Chapter I

INTRODUCTION

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Corrosion of steel has an enormous economic impact, hence, great efforts have been ongoing throughout this century [1, 2], to develop more efficient and environmentally compliant methods for corrosion prevention.

We live in the technological age, so the effect of unchecked corrosion is not only confined to the state of the corroding utility it self but it also influences, profoundly, man and his economic and social welfare, hence, the study of corrosion control has great importance and any improvement that can be brought about is welcomed.

One of the most convenient and certainely the oldest method of protecting a substrate from the detrimental effects of the environment, is coating it with a barrier to isolate it from its surroundings. This barrier principle represents the most common and wide spread use of corrosion prevention [3]. The protection provided by functional coatings saves the natural resources and is friendly to the environment because it minimizes corrosion and other means of degradation, thus allowing a substrate to last for a much longer period than it would without protection. It has been accepted that coatings serve as an insurance policy on the life of the structure, as the coating cost amounts to a very small percentage of any structure's total cost, and this small incremental cost protects the structure against disintegration for many years.

PART (I)

1.1. Corrosion Definition:

Corrosion is the destructive attack of a metal by reaction with its environment [4].

The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our every day encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive over design, it also jeopardizes safety and inhibits technological progress [5].

1.2. Electrochemical Basis of Corrosion:

Corrosion process occured as a result of the operation of galvanic corrosion cells on the metal surface [6]. The anodic reaction in every corrosion process is the oxidation of metal to its ions. This can be written in the general form:

$$M \longrightarrow M^{n+} + ne^- \qquad (1.1)$$

There are different cathodic reactions which are frequently encountered in metallic corrosion. The most common cathodic reactions are:

Hydrogen evolution $2H^+ + 2e^- \longrightarrow H_2$ (1.2)

Oxygen reduction $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (acidic solution) (1.3)

Oxygen reduction $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (neutral or basic solution) (1.4)

Metal ion reduction $M^{3+} + e^{-} \longrightarrow M^{2+}$ (1.5)

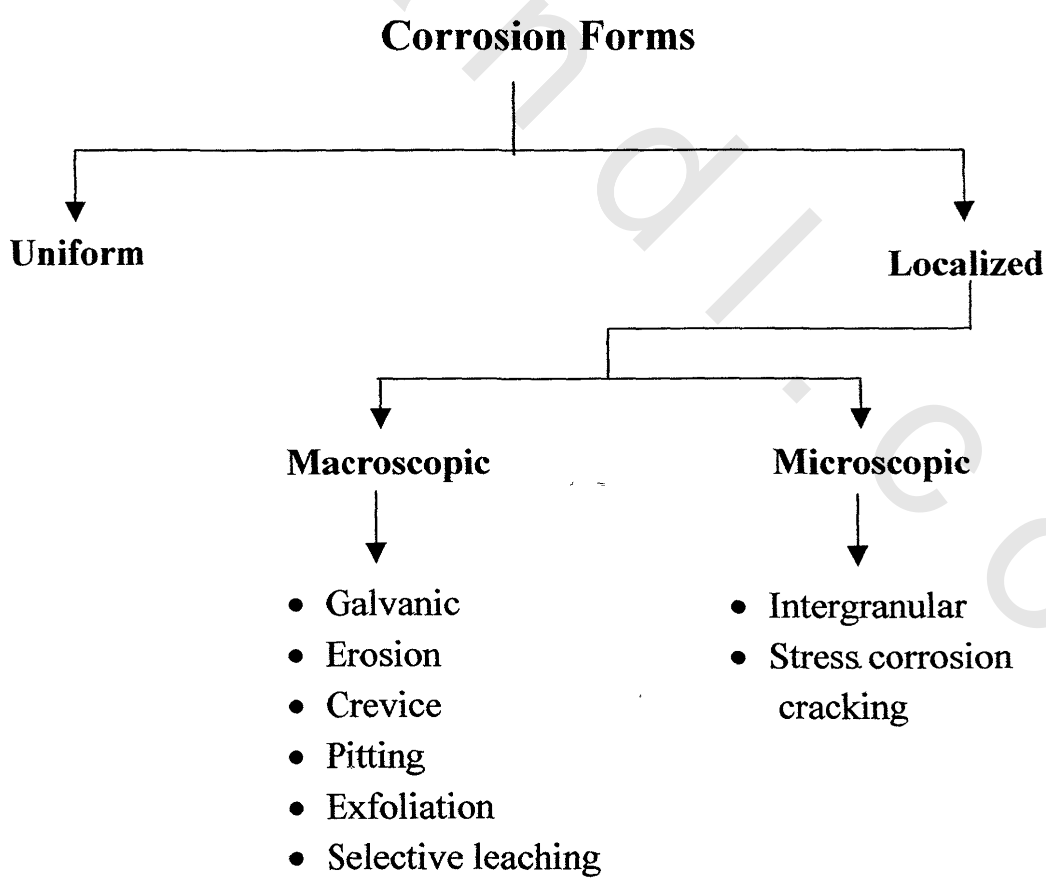
Metal deposition $M^{+} + e^{-} \longrightarrow M$ (1.6)

Hydrogen evolution and oxygen reduction are the most common cathodic reactions. Different cathodic reactions can occur simultaneously on a corroding metal surface.

1.3. Forms of Corrosion:

Corrosion occurs in several widely differing forms. Classification is usually based on one of three factors: nature of the corrodent, mechanism of corrosion, or appearance of the corroded metal (7) .The various types of corrosion, classified according to appearance, are listed in Table (1.1).

Table (1.1) -Forms of corrosion.



1.3.1. Uniform corrosion:

Uniform attack over large areas of a metal surface is the most common form of corrosion, where the metal corrodes at the same rate over its entire surface. Uniform corrosion is the easiest form of corrosion to measure, and failures can usually be avoided by regular inspection [8].

1.3.2. Localized corrosion:

Localized corrosion can be described as corrosion occuring at one part of a metal surface at a much higher rate than that over the rest of the surface. Localized corrosion damage can have a serious effect upon the mechanical properties of a metal [9].

1.3.2.1. Macroscopic forms:

a- Galvanic corrosion:

This form of corrosion takes place when two different incontact metals (or connected by an electrical conductor) are exposed to a conductive solution. A difference in electrical potential exists between different metals, and serves as the driving force to pass current through the corrodent. This current flow results in corrosion of one of the metals in the couple.

b- Erosion corrosion:

The role of erosion is usually attributed to the removal of protective surface films due to mechanical wear. Cavitation and fretting are two special forms of erosion. Cavitation is caused by the formation and collapse of vapor bubbles at the metal surface. The high pressures produced by this collapse can deform the underlying metal or remove protective films. Fretting corrosion occurs when metals slide over each other and cause mechanical damage.

c- Crevice corrosion:

An aggressive environment may develop and cause local corrosion in the crevice, it is usually attributed to one or more of some factors that may take place in the crevice such as, changes in acidity, lack of oxygen, build up of a detrimental ion species and finally depletion of an inhibitor. Crevice corrosion occurs to metals that depend on air-formed oxide film to achieve their corrosion resistance such as stainless steel and titanium, these materials can be alloyed to minimize crevices and to improve their resistance.

d- Pitting corrosion:

Pitting occurs when the metal undergoing corrosion suffers metal loss at localized areas rather than over the entire surface and the driving force of the corrosion reaction is concentrated at these localized areas (10). Pitting is much more dangerous than general corrosion because the pitted area can become penetrated in a short time. To minimize pitting, a clean and homogenous surface is desirable.

e- Exfoliation and selective leaching:

Exfoliation is subsurface corrosion that begins on a clean surface but spreads below it, this attack has a laminated appearance and it is usually recognizable by a flaky and sometimes blistered surface (11). It can be combatted by heat treatment and alloying. On the other hand selective leaching is the removal of one element in an alloy, this kind of corrosion is detrimental largely because it yields a porous metal with very poor mechanical properties.

1.3.2.2. Microscopic forms:

In microscopic local attack, the amount of metal dissolved is minute but a considerable damage can occur before the problem becomes visible to the naked eye. Intergranular and stress corrosion cracking are the two well known types of microscopic corrosion.

a- Intergranular corrosion:

As the name implies, intergranular corrosion is a preferential attack of metal's grain boundaries [(12)] .In most cases, it results from a metallurgical structure that causes the grain boundaries to be more susceptible to attack than the grain themselves.

b- Stress corrosion cracking:

Stress corrosion cracking is an interaction between chemical and mechanical forces that results in a failure which, otherwise would not occur. It is caused by the "synergistic" action of corrosion and applied tensile stress, the result of this combined effect is the cracking of a metal alloy [(12)]. The cracks may follow intergranular or transgranular paths and there is often a tendency for crack branching. In general, the time to failure and the extent of cracking vary with corrosive concentration, temperature, and stress intensity.

1.4 Corrosion Environments:

Practically all environments are corrosive to some degree and the severity of the resulted corrosion tends to vary significantly according to the environment [(13)]. In general, the inorganic materials are more corrosive than the organics; for example, corrosion in petroleum industry is due to sodium chloride, sulfur, hydrochloric and sulfuric acids, and water, these materials have more corrosive effect than oil, naphtha, or gasoline. The other important corrosion environments are as following [14]:

a-Atmosphere:

The degree of humidity and the contents of the atmosphere are the two important factors that determine the extent of atmospheric corrosion, hence, atmospheric environments have been classified into rural, urban, industrial, marine, or combinations of all [15]. In rural atmosphere the principal corrodents are moisture, oxygen, and carbon dioxide, while in urban there are additional contaminants of SO_x and NO_x resulted from motor vehicle and domestic fuel emissions. Industrial atmospheres are associated with high concentrations of sulfur dioxide, chlorides, phosphates, and nitrates. Finally, the marine atmosphere is characterized by fine windswept chloride particles that deposited on surfaces. The atmospheric corrosion attracts much attention because it has a considerable economic importance and because of the continuous increase in the number of environmental pollutants [16].

b- Soils:

Soil is an aggregate of minerals, organic matter, water, and gases (mostly air). It is formed by the combined weathering action of wind and water, and also organic decay. The properties and characteristics of soil obviously vary as a function of depth. Corrosion in soils is a major concern because most of the buried infra-structures are aging [17]. Typical examples of soil corrosion are related to oil, gas, and water pipelines, buried storage tanks (used by gas stations), electrical communication cables and anchoring systems. Corrosion in soils is a complex phenomenon due to the multitude of variables involved in it. These variations in soil characteristics can have a major impact on corrosion of buried structures, thus soils represent highly corrosive environments leading to the necessity of using additional corrosion protection for metals and alloys.

c- Microbes and biofouling:

Organisms pervade our environment and readily invade industrial systems wherever conditions permit [18]. The micro-organisms of interest in microbiologically influenced corrosion are mostly bacteria, fungi, algae, and protozoans [19], they are responsible for the degradation of a wide range of materials. These organisms are largely invisible, so it has taken considerable time for defining their role in material degradation.

d- Natural waters:

Metals immersed or partly immersed in water tend to corrode because of their thermodynamic instability. Natural waters contain dissolved solids and gases and sometimes colloidal or suspended matter. All these may affect the corrosive properties of the water in relation to the metals with which it is in contact [20].

e- Sea water:

Marine corrosion is a constant and continuous process. All marine structures are subjected to it and must be protected against disintegration by corrosion, not only to avoid the high cost of replacement, but also to maintain them in a safe operating conditions [21].

There are many factors influence the corrosion of carbon steel in sea water [22]. The most important one is chloride ion, which is highly corrosive to iron as well as carbon steel. The high conductivity of seawater makes it possible for anodes and cathodes to operate over long distances, thus corrosion possibilities are increased. Some other factors, which affect the corrosion of steel, are soluble oxygen and velocity. High oxygen content increases the corrosivity, also the increase in the velocity of moving sea water may destroy rust barrier and provide more oxygen leading to an increase in corrosion rate. There are other parameters, which play an important role in corrosion of steel in seawater such as, temperature, stress, presence of sulfides in polluted seawater, and suspended sediment [23].

1.5 Corrosion Prevention:

The cost that industry incurs each year in the restoration and maintenance of existing structures and equipments that are subjected to corrosion is enormous [24]. Accordingly, increased emphasis has been placed on the latest corrosion protection technology to reduce the cost of corrosion. There are four ways to control and avoid corrosion:

(a) Control of process variables that may accelerate the corrosion rate such as temperature, impurities, and pH.

(b) Good engineering design, i.e., to provide proper design for the process equipment to minimize corrosion.

(c) Materials selection, so that to choose ones which are less susceptive to corrosion.

(d) Protection by various corrosion prevention methods.

The most popular techniques applied to slow down the corrosion process are: corrosion inhibitors, cathodic protection, anodic protection, and coatings[25].

1.5.1. Corrosion inhibitors:

An inhibitor is a substance, which retards or slows down a chemical reaction when relatively small amounts of it are added to the corrodent [26].

Inhibitors can be classified according to their composition into organic and inorganic, or according to the mechanism of action into anodic, cathodic and mixed inhibitors [27]. It is important to know the mechanism of inhibition in the definition of a corrosion inhibitor because inhibition is accomplished by one or more of several mechanisms [28]. The inhibitors are widely used to protect metals and their alloys in different media [29].

1.5.2. Cathodic protection:

Cathodic protection may be defined as a technique to reduce corrosion of a metal surface by passing sufficient cathodic current to it in order to let its anodic dissolution rate becomes negligible.

There are two types of cathodic protection: impressed current and galvanic or sacrificial anode. Impressed current cathodic protection takes place by the passage of an electrical current into a metal at an equal or greater rate than it was flowing out of the corroding metal. This can be accomplished by connecting a large enough d.c. source to the metal and an electrode that becomes the anode [30, 31]. Galvanic protection uses a more active metal than that in the protected structure to supply the current needed for stopping corrosion. The more active metal is called a sacrificial anode. Metals that are commonly used as sacrificial anodes are zinc, magnesium, aluminum, and their alloys [32].

1.5.3. Anodic protection:

A very significant form of corrosion control is to passivate the metal by applying current in a direction that makes it more anodic. This technique is only applicable to metals and alloys that show active – passive behavior [33]. A well known phenomenon is passivation, it is the ability of a metal to corrode at a rate many times lower than that expected from simple thermodynamic considerations [34]. Anodic protection has been applied on iron, stainless steel, titanium, aluminum, and chromium, and it is used in a wide range of situations. The main advantages of anodic protection are: low operating costs, applicability to a wide range of sever corrodents, high throwing power, feasibility, predictable in the laboratory, and the protection current can be a good guide to corrosion rate [35].

1.5.4. Corrosion protection by coating:

Protective coatings are used to provide long – term protection under a broad range of corrosive conditions extending from atmospheric exposure to the most demanding chemical processing conditions [36], hence coatings are probably the most widely used products for corrosion control.

A coating is any thin material applied on a substrate to provide corrosion protection by acting as a barrier between a corrosive environment and the metal structure to which coating is applied. A coating that can protect metals efficiently against corrosion for a practical period of time must have the following properties [37]: (a) Excellent water resistance: as the coating must withstand continuous immersion in water or seawater and it must do so without swelling, blistering, cracking, softening, or loss of adhesion; (b) Low water absorption: each coating has its own level of water absorption which is the amount of water picked up and retained within the molecular spaces in the basic structure. The water absorbed, though not critical, can contribute to corrosion when combined with other factors, therefore, the less water absorption the better the coating [38]; (c) Moisture vapor transfer rate (MVT): it is the action of water vapor in molecular form passing through an organic substances. Each coating material has its characteristic MVT rate and generally, the lower the moisture vapor transfer rate the better the protection provided by an organic coating; (d) Resistance to ionic passage: the coating must act as a barrier to the penetration of different ions such as, chloride, sulfate, carbonate, or similar ions which on penetrating the film would start underfilm corrosion; (e) Resistance to osmosis: this phenomenon greatly affects coating life and it can be defined as the passage of water through a semipermeable membrane from a solution of lower concentration to a solution of higher one; (f) Resistance to electroendosmosis: which is defined as the forcing of water through a membrane by an electrical potential in the direction of the pole that has the same charge as the membrane; (g) Dielectric strength: whereas, the coating must be highly dielectric to resist the passage of any existing electrons from anodes set up through breaks in the coating; (h) Weather resistance: the coating must retain original properties of gloss, thickness, color, and film continuity for several years without chalking appreciably, embrittlement, checking or cracking. Finally, there are some other essential properties that protective coatings must have to perform effectively [39] such as: chemical resistance, adherence, abrasion resistance and inhibition. It must also be easily applied, resistant to fungus and bacteria, easily repaired and age resistant.

The cost of a coating is always given a serious consideration in coating selection, but it should be less important than the coating properties that provide the basis for long time effective coating protection.

1.5.4.1. Types of coating materials:

At the present time most corrodible surfaces are protected with synthetic coatings, these coatings are manufactured primarily with resins or binders which are the reaction products of some basic organic chemicals. It is useful to classify coatings into a number of groups: metallic, inorganic, and organic compounds.

a- Metallic coatings:

Metals, and in some cases their alloys, can be applied to almost all other metals and alloys by using one or more of different techniques such as hot dipping, metal spraying, cladding or electroplating. Metallic coatings can be divided into two groups: anodic group; in which they are more active to the metal being coated, and those cathodic, i.e., more noble to it. For steel, metals such as zinc fit for the former category, while nickel, copper, and chromium are typical of the latter. If a small gap in the coating exposes the base metal the more active coating will galvanically protect it whereas, a more noble coating may accelerate attack at the bare spot and produce a pit. This is an important factor when selecting a technique and establishing quality control methods, because a porous coating that contain defects will be dangerous if it is more noble than the base metal while, if a such coating is more active it will sacrificially corrode.

A well known example is the zinc – coating of steel, a metallurgical bond is formed between the coating and the underlying metal. Zinc coatings, as reconstruction and permanent primers have been a major part of the protective coatings markets for several decades [(40)].

b- Inorganic coatings:

There are many different types of inorganic coatings used in a variety of industrial applications. A typical example is ceramic coatings that when properly applied are effective against corrosion, but because of cost and fragility their use has been generally limited to relatively small equipments. Another system is Portland cement, which is used for protecting steel from water and soil corrosion [(41)]. It has been effective for external pipe protection.

Also porcelain enamels and glass coatings are fused onto metals to protect them. Glass coatings can resist a wide variety of chemicals, including strong acids, but may be unsuitable in hot and concentrated alkalis. Glass coating for chemical service is predominantly silica and it is applied primarily to iron and nickel – base alloys.

c- Organic coatings:

The organic coatings most frequently used for corrosion control are asphalt enamels, coal tar enamels, epoxies and plastic coatings [(42)]. Asphalt and coal tar have a long history in the protection of buried pipe lines and tank bottoms. They are usually applied in a molten state and strengthened with wraps of fabrics. Epoxies, in various forms, are perhaps the most widely used generic coatings in industry, they are so popular because they are tough and water resistant, they also resist alkalis, solvents, and most chemicals. Plastics include a wide range of organic compositions that give a good service for external protection of buried pipelines. The vinyls and acrylics may be considered as the most common types in this group, they are nontoxic, unflammable, and have good flexibility and abrasion resistance. Also, polyethylenes, polypropylenes, polyesters, and polyurethanes are growing in use as coatings, especially for applications where wear resistance is important and they are often applied as topcoats. Additional developments are expected in the continuous film plastic coating field, these developments probably will involve both new plastic materials and new application techniques with even better performance at reasonable cost. However recent developments indicate that polymer coatings are effectively used to protect steel structures from corrosive environments, as it will be mentioned in the next part.

It was emphasized that the most favorable coating system for any given structure is the most stable one, i.e., the coating system whose electrical and mechanical characteristics will deteriorate at the slowest rate with time (under the specific installation conditions), will be the most economical system.

PART (II)

1.6. Polymers :

Polymers are materials of very high molecular weight that are found to have multifarious applications in our modern society [43]. World consumption of polymers has significantly increased in the past twenty years because of their numerous advantages including excellent corrosion resistance, competitive cost, low weight, easiness of installation, and higher specific strength than many other materials [44]. Exploitation of many of these unique properties of polymers has made them extremely useful to mankind and hence, they represent an area where chemists continue to make major important contribution [45]. Polymers are used extensively in food packaging, clothing, home furnishing, transportation, medical devices, information technology and they have a long commercial history in coatings and adhesives industries. Polymeric construction consists of several structural units bound together by covalent bonds. They can be subdivided into three main categories [46]: (i) Thermoplastics which consist of individual long chain molecules where, any product can be reprocessed by chopping it up and feeding it back into the appropriate machine, (ii) Thermosets which include an infinite three dimensional networks that can be created only when the product is in its final form and can not be broken down by reheating, (iii) The last category is rubber which contain looser three dimensional networks where, the chains are free to change their shapes.

Ethylene propylene diene monomer (EPDM) can be considered as one of the most interesting elastomers that appear in recent years. EPDM is an artificial rubber that can be prepared by random copolymerization of ethylene with propylene in presence of diene monomer [47]. The most important characteristic of EPDM is its high oxygen, ozone, and UV resistance and hence, it is favorable for outdoor applications. Also EPDM has excellent adhesion to metals, excellent electrical resistance characteristics as well as favorably good tensile properties, hence the areas of application where the use of EPDM is now accepted are numerous [48], Table (1.2) shows the main EPDM applications and indicating its relative consumption percentage.

Table (1.2) - EPDM application fields

Field of Application	%
Automotive	42
Electrical cable	15
Building	10
Appliance	10
Industrial	9
Blends with plastics	9
Other	5

Polyethylene is the most widely used thermoplastic material [49] and it is manufactured by polymerization of ethylene under high pressure and elevated temperature in the presence of oxygen as free-radical initiator [50]. Polyethylene has many excellent characteristics, which have led to its wide spread use such as low cost, easy processability, excellent electrical insulation properties, toughness and flexibility (even at low temperatures), freedom from odor and toxicity, and the reasonable clarity of thin films. The most two important properties of PE for our study are the high chemical resistance (as it is not attacked by acids, bases, or salts) and its low permeability to water [51].

Major markets of LDPE are in packaging and sheeting also, cross linked LDPE foam has been used in the automotive industry for carpeting, sound deadening, and pipe insulation. It can be used as flotation media for oil carrying and dredging hose and it can act effectively in coating fields [52].

1.7. Polymer Blending:

Blending of polymers together has proved to be one of the methods that have been applied successfully for obtaining new polymeric materials with special or specific properties, i.e., up grading its quality. Product performance requirements will dictate the initial selection of formula ingredients [53]. These materials must be environmentally safe, meet occupational health and safety requirements, processable in the product manufacturing facilities, and must be cost effective.

Several techniques can be applied for the preparation of polymeric blends such as [54]: latex blending, solution blending, latex and solution blending, mechanical blending, mechanical chemical blending, and powdered rubber blending. The properties of the polymers to be blended together as well as the purpose of blending define the method to be used for blend preparation.

The mechanical blending method is the most widely used in industry because of its easy operation and high capacity for industrial production. It is also the method that has been used in this study and hence it will be reviewed in detail. It was recognized that although two high molecular weight polymers may be mutually insoluble, blends with macroscopic homogeneity and useful properties can be produced by mechanical blending, provided that mechanical mixing is sufficiently intense and that the viscosity after mixing is sufficiently high to prevent gross phase separation. High shearing forces that are required for the mechanical blending of high molecular weight elastomers necessitate the use of open roll mills and internal mixers, e.g., Banbury and extruders [55].

The open roll mill mixing process is to masticate the polymers until an even and smooth band is formed around the front roller and it is desirable to have similar polymer viscosity (at the mixing temperature) for ease of dispersion. Dealing with internal mixers, they are the most widely used mixing operations for reasons of speed, output and economy. This technique has the advantage of excellent dispersion with greater reproducibility of results, as well as, improved physical properties. It is very necessary to be able to keep an open mind on the exact technique to be used for mixing and to select the best combination of circumstances [56].

1.8. Fillers:

Fillers or reinforcement aids are added to rubber formulations to meet materials property targets such as tensile strength and abrasion resistance. There are many well known types of fillers like silica, silicates, clays, ceramic, non black fillers, and carbon black which is the most reinforcing agent used for rubber. Carbon black is made by incomplete combustion of hydrocarbon such as natural gas or heavy aromatic residue oils from petroleum or coal. Reinforcement by carbon black involves an increase in the resistance of rubber to abrasion, tearing, and other types of tensile failure. Also, it leads to an increase in the hardness, modulus of elasticity, and related viscoelastic properties [57] .Electrically insulating rubbers and plastics can be rendered conductive by the incorporation of adequate loading of carbon black.

The most important properties of carbon black that affect the applications are particle size, structure, physical and chemical nature, and porosity. The smaller the particles size the poorer the processibility and the higher the reinforcement. Also electrical conductivity and rate of cure are affected to a considerable degree by the surface chemistry of carbon black [58].

1.9.Vulcanization:

Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force [59]. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network, i.e., vulcanization is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. The crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, carbon - to - carbon bond, a polyvalent organic radical, and 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 sunder pressure.

A typical vulcanization system in a compound consists of three components: activators, accelerators, and vulcanizing agents (typically sulfur). The vulcanization activator system consisting of zinc oxide and stearic acid has received much less research effort than other components in the rubber compound. Stearic acid and zinc oxide levels of 2.0 and 5.0 phr, respectively are accepted throughout the rubber industry as being adequate for achievement a compound of optimum physical properties.

Accelerators used in vulcanization are products, which increase both the rate of sulfur crosslinking in a rubber compound and crosslinking density. Secondary accelerators, when added to primary accelerators, increase the rate of vulcanization and degree of crosslinking, with terms primary and secondary being essentially arbitrary. A feature of such binary acceleration systems is the phenomenon of synergism, where a combination of accelerators is synergistic, its effect is always more powerful than the effect of the individual components. Accelerators can be readily classified according to the rate of vulcanization into ultra, semi-ultra, fast, medium, and slow accelerators.

Special compounding ingredients are added for rubber curing, they are secondary materials such as processing aids, plasticisers, and peptisers. These materials are added to rubber compounds primarily to aid the processing operations of mixing, calendaring, extruding and molding [60].

One of the most important vulcanizing agents are peroxide groups, they are used for curing saturated or low unsaturated polymers, commercial peroxides are dicumyl peroxide, benzoyl peroxide, Luperco 230, and Lupersol 118 [61]. Vulcanization can also be induced by radiation, where reactive side groups are formed which subsequently serve to link polymer molecules together, i.e., crosslinking.

The most widely used method for many applications is accelerated sulphur vulcanization. It is the only rapid crosslinking technique which can, in a practical manner, give the delayed action required for processing and shaping before the formation of the vulcanized network.

The chemistry of sulphur vulcanization is so complex [62], the initial step in vulcanization seems to be the reaction of sulphur with the zinc salt of the accelerator to give a zinc perthio-salt $XS_x ZNS_x X$, where X is a group derived from the accelerator (e.g. thiocarbamate or benzothiazyl groups).

This salt reacts with the rubber hydrocarbon RH to give a rubber-bound intermediate

$$XS_x ZNS_x + RH \longrightarrow XS_x R + ZnS + HS_{x-1} X$$

and a perthio-accelerator group which, with further zinc oxide will form a zinc perthio-salt of lower sulfur content, this may nevertheless again be an active sulphurating agent, forming intermediates XS_{x-1} R. In this way each molecule of accelerator gives rise to series of intermediates of varying "degrees of polysulphidity". The intermediate XS_x R then reacts with a molecule of rubber hydrocarbon RH to give a crosslink and more accelerator is regenerated:

$$XS_x R + R H \longrightarrow RS_{x-1} R + XSH$$

Even this is not the whole story, for on further heating, the degree of polysulphidity of the crosslinks declines. This process is catalysed by $XS_x ZnS_x X$ and can result in additional crosslinks.

1.10. Classification of Polymer Blends:

Development of polymeric blends has become very important for polymer industries because they have been shown to be successful and versatile alternatives to obtain new polymers [63]. The most important types of polymeric blends are elastomer-elastomer blends and elastomer-plastic blends.

a- Elastomer - Elastomer blends:

Elastomers are large number of polymers, with rubber-like characteristics at ambient temperature [64]. They possess several significant properties such as the ability to stretch and retract rapidly and they have high modulus and strength when stretched. Also they have a low or negligible crystalline content, and their molar mass is large enough for network formation. From the practical point of view, elastomers have deficiency in one or more properties and blending is a way of obtaining all-round performance. Elastomer blends are one class of composite materials that are used in polymer based industrial products,these blends have a long commercial history in the rubber coatings and adhesives industries [65].

b- Elastomer - Plastic blends:

Mechanical blends formed from elastomeric rubber and plastic material would be expected to possess a wide range of properties depending not only on the properties of the individual components but also on the extent as well as the ratio of mixing [66]. Such blends would have rubbery properties, at the same time they can be processed as a plastic material,hence, substantial economic advantage is gained with respect to the fabrication of such elastomer-plastic blends into its end-use products [67]. Moreover, the polymer which predominates, will determine the kind of end-use product, as one may get impact resistant plastic when the latter constitutes the continuous matrix in the blend; and on the other hand, when the elastomeric phase is the continuous matrix, one may get reinforced elastomer blend.

The polymer macromolecules forming the blend may be considered incompatible, semicompatible, or compatible. In the first case, two distinct or immiscible phases can be distinguished. Semicompatibility is attained when partial mixing of the two polymers takes place on the molecular level. Compatibility would be expected only when a single thermodynamically stable phase is obtained. This latter case is a rare one especially in case of mechanical blends due to the fact that an entropy increase is always obtained on mixing. From the practical point of view, it has been accepted in general practice to speak of a compatible blend when its mechanical properties are proportional to the ratio of its constituents in the blend. Such proportionality does not occur in case of incompatible blend and, hence, it leads to the reduction of mechanical properties [68].

The area of elastomer-plastic blends has been revolutionized by advances in thermoplastic elastomers (TPEs), where the use of chemically modified elastomers and plastics has led to new compositions with very useful properties for many and varied end use applications [69].

Finally, the role of the modern materials scientist in rubber industry is to use materials to improve current products and also to develop new ones. Four parameters govern this development process: (i) Performance: where the product must satisfy customer expectations; (ii) Quality: as the product must be durable and have a good appearance;(iii) Environment: products should be environmentally friendly in manufacturing, use and disposal; and (iv) The last parameter is cost: as the systems must provide a suitable value to the customer.