

**THE EFFECT OF CARBON BLACK LOADINGS ON TENSILE STRENGTH
OF RUBBER VULCANIZATES**

MOHD WAQIYUDDIN BIN MOHD SALLEH

UNIVERSITI MALAYSIA PAHANG

THE EFFECT OF CARBON BLACK LOADINGS ON THE TENSILE STRENGTH OF
RUBBER VULCANIZATES

MOHD WAQIYUDDIN BIN MOHD SALLEH

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

ABSTRACT

In this study, the effect of filler loadings (carbon black) on the tensile strength of SMR 10 was investigated. The carbon black grade was chosen N220 and the loading ranges were set 20, 40, 50, and 60 parts per hundred rubbers (phr). For the mixing and moulding process, the Two Roll Mill (Model LS-22005) and 25 Ton Hot Cold Molding Press (Model LS22025) was used which is supplied by Lotus Scientific. In order to determine the tensile strength values, a Universal Testing Machine (Model 133004600771) operating at 20 mm/min was used. It was found that the tensile strength increase with the increasing of carbon black loading until it reaches at the maximum interphase interaction between the polymer chains and filler. This observation is attributed to the rubber–filler interphase interaction of carbon black and rubber.

ABSTRAK

Dalam kajian ini, pengaruh bebanan pengisi (karbon hitam) pada kekuatan penarikan SMR 10 diselidiki. Kelas Karbon hitam dipilih N220 dan bebanan ditetapkan berkisar 20, 40, 50, dan 60 bahagian per seratus getah (phr). Untuk pencampuran dan proses pencetakan, Two Roll Mill (Model LS-22.005) dan 25 Ton Hot Cold Molding Press (Model LS22025) digunakan yang disediakan oleh Lotus Scientific. Untuk menentukan nilai kekuatan penarikan, Universal Testing Machine (Model 133.004.600.771) beroperasi di 20 minit/mm digunakan. Dijumpai bahawa peningkatan kekuatan penarikan dengan meningkatnya beban karbon hitam sebelum mencapai pada interaksi interphasa maksimum antara rantai polimer dan filler. Pengamatan ini disebabkan oleh interaksi interphasa antara getah karbon hitam dan getah.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF SYMBOLS	x
	LIST OF FIGURES	xi
	LIST OF TABLES	xii
	LIST OF APPENDICES	xiv
1	INTRODUCTION	1
	1.1 Background of the Study	1
	1.2 Problem Statement	2
	1.3 Objective	4
	1.4 Scope of the Study	4

2	LITERATURE REVIEW	5
	2.1 Introduction	5
	2.2 Vulcanized Rubber	6
	2.3 Filler and Reinforcement	7
	2.3.1 Filler properties	8
	2.3.1.1 Particles size	8
	2.3.1.2 Surface area	10
	2.3.1.3 Structure	10
	2.3.1.4 Surface Activity	11
	2.3.2 Filler effect	12
	2.4 Carbon Black Filler	12
	2.5 Reinforcement of rubber with carbon black	14
	2.6 Tensile Strength	16
3	METHODOLOGY	20
	3.1 Overview	21
	3.2 Measurement	21
	3.2.1 Materials	21
	3.2.2 Rubber formulation	24
	3.3 Mastication	25

	3.4 Compounding	26
	3.5 Molding	28
	3.6 Tensile Strength Test	29
4	RESULT AND DISCUSSION	30
	4.1 Introduction	30
	4.2 Results	31
	4.2.1 20 phr of carbon black loading	31
	4.2.2 40 phr of carbon black loading	32
	4.2.3 50 phr of carbon black loading	33
	4.2.4 60 phr of carbon black loading	34
	4.2.5 The Overall Data	35
	4.3 Discussion	36
5	CONCLUSION AND RECOMMENDATION	38
	5.1 Conclusion	38
	5.2 Recommendation	39
	References	40
	Appendix A - List of calculations	42
	Appendix B - Figures of experiment	50

LIST OF SYMBOLS

PHR (phr)	-	part per hundred rubber
CBS	-	N-(1, 3-dimethylbutyl)-N-Phenyl-P-Phenylenediamine
CB	-	Carbon Black
SMR	-	Natural Rubber
IPPD	-	Iso Propyl-N-P- Phenylenediamine

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1	Filler Classification Chart	9
2	The Fixed Head of the Universal Machine	29
3	The graph of tensile strength (Pa) versus carbon black loading (phr)	35

LIST OF TABLES

TABLE NO.	TITLE	PAGE
1	The production and consumption of rubber in year 1998 to 2007	2
2	The materials used in this study and its purposes	22
3.1	The standard formulation of rubber	24
3.2	The rubber formulation for 20 phr, 40 phr, 50 phr, and 60 phr of carbon black loadings	25
3.3	Mixing Cycles	27
4.1	The data for 20 phr CB loading	31
4.2	The data for 40 phr CB loading	32
4.3	The data for 50 phr CB loading	33
4.4	The data for 60 phr CB loading	34
4.5	The overall data for CB loading	35

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	List of calculations	12
B	Figures of experiment	50

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural rubber is a solid product obtained through coagulating the latex produced by certain plants, particularly the Brazilian rubber-tree (*Hevea Brasiliensis*). This raw material is usually tapped from the rubber tree, which is native to Amazonia. Although there a large number of species that exude secretions similar to latex when the bark is cut, only a few produce sufficient quantities of a quality adequate for exploitation on economic bases. NR exhibits outstanding properties such as green strength and tensile strength because it can crystallize spontaneously when it is strained. Besides that, it also has the ability to stick to itself and to other material which make it easier to fabricate.

The market growth of the rubber is shown an increasing steadily over the past 10 years and is expected to grow at a similar rate in the next decade. But with global economy crisis nowadays, the global demand for rubber is expected to be down by at least 5.5% this year and maybe more, as key end-markets, most notably automotive tires, and demand from its largest geography, China, continued to slump. World production and consumption of rubber continued to increase in 2007. The production of rubber increased by 2.46%, from 22.44 million tonnes in 2006 to 22.99 million tonnes in 2007. Natural rubber comprised 42.12% of total rubber production in 2007. Consumption of rubber in 2007 also rose by 5.73% to 22.90 million tones as shown in Table 1 below:

Table 1: The production and consumption of rubber in year 1998 to 2007

Year	Production			Consumption		
	Natural Rubber	Synthetic Rubber	Total Rubber	Natural Rubber	Synthetic Rubber	Total Rubber
1998	6,634	9,880	16,514	6,570	9,870	16,440
1999	6,577	10,390	16,967	6,650	10,280	16,930
2000	6,762	10,870	17,632	7,340	10,830	18,170
2001	7,332	10,483	17,815	7,333	10,253	17,586
2002	7,337	10,882	18,219	7,628	10,692	18,320
2003	8,033	11,390	19,423	8,033	11,371	19,404
2004	8,756	12,019	20,775	8,715	11,839	20,554
2005	8,892	12,151	21,043	9,082	11,895	20,977
2006	9,846	12,646	22,419	9,216	12,371	21,587
2007	9,725	13,583	23,489	9,735	13,197	22,932

With the increasing of production and the consumption of the rubber, the usage of the rubber can be widely expanded especially in the area of production. Rubber products are composed of many different mechanistic materials, e.g. steel belt, nylon fibers, gas barrier layers, to form an overall product. This research will investigate the effect of filler loading (carbon black) on tensile strength of rubber vulcanizates. Additives are used to increase the rubber's strength, wear resistance, performance and processing.

Fillers like carbon black and silica, which is used to enhance the properties of the rubber, aromatic oil for aiding the dispersion of fillers, and anti-degradants such as anti-oxidants and anti-ozonents are the additives that used in the research. Already it can be seen that combining all of these materials together results in a complex composite with end properties depending on the formulation used.

The processing of these materials also affects the end properties. The resulting properties desired for filled rubbers include good mechanical properties, both static and dynamic. Typically these properties are obtained through a series of experiments that

vary the ratios of filler and measure the effects of the hardness. Recently however, efforts have been directed at understanding the mechanistic role of fillers loading in order to predict their effect on reinforcement.

The reinforcement of elastomer by fillers loading has been reviewed by other researcher. They considered that the effect of filler loading is to increase the number of chains, which share the load of a broken polymer chain. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. There include particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the filler and the rubber matrix.

1.2 Problem Statement

Natural and synthetic in vulcanized form are used to prepare various rubber products such as mechanical goods, hoses, soles, V-belts, seals, gaskets, tyre treads, etc. in the vulcanization of the rubber, carbon black and silica are the main fillers used in the compounding recipes. They are normally used up to 50 phr. In spite of being well known for their capabilities as reinforcements, i.e, they impart strength and stiffness to the vulcanized rubber, these fillers are relatively expensive. Therefore, considerable R&D efforts are being carried out to investigate the possibility of replacing these fillers with the target to reduce the cost of rubber products while maintaining their desired properties. The different fillers can be used in the industry but the quality of using the carbon black fillers are still the best for production industry. Meanwhile, several of filler loading will give different values of properties. The desired values for tensile strength for application in the product should be in higher values. Specific tensile values are used in numerous industrial products just to keep their products in good quality. Many researchers have studied the rubber formulations in order to enhance the quality of the product. In this study, the rubber formulation is based on the standard formulation and

the effect of carbon black loadings are studied on rubber vulcanizates to know the range of the higher tensile strength.

1.3 Objectives

This study is to achieve the following objective:

- To study the effect of carbon black loading on the tensile strength of rubber vulcanizates

1.4 Scopes of Study

There are two scopes of study:

- To determine the effect of 20 phr, 40 phr, 50 phr and 60 phr of carbon black loading on tensile strength of rubber vulcanizates
- To study the relation between the filler loading and the tensile strength

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The rubber industry was the original user of additives, and much of current technology for plastics - both chemicals and equipment - derives from compounding rubber. This chapter gives a brief overview. Classically, rubber is a thermosetting polymer, which requires curing (crosslinking), in a reaction which must be controlled (by initiators, accelerators, retarders, and other agents). The discovery that sulphur-based compounds initiated the reaction was fundamental. The rubber compound also requires pigmentation (leading to the discovery that carbon black could also act as reinforcement), stabilization (against heat in processing and application, weathering and ozone), plasticizing (to improve processability) and extension (by means of low-cost fillers).

Experience in compounding rubber established many of the principles of compounding plastics (especially PVC), in particular the mechanism of interface adhesion between polymer matrix and particulate and fibrous additives, and the process of compounding materials of differing size, shape, and chemical composition. Rubber compounds are very elaborate, in which the rubber component often functions mainly as a binder for the additives. These may include: process aids (peptizers, plasticizers, softeners and extenders, tackifiers);

- accelerators;
- accelerator activators;
- curing agents;
- anti-degradants
- fillers;
- colorants; and
- Other additives (retarders, blowing agents).

Reinforcements, such as natural or synthetic fibres or fabrics and steel wires also play a key role in manufacturing of rubber products, but it is normal to mix the compound first and then lay it up in the 'green' state together with the reinforcement, before moulding and curing the whole in a press or by passing it through an extruder.

2.2 Vulcanized Rubber

Vulcanized rubber is a rubber that has been going vulcanization process where involving high heat and the addition of sulfur or other equivalent curatives. It is a chemical process in which polymer molecules are linked to other polymer molecules by atomic bridges composed of sulfur atoms or carbon to carbon bonds. The end result is that the springy rubber molecules become cross-linked to a greater or lesser extent. This makes the bulk material harder, much more durable and also more resistant to chemical attack. It also makes the surface of the material smoother and prevents it from sticking to metal or plastic chemical catalysts. When rubber is vulcanized, it becomes cross-linked in its chemical structure at the atomic level. This linking of stronger bonds makes vulcanized rubber over 10 times stronger than natural rubber would be. This is one of vulcanized rubber's greatest strengths, as it allows rubber to be used in making more heavy duty products since it can stand up to more punishment. While vulcanized rubber is elastic, meaning it will return to its original shape, it is also 10 times more rigid than normal rubber as a result of the vulcanization process. Rigidity means that vulcanized

rubber is more difficult to bend out of shape in the first place, adding to its use in heavier applications, such as tires.

2.3 Filler and Reinforcement

The basic purpose of fillers is to 'fill' a plastics that is increase the bulk at low cost, to improve the economics. With good adhesion between filler ad polymer, consequently the filler begins to play a role in improving mechanical properties (Murphy, 2001). Therefore, fillers are not only for reducing cost but also to modify properties such as stiffness, hardness, thermal stability and shrinkage. In this case, the fillers function as the non-reinforcing fillers in the composites. Non-reinforcing fillers are additive to improve the hardness strength of composite but reduce the tensile strength and tear strength.

The effect of fillers on the composite properties are largely dependent on the mean particle size, particle shape, particle size distribution of filler and the strength of the bond between filler particle and polymer matrix(Wypych, 1999). Most filler do not consist of particles which are all the same size and the same shape. The shape of the particles affects the modulus and the other mechanical properties significantly. Spherical particles are less likely to initiate cracking than more slender particles. However, flat platelet-type particles tend to produce stronger bond between the filler particle and matrix, due to increased surface area available for bonding. One measurement of shape is the aspect ratio. The greater aspect ratio, the greater the increase in bonding area is available which usually improved mechanical properties (Miller, 1996).

2.3.1 Filler Properties

The characteristics which determine the properties filler will impact to a rubber compound are particle size, surface, structure, and surface activity.

2.3.1.1 Particle Size

If the size of filler particles greatly exceeds the polymer inter-chain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Filler with particles size greater than 10,000 nm are therefore generally avoided because they can reduce performance rather than reinforce or extend. Fillers with particles size between 1,000 and 10,000 nm are used primarily as diluent and usually have no significant affect, positive or negative, on rubber properties. Semi-reinforcing filler, which range from 100 to 1,000 nm, improve strength and modulus properties, the truly reinforcing fillers, which range 10 to 100nm significantly, improve rubber properties

Of the approximately 2.1 million tons of filler used in rubber each year, 70% is carbon black, 15% is kaolin clay or china clay, 8% is calcium carbonate or whiting, 4% is the precipitated silicas and silicates and the balance is variety of miscellaneous minerals(D. T. Norman, 1978). Figure 1 classifies the various filler by particles size and consequent reinforcement potential.

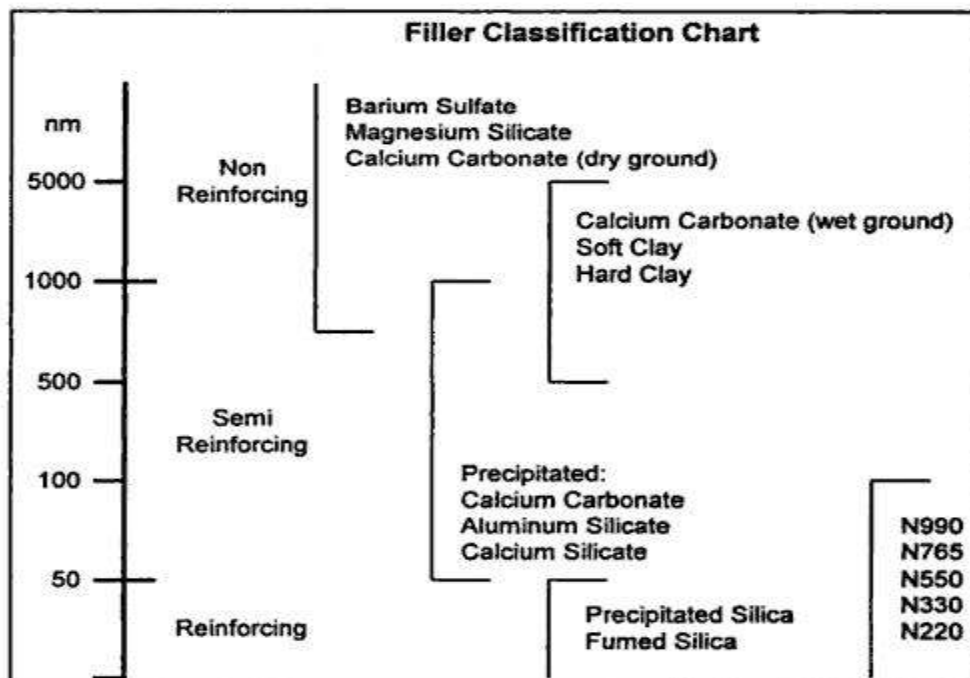


Figure 1: Filler Classification Chart

Most talcs and dry-ground calcium carbonates are degrading filler because of their large particles size; although the planar shape of the talc particles contributes some improvement in reinforcement potential. The soft clays would fall into a class of diluents fillers that do not contribute reinforcement, yet are not large that they degrade properties (D. T. Norman, 1978).

The hard clays contribute some reinforcement to rubber compounds, primarily because of their smaller particle size and are normally classified as the semi-reinforcing class. The carbon black is available in various particles sizes that range from semi-reinforcing to highly reinforcing. They generally exist as structural agglomerates or aggregates rather than individual spherical particles.

2.3.1.2 Surface Area

Particle size is generally the inverse surface area. Filler must make intimate contact with elastomer chains if it is going to contribute to reinforcement. Filler that have high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surfaces available for contacting the rubber than spherical particles with an equivalent average particle diameter. Clays have planar-shaped particles that align with the rubber chains during mixing and processing, and thus contribute more reinforcement than a spherical-shape calcium carbonate particle of similar average particle size (Z. H. Li, J. Zhang, S. J. Chen, 1998). Particles of carbon black or precipitated silica are generally spherical, but their aggregates are anisometric and are considerable smaller than the particles of clay. They thus have more surfaces per unit weight available to make contact with the polymer. Rubber grade carbon black varies from 6 to 259 m²/g.

2.3.1.3 Structure

The shape of an individual particle of reinforcing filler like carbon black is of less importance than the filler's effective shape once dispersed in elastomer. The black used for reinforcement have generally round primary particles but function as anisometric acicular aggregates. These aggregate properties-shapes, density, size-define their structure. High structure filler has aggregates favoring high particle count, with those particles joined in chain like cluster from which random branching of additional particle may occur. In simplest term, the more an aggregate deviates from solid spherical shape and the larger its size, the higher is its structure. The higher its structure, in turn, the greater it's reinforcing potential (Chayanoot Sangwichien.,2008; Z. H. Li, J. Zhang, S. J. Chen, 1998) .

For reinforcing, fillers which exist as aggregates rather than discrete particles, carbon black in particular, a certain amount of structure that existed at manufacture is lost after compounding. The shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates (Chayanoot Sangwichien,2008). The structure that exist in the rubber compound, the persistent structure, is what affects process ability and properties

2.3.1.4 Surface Activity

A filler can offer high surface area and high structure but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonpolar elastomer; polar filler work best in polar elastomers. Beyond this general chemical compatibility is potential for reaction between the elastomer and active sites on the filler surfaces. Carbon black particles, for example, have carboxyl, lactone quinone, and other organic functional groups which promote a high affinity of rubber to filler. This together with the high surface area of the black, means that there will be intimate elastomer-black contact. The black also has a limited number of chemically active sites (less than 5% of total surface) which arise from broken carbon-carbon bonds as a consequence of the methods used to manufacture the black. The close contact of elastomer and carbon black will allow these active sites to chemically react with elastomer chains. The carbon black particle effectively becomes a crosslink. The non-black filler generally offer less affinity and less surface activity toward the common elastomers.

2.3.2 Filler Effects

The principal characteristics of rubber fillers-particle size, surface area, structure, and surface activity-are interdependent in improving rubber properties. In considering fillers of adequately small particles size reinforcement potential can be qualitatively small particles size, reinforcement potential can be qualitatively considered as the product of surface area, surface activity, and persistent structure or anisometry(planar or acicular nature)

The general influence of each of these three filler characteristics above on rubber properties can be summarized as follows:

1. Increasing surface area or decreasing particle size gives lower resilience and higher Mooney Viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis.
2. Increasing surface activity including surface treatment gives higher abrasion resistance, chemical adsorption or reaction, modulus (at elongation>300%), and hysteresis.
3. Increasing persistent structure/anisometry gives higher Mooney Viscosity, modulus (at elongation<300%), and hysteresis, lower extrusion shrinkage, tear resistance, and resilience, and longer incorporation time

2.4 Carbon Black Filler

Carbon black is filler which is not easy to determine quantitatively because of its small particle size. The amounts of carbon black filler present in rubber vulcanizates can be determined by various methods and some reliable standard methods are now in practical use. Determination of insoluble residues, fillers or non-degradable residues via metathesis degradation of unsaturated crosslinked polymers has been reported. Etching

of crosslinked polybutadiene containing inorganic or organic fillers has been performed with 2-octene and the distribution of the filler in the polymer investigated by scanning electron microscopy. Polybutadiene crosslinked by dicumyl peroxide has been degraded for the determination of fillers such as glass beads, cellulose particles and carbon black. The crosslinked matrix was degraded to low molecular weight products with an excess of a low molecular weight olefin. This is one of the advantages of olefin metathesis with respect to carbon black determination because it is well-known that the more degraded the polymer, the less viscous the reaction mixture and the fewer degradation products remain adsorbed on the carbon black. Thus, the carbon black is more easily separated from the liquid phase.

The mixing of carbon black (CB) in rubber composites improves their performance-related properties. Depending on the material parameters and mixing technology CB undergoes different dispersion states, from large agglomerates to small aggregates. In order to obtain optimal vulcanizate properties, CB must be sufficiently dispersed in the mixture. Poor macrodispersion which is determined by agglomerates with a size larger than 6 μm is responsible for the decrease in ultimate tensile strength, breaking and tearing energy, or fatigue resistance. Small agglomerates and aggregates (microdispersion) influence the end use performance of many vehicle systems resulting in lower hysteresis properties and higher resistance to tearing, cut growth and abrasion. The time and temperature dependent mechanical behavior of filled vulcanizates has been investigated extensively by many researchers. Ronan proposed a method to separate physical and chemical relaxation processes. The basis of the method is to evaluate the continuous relaxation time spectrum for each test temperature in order to separate the relaxation processes. Vennemann developed a new test method, namely Temperature Scanning Stress Relaxation (TSSR) to characterize the thermomechanical behavior of filled vulcanizates. During TSSR tests, the temperature increases at a constant rate. During heating the decrease of the applied stress was explained as a result of different processes like break-down of filler network, desorption of bound rubber and thermo-oxidative chain scission. Using dynamic mechanical analysis and dielectric relaxation spectra on CB filled ethylene–propylene–rubber (EPDM) and chlorobutyl vulcanizates

Mahapatra and Sridhar found that debonding of the rubber chains in the vicinity of filler is essential for stress relaxation behavior. However, our comprehensive literature research revealed, in those works CB was always considered as well dispersed, the effect of CB dispersion degree has not been characterized so far.

2.5 Reinforcement of rubber with carbon black

One of the most important composite materials commercially available is rubber containing colloidal filler such as carbon black in quantities of up to 20 to 30% by volume of the rubber. Rubber by itself is unsuitable for a large number of important applications (eg tyres) and in these it must be manufactured into a composite material before it is of commercial use.

In contrast with the ordered and rigid crystalline arrangement of atoms in metals, elastomers are composed of a tangled mass of kinked, twisted and intertwined chain-like molecules. The basic element of an elastomer is the monomer -- the link in the chain which determines the chemical character of the material and its resistance to oil, ozone, solvents and chemicals.

Thousands of monomers link end-to-end to form a polymer, or molecular chain, free to bend or to rotate at most points where the chain links join. The tangled chains are free to slide past each other except where they are attached together here and there by cross-links. These cross-links tie the molecular chains together and limit the amount of stretch and increase the elasticity. Cross-links are formed by chemical reaction of the chain with certain materials (curatives and accelerators) mixed into the mass. Heating increases the rate and extent of cross-linking or curing and this process is termed vulcanisation.

Addition of inert materials, dispersed in the elastomeric mass prior to curing, can increase strength and hardness or resistance to deformation, usually with a reduction in elasticity and resilience. Size and shape of the particles and degree of dispersion are important factors; carbon black, for example, is useful in increasing strength and hardness for most elastomers. When an elastomer is stretched, the tangled mass of irregular, kinked and cross-linked molecular chains tend to straighten out, sliding and slipping past each other. When the external load is removed, the molecules tend to return to their original coiled-up and kinked condition. The amount and character of the added compounding materials have a strong influence on the elasticity.

The term 'reinforcement' as applied to natural and synthetic rubbers, though one of the most familiar in the rubber technologist's vocabulary is difficult to define; in fact, it does not necessarily mean the same thing to different people. This is because the properties of rubber vulcanisates are modified to different degrees by different reinforcing agents, and one's view of what constitutes high reinforcement is coloured by the particular kind of product in which one is interested. Thus certain rubber compounds (eg for engineering components) to which high stiffness is imparted by the incorporation of a suitable filler are sometimes said to be 'reinforced' because of the stiffening action of the filler, irrespective of its influence on other properties such as tensile or tear strength. On the other hand, most rubber technologists would probably agree that stiffness in itself is quite inadequate as a criterion of reinforcement. It should be accompanied by enhanced tensile strength (though the increase may be small in the case of natural rubber which, without fillers, has high tensile strength) and, in particular, by a high resistance to tearing and abrasion.

The mechanism by which carbon black improves the physical properties of rubber such as tensile strength, modulus, tear, abrasion resistance and stiffness is very complicated and has been the subject of numerous studies.