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Effect of Egg Shell Powder on Rheological and Mechanical Properties for some Rubbery Blends

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بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

ٱقۡرَأۡ وَرَبُّكَ ٱلۡأَكۡرَمُ ۝ ٱلَّذِى عَلَّمَ بِٱلۡقَلَمِ ۝ عَلَّمَ ٱلۡإِنسَٰنَ مَا لَمۡ يَعۡلَمۡ

صَدَقَ ٱللَّهُ ٱلۡعَظِيمُ

سورة العلق (الآية٣-٥)

Dedication

To My country with honor and dignity…

To who gave me the endurance to complete my road my father

To the best woman in the universe my mother, my God's mercy to her

To my beloved wife

To my dear daughters and sons

To my close friends

To my teachers

and

Everyone who has helped me …

Mohammed .. ✍□

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Thankfulness, praise be to Allah, the grace that befits his holy self, and peace and blessings be upon our Messenger, Muhammad Bin Abd Allah, May Allah's prayers and peace be upon him and his family and companions

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Mohammed .. ✍☐

Abstract

This study included preparation of four groups of rubber composites: the first (NR/SBR/ESP), which contains natural rubber (NR) and styrene-butadiene rubber (SBR) as basic materials. The second (NR/NBR/ESP) contains natural rubber (NR) and acrylonitrile butadiene rubber (NBR) as basic materials and eggshell powder (ESP) as reinforcement material with a particle size of less than (75µm) which contains 97% calcium carbonate in four groups with the loading ratio of the (ESP) material was(0, 10, 30, and 50 pphr)and with carbon black (CB)N375 at a loading ratio of (CB-20 pphr).

Fourier Transform Infrared spectroscopy (FTIR) was experimental, and measured the rheological properties such as minimum torque (ML), maximum torque (MH), scorch time (Ts2), optimum cure time (Tc90), optimum cure rate (CR), and viscosity according to [ASTM D-2705]. The mechanical properties were measured according[ASTM D412-88]such as hardness according[ASTM D1415]by shore A equipment, tensile strength, elongation at break, and elastic modulus according[ASTM D3182]by universal Tensometar, and thermal aging was carried out to measure hardness according[ASTM D573] for all specimens at 70 °C for 96 h with and without (CB)for two groups.

The results show that there were large effects of ESP and CB on the properties; some of these properties decreased with increasing loading ratios of ESP and CB, like rheological properties minimum torque (ML), maximum torque (MH), scorch time (Ts2), optimum cure time (Tc90), viscosity, and cure rate (CR), except the cure rate (CR),which were increasing in the second group. The mechanical properties such as tensile strength, elongation at the break, and elastic modulus wear decreased; on the other hand, hardness was increased in all samples with ESP and CB loading ratios increasing, and the thermal aging result shows that hardness was increasing as loading ratios of (ESP) material and (CB).

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List of Abbreviations

Symbols	**Description**
A	Cross section Area
ASTM	American Society for Testing Material
BR	Butadiene Rubber
CB	Carbon Black.
CR	Polychloroprene
E	Elastic Modulus (Youngs Modulus).
ESP	Egg Shell Powder
EPDM	Ethylene-Propylene Diene Terpolymer.
F	Force.
G	Shear modulus
IRHD	International Rubber Hardness Degree.
L	Final length
L_O	Initial length
MBS	N-oxydiethylenebenzothiazole.
Mpa	Mega Pascal.
NBR	Acrylonitrile Butadiene Rubber.
NR	Natural Rubber.
OSP	Oyster Shell Powder
OPF	Oil palm fiber
P	Depth of Penetration.
pphr	part Per hundred Rubber.
SBR	Styrene Butadiene Rubber.
SMR	Standard Malaysian Rubber.
Tg	Glass transition Temperature
Tm	Melting Temperature
t	Final thickness.
t_o	Initial thickness.
ΔL	Length Difference.
$\boldsymbol{\sigma e}$	Engineering Stress.
$\boldsymbol{\sigma t}$	True Stress
$\boldsymbol{\varepsilon}$	Strain.
Δ	Logarithmic Decrement.
μ	Dipole moment

Chapter One
Introduction
&
Review of Literature

1.1 Introduction

Rubbers have an important role in the advancement of contemporary technologies. Due to their lightweight, elastic, and other features, they are now employed in a variety of applications, including cables, tires, adhesives, household products, coatings, packaging materials, textile and sports goods transportation, building infrastructures, medical and optical technologies, etc. There are many different varieties of rubber, including Natural Rubber (NR), Synthetic Rubber as styrene-butadiene rubber (SBR), and nitrile rubber, among others. The chemical composition of a specific rubber determines its characteristics. A mix of raw rubbers with additives and the vulcanization process is important to the adjustment of rubber with requirement application[1].Vulcanization is one of the key factors in the technology of rubbers. It involves the conversion of raw rubber into a network through the formation of a cross-link between chains of rubber. This network is not sticky like raw rubber that does not harden with cold weather or soften much except at very high temperatures, it is elastic and highly resistant to abrasion, and it becomes tighter, and the forces necessary to achieve a given deformation increase[2,3].Most commonly used for its high mechanical properties due to its density and ease of manufacture. In addition to being lightweight, high durability, and low manufacturing cost. The polymeric basis was divided into materials, thermoplastics, and thermosetting materials [4].The term was used as an alternative to rubber where previously the term rubber was a rubber band that is used to refer to synthetic rubber. Flexible materials differ from other polymers with special specifications where they can deform when shedding stress on them and then regain their dimensions, quickly after removing these stresses . The mechanical properties can be significantly improved such as elasticity resistance to melting and bloating in the presence of temperature and appropriate vulcanization conditions [5]. The rubber material is not only flexible but also energy-dispersing materials because of the flexible viscous nature, yet plasticization reduces plasticity [6].

1.2 Polymers

Polymeric materials are among the most used materials at the present time, as polymeric materials are characterized by their cheap price, ease of manufacture, good specifications and often reach very good. It is known that most of the polymeric materials are insulating materials and that these materials have entered the electrical and electronic industries long ago. Long as an auxiliary material, but the good qualities of these materials have made polymeric materials a basic material that can be used in the electrical and electronic industries[6]. In addition to some polymeric materials having good thermal insulation characteristics as well as properties and characteristics mechanical and optical. Therefore, the process of enhancement the mechanical properties of polymeric materials can be considered an important matter that can be used in the electronic, electrical and among engineering industries [7].

1.2.1 Polymer Structure

The need to develop and comprehend new types of plastics, rubber, adhesives, fibers and coatings spawned polymer science in the industrial labs of the world's greatest companies. Polymer science did not enter the academic world until much later, may be as a result of its roots, polymer science is more multidisciplinary than other disciplines, mixing chemistry, chemical engineering, materials, and other subjects. Polymerization is the process of continuous connections to a chain or network structure of one or two, often more, forms of small molecules, resulting in a very large molecule with hundreds or thousands of atoms. These large molecules are classified as monomers, as the essential building blocks[8]. The size and shape of near to their properties are the polymers. The polymer form has a strong relationship with the size of the different units that make up the macromolecules and to the different primary and secondary bonding forces that are present within the chain and between the chains[9].

1.3 Classification of Polymers

Polymers cannot be classified under one category because of their complex structures, different behaviors and vast applications. We can, therefore, classify polymers based on the following considerations.

1.3.1 Thermal Classification of Polymer

According to the effect of temperature, polymers can be classified into three types as follows:

a. Thermoplastic polymers: The effect of temperature on these polymers affects their properties. As the temperature increases, the polymers be sticky and flexible polymers return to their solid state if the temperature decreases. This is due to the thermoplastic polymer's molecules being held together by intermolecular powers which are relatively weak (Van der Waals forces). These molecules, including polystyrene, polyethylene, polypropylene, and polyvinyl chloride, slip over each other when heated[10], as shown in the Fig.(1.1.a).

b. Elastomers Polymers: Elastomers are a form of network polymer that is lightly cross linked and can be extended to extreme lengths reversibly. They have very tightly randomly coiled molecules when not stressed, which are expanded polymers bent as they are stretched. This reduces the randomness of the chains resulting in a lower entropy in the material, and this entropy decrease is due to the molecules from moving past one another. The rubbers become glassy or crystal clear as they cool (partially). When heated they do not flow because of cross-links in a traditional sense. Vulcanized rubber and neoprene[11], as shown in Fig.(1.1.b)

c- Thermoset Polymers: These polymers have been modified chemically when heated thermosets are typically networked polymers with a high degree of interconnection between polymer chains. These polymers are insoluble after heating, they are not heater and electric conducting and hard because their molecules are connected by strong chemical bonds. Examples of this kind of polymers are phenol formaldehyde resin and urea formaldehyde resin[11,12], as show in Fig.(1.1.c).

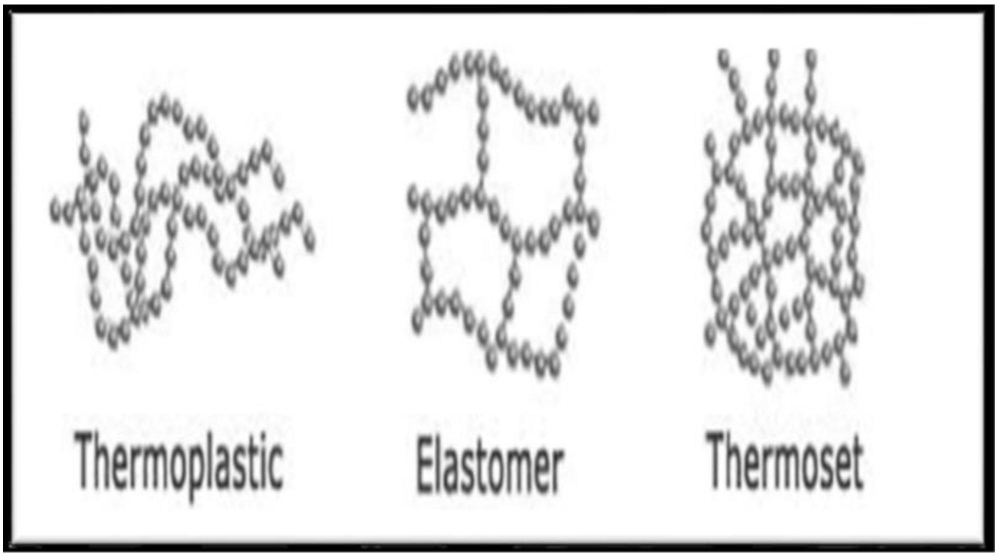


Figure (1.1): Schematic representation of (a-Thermoplastic polymer, b-Elastic polymer, c- Thermoset polymer)[12].

1.4 Polymer Blends

A polymer blend is a mixture of two or more polymers mixed to produce a new material with various physical properties, heat and thermoplastic-heat blends, and plastic–heat blends. Mixtures, Rubber-thermosetting, and polymer-filling mixtures are the five main categories of polymer blends. Polymer blending has attracted much attention as an easy and cost-effective way to create scalable polymeric materials for commercial applications. In other words, by correctly choosing the polymer materials, the properties of the mixtures can be manipulated according to their final application[13]. The goal of preparing polymeric mixtures is to obtain new qualities that cannot be found in individual polymers, and the preparation of polymeric mixtures depends largely on the miscibility of the polymers, for example, butadiene polymer is mixed with polystyrene in small proportions to obtain the elasticity of the polystyrene. Fragile, as well as the goal of preparing polymeric mixtures is to obtain polymeric materials possessing good mechanical, electrical and optical properties[14]. The phase of a solid state, where the first polymer is mixed with the second, also in powder form, and then dissolved together in an appropriate solvent, is the approach that is the most used in polymer mixture preparation. The liquid state method, also known as the reaction method, is used in industry, where the first polymer is blended in a liquid stage with the second polymer, the second polymer being polymerized after the first stage of mixing with the second polymer[15]. And the first approach has been implemented in our study. Fig.(1.2) provides an example of a mixture of polymers.

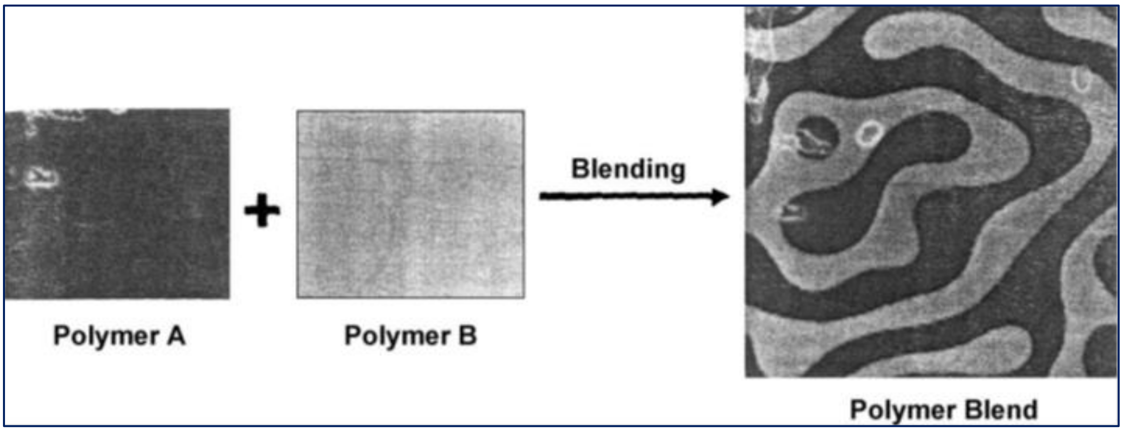


Figure (1.2) an illustration of a polymer mixture[15].

1.5 Composites

A composite material is a material system composed of a mixture or combination of two or more macro constituents differing in form material composition and that are essentially insoluble in each other[16,17]. The two constituents are normally reinforcements (fibers, particulates, whiskers, laminate, or flakes, or fillers). The term "reinforcement" refers to an improvement in the end–use performance of the rubber compound associated with an increase in modulus and the so–called ultimate properties including tensile strength, tear resistance, and abrasion resistance. A reinforcement filler is a particulate material that can increase tensile strength, tear strength and the abrasion resistance of rubber. A semi–reinforcing filler is a particulate material that can increase tensile strength and the tear strength but does not improve abrasion resistance. A non-reinforcing filler is unable to provide any increase in these properties and functions[18]. These are structural constituents that determine the internal structure of the composite, and the matrix is the body constituent serving to enclose the composite and give it its bulk form, maybe metal, polymer, or ceramics. There are modern classifications of composite used instead of various materials in the fields of different applications in medicine, civil engineering, and military due to their specific properties such as strength and stiffness[16].

1.5.1 Classification of Composites

Classification of composites can be set by several schemes including classification :

a. basic material combinations ,e.g., metalorganic ,or metal inorganic.
b. structural bulk –form characteristics ,e.g., matrix system or laminates.
c. function ,e.g., electrical or structural .
d. distribution of constituent .e.g., continues or discontinues .

The classification system gives four general classes that is based on the form of the structural constituent as shown in Fig.(1.3**)**[19].

So the classification according to the matrix system are[20].

1. **Metal matrix composite (MMCs)**, these materials can be used for operating temperatures up to (1250°C), where the conditions require high strength coupled with ductility and toughness for example boron fiber in aluminum basis or carbon fiber in magnesium basis.
2. **Polymer matrix composite (PMCs**), the most common composites matrix materials are thermosetting thermoplastic, elastomer and plastic reinforcing with carbon fibers or glass fibers, the technology of polymer composites has been driven to a large extent by aerospace arid military applications.
3. **Ceramic matrix composite (CMCs),** such as silicon nitride reinforcing with silicon carbide, offer lightweight, high temperature strength and good dimensional and environmental stability. The matrix provides high

temperature resistance .Glass matrices can operate at temperatures as high as (1500°C).

4. **Carbon – carbon composite (CCCs),** Graphite fibers in carbon matrix offer the possibility of a heat resistance material that could operate at temperatures up to (3300°C), with high strength and light.

5. **Intermetallic matrix composite (IMCs),** these composites have poor low-temperature ductility (1000°C), and marginal high-temperature oxidation resistance such as fiber compositions (Sic, Al_2 O_3 , Ti_3 Al) in aluminides of iron, titanium, nickel, and niobium.

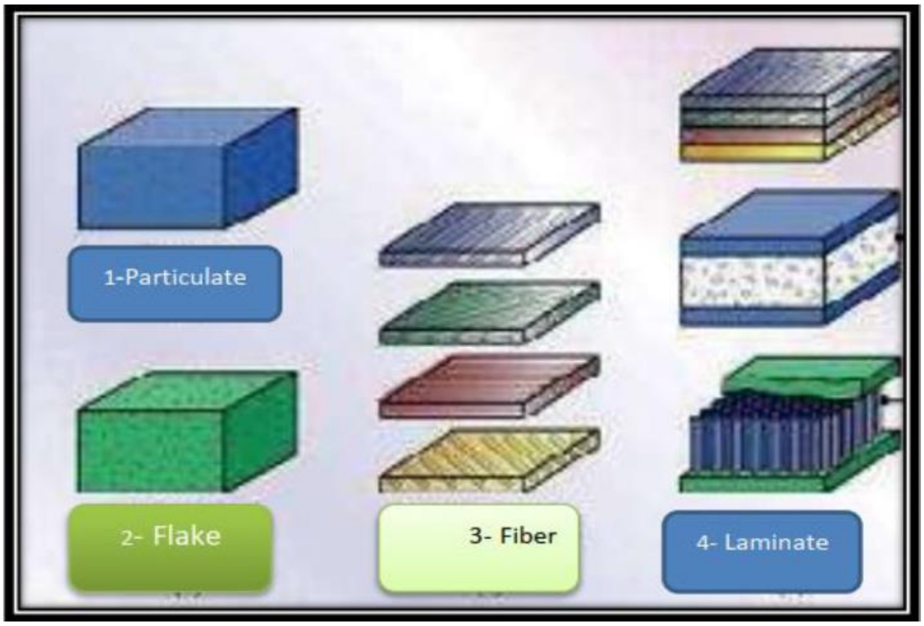


Figure (1.3) Classes of Composite Materials,1. Particulate composites, composed of particles with the matrix . 2. Flake composites, composed of flat flakes with the matrix. 3. Fiber composites composed of fiber with the matrix. 4. Laminate composites, composed of layer with the matrix[19].

1.5.2 Rubber composites

Goodyear and Hancock developed first rubber compound, it continues to develop as new materials , and new variations on old ones appear in the marketplace. The compound we see every day as rubber, such as in a tire or pencil eraser, is a mixture of a number of different ingredients. It starts with the raw gum elastomer, supplied by the plantation owner as NR, or by the petrochemical complex converting petroleum products such as ethylene, propylene, and butadiene into ‘raw’ bales or chips of rubbery polymers such as(EPDM, BR, SBR, NBR, or CR). It is shipped to the rubber processor that blends it with various ingredients. The raw gum elastomer itself has very limited use, although adhesives provide one example. Most are mechanically weak and subject to significant swelling in liquids, and will not retain their shape after molding[21].

Rubber has unique features like high extensibility, high strength, high energy absorption, and high resilience to fatigue, which contribute to its expanding use in engineering applications. High resilience and exceptional environmental resistance are other qualities. Engineered rubber items are made entirely of rubber or partly of rubber and other materials. A simple rubber band is considered to be a simple product, but complicated composites like radial tires or rubber-metal bearings for aerospace purposes are considered to be complex products [22]. Materials such as steel, aluminum, plastics, fabric, and cords are often combined with rubber to form composites. The purpose of these materials is generally to increase strength, minimize distortion [23].

High elastic polymer composites are very important in the applications of rubber industries, rubber composite materials with different types of rubber are used in dampers and support applications. Therefore: it is occupied wide field studies, because rubber has good characterization in the high elastic strain damping which is obtained from the suddenly impact loading because of different acceleration of the system. Therefore a different modification of a new type of rubber composite for loading resistance in addition to the interference of the usages conditions with the mechanical loads such as environmental effects at high temperatures in the presence of oils and friction result in the creation of blended polymers such as (NBR, SBR , NR , CR , … etc) [24,25].

1.6 Types of Rubber

Rubbers can be divided broadly into two types: Thermosets and thermoplastics. thermosets are three dimensional molecular networks, with the long molecules held together by chemical bonds. They absorb the solvent and swell, but do not dissolve; furthermore, they cannot be reprocessed simply by heating. On the other hand the molecules of thermoplastic rubbers, , are not connected by primary chemical bonds. Instead, they are joined by the physical aggregation of parts of the molecules into hard domains [26].

Hence, thermoplastic rubbers dissolve in unsuitable solvents and soften on heating, so that they can be processed repeatedly. In many cases, thermoplastic and thermoset rubbers may be used interchangeably. However, in demanding uses, such as tires, engine mounts, and springs, thermoset elastomers are used exclusively because of their better elasticity, resistance to set, and durability, the addition of various chemical materials to raw rubber to impart desirable properties is termed rubber compounding or formulation [27].

1.6.1 Natural Rubber (NR)

NR is only a natural product. It is a cis-polyisoprene but contains a variety of impurities such as proteins and resins. It crystallizes much more readily upon stretching compared to synthetic cis-polyisoprene, which does not contain impurities. NR has a very high molecular weight and contains long branches [28]. Natural rubber is collected in the form of latex that exudes from the bark of the tree when it is cut. The tree Havea Braziliensis is the largest producer of this latex. The average rubber content of latex may range between 30 – 45%. Latex concentrates are differentiated by the method of concentration and type of preservative used. Concentration is achieved by Centrifugation (most common), creaming, or by evaporation [29].

The elastomer used alone or with reinforcing filler, possesses first class mechanical properties with excellent process ability. It crystallizes easily at low temperatures and, so in subzero temperatures, it is necessary to thaw it by storing it in a hot room at (40 – 50) °C before the winter season. Both these operations are unnecessary with synthetic elastomers. NR requires lower curing temperatures and therefore longer vulcanization time. At mixing, NR has a sufficiently high viscosity to allow optimum dispersion of reinforcing fillers and other ingredients[30]. Chemical Structure: Natural rubber is high molecular polymer isoprene, C_5H_8. The repeating unit is (– CH_2 – C (CH_3) = CH– CH_2–). The Hevea rubber is the major naturally occurring form of cis 1.4–polyisoprene. This rubber contains more than 98% of its double bonds in the cis – configuration that is essential for elasticity in polyisoprene. Over 90% of all cis 1.4– polyisoprene used industrially is natural Hevea rubber[31].

The double bond in each repeating unit in the polymer chain is a site of steric isomerism since it can have either a cis or a trans configuration. The polymer chain segment on each carbon atom of the double is located on the same side of the double bond in the cis configuration and on the opposite sides in the tran configuration. See Fig.(1.4)[31].

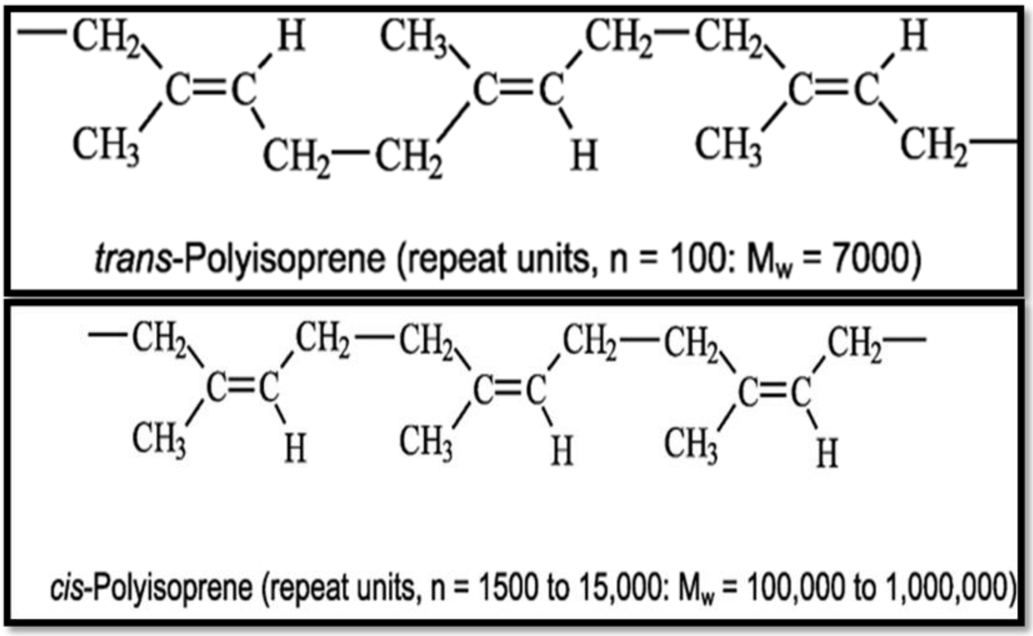
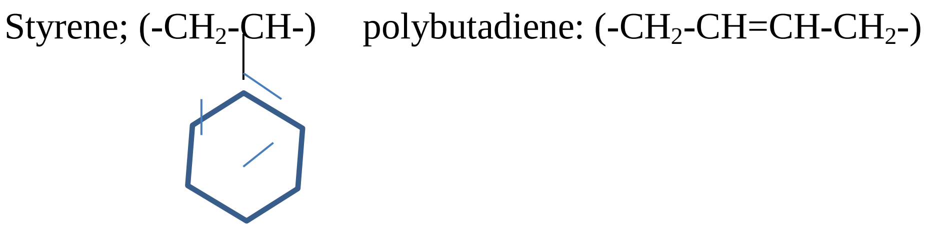


Figure (1.4): cis and trans isomers of natural rubber[31].

The trans isomer which has a higher molecular symmetry crystallizes to a greater extent and therefore has higher T_m and T_g Values and significant crystallinity. It is less an elastomer and more like a thermoplastic. The T_g of NR is about 200 K its T_m equal to 298 K and its structure is thought to be completely cis 1.4– polyisoprene, except for the chain ends, 1.4– poly isoprene is found in both the cis and transform [32].

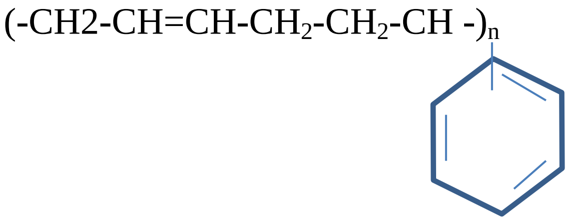
1.6.2 Styrene – Butadiene Rubber (SBR)

SBR is derived from petroleum oil, this applies to most elastomers, with the obvious exception of NR. SBR represents half of all synthetic rubber production, and is much consumed in tires, where it competes with and complements NR. There are many subgroups of the raw gum elastomer, depending on the method of synthesis of the polymer ،whether it is solution or emulsion polymerized, and the ratio of the two major chemical building blocks styrene and butadiene. The raw gum elastomer must have reinforcing fillers , such as carbon black, in order to obtain good mechanical strength and the filler increases hardness, at the same time. The properties of SBR are broadly similar to NR, for chemical, solvent, and weather resistance [33]. Chemical Structure :SBR is a synthetic copolymer, chemically SBR is a copolymer of styrene and butadiene typically containing about 23% styrene and 77% polybutadiene with a T_g is about -55 ^oC, see Fig,(1.2) [34].



Styrene; $(-CH_2-CH-)$ polybutadiene: $(-CH_2-CH=CH-CH_2-)$

Then the repeating unit (monomer) is:



$(-CH2-CH=CH-CH_2-CH_2-CH\ -)_n$

Figure (1.5) : SBR structure [34].

SBR is generally marketed at lower viscosity than NR ,owing to its irregular structure and does not crystallize. Reinforcing filler is needed to achieve good physical properties with SBR, the best reinforcing agent is carbon black. Abrasion resistance and resistance to degradation under heat are better for SBR than those of NR. SBR is less active chemically than NR and is thus slower curing, requiring more accelerators than NR[35].

1.6.3 Acrylonitrile Butadiene Rubber (NBR)

Nitrile rubbers(NBR) are copolymers of butadiene and acrylonitrile with the proportions ranging from 55% to 82% butadiene and 18% to 45% acrylonitrile. These rubbers are more costly than ordinary rubbers, also known by the name Buna-N, it was first founded in Germany at 1937 by I.G. Farbenindustrie . The structural formula of NBR is as shown in Fig.(1.6)[36].

BUTADIENE	ACRYLONITRILE
CH2=CH-CH-CH	CH2=CH-CN

NITRILE RUBBER (NBR)

(-----(CH2-CH=CH-CH2)---(CH2—CH)-----)

Figure(1.6): NBR Chemical Structure[36] .

Nitrile Rubber (NBR) is commonly considered the workhorse of the industrial and automotive rubber products industries.(NBR) is a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder variety of application areas requires oil, fuel, and chemical resistance. In the automotive area,(NBR) is used in fuel and oil handling hoses, seals and grommets, and water handling applications [37].With temperature range of –40°C to +125°C, NBR materials can withstand all but the most severe automotive applications. On the industrial side NBR finds uses in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications. Worldwide consumption of(NBR) is expected to reach 368,000 metric tons annually[38].

1.7 Vulcanization

Most useful rubber articles, such as tires and mechanical goods, cannot be made without vulcanization. Unvulcanized rubber is generally not very strong, The first commercial method for vulcanization has been attributed to Charles Goodyear. His process (heating natural rubber with sulfur) is first used in 1841. Thomas Hancock used essentially the same process about a year later in England. Since those early days, there has been continued progress toward the improvement of the process and the resulting vulcanized rubber articles. In addition to natural rubber, over the years, many synthetic rubbers have been introduced. Also, in addition to sulfur. many other substances have been introduced as components of curing (vulcanization) systems(e.g., natural rubber [NR], styrene-butadiene rubber [SBR], and butadiene rubber [BR])by sulfur in the presence of organic accelerators[39].

Vulcanization is a process generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process that increases the retractile force and reduces the amount of permanent deformation remaining after the removal of the deforming force. Thus vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a cross-linked molecular network as shown in Fig.(1.7). In vulcanization, the randomly oriented chains of raw rubber become cross-linked as indicated diagrammatically at the right[40].

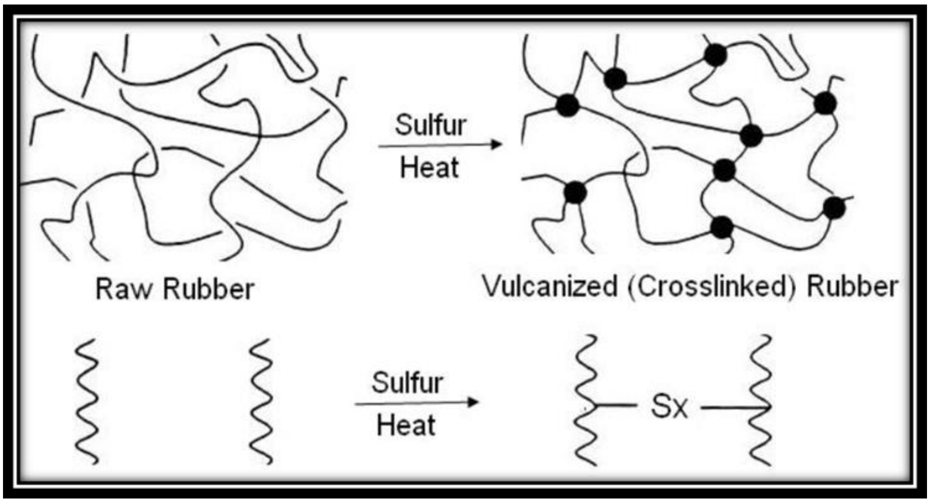


Figure (1.7) : Network vulcanization [40]

Vulcanization, thus, is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains, a crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, carbon to carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber, mixed with vulcanizing agents, in a mold under pressure[41]. The most important cross-linking agent is sulfur, which is relatively inexpensive and plentiful, and yet vital to the rubber industry. Sulfur links one chain to another through these double bonds. Elastomers such as NR and SBR need only a small percentage of these double bonds to be utilized to produce a useful product; however this leaves the larger percentage unused and therefore vulnerable to attack by oxygen, ozone and heat[42].

An elastomer, as synthesized, is basically a high molecular weight liquid with low elasticity and strength. Although the molecules are entangled, they can readily dissent angle upon stressing leading to viscous flow .Vulcanization or curing is the process in which the chains are chemically linked together to form a network, there by transforming the material from a viscous liquid to a tough elastic solid, strength and modulus of elasticity increase[43].

There are four principle changes which are brought about by vulcanization[44].

1- Rubber is converted from essentially a plastic substance of very low strength to an elastic of considerable strength and resilience.

2- The physical properties, such as tensile, modulus, hardness, abrasion resistance, elongation at break and stress relaxation undergo profound changes as vulcanization progresses, as shown in Fig.(1.8)[44].

3- The physical properties of vulcanizates are maintained over a much wider temperature range than in the case of unvulcanized rubber.

4- The cross linked polymer (vulcanizate) only swells in liquids which normally dissolve the uncross linked polymer.

There are many vulcanization systems for various elastomers , the conventional systems , sulfur vulcanization , peroxide crosslinke , resin vulcanization , electron beam vulcanization and metal oxides vulcanization .

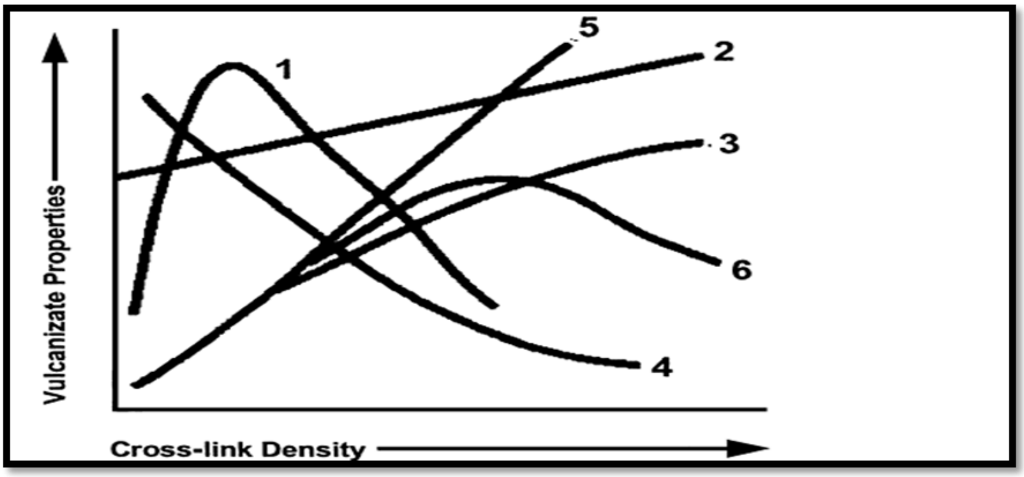


Figure (1.8) : Effects of vulcanization on physical properties. 1. Tear strength; 2.dynamic modulus; 3. hardness; 4. hysteresis, permanent set; 5. static modulus; tensile 6.strength[44]

1.8 Vulcanizing Agents

1.8.1 Sulfur Vulcanization

The most widely used vulcanizing agent is sulfur. For sulfur to effectively crosslink a rubber , an elastomer must contain double bonds with a hydrogen’s. General purpose rubber , Diene elastomers such as BR ,SBR, NR, and IR meet this basic requirement. Two forms of sulfur are used in vulcanization: soluble (rhombic crystals of S8 rings) and insoluble (amorphous, polymeric sulfur). Sometimes, in compounds containing high-levels of sulfur, insoluble sulfur is used to prevent sulfur blooming, a process by which the sulfur migrates to the surface of a compound and crystallizes there. Blooming can occur when large amounts of soluble sulfur are used, because a thigh mixing temperatures, the solubility of S8 is high, enabling large amounts to dissolve, but upon cooling the solubility decreases. When the solubility limit is reached, excess sulfur blooms to the surface. Insoluble sulfur does not bloom because it disperses in rubber as discrete particles, which cannot readily diffuse through the rubber. However, above 120^o C ,insoluble sulfur transforms in to soluble sulfur. Thus mixing temperatures must be kept below 120^o C to take advantage of the bloom resistance of insoluble sulfur as shown in Fig.(1.9)[44,45]**.**

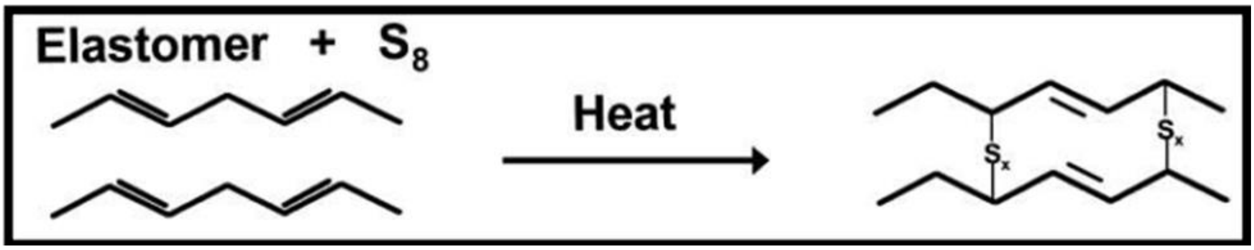


Figure (1.9) Sulfur Vulcanization[44].

Sulfur, S_8 in its normal crystalline state consists of (8) membered rings. It is thermally very stable, but upon heating, ring opening occurs at the activation energy of 270 KJ/mol. Very reactive free radical ends are created at the points of chain breakage[46].The free radicals at the chain are capable of linkage with the reactive sites on the rubber molecule in such a way that no intermolecular cross-links are formed initially sulfur attacks almost exclusively at the α – methylene carbon atoms. The sulfur–rubber interaction can be seen in Fig. (1.10)[47].

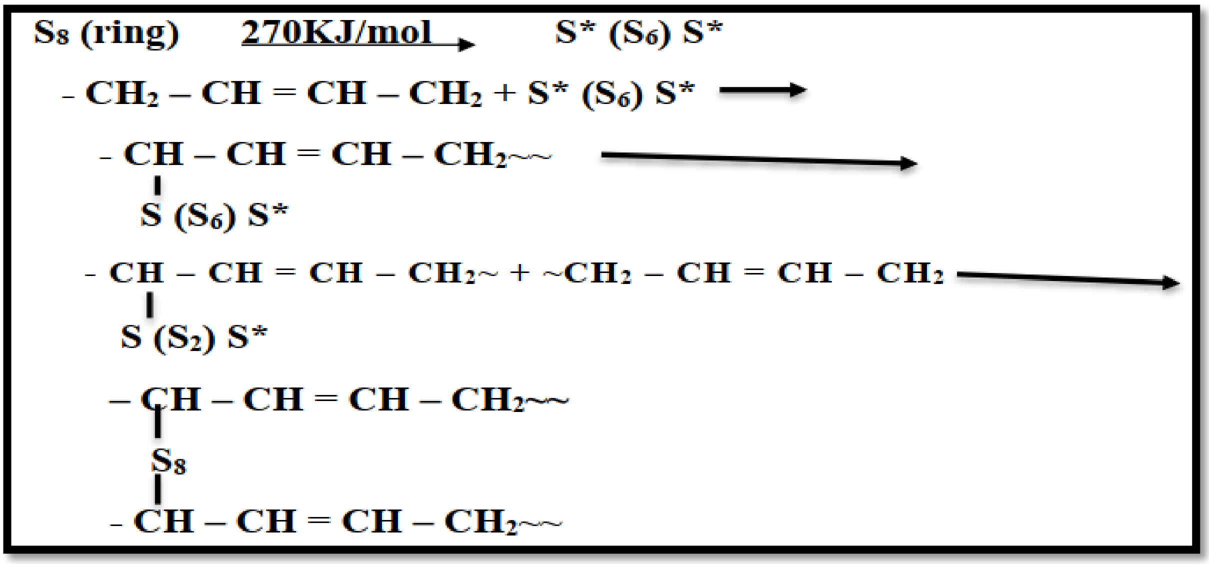


Figure (1.10) Sulfur – Rubber Reaction [47].

The general course of vulcanization is described as follows: Firstly, an active accelerator complex if formed by some prior interaction of accelerator and activator with the presence of soluble zinc. This complex can react with molecular sulfur to form a sulphureting agent[47,48]. Secondly, a sulphureting agent can react with rubber chains to form a cross linking precursor. The precursor as accelerator – terminated polysulfidic pendant group will be attached to the rubber chain [47,49]. Finally, the initially formed network matures during which similar desulfuration (cross link shortening, eventually leading to mono - sulfuridic cross links) and decomposition of poly sulfuridic cross links take place[50].

1.8.2 Activators

The two materials Zinc oxide and stearic acid, together with sulfur and accelerator, constitute the cure system for the formulation. Zinc oxide reacts with stearic acid to form zinc stearate (in some cases zinc stearate is used in place of zinc oxide and stearic acid) and together with the accelerator, they speed up the rate at which sulfur vulcanization occurs. With sulfur alone, the curing process might take hours. With this curing system, it can be reduced to minutes [44].

1.8.3 Antioxidants, Age Resistors and Antidegradant

In the human body free radicals (which play a part in the aging process) are neutralized by antioxidants (in the form of some vitamins). In the same way antioxidants are also necessary to protect other organic materials, such as most elastomers' from aging. Many vulcanizates become brittle when they age. Aging can be caused by the ravages of oxygen, accelerated by heat[51].

Antioxidants are employed to slow oxidation .They fall into two classes, with different functions. The first type, called preventive antioxidants, react with hydroperoxides to form harmless, non-radical products.. The second type, chain-breaking antioxidants, destroy peroxy radicals that would otherwise propagate. Chain-breaking antioxidants are aromatic and contain labile protons, which are "donated" to the peroxy radicals. This occurs readily because the resulting antioxidant radical is highly resonance-stabilized[46]. Antioxidants such as N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), N-(1,3dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) ,N,N'-diphenyl-p-phenylenediamine(DPPD), etc, are designed to slow down this process and can act as free radical scavenger like accelerators, there are many antioxidants available grouped into a number of chemical classes[46].

The chemist must be cautious of some antioxidants' instability. Materials that evaporate at high temperatures are of little utility, while mixes that thrive in applications where the product must bend heavily (anti-flex cracking antioxidants) are. Antiozonants, which offer sacrificial defense against ozone and include the p-phenylene diamines, are also significant and frequently included in compounds. This chemical group also has very good antioxidant activity. An antidegradant is a compounding material used to retard the deterioration caused by oxidation, ozone, light or combinations of these[21].

1.8.4 Softeners

These materials are added at low dosage to rubbers primarily to improve the process in operations such as mixing, calendaring, and extruding without significantly affecting physical properties [51]. They are used along with fillers to reduce the cost of the compound. Softeners, which increase the mastication efficiency and reduce the Mooney viscosity level to the desired processibility. Paraffin waxes with a melting point of approximately 55^{o} C are used as plasticizers. They bloom to the surface and protect ozone sensitive rubbers against cracking under static stress. Various kinds of resins are used as plasticizers; for example, coumarone resins, petroleum resins, high styrene resins, and phenolic resins. They give excellent flow characteristics to rubber compounds during calendaring, extruding, and molding [52].

1.9 The Reinforcing Fillers

Almost every conceivable material has been added to rubber in attempts to cheapen and stiffen it. Major fillers used in the rubber industry are classified as:

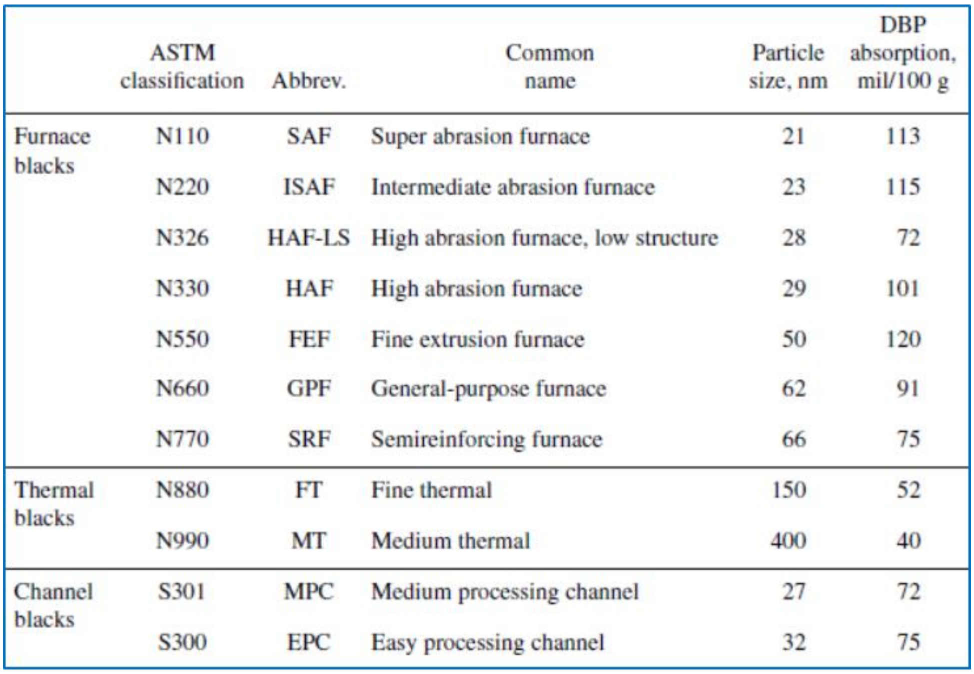
1- Carbon black.

2- Non-black fillers such as precipitated silica, fumed silica, alumina, china clay, magnesium carbonates, and inorganic fillers.

1.9.1 Carbon black

Carbon black is the general term used to describe a powdery commercial form of carbon; a lot like graphite, it is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Carbon black is used principally for the reinforcement of rubber, as a black pigment, and for its electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon, it is one of the most stable chemical products. In a general sense, it is the most widely used nanomaterial, with its aggregate dimension ranging from tens of nanometers to a few hundred nanometers, and imparts special properties to composites of which it is a part[53]. Carbon blacks are categorized, based on different production processes by which they are made, such as acetylene black, channel black, furnace black, lampblack, or thermal black over 95% of all carbon black produced today is furnace black. ASTM designations, the older nomenclature, particle size, surface area, and structure of some blacks are given in Table (1-1) [54].

Table(1-1): Colloidal properties of rubber-grade carbon[53].



	ASTM classification	Abbrev.	Common name	Particle size, nm	DBP absorption, mil/100 g
Furnace blacks	N110	SAF	Super abrasion furnace	21	113
	N220	ISAF	Intermediate abrasion furnace	23	115
	N326	HAF-LS	High abrasion furnace, low structure	28	72
	N330	HAF	High abrasion furnace	29	101
	N550	FEF	Fine extrusion furnace	50	120
	N660	GPF	General-purpose furnace	62	91
	N770	SRF	Semireinforcing furnace	66	75
Thermal blacks	N880	FT	Fine thermal	150	52
	N990	MT	Medium thermal	400	40
Channel blacks	S301	MPC	Medium processing channel	27	72
	S300	EPC	Easy processing channel	32	75

The type of carbon black filler such as (N375) was used in this thesis. The primary filler factors influencing elastomer reinforcement are:

1. The primary particle size or specific surface area, which, together with loading, determines the effective contact area between the filler and polymer matrix.

2. The structure or the degree of irregularity of the filler unit, which plays an essential role in the restrictive motion of elastomer chains under strain.

3. The surface activity, which is the predominant factor with regard to filler–filler and filler–polymer interaction.

The size of spherical particles is called particle size and the size of the aggregate is called structure. Various functional groups such as the hydroxyl or carboxyl group are found on the surface of carbon black, and their amount or composition is called surface chemistry. These three particle sizes, structure, and surface chemistry are the basic properties of carbon black, and together are called the three main characteristics Fig.(1.11). The three main properties have a large effect on practical properties such as blackness and dispensability when they are mixed with inks, paints, or resins[55,56].

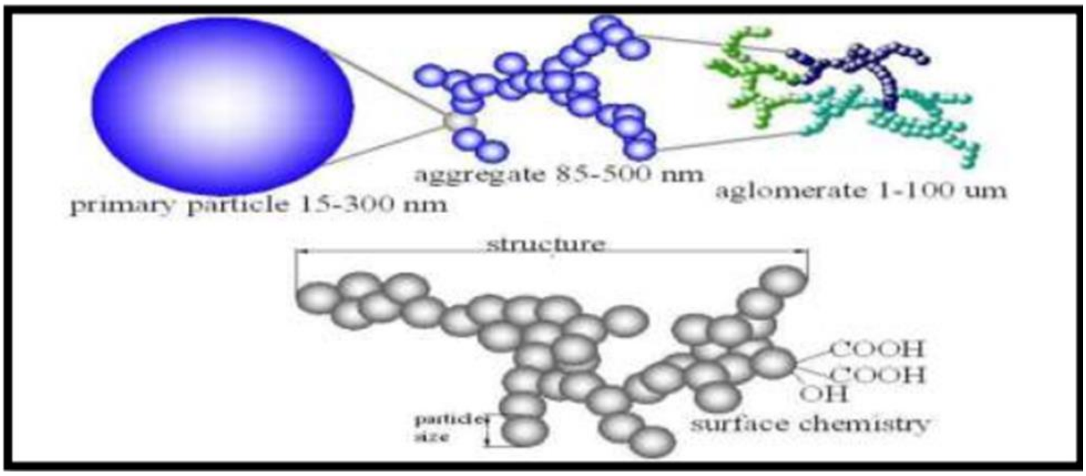


Figure (1.11) : Carbon Black structures [56].

1.9.2 Egg Shell powder

In an egg, the eggshell contributes around 11% of the overall weight of the egg, and calcium carbonate is abundant in the eggshell and is considered to be one of the major constituents present in it. With the addition of eggshell waste as filler into the natural rubber, studies were carried out to study the effect of eggshell filler on the mechanical and physical properties of natural rubber[57]. Low-cost fillers are added to polymers to reduce cost and improve their properties. One widely used inorganic filler is mineral limestone or calcium carbonate. An alternative to mined limestone is waste bio-materials such as chicken eggshells and seashells (marine mollusks, mussels, shellfish, oysters, scallops, and cockles) from the egg and seafood processing industries, respectively, which contain high calcium carbonate contents[58].

Eggshell powder(ESP) is a powder containing 97% of calcium carbonate (CaCO3). Eggshell CaCO3 powder can replace conventional limestone-derived CaCO3 for 100% in final products. Recovery of food waste eggshells to produce new materials is thus an ideal recycling strategy. To fulfill the cradle-to-cradle sustainability concept, the final products may need to be materials that can either completely degrade and serve as nutrients in the soil (e.g. composite with eggshell particles and biodegradable polymer matrix) or products that can be fully recycled[59,60].

1.10 Literature review

Many investigators have studied the effect of additives on the mechanical properties of the polymer and the new usage of eggshell powder in engineering applications.

Hanim. *et al.*, (2008)[61] prepared polypropylene/calcium carbonate (PP/NPCC) nanocomposites using a co-rotating twin screw extruder at filler loadings of 5, 10, and 15 weight %. The impact strength and modulus of PP showed some improvement with the incorporation of the nanofiller while the tensile strength deteriorated.

M. Reza Saeb. *et al.*, (2008)[62] studied the effect of using various types of eggshell powder including after and before hatching eggshell and boiled eggshell on the mechanical properties and vulcanization characteristics of SBR compounds has been investigated. The obtained results were compared with calcium carbonate-filled compounds. The results of this research showed that all kinds of eggshell powders can be used in SBR-based compounds successfully.

Masar Najm (2010) [63] studied the design of a rubber knead suitable for the manufacture of sports surfaces by adding cheap plant extracts, where a sample of natural rubber type SVR3 was prepared with vulcanizers and accelerators, then it was developed by adding different proportions of the substance extracted from the remnants of the Okra fruit as a blowing material. Some of its physical and mechanical properties such as (specific weight, tensile properties, and rebound hardness) were studied and compared to the properties of a commercial product, then exposed to UV rays for different periods, and tests were conducted. Physical and mechanical after irradiation, a spongy rubber was obtained that caused a decrease in the specific weight, tensile strength, modulus of elasticity, hardness, and resilience.

Mohammed R. M. and Ahmed N. Hadi (2012)[64]studied the effect of egg shells powder on some mechanical and physical properties of natural rubber (nr), tensile strength, modulus of elasticity, elongation, hardness, resilience and specific gravity, the egg shell powder was added to NR from 5 wt % to 25 wt %.The results showed that the hardness and modulus of elasticity, specific weight increased with increasing of the powder. The hardness was (35 IRHD) for pure rubber, while was (49.3 IRHD) at percent of powder (25 wt %) . It was observed that the tensile strength, elongation and resilience decreased with increasing of powder. The tensile strength was (21.96 MPa) for pure rubber, while was (9.21 MPa) at percent of powder 25 wt %.

H. Ismail and H. S. Ahmad (2013)[65] studied the properties of Acrylonitrile-Butadiene Rubber (NBR) composite with Halloysite Nanotubes (HNTs) and silica or carbon black five different compositions of NBR/HNTs/Silica or NBR/HNTs/CB (i.e., 100/5/0, 100/4/1, 100/3/2, 100/2/3, 100/0/5 parts per hundred rubber (phr)). The tensile strength and modulus (M100) of both composites decreased, whereas elongation at break increased and maximum torque with increasing the silica or carbon black content. However, both composites show opposite trends for cure time and scorch time, where NBR/HNTs/Silica composite exhibited an increasing trend, while NBR/HNTs/CB composite shows the decreasing trend. The rubber-filler interaction studies showed that carbon black is a more reinforcing filler than silica.

Sameer H. AL-Nesrawy (2014)[66] studied the effect of adding some industrial waste, which is cement kiln dust and recycled rubber as fillers, in addition to carbon black (N375) to support the rubber kneaders consisting of synthetic rubber (styrene – Butadiene) (SBR 1502 and (cis BR) in addition to natural rubber (NR SMR 20). They are,(SBR/NR/BRCIS),(SBR/NR SBR/BRCIS) used in the manufacture of fenders for ships, where the mechanical properties of hardness, tensile strength, elongation, tear resistance, compression, frictional wear, modulus of elasticity, fatigue, and rebound were studied. Through the extensive study of this research and conducting solubility and aging tests, the result was that the rubber compounds (SBR50/NR50) (SBR60/NR40) (SBR80/NR20) achieved the best results that can be used in this application.

Amal S.M. Bashir.*et al.*, (2017)[67] studied the use of ES powder (ESP) as filler in natural rubber latex foam (NRLF). Tensile strength of NRLF incorporated with ESP initially drops at low ESP filler loading and then increases with the increment of filler loading from 5 to 10 parts by weight per hundred parts of resin (phr). As the ESP filler loading increases up to 10 phr, M100, compression stress, compression set, hardness, rubber filler interaction, and density increase. Meanwhile, elongation at break and recovery percentage of compression set decrease, as the filler loading increases up to 10 phr. Field emission scanning electron microscopy results indicate that even at 10 phr of ESP loading, the fillers are homogenously dispersed in the matrix without agglomerations. However, the thermal stability of NRLF decreases with the incorporation of ESP.

Nyein C.A. *et al.*, (2019)[68] concerned with the characterization of banana stem fiber(BSF) and eggshell powder(ESP)- natural rubber composites. Banana stem fiber and eggshell powder were used as fillers in the process of preparation of natural rubber composites. The banana stem fiber and eggshell powder-natural rubber composites were prepared by molding method with various weight ratios (5 %, 10 %, 15 %, 20 %) of banana stem fiber and eggshell powder and were also characterized by modern techniques such as SEM. The mechanical properties such as hardness, specific gravity, tensile strength, and elongation at break and tear strength of banana stem fiber and eggs powder-natural rubber composites were determined by standard rubber testing methods, results show that as the BSF and ESP loading increased, hardness and specific gravity also increased. The tensile strength of BSF and ESP composites decreased as BSF and ESP loading increased. Scanning electron micrograph results of both revealed that the distribution and adhesion interaction between the fillers and rubber matrix was good.

Xianjie Rena and Katrina Cornisha (2019)[69] studied bifunctionally silanized silica micro-sized eggshell (ES), at three different loadings, in guayule (Parthenium argentatum, Gray) natural rubber (GNR) composites, and the dynamic mechanical properties and durability (resistance to aging, fatigue, and ozone) were characterized. Replacement of BSS with ES decreased the dynamic property of estimated rolling resistance, more than BSS by itself, and, unusually, concomitantly increased the estimated wet grip of GNR composites. The composites filled with ES and BSS had comparable resistance to aging and fatigue. However, ozone resistance was greatest in composites made with a mixture of the two fillers. Durable GNR composites made with ES and BSS with improved dynamic mechanical properties may support further expansion of the GNR industry.

S.H. Al-Nesrawy and M.H. Naeem (2019)[70] studied and prepared rheological properties for (NR50/SBR50/OSP) composites while the loading ratio of OSP were(0, 5, 10, 15, 20, 25, 30, 40, 60, 80, 100 pphr. The examination of FTIR were carried out and studied the effect of calcium carbonate (Oyster Shell Powder OSP) grain size <225 μ on the rheological properties with different loading ratio of (OSP). The device used to examine the characteristics is oscillating disc rheometer according ASTM D-2705 and temperature 185°C, pressure 10 bar and time 6 min. These rheological properties included the scorch time (ts2), cure time (tc90), viscosity, Maximum torque (MH), Minimum torque (ML) while the results of all these properties were decreasing with increase the loading ratio of OSP with or without C.B 10 pphr also all these properties were decreasing after addition C.B = 10 pphr for the same loading ratio of OSP except maximum and minimum torque at high loading ratio.

Shamsul K.*et al.*, (2020)[71] developed ENR-25, ENR-50, deproteinized natural rubber (DPNR), and NR rubber compounds, and a comparative study was carried out to determine the rheological properties, mechanical and dynamic behavior of the compounds. Oil palm fiber (OPF) and eggshell powder (ESP) were incorporated as hybrid biofillers with a ratio of 10/30 due to their superior findings. The ENR and DPNR compounds showed lower curing time and scorch time than NR indicating their improved processibility performance. NR resulted in the highest hardness, tensile strength, and compression set as expected.

Gbadeyan O. J.*et al.*, (2020)[72] studied mechanical and absorption properties of composites reinforced by achatina fulica snail (S-shell) and eggshell particles (E-shell). Epoxy composites of snail and eggshell particles were prepared separately with the filler content ranging from 5 to 20% by weight. Hybrid composites of both fillers were also prepared and assessed. Specimens of the composites and hybrid composites with different percentage weights of the reinforcing materials were fabricated using the resin casting method. Mechanical properties such as tensile strength, Young’s modulus, impact strength, hardness, and water absorption properties of the specimens were evaluated experimentally. It was observed that the addition of nano-size shell particles improves the mechanical properties of neat epoxy irrespective of the percentage weight of the reinforcement.

E. F. Al-Nesrawy and S. H. Al-Nesrawy (2021)[73] studied the impact of adding materials such as carbon black(C.B) and polymer of carboxyl methylcellulose(CMC) on the the rheological properties of styrene butadiene rubber (SBR) and natural rubber (NR) which was studied as a matrix. The present study was a carried out by two groups according to the loading level of (CMC) and (C.B) its molecular weight (N660) which their used as stiffeners in the composites. The purpose is to use these composites in various tire making and fender ship. The results revealed that the parameters differ according to the level of loading. Viscosity, lower torque, maximum torque and optimal curing where (BSS), a commercial synthetic filler, was partially or completely replaced by reduced for increasing loading ratio of the C.B and CMC. As well, an optimal curing time of the TC90 burning time was reduced as addition ratios of the carbon black (C.B) and carboxyl methyl cellulose (CMC) increased.

Cindy S. B. and Janice L.T (2022)[74] investigated the effect of eggshells, a widely available renewable material, as partial and complete replacements of petroleum-derived carbon black in natural rubber composites for automotive anti-vibration applications. At a fixed equal total filler weight, a comparable level of reinforcement was achieved at low replacements (up to 20%) of carbon black (N330) with eggshells in the reference formulation. Furthermore, pairs of composites formulated for similar hardness had similar mechanical properties, and improved isolation performance with very similar damping and static stiffness (Ks), despite the difference in carbon black/eggshell ratio among them. Particularly, composites made with 20 phr (parts per hundred rubber) of eggshell and 40 phr of carbon black (C40E20) had remarkable mechanical performance.

Suhas K.*et al*., (2023)[75] studied the effects of eggshell filler addition and post-curing on polymer composites that could be utilized for domestic applications. Herein, uncarbonated and carbonized eggshell filler material was processed from waste eggshells. Hybridization of the carbonized and uncarbonated eggshell filler was carried out. All three variants of eggshell fillers (10 wt.%) were used to fabricate composites. A hand lay-up technique was employed in the fabrication of unfilled composites along with three variants of filled composites, namely, uncarbonated, carbonized, and hybrid eggshell-filled composites. The fabricated and cured composites were further subjected to post-curing at a temperature of 60 °C for 2 h. All four variants of post-cured composites were then subjected to mechanical testing. The tests revealed that all three variants of filled composites possess better mechanical properties in comparison with unfilled composites. Further, in comparison with unfilled composites, the carbonized eggshell-filled composites showcased 42% and 49% improvement in flexural and tensile properties, respectively.

1.11 Aims of study

1.Preparation(NR/SBR/ESP),(NR/SBR/ESP/CB-20pphr),
(NR/NBR/ESP)and(NR/NBR/ESP/CB-20pphr)hybrid Rubber Composites.

2.Using Egg Shell Powder as reinforcement material with different loading ratio

3. Reducing the environmental pollution for this material.

4.Using of new fillers Egg Shell Powder as reinforcement material for improving the mechanical and Rheological properties of instead of traditional materials for engineering applications.

Chapter Two

Theoretical Background

2.1 Introduction

This chapter includes a general description of the theoretical aspect of the subject of the current study, in terms of theoretical physical ideas and concepts, scientific explanations, and mathematical relationships and laws through which the results obtained can be interpreted in practice. Fourier transform infrared (FTIR) spectroscopy, rheological properties such as minimum torque(ML), maximum torque(MH), scorch time(Ts2), optimum cure time(Tc90), cure rate index(CR)and viscosity, mechanical properties like tensile strength, elongation at break, elastic modulus and hardness, thermal aging were explanations.

2.2 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a nondestructive chemical characterization technique that covers the electromagnetic spectrum's wave number range of 14000 cm^{-1} to 10 cm^{-1} Fig.(2.1). This spectral zone is divided into three regions: near-infrared (14000 – 4000) cm^{-1}, mid-infrared (4000 –200) cm^{-1}, and far-infrared (200 - 10) cm^{-1}. This instrumental technique is based on the dipole moment (μ) and the molecular vibrational frequency[76,77,78].

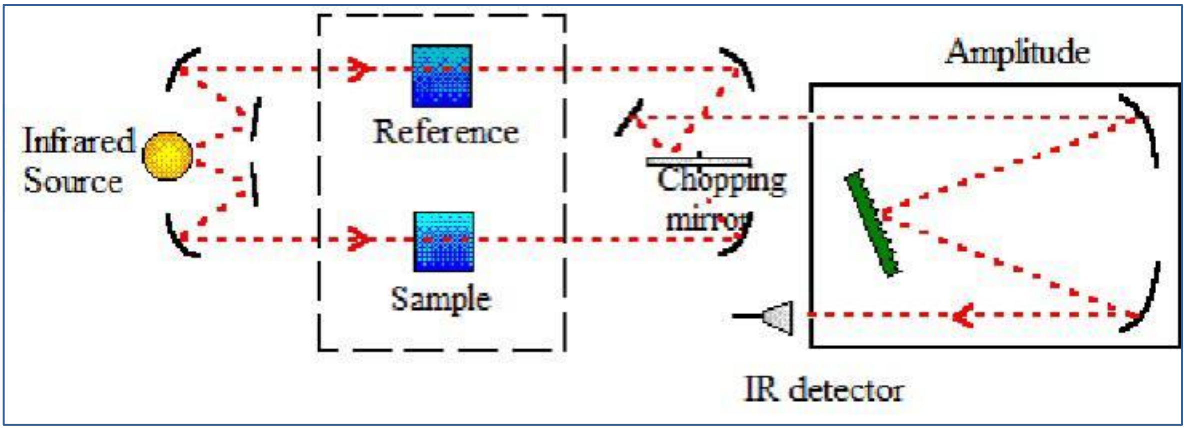


Figure (2.1): A schematic diagram of the classical dispersive IR spectrophotometer[78].

2.3 Rheological Properties

Rheology is the science of flow and deformation , not deformation is associated with elasticity, and flow is associated with viscosity. The term rheology is synonymous to the term viscoelasticity. Always what, these names of terms are often used interchangeably. However, the performance of a pharmaceutical solution is determined by its rheological qualities. The viscoelastic behavior of gum rubbers and compounds has already been well investigated[79]. Due to the following properties such as high strength-to-weight ratio, high modulus, chemical stability, fatigue resistance, resistance to deformation, high ductility, and ease of manufacturing. Carbon black reinforced composite materials have been widely used as engineering materials for various forms of tires or other rubber industries, such as the manufacture of ships, cars, planes, children's toys, and others[80].

A "Oscillating Disc Rheometer," which is one instrument for evaluating kinetic crosslinking, is used to obtain a treatment phase curve. The test chemicals are encapsulated by an oscillating rotor that is contained inside a heated box. The amount of torque for oscillating the rotor is calculated as a function of time[80]. All of the vulcanization properties of the rubber compound can be calculated directly from the torque versus cure time curve. Rheography is divided into three phases, which are showed below in Fig.(2.2) [81]:

1. Phase -1- : It represents the rubber compound's processing behavior.
2. Phase -2- : It defines the rubber compound's curing properties.
3. Phase -3- : It gives an indicator of the rubber compound's physical qualities.

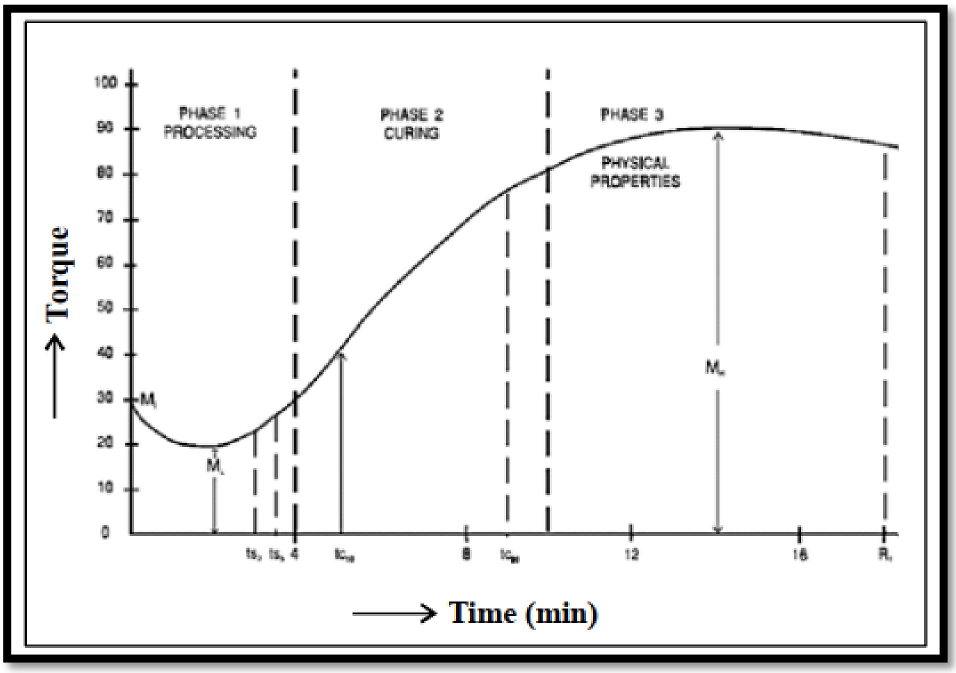


Figure (2.2) : Rheography (Cure Curve) [81]

Fig.(2.3) shows the relationship between the torque of the (Rheometer) device (Ibf-in) and the ripening time (min) of the rubber kneaders, which is called the elastic modulus time[82].

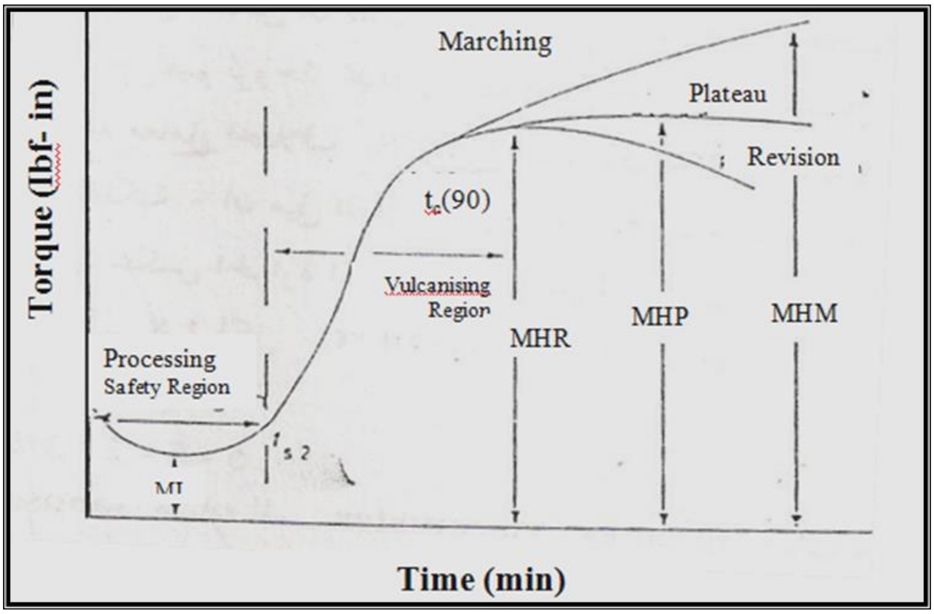


Figure (2.3) shows the relationship between the torque and the ripening time(min)[82]

1. A region in which the rubber is immature and where the lowest torque (ML) occurs, which is an indicator of the lowest viscosity value. In this region, scorch

resistance occurs within the period (ts2) and is called (Processing Safety Region).

2. The region in which the ripening occurs and the modulus of elasticity begins to rise and the mechanical properties of rubber improve. This region is within the time period (tc90) and is called the (Vulcanizing Region)[83].

The plot of torque versus time is studied to acquire the varied outcomes. The rheography is presented in real-time on an oscillating disc rheometer, and at the end of the test, the computer analyzes the graph, and the findings are automatically generated and shown on the screen or printer. Rheography's exhibited results are divided into three reports [84,85]:

1. Torque Report in (Ib.In).
2. Time Reports in minutes.
3. Derived Reports.

2.3.1 Torque Reports

a- ML (Minimum Torque)

The viscosity of the compound lowers when it is heated under pressure, and the torque reduces. The torque value that has been recorded at the lowest level is referred to as ML. Essentially, it is a measure of the stiffness and viscosity of vulcanized material, derived from torque measurements using the relation[85]:

$$\boldsymbol{Viscosity} = \mathbf{ML} * \mathbf{2.7} \qquad \ldots\ldots\ldots\ldots\ldots(2.1)$$

b- MH (Maximum Torque)

This type of curve with reversion is called the “reverting curve”. The slope of growing torque changes depending on the type of compound. After a period, the torque normally reaches its maximum value; this is referred to as the "plateau curve." If a test is continued for sufficient time, the reversion of cure occurs and torque tends to fall. The term "Revision curve" refers to a reverting curve during the period of record, the torque has shown a continuously rising trend at times. The term "rising or marching curve" describes this sort of curve. The greatest torque measured in the plateau curve is MH. When it comes to retracting curves, the Max. MH is the abbreviation for measured torque. The maximum torque may be stated as a measure of the vulcanized material's stiffness[85].

2.3.2 Time Reports

a- Scorch Time TS2

During the cure process, when the torque increases 2 units above ML, scorch time TS2 is registered. Scorch is premature vulcanization in which the rubber becomes partly vulcanized until the product is in its final state and ready for vulcanization. It causes the compound's plastic properties to deteriorate to the point that it can no longer be recycled. Scorching is caused by a rise in temperature during fermentation as well as the length of time the compound is subjected to high temperatures. This time interval before vulcanization begins is known as "scorch time." since scorching ruins the rubber, it is important that vulcanization does not start until this process is complete[86].

b- Optimum Cure Time TC90

It is the time at which 90% of cure has taken place[87].

c- Reversion Time RT

Since reaching MH, it is time to cross 98 percent of MH. When a substance is exposed to heat aging, how long it preserves its physical properties. It gives us an indication of the quality of the compound. Reversion occurs with over cure, which results in a reduction in modulus and tensile power.

2.3.3 Derived Values

a- Cure Rate Index CR

Cure rate is simply a measure of the rising curve's linear slope. When the compound is heated past the scorch point, the characteristics of the compound change from a soft plastic to a strong elastic material necessary for usage, and the rate of cure is the pace at which cross-linking and the development of stiffness(modulus) for the composites. Crosslinks join the lengthy polymer chains of the rubber during the curing process. The polymer chains become more tightly coupled as more crosslinks are generated, increasing the stiffness (modulus) of the composite. The rate of cure is an essential vulcanization characteristic since it dictates the amount of time necessary for the entire curing process to be completed. The cure rate index (CRI) is a simple metric that can be given by the following equation[84]:

$$\boldsymbol{CR} = \frac{\mathbf{100}}{\boldsymbol{TC}\mathbf{90} - \boldsymbol{TS}\mathbf{2}} \qquad \ldots\ldots\ldots(2.2)$$

b- Difference between maximum and minimum torque ΔM

The difference between maximum and minimum torques can be expressed as a parameter of crosslink density. In crosslink density tests, we used this value as an indicator for measuring crosslink density[84].

2.4 Mechanical Properties

Mechanical properties are of particular importance for composite materials because show the behavior of those materials when a force is applied to them**.**

2.4.1 Tensile properties

a-Tensile strength

The tensile strength of a rubber compound is defined as the maximum tensile stress applied in stretching a specimen of rubber compound to rupture. It is expressed by Newton per square meter (Pascal) or pound per square inch of the cross-section. This property has an absolute value in some applications where the product is subjected to tension in service, but like the other tensile properties, it is most frequently used in evaluating compounding materials on a comparative basis. The tensile strength may be considered either separately or together with the modulus and elongation in defining an optimum state of a cure for any specific compound[88]. The modulus values should not be determined from the results of one stress – strain curve, several tests should be made on the material and the average modulus where calculated which indicate the standard deviation Fig.(2.4) Typical, generalized tensile stress–strain curve for polymers. The molecular orientation has a significant effect on tensile strength values. Therefore these values should be indicated by the direction of orientation. On the other hand, the stress–strain parameters are extremely temperature dependent [88].

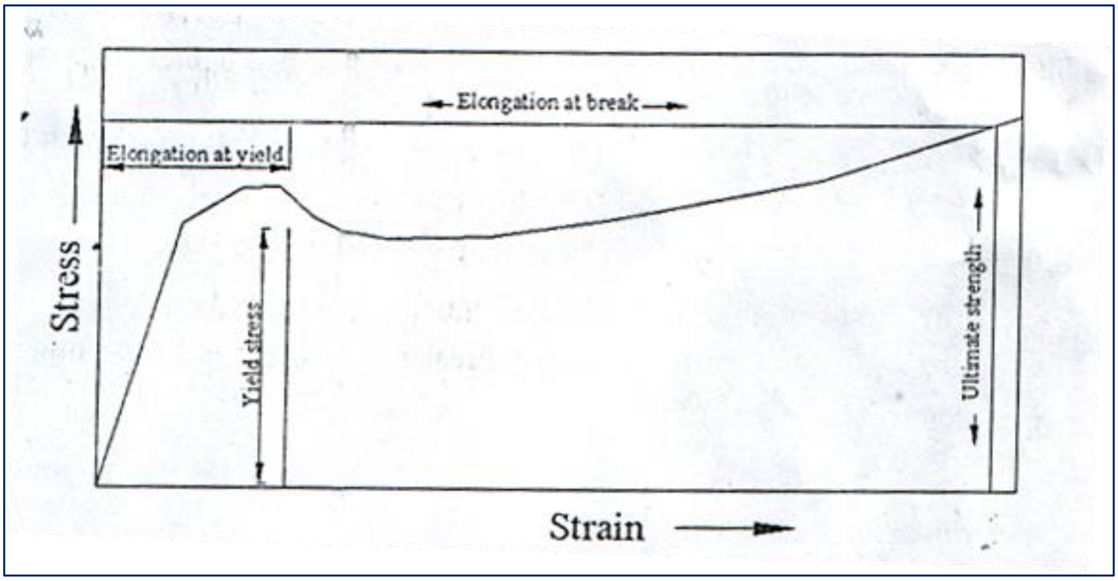


Figure (2.4) Typical , generalized tensile stress – strain curve for polymers[88]

b-Elongation at break

Elongation is used to describe the ability of a rubber compound to stretch without breaking. It is equal to the difference between the final and initial lengths expressed as a percentage of the latter[88]. The Dumbbell-shaped specimens for tensile test with determined dimensions as shown in Fig.(2.5)[88].

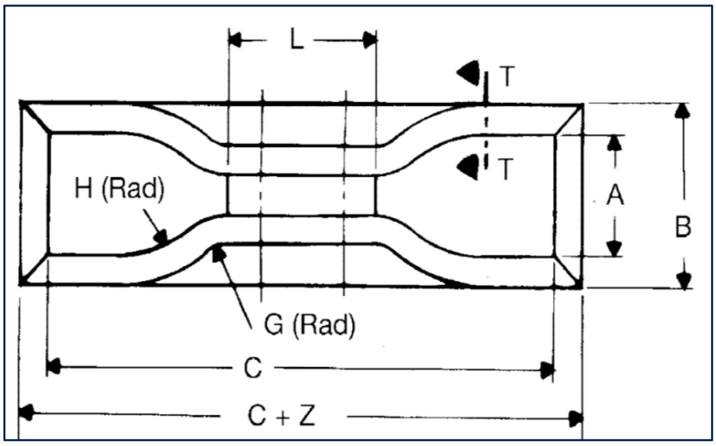


Figure (2.5) Dumbbell-shaped specimens for tensile test with determined dimensions[88].

Table(2-1) the value of Dumbbell-shaped specimens for tensile test[88]

Value	Tolerance	Units	Dimension
16	±1	mm	A
30	Max	mm	B
100	Min	mm	C
104	Min	mm	C+z
14	±1	mm	G
16	±2	mm	H
33	±2	mm	L

c-Modulus

Modulus is the quantity of stress required for a given elongation (frequently 300%100) and is used as a supplement to modulus in comparative evaluations. This value is determined during the test[88].

2.4.2 Tensile, Elongation and Elastic Modulus

The tensile test consists of stretching rubber samples at a uniform speed in a tensile tester and recording the values of stress on the samples and the resulting elongation at more or less regular time intervals. The curve drawn with the elongation on the abscissa and the stresses on the ordinate axis is called the tensile curve. The tensile stress is the ratio of the total force acting on the sample to the initial cross-section of the sample. The tensile stress at the breaking point of the rubber sample is called tensile strength. It is defined as the force per unit area of the original cross-section, which is applied when the specimen is ruptured [89].

Can calculate the tensile strength by the equation[89];

$$\boldsymbol{Tensile\ Strength = \frac{F}{A}} \qquad \ldots\ldots\ldots\ldots\ldots(2.3)$$

Where F : observed force(N) required to break the specimen of the cross section area A(mm^2).

Young's modulus is defined as the ratio between the applied stress and the strain resulting from it in the elastic region in the stress elongation. In the elastic deformation of solid material, the elongation relates to the stress by a quantity called elastic modulus (E) which is the straight region in the Stress - Elongation Curve. The Engineering stress and strain are described by the following expressions[90] :

$$\text{Engineering } Stress\ \sigma e = \frac{Force\ or\ load\ F}{Cross\ sectionalarea\ A} \quad \text{……….(2.4)}$$

$$\text{Engineering } Strain\ \varepsilon e = \frac{(L-Lo)}{Lo} \quad \text{…………(2.5)}$$

Where Lo=initial length and L=final length.

The relationship between true stress and engineering stress once no volume change is assumed in the specimen described by the following expressions.

$$\text{True stress } \sigma t = \sigma e\ (1 + \varepsilon t\ ) \quad \text{………………………..(2.6)}$$

Thus, Young's modulus in a tensile test is given by;

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} \quad \text{…………………..(2.7)}$$

The maximum elongation is called “elongation at break” or “ultimate elongation” Therefore; the mathematical relation to calculate the ultimate elongation is[89]:

$$Ultimate\ elongation = \frac{L-Lo}{Lo} * 100\% \quad \text{……….(2.8)}$$

2.4.3 Hardness

The measurement of hardness is perhaps the most extensively utilized test in the rubber business. ASTM defines hardness as the resistance of a material's surface to indentation when tested under certain conditions. Hardness is a practical way for rubber used technologists to classify rubber materials. The international rubber hardness tester and the durometer are two hardness measurements that have almost universal approval. Different durometers are depicted in Fig.(2.6), to cover the full spectrum of hardness found in rubbers[21]. The shore A scale is the most appropriate for rubber compounds commonly used in engineering. The shore D scale is appropriate for harder rubber compounds such as ebonite, plastics. Hard urethane is also measured using the Rockwell scale [91].

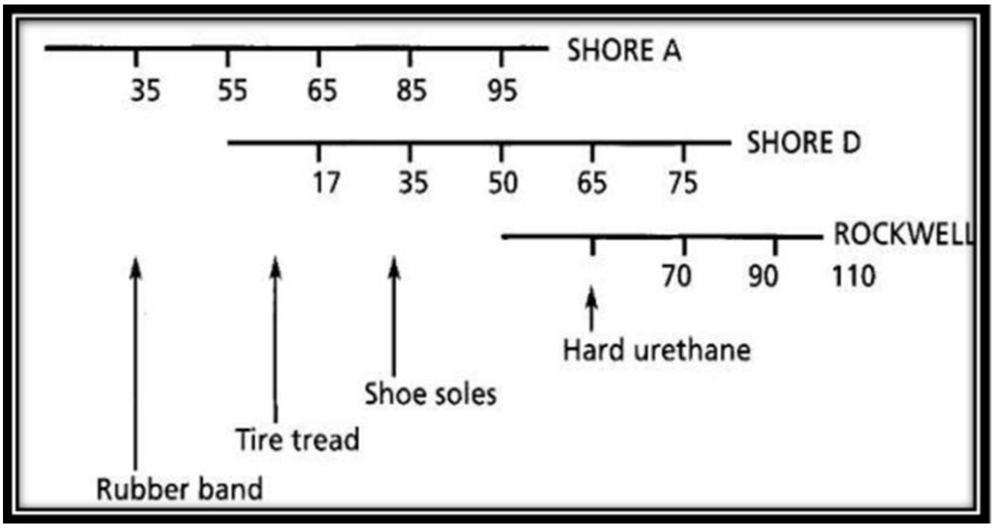


Figure (2.6) Approximate Equivalence of Hardness Scales [91]

In some main ways, the International Rubber Hardness Tester varies from the durometer. It is a small benchtop instrument that uses dead weights to apply given loads to a spherical indenter while a dial gauge measures penetration. In most cases, the dial gauge is specifically measured in International Rubber Hardness degrees (IRHD). The IRHD scale was selected because it has numerical readings that are numerically equal to the common A scale across the spectrum of functional engineering compounds. Although the IRHD and A scales are roughly equivalent for highly elastic materials, substantial variations can be predicted for materials with pronounced time-dependent properties[91].

According to the ASTM norm, the indenter's penetration is proportional to the rubber's Young's modulus. This is an empirical relation discovered by Scott in 1948[92].

$$\frac{\mathbf{F}}{\mathbf{E}} = \mathbf{1.9\ P^{1.35}\ r^{0.65}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.9)$$

Where F is the indenting force(N),(E) is Young's modulus (Mpa),(P) is the depth of Penetration (mm) ,and(r)is the radius of the indenter (mm) showed that a theoretical relation may be derived from the classical theory of elasticity in the form[93].

$$\frac{F}{E} = 1.78\ P^{1.5}\ r^{0.5} \qquad \ldots\ldots\ldots\ldots\ldots(2.10)$$

If we take Young's modulus to be equal to three times The shear modulus G ,we may write:

$$\frac{F}{G} = 5.33\ P^{1.5}\ r^{0.5} \qquad \ldots\ldots\ldots\ldots\ldots(2.11)$$

These empirical or theoretical relationships between hardness and Young's or shear modulus should be regarded as just approximate. The way Young's modulus is defined and measured hardness might cause significant disparities. Discrepancies are also predicted when a material's behavior deviates significantly from that of a completely elastic material [93].

2.5 Thermal Aging

Thermal aging of rubbers is very complicated because there are two competitive processes taking place: crosslinking and chains scission [94].

Crosslinking induced an increase in the elastic modulus and a consequent decrease in the extensibility of the material. It was found that the sulfur of the polysulfide -C-SX-C- bond led to further cross-linking. The aging process is defined by a set of irreversible physical and chemical changes in the observed material. Test procedures of aging consist in exposing samples to the effect of harmful factors in a given time interval. During the aging process rubber's mechanical properties become worsen, due to changes in the basic structure of the polymer, Polysulfidic, disulfidic, and monosulfide types of crosslinks in the vulcanizates exist [94].

As for rubber crosslinked with sulfur systems under conditions of elevated temperature conversion of polysulfide bonds in monosulphidic is observed. The reaction is followed by the separation of low molecular weight groups such as hydrogen sulfide, sulfur dioxide, and carbon disulfide. Monosulphidic connections are broken under the influence of stress and they react with neighboring hydrogen atoms, thus building a stable functional group. During subsequent crosslinking regardless of increasing of crosslinking degree, due to the dominating process breaking crosslink fact, in most cases, the strength and elasticity decline. Crosslink’s formed during cross-linking, under the influence of heat and prolonged time networking, can be torn. In this case, first -S-S- bonds are broken, followed by -C-C- bonds, which is explained by a lower value of energy connection. Scission process of -S-S- bonds provide radicals that can react with each other giving the chains of the smaller length of the starting molecules polymers that can react with each other by building the ring (cyclization) of different size and structure. The final properties of cross-linked materials strongly depend on the structure of cross-connections. If the presence of polysulfide bridges is bigger, changing the mutual arrangement of the parts chain between crosslink nodes is much easier[95].

Chapter Three
Materials and Experimental Techniques

3.1 Introduction

To make a rubber (batch) dough according to the prescribed methods after carrying out rheological tests like scorch time, cure time, and viscosity on the suggested kneaders that are made under various preparation settings, where the major variable is the proportions of its components, the dough will be acceptable for the proposed uses. Also, mechanical tests including tensile, hardness, and elongation at the rubber compound, followed by compliance with international standard requirements. In this chapter, the materials and processes used in the production of rubber kneading are presented, along with techniques and methods for analyzing the rubber's qualities.

3.2 Specification of mechanical properties

Table (3-1) includes the specifications of the mechanical properties of the rubber batch overlay by the American International Standards for Materials Inspection[96].

Table (3-1) The specifications of the mechanical properties[96]

Mechanical properties	Specification
Tensile strength	ASTM-D 4129
Hardness (IRHD)	ASTM-D 1415
Elongation	ASTM-D 4129
Modulus of Elasticity	ASTM-D 4129
Thermal aging	ASTM-D 573

3.3 Experimental part

3.3.1 Materials

The materials were used in experimental part shown in table(3-2)

Table(3-2) The material used in experimental part

Materials	PPHR
NR	50
SBR	50
NBR	50
Zinc oxide	4
Stearic acid	1
MBS	1
6PPD	0.5
Carbon black	20
Oil process	3
Sulfur	1.5
ESP	0,10,30,50

1. **NR** used in this study is Standard Malaysian Rubber (SMR 20) which has a specific gravity or density 0.92 g /cm^3, supplied by the Perlis, Malaysia.

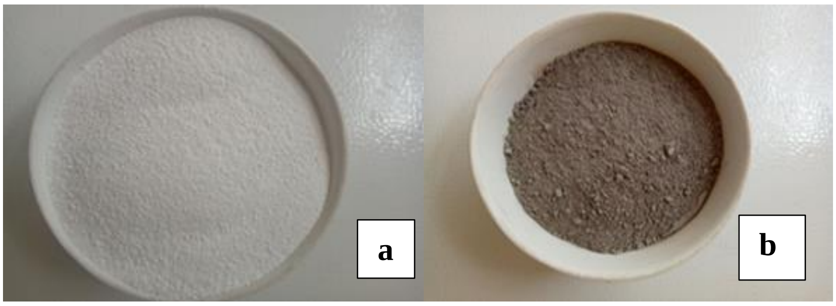
2. **SBR** used in these experiments is SBR 1502 (with 23.5% styrene content and 75% butadiene), with specific gravity (0.95 g/cm^3), supplied by the Kumho CO. Koria.

3. **NBR** (1052, acrylonitrile content 33%) was purchased from Nantex Industry Co., Ltd., China.

4. **Carbon black(CB**) N375 supplied by Doudah, Iran. It is examined in accordance with DBP absorption (ASTM D136) and Iodine absorption (ASTM D135).

5. **Eggshell powder(ESP**),the eggshell wastes collected locally were washed thoroughly with water several times and dry in the sun for many days and crushed into smaller pieces. The pieces of eggshell wastes were then stirred mechanically to separate the eggshell and its membranes. The membranes were removed and the eggshell pieces were dried in the furnace for 1 hours at 100°C . After the drying process, the eggshell pieces were grounded into powder form using ultra centrifugal mill. The eggshell powder were placed in a box furnace for 2 hours at 400°C. Heat treatment was done onto the(ESP)

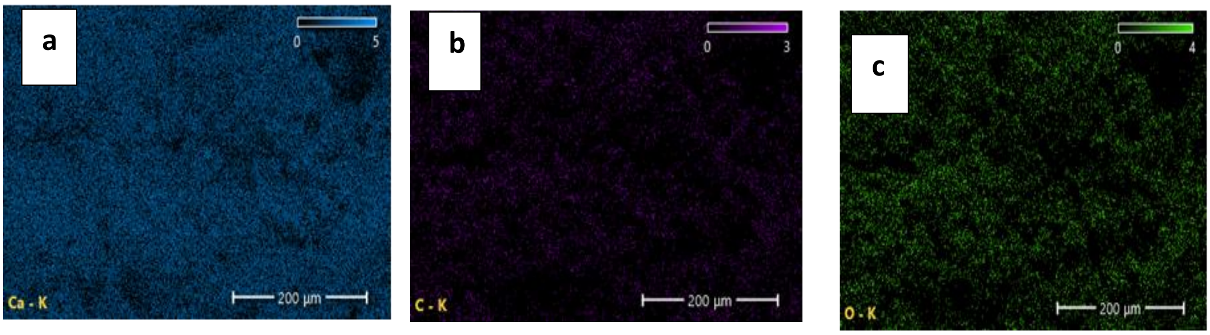
to enhance the properties of the eggshell powder. Fig(3.1,a,b) show the eggshell powder (ESP) before and after heat treatment respectively.



Figure(3.1) a-before heat treatment.

b-after heat treatment.

Egg shell powder(ESP) it is a powder containing 97% of the calcium carbonate ($CaCO_3$) that was carried out in the laboratory of Alkhora Company in Baghdad, detected by Energy Dispersive X-ray Spectroscopy (EDS), Fig(3.2,a,b,c) shown the elements of($CaCO_3$).



Figure(3.2,a,b,c)the elements of(CaCO3)

Table(3-3) shows the weight percentage of($CaCO_3$)in the(ESP) elements with the presence of other elements present in very small percentages.

Table(3-3)weight percentage of(ESP)elements.

Element	Weight %	Weight % Error
$CaCO_3$	97	0.1
MgO	0.8	0.1
SiO_2	0.7	0.1
SO_3	0.9	0.1

6. Zinc oxide (97%) and stearic acid (99.4%) were supplied by Acidchem-International CO. Malaysia. 6PPD N- (1, 3 – Dimethyl butyl) – N – Phenyl – Para – Phenylenediamine (98%) was supplied by Shenyang Sunnyjoint Chemicals CO. China. MBS N- oxy diethylene benzothiazole 2- sulfonamide (98.2%) supplied by ITT, India. The South Patrol Company supplied Paraphenic wax, processing oil. Sulfur was supplied by Al-Meshrak CO. Iraq.

3.4 Composites preparation

In this study was prepared two types composites. The first composite.

1. **Group(A)**(NR50/SBR50/ESP)composite the loading ratio of (ESP) was (0,10,30,50pphr),without (CB), the ingredient is shown in table (3-4).

Table (3-4) Composites ingredient (group A) (pphr)

Materials	A1	A2	A3	A4
NR	50	50	50	50
SBR	50	50	50	50
Zinc Oxide	4	4	4	4
Stearic acid	1	1	1	1
MBS	1	1	1	1
6PPD	0.5	0.5	0.5	0.5
Carbon black	0	0	0	0
Process oil	3	3	3	3
ESP	0	10	30	50
Sulfur	1.5	1.5	1.5	1.5

2. **Group(B)**(NR50/SBR50/ESP/CB-20pphr), with same loading ratio of(ESP) and with (CB-20pphr), the ingredient is shown in table (3-5).

Table (3-5) Composites ingredient (group B) (pphr)

Materials	B1	B2	B3	B4
NR	50	50	50	50
SBR	50	50	50	50
Zinc Oxide	4	4	4	4
Stearic acid	1	1	1	1
MBS	1	1	1	1
6PPD	0.5	0.5	0.5	0.5
Carbon black	٢٠	20	20	20
Process oil	3	3	3	3
ESP	0	10	30	50
Sulfur	1.5	1.5	1.5	1.5

The second composite.

1. **Group(C)**(NR50/NBR50/ESP)composite the loading ratio of(ESP)was(0,10,30,50pphr), without (CB), the ingredient is shown in table (3-6).

Table (3-6) Composites ingredient (group C) (pphr)

Materials	C1	C2	C3	C4
NR	50	50	50	50
NBR	50	50	50	50
Zinc Oxide	4	4	4	4
Stearic acid	1	1	1	1
MBS	1	1	1	1
6PPD	0.5	0.5	0.5	0.5
Carbon black	0	0	0	0
Process oil	3	3	3	3
ESP	0	10	30	50
Sulfur	1.5	1.5	1.5	1.5

2. **Group(D)**(NR50/NBR50/ESP/CB-20pphr),with same loading ratio of(ESP)and with(CB-20pphr), the ingredient is shown in table (3-7).

Table (3-7) Composites ingredient (group D) (pphr)

Materials	D1	D2	D3	D4
NR	50	50	50	50
NBR	50	50	50	50
Zinc Oxide	4	4	4	4
Stearic acid	1	1	1	1
MBS	1	1	1	1
6PPD	0.5	0.5	0.5	0.5
Carbon black	٢٠	20	20	20
Process oil	3	3	3	3
ESP	0	10	30	50
Sulfur	1.5	1.5	1.5	1.5

3.5 Equipment and Instruments

3.5.1 Laboratory mill

A two -roll mill was used as shown in Fig.(3.3), it consists of two hollow cast iron rolls of cylindrical shape of 150mm in diameter and 300mm in length, having provision for passing cold water or steam through the rolls.

The mixing of materials takes place at the compressive zone of the roll nip, where the mixing takes place along the circumferential direction of the rubber bank on the mill. In mill mixing temperature control is very important so, chilled water is passed through the rolls at a regulated flow rate to remove excessive heat developed during mixing, and prevent scorching of the compound, and heat is also necessary for some processes to warm up the rolls instead of cooling them[97].

Figure (3.3) Laboratory mill

3.5.2 Preparation of rubber composites(batches) group(A), (B), (C)and(D)

The batches recipe were prepared by using mill laboratory as shown in Fig (3.3) and the compounding ingredients are shown in Tables (3-4) , (3-5),(3-6),(3-7).

The steps of processing recipe master batch with different mixing time were carried out on(NR50/SBR50/ESP)and(NR50/SBR50/ESP/CB-20pphr).

1. Passing of(NR50)and (SBR50) rubber between the two rolls for several times with decreasing the distance between the two rolls to the extent of (0.5-1) mm at room temperature of laboratory.
2. During the process, rubber pieces are passed between rollers in horizontal and vertical state alternatively for several times for obtaining homogenous materials
3. Adding the zinc oxide and repeat mixing for 2 minute, then addition of stearic acid.
4. Adding the carbon black(CB-20pphr) in group(B) alternatively and repeating mixing for 5minutes.

5. Adding of accelerator(MBS) and repeating mixing for 5 min, then adding of antioxidant(6PPD).

6. Adding the reinforcing fillers(ESP) and repeating mixing for 5 min.

7. Finally, adding the sulfur .

8. The mixing process continues for more time in order to get a good homogenization and decrease mill opening to (0.5-1 mm) for increasing the homogenously and the efficiency of mixing.

9. The same steps processing on recipe master batch wear carried out on (NR50/NBR50/ESP)and(NR50/NBR50/ESP/CB-20pphr)composites.

3.6 FTIR analyses

FTIR spectra were recorded by FTIR (Bruker company, German origin, type vertex -70) Fourier Transform Infrared Rays exited in Babylon University/College of Education for Pure Sciences/Department of Physics. The wave number range (400-4000) cm^{-1} as shown in Fig.(3.4).

Figure (3.4): Image of (FTIR) spectroscopy

3.7 Preparation samples for rheological properties

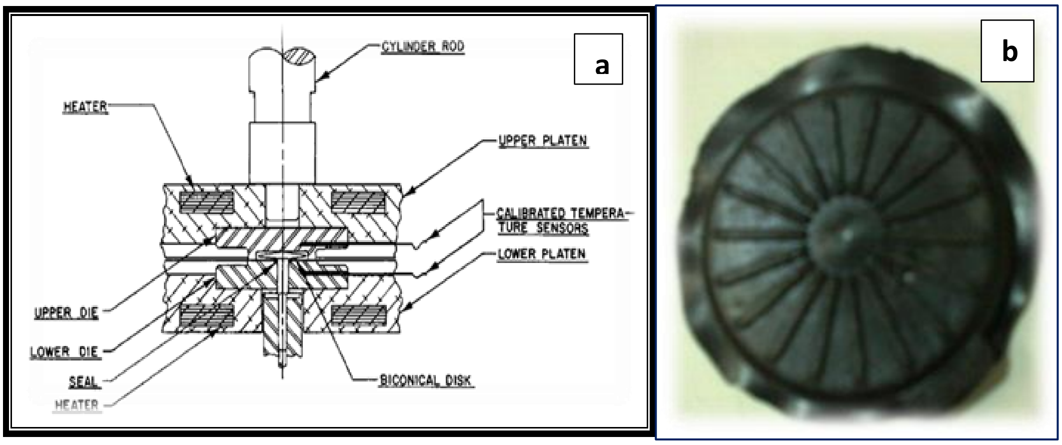
Cure characteristics test carried out in College of Materials Engineering, University of Babylon, and the cure characteristics of the different compounds were measured at(160°C) at time(12 min), by MV-ODR- (Micro vision Enterprises-India) according ASTM D2705. The optimal vulcanization time, minimum time(ML),maximum time(MH). scorch time(Ts2),cure time(CR) and torques of the compounds were determined by this rheometer. Fig.(3.5) this equipment consists of the following major components:

(specimen chamber, temperature control system, rotor drive, and torque measuring system[98].

1. Specimen chamber consists of two platens, two dies, and a biconical disk. They are explained in Fig.(3.5).
2. Die Closing Mechanism consists of a pneumatic cylinder to close the dies and hold them closed during the test with a force of (11.0 ±0.5) KN (2500 ± 100) lbf, and it is explained in Fig.(3.6, a).
3. Rotary drive system shall be provided for the oscillatory rotation of the disk.

The equipment was used in cure characteristics by MV-ODR- (Micro vision Enterprises-India). It is explained in Fig.(3.6, a).

Figure (3.5) (Monsanto Rheometer MV-ODR)



Figure(3.6) a- Monsanto Rheometer Assembly. b-specimen after testing.

3.7.1 Procedure of cure characteristics test:

1- The temperature of the Monsanto Rheometer was determined and it equaled 160ºC, the time of the test was 12 minutes[99].

2- A test specimen cut from the sheet of the compound.

3- A test specimen was inserted into the rheometer test cavity and contained in a sealed cavity under positive pressure. The cavity is maintained at some elevated vulcanization temperature. The rubber surrounds a biconical disk after the dies are closed.

4- The disk oscillates through a small rotational amplitude, and this action exerts a shear strain on the test specimen. The force required to oscillate or rotate the disk to maximum amplitude is continuously recorded as a function of time, with force being proportional to the shear modulus (stiffness) of the test specimen at the test temperature, and Fig.(3.6,b) is explained the effect of shear stress on the specimen. This stiffness first decreases as it warmed up; then increases due to vulcanization.

5- The test is completed when the recorded torque either rises to an equilibrium or maximum value or when a predetermined time has elapsed.

6- The curve of torque against time obtained by printer with minimum torque (ML), maximum torque (MH), scorch time(Ts2), and optimum cure time(Tc90).

3.8 Mechanical properties

3.8.1 Preparation samples for mechanical properties

Vulcanization processes were carried out in the laboratory of Materials Engineering / University of Babylon, and according to ASTM D3182 [100]. The equipment used in the Vulcanization processes was:

a-Platen Press

The press with electrically heated platens is operated by a hydraulic power unit, Fig.(3.7).

Figure (3.7) Platen Press

b- The mold of specimens of hardness tests

This mold with dimensions (200×180×6.5) mm has nine holes, any hole has dimensions (diameter 40 mm, thickness 4mm) for inserting the specimens inside the holes, Fig.(3.8).

Figure (3.8)mold of hardness

C. The mold of specimens of tension tests

This mold has two cavity sections, the first part has dimensions mm (395×160×2.5) and contains two sections, the dimensions of one section are mm (150×150×2.5), while the second part represents the upper cover. It has dimensions mm (395×160×10), Fig.(3.9).

Figure (3.9)mold of tensile

3.8.2 Preparation samples for Hardness testes

These samples are prepared using a mold with dimensions of mm (200 x 180 x 6.5) containing nine circular holes of equal size with a diameter of 40 mm and a thickness of 4 mm as shown in Fig.(3.8). The mold is cleaned first using acetone and a clean cloth, then filled with the required amount of dough, then the mold is placed in the hydraulic piston shown in Fig.(3.7) under(10MPa) pressure and a temperature of (155°C) for(40min) to complete the vulcanization process. The samples are taken out in the form of Discs in shape, with a thickness of(4mm) and a diameter of(40mm), as shown in Fig.(3.10).

Figure(3.10)sample of hardness

3.8.3 Hardness devise

The International Hardness test is used to determine the penetration of a hard ball into a rubber specimen (According to Brinall method). The ball's diameter is 2.5 mm. The apparatus illustrated in Fig.(3.11) was used to convert the observed penetration to Shore A. The degree scale is set up so that zero represents a material with an elastic modulus of zero and 100 indicates a material with an elastic modulus of infinite. The scale encompasses the entire range of normal hardness. The tests were carried out in laboratory of College of Education for Pure Sciences /Department of Physics/ University of Babylon accordance with ASTM D 1415 [101].

Figure(3.11)hardness devise

3.8.4 Procedures of Hardness Test

1. The test carried out at (25±2)°C.
2. Any test sample which used in hardness test had upper and lower surface flat, smooth and parallel.
3. The test sample placed on the table of the instrument.
4. The operating wheel was turned by hand to lower the foot to rest on the surface of the test sample.

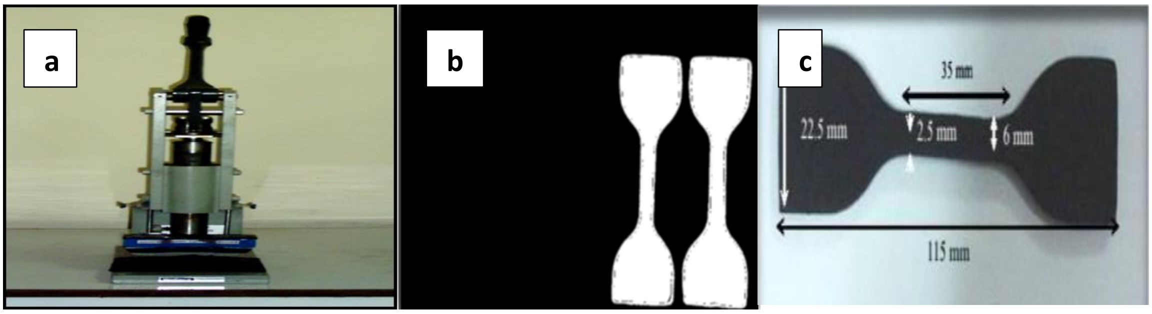
5. The plunger pressed, with the minor force on the indenting ball, vertically onto the sample for 5 seconds.

6. The reading on the gage recorded as a value of the hardness in IRHD.

7. The measurement was carried out in four different points distributed evenly over the sample and took the average of the measurement.

3.8.5 Preparation samples for Tensile, Modulus of Elasticity and Elongation tests

The samples were prepared for the above examinations using the mold shown in Fig.(3.9). The mold is cleaned first and then filled with the required amount of dough, after which the cover is placed on the mold and placed in the hydraulic piston Fig.(3.7) at a temperature of(155ºC) and a pressure of (10MPa) for a period of(40min) according to the American standard ASTM-D3182 as well as ASTM-D13192. The mold was taken out From the press, then take out the slice, which has dimensions of mm (150×150×2), and leave it for(24) hours to be ready for laboratory tests. The slide was cut into four standard test samples (Dumbbell Specimen), the cutting was done by the manual cutter shown in Fig.(3.12,a) and Fig.(3.12,b) shows the slide after cutting the samples. The sample dimensions are (115 mm) long,(22.5 mm) wide,(35mm) long and(6mm) wide, and the thickness is(2.5mm). Fig.(3.12,c) shows the dimensions of the tension sample.



Figure(3.12), a-manual cutter, b-slice after cutting, c-sample of tension

3.8.6 Tensile, Elasticity Modulus and Elongation tests

Tensile test was carried out in State Company for Tire Industry in Najaf and according to ASTM D4129[102] .The equipment, which was used in this test (a-Monsanto T10 Tensometer) and Dial Gauge device. The equipment, which was used in this test is Monsanto(T10 Tensometer) ,Fig.(3.13,a).This device is manufactured by Monsanto CO. England. It can be controlled by a microprocessor. It has a plotter to plot the stress-strain curve and a pneumatic sample Holder to hold the dumbbell specimen during the test. This device works by tension the dumbbell with a determined speed to break the dumbbell and recording the results[103]. The micrometer is to be a hand-held dial gauge instrument with a range (0 - 25 mm), calibrated in a division of 0.01mm. It was used to measure the thickness of dumbbells, Fig.(3.13,b).

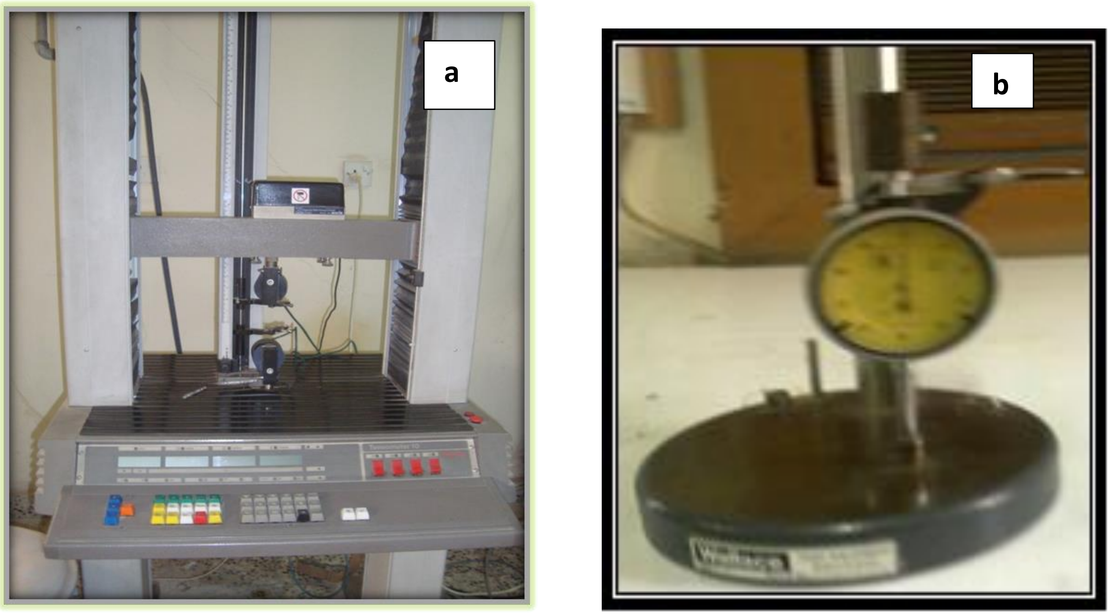


Figure (3.13,) a- Monsanto .b-Dial Gauge

3.8.7 Procedures of Tensile, Elasticity Modulus and Elongation tests

1. The test was carried out at 23±2 ºC.
2. The dumbbell was obtained by cutting the vulcanized sheets with Wallace Test Specimen Cutting Press.
3. The thickness was measured of the dumbbell by a dial gauge.
4. The dumbbell was placed in two grips of the tensometer.

5. The speed of the moving grip was determined at 100 mm/minute.
6. Data of the dumbbell (dimensions of dumbbell determined speed 100 mm/minute, number of dumbbells, and the date of test) was entered into the controlled board of tensometer.
7. When the tensometer was operated, the dumbbell elongated and broke down.
8. The results were recorded by the printer which was connected to the tensometer.

The values which are recorded, tensile strength, elongation, modulus at 100%, modulus at 200%, and modulus at 300%.

3.9 Thermal aging tests

The study for samples were carried out in an air oven of the type Jinyu 1700. The basic test method for the degradation of rubber in an air oven due to the combined effects of oxidative and thermal aging is defined in ASTM D573. The test's fundamental premise is to expose rubber test parts to air at a high temperature for a set amount of time. Their mechanical properties are determined after aging and compared to those seen on the initial test bits. The hardness wear measured at room temperature before and after aging. The temperature(70ºC)for (96h) was used for hardness, samples according to the aging state**.**

Chapter Four
Results and Discussion

4.1 Introduction

This chapter presents all the results obtained for rheological and mechanical properties and the discussion of theoretical and experimental results for the following of the group (A) (NR50/SBR50/ESP) and group (B) (NR50/SBR50/ESP/CB-20pphr) and group (C) (NR50/NBR50/ESP) and group (D) (NR50/NBR50/ESP/CB-20pphr) composites with the addition of different ratios of (ESP) (0,10,30,50pphr) with carbon black (CB-20pphr). The results of FTIR analyses are included, and rheological properties such as minimum torque (ML), maximum torque (MH), scorch time (Ts2), optimum cure time (Tc90), cure rate time (CR), and viscosity. The results of mechanical properties such as tensile strength, elongation at break, elastic modulus, and hardness, and the results of thermal aging effects on the mechanical properties, such as the hardness of prepared samples, are also included in this chapter.

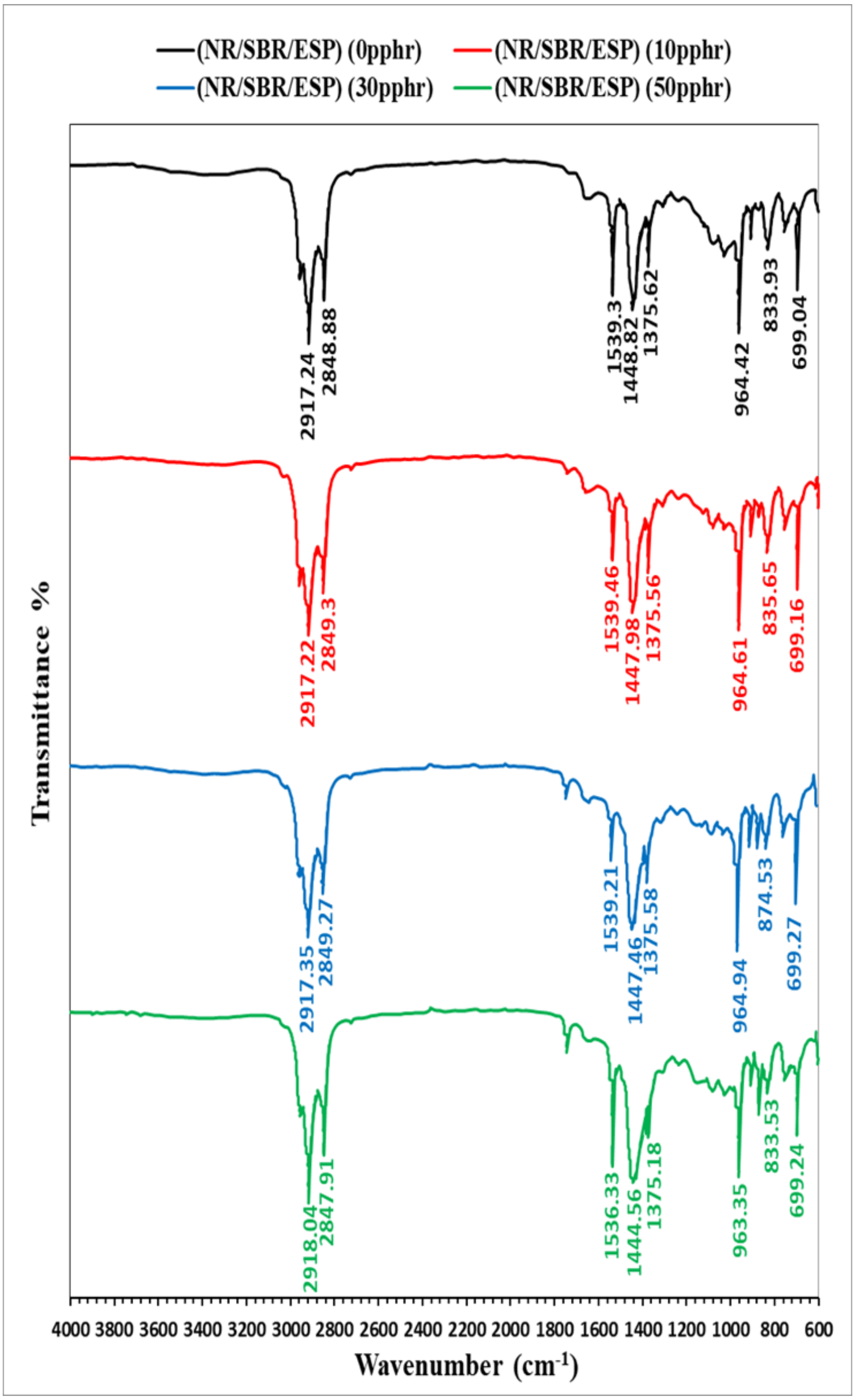
4.2 Results and discussion

4.2.1 FTIR analyses results of group(A)and(B)

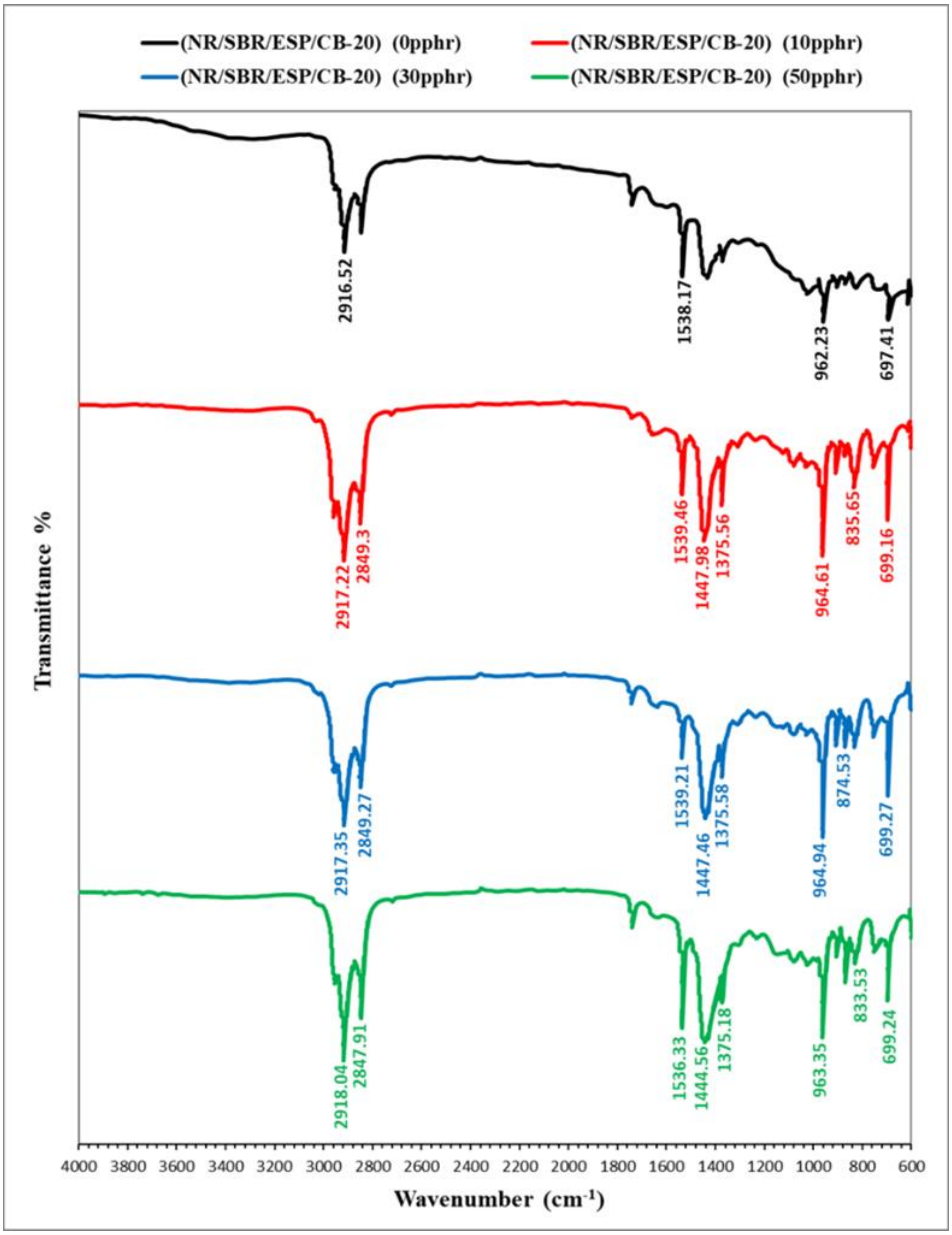
FTIR spectra of (NR50/SBR50/ESP) and (NR50/SBR50/ESP/CB-20pphr) composite with different loading (0,10,30 and 50pphr) are shown in Figs.(4.1,a),(4.1,b) respectively, at the wavenumber range (400-4000) cm^{-1}

The strong asymmetrical (νas CH_2) and symmetrical (νs CH_2) stretching of methylene group vibrations present in NR are observed near 2950, 2853 cm^{-1} and 2916.52, 2849.3 cm^{-1} in Figs. (1,2) respectively. The band 1539.3, 1539.46 cm^{-1} due to the stretching vibration of the CH_2 and CH_3 . The bands around 1448.82, 1375.62 $cm^{-1}$and 1447.98, 1375.75 cm^{-1} are assigned to $–CH_2$ scissoring vibrations and C–H bending vibrations of $–CH_3$, which attributed to the (NR/SBR) composite respectively, and the bands 964.42 and 962.23 cm^{-1} attributed to the trans –CH=CH– group vibrations of butadiene present in SBR. The presence of calcium carbonate was assigned by bands at

833.93 and 835.65 cm^{-1} (CO_3^{-} out of plane deformation). The bands 699.04, and 697.41 cm^{-1} ascribed to aromatic C-C stretching of SBR [104]. After different loading (0,10,30, and 50pphr) as shown in Figs.(4.1,a),(4.1,b) leads to shift of some of the bonds and not the emergence of new peaks. these results agree with the researchers [105].



Figure(4.1,a)FTIR of group A-(NR50/SBR50/ESP)composite with different loading ratio of ESP

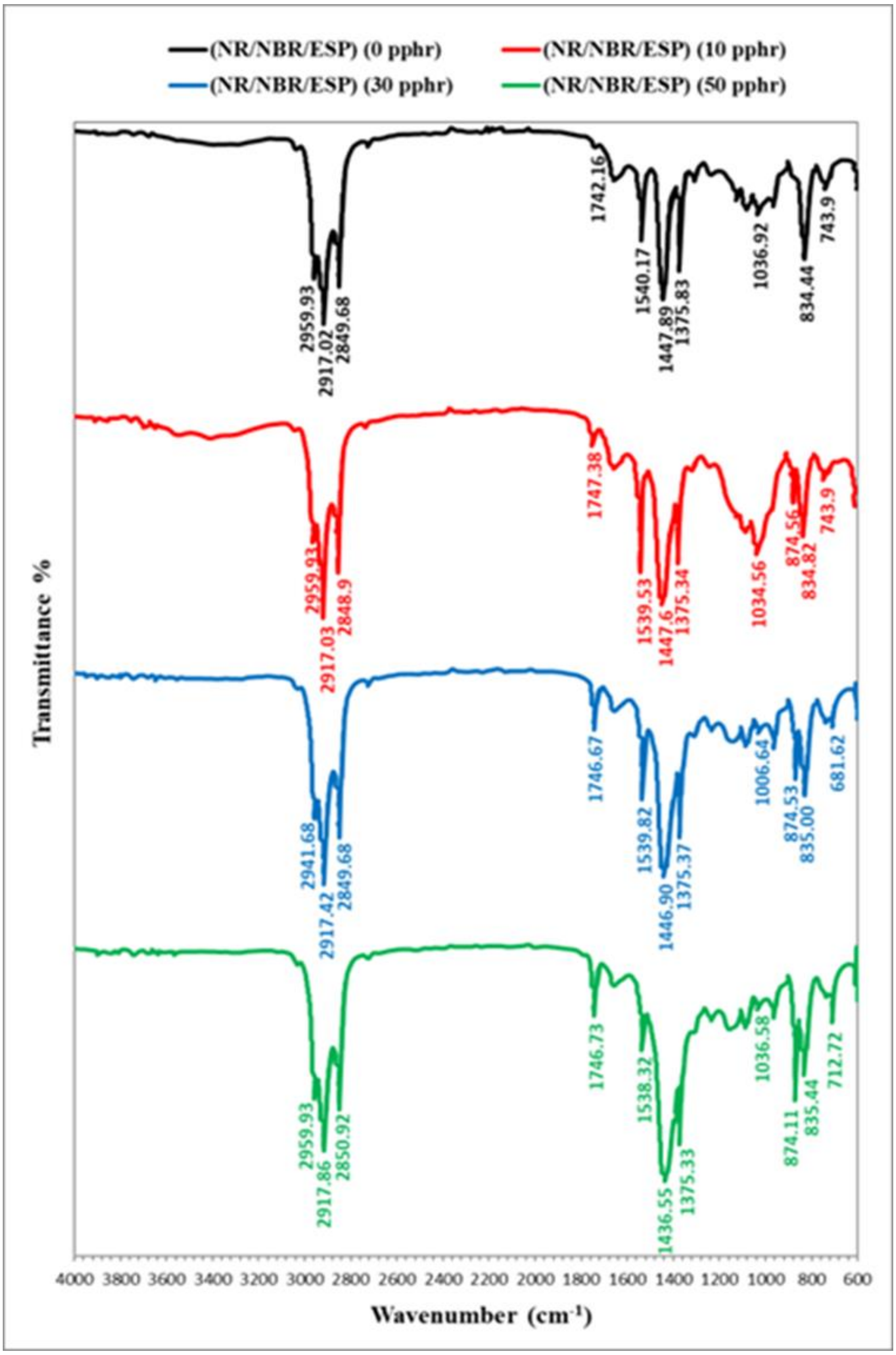


Figure(4.1,b)FTIR of group B-(NR50/SBR50/ESP/CB-20pphr)composite with different loading ratio of ESP

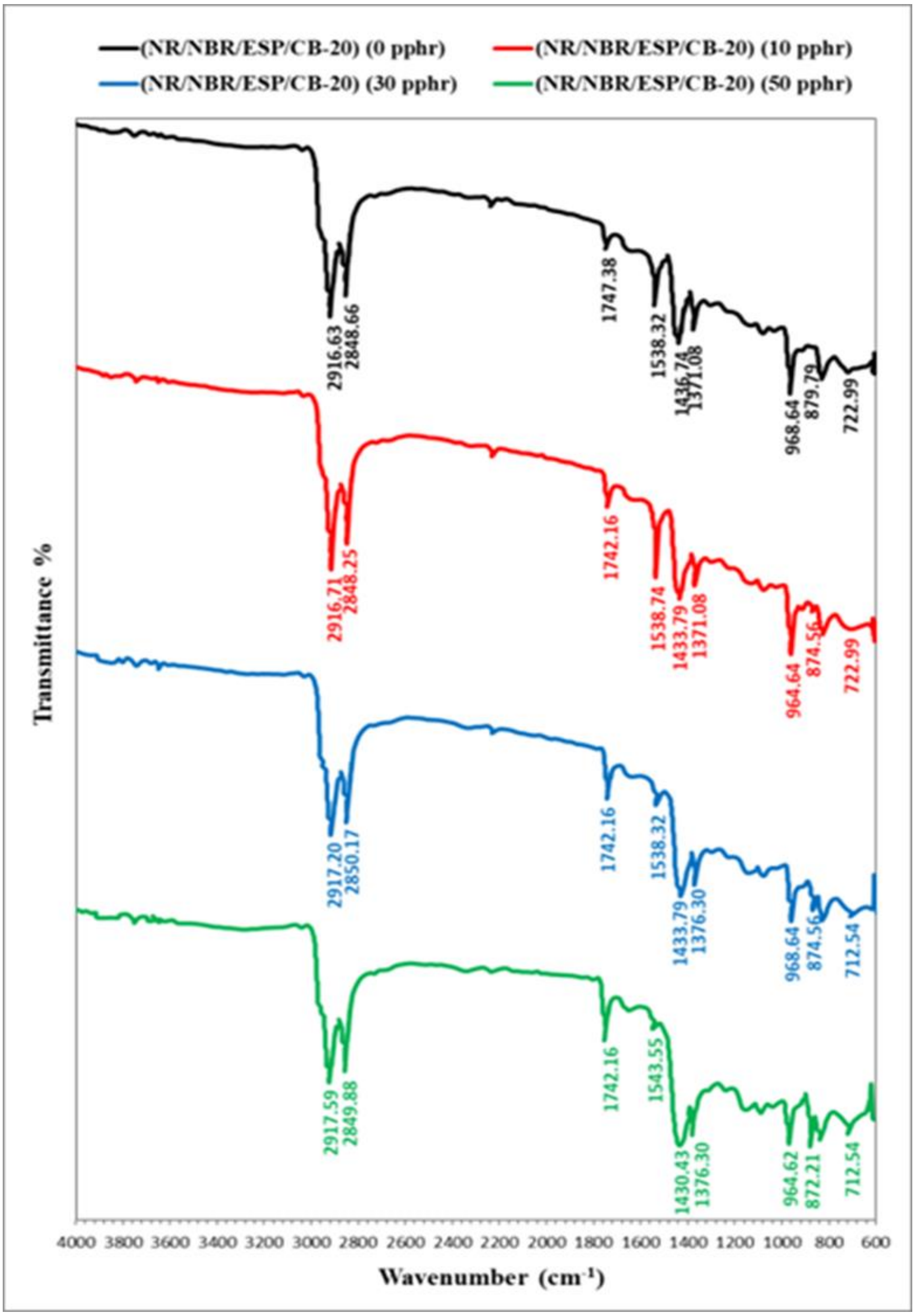
4.2.2 FTIR analyses results of group(C)and(D)

FTIR spectra of (NR50/NBR50/ESP) and (NR50/NBR50/ESP/CB-20pphr) composite with different loading (0,10,30 and 50pphr) are shown in Figs.(4.2,a,b) respectively, at the wavenumber range (400-4000) cm^{-1}.

The strong asymmetrical (νas CH_2) and symmetrical (νs CH_2) stretching of methylene group vibrations present in NR are observed near 2959, 2849 cm^{-1} and 2916, 2848 cm^{-1} in Figs. (4.2,a,b) respectively. The band 1742, 1540 cm^{-1} and 1747, 1538 cm^{-1} due to the stretching vibration of the CH_2 and CH_3 . The bands around 1447, 1375 cm^{-1} and 1436, 1371 cm^{-1} are assigned to $–CH_2$ scissoring vibrations and C–H bending vibrations of $–CH_3$, which attributed to the(NR/NBR) composite respectively, the band at 960 cm^{-1} is due to the C–H wagging motion vibrations of butadiene. The presence of calcium carbonate was assigned by bands at 834, 743 cm^{-1} and 879, 722 cm^{-1} ($CO_3{}^{-2}$ out of plane deformation). After different loading (0,10,30, and 50pphr) as shown in Figs.(4.2,a,b) leads to the displacement of some of the bonds and not the emergence of new peaks, these results agree with the researchers [106,107].



Figure(4.2,a)FTIR of group C-(NR50/NBR50/ESP)composite with different loading ratio of ESP



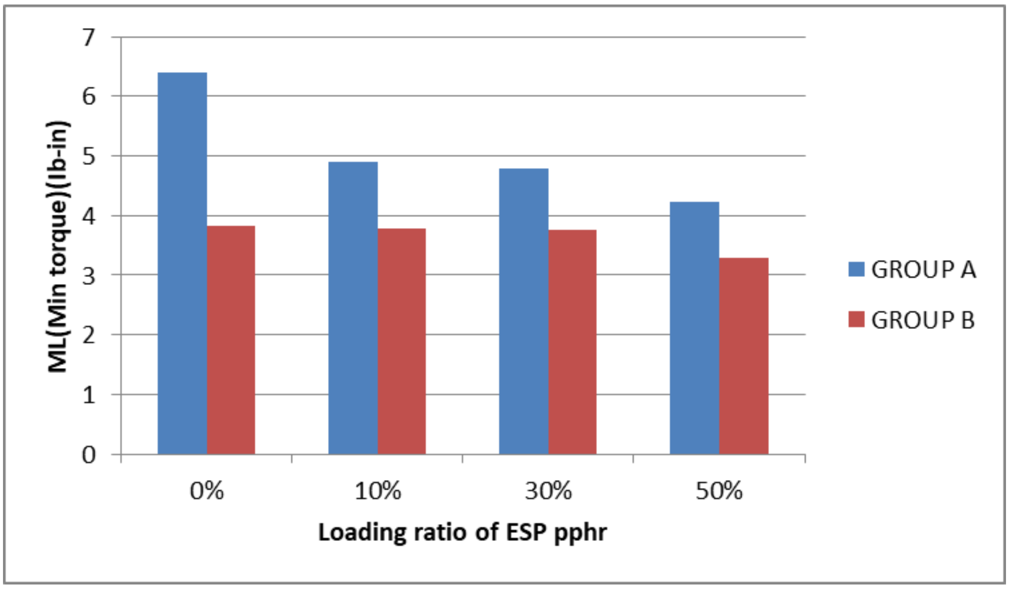
Figure(4.2,b)FTIR of group D-(NR50/NBR50/ESP/CB-20pphr)composite with different loading ratio of ESP

4.3 Rheological properties

4.3.1 Rheological properties of group(A)and(B)

1. Minimum Torque(ML)

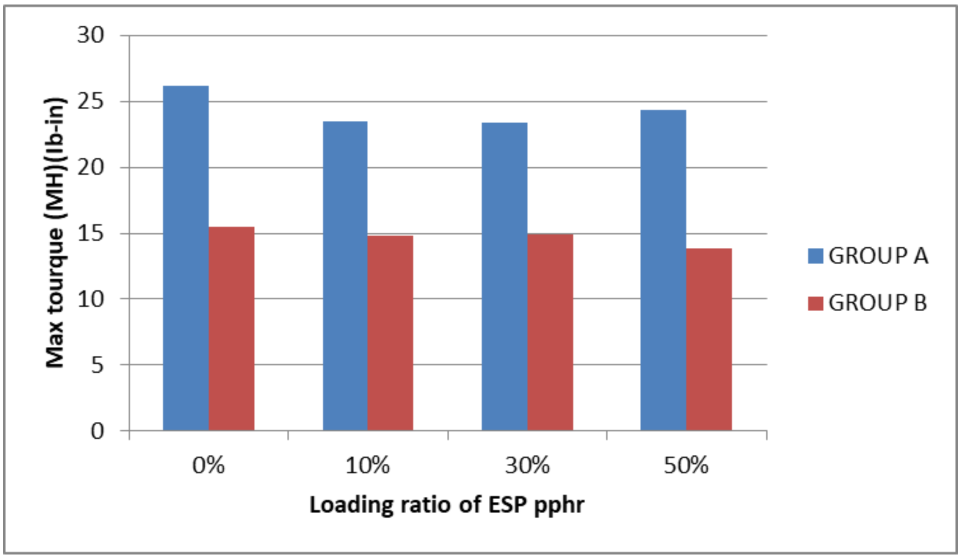
Fig.(4.3) shows the variation of (ESP)and(CB-20pphr) loading ratio with minimum torque (ML) that was observed (ML) decreases as (ESP) and(CB) loading ratio increased. This behavior was due to a rise in cross-linking density and correlations between the rubber chain and loading ratio of(ESP) and(CB) then, cause torque and viscosity to decrease, allowing the vulcanization process to speed up. As a result, the consequence of the continuous rise in (ESP) loading ratios on these samples was to increase the rate of vulcanization in a short period, this behavior agreement with the researcher [108].



Figure(4.3) The variation of minimum torque (ML)with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

2. Maximum Torque(MH)

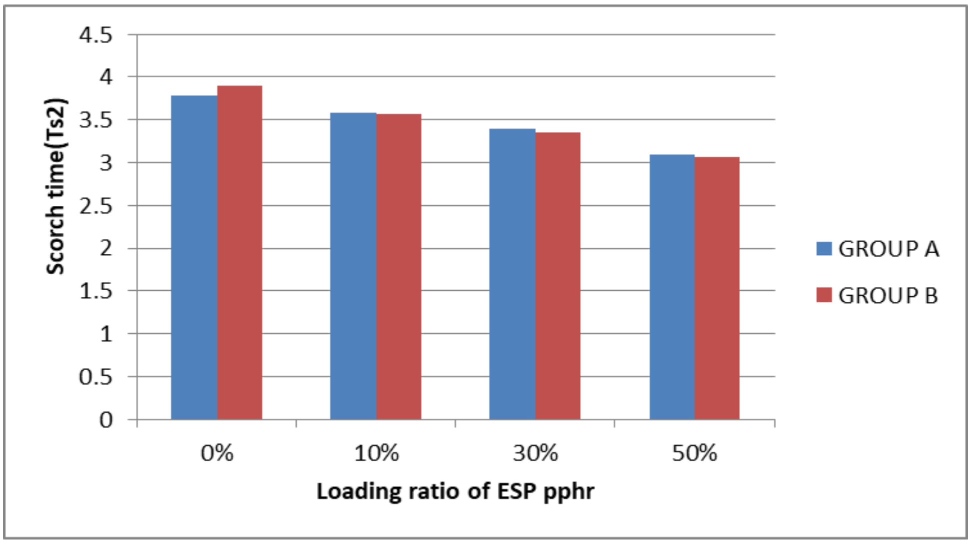
Fig.(4.4) shows the result of maximum torque(MH) decreasing as (ESP) and(CB-20pphr) loading ratios increasing, this behavior was due to the rubber compound starts to volcanize and converted to an elastic solid and the torque increase, Molecular chain detachment may occur, this behavior is in agreement with the researcher [108].



Figure(4.4) The variation of maximum torque (MH)with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr).

3. Scorch time(Ts2)

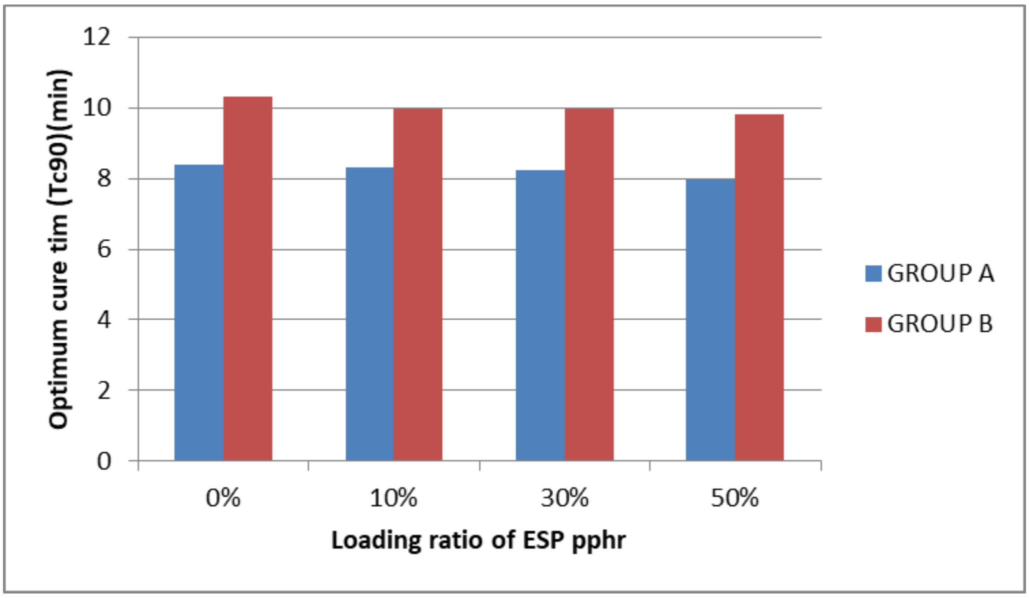
Fig.(4.5) shows the relation between scorch time(Ts2) against the loading ratio of(ESP) and (CB-20pphr) means the start of the treatment against continuously increasing the loading ratio of(ESP) as can be observed, this was caused to an increase in the rate of vulcanization and a decrease in the values of the treatment time and optimum scorch time (Ts2), this behavior agrees with the researcher [109].



Figure(4.5)The variation of scorch time (Ts2)with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

4. Optimum cure time(Tc90)

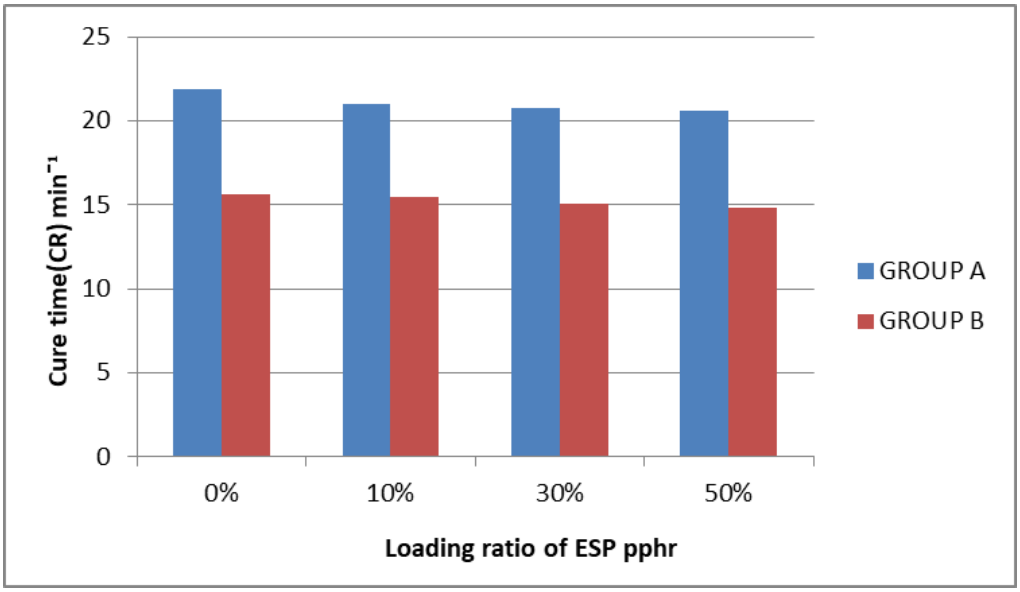
Fig.(4.6)show that optimum cure time(Tc90) it was decreasing with increasing loading ratio of(ESP) and(CB-20pphr), this was due to an increase in the rate of vulcanization and a decrease in the values of the Optimum cure time (Tc90). This behavior is in agreement with the researcher [1010].



Figure(4.6) The variation of optimum cure time (Tc90)with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

5. Cure rate time(CR)

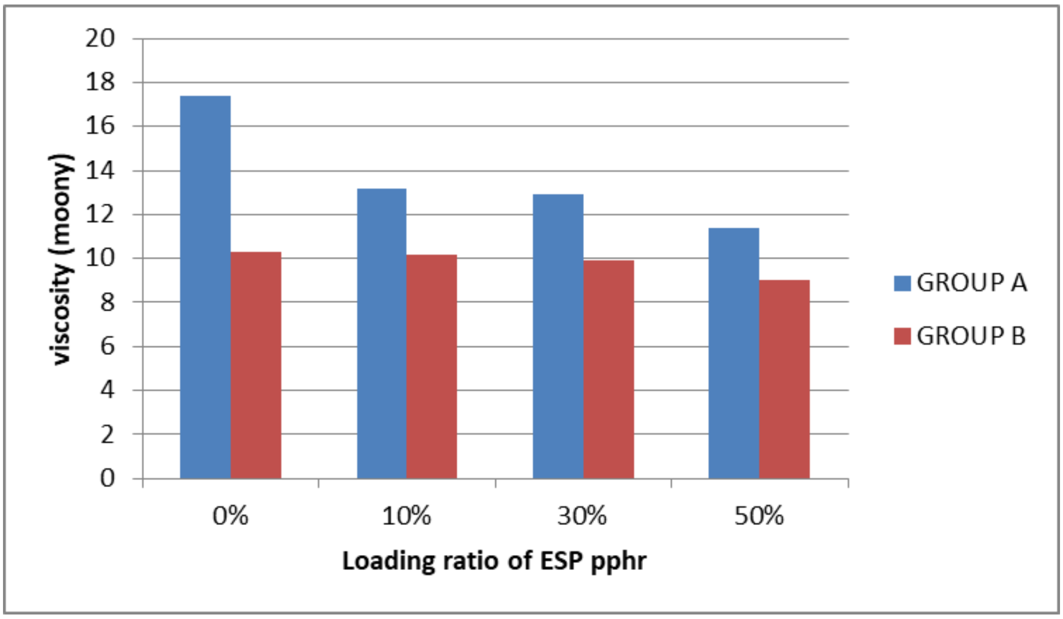
Fig.(4.7)represents the relation between cure rate time(CR)and loading ratio of(ESP)and(CB-20pphr) , it is clear that the(CR) values decreased with increasing loading ratio of(ESP), this behavior attributed to increasing the vulcanization rate and decreasing the values of cure time(CR) this is in agreement with researcher [1010].



Figure(4.7) The variation of cure time (CR)with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

6. Viscosity

Fig.(4.8)shows the result of viscosity wich was decreasing as (ESP)and(CB-20pphr) loading ratio increasing , this behavior attributed to an increasing the cross linking density and correlations between the (ESP) and the rubber chain, this leads to increasing the torque and viscosity and then leads to increase the vulcanization process, and that is in agreement with researcher [109].

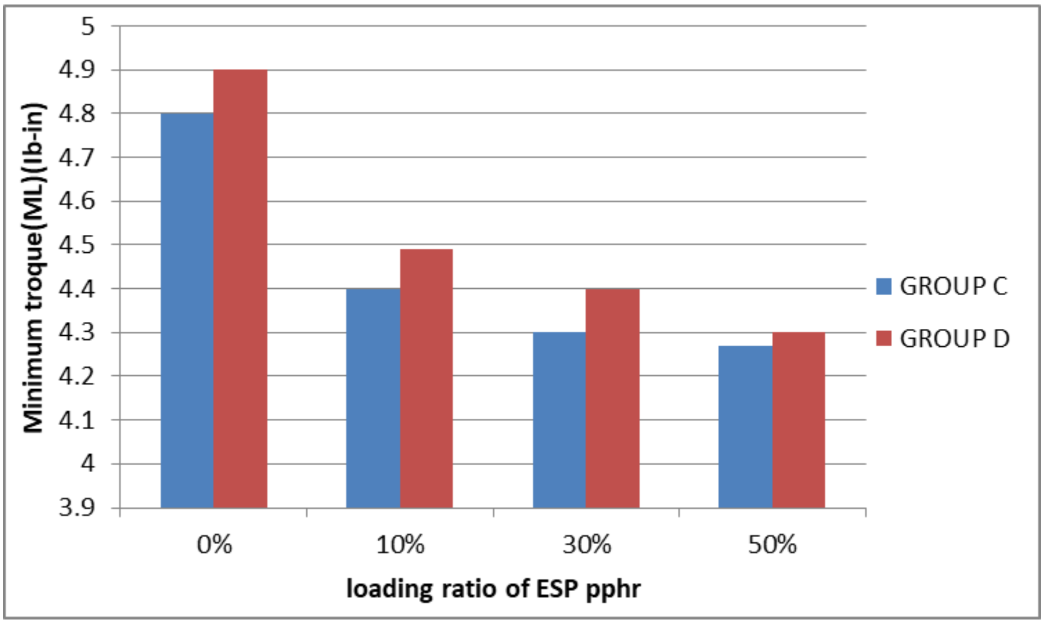


Figure(4.8) The variation of viscosity with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

4.3.2 Rheological properties of group(C)and(D)

1. Minimum Torque(ML)

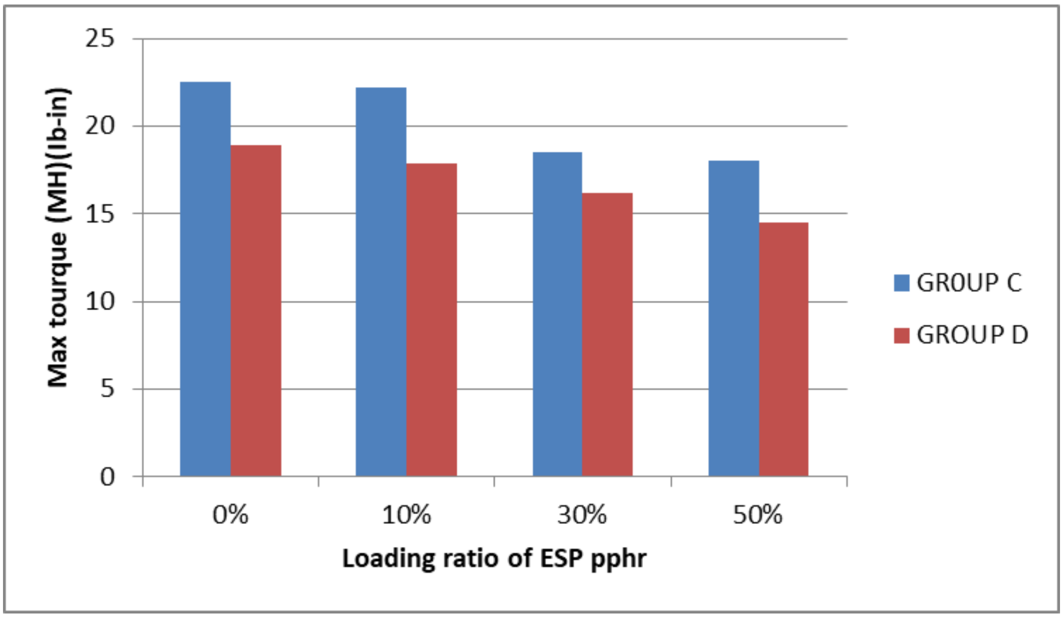
All the rheological properties were measured by oscillating disc rheometer according ASTM D-2705 (ASTM., 2012) and temperature 160 C^o, pressure 10 bar and time 12 mint, Fig.(4.9)shows the variation of (ESP)and(CB-20pphr) loading ratio with minimum torque (ML) that was observed(ML) decreases as (ESP) and(CB) loading ratio increasing , this behavior was due to a rise in cross-linking density and correlations between the rubber chain and loading ratio of(ESP) and(CB) then, cause torque and viscosity to decrease, allowing the vulcanization process to speed up. As a result, the consequence of the continuous rise in (ESP) loading ratios on these samples was to increase the rate of vulcanization in a short period, this behavior is in agreement with researcher [109].



Figure(4.9) The variation of minimum torque (ML)with loading ratio of ESP group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

2. Maximum Torque(MH)

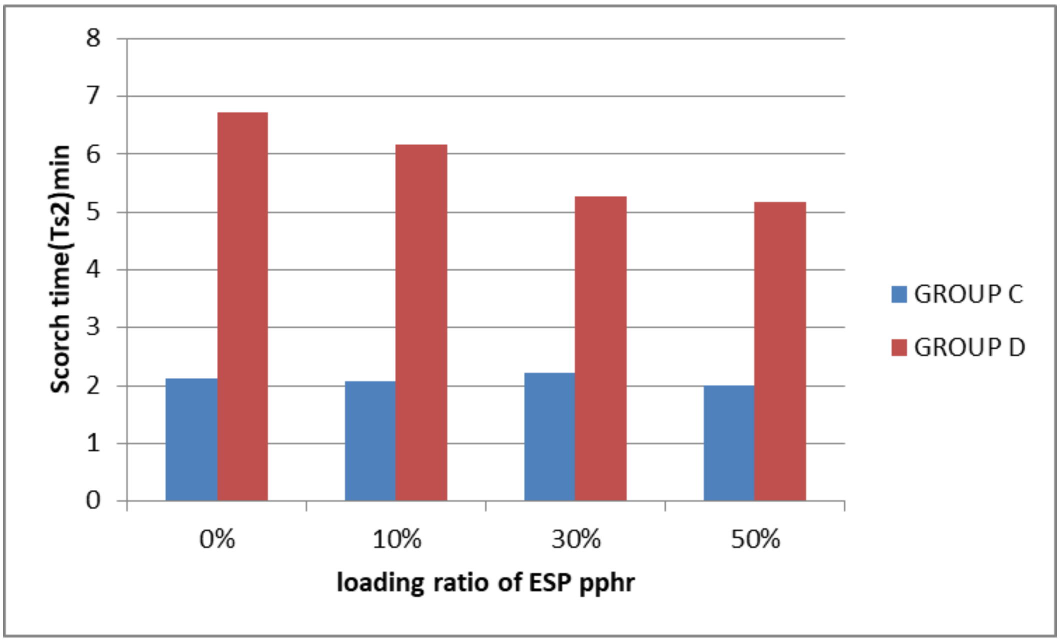
Fig.(4.10) shows the result of maximum torque(MH) decreasing as (ESP) and(CB-20pphr) loading ratios increasing, this behavior was due to the rubber compound starts to volcanize and converted to an elastic solid and the torque increase. Molecular chain detachment may occur, this behavior is in agreement with the researcher [109].



Figure(4.10) The variation of maximum torque (MH)with loading ratio of ESP group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr).

3. Scorch Time(Ts2)

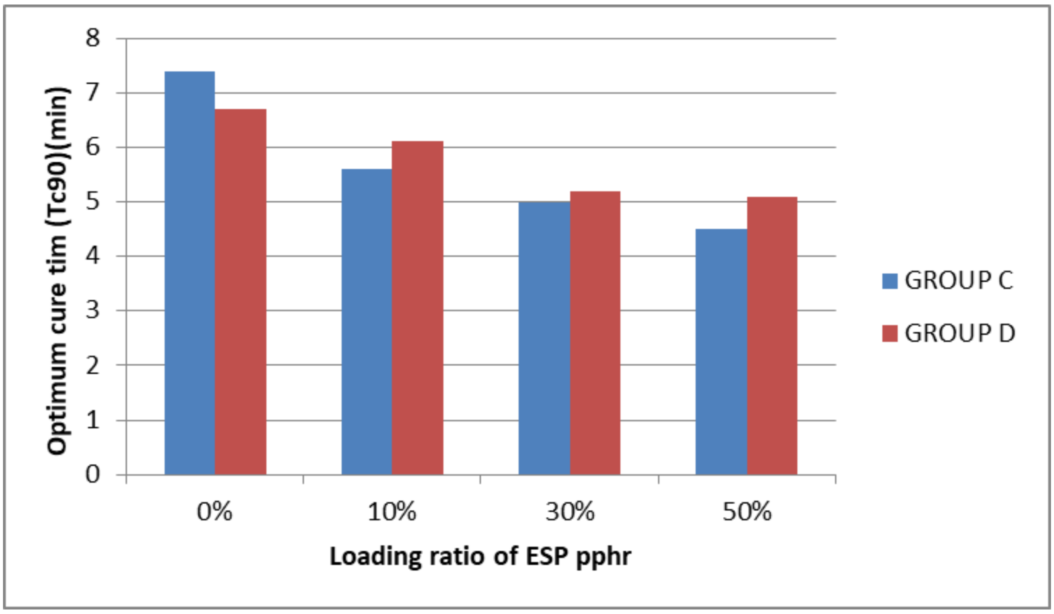
Fig.(4.11) shows the relation between scorch time(Ts2) against the loading ratio of(ESP) and (CB-20pphr) means the start of the treatment against continuously increasing the loading ratio of(ESP) as can be observed, this was caused to an increase in the rate of vulcanization and a decrease in the values of the treatment time and optimum scorch time (Ts2), this behavior agrees with the researcher [113].



Figure(4.11)The variation of scorch time (Ts2)with loading ratio of ESP group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

4. Optimum cure time(Tc90)

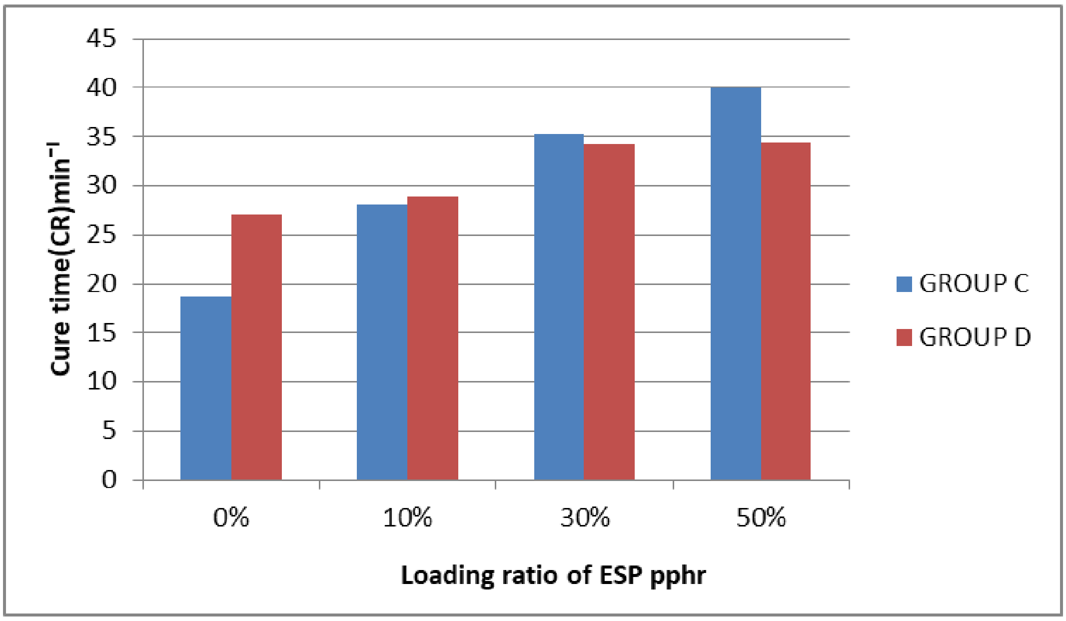
Fig.(4.12)shows that optimum cure time(Tc90) it was decreasing with increasing loading ratio of(ESP) and(CB-20pphr), this was due to an increase in the rate of vulcanization and a decrease in the values of the Optimum cure time (Tc90). This behavior is in agreement with the researcher [112].



Figure(4.12) The variation of optimum cure time (Tc90)with loading ratio of ESP group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

5. Cure rate time(CR)

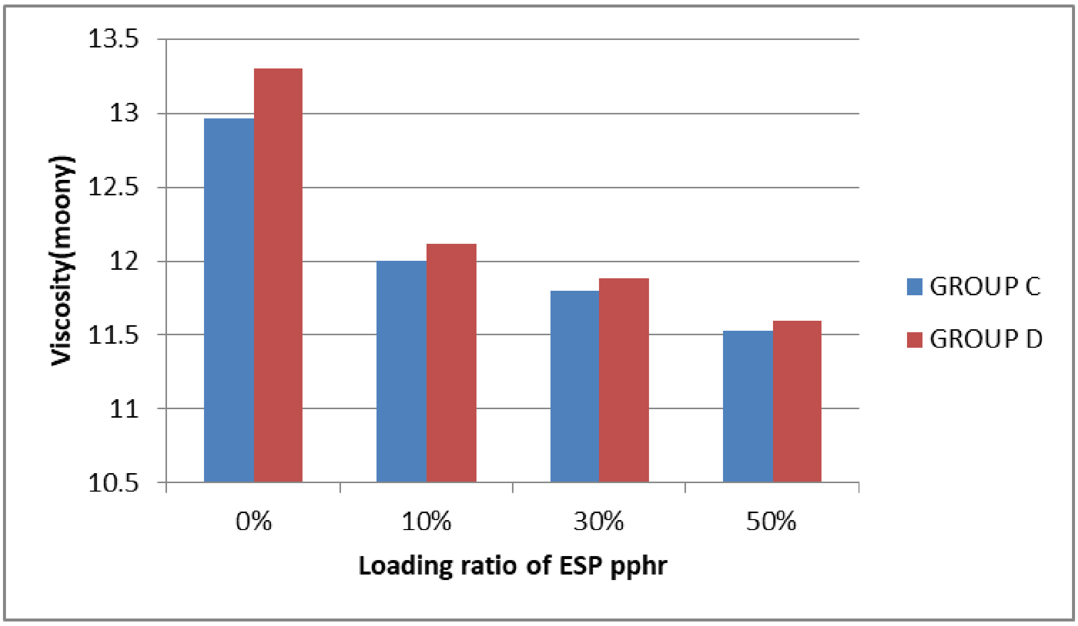
Fig.(4.13)represents the relation between cure rate time(CR)and loading ratio of(ESP)and(CB-20pphr) , it is clear that the(CR) values increased with increasing loading ratio of(ESP), this behavior attributed to increasing the vulcanization rate and decreasing the values of cure time(CR) this is in agreement with researcher [113].



Figure(4.13) The variation of cure time (CR)with loading ratio of ESP group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

6. Viscosity

Fig.(4.14)shows the result of viscosity was decreasing as (ESP)and(CB-20pphr) loading ratio increasing , this behavior attributed to an increasing the cross linking density and correlations between the (ESP) and the rubber chain, this leads to increasing the torque and viscosity and then leads to increase the vulcanization process, and that is in agreement with researcher [108].



Figure(4.14) The variation of viscosity with loading ratio of ESP group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

4.4 Mechanical properties

4.4.1 Mechanical properties of group(A)and(B)

1. Tensile strength

The tensile strength was calculated via the equation (2.3). The variation tensile strength of (NR50/SBR50/ESP) and (NR50/SBR50/ESP/CB-20) composite with loading ratio are demonstrated in Fig.(4.15). This figure shows a decrease in the tensile strength as(ESP) and (CB-20pphr) loading ratio increases. This result attributed to the strength of particulate-filled polymer composites depends, to a great extent, on the interfacial adhesion between the matrix and the filler which will facilitate the transfer of a small section of stress to the filler particle during deformation. Without the chemical modification, there is simply adhesion of the polymer to the filler through weak bonding, i.e., Van der Waals or induction interactions. This result is in agreement with the researcher [114].

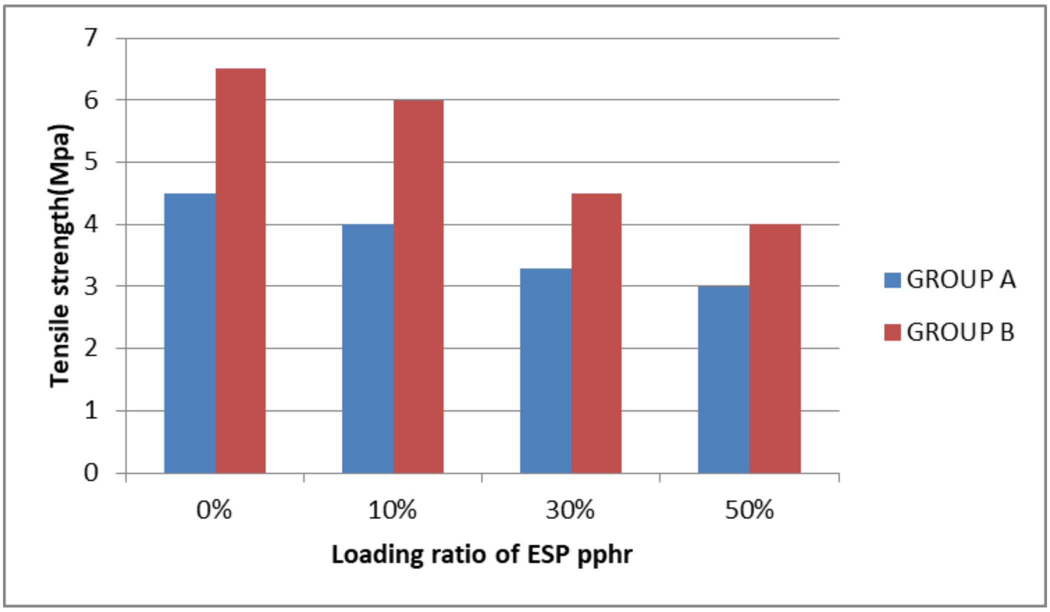


Figure (4.15) The variation tensile strength with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

2. Elongation at break

Fig.(4.16) shows the results of elongation at break decreases as (ESP) and(CB-20pphr) filler loading increases, when more (ESP) is incorporated into the compound, the(ESP) particles will place themselves in between the flexible rubber chains. This will hinder the movement of the rubber chains. The elasticity is reduced, resulting in a stiffer and more rigid compound, the reduction of elongation at break is due to the stiffening of the polymer matrix by the filler. A further increase in filler loading causes the molecular mobility to decrease, owing to the extensive formation of the physical bond between the filler particles and the polymer chain that stiffens the matrix[115].

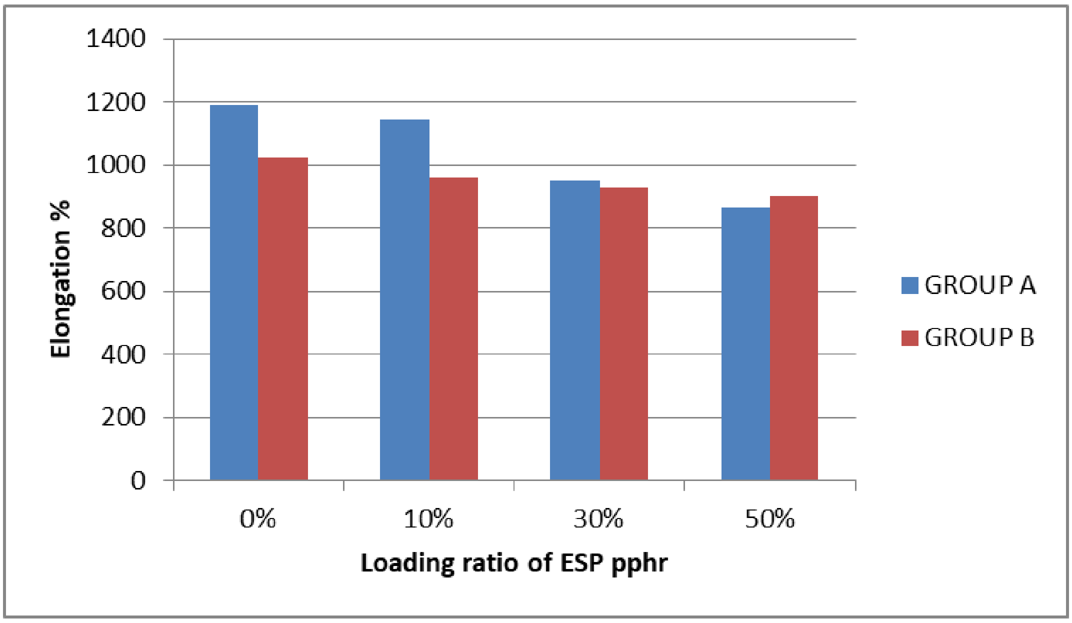
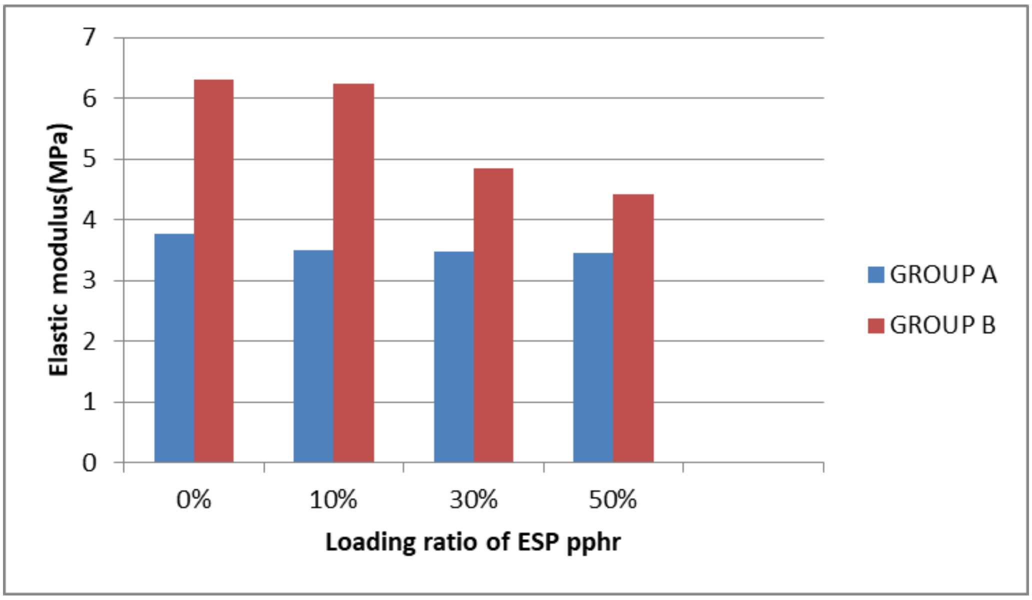


Figure (4.16) The variation elongation at break with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

3. Elastic modulus

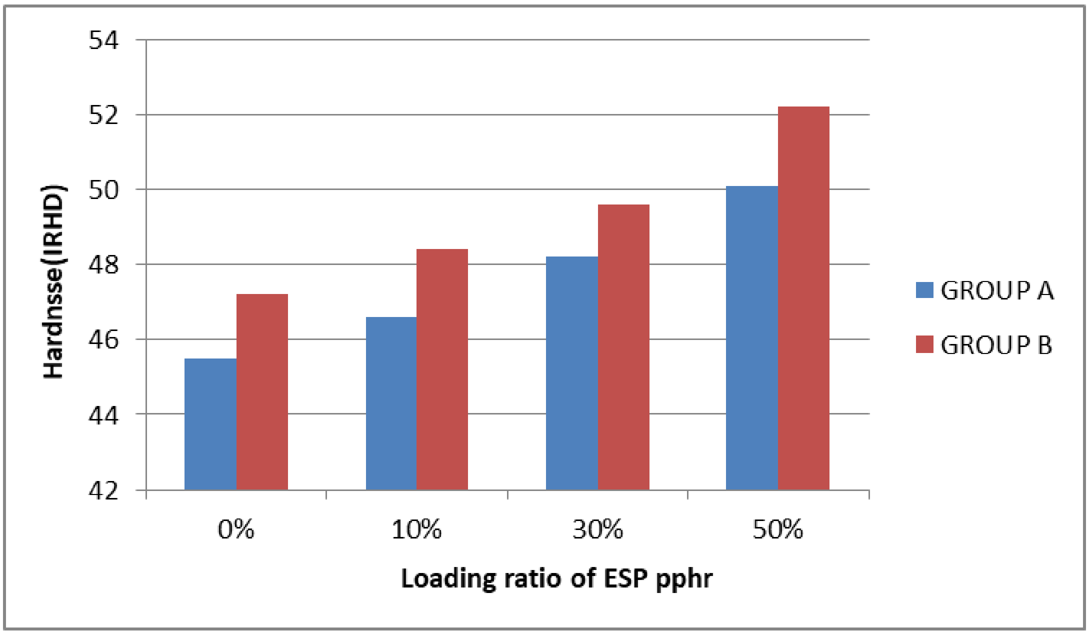
Fig.(4.17) shows the result of elastic modulus decreases as (ESP) and(CB) loading ratio of filler increasing, this result is in agreement with researcher [116].



Figure(4.17) The variation elastic modulus with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

4. Hardness

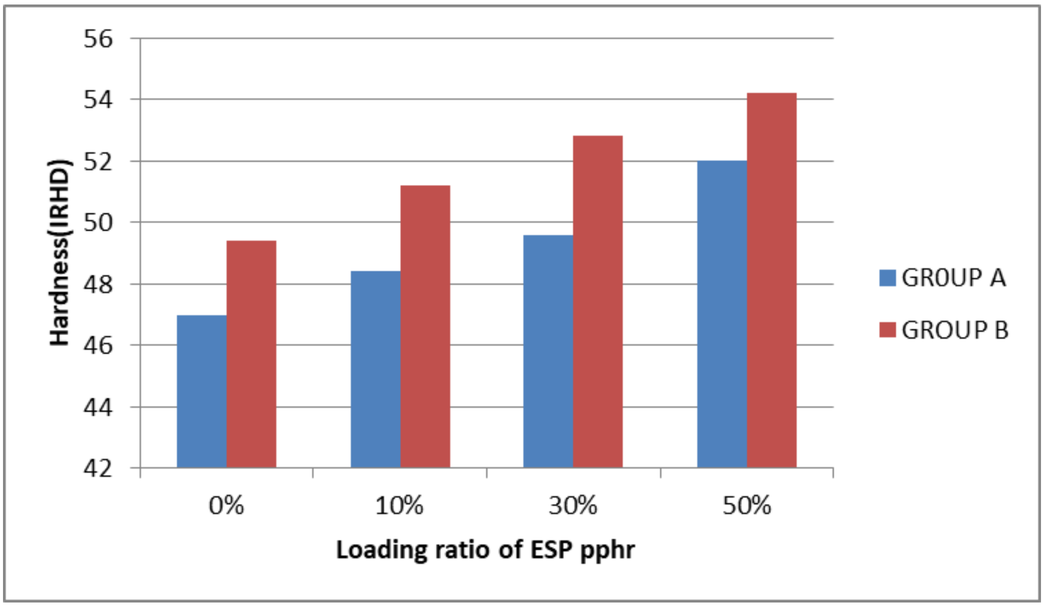
Fig.(4.18) shows the result of hardness increasing as (ESP)and(CB-20pphr) loading ratio of filler increasing, this can be attributed to the physical cross-linking that presents between the rubber chains and CB and the ESP materials fill the free volume between rubber series this leads to increase hardness. This behavior agrees with the results of researcher [114].



Figure(4.18) The variation of hardness with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

4.4.2 Thermal aging results of group(A)and(B)

Fig.(4.19) shows that the result thermal aging of hardness was increasing as (ESP)and(CB-20pphr) loading ratio increasing , this behavior attributed to an increasing the cross linking density and the effect of temperature to complete vulcanization process of rubber composites and this leads to increase hardness, that is in agreement with researcher [117].



Figure(4.19) The variation of hardness after thermal aging with loading ratio of ESP group A-(NR50/SBR50/ESP) and group B-(NR50/SBR50/ESP/CB-20 pphr)

4.4.3 Mechanical properties of group(C)and(D)

1.Tensile strength

The tensile strength was calculated by equation (2.3). The variation in tensile strength of (NR/NBR/ESP) and (NR/NBR/ESP/CB) composites with loading ratio is demonstrated in Fig.(4.20). This figure shows that the increasing loading of (ESP) and (CB-20pphr) fillers in the rubber matrix resulted in a decrease in tensile strength, and this was due to the higher filler content, which may lead to a larger interfacial area with filler loading across the matrix, which caused increasing and promoting the stress in the continuous phase, which will facilitate the transfer of a small section of stress to the filler particle during deformation. Without the chemical modification, there is simply adhesion of the polymer to the filler through weak bonding, i.e., Van der Waals or induction interactions, this finding is consistent with that of the researcher [118].

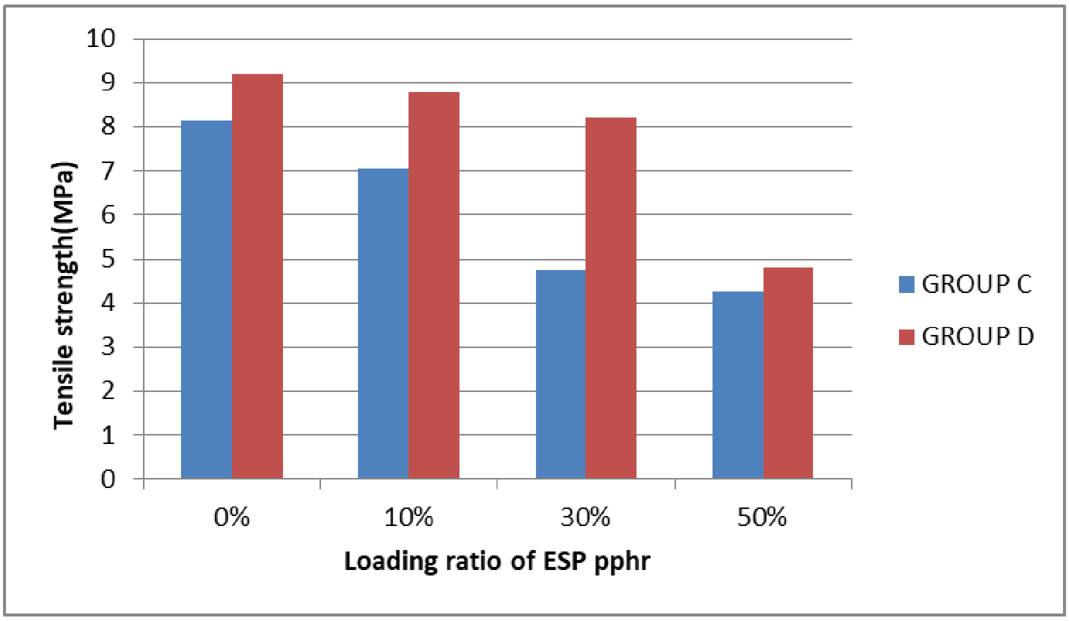


Figure (4.20) The variation tensile strength with loading ratio ESP for group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

2. Elongation at brake

Fig.(4.21) shows the results of elongation at break decreasing as (ESP) and(CB-20pphr) filler loading ratios increase. As more ESP is incorporated into the compound, the ESP and CB particles will place themselves in between the flexible rubber chains. The increase in filler loading ratios regardless of filler caused a decrease in elongation at break, as expected. This decrease was due to the promotion of brittleness and rigidity with filler loading ratios, resulting in a reduction of the elasticity of the rubber vulcanizates. A further increase in filler loading causes the molecular mobility to decrease, owing to the extensive formation of the physical bond between the filler particles and the polymer chain that stiffness the matrix[119].

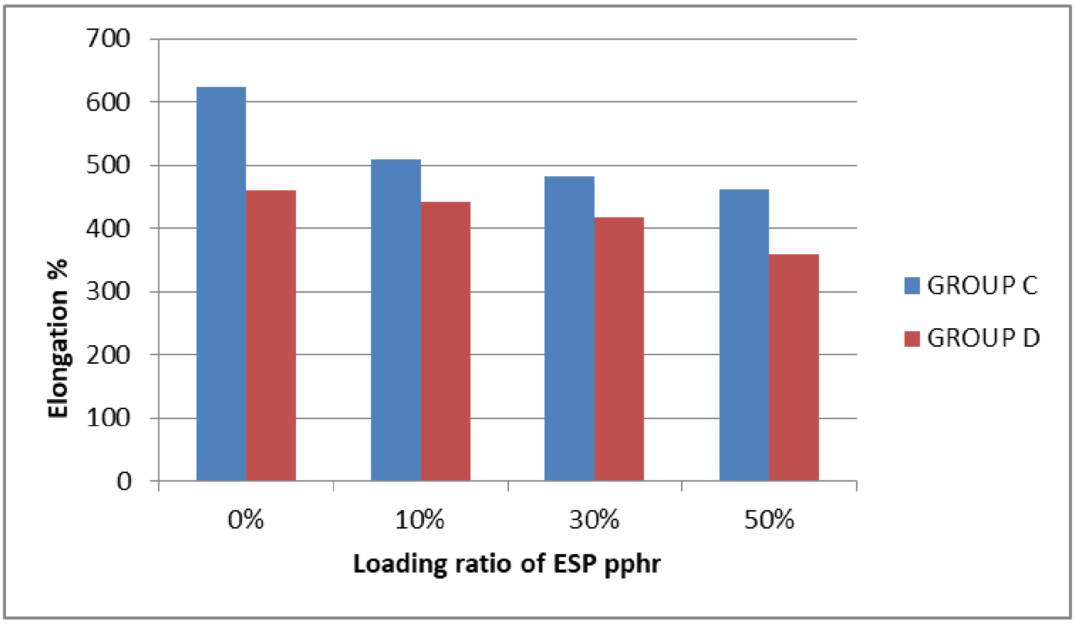
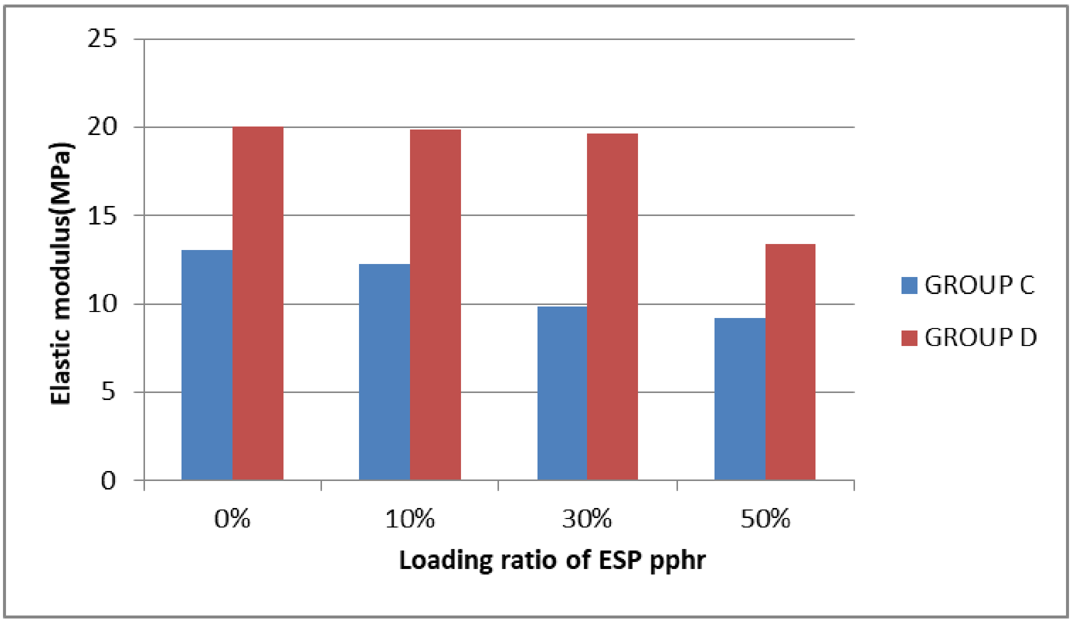


Figure (4.21) The variation elongation at break with loading ratio ESP for group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

3. Elastic modulus

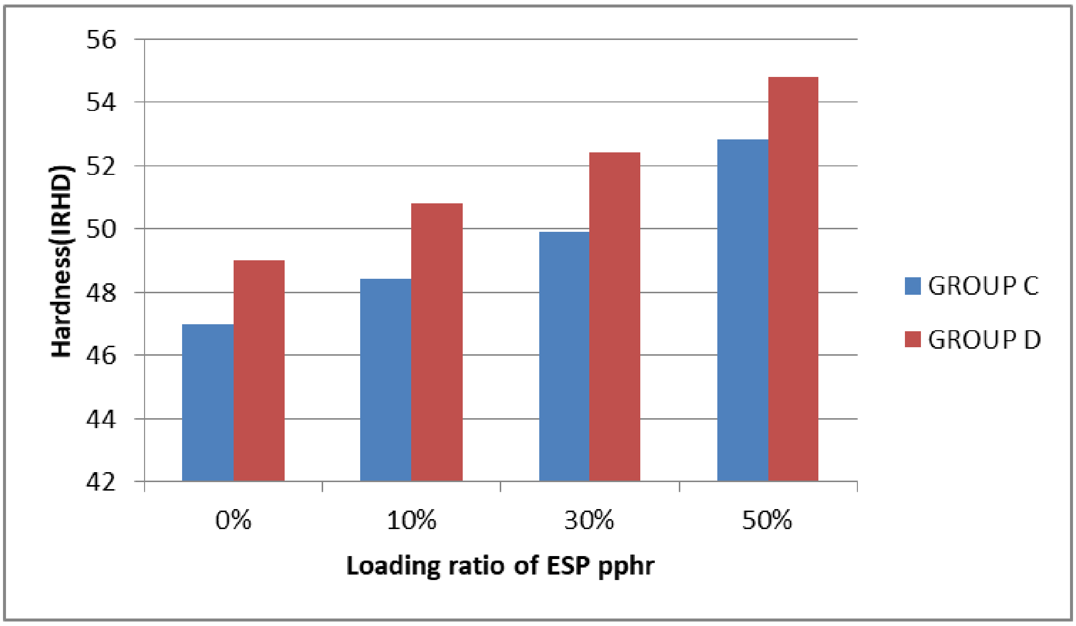
Fig.(4.22) depicts the decrease in elastic modulus as the (ESP) and (CB-20pphr) loading ratios of the filler increase. It is well documented that the mechanical properties of the vulcanized rubbers are mainly controlled by the type of inclusions, the filler content, and particularly the strengths of the interfacial interactions between the rubber matrix and the fillers. To understand the role of ESP and CB on the elastic modulus of the(NR/ NBR/ESP) composites, we study the mechanical properties of the composites. Overall, the elastic modulus of the composites decreases by increasing the filler content, independent of the filler type. This result is in agreement with the researcher [120].



Figure(4.22) The variation elastic modulus with loading ratio ESP for group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

4. Hardness

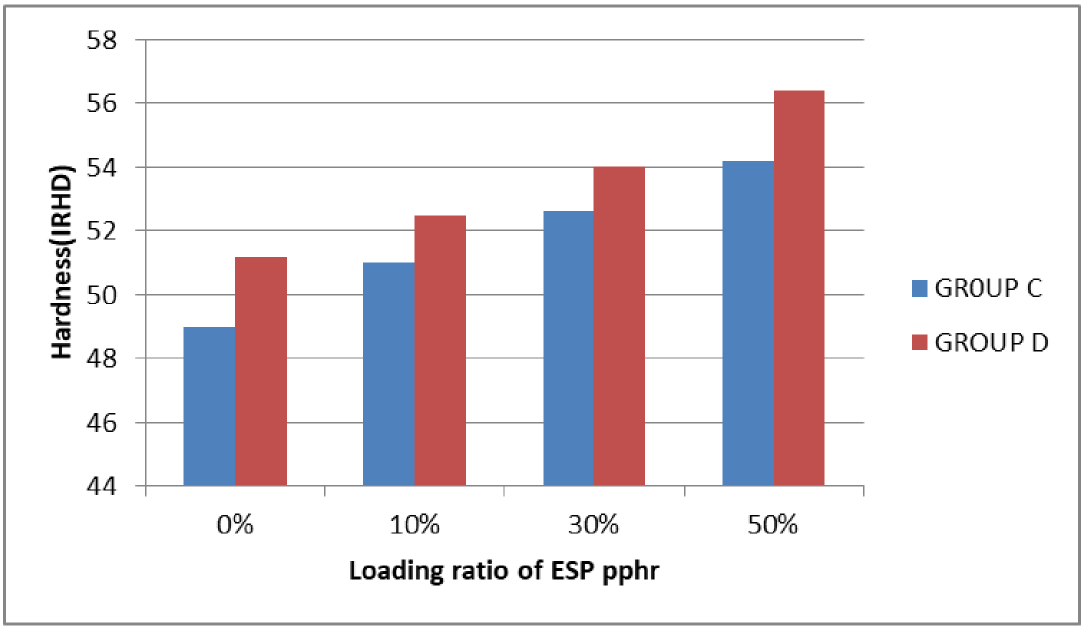
Fig.(4.23) shows the result of hardness increasing as the(ESP) and (CB-20pphr) loading ratios of filler increase. The figure depicts the variation in hardness of(NR/ NBR/ ESP) filled with different loading ratios of ESP and CB filler. It can be seen that the addition of fillers was due to increased hardness with increased filler content. This indicated that the hardness property of the vulcanizate was typically dominated by the filler loading. It was due to the presence of rigid calcium carbonate particles $CaCO3$ that caused increasing brittleness and the trend toward hardness. For the rubber elasticity of the rubber vulcanizates. This can be attributed to the physical cross-linking that occurs between the rubber chains, which leads to increased hardness. This behavior agrees with the results of the researcher [121].



Figure(4.23) The variation of hardness with loading ratio ESP for group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)

4.4.4 Thermal aging results of group(C)and(D)

Fig.(4.24) shows the result of the thermal aging of hardness increasing as the (ESP)and(CB-20pphr) loading ratios increase. Sample surfaces were subjected to the impact of thermal aging load during aging. Improved hardness was obtained with increasing aging temperatures and time, attributing to the correspondingly enhanced crosslinking densities. The molecular chains of NBR were sensitive to heat and oxygen due to the presence of unsaturated bonds in the butadiene fragments[122].



Figure(4.24) The variation of hardness with loading ratio ESP for group C-(NR50/NBR50/ESP) and group D-(NR50/NBR50/ESP/CB-20 pphr)after thermal aging

4.5 Conclusions

Eggshell powder(ESP) was incorporated as biofillers in composites. The mechanical properties and Rheological properties of eggshell powder(ESP)and(CB-20pphr)as reinforced in group(A),(B),(C)and(D) composites have been investigated.

1.The rheological properties such as minimum torque(ML), maximum torque(MH), scorch time(Ts2), optimum cure time(Tc90), viscosity and cure rate time(CR) decreases as the (ESP)and(CB-20pphr) loading ratios increased, excepted cure rate time(CR) in group (C)and(D) was increasing.

2.The mechanical properties such as tensile strength, elongation at break and elastic modulus wear decreased as the (ESP)and(CB) loading ratios increased in all groups.

3.The hardness increased as the (ESP)and(CB) loading ratios increased in all groups.

4. The thermal aging causes increasing cure time that leads to hardness increasing as (ESP)and(CB) loading ratios increase.

4.6 Recommendations for Future Works

Several recommendations can be suggested for future work, they can be summarized in the following points:

1. Preparation and study the rubber composites (NR\SBR\ESP) and (NR/NBR/ESP) reinforced with different ratio of eggshell powder and different ratio of (CB-pphr).
2. Synthesis rubber composites (SBR/ESP)and(NBR/ESP) with different ratio of (CB).
3. Study the rheological properties of (NR\SBR/ESP) and(NR/NBR/ESP) rubber composites, reinforcement with different type of(CB)
4. Synthesis the blend(NBR/SBR)and reinforced with different type of (CB)such as N660,N326,N220
5. Study the effecting of thermal aging on mechanical properties (SBR/NBR/ ESP) reinforced with different loading ratio of(CB)N326.

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الخلاصة

تضمنت هذه الدراسة تحضير اربعة مجموعات من متراكبات المطاط: الأولى (NR / SBR /ESP) والتي تحتوي على المطاط الطبيعي (NR) ومطاط الستايرين بوتادين (SBR) كمواد أساسية ، والثانية (NR / NBR /ESP) ، والتي تحتوي على المطاط الطبيعي (NR) ومطاط البوتادين الأكريلونيتريل (NBR) كمواد أساسية ومسحوق قشور البيض (ESP) كمواد تقوية بحجم جزيئات أقل من (٧٥ ميكرومتر) والتي تحتوي على ٩٧٪ كربونات الكالسيوم في مجموعتين مع التحميل كانت نسبة مادة(ESP)(٠، 10، 30، 50 pphr) ومع أسود الكربون (CB(N375 بنسبة تحميل (CB-20 pphr).

تم فحص جميع العينات بواسطة مطياف الأشعة تحت الحمراء (FTIR) وقياس الخصائص الريولوجية مثل الحد الأدنى لعزم الدوران (ML) وعزم الدوران الأقصى (MH) ووقت الاحتراق (Ts2) ووقت المعالجة الأمثل (Tc90) ومعدل المعالجة الأمثل (CR) واللزوجة وفقًا لـ [ASTM D-2705] ، وكذلك تم قياس الخواص الميكانيكية وفقًا لـ [ASTM D412-88] مثل الصلابة وفقًا لـ [ASTM D1415]بواسطة جهاز Shor A، وقوة الشد ، والاستطالة عند الكسر ، ومعامل المرونة وفقًا إلى [ASTM D3182] بواسطة Tensometar العالمي ، وتم إجراء التقادم الحراري لقياس الصلابة وفقًا لـ [ASTM D573] لجميع العينات عند ٧٠ درجة مئوية لمدة ٩٦ ساعة مع وبدون (CB) لمجموعتين.

أظهرت النتائج أن هناك تأثيرات كبيرة لـ ESP و (CB-20pphr) على الخصائص ؛ انخفضت بعض هذه الخصائص مع زيادة نسب التحميل من ESP و (CB-20pphr)، مثل الخصائص الانسيابية لعزم الدوران الأدنى (ML) ، وعزم الدوران الأقصى (MH) ، ووقت الاحتراق (Ts2) ، ووقت المعالجة الأمثل (Tc90) ، واللزوجة ، ومعدل المعالجة (CR) ، باستثناء معدل المعالجة الامثل (CR) ، كانت تتزايد في المجموعة الثانية ، وتناقصت الخواص الميكانيكية مثل مقاومة الشد ، والاستطالة عند الكسر ، و معامل المرونة ؛ من ناحية أخرى ، تمت زيادة الصلابة في جميع العينات مع زيادة نسب تحميل ESP و (CB-٢٠pphr)، وأظهرت نتيجة التقادم الحراري أن الصلابة كانت تزداد مع زيادة نسب تحميل مادة (ESP) و (CB).

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
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قسم الفيزياء

تأثير مسحوق قشور البيض على الخصائص الريولوجية والميكانيكية لبعض الخلائط المطاطية

رسالة مقدمه

إلى مجلس كلية التربية للعلوم الصرفة في جامعة بابل وهي جزء من متطلبات درجة الماجستير في التربية\ الفيزياء

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