

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber (NR)

Natural rubber (NR) derived from the tree *Hevea Brasiliensis* is indigenous to Brazil. NR occurs in *Hevea Brasiliensis* as minute particles, dispersed in a milky fluid (latex). These particles range in size from about 5 nm to about 3,000 nm [5]. Latex is a colloidal suspension of rubber particles in an aqueous serum phase. This latex is about 55-60% water, 30-40% rubber, 1.5-3.0% resins, 1-1.5% proteins, 0.8-1.0% carbohydrates and 0.7-0.9% minerals. Fresh latex is treated with a stabilizer to prevent premature coagulation. Ammonia is the most common stabilizer. To prepare dry rubber, the rubber latex is diluted with water to solids content of up to 12-18%. Then the diluted rubber latex is coagulated using acid. The more diluted the latex, the greater amount of acid is required for coagulation. The iso-electric point is reached at a pH of 5.1 to 4.8. The coagulated rubber is then processed into dry rubber. Due to a variety of processing methods, dry rubbers are classified into several types such as ribbed smoke sheets (RSS), air-dry sheets (ADS), pale crepes and block rubbers.

The chemical structure of natural rubber is ~100% cis-1,4 polyisoprene consisting of long sequence isoprene units as shown in Figure 2.1.

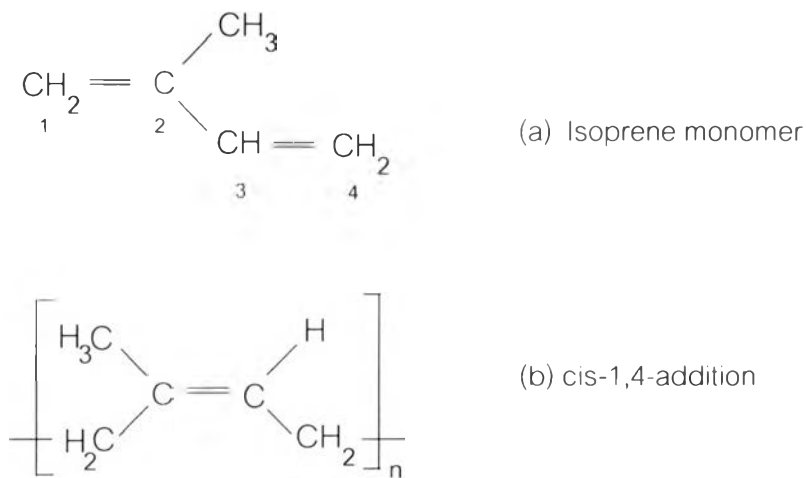


Figure 2.1 Chemical structure of (a) isoprene monomer and
(b) natural rubber (cis-1,4-addition)

2.2 Properties and Applications of NR Vulcanizates

NR is a translucent, light yellow to dark brown, soft and extensible material. The molecular weight is basically in the ranges of 10^4 - 10^6 [6]. The T_g (glass transition temperature) of NR is about -70°C [7]. Generally, NR is high stereoregularity and amorphous polymer but it crystallizes spontaneously when stored at low temperatures or upon stretching which is called low temperature crystallization and strain induced crystallization, respectively.

Due to strain induced crystallization, this results NR in having good mechanical properties such as high tensile strength, tear resistances, resilience and abrasion resistance. Therefore, NR is the best choice for any application when the high strength is required. NR is also a good choice for applications that require low heat build up, such as tires for passenger-cars, vibration mounts, springs and bearings. Other applications that highly use NR include dipping goods such as condoms and gloves and pharmaceutical goods for example, urinary drainage catheters [7, 8, 9].

2.3 Vulcanization

Vulcanization is the chemical process of crosslinking the chain-like rubber molecules to form an elastic three-dimensional network as shown in Figure 2.2 which prevents permanent deformation after removal of the deforming force. Therefore in order to develop the full potential of rubbers, rubber molecules must be crosslinked. The first method of vulcanization was based on the discovery of Charles Goodyear in 1841. It was found that addition of sulfur to rubber, followed by heating, led to an improvement in the properties. Thomas Hancock used essentially the same process about a year later [10]. For rubbers containing unsaturated carbon-carbon bonds in the backbone, a variety of curing agents are available to choose with some common ones being sulfur [11, 12], peroxides [13], phenolic resin [14], and metallic oxides [15]. In most cases, the cure reaction is achieved by a chemical reaction between the rubber and curing agent [16]. Among them, sulfur is the most popular curing agent employed in rubber industry.

Vulcanization results in the increase of tensile strength, modulus (stiffness), hardness, abrasion resistance and rebound, but the decrease of elongation, hysteresis (heat buildup), compression set and solubility. It also makes rubber impermeable to gases and resistant to heat, electricity and chemical action. The improved frictional properties of rubber by vulcanization are highly desired for pneumatic tire application.

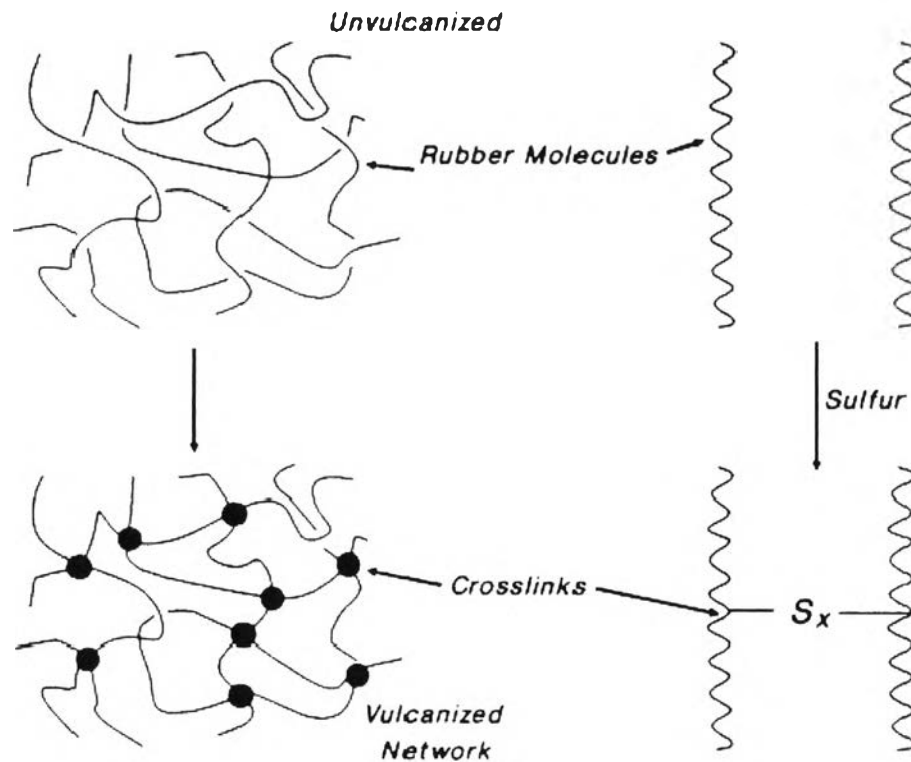


Figure 2.2 Network formations [17]

2.3.1 Sulfur Vulcanization

Generally, sulfur vulcanization is the most widely used in rubber industrials because it provides rubber vulcanizates with good mechanical properties. However, sulfur can vulcanize only diene rubber. Two forms of sulfur are used in vulcanization: amorphous and rhombic. The amorphous sulfur, also known as insoluble sulfur, is insoluble in rubber and most solvent. Rhombic sulfur, a ring of eight sulfur atoms usually in its normal crystalline state, is the form normally used for vulcanization [18]. Vulcanization of rubber by sulfur alone is quite inefficient and curing times of several hours. Commercial sulfur vulcanization uses special additive, which accelerates cure. This is called accelerator. Accelerator increases crosslink efficiency and rate. Several common accelerators are listed in Table 2.1.

Table 2.1 Several common accelerators used in sulfur vulcanization [19]

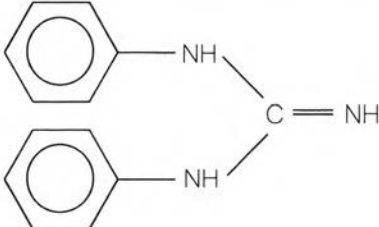
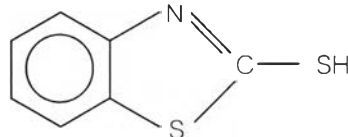
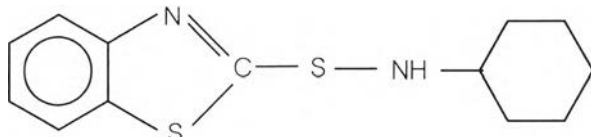
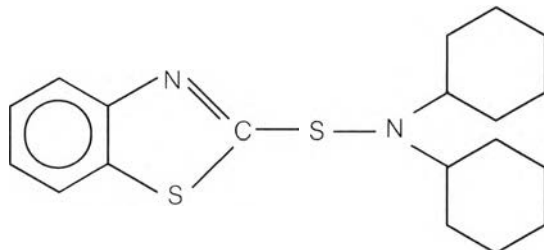
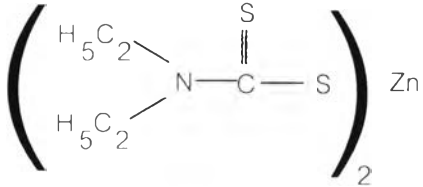
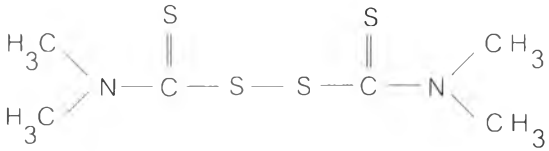
Type and example	Chemical formula
<p><i>Guanidine</i></p> <p>-Diphenyl guanidine (DPG)</p>	
<p><i>Thiazole</i></p> <p>- Mercaptobenzothiazole (MBT)</p>	
<p><i>Sulfenamide</i></p> <p>- N-cyclohexyl benzothiazyl sulfenamide (CBS)</p>	
<p>- N, N-dicyclohexyl benzothiazyl sulfenamide (DCBS)</p>	

Table 2.1 (continued)

Type and example	Chemical formula
<p><i>Dithiocarbamate</i></p> <p>- Zinc diethyl dithiocarbamate (ZDC or ZDEC)</p>	
<p><i>Thiuram</i></p> <p>- Tetramethyl thiuram disulfide (TMTD)</p>	

Each type of accelerator has a different effect on the vulcanization process. Then, the choice of vulcanization accelerator will affect the scorch safety, the cure rate and the crosslink length formed as shown in Table 2.2.

Table 2.2 Accelerated sulfur vulcanization [19]

Accelerator type	Scorch safety	Cure rate	Crosslink length
None	-	Very slow	Very long
Guanidines	Moderate	Moderate	Medium-long
Mercaptobenzothiazoles	Moderate	Moderate	Medium
Sulfenamides	Long	Fast	Short-medium
Thiurams	Short	Very fast	Short
Dithiocarbamates	Least	Very fast	Short

Vulcanization of NR is normally achieved by heating at 100-180°C. Crosslinking is accompanied by chemical modification of the rubber backbone. The vulcanization leads to a variety of crosslink structures with different lengths and distribution [18] as shown in Figure 2.3. There are mono-, di-, and polysulfide crosslinks (a, b, and c, respectively), cyclic monosulfide (d) and disulfide groups (e), pendent sulfide groups terminated by accelerator moieties (f) and conjugated diene (g) and conjugated triene units (h). There is also sometimes evidence of 1,4 trans configuration, and double bond movement.

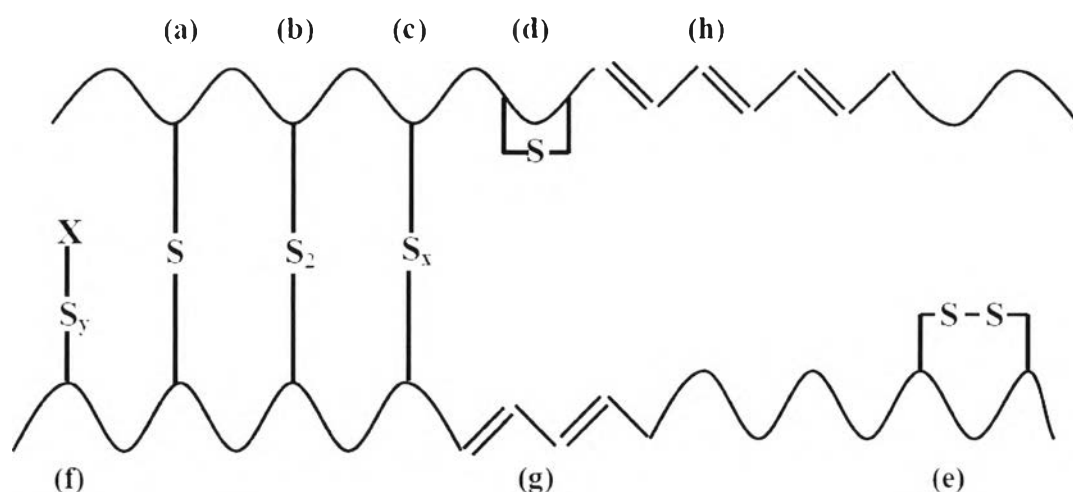


Figure 2.3 Structural formed during accelerated sulfur vulcanization of NR

(X accelerator fragment, $x \geq 3$, $y \geq 1$) [18]

Accelerated sulfur vulcanization systems can be classified based on the ratio of accelerator to sulfur (A/S ratio) into three types, conventional (CV), semi-efficient (semi-EV) and efficient (EV) systems, as shown in Table 2.3

Table 2.3 Sulfur and accelerator of different vulcanization systems for NR [20]

Vulcanization systems	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
Conventional (CV)	2.0-3.5	1.2-0.4	0.1-0.6
Semi-EV	1.0-1.7	2.5-1.2	0.7-2.5
Efficient (EV)	0.4-0.8	5.0-2.0	2.5-12

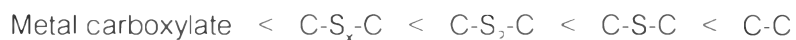
Conventional sulfur vulcanization (CV) system contains a much higher concentration of sulfur (S) than accelerator (A). The A/S ratio is between about 0.1-0.6 [20]. CV system gives most vulcanizes containing longer (polysulfidic) crosslinks. In contrast, efficient sulfur vulcanization (EV) system leads to shorter (mono- or di- sulfidic) crosslinks which are more stable (less prone to scission). For EV system, the A/S ratio can be varied between 2.5 and as high as 12 [20]. Semi-efficient sulfur vulcanization (semi-EV) system, having accelerator to sulfur ratio between about 0.7 and 2.5 [20], is an alternative to give the vulcanizate properties intermediate between both systems. Therefore, this system is compromised design to produce, in structural terms, a vulcanizate which contains an equal concentration of polysulfidic and monosulfidic crosslinks at the optimum cure. Typical NR vulcanizate structures at the optimum cure time and some properties are shown in Table 2.4 [20].

Table 2.4 Typical NR vulcanizate structures and properties at the optimum cure time [20]

	CV	semi-EV	EV
Poly- and disulfidic crosslinks, %	95	50	20
Monosulfidic crosslinks, %	5	50	80
Cyclic sulfidic concentration	High	Medium	Low
Tensile strength	High	Medium	Low
Low temperature crystallization resistance	High	Medium	Low
Heat-aging resistance	Low	Medium	High
Reversion resistance	Low	Medium	High
Compression set, 22 hours at 70°C , %	30	20	10

When a rubber is crosslinked to the same extent by different sulfur vulcanization systems, the resulting vulcanizates can have widely differing strengths, apparently due to differences in the nature of the crosslinks. Vulcanizates containing high levels of

polysulfidic crosslinks often give higher strengths than those containing mono- and disulfidic crosslinks, which in turn give higher strengths than vulcanizates containing carbon-carbon crosslinks. The strength of crosslinks is as follows [21]:



According to bond energies shown in Table 2.5, polysulfidic crosslinks give the vulcanizates with a low heat-aging and reversion resistance. This is because polysulfidic crosslinks have lower bond energy than disulfidic, monosulfidic and carbon-carbon crosslinks, respectively.

Table 2.5 Bond energy [10]

Type of linkage	Bond energy (kcal/mol)
-C-S _x -C-	< 64
-C-S ₂ -C-	64
-C-S-C-	68
-C-C-	84

Besides accelerator, many reagents which are associated with the sulfur vulcanization have been developed [22]. Accelerated sulfur vulcanization is more efficient when the activators, i.e. zinc oxide and stearic acid are incorporated. It is thought that these additives combine to create soluble zinc ions that activate intermediate reactions involved in crosslink formation [23].

2.3.2 Mechanism of Accelerated Sulfur Vulcanization

Generally, accelerated sulfur vulcanization involves a combination of zinc oxide, fatty acid, sulfur, and at least one accelerator. A general scheme for free radical accelerated sulfur vulcanization is shown in Figure 2.4. The active sulfurating agent (Ac-S_x-Ac), formed by reaction of sulfur with an accelerator complex or from a sulfur donor and zinc oxide, reacts with the rubber to give a polysulfidic pendent group

terminated by a fragment derived from the accelerator or sulfur donor (rubber-S_x-Ac). These are precursors to polysulfidic crosslinks, which are formed either by direct reaction with another rubber hydrocarbon molecule or by disproportionation with a second pendent group on a neighboring rubber chain. The final networks are formed through mainly two reactions which are desulfuration and thermal decomposition of initial polysulfide crosslinks. The additional crosslinking is taken place by desulfuration process which gives a short sulfur crosslink. And thermal decomposition gives the vulcanizates with main-chain modification (cyclic mono-, and disulfides and conjugated diene and triene). The final structure of the vulcanizate depends on the time and temperature of vulcanization. [4, 17]

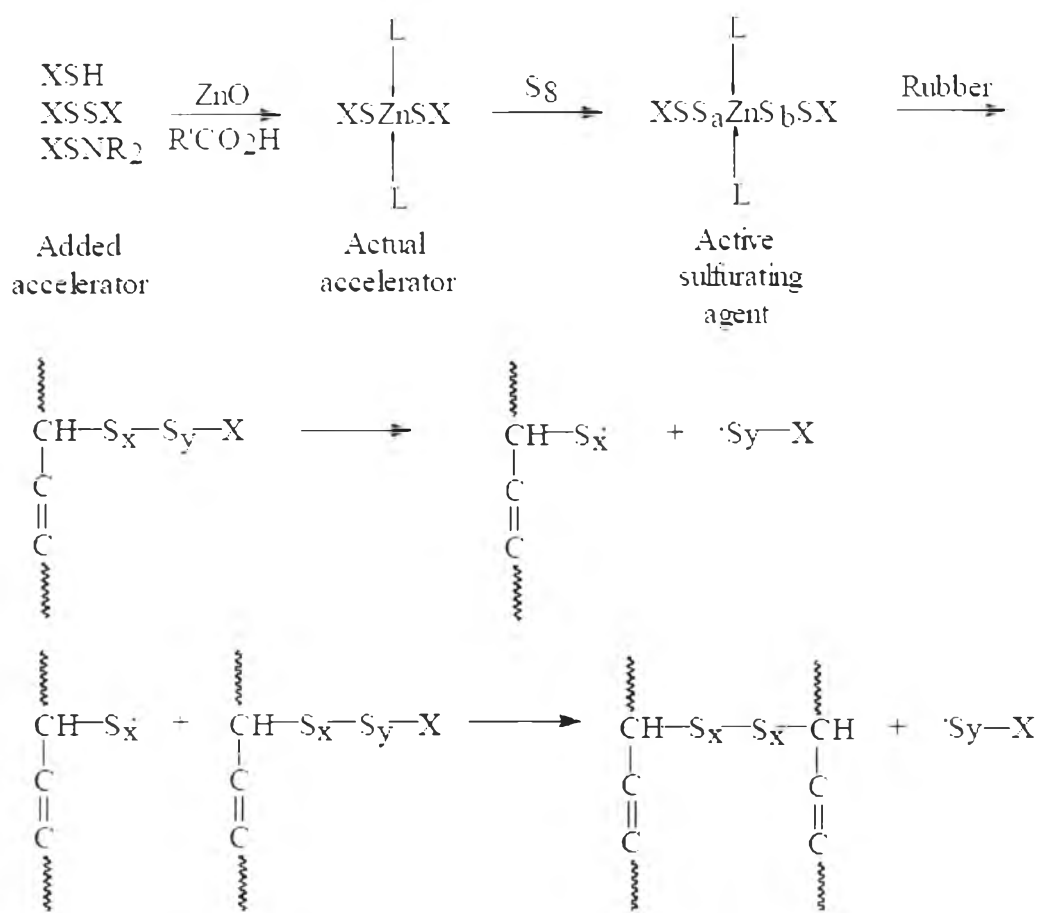


Figure 2.4 Free radical mechanism for accelerated sulfur vulcanization

X = accelerator residue, L = ligand (basic nitrogen or zinc carboxylate) [17, 24]

2.3.3 Effect of Vulcanization on Properties

In practical vulcanizates, the average molecular weight between crosslinks is typically about 4,000 to 10,000. Vulcanized rubber is insoluble in solvent and it does not flow. Thus, vulcanization must occur after a rubber article is in its final shape.

The effect of vulcanization extent a crosslink density on some properties is shown in Figure 2.5 [17]. It can be seen that vulcanizates properties depend on crosslink density significantly. Stiffness increases monotonically with increasing crosslink density. Tear strength, tensile strength, fatigue life, and toughness first increase with crosslink density and then decrease. Hysteresis decreases monotonically with increasing crosslink density.

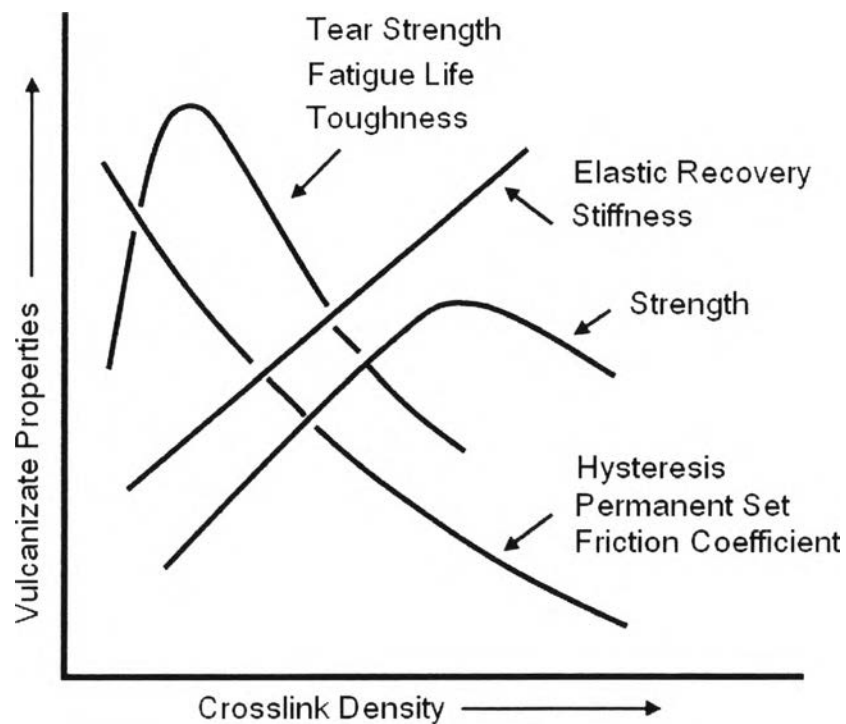


Figure 2.5 Vulcanizate properties as a function of the extent of vulcanization [17].

The reason why the strength of vulcanized rubber passes through a maximum as crosslinking is increased can be explained by considering energy dissipation. Uncrosslinked rubber chains can disentangle upon stressing. So the fracture of uncrosslinked rubber under stressing at slow rate is because viscous flow without breaking chemical bonds. The effect of a few crosslinks is to increase the molecular

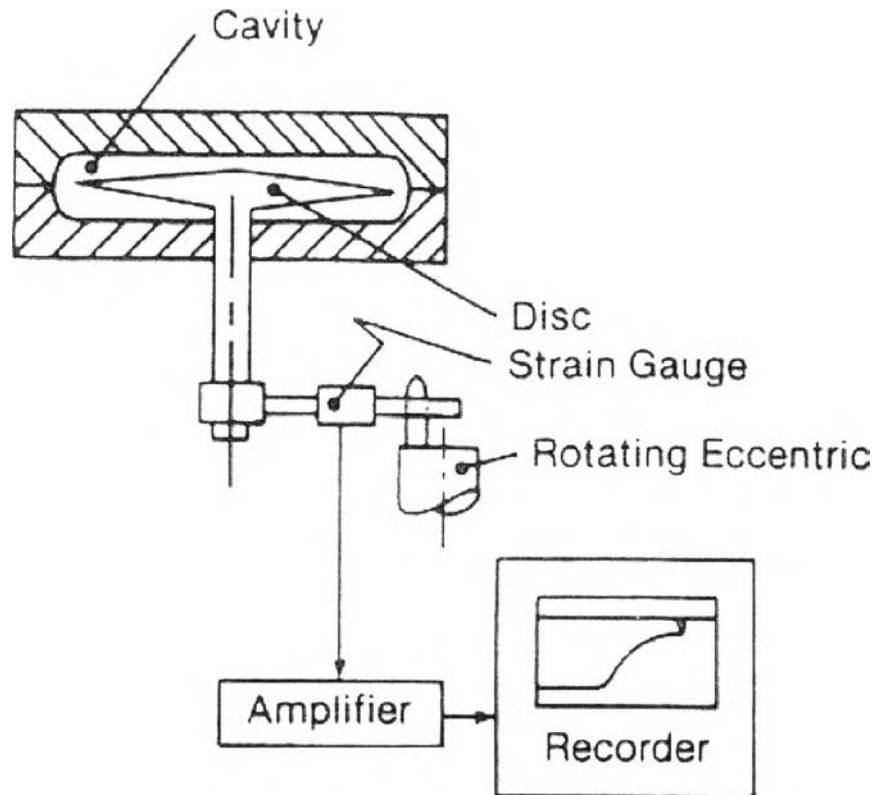
weight, create branched molecules and a broader molecular weight distribution. It is more difficult for these branched molecules to disentangle and hence, strength increases. As crosslinking is increased further, the gel point is eventually reached when a three-dimensional network forms. A gel cannot be fractured without breaking chemical bonds. Thus, strength is higher at the gel point, because chemical bonds must be ruptured to create fracture surface. However, strength does not increase indefinitely with more crosslinking. When an elastomer is deformed by an external force, part of the energy is stored elastically in the network chains, and the rest energy dissipates through molecular motions into heat. When crosslink density is too high, molecular motion is restricted and energy dissipation is minimal. Therefore, vulcanizates become brittle and strength is low.

2.3.4 Measurement of Vulcanization and Cure Characterization of Vulcanizates

The extent of cure is measured as a function of cure time by using a curemeter: oscillating disk rheometer (ODR) or moving die rheometer (MDR). In ODR testing, a piece of rubber is placed in a closed cavity preheated to the cure temperature and containing a conical disc (rotor) which is oscillated through a small arc. Vulcanization is followed by recording the torque required to maintain a rotor at a given amplitude. An ODR is shown in Figure 2.6(a). MDR is a newer curemeter. The cavity is much smaller and there is no rotor. In this type of curemeter, one-half of the die is stationary and the other half oscillates. Heat transfer is faster and the temperature of the cavity and sample can be changed more rapidly. A sketch of an MDR is shown in Figure 2.6(b).

Torque is plotted against time to give a so-called cure curve. Typical cure curves are given in Figure 2.7. The type of cure curves can be categorized into three types; plateau, reversion and creeping. In a plateau curve is complete and crosslinks are stable, with equal rates of reforming and breaking of crosslinks. Reversion is a drop in torque; there is a loss of network at long vulcanization time. A creeping curve, torque continually increases with time as more crosslinks are formed due to rearrangement of polysulfidic crosslinks. The general cure parameters taken from cure curves are given in Table 2.6.

(a) Oscillating Disk Rheometer (ODR)



(b) Moving Die Rheometer (MDR)

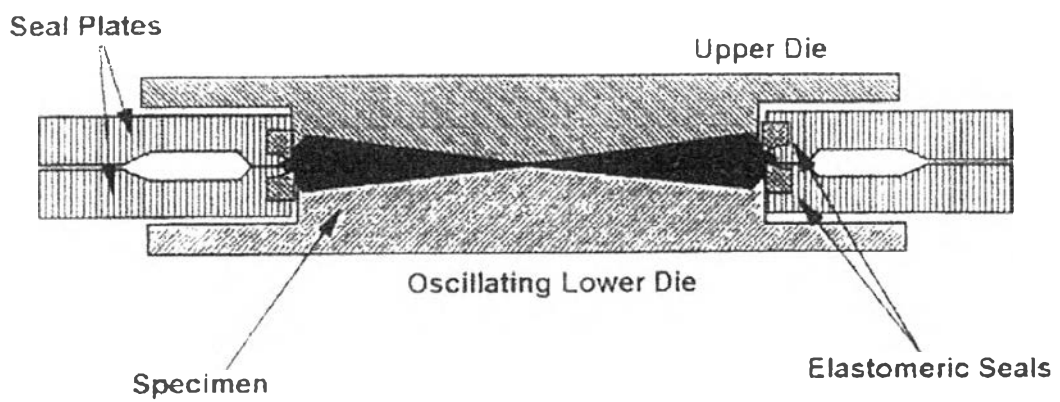


Figure 2.6 Curemeters: (a) Oscillating Disk Rheometer [17], (b) Moving Die Rheometer [25]

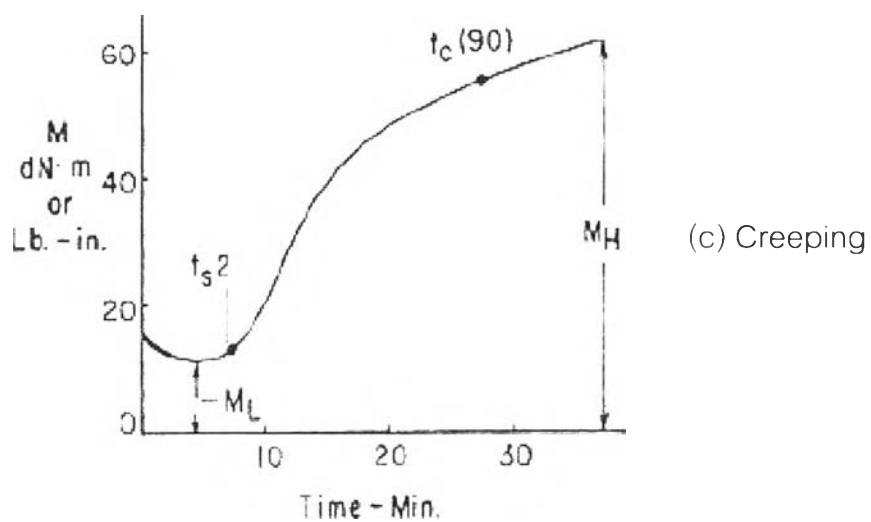
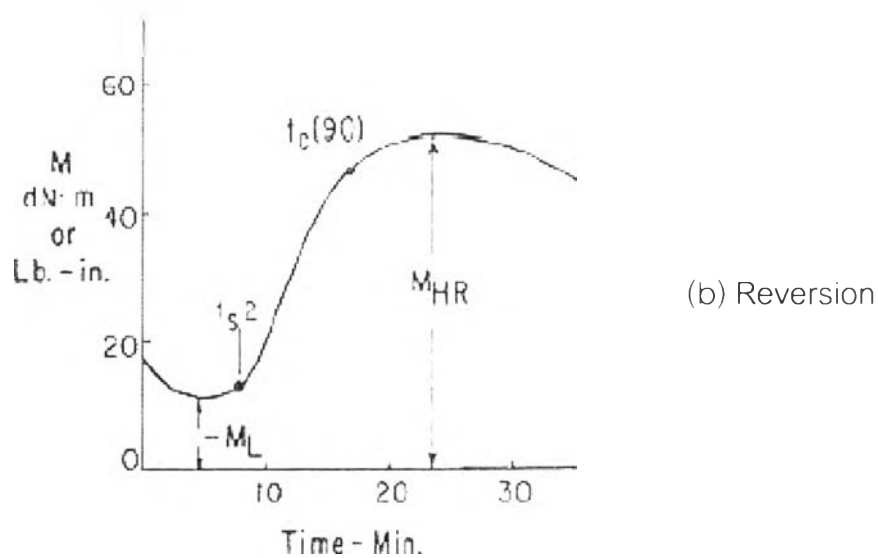
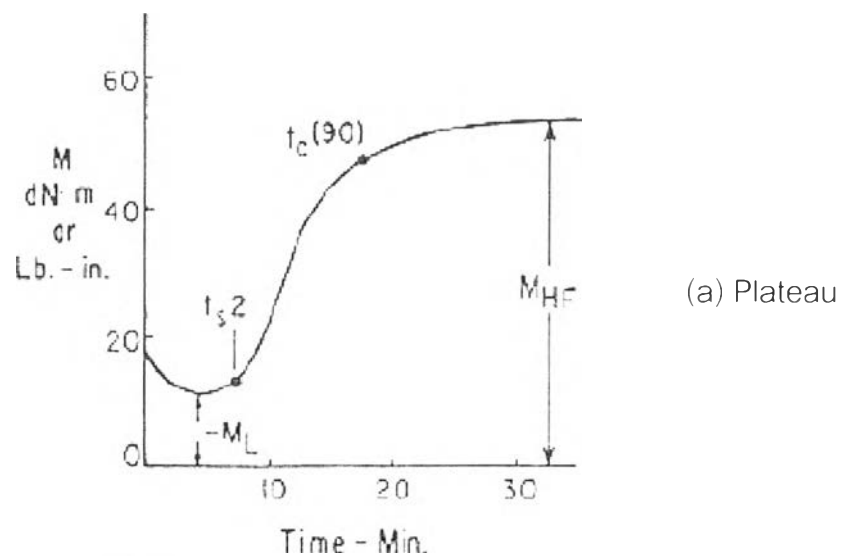


Figure 2.7 Type of curves: (a) Plateau (cure to equilibrium torque),
 (b) Reversion (cure to maximum torque with reversion),
 (c) Creeping (cure to no equilibrium or maximum torque) [26].

Table 2.6 Cure parameters taken from the cure curves.

Symbol	Definition and units
M_L	Minimum torque (dN.m or lbf.in)
M_{HF}	Maximum torque where curve plateau (dN.m or lbf.in) (Fig 2.7(a))
M_{HR}	Maximum torque of reverting curve (dN.m or lbf.in) (Fig 2.7(b))
M_H	Highest torque attained during specified period of time when no plateau or maximum torque is obtained (dN.m or lbf.in) (Fig 2.7(c))
ts_2	Scorch time; time when torque increases 2 units from minimum torque (min)
tc_x	Time to reach X percent of torque increase (min) (time to reach $M_L + (X(M_{HF}-M_L)/100)$)

2.4 Reversion Behavior

Reversion is a well-known phenomenon in the accelerated sulfur vulcanization. It is associated with a loss of network integrity. Usually, the degradation of linkages is mainly from polysulfidic ones. This is attributed to their low heat stability, as shown in Table 2.5. The reversion process is thermally initiated and primarily associated with overcure or high temperature service conditions. The reversion behavior can be observed from the cure curve. When crosslink breakage becomes dominant during prolonged heating, the decrease of torque after reaching maximum value indicates the initiation of reversion. Datta and Ivany [27] showed that the reversion of natural rubber is initially observed when curing temperature is above 130°C, and the extent of reversion increases with increasing curing temperature.

Henning and Shapot [28] studied reversion behavior in many rubbers vulcanized by sulfur. The result showed that the extent of reversion is dependent on the number of allylic hydrogen of rubber as shown in Figure 2.8. The rubber with the highest allylic hydrogen concentration, cis-1,4 polyisoprene including both synthetic and natural rubber, showed the highest reversion.

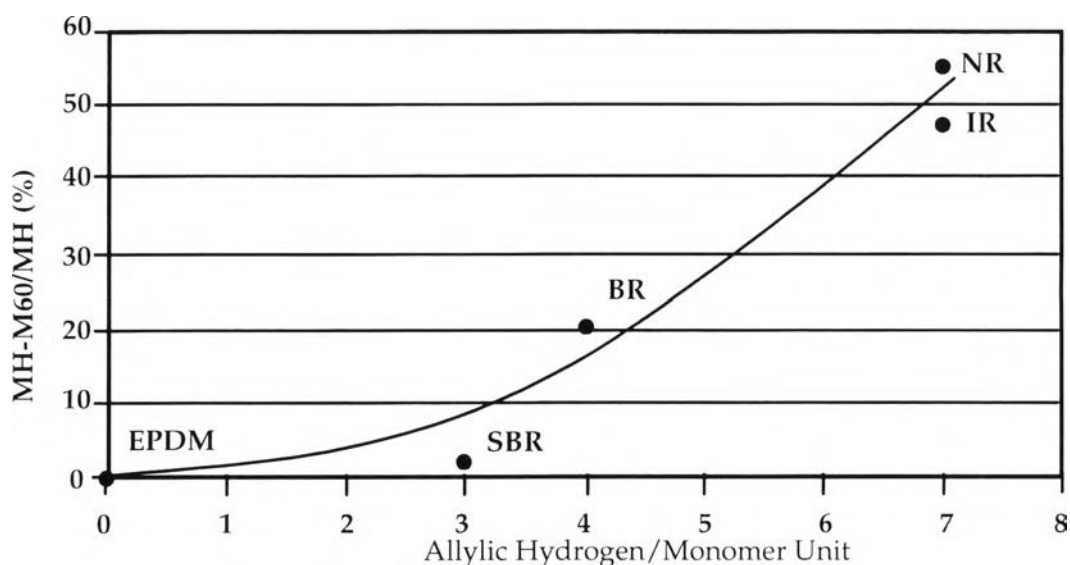


Figure 2.8 Extent of reversion as a function of allylic hydrogen for a series of elastomers (EPDM = ethylene-propylene-diene monomer, SBR = emulsion styrene-butadiene rubber, BR = cis-butadiene rubber, IR = cis-isoprene rubber, NR = natural rubber) [28].

Fath [29] showed that the reversion of rubber is found only when the certain accelerator class are used as shown in Figure 2.9. Thiuram and dithiocarbamate classes lead to stable linkages, while sulfenamide type causes reversion at the prolonged cure time. And guanidines cause creeping behavior.

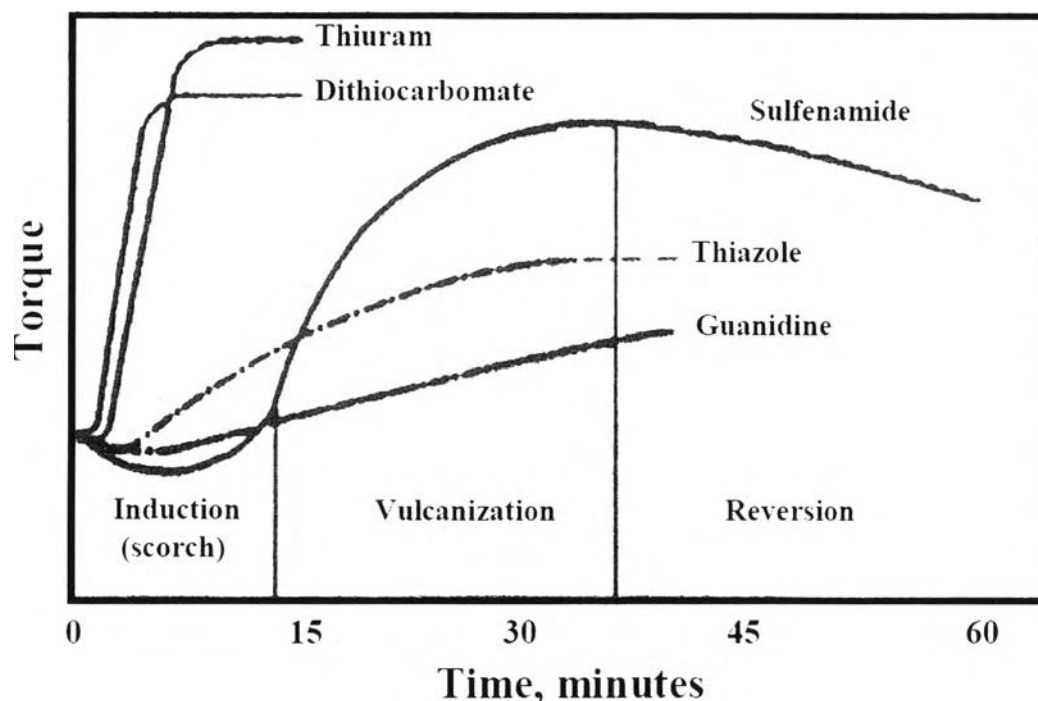


Figure 2.9 Cure characteristics of various accelerators [29]

Sloan [30] has investigated the effect of carbon black on reversion. It was found that the presence of carbon black can suppress the reversion. Moreover, a decrease of reversion increases with an increase in carbon black loading. Chen and coworker [31] also reported that the addition of carbon black can improve reversion resistance. They proposed that the reversion improvement might be due to adhere of rubber chains onto the carbon black surface, causing less desulfuration of polysulfidic linkages. The polysulfidic linkages now have greater thermal stability. So the reversion resistance is improved. Studebaker [2] and Porter [3] also found that the network filled with carbon black consists of the higher proportion of stronger linkages, mono- and disulfidic linkages than one without carbon black. So this leads to higher thermal and reversion resistance.

Although it is widely understood in the rubber industry that carbon black can improve reversion resistance of natural rubber. However, Boonkerd [4] showed that adding 50 phr of carbon black N330 into NR cured with the DCBS accelerated sulfur cure system significantly increased in the reversion behavior as shown in Figure 2.10.

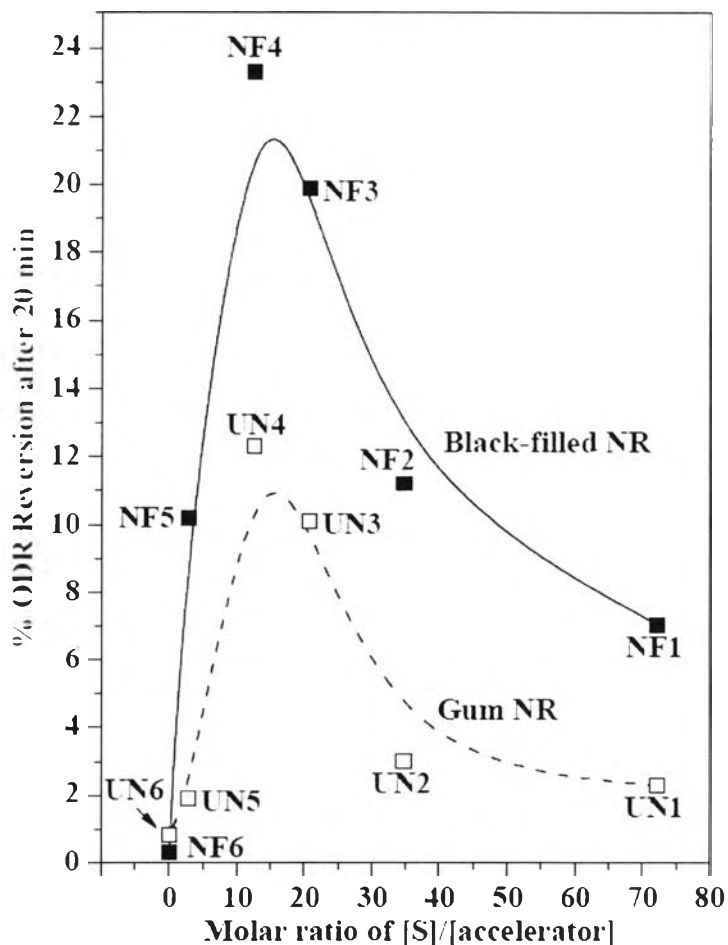


Figure 2.10 Comparison of reversion between gum and black-filled NR vulcanizates [4].

2.5 Reinforcement of Rubber

In rubber technology, reinforcement is often defined as the character of improvement in the properties of rubber which generally means an increase in modulus, hardness, tensile strength, abrasion resistance and tear resistance or other properties. It is a well known that reinforcement can be achieved by the addition of fillers. Typically, fillers used in rubber are classified into reinforcing and non-reinforcing fillers. In some cases, they are divided into black and non-black types.

2.5.1 Degree of Reinforcement

Even though the reasons for reinforcement are not completely known, it is believed that the reinforcement is caused by interaction force between the elastomer and the fillers. So degree of reinforcement depends on [32-35]:

2.5.1.1 Surface area and particle size of filler

Particle size is directly related to the reciprocal of surface area per gram of filler; thus the effect of smaller particles actually reflects their greater extent of the interface between polymer and filler. In Figure 2.11, carbon black (some carbon black grades) and silica having small size are sorted as reinforcing filler while other larger fillers such as calcium carbonate (CaCO_3) and talc are not able to reinforce rubber products. Semi-reinforcing filler as clay or non-reinforcing filler such as (CaCO_3) are used mainly as diluent fillers [36-39].

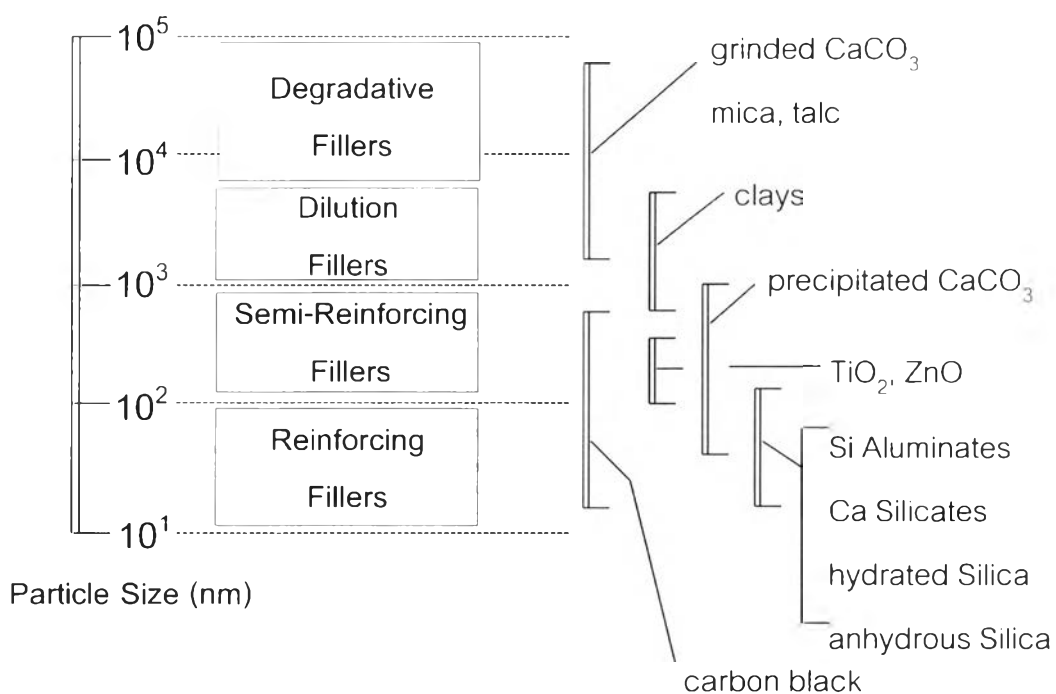


Figure 2.11 Classification of fillers according to average particle size [39]

2.5.1.2 Specific activity of filler surface

Carbon black surface is primary carbon. Other hydrocarbon or oxygen-containing groups make up a low percentage of the surface. For example, carbon black surface consists of phenolic, hydroxyl, quinone, carboxyl, lactone and free radicals which can react chemically with rubber molecules as shown in Figure 2.12. However, the filler-rubber interaction is effected by the reactivity of the rubber also.

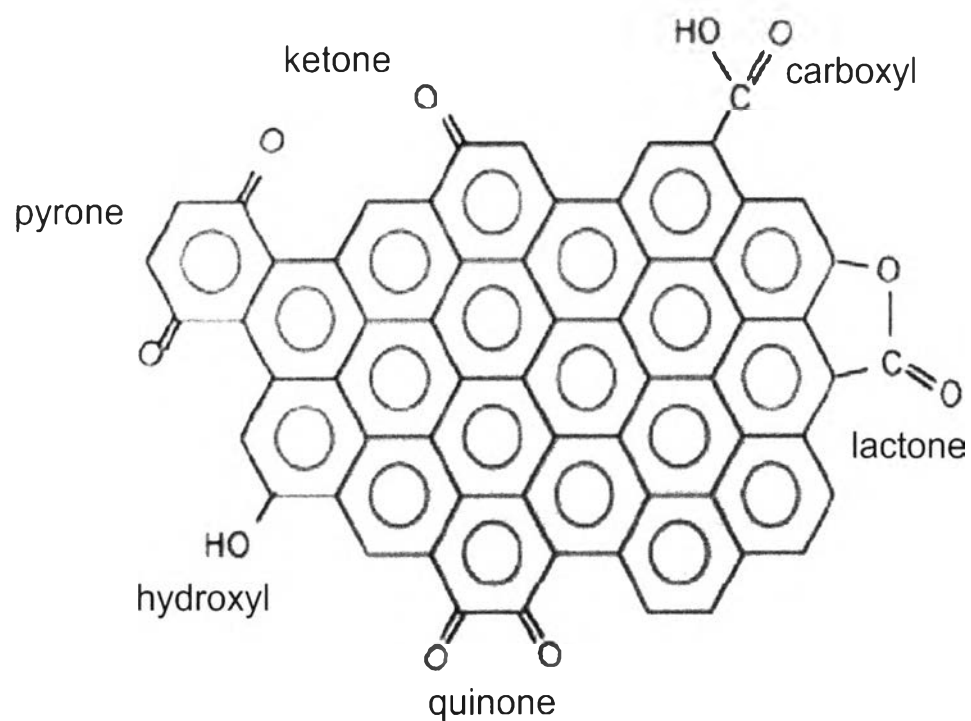


Figure 2.12 Surface chemistry of carbon black [40]

The surface activity can be influenced by heat treatment. It is well-known that heat treatment of carbon blacks at temperatures ranging between 1500 and 2700°C [41] profoundly changes the carbon black influence on rubber compound properties. The result is a low level of bound rubber, a drastic reduction in high strain modulus, tensile strength and abrasion resistance. The explanation for this behavior is that during heat treatment the size of the nanocrystallites, building up the primary particles of carbon blacks, drastically increases and the arrangement of these crystallites becomes more ordered. As a consequence the microstructure is totally changed and the number of high energy sites, located at the edges of the crystallites, decreases drastically.

2.5.1.3 Structure of filler

The primary particles formed during the initial carbon black formation stage fuse together building up three dimensional branched clusters called aggregates. High structure blacks exhibit a high number of primary particles per aggregate, which is called a strong aggregation, low structure blacks show only a weak aggregation. These aggregates again may form loose agglomerates linked by van der Waals interactions. The empty space (void volume) between the aggregates and agglomerates, usually expressed as the volume of dibutylphthalate (DBP) absorbed by a given amount of carbon black, is described by the term 'structure' of carbon black. It is assumed that the DBP absorption reflects the total carbon black structure which comprises both aggregates and agglomerates, whereas the crushed DBP absorption test eliminates loose agglomerates and easily destroyable aggregates.

The effect of the structure is attributed to the 'in-rubber structure', which can be understood as a combination of the structure of the filler in the in-rubber state ('in-rubber DBP') and the extent of filler-polymer interaction. The in-rubber structure is the measure for the occluded rubber, which is shielded from deformation and therefore increases the effective filler content leading also to a strain-independent contribution to the modulus. The filler-polymer interaction can be attributed to physical (Van der Waals) as well as to chemical linkages or a mixture of both.

2.5.1.4 Filler content

The reduction in properties at higher loading is a dilution effect, general to all fillers, merely due to a diminishing volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength approaches zero.

2.5.1.5 pH-value

The pH-value does not affect directly on degree of reinforcing. However, it can give important clues for vulcanization behavior and the possible adsorption of accelerator by the filler; this can upset the vulcanization process and result in poor properties of the vulcanizates.

2.5.2 Carbon Black

Carbon black is a well-known filler extensively used in rubber industry. Carbon black is a material composed essentially of elemental carbon in the form of quasi spherical particle that fused together into aggregate [32]. Figure 2.13 shows carbon black morphology [42]. The smallest unit of carbon black is primary particle. The average size ranges from 10 to 100 nm. It is constituted of carbon atoms arranged in plane layers of aromatic rings. The layers are seldom connected in three-dimensional network like in the crystalline carbon form graphite but rings randomly oriented and loosely held. It is semi-graphitic structure [32]. These primary particles are usually fused together into aggregate during production. Aggregate is a clustering or bonding of the primary particles. They are not broken down into primary particles upon mixing with rubber. The degree of aggregate branching is referred to as structure. Moreover, carbon black aggregates interact together with Van der Waals force, thus leading to agglomerate formation. However the agglomerates can be broken into aggregate upon mixing with rubber.

2.5.2.1 Classification of carbon black by manufacturing process

The characteristic of carbon black varies depending on manufacturing process, and therefore carbon black is classified by manufacturing process [32, 43-44].

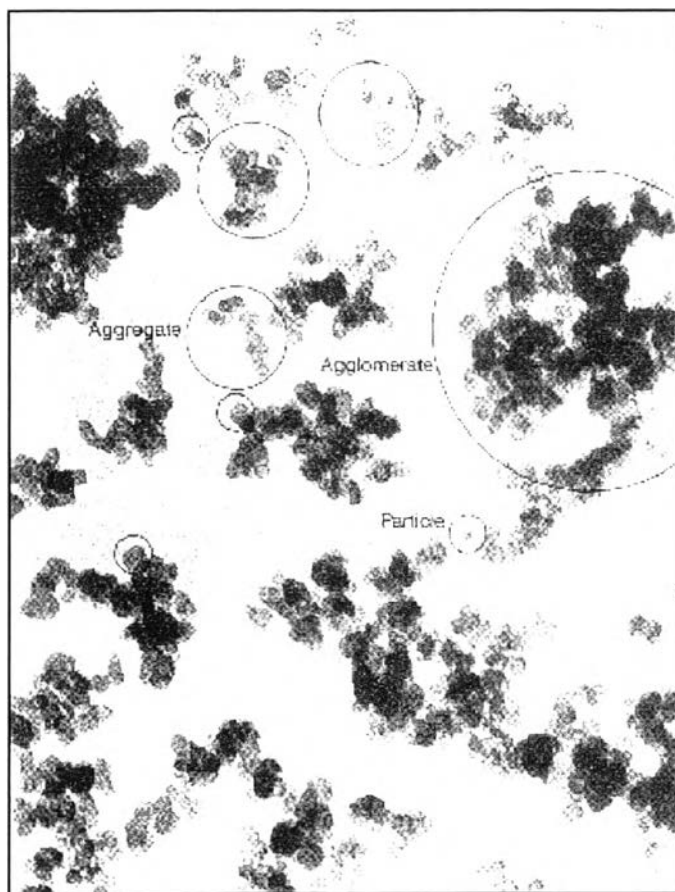


Figure 2.13 Carbon black morphology [42]

a) Furnace blacks

Furnace blacks are produced from liquid aromatic feedstock. In the process, the first step is to produce an intensely hot combustion zone with a convenient fuel. After combustion is complete, aromatic feedstock is injected into intensely hot zone. It will be burned in a reaction zone with insufficient air supply, resulting in carbon black formation. Reaction is quenched with water. Furnace blacks are finely divided carbons with low oxygen contents. Their surface is neutral or alkaline.

b) Thermal blacks

The thermal black process is carried out at a comparatively low temperature (about 1300°C) in absence of oxygen and longer residence time than the furnace process. Therefore thermal blacks are unoxidized blacks with relatively large size (1,000 to 5,000 Å).

c) Channel blacks

Natural gas is burned to form a sooty diffusion flame, and the carbon is collected on cooled iron channel. Relative free access of the hot product to air leads to oxidation of the surface, giving channel black an acidic character. They cause a more or less strong vulcanization retardation.

d) Acetylene blacks

Decomposition reaction is started by burning a mixture of acetylene and air in steel pressure vessels. It provides carbon black with higher structures and higher crystallinity, and is mainly used for electric conductive agents.

In Table 2.7, carbon black used in rubber industry can be categorized into three grades; reinforcing, semi-reinforcing and none-reinforcing grades. The smallest particle size leads to the highest surface areas and the corresponding carbon blacks are the most reinforcing but also the most difficult to disperse. Table 2.8 lists various carbon black grades with physical characteristics [45].

Table 2.7 Main categories of carbon black for the rubber industry

Reinforcement level	Suitable grades
Reinforcing grades	N100 to N300
Semi-reinforcing grades	N550 to N700
None-reinforcing grades	N880 to N990

Table 2.8 Physical characteristics of carbon blacks [45]

Code	ASTM Designation	Carbon black type	Particle diameter (nm)
SAF	N110	Super abrasion furnace	11-19
ISAF	N220	Intermediate super abrasion furnace	20-25
HAF	N330	High abrasion furnace	26-30
FF	N440	Fine furnace	31-39
FEF	N550	Fast extrusion furnace	40-48
GPF	N660	General purpose furnace	49-60
HMF	N601	High modulus furnace	49-60
SRF	N770	Semireinforcing furnace	61-100
FT	N880	Fine thermal	101-200
MT	N990	Medium thermal	201-500
EPC	S300	Easy processing channel	26-30
MPC	S301	Medium processing channel	26-30

2.5.2.2 Effect of carbon black on vulcanization

Carbon black also has influence sulfur vulcanization. Studebaker [2] showed carbon black containing stocks are scorchier than corresponding gum stocks. Scorch time decreases with increased specific surface of the carbon black. Wampler and coworkers [46] found that carbon blacks also enhance cure rate. There are two reasons for these behaviors [2]. With delayed action accelerators of the sulfenamide type, it is necessary to break the S-N bond before the accelerator becomes active. Carbon black catalytically promotes the rupture of the S-N linkages when heated. Second, most sulfur-containing

vulcanizing systems can be activated by trace amounts of hydrogen sulfide. Carbon black promotes the formation of hydrogen sulfide.

2.5.2.3 Effect of carbon black on rubber properties

In the processing, carbon black increases viscosity of a rubber compound. Carbon black filled compounds are highly non-Newtonian. Carbon black causes shear strain amplification (hydrodynamic effect). This increases viscosity. Filler-filler networking is also a factor that increases viscosity. Carbon black reduces die swell, due to reduction of the elastic component of flow.

For rubber vulcanizates, Bueche [47] proposed that the inclusion of a rigid adhering filler in a soft matrix will cause the average local strain in the matrix to exceed the macroscopic strain. Thus, rubber in filled vulcanizate is more highly strained and responds with a higher stress. This phenomenon is called strain amplification. Strain amplification also increases the mean rate at which the matrix is strained, leading to a further increase in stress. In addition to the expected increase in the modulus resulting from the inclusion of rigid filler particles in the soft matrix, another contribution arises from filler-rubber interactions, effectively leading to additional crosslinks.

A summary of the effect of carbon black on rubber properties is given in Table 2.9.

Table 2.9 Effect of carbon black on rubber properties [44]

Property	Effect of increase in carbon black		
	Surface area	Structure	Loading
<i>Processing characteristic</i>			
Mixing temperature	Increases	Increases	Increases
Die swell	Decreases	Decreases	Decreases
Mooney viscosity	Increases	Increases	Increases
Dispersion	Decreases	Increases	Decreases
Load capacity	Decreases	Decreases	-
Green strength	Increases	Increases	Increases
<i>Physical property</i>			
300% modulus	Insignificant	Increases	Increases
Tensile strength	Increases	Variable	Increases ^a
Elongation	Insignificant	Decreases	Decreases
Hardness	Increases	Increases	Increases
Tear resistance	Increases	Decreases	Increases ^a
Hysteresis	Increases	Variable	Increases
Abrasion resistance	Increases	Variable	Increases ^a
Low strain dynamic modulus	Increases	Insignificant	Increases
High strain dynamic modulus	Insignificant	Increases	Increases

^a Increases to an optimum before decreasing.

2.6 Determination of Sulfur Crosslink Distribution by XANES

XAS measures the probability that a photon is absorbed by the sample as a function of its energy. A spectrum obtained from XAS technique can be separated into two parts, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). XANES is useful for identifying chemical forms (as fingerprints) and oxidation states as well as studying valence states [48] and symmetry of unoccupied orbital whereas EXAFS, appearing as oscillation part seen above the absorption edge [49], is useful for analysis of local atomic structure. XAS is non-destructive to sample and can be used with various types of the sample such as solid, liquid, and gas.

Over the years, there have been a number of XANES studies at the sulfur K-edge of the sulfur crosslink in the vulcanized rubber. Chauvistré et al. [50] and Hormes and Modrow [51] reported that the peak shift is related to the number of sulfur atoms within the sulfur crosslink. The absorption peak of XANES spectrum is shifted to lower photon energy when the number of sulfur atoms is increased as shown in Figure 2.14. According to the shifting of sulfur peak due to the change in the number of sulfur atoms within the crosslink, many researches try to use this technique to examine the crosslink distribution [51-52].

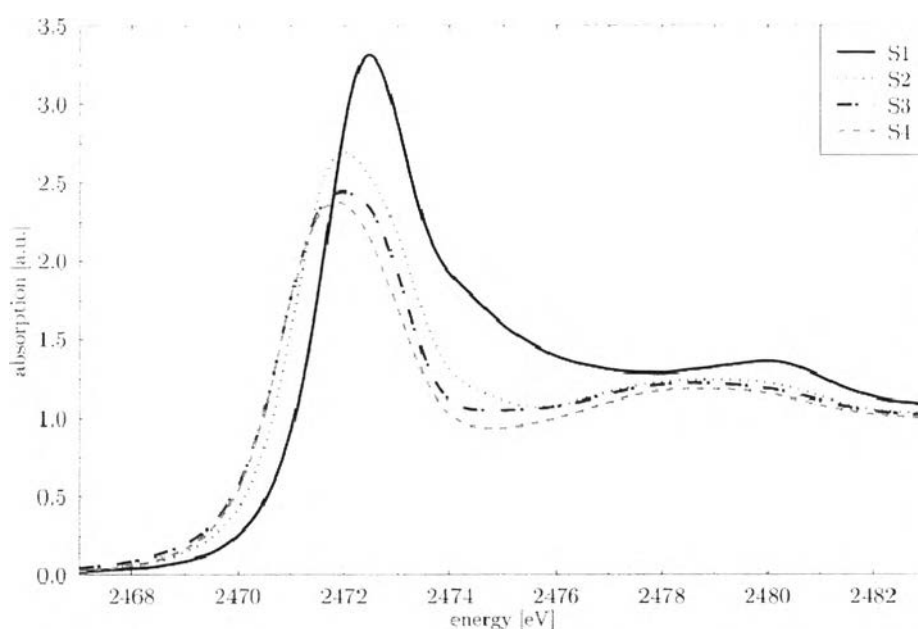


Figure 2.14 XANES spectra of dioctenyl- n -sulfanes ($n=1-4$) [52]

Furthermore, Brendebach and Modorw [52] investigated the influence of carbon black on vulcanization process, using XANES spectroscopy. As shown in Figure 2.15, the absorption peak of XANES spectrum of the sample containing carbon black shifts to lower photon energy. This can explain that the amount of sulfur bonds or chain length of sulfurs increased when carbon black was added to the sample. Surface activity of carbon black, which correlates to high surface energy, allows a chain clipping reaction of sulfur bonds in element sulfur rings to take place and then accelerates formation of polymeric sulfur chain and crosslinks with four or three bound sulfur atom.

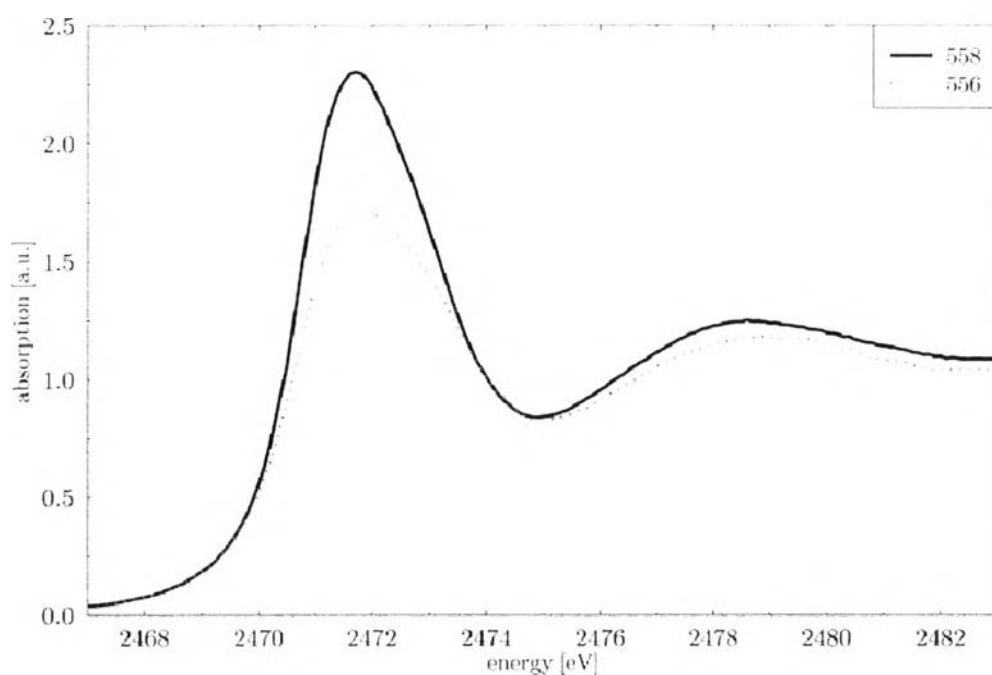


Figure 2.15 XANES spectra of compounds 556 (without filler) and 558 (with a contribution of 10 phr carbon black) [52]