CHAPTER 1
INTRODUCTION

The environment forms the background and support system on which all life forms sprout and grow. Until recently what affected environment were exclusively the natural phenomena, the complex seasonal changes together with some short-term natural upheavals like cyclones, earthquakes, floods and the like. In recent times with advances in science and technology, man made newer and highly versatile materials with attractive properties and almost infinite stability. Synthetic polymers are a class fall under this category. In a very short time, proliferation of these materials into the various aspects of the human life has reached to such an extent that these form one of the biggest threat to environment, as the nature meet its limited resources failed to absorb the accumulated waste from these materials. Discarded and scrap tyres and other rubber products prepared from different elastomers contribute one of the larger source of pollution and calls for urgent remedial action.

1.1 Reclaimed Rubber

According to recent estimates the world's rubber scrap amount to 10 million tons. Among the scrap rubber, used and scraped tyres form a major chunk. Earlier these were disposed of as landfill. Another method was to reduce them to crumbs by a variety of methods such as cryogrinding, irradiation and pulverization. Other disposal methods were pyrolysis to recover raw materials and incineration for energy recovery. Incineration of tyre products leads to release of large quantity of carbon and toxic chemicals. This procedure change the state of pollutant from solid to gas, along with carbon dust.
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Yet another route for disposal of these materials is to recycle them i.e. to convert them to some form that can be used to substitute virgin rubbers at least partially in rubber compounds. The rubber reclaiming industry started shortly after 1844\(^7\), the year in which Good Year obtained patent for the vulcanization of natural rubber with sulphur\(^8\). In spite of many efforts to reverse the vulcanization process and remove the sulphur no true devulcanization of the rubber hydrocarbon could be demonstrated\(^9\). Recently techniques have been developed to recycle the waste and scrap rubbers to reclaimed rubber. The motivation for the recycling was primarily the generation of useful rubber compounding material.

Application of heat and chemicals to ground vulcanised rubber leads to substantial depolymerisation which leads to the regeneration of the rubber compounds to a soft, plastic - processable state.\(^{10-12}\) A few other methods also have been patented.\(^{14-15}\) Rubber so regenerated for reuse is commonly known as Reclaimed Rubber. When the same processes is conducted on scrap and used tyres resultant material is known as Whole Tyre Reclaimed Rubber (WfR). WfR is a good source of rubber hydrocarbon and carbon black filler. It contains approximately 50% of rubber hydrocarbon and 30 % carbon black and can easily be processed, compounded and vulcanised along with other rubbers.

Recently, vulcanised rubber powders have been arousing interest as an active or passive ingredient of thermoplastics. Formulations including fine-grained rubber yield products that show enhanced elasticity, vibration absorption, porosity and anti slip behavior.

Reclaiming processes impart necessary degree of plasticity to vulcanised rubber there by enabling it to be blended with natural rubber or synthetic rubber.\(^{10}\) Reclaimed rubber is used in rubber compounds to reduce cost and also to improve the processing characteristics. It mixes faster than virgin rubber because all the fillers of the original product are already incorporated and hence the power consumed for mixing is less. The three dimensional nature of the rubber fragments and the reduced nerve of the reclaim imparts rate and gauge stability to the calendared and extruded stocks. But mechanical properties of the reclaimed rubber are very inferior to
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those of the virgin rubber due to the degradation of rubber during reclaiming. Hence reclaimed rubber is added in small percentage to virgin rubbers.

Several workers have explored possibility of utilising the rubber hydrocarbon available in the reclaimed rubber. Grant Crane et al\(^{49}\) reported that scrap rubber vulcanizates can be depolymerised to give a product known as 'Depolymerised Scrap Rubber (DSR), which could be used as a rubber compounding ingredient and to extend fuel oil to yield a fuel which could be utilized in conventional boilers. Burgongenoe et al\(^{50}\) reported that mechanically ground scrap rubber having a broad spectrum of particle size could act as a cheap filler having approximately the same effect on the properties as soft kaolin clay. According to Bleyie\(^{51}\) as particle size of ground rubber decreases, mixing behavior and mechanical properties of vulcanizates are improved. Swor et al\(^{52}\) showed that the utilisation of dry rubber reclaim in SBR improved the cure rate of SBR vulcanize. Kazarnowick et al\(^{53}\) found that blends of reclaim or ground vulcanizates with NR had processing as well as economic advantages. Accepta et al\(^{54}\) showed that reclaimed rubber in the form of cryoground rubber could be blended in a two roll mill and compounded with common rubber ingredients. They developed a process to improve quality of scrap rubber powder recovered from old tyres.\(^{55}\) Phadke et al\(^{56}\) reported that physical properties of reclaimed rubber vulcanizate were inferior to those of control vulcanizates. The poor physical properties and processing characteristics could be improved by blending with fresh rubber. However high proportion of reclaimed rubber increased the stiffness and caused brittle failure. The addition of cryoground rubber caused changes in curing characteristics and showed detrimental effects on most of the vulcanizate properties.\(^{57}\) Higher dose of curatives and addition of reinforcing carbon black made up the loss in physical properties. Reclaimed rubber could partially replace butyl rubber in the manufacture of inner tube.\(^{58}\) Margryta\(^{59}\) studied the processing and mechanical properties of rubber vulcanizates containing reclaimed rubber and concluded that the addition of reclaimed rubber resulted in some deterioration of mechanical properties but improved thermo-oxidative stability and decreased price of vulcanizates. Waste
rubber powder (WRP)/SBR/Black compound has been studied by Zhao et al. (60) Addition of WRP ≤ 20 phr with a grain size ≤ 160 µm did not significantly affect the compound properties. The presence of waste rubber powder in SBR resulted in improvements in its tear strength and elongation at break. (61) Modification of rubber powder improved the mechanical properties of rubber compounds. Decrease in scorch time and maximum rheometer torque were observed when ground vulcanizate were added to SBR Compounds. (62) It has been reported that 20 % of reclaimed rubber could be used in place of NR in the blend without greatly affecting mechanical properties of the products. (63) The use of reclaimed rubber in powder form gave rubber blends better mechanical properties. The presence of NR latex modifiers improved mechanical properties and thermal stability of NR/reclaimed rubber blends. Cure and physical properties of EPDM vulcanizates containing ground rubber were studied with respect to particle size and amount of ground rubber by Seo et al. (64) The mechanical properties of the rubber blends containing post consumer recycled polymer and NR, Bromobutyl rubber, isobutylene rubber or EPR were studied by Theodore et al. (65) Gibale (66) et al studied the effect of black filled SBR ground vulcanizates on the tensile and tear strength of rubber compounds. They reported that the compound exhibited reduced tensile strength and enhanced tear strength.

1.2 Types of Reclaimed Rubber

Different types of reclaimed rubber are in use and the most important ones are the following

1.2.1 Whole tyre reclaim (WTR) It is the most important reclaimed rubber. WTR contains about 50 % of rubber hydrocarbons and the rest consists of minerals fillers, carbon black, softeners etc, which remain unchanged during the reclamation process.

1.2.2 Minimum Staining Reclaim(MSR): Minimum staining reclaim is used in some times in place of whole tyre reclaim. As the name implies it has a much lower tendency to stain either by migration or contact. This reduction in staining characteristics is achieved by the use of activated
carbon, non-staining oils and by selecting tyres containing a higher proportions of natural to synthetic rubber.

1.2.3 Drab and Coloured Reclaims: These reclaims are made from non-black scraps. These are usually made by the digester process. Digestion is carried out with some caustic if fibers are present and digestion is carried out at 195 °C for several hours.

1.2.4 Butyl Reclaim: Butyl reclaim is made from butyl inner tubes. A modified digester process is used and precautions are taken to avoid contamination by natural or SBR rubber as they exert adverse effect on the curing characteristics of the butyl rubber. Extensive control test are necessary to ensure that curing properties are satisfactory. The nerve of butyl reclaim is much reduced compared to that of the original polymer. Hence compounds containing butyl reclaim mix, calender and extrude faster and more smoothly than similar compounds based on virgin rubber.

1.3 Production of Whole Tyre Reclaim

Reclaiming and devulcanization enables the conversion of vulcanised rubber into new rubber compounds that can be compounded and re-vulcanised, much like virgin rubber, into relatively high quality polymers. Reclaiming and devulcanization are related, but quite separate processes. Reclaiming generally result in the scission or fracture of long chains to produce rubber of lower molecular weight while devulcanization targets the cross links in vulcanised rubber (i.e. C-S, S-S bonds), which are cleaved so that the rubber can be re-moulded. Traditionally, the rubber molecule and cross-links are broken by catalytically accelerated oxidation of the rubber at high temperature. Diarylsulphide catalysts are usually employed which allow the rubber to be reclaimed at a lower temperature and at a faster rate.\(^{(67)}\)

Different types of techniques are applied for the production of tyre recycling. Treating scrap-vulcanised rubber with devulcanizing agent and plasticizers under pressure and heat and simultaneously working the material, subsequently produces reclaimed rubber. Devulcanizing agents include xylyl mercaptan, dixylyl disulphide, dodecyl mercaptan, pine tar, coal tar, naphtha, etc.
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Common to most of the reclaiming process, removal of metals, such as beads in tyres, and fibers is conducted prior to devulcanization. Powerful corrugated rolls or crackers operating at differential speeds tear the tyres apart exposing the fabric and the bead wire. The material is subdivided into 1 in. size or less. Magnets remove ferrous metal, and air flotation table removes non-ferrous metals. However fine wires from tyres containing steel fabric are extremely difficult to remove once they get into the process; Such tyres are customarily removed by a metal detector prior to cracking. The fiber removal is frequently associated with a particular process.

There are a number of commercial processes for whole tyre reclamation. Important processes for whole tyre reclaiming are

1.3.1. Digester Process (Neutral or Alkali)\textsuperscript{(68,69,70)}: - For the digester process alkali digestion or neutral digestion method de-beaded tyres and scraps are cut into small pieces. The materials are mixed with a peptizer and heavy naphtha. The crumbs are then charged into spherical autoclave with required quantities of water containing caustic soda for the purpose of alkali digestion or zinc chloride for the neutral process. Steam pressure and amount of air or oxygen in the autoclave greatly influence the period necessary for the reclamation. On completion of the process, the pressure is released, the content is discharged in to water, centrifuged, pressed to squeeze out water and dried. They are finally passed through a two-roll mill for a refining process during which mineral fillers and oil may be added to give a product for a standard specific gravity and oil extension.

1.3.2. Thermal Process\textsuperscript{(71)}

This procedure gained popularity in Europe during the World war. It involves conjoint destruction of fibers and softening of vulcanised rubber in a medium of superheated steam. Temperature employed is substantially higher than those used in the digester method. Tyre scrap is loaded into steam autoclaves in which electric heaters are fitted. Steam is raised to low pressure and the electric heaters located in the autoclaves increase the temperature to 220-250°C. Tyre scrap is charged into the digester without fiber removal. It is found that thermal reclams are inferior to those prepared from more conventional process.
1.3.3. **Reclaimator Process** 

Reclaimator process is the only commercially successful continuous technique for the devulcanization of the scrap. Tyres are ground, the metal and fiber are mechanically separated and then the rubber is further ground to fine particle size. This fine ground rubber and the various reclaiming agents such as xylol or other mercaptans are all metered into a blending system and conveyed to the reclaimator. Ground vulcanised rubber heated in a temperature range of 120-200°C undergoes a rapid initial increase in plasticity and on continued heating passes through an inversion point. After prolonged heating, a further but slower increase in plasticity is attained.

1.3.4. **Pan Process**

The pan process is the oldest and simplest reclaiming methods and is based on heating rubber crumb at temperature in the range 150°-180°C in the presence of saturated steam, reclaim oil and catalyst. The presence of oxygen is also necessary for the process to work. The mild condition results in superior reclaim properties due to the lower content of thermally degraded materials.

A heater is a large, single-shell horizontal pressure vessel or autoclave. The ground rubber is mixed with reclaiming agents in an open ribbon mixer then placed into containers rolled into the vessel. The main consideration is to allow an even penetration of heat on the mass of rubber. To achieve this uniform steam penetration, shallow pans or boats equipped with hollow metal pipes or inverters “V” sections are used as the stock containers. Live steam at pressures of 100 to 250 psi with cycle time of 5 to 12 hours are typical.

This process yields good results with some types of rubber scraps such as butyl inner tubes and marginally quality with other types such as fine ground tires or low-specific gravity natural-rubber scrap.

1.3.5. **Chemical devulcanization**

The chemical devulcanization method are reported to uncouple sulphur linkages in vulcanised rubber at mild temperatures using the Sekher-Kormer method.
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Sotnikova (SKS) reaction. This is a mechanico-chemical reaction involving a proprietary reactant, which can cleave the sulphur bond in the rubber allowing the resulting compound to be re vulcanised without addition of vulcanizing agent. This process has been commercialised by STI-K Polymers and is known as De – Link™ process (74).

The figure (1.1) shows SKS reaction leading to uncoupling of the sulphur links and then on subsequent moulding, reformation of cross links with less sulphur atoms occurs. The rubber produced by this process therefore shows characteristics such as increased reversion resistance, lower compression set, higher resilience and lower rolling resistance. This process gives a decrease in tensile strength of the remolded rubber but it remains within acceptable values. Virgin vulcanized rubber with tensile strength of 25-28 MPa shows tensile strength of 16-18 MPa after the De-Link process. The recycled material can give 50-85% of rubber's original properties.

Figure 1.1 The devulcanization of scrap rubber by the De-Link process catalytically uncouples the polysulphidic (Sx-n and Sn) cross links re vulcanised product with shorter cross links.

1.3.6. Ground Rubber

The technology involves grinding rubber articles into crumb and then reusing it as particular filler in low-performance rubber articles and as a toughing agent in asphalt. Up to 60% of the original weight of a tyre can be recovered as a powder known as Ground rubber tyres (GRT).
Many rubber manufactures currently carry out primarily recycling on a small scale by adding in-house ground rubber scrap to fresh compounds. This can be done at loading of up to 10 % wt. However beyond this, the physical properties of the rubber end product begin to deteriorate since the rubber crumb acts primarily as an inter filler.

Untreated ground rubber crumb when added to virgin rubber products increases viscosity and decreases tensile strength. Hence it is used in non technical applications such as flooring, mats and footwear. These poor proprieties can be attributed to lack of adhesion across the crumb – matrix interface. Thus, untreated rubber crumb is mainly used as low loading filler extender in application were a modest reduction in properties is acceptable. Small size crumbs do allow greater loading levels but at greater expense due to the increased granulation involved. The smallest particle size rubber crumb commercially available at present is 75 μm.

The addition of crumb rubber, even at low concentration, to the virgin rubber, generally results in a decrease in physical properties.\(^{73,77}\) It has been shown that the addition of 10% rubber crumb to a virgin compound leads to 15 % reduction in tensile strength.\(^{78}\) Phadke\(^{76}\) attributed the poor properties of virgin rubber –rubber crumb vulcanizates to poor adhesion and the relatively large crumb particle size.

It has also been found that the addition of ground rubber crumb to virgin SBR compounds leads to decreased maximum rheometer torque and increased tendency to scorch.\(^{79}\) These effects are attributed to the migration of the curatives from the matrix to rubber particles. The migration of sulphur into ground vulcanised rubber particle triggers the release of bound accelerators fragments from the rubber crumb and these diffuse into the matrix speeding vulcanization.\(^{112}\)

In the case of tyres rubber crumb can be used as low volume filler in new tyres but only in the tread and the sidewall. The loading of scrap crumb in these applications is restricted to a maximum of 1.5 weight % because of the chemically combined sulphur cross-link it contains.\(^{80}\)

The use of untreated rubber crumbs as filler in tyres at higher loading causes a lowering of tensile strength, an increase in heat build up and
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Increase oxidative ageing. It has been demonstrated that in a new tyre, for each percentage of recycled rubber, there is approximately 1% reduction in the life of the tread. In addition, rolling resistance of the tyres is increased and this results in greater fuel consumption.\(^{(8)}\)

1.4. Rubbers

1.4.1. Nitrile rubber (NBR)

Nitrile rubber is a product of copolymerisation of acrylonitrile and butadiene developed in the 1930. The commercial product developed in Germany\(^{(82)}\) initially was known as Buna N. The discovery occurred during an effort to obtain useful rubber via emulsion polymerisation of butadiene and it was shortly thereafter that the combination of properties provided by nitrile elastomers was revealed. In addition to providing good strength properties in the vulcanizates these elastomers also out performed ordinary rubbers in oil and gasoline resistance, abrasion resistance, gas permeability and thermal stability. These properties stem from the highly polar character of the acrylonitrile group. A review\(^{(83)}\) gives worldwide production of nitrile rubber.

Various workers explored the utility of blends of nitrile rubbers with different polymers. K.E. George et al studied the NBR/PVC blends.\(^{(84-86)}\) Sreeja and Kutty reported blends of nitrile rubber with reclaimed rubber.\(^{(87-88)}\)

1.4.2 Styrene Butadiene Rubber

Styrene butadiene rubber is a copolymer of styrene and butadiene. At present SBR constitutes about 40% of the total synthetic rubber. Formulations of the monomers are 70-75% butadiene and 30-25% parts of styrene. Polymerisation may be done at 40-50°C giving hot SBR or it may be conducted at lower temperature 5°C or even at lower temperature (-10 to 15°C). The product of low temperature polymerisation is called cold SBR rubber.

SBR containing 30-50% bound styrene is useful as rubbers in the design of tread compounds for tyres with improved road grip. These rubbers are seldom used alone; they are blended in appropriate proportions
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with normal SBR or NR for the production of hard vulcanizates. Copolymers with still higher bound styrene contents (up to 90%), better known as high styrene resins, serve as useful compounding ingredient for imparting improved hardness and stiffness to NR and SBR vulcanizates.

SBR is much superior to NR with respect to ageing and ozone resistance. However cuts and cracks are faster in SBR than in NR. SBR is also characterized by relatively high hysteresis or heat build up and poor resilience. The abrasion resistance of SBR is as good as that of natural rubber or slightly better.

The original development of SBR was for the production of tyres. A good balance of desirable properties, favorable production economics of the raw rubber grades and easy processing characteristic contributed to the growth in popularity of SBR.

Large number of workers studied different types of blends of styrene butadiene rubber with other rubbers. K.E George et al studied properties of blends of styrene butadiene rubber with NBR. (81) Rani J. et al studied properties of blends of natural rubber with styrene butadiene rubbers. (89-90)

1.4.3. Chloroprene rubber (CR)

Chloroprene is the world’s first commercial synthetic rubber made available in the market by Dupont in 1935. The commercial elastomeric polymer and monomer of chloroprene i.e. 2-chloro 1,3, butadiene is known in the trade by the generic term Neoprene. The monomer is conveniently prepared from butadiene in two steps. The first step is the chlorination of butadiene to 3, 4 dichlorobutene-1 which is dehydrohalogenated to chloroprene by heating with aqueous alkali in a subsequent step. The molecular structure of chloroprene polymer is primarily trans 1,4 chloroprene units (88-92 %). But three other configurations viz cis 1,4 (7-12%), 1,2 (1.5%) and 3,4 (1%) also occur. 1,2 addition of chloroprene results in polymer having some chlorine available in allylic position. This labile form is believed to be the main site of vulcanization. The degree of crystallinity in chloroprene is largely depending upon the amount of trans configuration in the polymer. Presence of chlorine atom in the monomeric
unit makes it a polar polymer. Therefore, by comparison with non-polar diene rubber, CR has a better resistance to swelling in mineral and vegetable oils and fats. Chlorine atom also imparts to chloroprene better flame, weather and ozone resistances.

Vulcanization of CR, as commercially practiced, is much different from that of other diene rubbers. Vulcanization is conveniently accomplished by heating with zinc oxide and magnesium oxide. Five parts of ZnO and with four parts of MgO per 100 parts of chloroprene is a standard curative. The use of small portions (0.5 to 1.0 parts) of certain other chemicals such as ethylene thiourea and antimony sulphide gives faster and effective press cure at 150°C.

Chloroprene may be vulcanised with sulphur and accelerator. However product exhibits poor ageing resistance. Cross linking with sulphur probably occurs at the double bond in the linear polymeric chain rather than at the allylic position. In contract to most synthetic rubbers, unfilled chloroprene vulcanizate exhibit high tensile strength. The resilience of pure gum vulcanizate of chloroprene is lower than that of similar gum vulcanizates of NR. With the increase in filler loading in each case, however, the resilience drops, though to a lesser extent for CR system.

Blends of chloroprene rubber with other polymers was studied by different workers. Rani.j et al studied blends of chloroprene with polyvinyl chloride.(92-93)

1.4.4 Butadiene Rubber (BR)

Three types of Polybutadiene are manufactured. The high cis (97%) 1-4 Polybutadiene polymerized by Ziegler-Natta type catalyst system consisting either a cobalt or nickel salts or organic compounds of these metals, with alkyl aluminum halide. The medium high-cis (92%) 1-4 Polybutadiene, also polymerized by a Zeigler Natta type catalyst system, transition metal used being here is titanium instead of cobalt or nickel.) The low cis (around 40 %) 1-4 Polybutadiene polymerizes in the presence of alkyl lithium initiator.
Different blends of butadiene rubbers are prepared with other rubbers by many workers, Rani J et al studied the properties of the blends of butadiene rubber with natural rubbers. (94-96)

1.4.5. Natural Rubber (NR)

Natural rubber is a polymer of isoprene units (C₆H₈), which is 2 methyl 1,3 butadiene. It is chemically unsaturated and amorphous when unstretched and oriented crystal structure on stretching. Due to the high stereo regularity, natural rubber crystallizes spontaneously when stored at low temperature or when it is stretched. Unstrained rubber has a maximum rate of crystallization at about −26°C. But even at 0 °C natural rubber can crystallize. The maximum degree of crystallinity reached is only about 25-30 %. Rapid crystallization on stretching gives natural rubber its unique high tensile strength and tear resistance in pure gum or in non – reinforcing vulcanizates.

Originally natural rubber was used un-vulcanised. But it suffered from drastic softening in warm water and high rigidity in cold water. After the discovery of sulphur vulcanization by Goodyear in U.S and Hancock in England, considerable improvements of the property was obtained. Although natural rubber can also be cross-linked with peroxide or high energy radiation, in practice sulphur accelerators are predominantly used.

Blends of natural rubber with synthetic rubbers such as styrene butadiene, butadiene rubbers are prepared by different workers and its properties were studied. (79,84,87)

1.5. Vulcanization and chemicals used for vulcanization

The vulcanization is a process which transforms the predominantly thermoplastic raw rubber into an elastic rubbery state. This process which involves the association of macromolecule through their reactive sites is also called cross linking or curing. Vulcanization agents are necessary for the formation of cross link formation. The most commonly used one are sulphur, peroxide or metal oxide and high-energy radiation. The cross links formed by the peroxide are purely carbon- carbon linkage. The importance of peroxide linkage is their ability to cross link saturated
elastomers such as Ethylene Propylene Rubber, Silicon rubber etc. which cannot be cross-linked by other vulcanizing agents. As long as molecules are not tied to each other they can move more or less freely. They exhibit mechanical and thermo dynamical irreversible flow. By the cross links the vulcanizate becomes tough and stiff.

The number of cross links formed depends on the amount of vulcanizing agents, its activity and the reaction time. These cross links can be anything between mono sulphidic to polysulphidic. The resulting properties of the vulcanizate depend on the number and nature of cross-links.

Depending on the vulcanization system used different cross-link structures are obtained. In high sulphur system (conventional systems) poly sulphidic cross-links are formed. In the semi-efficient vulcanizations systems (semi E-V) disulphide cross link are formed. And in efficient vulcanization systems (E-V) with very low sulphur and in sulphur less thiouranum vulcanization mono sulphidic and di sulphidic cross-links are predominant. The nature of cross-links influences mechanical properties and aging behavior of vulcanizates.

1.5.1 Accelerators

Rubber can be vulcanized with sulphur alone, but the rate of reaction is found to be very low and it requires large amount of sulphur for vulcanization. Substances that are added in small amounts during compounding to accelerate the vulcanization reaction and to improve the physical properties of the finished products are called accelerators. These substances can reduce the cure time from days or hours to minutes or seconds at the same vulcanization temperature. Different types of accelerators are now common in use. A major development came with the discovery of the organic nitrogen containing compounds acting as accelerators for the vulcanization process. An intense search for the vulcanization accelerators started around 1906 by Oenslager. Accelerators are classified on the basis of the speed of the vulcanization reaction. They are slow accelerators (Thiourea derivatives), Medium accelerators (Guanidines), Semi fast accelerators (Benzothiazoles derivatives), Fast delayed action (Sulphenamides derivatives) Fast
Accelerators (Xanthates)\(^{(105)}\) and (Dithiophosphates),\(^{(106)}\) Very fast (Thiurams),\(^{(107)}\) (Dithiocarbamates).\(^{(108)}\)

Along with many of organic accelerators certain inorganic compounds such as Magnesium oxide, Calcium hydroxide, Lead oxide and Antimony tri and penta sulphide can act as accelerators for the vulcanization reactions.\(^{(109)}\)

1.5.2 Accelerator Activators / Co Activators

In order to attain maximum potential of accelerators, accelerator activators are generally used along with accelerators. Accelerators may be either inorganic or organic. Most common activators used are Zinc oxide, Magnesium oxide, Lead oxides etc.\(^{(110)}\) Zinc oxide is the most important of these additives. Originally zinc oxide was used as an extender for cost reduction. Later on it was found to reduce vulcanization time.\(^{(111)}\) Usually in an activator system, a combination of zinc oxide and a long chain fatty acid such as stearic acid that acts as a co-activator is used.

1.5.3 Antioxidants

Ageing is a collective term for the change of property of materials that occur on longer-term storage without the action of chemicals that lead to partial or complete degradation. These changes can occur in the form of degradation process, embrittlement, softening and fatigue processes and the like. Uncured and cured rubber are especially prone to such ageing effects. The unsaturated groups in diene rubber make it possible to cure with sulphur, but at the same time show a sensitivity toward oxygen, ozone and other reactive substances. These reactions cause changes in the rubber. Since soft rubbers based on diene rubber contain free double bonds even after vulcanization they remain sensitive to the above agent. Higher temperatures make these effects more reactive. In the presence of oxidation catalyst like Cu, Mn compounds these ageing phenomena occurs rapidly. When reversion occurs these effects become more apparent. Diene rubber vulcanizates take up oxygen from the air during storage and it is partially bound to the vulcanizates and partly given off as carbon dioxide and water and other low molecular weight oxidation products. Diene rubbers are
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easily attacked by oxygen or ozone compared to the saturated rubbers. Type and amount of filler used also influence the stability of the vulcanizates.

In a given rubber compound the degradation process can be retarded by the addition of chemicals that called ageing protectors or antioxidants. These antioxidants are added to rubber mixtures in amounts of 1-3 phr, there by the rubber part is more or less protected against the influence of the aging condition. The degree of protection depends on the composition of the antioxidant. The majority of the commercial anti oxidants are of the two types chemically amine type representing the staining variety and phenol type representing the non-staining variety.\(^{(112)}\)

1.5.4. Fillers

Fillers are usually organic and inorganic powders of small particle size incorporated during compounding for various purposes like improvement in strength, cheapening the product etc. Choice of the filler to be used depends on the hardness, tensile strength and other properties required for the product. Addition of fillers to the vulcanizates generally results in the reinforcement ie improvement in various properties like tensile strength, tear resistance, abrasion resistance etc. At the same time ultimate elongation and resilience decreases with the addition of reinforcing filler to the vulcanizates.

Reinforcing effect of filler is also reflected in its ability to change the viscosity of a compound. The vulcanizates properties like tensile strength, tear resistance and abrasion resistance increase with filler loading. The reinforcing effect of an active filler as well as the dosage required can be quite different for different elastomers. For synthetic rubbers such as BR, SBR and NBR the tensile properties of the vulcanizates increase up to 10 times with the addition of the reinforcing fillers, where as in the case of natural rubber and chloroprene rubber improvement in tensile strength is not as much.\(^{(113)}\) The variation in the effectiveness of filler in natural rubber and synthetic rubbers can be explained by the theory of over stressed molecules.\(^{(114-117)}\)

It has been reported that different types of interaction including van der waal's and chemical are existing between the filler and elastomer in the
vulcanized material. The active centers of the filler surface can polarize the double bonds of the rubber molecules and can thus influence reactions. Fillers can have chemically or adsorptively bound functional groups on their surface, depending on their origin. On carbon black surfaces, for example, phenolic, hydroxyl, quinone, carboxyl, lactone groups as well as free radicals have been formed which can react chemically with rubber molecules. These results show the surface structure and its active centers are responsible for the reinforcement effects.

The fillers are primarily classified as carbon black and light coloured fillers. Among the light coloured fillers chemical composition is primarily the basis for classification. With each class of filler different degree of activity is present. Basically, most carbon blacks, colloidal silica and most small particle size silicates belong to the high and medium active fillers, while chalk belong to the inactive or inert fillers. Inert fillers do not give sufficient reinforcement, are used to adjust the volume and processibility.

1.5.5 Effects of Filler Characteristics on Vulcanizate properties

Properties of the vulcanizate are related to the properties of the rubber and the properties of the fillers. Smaller particle size (larger external surface area) results in higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity and higher Mooney viscosity. An increase in surface activity (physical adsorption) results in higher modulus at the higher strains and higher abrasion resistance. An increase in persistence structure (bulkiness) results in higher Mooney viscosity and higher mixing time. Porosity results in higher viscosity and higher electrical conductivity in the cases of carbon black.

1.5.6 Influence of Fillers on Cross link Density

Influence of fillers on cross link density can be evaluated from the change in torque with the addition of addition of fillers to the gum vulcanizates. Work by Cotton shows that reinforcement by fillers can be evaluated as the ratio of difference in maximum torque of gum and filled vulcanizate to that of the gum vulcanizates.
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\[ \alpha = \frac{\Delta T \text{(max of filled vulcanizate)} - \Delta T \text{(gum)}}{\Delta T \text{(gum)}} \]  

(1.1)

When this entity is plotted against amount of reinforcing filler a straight line is obtained. The slope of the line called \(\alpha F\), is a characteristic structure of the filler.

Comparison of filled vulcanizates with gum vulcanizates shows two important differences the modulus at 300 % is greatly increased and the swelling of the elastomer in solvent is reduced. Both the modulus and swelling are used to determine cross link density. The modulus is related to cross link density by the well known formula from the kinetic theory of elasticity in its simplest form

\[ \sigma = RT \nu (\lambda - \frac{1}{\lambda^2}) \]  

(1.2)

where \(\nu\) is the number of cross link per cubic centimeter, \(\sigma\) is the modulus and \(\lambda\) is the extension ratio. According to the equation (1.2) modulus at certain extension ratio and at a given temperature can only be increased by increasing the cross-link density \(\nu\).

An uncross linked rubber dissolves in a suitable solvents. But if the rubber is held together by cross-links between the molecular chains it cannot be dissolved; instead it swells to an extent determined by the solvent power of the liquid. Evidently, for a given solvent higher the cross link density of the rubber lower the swelling and conversely for a given degree of cross linking density a more powerful solvent will give a higher degree of swelling. Flory Rehner (124,125) equation can be used to determine cross link density of the vulcanizates.

\[ -\ln (1-Vr) + Vr + \chi Vr^2 = \frac{\rho r Vs (Vr)^{1/3}}{Mc} \]  

(1.3)

where \(Vs\) is the molar volume of the solvent \(\chi\) is the parameter characteristic of the interaction between rubber and solvent and \(Mc\) is the number average molecular weight of rubber chains between adjacent cross links.
The most common and effective reinforcing filler is carbon black. There are different types of carbon black characterized by the particle size, method of manufacture etc. They are essentially elemental carbon and are composed of aggregated particles. During the vulcanization carbon black enters into chemical reaction with sulphur, accelerators etc participating in the formation of net work. Thus, filler will influence the degree of cross-linking also. Carbon black also interacts with the unsaturated hydrocarbon rubber during milling and the rubber is adsorbed on to the filler. This alters the stress-stain properties and reduces the extent of swelling of the product in solvents. Porter reported that the cross link density of a black reinforced vulcanization system increased about 25% compared to the corresponding unfilled systems. Carbon black generally increases the state of vulcanization and improves the reversion resistance. However, carbon blacks can be used in dark coloured product only.

1.6. Rubber Blends

Almost all polymers in industrial and transportation applications are used as polymer blends. One of the main advantages of polymer blend is the great variability of their properties. Mixing together of two or more different polymers is known as blending. Blending is a process similar to mixing. In a polymer blend the constituent polymers are usually present in significant weight proportion with respect to each other. Blending of different polymers results in the production of new material with a properties far different from that of constituent polymers.

Different types of polymeric blends are mechanical polyblends, chemical polyblends, mechano-chemical polyblends solution cast polyblends and latex polyblends. Mechanical polyblend is made by melt blending of the constituent polymers. A chemical polyblends is given by polymeric systems in which long monomeric sequence of one kind are chemically linked to similar long monomeric sequence of a different kind either in the axial direction, or in the cross direction, giving block copolymer or graft copolymers structure respectively.
1.7. Compatibility

In the preparation of polymer blend the most important attention is given to the compatibility of the blend components \(^{(129)}\). In a very manner it may be said that polymer – polymer incompatibility is more a rule than an exception. Even if two different polymers are by and large compatible under a specified condition, they slowly develop incompatibility as they are put to use at different set of conditions. Complete miscibility or compatibility between the component polymers in a blend is the entire most desired feature.

Frequently, a blend of two polymers is neither totally miscible not totally immiscible, but falls some where in between. A blend of this type is partially miscible. Partially miscible polymers may form completely miscible blends when either polymer is present in small amounts. However as ratios progress towards equality, the phase separates. At compositions where partially miscible polymer blends are in two phases, the phases may not have a well-defined boundary since polymer A significantly penetrates into the polymer B phase or vice versa. The molecular mixing that occurs at the interface of a partially miscible two phase blend can stabilize the domains and improve interfacial adhesion, which in turn explains why these two phases blend generally have good bulk properties.

A useful blend has a characteristic of a uniform dispersion – fine discrete particle of one component being uniformly dispersed through the medium or matrix of the other component. It would be advantages if the size distribution of the domain or the dispersed phase remains practically unaltered over a long time. Use of selected compatibilizers\(^{(130,131)}\) in the form of appropriate block polymers or coupling agent such as silane coupling agent may minimize phase separation in multi component polymer blends.

The behavior of two polymers in a blend is not necessary the same as expected from the behavior exhibited by the components in their isolated forms. The ultimate behavior pattern of polyblends is dependent on the extent of phase separation, nature of the phase provided by the matrix, character of the dispersed phase and interaction between the component
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polymers. It has been observed that for miscible polyblends, the following arithmetic semi empirical rule hold good ($^{132,133}$)

$$P = P_1 \phi_1 + P_2 \phi_2 + l \phi_1 \phi_2$$  \hspace{1cm} 1.4

Where $P$ is the property of interest, $\phi$ is the concentration and $l$ is the interaction term. It can be positive, negative or zero. If $l$ is zero, the rule of mixtures is observed. If it is positive the polyblend property would be higher than the weight average of the constituent polymers and the polymers produce a synergetic effect in the blend. If $l$ is negative the polyblend property would be lower than simple average and the blend system is anti-synergistic.

For an immiscible polyblend having continuous phase and a dispersed phase equation 1.4 is not acceptable for property analysis. In such cases, the semi empirical relationship to analyze the physical properties is given by equation 1.5

$$\frac{P}{P_1} = \frac{1 + AB\phi_2}{1 - B\Psi \phi_2}$$  \hspace{1cm} 1.5

Where $\phi_2$ is the concentration of the dispersed phase constituent. The value of $A$ varies between zero and $\infty$ depending on the shape and orientation of the dispersed phase as well as the nature of the interface. $B$ depends on the relative values of the $P_1$, $P_2$ and $A$ and $\Psi$ is reduced concentration term that is a function of the maximum packing fraction. It is common experience if $A \rightarrow 0$, the dispersed phase is soft and if $A \rightarrow \infty$, the dispersed phase is hard. Equation 1.5 is useful for analysis of almost all physical properties of immiscible blend excepting the failure and toughness properties.

Properties of a blend generally depend on the compatibility of the blend components. Filler -matrix interactions can be improved substantially by treating with coupling agent or compatibilising agent. ($^{134,135}$) Stable polymer blends can be produced from immiscible polymers using compatibilizers, just as a surfactant can stabilize oil water mixture.
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1.7.1. Grafting / Functionalisation reactions

Grafting of vinyl silanes to poly olefins substrate in the presence of peroxide is the common example of graft reaction performed in extruder reactors. Reviews summarizing aspects of the various grafting and cross linking processes have been published (137-145). Jones and Nowak (146) have grafted styrene to polyethylene in a reactive extrusion process. Thames, et al (147) studied the reactions of low molecular weight Guayule rubber (LMWGR) and maleic anhydride (MA) at varying mole ratios in polar solvent. Balakrishnan. et al (148) investigated the crack resistance of blends of polycarbonate (PC) and acrylonitrile-butadiene-styrene terpolymer (ABS) with and without maleic anhydride grafted ABS at two different weight fractions. Sanchez-et al (149) investigated the rheological properties of polyethylene terephthalate (PET)-styrene butadiene rubber (SBR) blends and the blend of PET and maleic anhydride-functionalized SBR.

Machado et al (150) investigated a series of polyolefin with different ethene/propene ratios grafted with maleic anhydride (MA) both in melt and in solution and studied cross linking and degradation with FTIR spectroscopy and rheometry. Loyens. et al (151) studied functionalisation of ethylene propylene rubber using maleic anhydride. Phinyocheep et al (152) found that the presence of 6-10% MA grafted styrene -ethylene-butylenes-styrene shows improved the physical properties of blends of polypropylene containing scrap rubber ducts. Naskar et al (153) reported that maleic anhydride grafted ground tire rubber improved the better physical properties when it was blended with high density poly ethylene. Mishra et al (154) studied the shrinkability of MA grafted low density polyethylene and ethylene acrylic elastomer. John et al (155) successfully used maleic anhydride as a compatibilizers for the binary blends of polyester (PBT) and polyamide (PA66).

Kim et al (156) studied the mechanical and dynamic mechanical properties of a waste rubber powder-filled high-density polyethylene (HDPE) composite. They found that maleic anhydride grafted polypropylene could be used as compatibilizers Grigoryeva. et al (157) al studied grafting of maleic anhydride on EPDM using Brabender Plasticorder. Grafting efficiency was established by FTIR spectroscopy. Naskar. et al (158) investigated mechanical properties of blends of maleated ground tyre and
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acrylated high density polyethylene in the ratio 60:40 and ethylene propylene diene rubber containing maleated GRT.

1.7.2. Coupling agents

Coupling agents are compounds containing both organic and inorganic groups. They bridge the interface between matrix and reinforcement. Organo functional silanes have R groups that form covalent bonds with the matrix where as hydroxyl groups (or alkoxy) bond to the mineral. Coupling agents are primarily materials that improve the adhesive bond of dissimilar surfaces. This must involve an increase in true adhesion. Coupling agents may also modify the inter phase region to strengthen the organic and inorganic boundary layers. Minakgawa, et al studied the effect of silane coupling agent in natural rubber containing silica filler. Ismail H. et al studied the effect of Silane coupling agent on cure characteristics and mechanical properties bamboo filled natural rubber composites. They found that cure time and scorch time decreased with the increase in filler loading in presence of silane coupling agent. Bokobza L. et al investigated swelling properties of silica filled styrene butadiene rubber in presence coupling agent Si 69.

1.8. Thermal analysis

Thermal stability of rubber vulcanizates is evaluated by thermogravimetric analysis. Achary, et al investigated the stability of nitrile rubber vulcanizates containing precipitated silica as filler by TGA. Sierra et al studied the reinforcing capacity and stability of mesoporous silica mixtures filled styrene butadiene rubber vulcanizates using TGA, NMR, FTIR techniques and SEM. Shield et al studied pyrolysis of styrene butadiene rubber /acrylonitrile butadiene rubber blends using gas chromatographic, mass spectrometric techniques and T.G.A methods. Dileep et al conducted thermogravimetric analysis of maleic anhydride grafted depolymerised natural rubber. Ahmed et al studied comparison of thermal stability of sulphur, peroxide and radiation cured NBR and SBR vulcanizates by thermogravimetry.
1.9. Scope of the Work

The unprecedented growth in the transport industry has resulted in the accumulation of large quantities of worn out and scrap tyres. Converting these materials into some reusable forms not only reduces the damage to environment but also saves energy and preserves precious natural resources.

Whole tyre reclaim (WTR) is prepared by digesting the used and scraped tyres by simultaneous applications of high temperature and pressure in the presence of oil and chemicals.

Analysis of WTR shows that it contains 50% of rubber hydrocarbon and 30% of carbon black filler. Hence WTR can be used to partly replace virgin rubber and also as a source of carbon black filler in rubber compounds.

Being lower in price, the introduction of WTR in rubber blends is expected to reduce the cost. Moreover, the low viscosity of WTR permits easy blending with other rubbers. The presence of some amount of filler, plasticizer and accelerator relics in the WTR can influence the ultimate properties of the blends.

One of the problems to be tackled in preparing such blends is the compatibility of the individual components. WTR being inherently non polar, its compatibility with polar matrices is to be improved by giving suitable treatment to either of the component matrices. Some of the accepted routes such as grafting of polar groups or the use of coupling agent can improve the properties of the resultant blends.

Thus, it is important to prepare blends of WTR with other rubbers over a range of compositions and characterize them in terms of cure behavior, mechanical and thermal properties in order to arrive at optimum blend ratios for different blends. It is also important to prepare and evaluate blends with modified WTR and different coupling agents in order to make right choice of blend compositions.
1.10. Objectives of the work

- Preparation of whole tyre reclaim blend with natural rubber and synthetic rubbers such as Butadiene rubber (BR), Styrene butadiene rubber (SBR), Acrylonitrile butadiene rubber (NBR) and Chloroprene rubber (CR).

- Study of cure characteristics and mechanical properties of blends of WTR with NR, BR, SBR, NBR and CR.

- Modification of whole tyre reclaimed rubber by maleic anhydride grafting.

- Preparation of blends of Styrene butadiene rubber (SBR), Acrylonitrile butadiene rubber (NBR) and Chloroprene rubber (CR) with modified whole tyre reclaimed rubber.

- Study of cure characteristics and mechanical properties of blends of modified WTR with SBR, NBR and CR.

- Optimisation of silane coupling agent in blends of WTR with NBR, SBR, and CR.

- Thermal characterization of blends of the reclaim with NR, BR, NBR and SBR.

Chapter wise description of the study is given below.

Chapter 1.

This chapter gives a general introduction to the whole tyre reclaim, preparation and properties and review of the previous work done in this area. Discussion on the different rubbers used in this study is also included.
Chapter 2

Materials used and the various experimental procedures adopted in the present study are given in detail in this chapter.

Chapter 3

In this chapter, studies of cure characteristics and mechanical properties of blends of whole tyre reclaim with acrylonitrile butadiene rubber, chloroprene rubber, styrene butadiene rubber, butadiene rubber and natural rubber are included. It consists of five parts, which deal with cure characteristics, mechanical properties and ageing studies of NBR/WfR blends, CR/WfR blends, SBR/WfR blends, BR/WfR blends and NR/WfR blend.

Chapter 4

In this chapter, the effect of using maleic anhydride grafted whole tyre reclaim in blends with acrylonitrile butadiene rubber, chloroprene rubber, styrene butadiene rubber is given. It consists of three parts, which deal with cure characteristics, mechanical properties and ageing studies of NBR/MA-g-WfR blends, CR/MA-g-WfR blends and SBR/MA-g-WfR blends.

Chapter 5

In this chapter, effect of silane coupling agent on cure characteristics and mechanical properties of blends of whole tyre reclaim with acrylonitrile butadiene rubber, chloroprene rubber, styrene butadiene rubber, is discussed. The results are discussed in three parts, which deal with influence of coupling agent on cure characteristics, mechanical properties and ageing studies of NBR/ WfR blends, CR/ WfR blends, SBR/ WfR blends.

Chapter 6

This chapter discusses the thermal analysis of blends of whole tyre reclaim with natural rubber, butadiene rubber, acrylonitrile butadiene rubber and Styrene butadiene rubber. It consists of two parts, which deal on thermal stability and order of decomposition of blends of NR/WfR, BR/WfR, NBR/WfR and SBR/WfR blends.
Chapter 7

Overall summary and conclusion of the present study are given in the chapter.

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