

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

ASTM D 1566-90 defines elastomers as “macromolecular material that returns rapidly to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress”. A rubber in its modified state, free of diluents, retracts within 1 min to less than 1.5 times its original length after being stretched at room temperature to twice its length and held for 1 min before release. More specifically, an elastomer is a rubber like material that can be or already is modified to a state exhibiting little plastic flow and quick and nearly complete recovery from an extending force. Such material before modification is called, in most instances, a raw or crude rubber or a basic high polymer and by appropriate processes may be converted into a finished product. The rubber definition with its swelling test certainly limits it to only the natural latex-tree source, whereas the elastomer definition is more in line with modern new synthetics [1].

Natural rubber is a white milky fluid produced by specialized cells in a variety of plants, throughout the world, in totally unrelated families, including the *Compositae* and *Moraceae* as well as the Euphorbiaceae [2]. Although in the past many different species have been used for obtaining crops of latex. The principal source of natural rubber, today, is *Hevea Brasiliensis*, which is a native of the tropical rain forest of the Amazon Basin in Brazil. Most of the world’s natural rubber comes today from South East Asia, mainly Thailand, Malaysia, and Indonesia [3].

Hevea Brasiliensis, the commercial rubber tree, is a tall tree, growing naturally up to forty metres (130 feet) and living for one hundred years or more. *Hevea Brasiliensis* requires temperatures of 20-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity. This naturally occurring polymer is known chemically as cis-1,4-polyisoprene [2].

2.2 Processing and Rubber Compounding [4]

The optimization of properties for natural and synthetic rubber by the incorporation of non-rubber ingredients, process referred to as compounding, has always been historically important. Rubber compounding is day practiced predominately on the basis of scientific principles elucidated over many years of research.

The mixing and processing of rubber play a vital role in achieving and controlling particular flow characteristics for the uncured compound and also the engineering properties in the final vulcanisate, and control the mixing and processing conditions, if reproducibility of optimum properties is to be achieved between different manufacturing plants and/or laboratories.

Compounding ingredients are used to influence and control mixing/processing parameters and are of great importance in rubber compound design, since in manufacturing ease of processability often ranks in equal importance to final vulcanisate properties and cost.

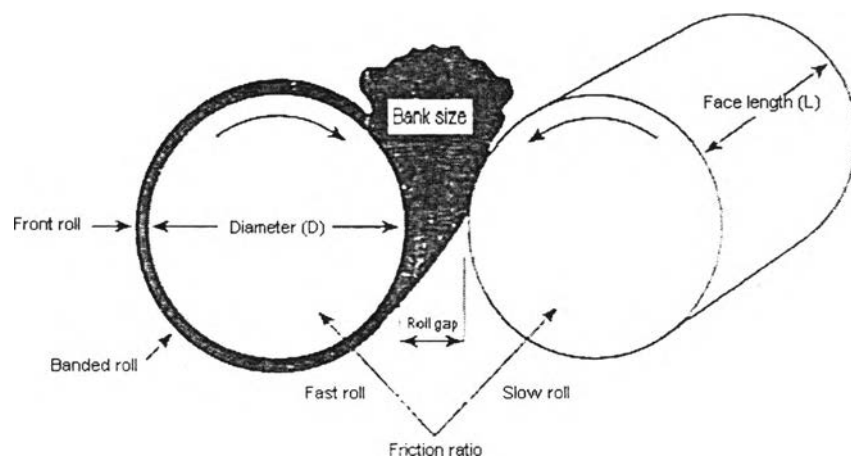


Figure 2.1 Two Roll Mill [5].

2.3 Vulcanisation and Acceleration [4]

The concept of rubber vulcanisation is the conversion of a fully mobile entanglement of rubber macromolecules into a chemically stable network by the insertion of covalent bonds or crosslinks to give an elastic material. Such a phenomena is illustrated in Figure 2.2 and 2.3.

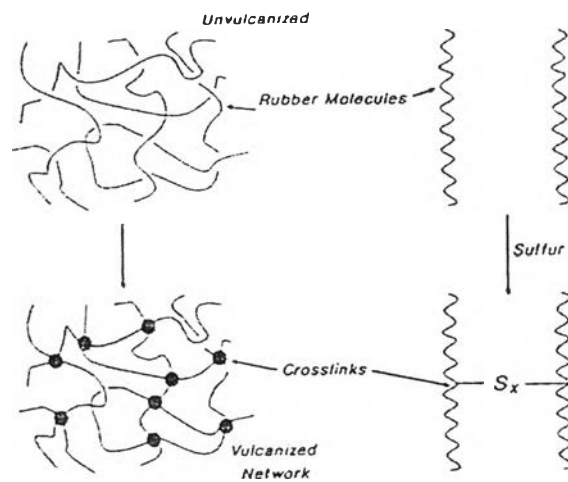


Figure 2.2 Network Formation [6].

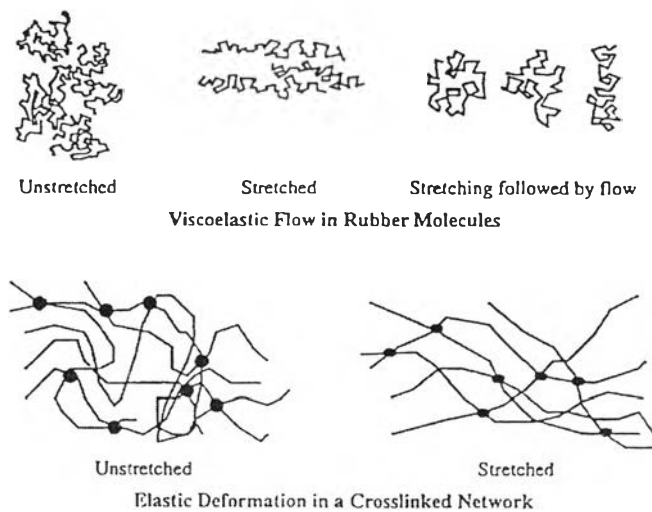
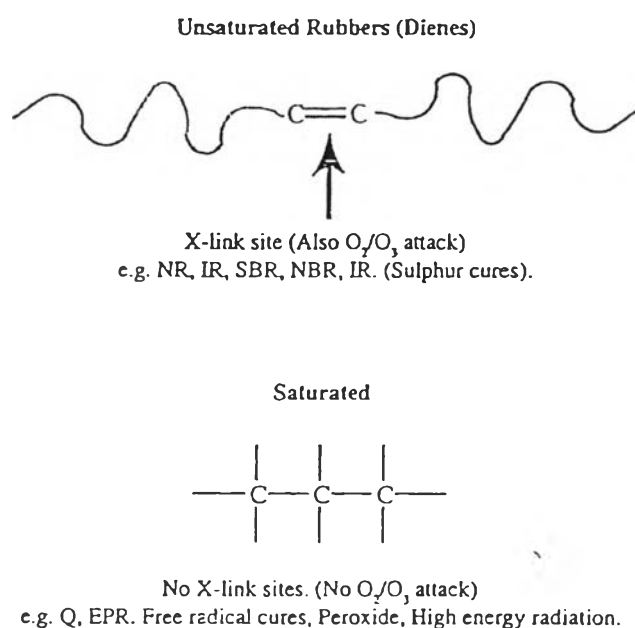


Figure 2.3 The Concept of Rubber Vulcanisation [4].

For vulcanisation purposes most common rubbers can be classified into one of the two structures as shown in Figure 2.4. Of these the main chain unsaturated diene structure, historically the oldest, is the most common and is still commercially the most importance. The combination of saturated main chain with unsaturated side chain represents a versatile technical alternative, although rubbers in this group, whilst being more stable to environmental attack usually less strong and have poorer adhesion properties. Vulcanisation of these unsaturated rubbers will be discussed initially, as they are predominantly sulphur based.



- NR = natural rubber
- IR = isoprene rubber
- SBR = styrene-butadiene copolymer
- NBR = nitrile rubber
- EPR = ethylene propylene rubber

Figure 2.4 Common Rubber Structures for the Classification of Vulcanisation Properties [4].

2.3.1 Sulphur Vulcanisation and Acceleration

Organic chemical accelerators were not used until 1906, when the effect of aniline on sulphur vulcanization was discovered by Oenslager. This could have been, at least partially, in response to the development of pneumatic tires and automobiles near the turn of the century. Further developments lead to guanidine accelerators. Reaction products formed between carbon disulfide and aliphatic amines (dithiocarbamates) were first used as accelerators 1919. These are still the most active accelerators with respect to both crosslinking rate and extent of crosslink formation [6].

The different stages of vulcanisation are shown in Figure 2.5. They give rise to the mixture of the various crosslink structures shown in Figure 2.6. In Figure 2.6 usually one or two structures can be made to be dominant by the appropriate selection of particular vulcanisation accelerators and by specific accelerator/ sulphur ratios.

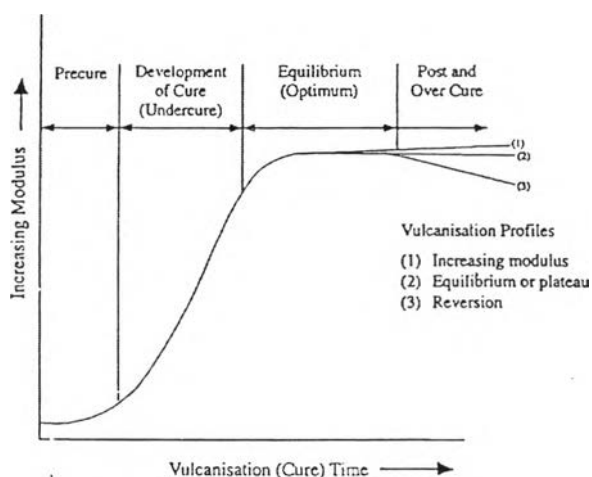


Figure 2.5 The Progressive Stage of Rubber Vulcanisation [4].

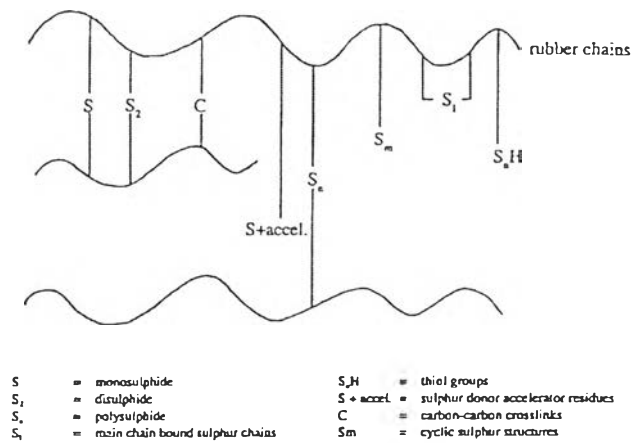


Figure 2.6 Sulphur Crosslink Structures [4].

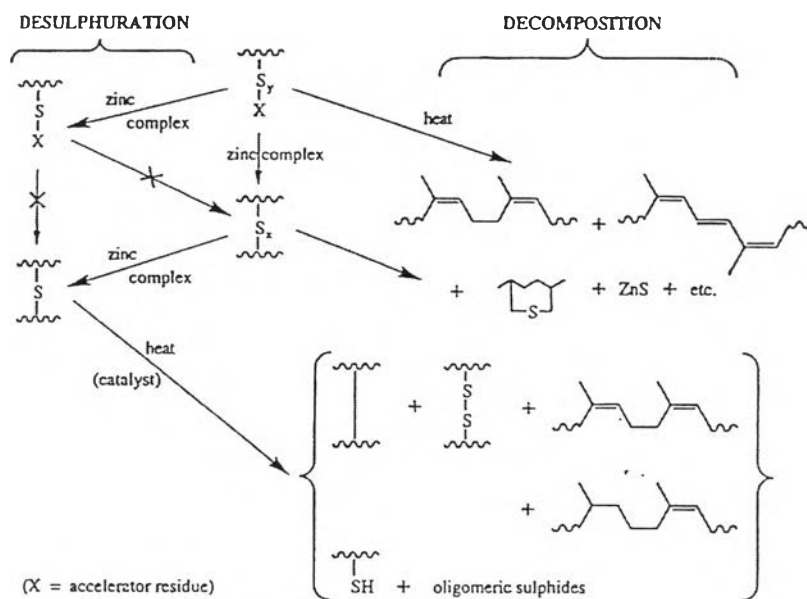


Figure 2.7 Crosslinking, Decomposition and Desulphuration Reactions that Proceed in a Rubber Vulcanisation Process [4].

Additionally the rate of vulcanisation is controlled by the choice of accelerators and the influence of the different primary classes of accelerators (Figure 2.8).

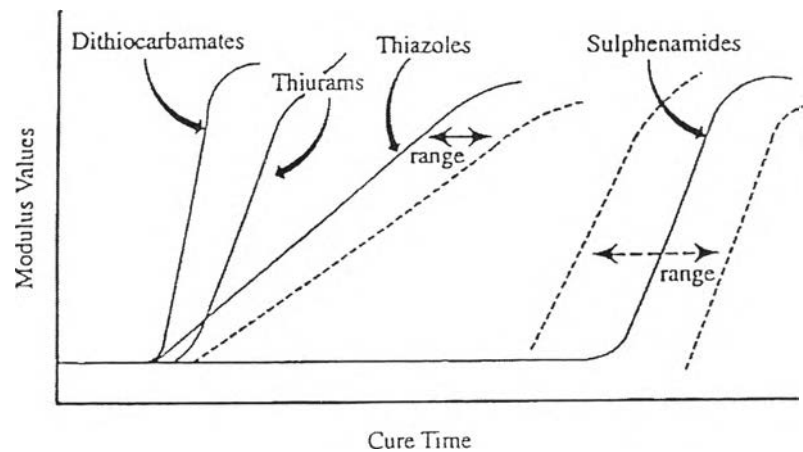


Figure 2.8 Delayed Action Vulcanisation According to Choice of Accelerator [4].

2.3.2 Peroxide of Free Radical Vulcanisation Systems

a) The Carbon-Carbon Crosslink

The type of crosslink is available when a peroxide is used to crosslink a rubber, and one carbon atom is directly bonded to another carbon atom, giving vulcanisates which have better thermal stability than sulphur vulcanisates though accompanied by lower strength. The mechanism of peroxide crosslinking can be seen that in addition to the formation of C-C crosslinks decomposition, by-products are formed and can remain in situ within the rubber vulcanisate after cure. Their presence can be detrimental on several grounds.

- 1) Free radicals are left within the rubber and hence form the focus for long term oxidative degradation sites unless they are removed.
- 2) The vulcanisates may possess an unpleasant odor due, for example, to the presence of acetophenone if dicumyl peroxide (DCP) is used.

Removal of such decomposition products is therefore paramount if an optimally cured vulcanisate is to be obtained and hence post-curing of the set cured vulcanisate in hot air ovens at atmosphere pressure, or under vacuum, is usually carried out to achieve maximum stability.

b) Saturated Rubbers

The only practical way of vulcanizing saturated rubbers is by the use of a free radical generating technique. Only two such techniques presently exist, namely the use of peroxides or the use of high energy radiation such as gamma radiation or electron beam bombardment.

c) Co-Agents for Peroxide Vulcanisation

The crosslinking efficiency of many peroxide-initiated free radicals is low, due to their short lifetime. These labile radicals can be converted to more stable radicals by contact *in situ* in the rubber mix with polyfunctional monomers to form a three-dimensional polymer network. Crosslinking efficiency is thus increased by about 20%. Examples of co-agents include triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), ethylene glycol diacrylate and glycerol trimethacrylate, all usually used at levels of 3 phr.

d) Urethane Crosslinking

Urethane crosslinking agents are formed by an addition reaction between a nitrosophenol and diisocyanate. On heating to vulcanisation temperatures this addition reactions reversed to liberate the nitrosophenol which forms pendant aminophenol groups on the rubber molecule. Simultaneously the diisocyanate liberated reacts with these main chain aminophenol to form crosslinks.

2.3.3 Crosslinking Density [7]

The crosslinking density was determined by Flory-Rhener equation (2.1).

$$-\left[\ln(1-V_{2m}) + V_{2m} + \chi_1 V_{2m}^2 \right] = \frac{V_1[\rho_2]}{M_c} \left[V_{2m}^{1/3} - \frac{V_{2m}}{2} \right] \quad (2.1)$$

Or

$$Mc = \frac{V_1 \rho_2 \left[V_{2m}^{1/3} - \frac{V_{2m}}{2} \right]}{- [Ln(1-V_{2m}) + V_{2m} + \chi_1 V_{2m}^2]} \quad (2.2)$$

Swelling can be determined gravimetrically, by weighing the polymer sample before the experiment (w_0) and subtracting this value from the solvent swollen polymer weight (w_s) as in equation 2.3.

$$V_{equil} = \frac{W_0}{\rho_2} + \frac{W_s - W_0}{\rho_1} \quad (2.3)$$

and

$$V_{2m} = \frac{W_0}{V_{equil} \cdot \rho_2} \quad (2.4)$$

Where

V_1 = molar volume of solvent

χ_1 = polymer-solvent interaction parameter

W_0 = original polymer weight

W_s = swollen polymer weight

ρ_1 = solvent density

ρ_2 = initial density of polymer

2.4 Reinforcing Fillers for Rubber

This is a fundamental part of rubber compounding and an understanding of the basic theory of rubber reinforcement is necessary to comprehend why such a large variety of

particulate filler materials are commercially viable in this aspect of rubber compounding. The field is one of continual advances in filler materials, their treatments and various processes.

2.4.1 Strain Crystallization in Rubber

All rubbers can be classified as either strain crystallisable (i.e. self-reinforcing) or non strain crystallisable (i.e. non self-reinforcing); in the latter case it is necessary to artificially provide some form of simulated in situ crystallites to provide the reinforcing effect of the natural crystallite which exists or the case of the strain crystallisable material.

2.4.2 The Interaction of Strain Crystallization and Filler Particles in a Rubber

Then filler particles are very large the rubber chains cannot fully envelop them. However if the filler particles are reduced in size a critical size is eventually reached such that the particles can then fit within crosslinked segments in the vulcanized rubber. In Figure 2.9, three chains of rubber crosslinked together are shown. When a strain crystallisable rubber such as natural or chloroprene rubber is stretched, crystallites develop, which tend to reinforce the rubber (see Figure 2.9b). Sufficiently small filler particles can be accommodated within the crosslinked segments as shown in Figure 2.9c. Upon applying a stress, the filler particles effectively take up the slack in the crosslinked chains permitting a greater degree of crystallization, Figure 2.9d.

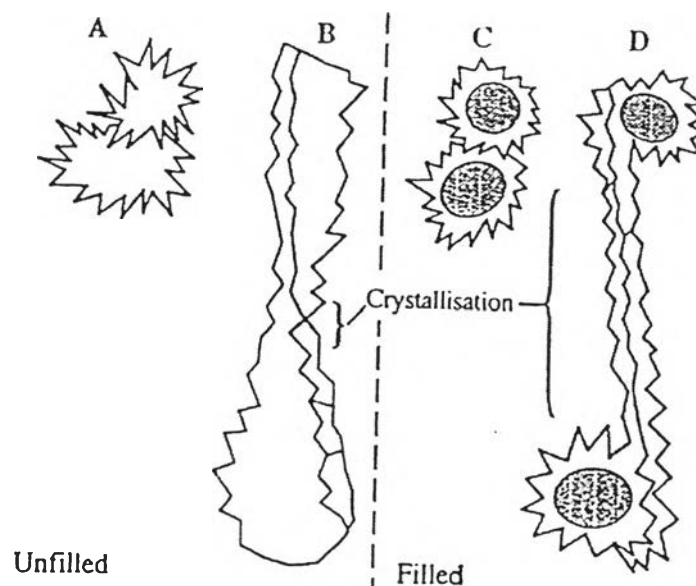


Figure 2.9 A Schematic Diagram of the Stretching Process in Natural Rubber with Active Fillers [4].

2.4.3 Tear Strength and Filler Reinforcement

Figure 2.10 illustrates one way in which fillers and crystallization can act together. If the central chain were to break at A without the filler particles being present, the ends of the broken chain would retract a sizeable distance. Most of the load held by chain A would be thrown on to chains B and C the broken chain will only retract a short distance, and most of the load held by chain A will be distributed over all the chains attached to the filler particles. Hence the filler particles act effectively as a means of distributing the load more equitably, thus decreasing the chance for a 'break' to propagate, and consequently increasing the strength of the sample. The above remarks concerning the load-sharing acting of filler can be applied equally well to crystallites.

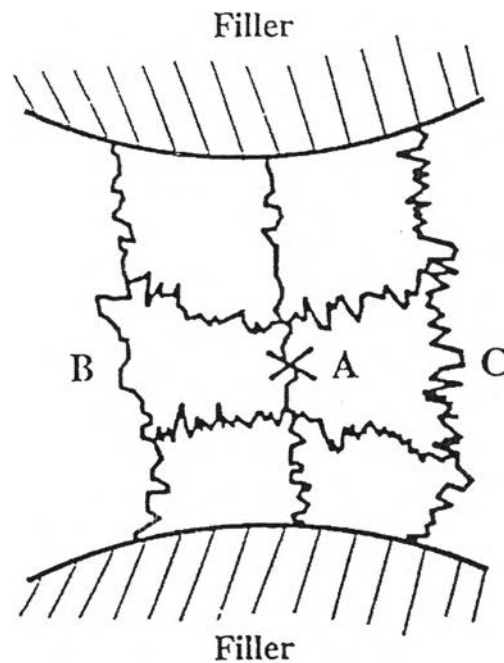


Figure 2.10 The Load-Sharing Actions of Fillers when a Rubber Chain Breaks [4].

2.4.4 Stress Softening or Mullins Effect

Rubbers that contain reinforcing fillers display a curious effect, the ‘Mullins effect’ or ‘Stress-softening effect’, which gives considerable information concerning the modulus reinforcing action of the filler. It may be described best by reference to the stress-strain curve shown in Figure 2.11.

If a vulcanized rubber filled with carbon black is stretched slowly for the first time, it gives a stress-strain curve somewhat like curve OABC of Figure 2.11. Suppose that a particular rubber is only stretched to B on this curve during the first stretching cycle. If the sample is now relaxed to facilitate complete recovery the rubber will follow curve ODBC in the next stretching cycle. Obviously, although the curves do not differ much at very small elongations, the rubber has been softened by the first stretching process.

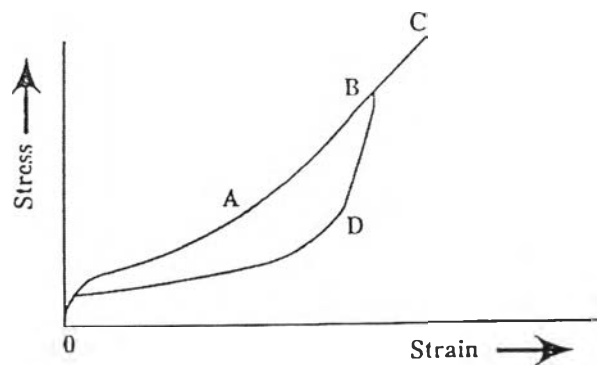


Figure 2.11 The Action of Reinforcing Fillers (Stress-Softeners) [4].

If the chains connecting the surfaces of two adjacent filler particles are examined, some of these chains will be rather highly elongated, while others will be very loosely coiled, since they must conform to the Gaussian distribution of chain-end lengths. This is shown in Figure 2.12. If the rubber is now stretched, the filler particles will almost certainly separate in proportion to the overall elongation of the rubber.

Obviously, chain A must break at a relatively small elongation, but before breaking, together with similar chains will hold an enormous load and give rise to a high modulus. On the second stretch, however the broken chains will not be holding any load, and consequently the modulus will be lower.

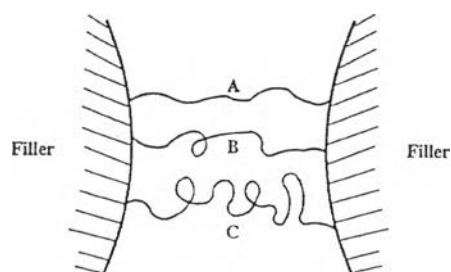


Figure 2.12 The Mechanism of Stress Softening [4].

2.4.5 Conditions for Reinforcement

a) Particle Size Influence

The primary property of particulate filler which is able to reinforce rubber is a sufficiently small particle size. Tensile strength properties vary inversely with particle size for a given loading. The problem generally applies irrespective of all other filler/particle morphology and chemical or physico-chemical properties. The relative reinforcing abilities of the different particle size fillers are given in Table 2.1.

Table 2.1 Particle Size for Rubber Reinforcement [4].

Particle Size	Effect
Particles > 5000 nm	Degraded rubber
1000 < Particles < 5000 nm	Have little effect on strength-hence large volumes can be used with little degradation of rubber
Particles < 1000 nm	Reinforcement
Particles < 1 nm	Real reinforcing agent

b) Filler Reinforcement Factors

- i) Extensity - Surface area
- ii) Intensity - Chemistry of surface
- iii) Geometric – Shape and porosity of particles

Primary concept

Reinforcement factor = Total area x Specific surface activity

It is known that chemical bonding at the filler-rubber interface is not a necessary condition for reinforcement. However chemical bonding will lead to unique combinations of mechanical properties which gives the best overall reinforcing effect.

2.4.6 Measurement of Reinforcement in Rubber Vulcanisates

Reinforcement effects in vulcanisates containing active fillers are generally measured by the resistance to abrasion, tearing, cut growth, flex cracking and tensile fracture. These are all failure phenomena which appear to involve, in complex ways, the common process of rupture propagation through the rubber. A widely used method to assess the relative ability of fillers to reinforce rubber is shown in Figure 2.13 which demonstrates the 'optimum loading concept' of a filler. As can be seen the reinforcement conveyed to a rubber by a reinforcing filler increases initially until a maximum is reached after which dilution effects predominate and the strength of the rubber composite reduces. Fillers can be compared for their relative performances in any rubber polymer on this basis.

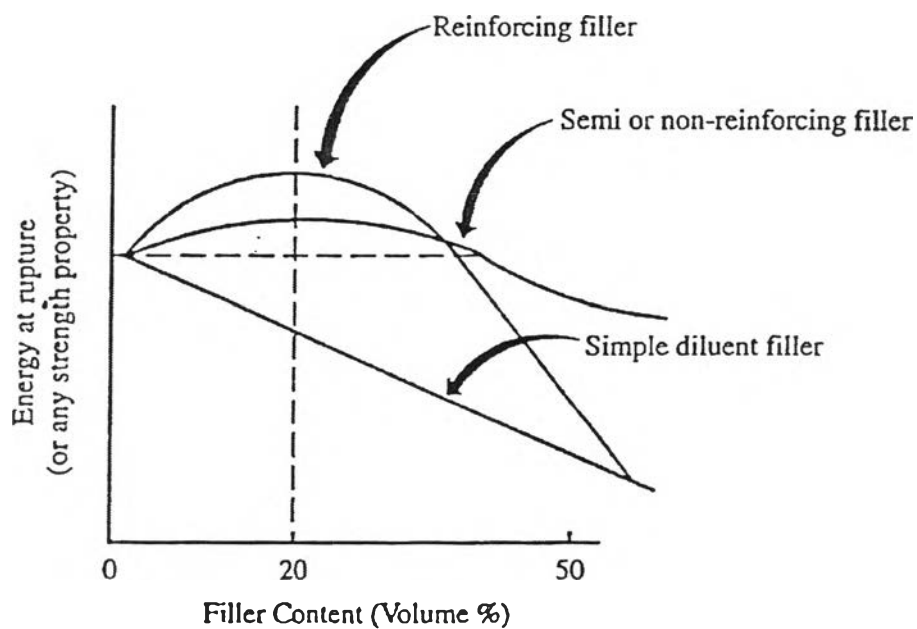


Figure 2.13 The Optimum Loading Concept [4].

2.4.7 Filler Activity and Reinforcement

Particulate fillers can be classified as active, semi-active and active. The activity of a filler is a phenomenon which can be described in terms of bound rubber content.

When rubber and filler are mixed together under conditions of high shear (e.g. in a mill or in an internal mixer), it is observed that a percentage of insoluble gel is present in the rubber mix which can be used to quantify rubber-filler interaction. This gel is referred to as the bound rubber content and is used as an indication of the filler's ability to reinforce the rubber.

The definition of bound rubber is as follows:

$$\text{Bound Rubber} = \frac{\% \text{ insoluble fraction} - \text{filler fraction}}{\% \text{ total rubber}} \times 100 \quad (2.5)$$

The general empirical relationships between inactive and active fillers and rubber properties are shown in Figure 2.14. Structure and particle size influence of fillers are given in Table 2.2.

Table 2.2 Influences of the Structure and Particle Size [4].

Increasing Structure	Decreasing Particle Size
- increase of Mooney viscosity	- increase of tensile strength
- better shape stability and surface quality during extrusion	- decrease of elongation
- decrease of elongation	- increase of hardness
- increase of hardness	- increase of tear strength
- increase of modulus	- decrease of abrasion

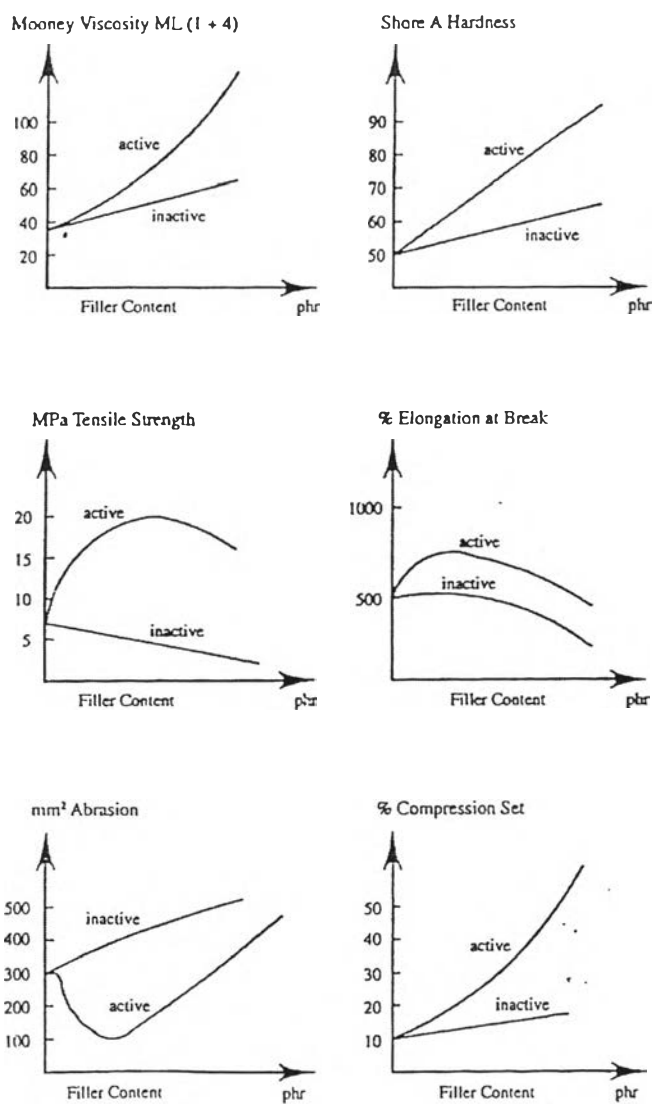


Figure 2.14 General Relationship Between Inactive and Active Fillers and Rubber Properties [4].

2.4.8 Filler Structure

Real fillers are not round particles but have complicated geometric shapes and may also be porous. However, calculated values assuming a filler particle to be ideal or round are useful theoretical concepts, as:

$$\text{Measure surface} - \text{Calculated surface area} = \text{the inner surface area} \quad (2.6)$$

The measured surface area is obtained by a nitrogen absorption methods called the BET (Brunauer-Emmett-Teller) technique, and results are in m^2/g . For white fillers (black fillers use a different classification technique) typical BET values for inactive to very active fillers are given in Table 2.3.

Table 2.3 BET Values for Inactive and Active White Fillers [4].

BET < 10 m^2/g	Inactive
BET 10- 60 m^2/g	Semi-active
BET > 60 m^2/g	Active
BET > 100 m^2/g	Very active

2.4.9 Physical and Chemical Interaction at the Filler Surface [8]

Whether or not reinforcement requires the formation of primary valance bonds, anchoring polymer chains to the filler surface, has been the subject of much controversy. The origin of this controversy can be traced to differing view of what constitutes ‘true’ reinforcement. The experimental evidence is quite clear:

- (1) chemical bonding at the filler-rubber interface is not a necessary condition for reinforcement:
- (2) chemical bonding leads to the unique combination of mechanical properties associated with carbon black, the best overall reinforcing agent known.

If the existence of chemical bonding can be established for a filler-polymer system with a high degree of probability, and if means for 'deactivating' the surface can be found which do not fundamentally alter the filler morphology, then a comparison of vulcanisate physical properties permits the effects of bonding to be established. Conversely, chemical filler-polymer linkages can be introduced into a system devoid of (or at least deficient in) such linkages.

2.4.10 Chemical Functionality of Rubber Surfaces [9]

a) Carbon Blacks

The most important synthetic fillers used in rubber are the carbon blacks. These are principally made by the chemical decomposition of natural gas or oil. Two classes predominate, namely the furnace blacks which are active and thermal blacks which are inactive. There are a substantial number of other carbon blacks available such as electrically conducting and printing ink blacks.

b) Non-Black and Mineral Fillers

In the rubber compounding field naturally occurring mineral fillers are important in reducing cost and are usually classified on the basis of their origin.

They are usually classified as:[10]

1. Fillers used mainly to reduce cost.
2. Certain unique properties are required like thermal conductivity by the use of zinc oxide.
3. Reinforcing fillers used to achieve high performance in non-black products.

This classification is not rigid as materials derived from similar sources may vary in

function according to their methods of preparation and treatment. It has been considered expedient, therefore, to group them here according to their source.

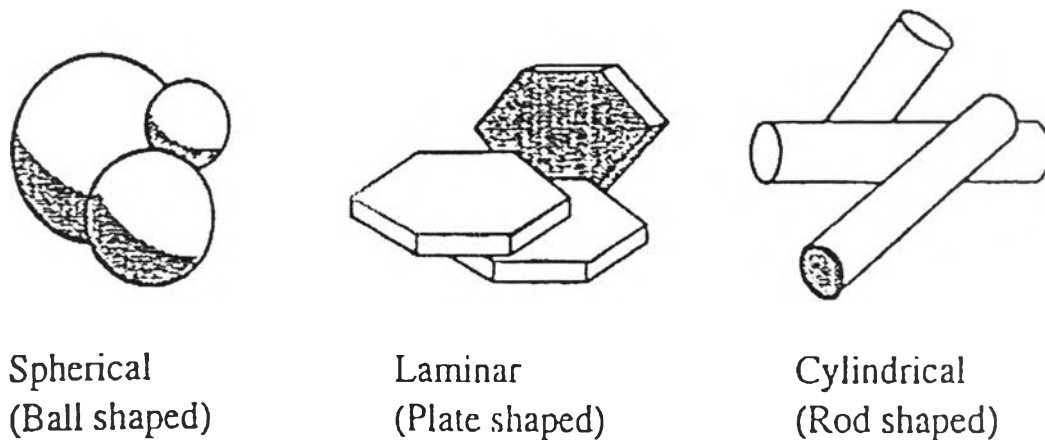


Figure 2.15 Basic Types of Mineral Filler Shapes [10].

I) Calcium Carbonates

The large particle size is obtained either by grinding or water flotation, particle shape is corpuscular and with a relatively small surface area it has to be regarded as inactive filler except when involved with highly acidic medias. Calcium carbonate can be regarded as a cheap inert filler capable of easy processing. It is the most widely used extender in the rubber industry.

II) Synthetic Calcium Carbonates

These are produced by precipitation and are then referred to as precipitated calcium carbonates and are semi-active fillers. If these precipitated fillers are surface coated with stearic acid or polybutadiene rubber they become fully reinforcing fillers.

III) Clays

These usually kaolin clays called the kaolinites. They are based upon aluminum and are laminar in structure. Within the particle size range 1-5 microns two general categories of surface area are available namely:

- No reinforcement: Soft clay of surface area below $10 \text{ m}^2/\text{g}$. No activity.
- Some reinforcement: Hard clay of surface area approximately $30 \text{ m}^2/\text{g}$. Semi active.

IV) Silicas

Ground Mineral Silica. Mineral silica or sand (silicon dioxide) ground below 200 mesh is a cheap filler for heat-resistant compounds. It has no effect on cure.

- Hydrated Precipitated Silicas: These silicas are silicon dioxide containing 10-14% water, with particle sizes in the range 10-40 nm. They are reinforcing fillers giving compounds of high tensile strength, tear resistance, abrasion mechanical goods, and shoe soling. In combination with reinforcing blacks they improve tear resistance and adhesion to fabrics. Hydrated silicas retard cure and require increased dosage of accelerator or the addition of materials such as glycols or amines to promote curing. They respond to hot mixing techniques in a manner similar to reinforcing blacks giving increased modulus or resilience.

- Fume Silica or Pyrogenic Silica: Fume or pyrogenic silica is silicon dioxide, containing less than 2% combined water, usually prepared by burning volatile silicon compounds. These silicas are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance, and abrasion resistance, particularly to silicone rubbers. The retarding effect on cure in organic rubbers requires increased amounts of accelerators or the use of glycols or amines. The use of wax, polyethylene, or other lubricating materials is recommended to avoid sticking to rolls in processing and to moulds after cure.

2.5 Nanomaterial Technology

2.5.1 Nano-Technology [11]

Nanotechnology is very much in vogue now. The idea of manipulating material at the most fundamental level, the level of life itself, is very intriguing and seems to be financially attractive. The availability of tools and methods to study material at that level (e.g. Atomic Force Microscope, to name just one of a large group), the development of molecular biology and the shrinking size of complex electronic devices, have all contributed to that excitement.

2.5.2 Benefits of Nanoscopic Materials in Applications

- 1) Nano chemicals (specialty functional fillers/ additives)
 - Enhance properties in plastic (nano-composite), paint/coating, pulp and paper, ink, rubber and etc.
- 2) Nano drugs (drug delivery)
 - Enhance absorption into human body and improves therapeutic effectiveness
 - Reduce dosage/cost
 - Replace more invasive application methods
- 3) Nano ceramics
 - Reduce sintering temperature and component size
 - Improves electrical properties and reduce component size
- 4) Nano catalysts
 - Enhance catalyst reactivity (requires less active ingredient or lower reaction temperature)

2.6 Literature Reviews

Arroyo et al. [12] studied octadecylamine modified montmorillonite use as substitute of carbon black in natural rubber (NR) compounds. Rubber with 10 phr of clay and

octadecylamine modified montmorillonite (organoclay) were compared with 10 and 40 phr carbon black as filler. Vulcanometric curves show that the organoclay and carbon black accelerate the vulcanisation reaction and increase torque, indicating a higher degree of crosslinking as was also confirmed by swelling measurements. The mechanical properties of NR with 10 phr organoclay are comparable to the compound with 40 phr carbon black. Moreover, the organoclay improves the strength of the NR without hardly any reduction in the elasticity of the material.

Chan et al. [13] studied the polypropylene (PP) and calcium carbonate nanocomposites. The average primary particle size of the calcium carbonate nanoparticles was measured to be about 44 nm. The calcium carbonate nanoparticles are very effective nucleating agent for PP. Tensile tests showed that the modulus of the nanocomposites increased by approximately 85%, while the ultimate stress and strain, as well as yield stress and strain were not much affected by the presence of CaCO_3 nanoparticles.

The results of the tensile test can be explained by the presence of the two-counter balancing forces such as the reinforcing effect of the CaCO_3 nanoparticles and the decrease in spherulite size of the PP. Izod impact tests suggested that the incorporation of CaCO_3 nanoparticles in PP has significantly increased its impact strength by approximately 300%. J-integral tests showed a dramatic 500% increase in the notched fracture toughness. Micrographs of scanning electron microscopy revealed the absence of spherulitic structure for the PP matrix.

In addition, DSC results indicated the presence of a small amount of β phase PP after the addition of the calcium carbonate nanoparticles. The large number of CaCO_3 nanoparticles may act as stress concentration sites which can promote cavitation at the particle-polymer boundaries during loading. The cavitation can release the plastic constraints and trigger mass plastic deformation of the matrix, leading to much improved fracture toughness.

Poh et al. [14] studied the effect of filler loading on the tensile and tear properties of SMR L (one grade of natural rubber) /ENR 25 (epoxidized natural rubber) and SMR L/SBR (styrene-butadiene rubber) blends using a semi-efficient vulcanisation system. Carbon black (N330), silica (Vulcasil C) and calcium carbonate were used as the fillers and the loading range was from 0 to 40 phr. Results show that for the carbon black and silica-filled blends, elongation

at break decreases, but tensile strength, modulus 300 and tear strength increase with filler loading. The reverse behavior is obtained for the calcium carbonate-filled blends. This observation is attributed to the better rubber-filler interphase interaction of carbon black and silica compared to the non-reinforcing nature of calcium carbonate, the dilution effect of which becomes more significant as the filler loading is increased. For a fixed filler loading, SMR L/ENR 25 blend consistently exhibits higher tensile strength, modulus 300 and tear strength but lower elongation at break compared to SMR L/SBR blend. This finding is associated with the mutual rubber reinforcement between the two strain induced crystallizable rubbers (i.e. SMR L and ENR 25), coupled with good rubber-filler interaction, particularly between silica and ENR 25 in the former blend.

Frogley et al. [15] studied silicone based elastomers mixed with single-wall carbon nanotubes or larger carbon nanofibrils. Tensile tests show a dramatic enhancement of the initial modulus of the resulting specimens as a function of filler load, accompanied by a reduction of the ultimate properties. It was found that the unique properties of the carbon nanoparticles are important and effective in the reinforcement. The modulus enhancement of the composites initially increases as a function of applied strain and then at around 10-20% strain the enhancement effect is lost in all of the samples. This “pseudo-yield” in elastomeric (or rubber) composites is generally believed to be due to trapping and release of rubber within filler clusters. In Raman spectroscopy experiments show a loss of stress transfer to the nanotubes suggesting that instead. The “pseudo yield” is due to break-down of the effective interface between the phases. The reorientation of nanotubes under strain in the samples may be responsible for the initial increase in modulus enhancement under strain and this is quantified in the Raman experiments.

Wang et al. [16] studied two different preparation methods of rubber-clay nanocomposites and characterized with TEM and XRD. The TEM showed clay had been dispersed to one or several layers. The XRD showed that the basal spacing in the clay was increased. It was evident that some macromolecules intercalated to the clay layer galleries. The clay layer could be uniformly dispersed in the rubber matrix on the nanometer level. The mechanical tests showed that the nanocomposites had good mechanical properties. Some

properties exceeded those of rubber reinforced with carbon black, so the clay layers could be used as an important reinforcing agent as the carbon black was.

Hundiwale et al. [17] studied the mechanical properties of natural rubber filled with fly ash. The mechanical properties of fly ash-filled natural rubber were investigated and compared with those filled with calcium carbonate. A number of composites with varying percentage of the fillers were prepared using a two-roll mill and a compression molding press. Specimens were subjected to mechanical testing. The properties studied were tensile strength, modulus at various elongations, hardness, density, etc. In this work, it was observed that addition of filler increased the tensile strength and modulus reach maximum, and when the property decreased with increasing the volume fraction of the filler. The composites undergo transition from a continuous phase to a discontinuous phase as the volume fraction of the filler increases. The increase in properties is due to the wetting of the filler with matrix material while dewetting between the filler and matrix materials causes the decrease. Fly ash-filled natural rubber showed better results than those of calcium carbonate-filled composites. Hence, fly ash could be utilized as a filler, which is, of course, an economical one, and simultaneously, its consumption as filler will definitely help in reducing environmental pollution and financial burden involved in its disposal.