

**INVESTIGATION ON THE PROPERTIES OF  
THERMOPLASTIC ELASTOMERS (TPEs) BASED  
ON BLENDS OF RECYCLE POLYETHYLENE (rPE)  
/ ETHYLENE-PROPYLENE-DIENE TERPOLYMER  
(EPDM)**

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## LIST OF ABBREVIATIONS

ASTM	– American Society for Testing and Materials
CaCO <sub>3</sub>	– Calcium Carbonate
CB	– Carbon Black
CBS	– N-sikloheksil-2-benzol tiazosulfenamide
E	– Elastomer
E <sub>b</sub>	– Elongation at Break
EPDM	– Ethylene Propylene Diene Terpolymer
HDPE	– High Density Polyethylene
LDPE	– Low Density Polyethylene
MDPE	– Medium Density Polyethylene
PE	– Polyethylene
rPE	– Recycle Polyethylene
TMTD	– Tetrametiltiuram disulfide
TPEs	– Thermoplastic Elastomers
TPs	– Thermoplastics
vPE	– Virgin Polyethylene
XLPE	– Cross-linked Polyethylene

**KAJIAN SIFAT-SIFAT ELASTOMER TERMOPLASTIK DARIPADA ADUNAN  
POLIETILENA KITAR SEMULA/ ETILENA PROPILENA DIENA  
TERPOLIMER**

**ABSTRAK**

Polietilena kitar semula (rPE) telah diadun dengan etilena propilena diena terpolimer (EPDM) untuk menghasilkan elastomer termoplastik. Di dalam siri pertama, adunan dengan menggunakan polietilena baru (rPE) juga turut disediakan. Semua adunan disediakan dengan menggunakan Haake Rheomix pada suhu 180 °C dan kelajuan 50 putaran per minit. Kajian selanjutnya berkenaan kesan penggantian separa vPE oleh rPE di dalam adunan vPE/rPE/EPDM pada nisbah adunan tetap 70:30 daripada adunan plastik (vPE + rPE) dan EPDM telah dijalankan. Selain itu, kesan terhadap pemvulkanan dinamik (sulfur) dan pembebanan pengisi (hitam karbon, silika dan kalsium karbonat) ke atas adunan vPE/rPE/EPDM (40/30/30) telah dijalankan secara berasingan. Keputusan menunjukkan bahawa pada kandungan EPDM yang sama, adunan rPE/EPDM mempunyai kekuatan tensil, modulus Young, kestabilan tork dan kestabilan terma yang tinggi tetapi pemanjangan pada takat putus yang rendah berbanding adunan vPE/EPDM. Kajian pembengkakan menunjukkan bahawa adunan rPE/EPDM mempunyai ketahanan pembengkakan di dalam minyak dan pelarut kimia yang lebih tinggi berbanding adunan vPE/EPDM. Pemeriksaan permukaan rekahan tensil menggunakan mikrograf Scanning Electron Microscopy (SEM) telah menunjukkan lebih tenaga diperlukan oleh adunan rPE/EPDM untuk menghasilkan kegagalan katastropik

berbanding dengan adunan vPE/EPDM. Kesan penggantian separa vPE oleh rPE telah meningkatkan kekuatan tensil, modulus Young, ketahanan pembengkakan dan kestabilan tork dalam adunan vPE/rPE/EPDM. Kehadiran pengisi, pewarna dan bahan-bahan lain yang terkandung dalam rPE dipercayai bertanggungjawab atas sifat-sifat adunan di atas. Kesan pemvulkanan dinamik ke atas adunan vPE/rPE/EPDM telah menunjukkan pencapaian positif pada kekuatan tensil, modulus Young dan kestabilan tork. Pemerhatian ini adalah disebabkan oleh peningkatan ketumpatan sambung silang di mana dibuktikan dengan penurunan nyata indek dan peratus pembengkakan. Peningkatan dalam pembebanan pengisi yang melibatkan hitam karbon dan silika telah meningkatkan kekuatan tensil, modulus Young dan kestabilan terma tetapi penurunan dalam pemanjangan pada takat putus. Keputusan sebaliknya ditunjukkan oleh kalsium karbonat kecuali modulus Young dan kestabilan terma.

## ABSTRACT

Recycle polyethylene (rPE) was used to prepare thermoplastic elastomer (TPE) by incorporating it with ethylene propylene diene terpolymer (EPDM). A similar series of blends were also formulated by using virgin polyethylene (vPE). All the blends were prepared by using a Haake Rheomix at 180 °C and 50 rpm. Further studies were done on the effect of partial replacement of vPE with rPE in vPE/rPE/EPDM blends at a fixed 70:30 blend ratio of plastics (vPE + rPE) and EPDM. Besides, the effect of dynamic vulcanization (sulfur) and fillers loading (carbon black, silica and calcium carbonate) were performed separately based on vPE/rPE/EPDM (40/30/30) blends. The results indicated that at a similar EPDM content, rPE/EPDM blends have higher tensile strength, Young's modulus, stabilization torque and thermal stability but lower elongation at break than vPE/EPDM blends. Swelling study reveals that rPE/EPDM blends have better oil and toluene resistance than vPE/EPDM blends. Scanning electron microscopy (SEM) examination of the tensile fracture surface of rPE/EPDM blends indicates that higher energy is needed to cause catastrophic failure compare to vPE/EPDM blends. The partial replacement of vPE with rPE resulted improvement in the tensile strength, Young's modulus and swelling resistance with an increase in the stabilization torque of the vPE/rPE/EPDM blends. The presence of fillers, coloring agents and other materials in rPE is believed responsible for the above observation. The effect of dynamic vulcanization on vPE/rPE/EPDM blends shows an improvement in the tensile strength, Young's modulus and stabilization torque. This observation is due to the increase in crosslink density, which was evident from the significant

reduction in swelling index and swelling percentage. The increase in filler loading of carbon black and silica has improved the tensile strength, Young's modulus and thermal stability of vPE/rPE/EPDM blends with a concurrent decrease in elongation at break. However, a positive trend was observed for calcium carbonate except for Young's modulus and thermal stability.

# CHAPTER 1

## INTRODUCTION

### 1.1 Recycle and Reuse Waste Materials

#### 1.1.1 The Necessity for Plastic Recycling

Disposal of plastic waste into landfills has become increasingly prohibitive due to high costs, legislative pressure and public opinion. Growing environmental awareness and reductions in available landfill capacity have prompted plastics recycling programs in most developed countries. Incentives for using recycled plastics include ecological reasons, consumer demand, recycle-content legislation and lower cost. Much plastic is made from petroleum, recycling conserves a valuable resource. Until recently these incentives have had to be weighed against variable material composition, possibility of contamination, loss of mechanical properties due to degradation, lack of standards and variations in supply. Today, many of these problems have been solved through such measures as the use of sophisticated automated sorting, restabilization, implementation of recycle quality standards and integrated collection networks (Joseph, 1995).

Major producers of virgin polymers, e.g. petrochemical and chemical companies are just beginning to offer grades that contain recycled plastics. Undoubtedly, in future years these producers will increase their activities in recovery of plastics from waste and in marketing recycled polymers.

### 1.1.2 Plastic Recycle Process

In general, polymer recovery or recycling involves a variety of technologies as below (Jesse, 1992):

- Collection of discarded objects and parts

There are numerous alternative methods of collection including drop-offs, deposit returns, curbside collection, trash sortation and reverse distribution.

- Polymers separation – Sortation

Sortation, the separation of plastic objects in waste streams into groupings by generic resin type and colors has been the first step in recovering the polymer content of the object. However, plastic objects can be sorted only if they are recognizable to a sensor, human or mechanical/ electronic.

- Polymer separation – Reclamation

Reclamation processes are designed to produce high purity polymer resins from the plastic objects generated during sortation. A variety of separation techniques such as micro-sortation and solvent processes are under development to address the relevant issues involved. Micro-sortation processes utilize polymer properties such as density, surface energy / wetting, electrostatic and softening point to affect separation of ground or flake resins.

- Melt reprocessing

Reprocessing of generic thermoplastics recovered by sortation / reclamation from post-consumer discard streams and industrial scrap

regrind is done in conventional polymer processing equipment. The reclaimed resins are formulated in limited quantities with virgin resins and additives to obtain the desired properties in the plastic object being produced. Estimates of market penetration will depend on many factors in addition to cost, the nature of the market, desired properties for the plastic objects and the characteristics of the reclaimed resin will determine the permissible ratio of virgin / reclaimed resins, i.e. the recycle ratio.

## **1.2 Waste Polyethylene in Wire Industries**

Polyethylene (PE) has filled a long-standing need for a material which would effectively insulate electrical cables without introducing electrical losses at high frequencies. The nonpolar nature of the polymer makes it ideal for this purpose. Television, radar, and multicircuit long distance telephony might well have been impossible without such insulating materials. Weathering introduces polar impurities such as carbonyl groups into the polymer and must be carefully guarded against. In addition to the high-frequency uses, polyethylene is being more generally utilized for mechanical protection of wire and cables, where its chemical inertness and light weight are advantageous. About 10 % of the polyethylene produced is used for wire and cable insulation (Joseph, 1995).

In the wire industries, reprocessing waste material arising from normal processing operations is a common practice. This procedure known as primary recycling is done because it allows processors to maintain at high efficiency of the production cycle. Moreover, the recovery process comply with the most

recent environmental guidelines and directives that promote the reduction of waste arising at the source and the recycling of materials, whenever possible.

Although recycled polymers are generally used to produce goods for low value application, in primary recycling, it is possible to obtain high quality products. In fact, in this case, waste PE arising from the manufacturing operations is not contaminated.

The commodity plastic insulation is polyethylene, however, there are a large number of formulations including some that contain significant quantities of carbon black and reinforce fillers with purpose to enhance better properties which compare to virgin polyethylene. Therefore, it may be shown that properties of the products incorporating recycled polyethylene after the primary recycle were expected to drop but was believed able to retain the original virgin value or even perform higher.

### **1.3 Recycle PE**

Recycle PE (rPE) wire is collected from wire industries. Only the recycle PE wire insulation without copper and aluminum wire is delivered to the plant in bales. Sorting of scrap wire is required to ensure that a consistent, pure PE wire stream is attained. A purified stream of PE is slowly inserted into extrusion for re-pellet process. rPE is propelled continuously along a screw through regions of high temperature and pressure where it is melted, compacted and formed into a continuing stream of molten plastic.

rPE is fed into crusher for the size reduction step to form small pellet. Magnet between the crushing steps to remove any ferrous metal. rPE in pellet form is packed into 20 kg kraft paper bag.

#### **1.4 Problem Statement**

Waste plastics have created a series of serious environmental problems. Growing environmental awareness and reductions in available landfill capacity have prompted plastics recycling programs in most developed countries. Currently, however, only somewhere between 5 and 25 % of plastic waste is being reused. This is due to lack of incentives for reprocessing waste plastics. Recycle plastics show poorer mechanical properties after repeated recycling process, fluctuation of waste plastics properties, additional processes (sortation, reclamation and cleaning) and higher machine cost. Besides that, recycled plastic found to be not attractive in the market due to its limited applications.

The economic reuse or recycling of waste plastics is a great challenge nowadays. The research interest on this topic is fueled by environment concerns. There is a great need to find some value-added applications for waste plastic products. Polymer blending has proved to be one of the most simple and efficient means of developing high-performance composite systems. Blend composites whose performances surpass those of the initial polymers have served the base for solving a series of technical and economic problems. Thus, it is suggested to blend rPE with rubber. This plays an important role in the modern polymer industry not only for the development of new materials but also for practical recycling purposes.

Considering the wide spread application of ethylene propylene diene terpolymer (EPDM) with excellent weather and heat resistance, blending of rPE and EPDM was carried out in this study. In order to achieve a synergistic improvement in properties, such improvement in properties is reported in a number of reviews on polymer blends. For examples, ethylene propylene diene terpolymer has been blended with LLDPE (Kim et al., 1996). EPDM was proven to be compatible with HDPE due to the presence of ethylene group (Chandra et al., 1995). Thus, it is believed that rPE/EPDM blends would exhibit improved properties.

### **1.5 Research Objectives**

The primary objective of the study is to determine the feasibility of rPE in rPE/EPDM blends on a different composition with aim to develop thermoplastic elastomer materials. In order to obtain a basic understanding of the waste materials' characteristics and the effects when incorporated into EPDM, the mechanical, thermal, morphology and swelling behavior of these blends will be evaluated.

Besides, align to environment concerns, this study was intended to minimize the use of virgin PE (vPE) and partially replaced by rPE, which would not only generate interest in term of cost, but would be blending with other materials to create a new and unique material.

This work will also focus on the effect of dynamic vulcanization on vPE/rPE/EPDM blends and as a technological technique to get stable morphology and improved mechanical properties.

A comparison of carbon black (N330), Silica (Vulcasil S) and  $\text{CaCO}_3$  filled vPE/rPE/EPDM blends were made to assess the effectiveness of fillers in TPE blends.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Thermoplastic Elastomers

Thermoplastic elastomers (TPEs) are multi-functional polymeric materials that combine the elasticity of vulcanized rubber with processability of thermoplastics. They are processed like thermoplastics, yet perform like rubbers. TPEs are two-phase blends system: a rigid thermoplastic phase combined with a soft rubber phase, thermoplastic segments capable of forming rigid nanoscale domains or channels are covalently bonded to rubbery segments that provide a soft matrix in which the rigid domains reside. Due to the covalent linkages between the chemically dissimilar segments, the rigid domains can form a three-dimensional network of physical crosslink sites. The TPE, consequently, exhibits mechanical properties that are, comparable to those of a vulcanized (covalently crosslinked) rubber, with the exception that the network and, hence, the properties of the TPE are thermally reversible. Hence, they can be repeatedly melted and scrap reprocessed due to the absence of the chemical networks that normally exist in rubber. This feature makes TPEs ideally suited for conventional thermoplastic processes such as extrusion and injection molding (Bhowmick and Stephens, 1988).

The hard segments act as multifunctional tie points functioning both as physical crosslinks and reinforcing fillers, while the soft segments form an elastomer matrix which accounts for the elastic properties of TPE. Amorphous hard segments dissolve in the soft segments with increasing temperature. The

amorphous hard segments are understood to be the residual hard segments which exist in soft segments domains. Upon heating above the melting temperature of the hard segments, the polymer forms a homogeneous viscous melt, which can be thermoplastically processed, e.g. by injection moulding. Subsequent cooling again results in separation of soft segments and hard segments.

## 2.2 Polyethylene

PE is in the polyolefin family of semicrystalline thermoplastics (TPs). The largest volume plastics used worldwide, PE is available in many varieties with an equally wide range of properties. Some flexible, others rigid; some have low impact strength, whereas others are nearly unbreakable; some have good clarity, other are opaque, and so on. The service temperatures for PE range from  $-40$  to  $93$  °C ( $-40$  to  $200$  °F). In general they are characterized by toughness, excellent chemical resistance and electrical properties, a low coefficient of friction, near-zero moisture absorption, and good ease of processing. They are basically classified according to their density (Shedd, 1988).

There are others designed to meet different requirements, such as crosslink PE (XLPE), which by chemical or irradiation treatment becomes essentially a thermosetting resin with outstanding heat resistance and strength. There are various grades of PE can be found in market such as extra high-gloss HDPE (Fortiflex) produced by Soltex Polymer Corp. PE which retains its toughness at very low temperatures and performs at levels between the

commodity and engineering resins (Zemid) produced by Du Pont, and many others.

Table 2.1 shows three basic characteristics of PE determine their processing and end use properties: their density, melt index and molecular weight distribution (Jesse, 1992). Their range in density, from 0.890 to above 0.96 g/cm<sup>3</sup>, is a result of their crystalline structure. This difference accounts for their property variations. As one example, reducing PE's crystallinity increases its impact resistance, cold flow, tackiness, tear strength, environmental stress-crack resistance and heat-seal range. As its crystallinity is reduced, decreases occur in stiffness, shrinkage, brittleness temperature and chemical resistance.

Table 2.1: The effects on PE by increasing density, melt index and molecular weight

PE Property	Density	Melt Index	Molecular Weight
Tensile strength (at yield)	Increases	Decreases	
Stiffness	Increases	Decreases slightly	Decreases slightly
Impact strength	Decreases	Decreases	Decreases
Low-temperature brittleness	Increases	Increases	Decreases
Abrasion resistance	Increases	Decreases	
Hardness	Increases	Decreases slightly	
Softening point	Increases		Increases
Stress-crack resistance	Decreases	Decreases	
Chemical resistance	Increases	Decreases	
Melt strength		Decreases	Increases

### **2.2.1 High Density Polyethylene**

Today, medium density polyethylene (MDPE) and high density polyethylene (HDPE) are common in market. The higher the density, the higher the polymers are in temperature-use rating. The higher density polymers have higher stiffness and superior physical properties. The purity of these polymers was improved and the molecular weight distribution was controlled so that the polymer flow could be improved by narrowing the melt-temperature range. This property is significant important in injection and blow molding. LDPE using high-reaction pressure technology provided scientists with the opportunity to use the simplest unsaturated hydrocarbon monomer in a number of complex permeations to produce a wide range of commercially useful polymers with different properties.

### **2.2.2 Polymerization Process**

The polymerization processes developed by Karl Zeigler, the Phillips Petroleum Co. and the Standard Oil Co. of Indiana had in common the polymerization of ethylene at relatively low reaction pressures and temperatures with the use of a stereospecific catalyst. The resulting linear polymers were significantly higher in density than the products produced using the high pressure technology. This difference is due to the repeating polymer chain regularity and thus the efficient use of "molecular space". Specific control the extent of the reaction conditions and the type of catalyst leads to the variation of the molecular weight, or length of the polymer, and molecular-weight distribution.

The key to the wide range of HDPE materials offered by the plastic producers rests on the control of these three parameters: density, molecular weight and molecular weight distribution. There are many secondary characteristics that can be controlled to provide the final refinement of the polymer design (Billmeyer, 1984).

Commercial low pressure polymerization of ethylene with stereospecific catalyst takes place via three methods with a variety of catalysts. These methods are the result of much individual company development of the original three catalysts types (Billmeyer, 1984):

Ziegler – aluminum trialkyl / metal halides

Phillips – chromium oxide on a silica base

Standard Oil – molybdena on alumina support with sodium hydrides

The methods of a polymerization are slurry, solution and gas phase. The original and currently most widely used process is the slurry technique. In this case, the ethylene gas is fed to a stirred reactor in which a liquid hydrocarbon diluent containing the suspended catalyst particles allows even heat and mass distribution for the polymerization process to occur. The polymer is formed as a colorless particle in suspension. Typical process condition would be 500 to 600 pounds per square inch pressure and 200 °F to 250 °F (93 °C to 120 °C) temperature. The polymer is separated, the catalyst removed, the catalyst removed, and the resin is dried as a coarse particle. The polymer is then compounded with additives to produce a pellet or it can be supplied as an unpelletized powder, sometimes called fluff or granular. The process can be continuous or batch (Das, 1986).

### **2.2.3 HDPE Processing**

The HDPE supplied by resin producers normally will include processing and long-term heat stabilizers added for use during the manufacturing pelletization process to the degree dictated by the application for which the resin is designed. The addition of more than the basic stabilization usually is not needed unless higher than normal temperature and shear conditions are expected. In the event that several recycling cycles are anticipated for the product, additional stabilization would be recommended. In this case, the combination of a sterically hindered phenol as the primary stabilizer and an organic phosphite has proved to be the most efficient and cost-effective solution. The level of addition would be in the 1000- to 3500 parts per million ranges (Fried, 1995).

The polymer processes in the 190 to 245 °C range, depending on the process and the residence time, may require more antioxidant. Sustained processing above 250 °C is not recommended. Screw design varies widely but compression ratios of 2.5:1 and 3:1 are not uncommon with the use of different mixing-head designs. PE materials are thermally stable and do not decompose to give off harmful products.

### **2.2.4 HDPE Application**

The higher the density the higher the polymers are in temperature-use ratings. The higher density polymers have higher stiffness and superior physical

properties. It was eventually discovered that a wide range of products with controlled density and crystallinity could be manufactured that would have vastly improved end-use and processing properties. The purity of these polymers was improved. Also, the molecular weight distribution was controlled so that the polymer flow could be improved by narrowing the melt temperature range. This property is of significant importance in injection molding and in the manufacture of blow film for packaging uses.

HDPE has achieved wide application because of the wide selection of properties, its economical manufacturing process, the ease of processing, its excellent chemical resistance, the good electrical and dielectric properties and its light weight. Applications are summarized in the following lists, depending on the processing technique.

- Extrusion

Pipe and tubing, wire and cable, film and sheet.

- Blow molding

Fuel tanks, containers for industrial chemicals; milk, water and juices; household chemicals; lawn and agricultural chemicals; toys; oil and automotive fluids; and automotive hollow parts

- Injection molding

Tote boxes, buckets, beverage crates, housewares, toys, pallets, containers, closures

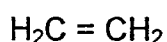
- Rotational molding

Large hollow containers (e.g., gas tanks), toys, trash-handling equipment

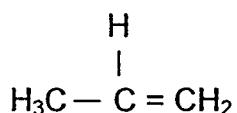
### 2.3 Ethylene Propylene Diene Terpolymer (EPDM)

EPDM rubber is usually called EPDM. This designation, which follows a nomenclature convention endorsed by the American Society for testing materials, the International Institute of Synthetic Rubber Producers, Inc., and the International Standards Organization, applies to the more common, sulfur vulcanizable product which includes in the rubber molecule a minor percentage of a diene monomer in addition to ethylene and propylene. The basic for the letter designation, EPDM, is: E for ethylene; P for propylene; D for diene; and M for methylene, which are the repeating units ( $\text{CH}_2$ ), or 'vertebrae' in the 'spine' of the polymer (Hanafi and Azanam, 1998).

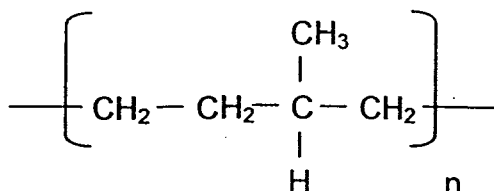
The structure of the regular, alternating amorphous copolymer of ethylene



and propylene



can be written



### **2.3.1 EPDM Properties**

EPDM is a durable geomembrane with a 20 year proven performance history in exposed applications, such as ponds and lakes, canals, fish stock ponds. It can be self-installed in residential water features.

EPDM exhibits high tensile strength and excellent resistance to punctures, ultra violet radiation, weathering and microbial attack. It is also highly flexible material with a low co-efficient of thermal expansion and contraction, enabling it to lay flat in a wide range of temperatures and terrains thereby conforming well to irregularities in the subgrade. EPDM is manufactured in panels up to 50 ' wide to 200 ' long, is installed as liners, caps and covers in environmental containment applications worldwide.

### **2.3.2 EPDM Application**

EPDM is ideal for outdoor applications because of its excellent resistance to ozone, oxidants, and severe weather conditions. Other outstanding characteristics of EPDM include excellent color stability, heat resistance, and dielectric qualities. It offers many of the advantages of neoprene, at a lower cost.

A relative newcomer to the geomembrane industry, this product exhibits excellent elongation characteristics and does not require a soil cover. EPDM is delivered to the project in panels that are up to 50 ' x 200 ' (10,000 sq.ft.). This product is available in custom sizes as well. 45 mil Pond Guard™ (Firestone Building Products) EPDM is gaining popularity in the custom waterfall and decorative pond market due to its high degree of flexibility. Its resistance to

weathering and ultra violet exposure comes into play around the waterline where the membrane can be exposed with rising and falling water levels. Its ability to expand and contract, while maintaining its integrity as water levels and temperatures change is another design asset.

EPDM is slightly lower than both natural rubber and polyisoprene in resilience and tensile. It is not recommended for applications involving petroleum derivatives, generally attacked by mineral oils, solvents, and aromatic hydrocarbons (Scott, 1995).

## **2.4 Dynamic Vulcanization**

Dynamically vulcanized blends, first described by Fischer (1973), have been widely used in the plastics and thermoplastic elastomer (TPE) industries because of their technical advantage in processing as well as their versatile end-use properties. Ever since Goodyear's first experiments in heating rubber with small amounts of sulfur, this process has been the best and most practical method for bringing about the drastic property changes described by the thermal vulcanization, not only in natural rubber but also in the diene synthetic elastomers. It has been found since, however, that neither heat nor sulfur is essential to the vulcanization process. Rubber can be vulcanized or cured without heat by the action of sulfur chloride, for example. A large number of compounds which do not contain sulfur can vulcanize rubber; these fall generally into two groups, oxidizing agents (selenium, tellurium, organic peroxides, nitro compounds) and generators of free radicals (organic peroxides,

azo compounds, many accelerators, etc.). Thus it is clear that there is no single method or chemical reaction of vulcanization (Hofmann, 1967).

Since the chemical reactions associated with vulcanization are varied and involve only a few atoms in each polymer molecule, a definition of vulcanization in terms of the physical properties of the rubber is necessary. In this sense, vulcanization may be defined as any treatment that decreases the flow of an elastomer, increasing its tensile strength and modulus, but preserves its extensibility (Hofmann, 1967). There is little doubt that these changes are due primarily to chemical crosslinking reactions between polymer molecules. As might be onset of these crosslinking reactions; tensile strength does indeed change tenfold during curing, but this is evidence of the profound alteration of polymer properties by the process. Tests based on melt flow are most sensitive to initial crosslinking reactions and are widely used in the rubber industry.

Although vulcanization can takes place by heating the rubber in the presence of sulfur alone, the process is relatively slow. It can be speeded many fold by the addition of small amounts of organic or inorganic compounds known as accelerators. Many accelerators require the presence of other chemicals known as activators or promoters before their full effects are realized. These activators are usually metallic oxides, such as zinc oxide. They function best in the presence of a rubber-soluble metallic soap, which may be formed during the curing reaction from the activator and a fatty acid. The most efficient combination of chemicals for sulfur vulcanization includes sulfur, an organic accelerator, a metallic oxide, and soap.

It is convenient to group vulcanization reactions into two categories: nonsulfur vulcanizations, in which peroxides, nitro compounds, quinines, or azo

compounds are the curing agents; and vulcanizations brought about by sulfur, selenium, or tellurium.

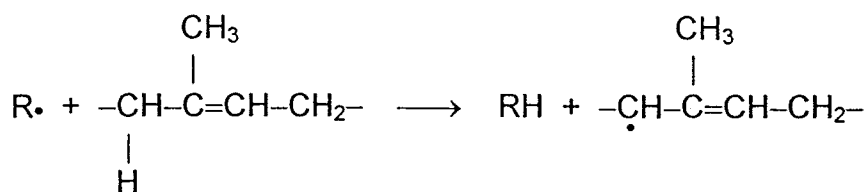
The understanding of vulcanization has been considerably advanced by the recognition of the following two concepts which arise from the analogy of vulcanization with the crosslinking and (oxidative) degradation of simple olefins (Hofmann, 1967):

- a. The point of initial attack in most vulcanization reaction is a hydrogen atom on a methylene group alpha to the double bond itself.
- b. Free radical mechanisms are involved in almost all cases.

#### 2.4.1 Nonsulfur Vulcanization

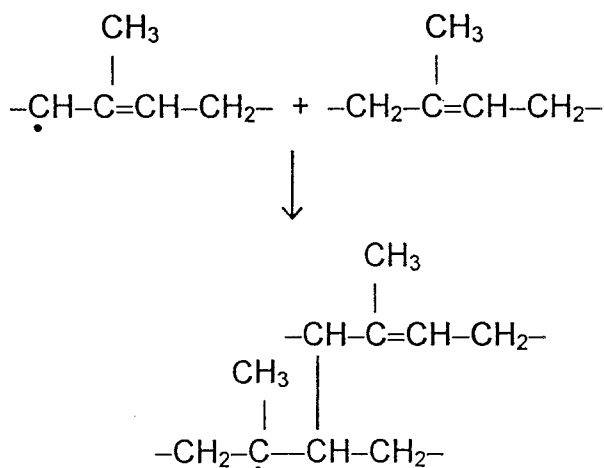
From the two concepts just given, the following scheme has been developed for nonsulfur vulcanization:

- a. A free radical  $R\cdot$  is formed by the decomposition or oxidation of the curing agent, or as a step in the oxidative degradation of the rubber.
- b. This free radical initiates vulcanization by abstracting a hydrogen atom from one of the  $\alpha$ -methylene groups (in natural rubber the methyl side group directs the attack to the methylene group nearest it):



- c. The rubber free radical then attacks a double bond in an adjacent polymer chain. This results in the formation of a crosslink and the

regeneration of a free radical in a recent analogous to propagation in an addition polymerization:



Vulcanization may continue by several such propagation steps. Chain transfer may also occur. Termination probably occurs by reaction of the rubber free radical with a free radical fragment of the curing agent. In contrast to addition polymerization in a fluid system, the termination reaction between two rubber free radicals is considered unlikely because of the low probability of two such radicals coming into position to react, owing to the high viscosity of the medium (Ismail, 2000).

## 2.4.2 Sulfur Vulcanization

Not all the reactions which take place in sulfur curing are well understood. It is clear that the sulfur can undergo a variety of reactions (Hofmann, 1967). Some, but not all, of it goes to form sulfide or disulfide crosslinks between chains, e.g:



### 2.4.3 Physical Aspects of Vulcanization

Vulcanization of the type just described takes place when 0.5 – 5.0 parts (by weight) of sulfur is combined with 100 parts of rubber. If the reactions are allowed to continue until considerably more sulfur has combined (30 – 50 parts per 100 parts rubber), a rigid, nonelastomeric plastic known as hard rubber or ebonite is formed. Tensile strength reaches a maximum, with elongation remaining high, in the early soft cure region; then both fall to much lower values with increasing amount of combined sulfur.

The region of maximum tensile properties in the neighborhood of 5 – 10 parts combined sulfur is known as the region of optimum cure for this mix. Beyond this point the stock (i.e., mixture) is said to be overcured and is likely to be leathery, i.e., stiffer and harder than at the optimum cure but weaker and less extensible. At high proportions of combined sulfur the strength of the material increase again, and the elongation becomes very low as the hard rubber region is reached.

Many properties of soft vulcanizates, including tensile and tear strength, stiffness, and hardness, go through a shallow maximum as the cure time is increased. Others, such as elongation and permanent set, drop continuously. The effect of increasing temperature is, as expected, to move the curves to shorter times. Experiments in which the composition of the mix is varied show that the initial rise in tensile strength is accompanied by the rapid incorporation of sulfur in the rubber, and that, as the rate of sulfur addition decreases, the rate of increase of tensile strength begins to decline. It is also known that the total amount of combine sulfur does not measure the extent of change in physical

properties during cure, and that the ratio of sulfur combined to double bonds used up varies widely from one mix to another.

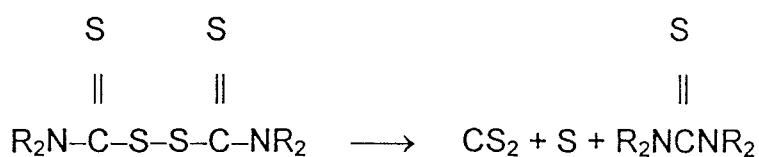
These facts suggest that processes of crosslinking and degradation occur simultaneously during vulcanization. Additional evidence for this view arises from the fact that badly overcured stocks may undergo reversion, i.e., become soft and tacky with notable loss in strength. Such stocks resemble oxidatively degraded rubber. Reversion differs from overcuring in that it usually takes place on prolonged heating when not enough sulfur is present to get into the region of leathery cures.

#### **2.4.4 Accelerators**

Until about year 1900, rubber vulcanization was a slow process. Large excesses of sulfur over the amount required for optimum cure were used. The remaining free sulfur diffused to the surface of the stock and caused bloom. The curing time was several hours, despite the fact that lead, calcium, magnesium, or zinc oxides (inorganic accelerators) speeded the reaction slightly.

The rubber industry was revolutionized by the introduction of organic accelerators for vulcanization. These include sulfur-containing compounds such as thioureas, thiophenols, mercaptans, dithiocarbamates, xanthates, trithiocarbamates, dithio acids, mercaptothiazoles and mercaptobenzothiazoles, and thiuram sulfides, plus a few nonsulfur types such as ureas, guanidines, and aldehydeamines.

Except for the generalization that accelerators are likely to contribute to vulcanization by initiating free radical chains or by abstracting protons, little is known about their specific action in speeding up vulcanization. Some accelerators, such as thiuram disulfides, are known to dissociate thermally at vulcanization temperatures:

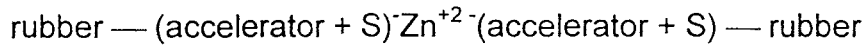


The sulfur is consumed in promoting vulcanization. Since the mechanism may involve free radical steps, further action is possible. Zinc salts of mercaptobenzothiazole and the dithiocarbamic acids may act similarly. On the other hand, an accelerator such as mercaptobenzothiazole itself, which is known not to decompose or to react with olefins at curing temperatures, must always be used with an activator.

#### 2.4.5 Activators

The presence of basic metallic oxides or salts of lead, calcium, zinc, or magnesium appears to be necessary to obtain the full effect of almost all organic accelerators. Solubility of the compound is important; for this reason the oxides are used with organic acids (stearic acids, rosin), or the soaps (stearates, laureates) of the metals are utilized instead. Aside from the specific need for an activator with an acidic accelerator such as mercaptobenzothiazole, as just

noted, the presence of the oxide appears to be important in determining the type of crosslinking reactions which take place. These appear to be strong ionic bridges of the type formed during vulcanization.



In cases in which the activator is important, these bridges may contribute substantially to the crosslinking in the vulcanizate.

## 2.5 Fillers

Many plastics are virtually useless alone but are converted into highly serviceable products by combining them with particulate or fibrous solids. Historically, the primary purpose for using a filler in a resin composite has been extend the plastic and make the end product more cost effective. Nearly all of the fillers do more than just take up space and extend the polymer resin. They will always modify the mechanical properties of the final composite, often improving such properties as flexural modulus, temperature resistance, and warpage. For this reason, they are more properly called functional fillers, mineral additives, or reinforcing agents.

A mineral-resin composite is made up of two very dissimilar materials. The resin is organic in nature, consisting of covalent bonds between atoms. The mineral is inorganic with ionic interactions between atoms. Resin surfaces are hydrophobic; mineral surfaces are hydrophilic. Other differences also exist, as in surface tension, coefficient of linear expansion, elasticity, and so on.