) and precise method of production. Popular grades are ribbed smoked sheet (RSS) and technically specified rubber such as SMR (Standard Malaysian Rubber) and SIR (Standard Indonesia Rubber). All of these are sub graded by dirt content. Grades are RSS1 to RSS5 and SMR 5, 10, 20 and 50; the lower number, the cleaner of the grade, and therefore the more expensive. To achieve more consistence viscosity control of NR a specialized grade known as SMR CV (constant viscosity) is available. This grade has 0.15% of a hydroxylamine salt added to prevent a 'cross linking' phenomenon known as storage hardening, which causes an increasing viscosity during storage.

Properties of vulcanized product made from natural rubber are as follows:
(Ciesielski, 1999)

- High mechanical strength and can be compounded to have excellent elasticity.
- Good abrasion resistance, low relative cost, significant choice for slurry pump liner and impellers as well as for tank lining.
- Good dynamic mechanical properties used in tires, rubber springs and vibration mounts.
- Very good low temperature resistance, down into the region of -57°C .
- Its high temperature heat ageing resistance limit for 'continuous' use in the region of 75°C .
- Inherent weather (UV light and ozone) resistance provided by the raw gum elastomer is poor.

- Electrical insulation is very good.
- Dilute mineral acid (although not oxidizing acids such as nitric) and dilute base resistance is good.
- Resistance to petroleum oils is poor while resistance to alcohols and ketones is much better.

Rubber also capable of adhering to textile fibres and metals; such as rayon, polyamide, polyester, glass or steel cord. Depending on the properties of the reinforcing member, the tensile strength is increased considerably with the presence reduction in extendibility (Hofmann, 1989). This use in most of the composites increases the range of applications of rubbers considerably.

1.1.2 Type of Natural Rubber

Natural rubber can be isolated from more than 200 different species of plants, however only one tree source, *Hevea Brasiliensis*, is commercially significant (Myers, 1973). Early in the century, a large tree *Funtumia elastica* was exploited in tropical Africa, as was the *Landolphia* species, a climbing shrub. In Mexico, the large tree *Castilloa elastica* also provided rubber. In South America, the Ceara Rubber tree, *Manihot glaziovii*, was another source. From all of it, none could compete with *Hevea Brasiliensis* in yield, frequency of tapping or longevity (Myers, 1973).

Most commercial natural rubbers have Mooney's Viscosity value of about 60 ± 5 when freshly coagulate. Commercial rubbers obtained from cloned blends may have average molecular weights of $1.0-1.5 \times 10^6$ and number average molecular weights of $3.0 \times 10^5 - 5.0 \times 10^5$. Sterols, ester and fatty acids in the natural rubber can be extracted by acetone. Fatty acids in natural rubber help in the vulcanization reaction while proteinaceous matters can serve as accelerator. Analysis of a representative sample of natural rubber is shown in Table 1.1.

In addition, natural rubber has a very good abrasion resistance. It also shows very good low temperature resistance, down into the region of -57°C at which its stiffness shows a considerable increase. The composition of a representative sample of natural rubber is shown in Table 1.1.

Table 1.1: Analysis of a representative sample of natural rubber (Mark, 1994).

Component	Percentage
Acetone Extract	2.7
Protein*	2.8
Ash	0.5
Rubber Hydrocarbon	93.6
<i>Total</i>	<i>100.0</i>

* calculated from percentage of nitrogen

Natural rubber obtain in 2 different stages; 1) latex is obtained by a process called tapping and ribbed smoked sheet. Latex flows for about 4 hours, and auto-coagulation is prevented by placing a small amount of liquid ammonia. 2) Ribbed smoked sheet is made from whole-field latex; diluted to about 15% solids and then coagulated with dilute formic acid (James Mark, 1994). In addition to the standard ribbed smoked sheets which are graded from 1 to 5, depending on the appearance and purity, there are the non-smoked grades which are 'air-dried' sheets. The latter has high degree of purity and vulcanization properties (Hofmann, 1989).

The smoked sheets rubber and pale crepe have different properties from different plantations vary with respect to process and cure rate. Therefore, the natural rubber has been classified by two standards such as Standard Malaysian Rubber (SMR) and Technically Classified Rubber (TCR) (Hofmann, 1989). TCR is a visually classified natural rubber, where cure properties evaluated and graded. SMR is the most important NR grade belongs to the

group of Technically Specified Rubber (TSR). The first SMR was introduced in 1965. The SMR graded shown on Table 1.2.

Table 1.2: Standard Malaysian Rubber Specification (Hofmann, 1989).

Parameter	SMR CV	SMR LV	SMR L	SMR WF	SMR 5	SMR GP	SMR 10	SMR 20	SMR 50
	Latex				Sheet material	Blend	Field Grade Material		
	Viscosity Stabilized								
Dirt retained	0.03	0.03	0.03	0.03	0.05	0.10	0.10	0.20	0.50
Ash content	0.50	0.50	0.50	0.50	0.60	0.75	0.75	1.00	1.50
Nitrogen content	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Wallace Rapid Plasticity	-	-	30	30	30	-	30	30	30
Plasticity Retention index	60	60	60	60	60	50	50	40	30

1.1.3 Usage and Application of Natural Rubber

Natural rubber is a very versatile raw material, had a widely application use on industry material and domestic. Natural rubber can be directly used for making adhesive tapes, rubber solutions or art gum but most is vulcanized. With the increasing and improvement of Synthetic Rubber (SR) grades, natural rubber has been slowly replaced in many applications which require heat and swelling resistance. But natural rubber is preferably used in large tyres due to its poor conductor of heat and heat build-up, always been of great important for producing truck tyres. With the introduction of passenger radial tyres and heavy radial truck tyres, the used of natural rubber has been increase. The excellent flexibility of natural rubber is suitable for sidewall compound and its low heat build-up results in cooler running tyres (Hofmann, 1989). Natural rubber also has important application in the production of thin walled such as balloons,

surgical gloves or sanitary rubber product due to its strain crystallization and self-reinforcing properties.

1.2 Fillers

The fillers are the primarily classified as carbon blacks and light colour fillers. Among the light colour fillers chemical composition is primarily the basis for classification. With each class of fillers, different degrees of activity are present. Basically, most carbon black, colloidal silica and most small particle size silicates belong to the high and medium activity fillers, while chalk belongs to inactive fillers.

1.2.1 Carbon black

Carbon black is a material that has been known and produced since olden days but only found its widespread manufacture and use in the last century when it was discovered that when mixed into rubber it improves its mechanical properties (Baranwal, 2001). The increase in strength of the rubber containing carbon black led to many practical application of the rubber throughout the world. The ability of tyres to last longer is primarily due to the strength imparted to rubber from carbon black.

Carbon black refers to a group of industrial product consisting of furnace black, channel blacks, thermal blacks and lampblacks. They are material composed essentially of elemental carbon in form of near-spherical particles of colloidal sizes, combined mainly into particle aggregates obtained by partial ignition or thermal decomposition of hydrocarbons. Furnace black are made in a furnace by partial ignition of hydrocarbons. Thermal black and acetylene blacks are produced by thermal decomposition of natural gas and acetylene,

respectively. Channel blacks are manufactured by impingement of natural gas flames on channel irons. Lampblack is made by burning hydrocarbons in open, shallow pans. Only the furnace and thermal decomposition processes are significant commercial important.

1.2.1.1 Carbon black classification

A classification system is used to classify rubber grade carbon blacks by use of a four-character nomenclature system. The first character in the nomenclature system for rubber-grade carbon blacks is the lettering indicating the effect of the carbon blacks on the cure rate of a typical rubber compound containing the carbon black. The letter "N" (Normal) is used to indicate a normal curing rate typical of furnace blacks and "S" (Slow) is used for channel blacks or for furnace blacks that have been modified to effectively reduce the curing rate of rubber.

The second character is a digit to designate the average surface area of the carbon black as measured by nitrogen surface area. The surface area range of the carbon blacks has been divided into ten arbitrarily groups. These groups are as shown in Table 1.3. The third and fourth characters in this system are arbitrarily assigned digits. It is to be noted that currently no ASTM grades cover. Indeed, the main carbon black manufacturers have been proposing grades on an experimental or commercial basis. Table 1.4 gives some samples of few commercial carbon blacks. Also given are their typical surface area and particle size ranges.

Table 1.3: Classification of carbon black by particle size (Baranwal, 2001).

Group No.	Avg. N ₂ Surface Area m ² /g
0	>150
1	121 to 150
2	100 to 120
3	70 to 79
4	50 to 69
5	40 to 49
6	33 to 39
7	21 to 32
8	11 to 20
9	0 to 10

Table 1.4: Classification and characterization of commercial carbon black (Baranwal, 2001)

ASTM Designation	Type Code	Type	Typical N ₂ SA m ² /g	Typical avg. particle, nm
N110	SAF	Supper abrasion furnace	130	11-19
N220	ISAF	Intermediate superabrasion furnace	115	20-25
N330	HAF	High abrasion furnace	79	26-30
N550	FEF	Fast extrusion furnace	41	40-48
N660	GPF	General purpose furnace	35	49-60
N762	SRF	Semi-reinforcing furnace	28	61-100
N990	MT	Medium thermal	9	200-500

1.2.1.2 Carbon black in rubber

Carbon black is generally incorporated into rubber by shear experienced in an open mill or Banbury mixer. It has been postulated that during the first stage of incorporation, carbon black agglomerates becomes encapsulated by polymer. In the next stage of incorporation the rubber is being forced through the channel between aggregates and agglomerates to form a reinforced rubbery composite. The consequence of this incorporation of carbon black into rubber is the creation of an interface whose total interfacial area and ability to have

interaction between the materials depends on the carbon black loading, structure, specific surface area and dispersion obtained through the mixing process.

The processing properties of rubber are very important in industry. The incorporation of carbon black into rubber greatly influences the properties of uncured rubber. Carbon black is known to significantly change the flow and viscosity of an uncured rubber compound. The hydrodynamic effect from the carbon black present reduces the volume fraction of the flow medium causing shear strain amplification when the compound is forced to flow thus increasing the viscosity. It is important that the asymmetric aggregate of carbon black increases the flow resistance and it is known that as the structure is increased to even higher level that the viscosity is increased (Baranwal, 2001). Filler-filler networking is also a factor that must be overcome when the compound flows which will again increase viscosity.

The effects of different carbon blacks on rubber properties are dominated by the carbon black specific area and structure. In general, higher surface area carbon black impact higher levels of reinforcement with resulting higher hysteresis (Barawal, 2001). Higher structure generally gives improved extrusion behavior, higher compounds modulus and higher compound viscosity. The rubber properties are also influenced by the amount of carbon black in the rubber compound. Some rubber properties like tensile strength, abrasion resistance, are increased with the increasing loading of carbon black to an optimum and then they decrease (Baranwal, 2001).

1.2.2 Non-black fillers

In general, fillers with the smallest particle size or highest surface area should contribute the greatest degree of reinforcement in a rubber compound. The first fillers used in rubber products were naturally occurring minerals that were readily available. These include zinc oxide, clay, mica and asbestos that were added to natural rubber to reduce tack, increase hardness and reduce the cost of the compound. Additional needs for reinforcing non-black fillers generated the usage of calcium silicates, fumed silica, precipitated silica and silicate and a variety of silane-modified products.

1.2.2.1 Silicas classification

There are three categories of commercially available synthetic silicas which are precipitated, fumed and surface treated silica. The precipitated silica is by far the most common variety for general rubber usage and is commonly called 'silica' as a generic term. Precipitated silica is made by acid precipitation of sodium silicate. The sodium silicate solution is usually produced by combining high purity sand and sodium carbonate in a high temperature furnace, then dissolving the molten 'glass' in water. Fumed silica is used primarily in silicone rubber and compounds with special polymers or cure systems. Fumed silica is produced by high temperature gaseous process and is more expensive. Lastly, the surface treated silicas are specialty products, used to advantage in certain function applications.

1.2.2.2 Non-black filler in rubber

At elevated temperatures, such as those encountered during mixing, the silanol groups on the surface of silicas, silicates, clays and talcs may attach to a number of chemical groups present in rubber compounds. Silanes are known to form strong chemical bonds while others, such as water and glycols, form fairly weak adsorption bonds via Van der Waals forces or hydrogen bonding (Barawal, 2001).

The reactivity features of non-black fillers with rubber compounding materials are characterized in Table 1.5. Some of the reactions with silanols can have a profound effect on the properties of the rubber compound, especially where the chemical involved is an important part of the cure system. Most of the accelerators in sulfur cure systems contain an amine group. Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reactions. This can give slower cure rates and a reduce state of cure.

Similar effects can result from the reaction of zinc ions with filler particles because zinc involve as an activator in the cure system. Zinc oxide and stearic acid react to produce zinc stearate, an intermediate in the vulcanization mechanism. The active silanols on the silica particle surface will react with zinc stearate. If the reaction is given enough time to progress, it would eventually rob all the zinc leaving none to activate the vulcanization reaction (Baranwal, 2001).

Table 1.5: Effect of the reactivity of silicas, silicates, clays and talcs on compounding materials (Baranwal, 2001)

Functional group	Effect on cure	Compounding Material
Silanes	+	Coupling silanes
Amines	-	Accelerators
	+	Hexa, HMMM, Triethanol amines
Metal ions	-	Zinc & Magnesium compounds
Polar compounds water, alcohols, glycols	+	Diethylene glycol, Polyethylene glycol

^aSurface silanols react with or adsorb other chemicals.

1.3 Rubber Compounding

1.3.1 History and Development

The rubber compounding begins in 1839 when Charles Goodyear subjected a rubber compound (with rubber 25, sulfur 5 and white lead 7) to heat of a hot stove. Since that Charles Goodyear proposed over 1000 items that could be made from his newly discovered, useful and versatile compound. The integrated of lumps of rubber need to be soften for easier chemical mixing process and permit moulding into desired product. Edwin M. Chaffee had invented the two-roll in 1836 for plasticizing raw rubber and for mixing pigments into the renewing of rubber to achieve desired finished compound (Baranwal, 2001). The unique features of rubber spontaneous the expansion of application and manufacturing of rubber products. Table 1.6 shows the trends in rubber product manufactured during the 20th Century.

Table 1.6: Rubber Use Product Trends (Baranwal, 2001)

1909	1919	1970
Mechanical Goods	Tires/Tubes	Tires
Belting	Mechanical	Footwear
Hose	Footwear	Latex Foam
Packing	Sundries	Latex Carpet Backing
Footwear	Clothing	Metal-to-Metal
Tires (solid and pneumatic)	Miscellaneous	Belting
Wire Insulation		Hose
Drug Sundries		Wire/Cable
Waterproof Fabrics		
Hard Rubber		
Sporting Goods		

B.F. Goodrich established the first company to make rubber products in Akron, Ohio in 1870; producing rubber fire hose to replace hose made of leather. The company rapidly moved to diversify product line and by the 1917 was proudly claiming the title, “World’s Largest Rubber Factory” (Table 1.7).

Table 1.7: B.F. Goodrich Product Manufacturing, 1917 (Baranwal, 2001).

WORLD'S LARGEST RUBBER FACTORY ^a (1917)					
No. Employees	No. Products	Production		Rate	Item
		Mix	Manufacture		
20,000	30,000	350,000		lbs/day	Compounded rubber
				60 miles/day	Insulated wire
				15 miles/day	Rubber hose
				60,000 pairs/day	Rubber heels
				15,000 pairs/day	Boots and shoes
				4,000 No./day	Water bottles
				18,000 No./day	Battery jars
				11,000 No./day	Golf balls
				1 tons/day	Rubber bands
				7,000 No./day	Syringe bulbs
				20,000 No./day	Automobile tires

^aB.F. Goodrich Rubber Factory, Akron, Ohio.

1.3.2 Classification of Rubber Compounding Ingredients

The objectives of rubber compounding are to produce an acceptable balance between properties in finish product to satisfy service requirement, processing characteristic for efficient utilization of available equipment, and to achieve the desirable properties and process ability at the lowest possible cost (Long, 1985). A practical compound formulation consists of 10 or more ingredients. Each ingredient has a specific function, required properties, process ability and price.

1.3.2.1 Elastomers

Elastomer is the major selection for the first step in compounding. Each elastomer has its own unique properties. All elastomer are elastic, flexible, tough, and relatively impermeable to both water and air. Elastomer is macromolecular material which can rapidly return to the approximate shape from which they have been substantially distorted by a weak stress. Usually, there are double bonds in the backbone that can be vulcanized to give elastic properties. Elastomer could be grouped according to their usage as shown in Table 1.8 (Baranwal, 2001).

Table 1.8: Type of elastomers (Baranwal, 2001)

Group	Type	Monomer	Application
General Purpose	Natural Synthetic Polyisoprene Polybutadiene Styrene-Butadiene Butyl Ethylene-Propylene-Diene (EPDM)	Isoprene Isoprene Butadiene Styrene, Butadiene Isobutylene, Isoprene Ethylene, Propylene, and diene monomer	Tyres, Belts, Hoses
Solvent Resistant	Nitrile Neoprene	Butadiene, Acrylonitrile Chloroprene	Oil seals, oil hoses, Automotive gaskets,

1.3.2.2 Vulcanization Agent

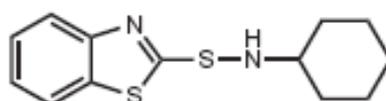
Vulcanization agents are the ingredient which must present to cause chemical reaction, resulting in cross linking of elastomer molecule. When it is used together with an accelerator and activator at elevated temperatures, thermally stable covalent bonds are formed between the elastomer chains at the carbon – carbon double bonds. Commonly, sulfur is used as vulcanization agent. Sulfur which is suitable for vulcanization has to be at least 99.5% pure and it must not contain more than 0.5% ash. There are two types of sulfur which are cyclic sulfur (S₈) and amorphous sulfur. Other important vulcanization agents are selenium, tellurium, thiuram disulphides, peroxides, metallic oxides and quinone dioximes.

1.3.2.3 Accelerators

Accelerators are ingredient used in compounding to reduce the vulcanization time, by increasing the speed of vulcanization. Accelerators are divided into five classes according to their chemical structure application in the rubber industry. They are:

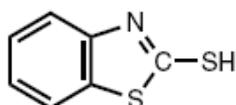
a) **Sulfenamides** – it plays dual role in the vulcanization; provide longer scorch time which avoids premature crosslinking during vulcanization and processing. This would be a good choice when mixing compounds which contain reinforcing furnace black which generate more heat.

Example: N-cyclohexylbenzothiazole-2-sulfenamide (CBS)



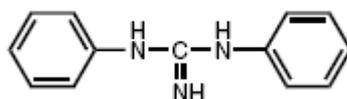
b) **Thiazoles** – thiazoles derivatives are versatile vulcanization accelerator used alone or combine with other accelerator in a compounding formulation. It gives moderate vulcanization rate and scorch time.

Example: 2-mercaptobenzothiazole (MBT)



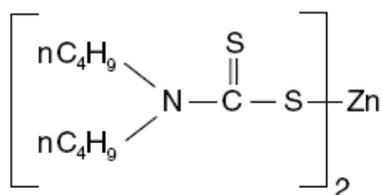
c) **Guanidine** – a secondary accelerator which is used with other accelerator of thiazoles class. The thiazoles – guanidine combinations are frequently used for technical goods.

Example: N,N'-Diphenylguanidine



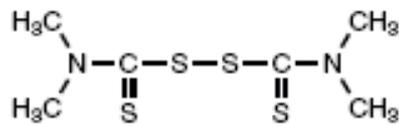
d) **Dithiocarbamates** – vulcanization with dithiocarbamates is faster than with thiurams. It is used as ultra accelerator.

Example: Zinc Dibutyldithiocarbamate

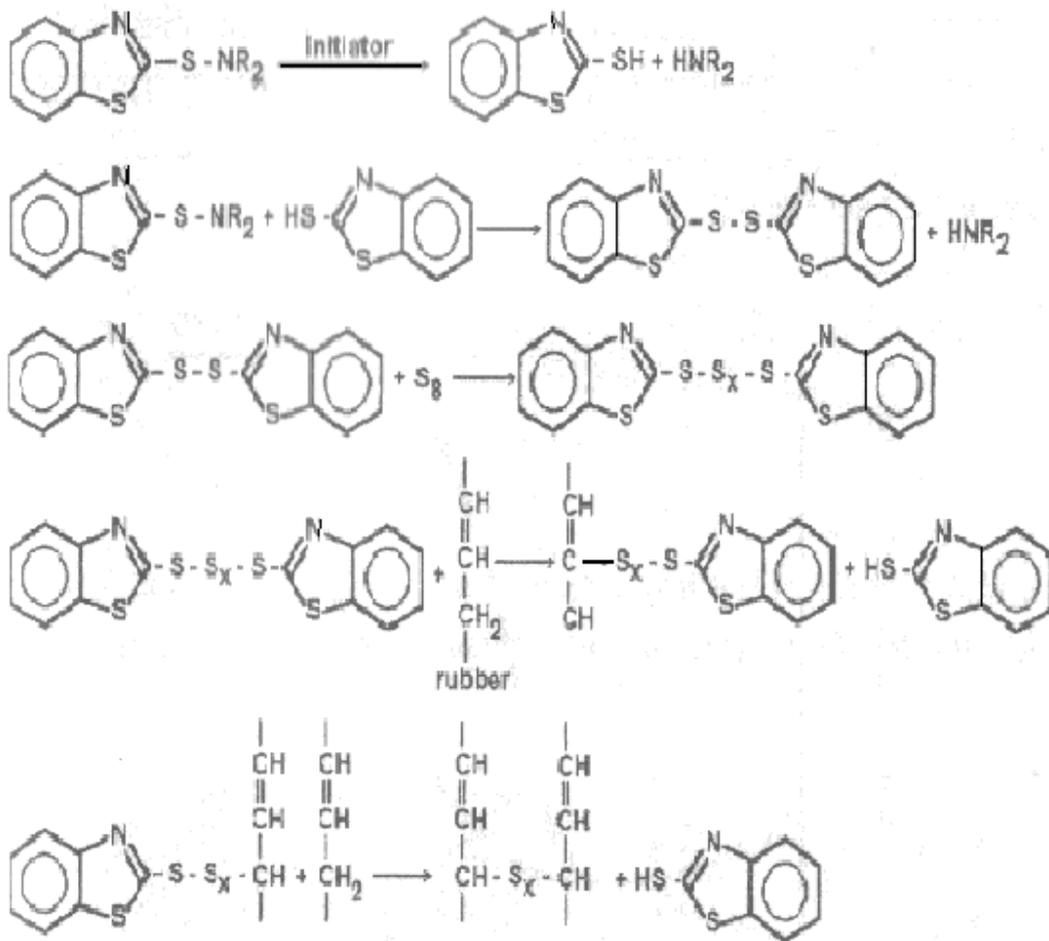


e) **Thiurams (others than disulfides)** – use as ultra accelerator
 accelerator with normal amount of sulphur.

Example: Tetramethylthiuram disulfide



An example of accelerator reaction is shown below (Barawal, 2001):

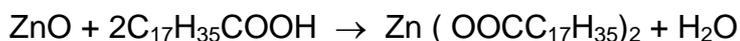


X = accelerator residue

Fig 1.1: Generalized course of accelerated sulphur vulcanization

1.3.2.4 Activators and Retarders

Activators are ingredient used to activate the accelerator and improve its effectiveness. Zinc oxide, stearic acid and amine are the mostly widely used activators. In a cure system consisting of sulphur; the presence of zinc oxide and stearic acid as accelerators are usually requires to attain a good crosslinking. It can be classified into organic and inorganic activator. Stearic acid is the most popular type of activator used in rubber industry while zinc oxide is common inorganic type activator used in the rubber compounding. Depending on the particle size, full activation of vulcanization is obtained with about 3 – 5% of zinc oxide (Hofmann, 1967). Zinc oxide activates the vulcanization by complexation with the sulfur accelerator system to give a faster cure rate. Fatty Acid is needed to solubilize the zinc to give Zn^{2+} which can form complex with sulfur and accelerator as shown below:



The retarders are the ingredient used to reduce the scorchiness of a compound. The most common used retarder is cyclohexyl-N-thiophthalimide. It makes a sulfenamide or thiazole accelerated compound much less scorchy and gives it more processing safety without affecting its cure rate or vulcanize properties.

1.3.2.5 Antidegradants

Antidegradants are ingredient used to retard the deterioration of rubber compound initiated by oxygen, ozone, heat, light, metal catalysis and mechanical flexing. In compounding, antidegradant is required to give good aging properties to a compound and prolong its useful life. In general, the more

saturated bond in the main chains of elastomer, will give the better the aging properties.

Antidegradant could be divided into two types; they are (i) antioxidants and (ii) antiozonants. Antioxidants are chemical which extend the life of rubber products by first reacting with polymeric free radicals and stopping propagation of polymer oxidation. Commercially available antioxidants fall in 3 groups: secondary amine, phenolics and phosphates. Antiozonants are chemical which diffuse to the surface and react with the ozone before rubber molecules have chance to react with ozone. Commonly used antiozonants are paraphenyldiamines (PPD) and petroleum waxes. In the selection of antidegradants, a few factor need to be considerate such as; type of protection require, chemical activity, persistence, discoloration and cost.

1.3.2.6 Processing Aids

Processing aids are the ingredient added to a rubber compound to facilitate processing operation, such as mixing, calendaring, 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 also been used to soften rubber and improve its

processing characteristic. Peptizers such as pentachlorothiophenol and phenylhydrazine 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 (Mark, 1994).

1.3.2.7 Fillers

Filler is the ingredient used to reinforce physical properties to impart certain processing characteristics or to reduce cost. Reinforcing filler will enhance the hardness, tensile strength, modulus, and tear strength and abrasion resistance of a compound. Selection of filler is the third most important task in compound after the elastomer and cure agent. Filler will influence on a compound physical and processing properties. Degree of reinforcement of fillers will increase with the decrease in filler particle size. The finer fillers require more energy for their dispersion into elastomer and therefore more difficult to process. The particle size of filler plays a major role in tensile strength of rubber compound and Mooney scorch.

There are two types of fillers used in the rubber industry which classified as (i) black filler and (ii) non-black filler. Example of black filler is carbon black while for non-black filler are silica, clay and titanium dioxide. In tyre manufacturing, carbon black and silica are widely use. The addition of active fillers to a rubber matrix leads to a considerably high reinforcement. This greater reinforcement manifests itself in a rise in the modulus, leading among other things, to higher strain value, greater tensile strength and lower abrasion.

- (i) Carbon Black – Carbon black is a colloidal form of element carbon consisting of 90 to 99 percent of carbon. The main non-carbon elements in carbon black are oxygen, hydrogen and sulfur. Carbon black can be obtained commercially. Carbon black is classified according to their particle size, surface activity, porosity and structure. These parameters affect the properties of a rubber compound. For example, the smaller the particle size, the greater the increase in modulus and tensile property, higher abrasion resistance, higher viscosity and high electrical conductivity (Myers, 1973). It reinforces the rubber compound besides lowering the compound cost. Reinforcement of rubber by carbon black improves the rubber properties due to a combination of physical and chemical interactions between carbon black and rubber (Stephen, 1993). Modulus is a primarily a function of carbon black structure and loading (Long, 1985). Compound containing higher structured blacks have highest modulus. Mooney viscosity in most elastomers is mainly dependent on carbon black structure. High structure black contribute the highest Mooney viscosity with the particle size having a lesser effect. The largest particle size black provide the greatest scorch resistance while high structure, small particle size black usually reduces the scorch resistance (Long, 1985).
- (ii) Non black filler - This includes precipitated silica, clay and calcium carbonate. Among the filler, precipitated silica had been widely used in rubber product especially in tyre. Silica used is in the form

of a synthetic, amorphous silicon dioxide (SiO_2). Sung (2002) stated that since silica has hydroxyl groups on its surface, this has resulted in a strong filler–filler interactions and adsorption of polar materials by hydrogen bonds. More over, the surfaces of silica are polar and hydrophilic; there is a strong tendency to adsorb moisture which adversely influences cure and therefore properties of vulcanized rubbers. Silica can be classified into two types which based on the amount of water remove by ignition, they are: i) hydrated and ii) anhydrous type. Silica is added to rubber as reinforcing filler; where it improves the tensile strength, hardness, tear strength and abrasion resistance. Fine particle silica blend with carbon black is finding increase use in commercial tyres. One reason is that silica filled vulcanizate shows a low hysteresis in comparison with carbon black (Fumito, 2001). Besides that, the resulting trends exhibit a useful combination of resistance to abrasion, cut growth, tearing, chipping, crack initiation and skidding.

1.3.2.8 Special Purpose Materials.

Special purpose materials are those used for specific purpose which is not normally required in the majority of rubber compound such as bonding agent and additive. This material requires providing a bonding between rubber compound and a steel cord. Hexamethoxymethylmelamine (HMMM) is an additive for cobalt neodecanoate/propionate (bonding agent) with will create a bonding with the brass that coated on a steel cord (Long, 1985).