STUDIES ON THE UTILISATION OF RUBBER RECLAIM IN ELASTOMERS

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To

My wife ***Joyce***
And
Children ***Anugraha*** *and* ***Astrid***

CERTIFICATE

*This is Certify that the thesis entitled "***Studies on the Utilisation of Rubber Reclaim in Elastomers"** *is an authentic report of the original work carried out by Mr. P.A.Nelson under my supervision and guidance in the department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 6820 22. No part of the work reported in this thesis has been presented for any other degree of any other institution.*

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DECLARATION

*I hereby declare that the thesis entitled "***Studies on the Utilisation of Rubber Reclaim in Elastomers***" is the original work carried out by me under the supervision of Dr. Sunil K. Narayanan Kutty, Senior Lecturer, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.*

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ABSTRACT

The thesis describes utilisation of reclaimed rubber, Whole Tyre Reclaim (WTR) produced from bio non- degradable solid pollutant scrap and used tyres. In this study an attempt has made to optimize the substitution of virgin rubber with WTR in both natural and synthetic rubber compounds without seriously compromising the important mechanical properties. The WTR is used as potent source of rubber hydrocarbon and carbon black filler. Apart from natural rubber (NR), Butadiene rubber (BR), Styrene butadiene rubber (SBR), Acrylonitrile butadiene rubber (NBR) and Chloroprene rubber (CR) were selected for study, being the most widely used general purpose and specialty rubbers. The compatibility problem was addressed by functionalisation of WTR with maleic anhydride and by using a coupling agent Si69.The blends were systematically evaluated with respect to various mechanical properties. The thermogravimetric analyses were also carried out to evaluate the thermal stability of the blends.

Mechanical properties of the blends were property and matrix dependant. Presence of reinforcing carbon black filler and curatives in the reclaimed rubber improved the mechanical properties with the exception of some of the elastic properties like heat build up, resilience, compression set. When WTR was blended with natural rubber and synthetic rubbers, as the concentration of the low molecular weight, depolymerised WTR was increased above 46-weight percent, the properties deteriorates.

When WTR was blended with crystallizing rubbers such as natural rubber and chloroprene rubber, properties like tensile strength, ultimate elongation were decreased in presence of WTR. Where as in the case of

blends of WTR with non-crystallizing rubbers reinforcement effect was more prominent.

The effect of functionalisation and coupling agent was studied in three matrices having different levels of polarity(NBR, CR and SBR).The grafting of maleic anhydride on to WTR definitely improved the properties of its blends with NBR, CR and SBR, the effect being prominent in Chloroprene rubber.

Improvement in properties of these blends could also achieved by using a coupling agent Si69. With this there is apparent plasticizing effect at higher loading of the coupling agent. The optimum concentration of Si69 was 1 phr for improved properties, though the improvements are not as significant as in the case of maleic anhydride grafting.

Thermal stability of the blend was increased by using silane-coupling agent.

PREFACE

The thesis "**Studies on Utilisation of Reclaimed Rubber in Elastomer**" is mainly intended to explore new avenues of applications of reclaimed rubber produced from worn out and discarded tyres, which is a major bio non-degradable source of pollution. According the recent survey, of the 250 million tyres produced every year only 15 percent is converted to some reusable form. The rest is mainly used as landfill and fuel. Both of these methods only leads to further pollution. One safe way out is to encourage the use of recycled material. Whole Tyre Reclaim (WTR) is one such recycled product prepared from tyres after the removal of metallic and fibrous materials. It is a good source of rubber hydrocarbon and carbon black filler.

In this study an attempt is made to replace the virgin rubber with the whole tyre reclaim in rubber compounds. When non-polar whole tyre reclaim is blended with polar rubbers such as NBR and CR, incompatibility of the blend can be reduced by introducing polar groups on whole tyre reclaim by grafting reaction or by the use of coupling agent. The coupling agent or grafting of polar group on whole tyre reclaim improves the mechanical properties of the blend. Thermal stability of the blends is also studied thermogravimetrically.

The results of investigation are presented in seven chapters.

Chapter 1 presents a review of the literature in the field and the scope of the present investigation.

Chapter 2 describes experimental techniques employed in the study.

Chapter 3 consists of five parts, which deals with studies on cure characteristics and mechanical properties of the blends of whole tyre reclaim with virgin rubbers such as natural rubber (NR), Butadiene rubber

(BR), Styrene butadiene rubber (SBR), Acrylonitrile butadiene rubber (NBR) and Chloroprene rubber (CR).

Chapter 4 describes a method for the improvement of compatibility of the blend components by maleic anhydride grafting on whole tyre reclaim. This chapter consists of three parts, which discusses cure characteristics and mechanical properties of blends of NBR, CR and SBR with MA-g-WTR respectively.

Chapter 5 describes the use of coupling agent to improve the properties of the blend components in the system. The effect of coupling agent on cure and mechanical characteristics of the blends of whole tyre with the NBR, CR and SBR is presented in three parts.

Results of thermal stability of the blends at higher temperature are presented in chapter 6. This chapter consists of two parts. First part deals with thermal study of blends of NR and BR with whole tyre reclaim. Second part deals on effect of silane coupling agent and maleic anhydride grafted WTR on thermal properties of blends of NBR and SBR with whole tyre reclaim.

Chapter 7 presents important conclusions of present investigation.

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Introduction

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 (1,2) 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.(3) Another method was to reduce them to crumbs by a variety of methods such as cryogrinding, irradiation and pulverization.(4) Other disposal methods were pyrolysis to recover raw materials(5) and incineration for energy recovery.(6) 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.

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 (WTR). WTR 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.(16) 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 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. (17- 30) Vulcanised rubber scrap has been used to prepare polyolefin based(31-38) and PVC based compositions.(39-48) 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 vulcanizate. 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.

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)(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 auto clave 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(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 reclaims are inferior to those prepared from more conventional process.

1.3.3.Reclaimator Process (72)

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 xylyl 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~~s~~ 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 (73)

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 place 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 a 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

–Sotniklva (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 with out addition of vulcanizing agent. This process has been commercialized 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.

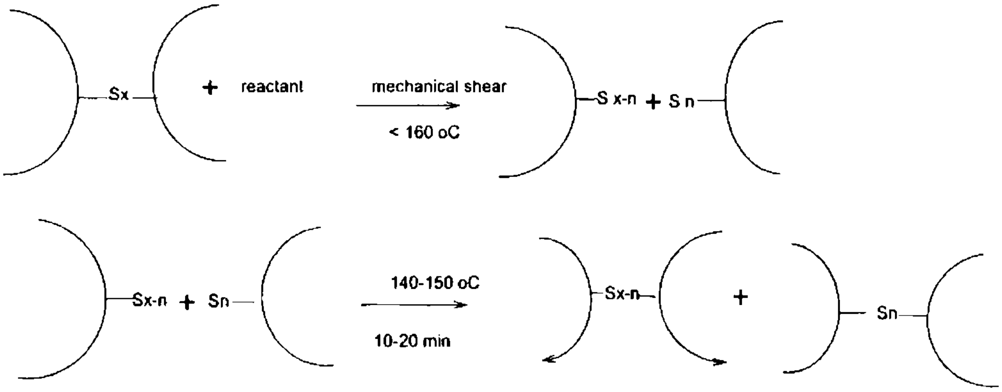

Figure 1.1 The devulcanization of scrap rubber by the De-Link process catalytically uncouples the polysulphidic (S x-n and Sn) cross links re vulcanised product with shorter cross links.

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.(75-77) 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 a 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 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.(81)

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 theses 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 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. (91)

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 (C_5 H_8), 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.(97) 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.(98-99) 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 links 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(100) Accelerators are classified on the basis of the speed of the vulcanization reaction. They are slow accelerators (Thiourea derivatives) (101), Medium accelerators (Guanidines) (102) Semi fast accelerators (Benzothiazoles derivatives), (103) Fast delayed action (Sulphenamides derivatives) (104) 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 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 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· (118) 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 (119-122) as well as free radicals (123)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.

$$\alpha = \frac{\Delta T\text{ (max of filled vulcanizate) } - \Delta T\text{(gum)}}{\Delta T\text{(gum)}} \qquad (1.1)$$

When this entity is plotted against amount of reinforcing filler a straight line is obtained. The slope of the line called αF, 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

$$\sigma = RT\,v\,(\lambda - \frac{1}{\lambda^2}) \qquad (1.2)$$

where v is the number of cross link per cubic centimeter, σ is the modulus and λ 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 v.

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.

$$-\ln(1-Vr) + Vr + \chi\,Vr^2 = \frac{\rho_r\ Vs\,(Vr)^{1/3}}{Mc} \qquad (1.3)$$

where Vs is the molar volume of the solvent χ 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.(126).Porter reported that the cross link density of a black reinforced vulcanization system increased about 25 % compared to the corresponding unfilled systems(127) Carbon black generally increases the state of vulcanization and improves the reversion resistance(128). 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 polymers. It has been observed that for miscible polyblends, the following arithmetic semi empirical rule hold good ([132,133])

$$P = P_1 \phi_1 + P_2 \phi_2 + I \phi_1 \phi_2 \qquad 1.4$$

Where P is the property of interest, ϕ is the concentration and I is the interaction term. It can be positive, negative or zero. If I 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 I 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

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

Where ϕ_2 is the concentration of the dispersed phase constituent. The value of A varies between zero and ∞ 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 P1, P2 and A and Ψ is reduced concentration term that is a function of the maximum packing fraction. It is common experience if A→0, the dispersed phase is soft and if A→∞, 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. ([134-136]) Stable polymer blends can be produced from immiscible polymers using compatibilizers, just as a surfactant can stabilize oil water mixture.

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 dusts. 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 (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 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 alkoxyl) bond to the mineral.(159) 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. (160). Minakgawa, et al (161) studied the effect of silane coupling agent in natural rubber containing silica filler. Ismail H. et al (162) 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 (163) 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(164) investigated the stability of nitrile rubber vulcanizates containing precipitated silica as filler by TGA. Sierra et al (165) 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 (166)studied pyrolysis of styrene butadiene rubber /acrylonitrile butadiene rubber blends using gas chromatographic, mass spectrometric techniques and T.G.A methods. Dileep et al (167) conducted thermogravimetric analysis of maleic anhydride grafted depolymerised natural rubber. Ahmed et al(168) 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/WTR blends, CR/WTR blends, SBR/WTR blends, BR/WTR blends and NR/WTR 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-WTR blends, CR/ MA-g-WTR blends and SBR/ MA-g-WTR 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/ WTR blends, CR/ WTR blends, SBR/ WTR 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/WTR, BR/WTR, NBR/WTR and SBR/WTR blends.

Chapter 7

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

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

A detailed description of the experimental procedures adopted, the material used, and the methods of sample preparation applied in the present investigations are given in this chapter.

2.1 Materials Used

2.1.1. Elastomers

2.1.1.a. Acrylonitrile Butadiene Rubber (NBR)

Acrylonitrile Butadiene Rubber (NBR), N553 grade used in this study was supplied by Apar Polymers Ltd., India. Nitrile content of the acrylonitrile rubber was of 33 % and the Mooney viscosity [ML (1+4) at 100°C] was 45.

2.1.1.b. Styrene Butadiene Rubber (SBR)

Styrene Butadiene Rubber (SBR), (Synaprene-1502) was supplied by Synthetics and Chemicals Ltd., Bareily., and the Mooney viscosity [ML (1+4) at 100 °C] was 52.

2.1.1.c. Chloroprene rubber (CR)

Chloroprene rubber (CR) (Neoprene rubber) W type was supplied by Du Pont, USA., and the Mooney viscosity [ML (1+4) at 100°C] was 47.

2.1.1.d. Butadiene Rubber (BR)

Butadiene Rubber (BR) CISAMER 220 was obtained from Indian Petrochemical Ltd., Baroda., and the Mooney viscosity [ML (1+4) at 100°C] was 45.

2.1.1.e. Natural Rubber

Natural Rubber (ISNR-5) was supplied by Rubber Research Institute of India, Kottayam, India. The Indian Standard specifications for the grade of rubber are given below. The Mooney Viscosity [ML (1+ 4) at 100 °C] was 82.

Dirt content, % by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass, max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity index, min.	30.00
Plasticity Retention Index (PRI), min	60.00

2.1.1 f. Whole Tyre Reclaimed Rubber (WTR)

Whole Tyre Reclaimed Rubber (WTR), was obtained from Kerala Rubber and Reclaims, Mamala, Kerala, India. The characteristics are given below.

Property	Value
Acetone extract (%)	15
Carbon black (%)	30
Gel content (%)	68
Mooney Viscosity	24
Particle size	30 mesh

2.1. 2. Other chemicals

2.1. 2. a. Zinc oxide (ZnO)

Zinc oxide was obtained from Meta Zinc Ltd., Bombay, India, had the following specifications

Specific gravity	5.5
Zinc oxide content	98 %
Acidity	0.4 % mass

Heat loss (2 hrs at 100 °C)	0.5 % max.

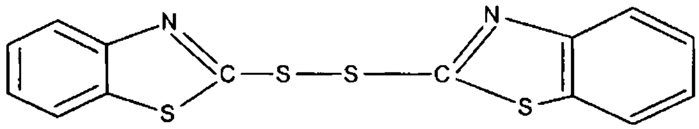
2.1. 2. b. Stearic acid ($CH_3 (CH_2)_{16} COOH$)

Stearic acid used in the study was procured from Godrej Soaps Pvt. Ltd., Mumbai. It had following specifications.

Melting point	50-69°C
Acid number	185-210
Iodine number	9.5 max
Specific gravity	0.85 ± 0.01
Ash content	0.1% max.

2.1.2.c. Mercaptobenzothiazoledisulphide (MBTS)

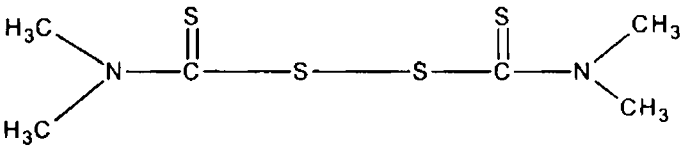
Mercaptobenzothiazoledisulphide, with a specific gravity of 1. 34 and melting point 165°C, was obtained from Bayer India Ltd., Mumbai, India.



MBTS

2.1.2.d. Tetramethylthiuramdisulphide(TMTD)

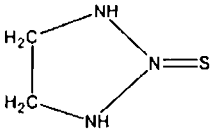
Tetramethylthiuramdisulphide, with a specific gravity of 1.42 and melting point 140°C, was procured from NOCIL, Mumbai, India.



TMTD

2.1.2.e. Ethylene thiourea (NA 22)

Ethylene thiourea, accelerator used in the chloroprene vulcanization was obtained from Akrochem Corporation, U.S.A



2.1.2.f. Sulphur

Sulphur was supplied by Sameera enterprises, Kottayam, India. The specifications of the sample are

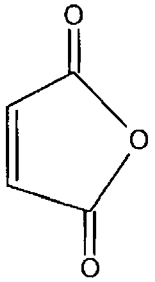
Specific gravity	2.05
Acidity	0.01 % max
Ash content	0.01 % max
Solubility in CS_2	98 %

2.1.2.g Magnesium oxide MgO (light weight)

Magnesium oxide used in the study was calcinated light weight magnesia with a specific gravity 3.6, supplied by Merk India Ltd., Mumbai, India.

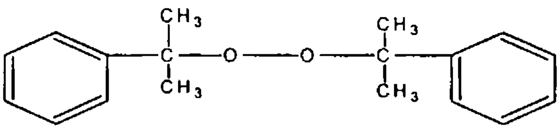
2.1.2.h. Maleic anhydride ($C_4H_2O_3$)

In this study maleic anhydride was used for grafting on whole tyre reclaim. The compound was supplied by Merk India Ltd Mumbai, India.



2.1.2.i. Dicumyl peroxide (DCP)

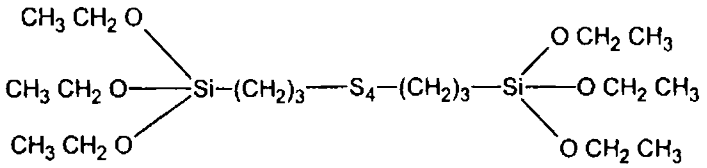
Dicumyl peroxide was commercial grade with 40% activity. This compound decomposes on exposure to heat and sunlight. It is commonly used as a free radical source. In the dicumyl peroxide one stage decomposition of the peroxide take place with the generation of free radicals. The material was supplied by Sameera enterprises, Kottayam, India.



2.1.2.j. Silane coupling agent, Si 69. [Bis(3-(triethoxysilyl) propyl) tetrasulphide]

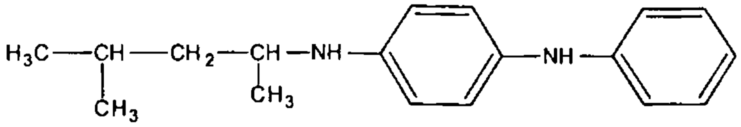
Silane coupling agent, Si69 was obtained from Degussa Corporation, Germany.

It is a pale yellow liquid with a pH value of 7-8



2.1.2.k. Antioxidant 4020 [N (1,3 dimethylbutyl) N' phenyl p- phenylenediamine]

Antioxidant 4020 was obtained from Bayer India Ltd, Mumbai, India.



2.1.2.l. Other chemicals used were Benzene, Toluene, Methyl ethyl ketone, Acetone and Silica gel.

2.2. Processing

2.2.1 Compounding

The blends of natural and synthetic rubbers with whole tyre reclaim were prepared on a laboratory size two-roll mill (150 x 330 mm) as per ASTM D 3184(1989)(1). Once a smooth band was formed on the roll, the ingredients were added in the following order: activators, antioxidants, accelerators and finally sulphur. For the preparation of blends of whole tyre reclaim and acrylonitrile butadiene rubber, sulphur was added initially due to its low solubility in the matrix. After the homogenous distribution of sulphur, all other ingredients were added.

After completion of mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out in a nip gap of 6 mm.

2.2.2 Assessment of processibility and state of cure

The process of vulcanization converts a predominantly plastic mass of a rubber compound into a elastic vulcanizate. The progress in the state of cure with time at a given temperature can be measured most conveniently by having a measure of the plasticity or viscosity of the compound. Such measurements are also useful in making an assessment and comparison of processibility of rubber compounds. Cure characteristics were determined by using a Goettfert Elastograph model 67.85 at 150°C. The machine has two directly heated, opposed bi-conical dies that are designed to achieve a constant shear gradient over the entire samples chamber. The specimen is kept in the lower die, which is oscillating though a small deformation angle (± 0.2°C) at a frequency of 50 oscillation per minute. The torque transducer on the upper die senses the force being transmitted through rubber. The chamber is kept closed by pneumatic pressure. Rheometer gives a plot of torque versus time. The minimum torque may be used for the assessment of processibility of the compound. Time -span over the bottom flat zone of the torque – time curve for10 % rise in torque from the minimum torque is taken as scorch safety. Lower the value, more scorchy the compound is. The maximum torque attained is a measure of degree of cure of a specific kind and the time required to attain 90% of the maximum torque is commonly taken as the optimum cure time. Whether the curing is characterized by a plateau effect, reversion or marching cure phenomenon can be readily judged from the nature of the torque –time curve given by the rheometer. In the rheometer curve, no change in torque, or a fall in torque with time after attainment of maximum torque is indicative of plateau effect or reversion respectively, while a slow monotonous increases in torque after the fast uptake zone is normally indicative of a marching curve. A typical cure curve is shown in the figure 2.1

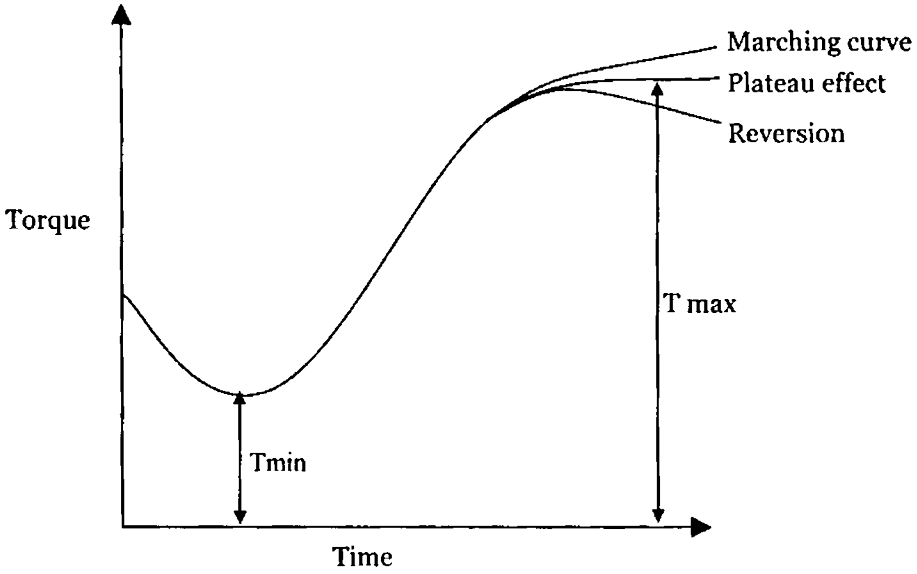


Figure 2.1. Three types of response from an oscillating disk cure rheometer

Minimum torque, maximum torque, or the slope of the curve (cure rate) can be taken from the cure curve, the most useful single figure is the time to achieve a given degree of cure, which is the time for the torque to increase to

$$\frac{Y}{100}\left(T_{max} - T_{min}\right) + T_{min}$$

Where Y is the percentage cure required (usually 90% for a 'practical' cure) T_{max} is the maximum torque and M_L is the minimum torque.

The following data can be obtained from the cure curve

Minimum torque (T_{min}): It is the lowest torque shown by the mix at the test temperature before the onset of cure.

Maximum torque (T_{max}) : It is the torque recorded when curing of the mix is completed.

Scorch Time (T_{10}) : It is taken as the time for 10% rise in torque from the minimum torque.

Optimum cure time T_{90} : corresponds to the time to achieve 90% of cure.

(Maximum torque - Minimum torque) Δt: Δt is the difference in maximum torque and minimum torque during the vulcanization. It represents improvement in degree of cross-linking on vulcanization ie. it is a measure of final cross link density of the vulcanizate.

Cure rate: Cure rate is the rate at which cross linking and the development of the stiffness of the compound occur after the scorch point. As the compound is heated past the scorch point, the properties of the compound changes from soft plastic to a tough elastic materials. During the curing step cross-links are introduced, which connect the long polymer chain of rubber together. As more cross links are introduced, the polymer chains become more firmly connected and the stiffness or modulus of the compound increases. The slope of the steepest portion of the cure curve is take as the cure rate.

2.2.3. Vulcanization

Test specimen marked with the mill grain direction were vulcanised at 150 ± 2°C and at a pressure of 180 kg/cm^2 in an electrically heated hydraulic press to their respective cure times. Sample was placed in the mould cavity and compressed under preset pressure and temperature so that it could flow and fill the mould cavity. (2-4) For thicker samples sufficient extra cure time was given to obtain satisfactory moulding. Mouldings were cooled quickly in water at the end of the curing cycle. Samples were kept in a cold dark place for 24 hours and were used for subsequent property measurements.

2.3. Physical properties

Vulcanised rubber is a complex material and differs considerably from other engineering materials. The vulcanizate materials were tested for different mechanical properties. Tensile strength, ultimate elongation, tear strength, compression set, abrasion resistance, heat build up and resilience were tested according to relevant ASTM standards.

2.3.1.Tensile Strength

Stress- strain test is the most commonly employed test method for evaluation of rubbers. Stress-strain measurements are generally carried out in tension in standard testing equipments using dumb-bell shaped specimens of specified dimensions (ASTM D 612 E type die) under specified conditions by stretching the test piece at a uniform rate and simultaneously measuring the force or stress on the specimen and the elongation or strain induced until specimen breaks.

The instrument used for the purpose was from Lloyd Instruments, LRX PLUS which digitally gave the tensile strength and ultimate elongation according to ASTM D 412 (1987) (5). The samples were punched out from the moulded sheets both along and across the grain direction. The grip separation speed was 500 mm/minute. All the tests were carried out at 28 ± 2°C. Thickness of the narrow portion was measured using a bench thickness gauge. The sample was held tight by the two grips and the lower grip being fixed. The grips were then separated at predetermined speed till the sample failed. The ultimate strength and elongation were noted.

2.3.2. Ultimate elongation

The ultimate elongation was calculated as

$$\text{Ultimate elongation} = \frac{L - Lo}{Lo} \times 100$$

Where L the length in millimeters, between benchmarks at break and L_0 is the initial length in millimeters between benchmarks.

2.3.3. Tear strength

For a vulcanised rubber tear strength or tear resistance is a property commonly assessed and it is a special form of tensile testing making use of the same equipments, Lloyd Instruments, LRX PLUS, and standard tear test pieces ASTM D 624 (die C). The samples were punched out from the moulded sheets. The test speed was 500 mm/minute. The tear strength was taken as the force per unit thickness of test piece required to extend until the piece was broken or torn and was expressed in the unit of N/mm.

2.3.4. Aging in air oven

Aging studies were carried out according to ASTM D 573-88(6) standard. Test pieces were subjected to air aging at elevated temperature (70°C) and at atmospheric pressure for a period of 48 hours after which the physical properties were measured and compared with those of unaged test pieces. Retention of the properties was then calculated as

$$\text{Retention} = \frac{\text{Property after aging}}{\text{Property before aging}} \times 100$$

2.3.5. Heat Build Up

Heat Build Up test was carried out using Goodrich Flexometer as per ASTM D 623-78(7) method A. The samples were 25 mm in height 19 mm in diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.05 kg/cm^2. The samples were preconditioned at the test temperature in the oven for 20 minutes prior to the test. The heat development at the base of the sample was sensed by a thermocouple and relayed to a temperature indicator. The temperature rise (ΔT °C) at the end of the specific time interval (20 minutes) was taken as the heat build up.

2.3.6. Compression set

Evaluation of compression set is technically useful for a vulcanised rubber. The compression set at constant strain was determined by compressing to a fixed percentage of the original thickness by clamping the test specimen in between rigid parallel plates using standard spacers. Compression set at constant strain was measured according to ASTM D395-86(8) method B. Samples with 6.25 mm thickness and 18 mm diameter were compressed to constant strain (25%) and kept for 22 hours in an air oven at 70°C. At the end of the test period, the test specimens were taken out, cooled to room temperature and the final thickness was measured. The compression set in percentage was calculated as follows.

$$\text{Compression set} = \frac{Ti - Tf}{Ti - Ts} \times 100$$

Ti and Tf are the initial and final thickness of the specimen and Ts is the thickness of the spacer used.

2.3.7. Rebound resilience

Rebound resilience was determined by vertical rebound method according to ASTM D 2832-88. In this method a plunger suspended from a given height h_o (400 ± 1 mm) above the specimen was released and the rebound height was measured. The resilience scale was marked in equally spaced division and hence the rebound height was equal to the resilience.

$$\text{Rebound resilience (\%)} = \frac{h}{ho} \times 100$$

2.3.8. Abrasion resistance

Abrasion resistance of the samples were measured using a DIN abrader based on DIN 53516. Samples having a diameter of 12 ± 0.2 mm and a thickness of 16-20 mm were placed on a rotating holder and a load of 10 N was applied. A pre run was given for conditioning the sample and the sample weight was taken. Weight after the test was also noted. The difference in weight is the weight loss of the test piece after it has traveled through 40 m on a standard abrasive surface. The results were expressed as volume loss per hour. The abrasion loss was calculated as follows

$$V = \frac{\Delta M}{\rho} \times 27.27$$

Where ΔM = mass loss, ρ = density of the sample and V = abrasion loss in cm^3/hr.

2.3.9. Density

Density of the samples was determined as per ASTM D 297 (1981)[9]. In this method the weight of the specimen in air was first noted and then specimen was immersed in water and its loss of weight in water was determined. The density of the sample was calculated as

$$\text{Density} = \frac{\text{Weight of specimen in air} \times \text{density of water}}{\text{Loss of weight of specimen in water}}$$

Density of water is taken as 1 g/cm^3

2.3.10. Gel content

Gel content was determined as per ASTM D 3616-88. In this method about 0.39 to 0.41 g ± 0.1 mg of compounded stock was punched out and allowed to swell in 100 ml of solvent for 20 hours. The solution was filtered and 25 ml of the filtrate was dried to constant mass. Gel content was calculated as follows:

$$A \times 4 = B$$

$$\% \text{ of Gel} = \frac{(C - B)}{C} \times 100$$

Where, A = mass of the dried sol, in 25 ml volume

B = Mass of the total dried sol

C = Mass of the original sample

2.4. Grafting of Maleic anhydride onto whole tyre reclaim

Brabender Plasticorder (torque Rheometer) model PS 3 S equipped with roller type rotors, having a capacity of 40g. was used for grafting maleic anhydride on reclaimed rubber. 40 grams of reclaimed rubber, 2 grams of maleic anhydride and 1 gram of dicumylperoxide (DCP) were mixed at a temperature of 150°C in Brabender Plasticorder at 30 rpm for 3 minutes. At the end of 3 minutes of mixing the samples were taken out and homogenized on a two-roll mill.

2.5. Determination of cross link density

Samples of WTR / virgin rubber blends were used for the determination of cross link density. Samples of approximately 10 mm diameter and 2mm thickness and 0.2 gm weight were punched out from the central portion of the vulcanizate and allowed to swell in a suitable solvent for 48 hrs. The swollen samples were taken out and weighed again. The solvent was removed in vacuum and the samples were weighed again. Volume fraction of the rubber, Vr, in the swollen network was then calculated by following equation. (10-11)

$$Vr = \frac{(D-FT)\ \rho_r^{-1}}{(D-FT)\ \rho_r^{-1} + A_o\ \rho_s^{-1}}$$

Where T is the weight of test specimen, D is the weight of deswollen test specimen, F is the weight of fraction of insoluble components. A_0 weight of absorbed solvent corrected for the swelling increment. ρ_r was density of the rubber and ρ_s was the density of the solvent.

Knowing the value of Vr, the total chemical cross link density was calculated using Flory-Rehner equation (12-13)

$$-\ln(1\text{-}Vr) + Vr + \chi\ Vr^2 = \frac{\rho_r\ Vs\ (Vr)^{1/3}}{Mc}$$

where Vs is the molar volume of the solvent χ is the parameter characteristic of the interaction between rubber and solvent Mc is the number average molecular weight of rubber chains between the cross links.

The value of the parameter χ (14)taken for

NBR –MEK system was 0.21

χ taken for SBR –Toluene system was 0.32

χ taken for CR –benzene system was 0.26

2.6. Characterisation of MA-g- WTR

A portion of maleic anhydride grafted whole tyre reclaimed rubber (MA-g- WTR) was dissolved in toluene and heated under mercury lamp for a period of 2 hrs, for the complete dissolution of the rubber in the solvent. The residue was removed by filtering the solution in a Gooch crucible using powdered asbestos as a filtering medium. Filtrate obtained from the Gooch crucible was then purified by chromatographic techniques using silica gel as a stationary phase in the chromatographic column and toluene as mobile phase. The pure solution obtained from the chromatographic column was then concentrated in a vacuum oven. The solid rubber thus obtained by the complete removal of solvent was then extracted with acetone in a soxhlet apparatus for 12 hours to remove all acetone soluble curatives present in the rubber. After drying the rubber, the FTIR spectrum of the sample was taken using a FTIR spectrometer. A blank was also conducted for comparison.

2.7. Thermal Analysis

Thermogravimetry of blends of natural rubber, butadiene rubber, styrene butadiene rubber and acrylonitrile rubber with whole tyre reclaim was conducted in a Universal V3.2B, T A Instruments.

All the analyses were carried out using 10 mg samples on platinum pan in an atmosphere of Nitrogen at a heating rate of 10 °C/minute. The following characteristics were determined from the thermogravimetric curves the temperature of onset degradation, the temperature at peak rate of decomposition, the weight of residue. Using Freeman –Carroll equation, the order of decomposition reaction of rubber hydrocarbon is evaluated.

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CHAPTER 3

BLENDS OF WHOLE TYRE RECLAIM WITH NATURAL AND SYNTHETIC RUBBERS

Whole tyre reclaim (WTR) is prepared from scrap and used tyres. Rubber hydrocarbon present in the tyre is heavily cross-linked and hence devulcanization of waste tyre produce elastomer with high processibility, commonly known as Whole Tyre Reclaim (WTR). Use of reclaim in rubber compounding is a method of waste utilisation. Reclaim or regenerated rubber is recognized as a raw material having some processing and economic advantages to make them highly valued in rubber compounding.(1). Characterization of whole tyre reclaimed rubber shows that it is an important source of rubber hydrocarbon (about 50 %) and reinforcing filler, carbon black (about 30 %). WTR contains all the fillers present in the original scrap rubber. Usually, rubber is compounded with fillers to improve properties or reduce cost. When the elastomers are blended with reclaim, it contributes both rubber hydrocarbon and carbon black filler. In the whole tyre reclaim, carbon black filler present is homogenously distributed. This results in easy compounding, low power consumption and low manpower that lead to low cost products.

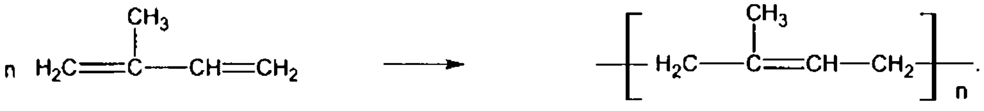
This chapter discusses the cure characteristics and mechanical properties of blends of whole tyre reclaim with natural rubber and synthetic rubber such as Acrylonitrile butadiene rubber (NBR), Chloroprene rubber (CR), Styrene butadiene rubber (SBR), and Polybutadiene rubber (BR). This chapter consists of five parts which deal with the cure characteristics and mechanical properties of Acrylonitrile butadiene rubber/WTR blends, Chloroprene/WTR blends, Styrene butadiene rubber/ WTR blends, Butadiene/WTR blends and Natural rubber/WTR blends.

In all the experiments, the amount of rubber hydrocarbon is fixed at hundred grams i.e. When blends are prepared by substituting reclaim in place of virgin rubber, concentration of rubber hydrocarbon is maintained by taking twice the amount of reclaimed rubber. (Reclaim contain 50 % rubber hydrocarbon). In this study different blends are prepared by substituting up to 66 percentage of the virgin rubber with WTR

PART 1

3. 1. Natural rubber (NR)/ Whole tyre reclaim (WTR) blend.

Natural rubber is chemically polymer of 2 methyl 1,3 butadiene



$$n\ H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow \left[H_2C{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2 \right]_n$$

Natural rubber is a versatile elastomer with many interesting properties and find applications in wide range of areas such as tyres, belts, bushes etc.

3.1.1 Preparation of blends

Formulation of the mixes is given in the table 3.1.1. Samples preparation and various test method employed are given in the chapter 2.

Formulation of the mixes is given in the table. 3.1.1

Ingredient	Mix. No					
	A	B	C	D	E	F
NR	100	90	80	70	60	50
WTR	---	20	40	60	80	100

Note: NR - Natural rubber, WTR - whole tyre reclaim, weight of rubber is adjusted so as to get 100 grams of rubber hydrocarbon. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS – 0.5 g, TMTD - 0.2 g, Sulphur – 2.5 g are common to all mixes.

3.1.1 Cure Characteristics

Figure 3.1.1 shows the variation of minimum torque with reclaim loading. Minimum torque decreases from 0.04736N.m to 0.02979 N.m with a major drop at 33 weight percent of reclaim loading. At all reclaim loading minimum torque is lower than that of the gum compound indicating an improved processibility of the blends. The higher plasitcizer content of the reclaimed rubber (2.1.1.f) explains the initial reduction of torque values. However at higher reclaim loading the effect of carbon black filler present in the reclaim seems to offset the increased plasticity resulting in an almost constant torque value.

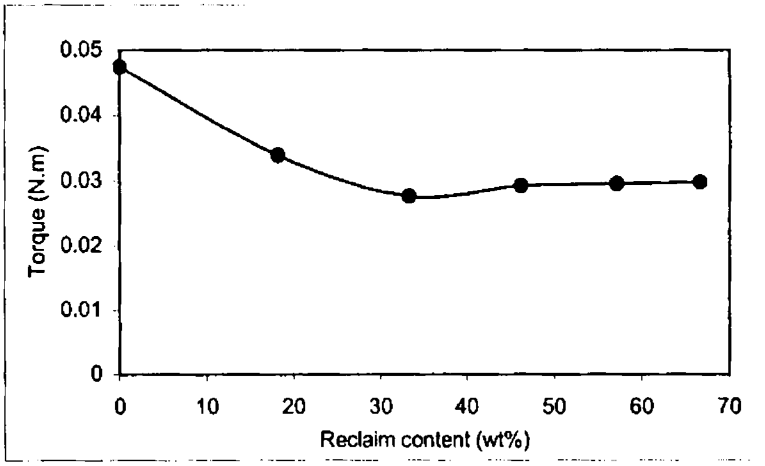


Figure 3.1.1 Variation of minimum torque with reclaim loading

The Figure 3.1.2 shows variation of (maximum – minimum) torque (Δt) for the mixes A-F. The (max – min) torque value shows a reduction with the increase in reclaim content. Though the reclaim contains carbon black as filler, the oil present in the reclaim seems to reduce the (max-min) torque. Again, the (Δt) value is also related to the cross-links during the vulcanization reaction. The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking.

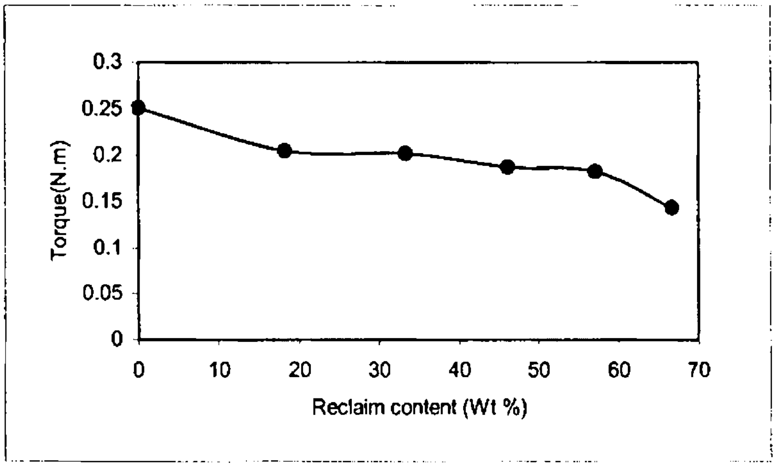


Figure 3.1.2 Variation of (Max-min) torque with reclaim loading

Figure 3.1.3 gives a plot of cure time versus reclaim loading. The cure time is reduced gradually from 4.6 minutes to 3.7 minute at 66 weight percentage of reclaim loading. The reclaim normally contains some amount of unreacted sulphur and accelerators relics, which can increase the cure rate and hence reduce cure time. (Figure 3.1.4). The scorch time is only marginally reduced even at higher loading of reclaim i.e. from 3.0 minutes to 2.0 minutes. The reduced scorch safety with increased cure time indicates higher cure rate. (Figure 3.1.5)

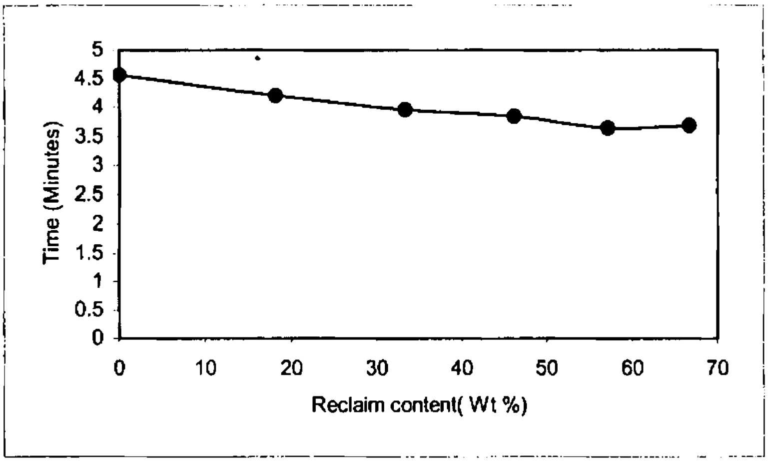


Figure 3.1.3 Variation of cure time with reclaim loading

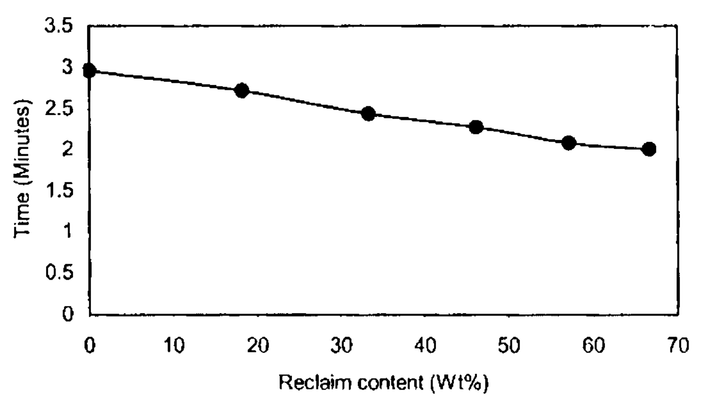


Figure 3.1.4 Variation of scorch time with reclaim loading

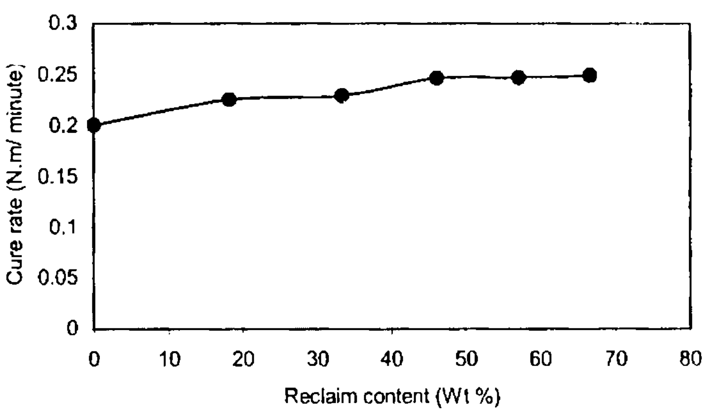


Figure 3.1.5 Variation of cure rate with reclaim loading

3.1.3.Mechanical Properties

Figure 3.1.6 shows the variation of tensile strength with reclaim loading. Tensile strength shows almost a linear decrease from 19.8 MPa to 14.2 MPa at 66-weight percentage of reclaim loading. The decrease in tensile strength with the addition of reclaimed rubber is due to the lower molecular weight of the reclaimed rubber (1). The high shear and temperature during the reclamation process severely breaks down the molecular chains to shorter segments. Incorporating more of this low molecular weight fraction results in progressive reduction in the tensile strength. The reclaim contain about 30 % of carbon black. However this does not seem to improve the tensile strength of the blend.

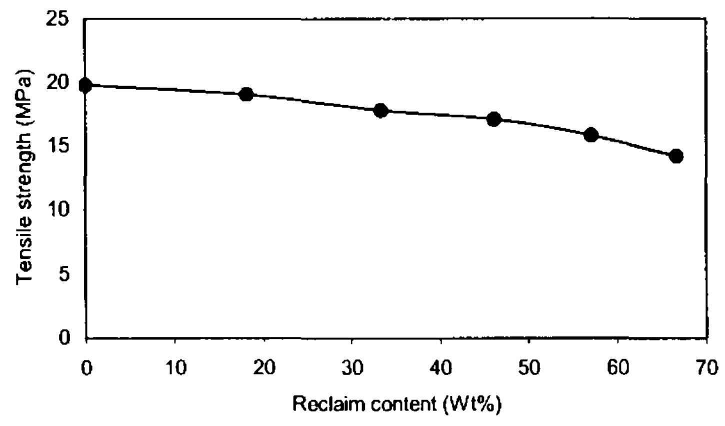


Figure 3.1.6 Variation of Tensile strength with reclaim loading

Figure 3.1.7 gives a plot of ultimate elongation versus reclaim loading. A linear decrease in the ultimate elongation of the blend with increase in reclaim content points to the lower molecular weight of reclaimed rubber.

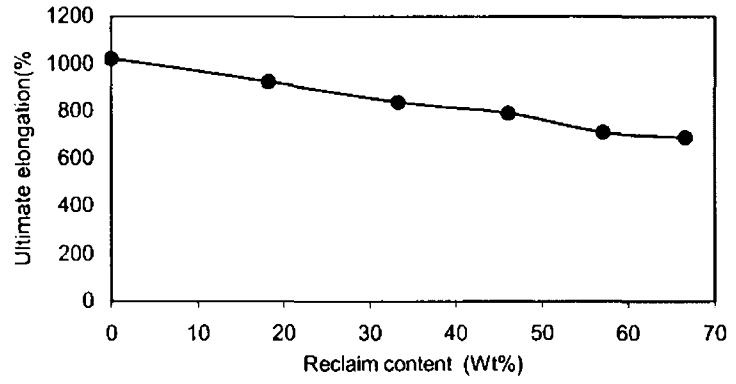


Figure 3.1.7 Variation of ultimate elongation with reclaim loading

Tear strength increases from 24.3 N/mm to 40.1 N/mm at 66-weight percentage of reclaimed rubber (Figure 3.1.8). Increased tear strength in case of blends indicates the reinforcing capacity of the reclaim rubber, arising from the presence of carbon black filler.

Crosslinked dispersed domains, agglomerates which act as crack stoppers.

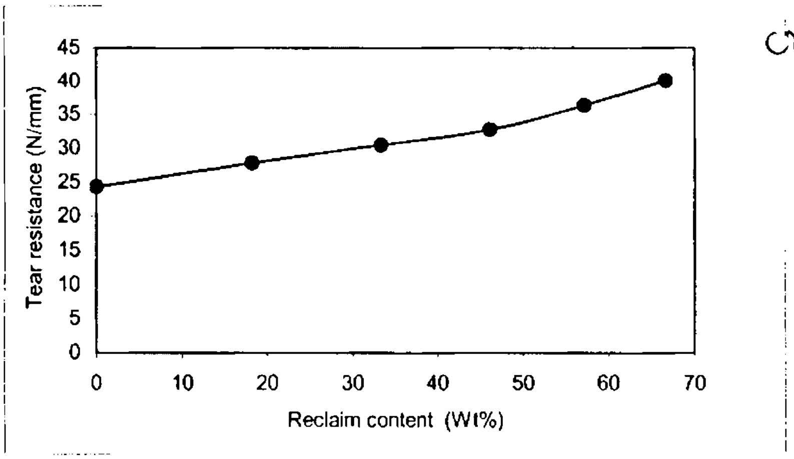


Figure 3.1.8 Variation of tear resistance with reclaim loading

Figure 3.1.9 shows a plot of abrasion loss versus reclaim loading. There is an increase in the abrasion loss with the increase in reclaim content. The abrasion loss for the gum sample is 8.0 cm^3/hr where as the same in the 66- weight percentage of reclaim is 11.62 cm^3/hr. The increased abrasion loss with the increased reclaim loading can also be attributed to the poor strength of the reclaim.

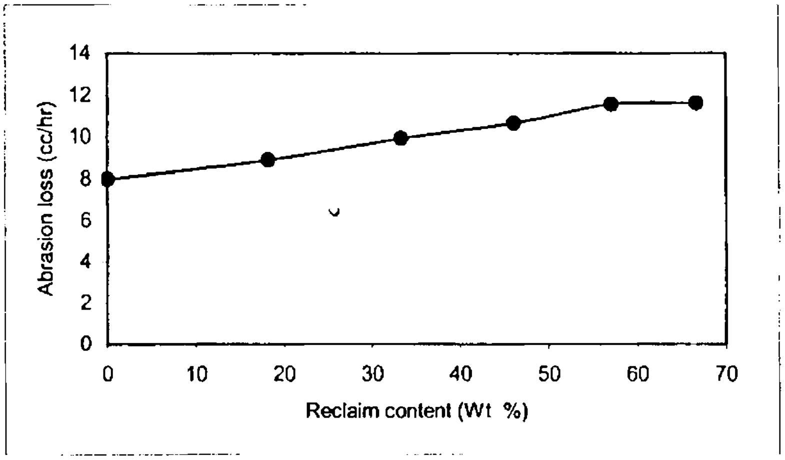


Figure 3.1.9 Variation of abrasion resistance with reclaim loading

Figure 3.1.10 shows the variation of compression set with reclaim loading. This marked increase in the set at higher reclaim loading may be resulting from combined effect of filler, plasticizer and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values.(2).

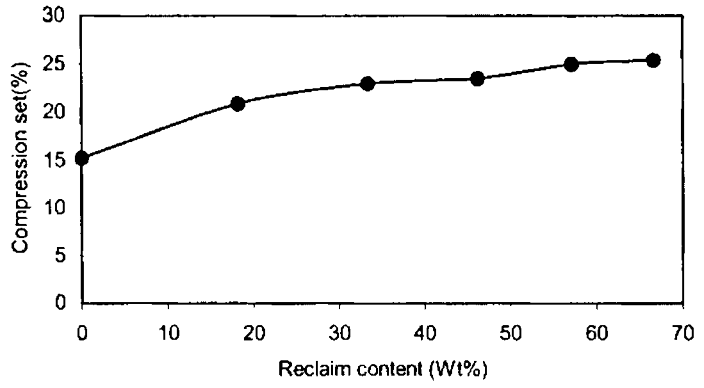


Figure 3.1.10 Variation of compression set with reclaim loading

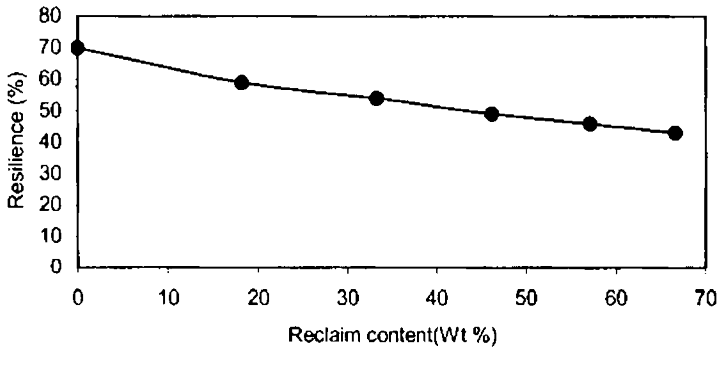


Figure 3.1.11 Variation of resilience with reclaim loading

The reduced elasticity is also evident from figure 3.1.11, which is a plot of resilience versus reclaim loading. Resilience gradually decreases with the addition of the reclaim to the natural rubber matrix.

Figure 3.1.12 shows an increase in heat build up with the reclaim loading. The increase in heat build is again due to the presence of reinforcing filler in the reclaim. The filler - matrix interface is an area of energy dissipation. More is the filler, more is the interface area and hence more is the dissipation of energy by heat due to friction.

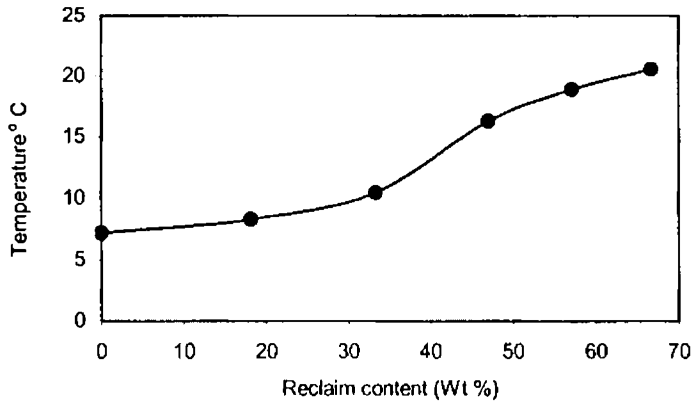


Figure 3.1.12. Variation of heat build up with reclaim loading

3.1.3.Ageing Resistance

Table 3.1.2 shows the tensile strength of the blends before and after ageing. In all the cases the tensile strength value is found to be reduced after ageing.

Table 3.1.2 Tensile strength of mixes before and after the ageing.

Mix No.	Tensile strength (MPa)		Percentage retention
	Before ageing	After ageing	
A	19.8	18.7	93
B	19.0	17.8	94
C	17.7	16.7	94
D	17.1	16.1	95
E	15.8	15.3	97
F	14.2	13.9	98

The percentage retention is the ratio of aged property to unaged roperty, shows a gradual reduction from 107% to 101% at a reclaim ontent of 66- weight percent. In the case of blends, the presence of eclaim, which is relatively more prone to degradation, lowers the retention alues. Similar trend is also observed in the case of retention of tear esistance on ageing (Table 3.1.3).

Table 3.1.4 shows the retention values of ultimate elongation of the nixes A - F. Ultimate elongation values of the aged sample are lower than hat of the unaged sample.

Table.3.1.3 Tear resistance of mixes before and after the ageing

Mix No.	Tear resistance (N/mm)		Percentage retention
	Before ageing	After ageing	
A	24.3	23.0	95
B	27.8	25.3	91
C	30.5	26.4	86
D	32.7	28.3	86
E	36.4	30.8	85
F	40.0	33.8	84

Table. 3.1.4 Ultimate elongation of mixes before and after the ageing

Mix No.	Ultimate elongation (%)		Percentage retention
	Before ageing	After ageing	
A	1024	1021	100
B	925	928	100
C	837	790	94
D	791	729	92
E	710	634	89
F	688	583	84

PART 2

3.2. Butadiene rubber (BR) /Whole tyre reclaim (WTR) blend*

The synthetic rubbers developed initially were based on diene, and had unsaturated structural units in their molecules similar to that present in the repeating units of natural rubbers. Polybutadiene rubber is made by polymerizing 1,3 butadiene with a stereo specific organometallic catalyst.

$$n\ H_2C{=}CH{-}CH{=}CH_2 \longrightarrow \left[-H_2C{-}CH{=}CH{-}CH_2-\right]_n$$

It is used mostly in tyres blended with natural rubber and styrene butadiene rubber. Compared to natural rubber, butadiene rubber has relatively high elasticity, high resilience, and improved resistance to oxidation.

3.2.1 Preparation of blends

Formulation of the mixes are given in the table 3.2.1.Samples preparation and various test method employed are given in the chapter 2.

Formulation of the mixes are given in the table.3.2.1

Ingredient	Mix. No					
	A	B	C	D	E	F
BR	100	90	80	70	60	50
WTR	---	20	40	60	80	100

Note:- Note: BR - Butadiene rubber, WTR - whole tyre reclaim, weight of whole tyre reclaim is adjusted so as to get 100 grams of rubber hydrocarbon. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g are common to all mixes.

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* Results of this chapter has been published in Progress in Rubber, Plastics and Recycling Technology, **18** (2)p 85 (2002)

3.2. 1.Cure Characteristics

Figure 3.2.1. shows the variation of minimum torque with reclaim loading. Minimum torque, a measure of the stock viscosity, shows a gradual reduction with respect to reclaim loading. This increased flowability of the mixes can be attributed to the plastizicer present in the matrix. The reclaim contains 15% plasticizer. Increasing reclaim loading increases plastizicer content of the mixes and hence the minimum torque decreases.

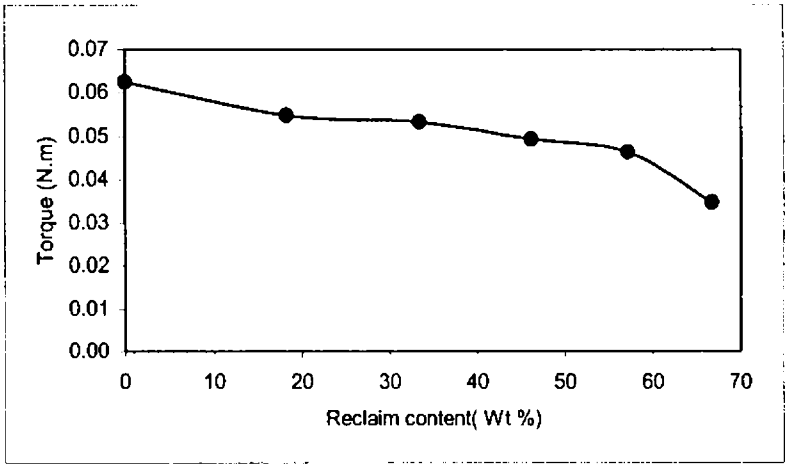


Figure 3.2. 1 Variation of minimum torque with reclaim loading

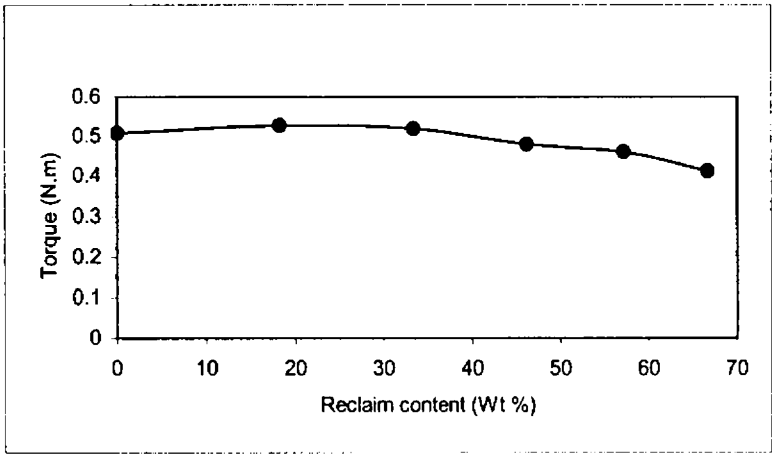


Figure 3.2.2 Variation of (max-min) torque with reclaim loading

The Figure 3.2.2 shows variation of (maximum – minimum) torque (Δt). The (max– min) torque value shows a marginal reduction beyond 33-weight percent of reclaim content. The (Δt) value is a measure of cross-links that are formed during the vulcanization reaction. The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking.

Figure 3.2.3 gives a plot of cure time versus reclaim loading. The cure time is reduced gradually from 9.5 minutes to 4.4 minute at 66- weight percent reclaim loading. The reclaimed rubber normally contains some amount of unreacted sulphur and accelerators relics, which can increase the cure rate and hence reduce cure time and scorch time. (Figure 3.2.4). The reduced cure time indicates an increased rate of cure reaction. (Figure 3.2.5)

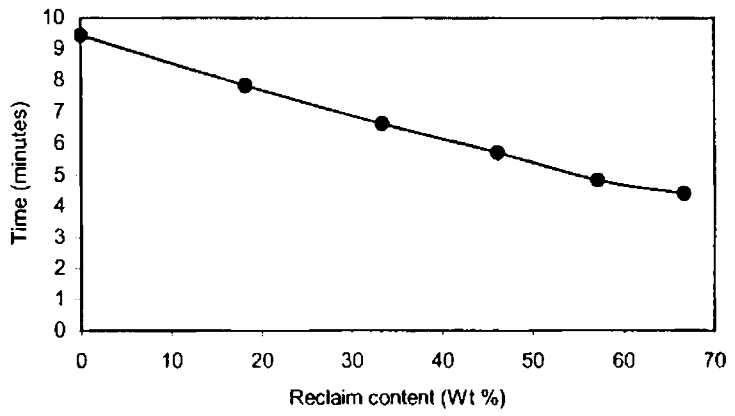


Figure 3.2.3 Variation of cure time with reclaim loading

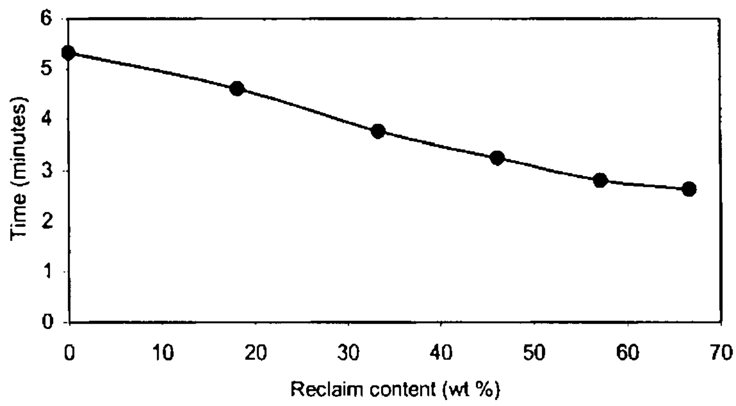


Figure 3.2.4 Variation of scorch time with reclaim loading

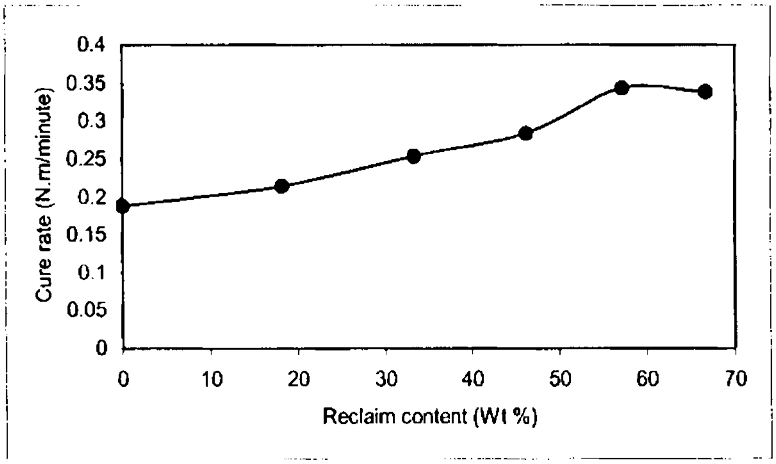


Figure 3.2.5 Variation of cure rate with reclaim loading

3.2.3.Mechanical Properties

Figure 3.2.6 show the variation of tensile strength with reclaim loading. Tensile strength shows almost a linear increase from 1.2 MPa to 5.7 MPa at 66- weight percent of reclaim loading. The increase in tensile strength may be attributed to the presence of reinforcing filler in the reclaim. Reclaim contains about 30 % of carbon black filler (2.1.1.f).

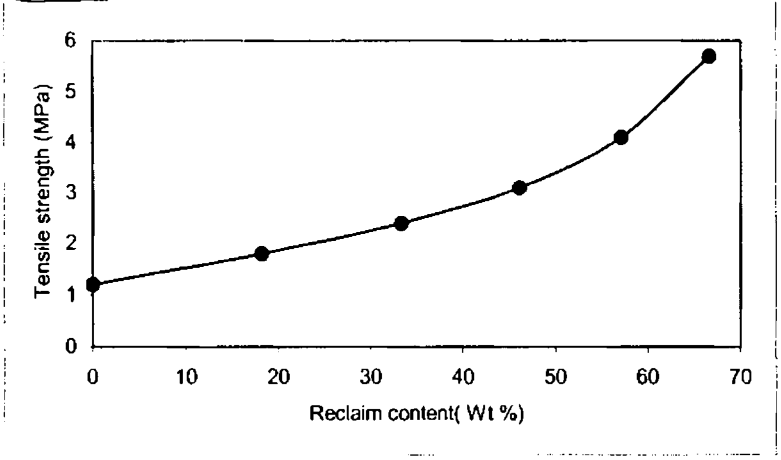


Figure 3.2. 6 Variation of tensile strength with reclaim loading

Figure 3.2.7 gives a plot of ultimate elongation versus reclaim loading. Linear increase in the ultimate elongation of the blend with increase in reclaim content points to increased extensibility of the matrix. This may be resulting from the presence of about 15 % plasticizer in the reclaim. (2.1.1.f.)

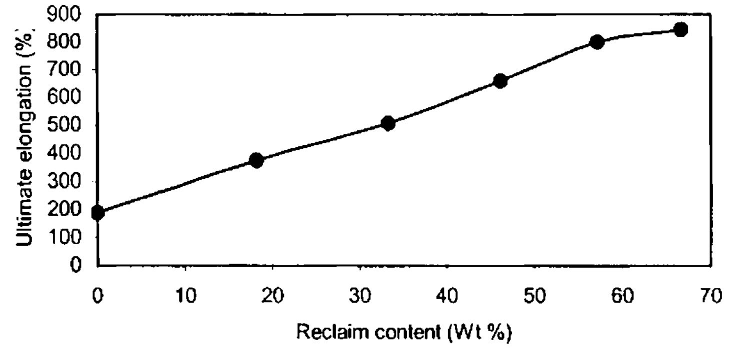


Figure 3.2.7 Variation of ultimate elongation with reclaim loading

Tear strength increases with increase in reclaim loading (Figure 3.2.8). Increased tear strength in case of blends indicates the reinforcing capacity of the reclaim, arising from the presence of carbon black filler.

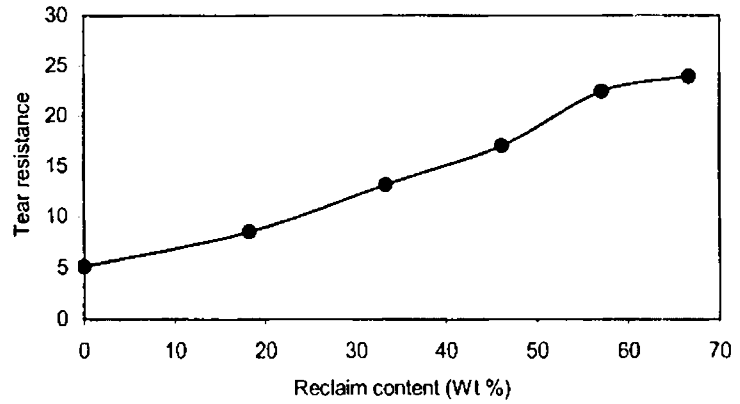


Figure 3.2.8 Variation of tear resistance with reclaim loading

Figure 3.2.9 shows a plot of abrasion loss versus reclaim loading. There is a drastic reduction in the abrasion loss at 33- weight percent of the reclaim beyond which further increase in reclaim content has only a marginal effect in the abrasion loss. The increased abrasion resistance with the increased reclaim load can also be attributed to the presence of reinforcing filler in the reclaim. A low gum strength matrix can be reinforced more efficiently with the carbon black filler.

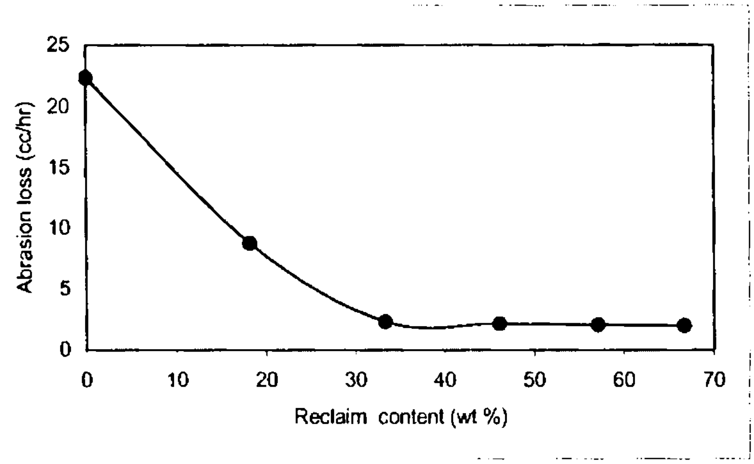


Figure 3.2.9 Variation of abrasion resistance with reclaim loading

Figure 3.2.10. shows the variation of compression set with reclaim loading. This marked increase in the set values at higher reclaim loading may be resulting from combined effect of filler, plasticizer and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values. Similar results have been reported by Phadke et al in natural rubber.(2)

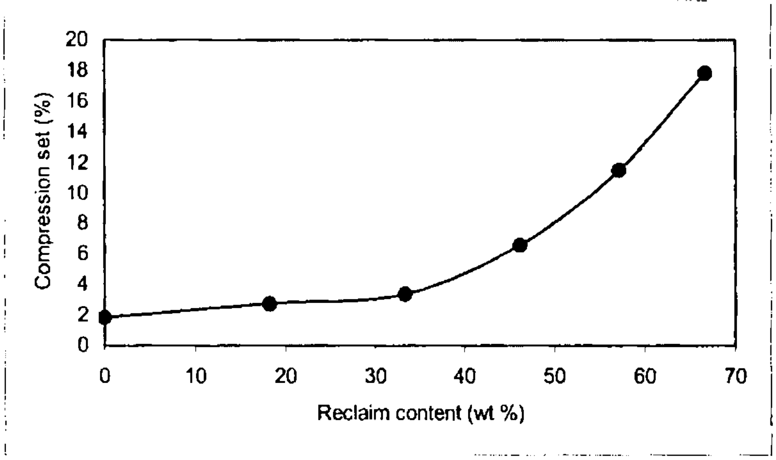


Figure 3.2.10 Variation of compression set with reclaim loading

The reduced elasticity is also evident from figure 3.2.11, which is a plot of resilience versus reclaim loading. As expected, the resilience decreases with the addition of the reclaim.

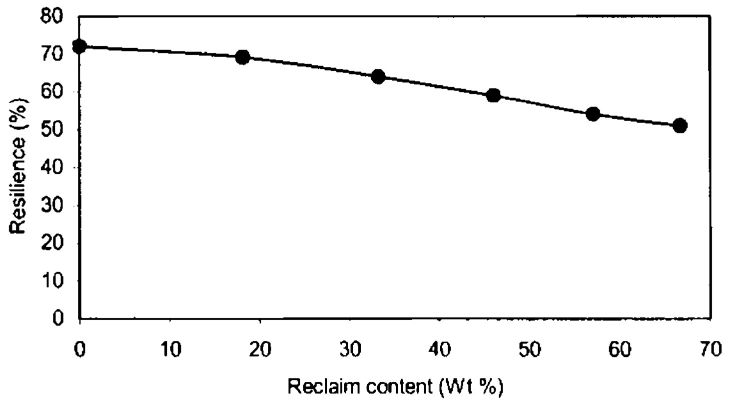


Figure 3.2.11 Variation of resilience with reclaim loading

Figure 3.2.12 shows a linear increase in heat build up with the reclaim loading. The increase in heat build is again due to the presence of reinforcing filler in the reclaim. The filler - matrix interface is an area of energy dissipation. More is the filler, more is the interface area and hence more is the dissipation of energy by heat due to friction.

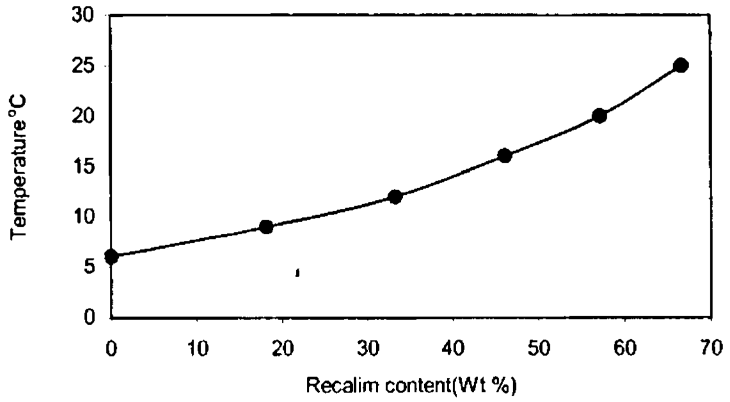


Figure 3.2.12. Variation of heat build up with reclaim loading

3.2.4. Ageing Resistance

Table 3.2.2. shows the tensile strength of the blends before and after ageing. In all the cases of blends the tensile strength value is found to be reduced after ageing. The percentage of retention, calculated as the ratio of tensile strength after and before ageing, shows a gradual reduction from 100 % to 74 % at a reclaim content of 66 weight percent.

Table 3.4.2 Tensile strength of mixes before and after the ageing.

Mix No.	Tensile strength (MPa)		Percentage retention
	Before ageing	After ageing	
A	1.2	1.2	100
B	1.8	1.5	83
C	2.4	1.9	79
D	3.1	2.4	77
E	4.1	3.1	76
F	5.7	4.2	74

A synthetic matrix with better resistance to degradation, the BR gum compound (mix A) gives a percentage retention of 100.Where as in the case of blends, the presence of reclaim which is relatively more prone to degradation, lowers the retention values. A similar trend is also observed in the case of retention of tear (Table 3.2.3).

Table.3.4.3 Tear resistance of mixes before and after the ageing

Mix No.	Tear resistance (N/mm)		Percentage retention
	Before ageing	After ageing	
A	5.1	4.8	94
B	8.5	6.8	80
C	13.1	10.1	77
D	17.0	12.6	74
E	22.4	16.2	72
F	22.9	16.4	71

Table 3.2.4 shows the retention of ultimate elongation of the mixes A-F. Ultimate elongation of the aged sample are lower than that of the unaged sample. This is in agreement with the reduced tensile strength values, of the aged samples.

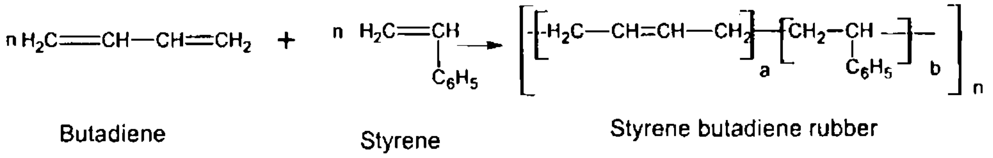
Table.3.4.4 Ultimate elongation of mixes before and after the ageing

Mix No.	Ultimate elongation (%)		Percentage retention
	Before ageing	After ageing	
A	75	75	100
B	150	105	70
C	217	133	66
D	263	166	63
E	320	187	62
F	338	249	61

PART 3

3.3. Styrene butadiene rubber (SBR) / Whole tyre reclaim (WTR) blend

In this study whole tyre reclaim (WTR) is blended with Styrene butadiene rubber (SBR). Styrene butadiene rubber is produced by the copolymerisation of butadiene and styrene.



$$n\,H_2C{=}CH{-}CH{=}CH_2 + n\,H_2C{=}\underset{C_6H_5}{CH} \longrightarrow \left[\left[-H_2C{-}CH{=}CH{-}CH_2-\right]_a\left[-CH_2{-}\underset{C_6H_5}{CH}-\right]_b\right]_n$$

The sequence of the monomer is irregular in the chains of the polymer. Due to the irregularity of the monomeric units in the polymer, SBR gum vulcanizates have low tensile strength. (3) These irregularities of the chain structure results in weak inter chain forces in the polymer.

3.3.1 Preparation of blends

Formulation of the mixes is given in the table.3.3.1. The preparation of the samples and the experimental techniques employed are explained in the chapter2.

Table 3.3.1 Formulation of the mixes

Ingredient	Mix. No					
	A	B	C	D	E	F
SBR	100	90	80	70	60	50
Reclaim	---	20	40	60	80	100

Note:- Note: SBR = Styrene butadiene rubber, WTR- whole tyre reclaim, Weight of whole tyre reclaim is adjusted so as to get 100 grams of rubber hydrocarbon. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g are common to all mixes.

3.3.2.Cure Characteristics

Figure 3.3.1 shows the variation of minimum torque with reclaim loading. Minimum torque decreases from 0.03638 Nm. to 0.02417 N m. and it is a measure of the stock viscosity.

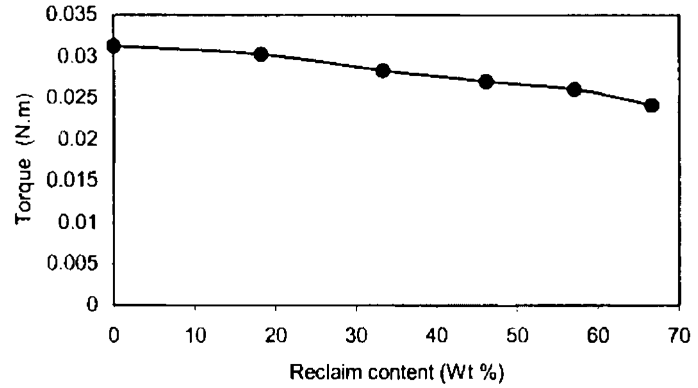


Figure 3.3.1 Variation of minimum torque with reclaim loading

The decreased minimum torque value indicates improved processibility in the case of blends. This improved processibility of the mixes can be attributed to the plasticizer present in the matrix. The acetone extractable fraction of the reclaim, which is an indication of plasticizer content of the reclaim is given in the table 2.1.1.f. Increasing reclaim loading increases plastizicer content of the mixes and hence the minimum torque decreases.

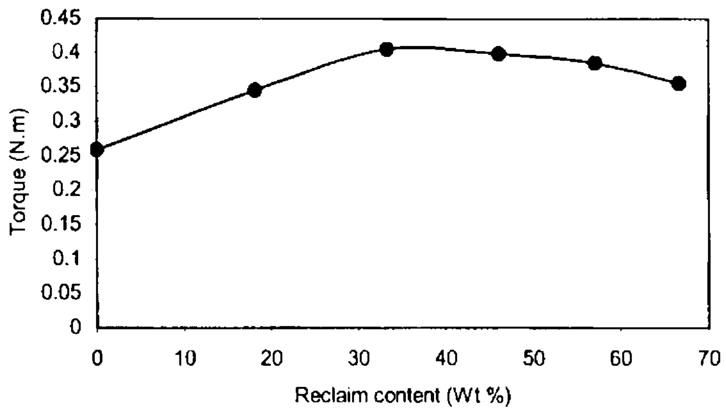


Figure 3.3.2 Variation of (max –min) torque with reclaim loading

The Figure 3.3.2 shows variation of (maximum – minimum) torque (Δt). The (max – min) torque value increases with the reclaim loading. After 33 weight percent of reclaim, further additions of reclaim results in decrease in torque. The (Δt) value is a measure of cross-links that are formed during the vulcanization reaction. The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking. Increase in concentration of low molecular weight reclaimed rubber lead to the lower (max-min) torque values. Gibale et.al reported that addition of reclaim to the SBR compounds decreases the maximum torque (4). Decrease in (Δt) is again accounted for the basis of higher oil content of the reclaimed rubber.

Figure 3.3.3 gives a plot of cure time versus reclaim loading. The cure time is decreased gradually from 8.9 minutes to 4.6 minute at 66.6 weight percent of reclaim loading. The reduced cure time may be attributed to the presence of accelerator relics present in the reclaimed rubber. Scorch time decreases from 4.9 to 2.6 minutes with increase in reclaim loading. Figure (3.3.4) represents the variation of scorch time with increase in reclaim content. Decrease in scorch time can be attributed to the cross-link precursors or unreacted curatives in reclaimed rubber. Decrease in scorch time on the addition of ground vulcanizate to SBR compounds is reported by Gibale earlier.(4)

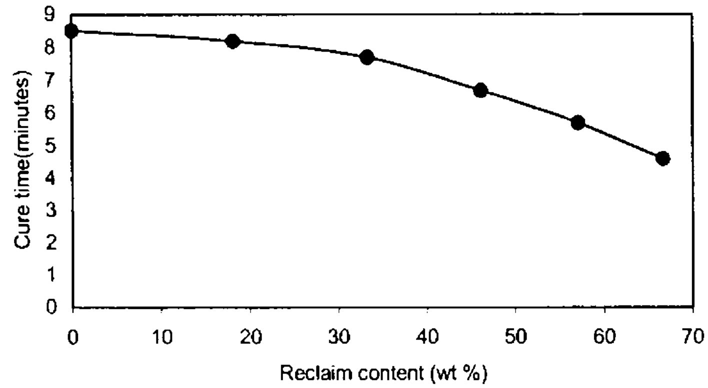


Figure 3.3.3 Variation of cure time with reclaim loading

Figure (3.3.5) represents variation of cure rate with reclaim loading. The increase in cure rate is expected from the decrease in cure time and it may be attributed to for presence of accelerator relics present in the reclaimed rubber.

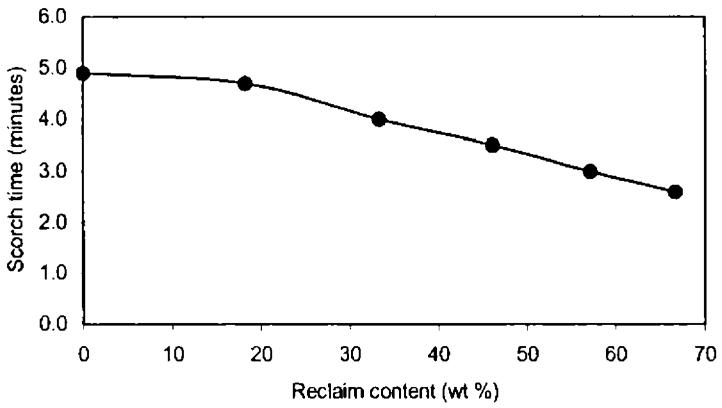


Figure 3.3.4 Variation of scorch time with reclaim loading

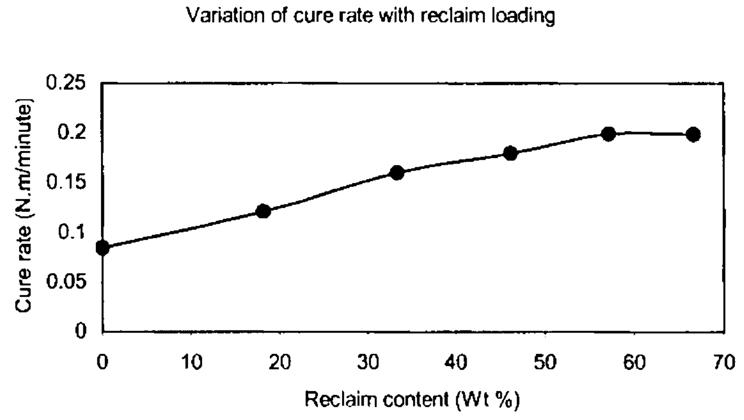


Figure 3.3.5 Variation of cure rate with reclaim loading

3.3.2.Mechanical Properties

Figure 3.3.6 shows the variation of tensile strength with reclaim loading. Tensile strength shows a linear increase from 2.11 MPa to 5.14 MPa at 66.6 weight percent of reclaim loading. SBR, a typical non -crystallizing rubber with low gum tensile strength, is effectively reinforced by carbon black present in the whole tyre reclaimed rubber. Improvements in tensile strength and tear strength on the addition of ground vulcanizates to SBR is reported by Gibale.(5)

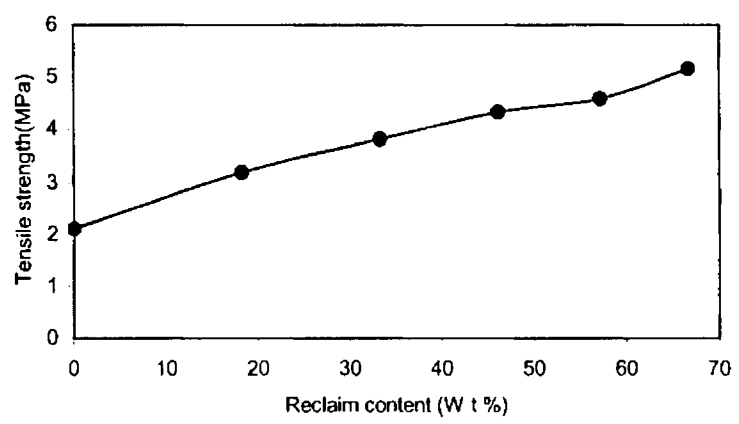


Figure 3.3.6. Variation of tensile strength with reclaim loading

Figure 3.3.7 show the variation of ultimate elongation with reclaim loading. The ultimate elongation values show an increase with increase in reclaim content which can be attributed to the presence of plasticizer present in the reclaim. At 46 weight percent of reclaimed rubber the ultimate elongation attains a maximum value and further addition of reclaim reduces the ultimate elongation. It may be partially due to the increased concentration low molecular weight reclaim.

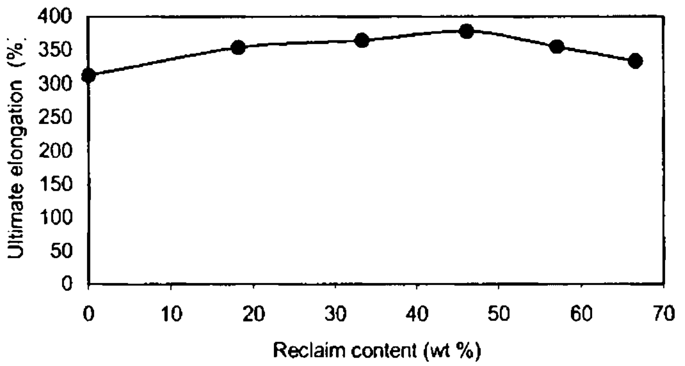


Figure 3.3.7. Variation of ultimate elongation with reclaim loading

Figure 3.3.8 shows variation of tear strength with reclaim loading. The tear strength of the blends increases from 11.4 N/mm to 30.9 N/mm at 66 weight percent of reclaim. The improved tear resistance can be attributed to the presence of reinforcing carbon black filler present in the WTR matrix. A plot of abrasion loss versus reclaim content is shown in the figure 3.3.9. The abrasion loss on reclaim loading increases from 4.9 cm^3/hr to 8.5 cm^3/ hr at 66 weight percentage. The increase in abrasion loss may be attributed to the relatively lower molecular weight of the reclaimed rubber. The higher hysteresis loss, as indicated by lower resilience of the blend, may also contribute to the increased abrasion loss. Similar results have been reported in the case of NR/reclaim by Phadke et.al (3)

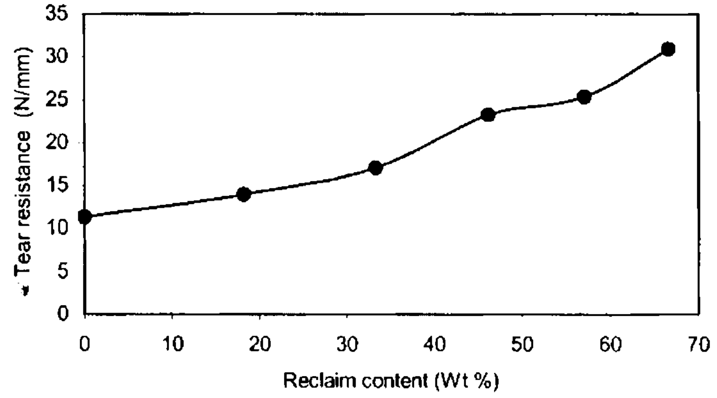


Figure 3.3.8 Variation of tear resistance with reclaim loading

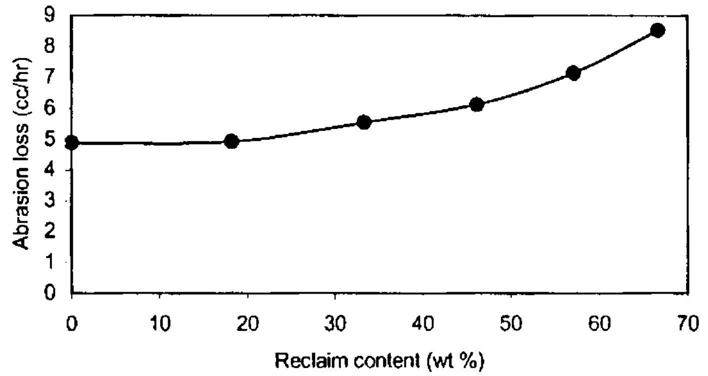


Figure 3.3.9 Variation of abrasion resistance with reclaim loading

Figure 3.3.10 shows variation of resilience with reclaim loading. The resilience, a measure of material elasticity, is found to decrease with increase in reclaim loading. The value changes from 63 % at zero parts to 49% at 66-weight percentage of reclaim. Higher the concentration of filler and plasticizers, higher is the chance of energy dissipation. The energy dissipation can be through loss at filler – matrix interfaces, friction between the chains and breakdown of filler structure. This is manifested as the lower resilience value.

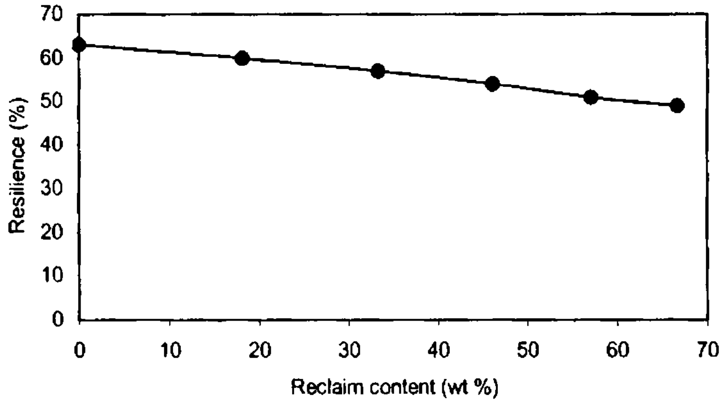


Figure 3.3.10 Variation of resilience with reclaim loading

Figure 3.3.11. shows the variation of compression set at constant strain with reclaim loading. The compression set increases with increase in reclaim loading and attain a maximum value at 57 percent of reclaim, in agreement with the observed reduced resilience. The increased compression set arises from the flowabillity of the compound under load at elevated temperature. The relatively lower molecular weight of the reclaim renders the blend more plastic. Similar results have been reported by Chakraborthy et.al.(2)

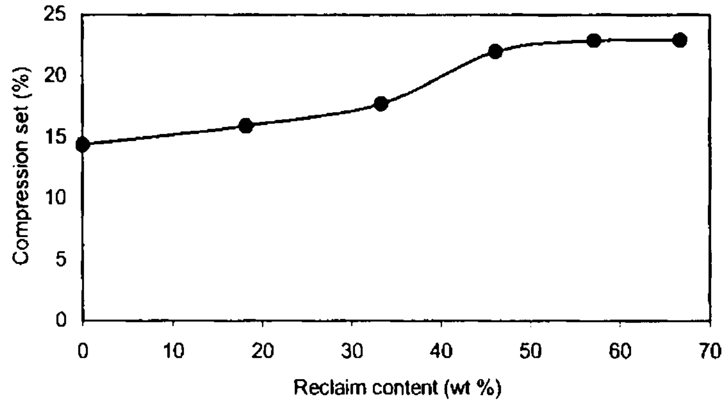


Figure 3.3.11. Variation of compression set with reclaim loading

Figure 3.3.12 shows increase in heat build up with the reclaim loading. The increase in heat build is again due to the presence of reinforcing filler in the reclaim. The filler - matrix interface is an area of energy dissipation. More is the filler, more is the interface area and hence more is the dissipation of energy as heat due to friction

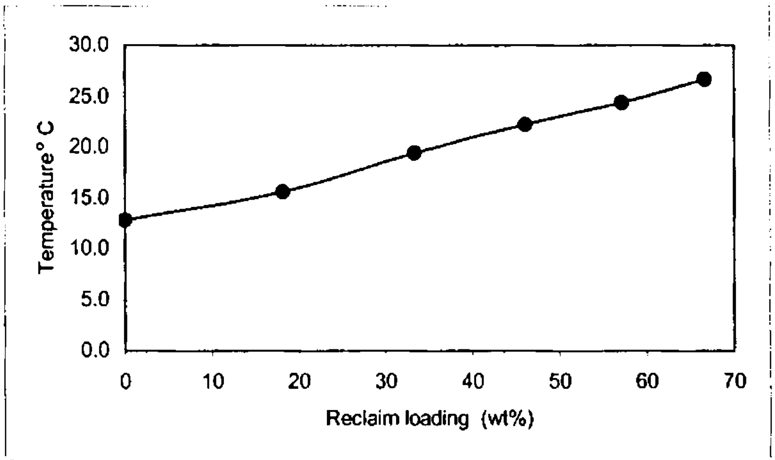


Figure 3.3.12.Variation of heat build up with reclaim loading

3.3.3. Ageing Resistance

The percentage retention, calculated as the ratio of aged properties to the unaged properties is given in the tables 3.3.2 to 3.3.4. Table 3.3.2 represents percentage retention of tensile strength. The retention value indicates the nominal level of post curing taking place during aging. This is to be expected because of the marching cure pattern of SBR

The tear strength before and after ageing is shown in the table 3.3.3. In all cases the percentage of retention of the blend is less than gum compound.

The aged values of ultimate elongation are also found to lower than that of unaged sample at all mix ratios.

Table 3.3.2. Tensile strength of mixes before and after the ageing

Mix No.	Tensile strength (MPa)		Percentage retention
	Before ageing	After ageing	
A	2.1	2.4	114
B	3.2	3.4	106
C	3.8	3.9	103
D	4.3	4.3	99
E	4.6	4.5	98
F	5.1	5.2	102

Table.3.3.3 Tear resistance of mixes before and after the ageing

Mix No.	Tear strength (N/mm)		Percentage retention
	Before ageing	After ageing	
A	11.3	10.2	90
B	13.9	13.3	95
C	17.0	15.9	93
D	21.2	19.1	90
E	25.3	22.6	89
F	30.9	28.3	92

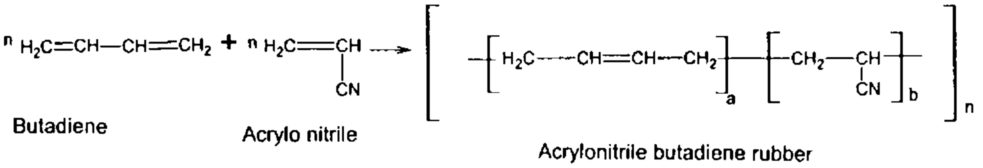
Table.3.3. 4 Ultimate elongation of mixes before and after the ageing

Mix No.	Ultimate elongation (%)		Percentage retention
	Before ageing	After ageing	
A	313	252	81
B	355	359	73
C	364	266	73
D	378	276	73
E	355	287	81
F	334	322	96

PART 4

3. 4. Acrylonitrile butadiene rubber (NBR) / Whole tyre reclaim (WTR) blend.

NBR is a synthetic rubber made by random polymerisation of acrylonitrile with butadiene by free radical catalyst. The main raw materials used for the monomer are butadiene and acrylonitrile. Theoretically the polymerisation reaction can be written as



The value a and b depends on precise formulation recipe and temperature of polymerisation. As the ratio of monomers in the polymer largely controls the properties, the design of the polymerisation recipe and the temperature at which this is carried out are important features of nitrile rubber.

Ntrile rubber is an oil resistant rubber. It offers broad balance of low temperature, oil, fuel and solvent resistance as related to acrylonitrile content. These characteristics combined with their good abrasion resistance and water resistance qualities, make them suitable for the use in a wide variety of applications.

3.4.1.Preparation of blends

In this experiment nitrile rubber is blended with the whole tyre reclaim Formulation of the mixes is given in the table 3.4.1. Sample preparation and various test method employed are given in the chapter 2.

Table 3.4.1. Formulation of the mixes

Ingredient	Mix. No					
	A	B	C	D	E	F
NBR	100	90	80	70	60	50
WTR	---	20	40	60	80	100

Note:- Note: NBR - Acrylonitrile rubber, WTR- whole tyre reclaim, Weight of whole tyre reclaim is adjusted so as get 100 grams of rubber hydrocarbon.

ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g are common to all mixes.

3.4.2 Cure Characteristics

Figure 3.4.1 shows the variation of minimum torque with reclaim loading. Minimum torque value decreases from 0.02954 to 0.01514 N.m. It is a measure of the stock viscosity and shows a gradual reduction with respect to reclaim loading. This increased flowability which results in decrease in torque values of the mixes can be attributed to the plastizicer present in the matrix. The reclaim contains 15 % plasticizer (2.1.1.f). Increasing reclaim loading increases plastizicer content of the mixes and hence the minimum torque decreases.

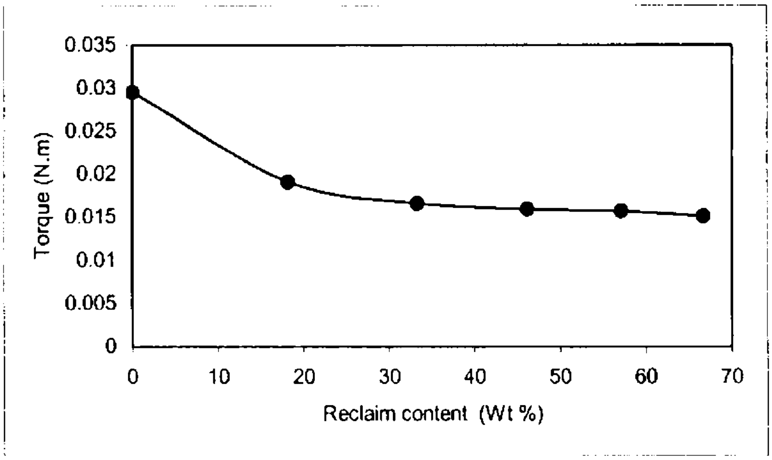


Figure 3.4.1 Variation of minimum torque with reclaim loading

Figure 3.4.2 shows variation of (maximum – minimum) torque (Δt). Torque value decrease from 0.42773 N.m to 0.24072 N.m with the 66.6 weight percent of reclaim loading. The (max– min) torque value shows a marginal reduction at 33.3 weight percent of reclaim content. The (Δt) value is a measure of cross-links that are formed during the vulcanization reaction. The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there are relatively less reaction sites available for further cross linking.

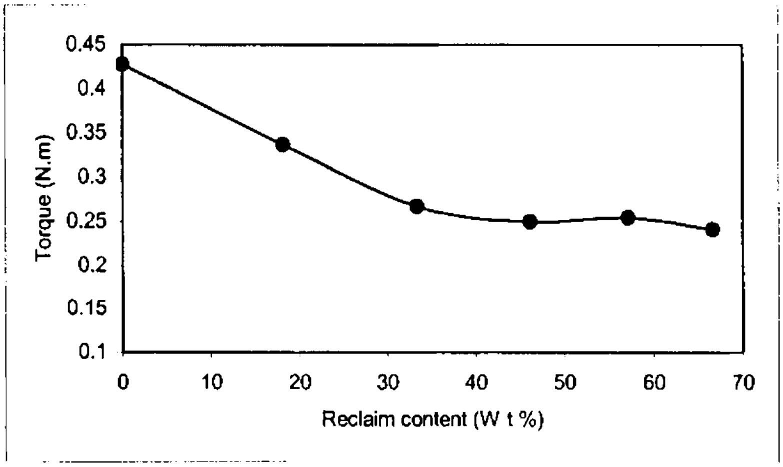


Figure 3.4.2. Variation of (max-min) torque with reclaim loading

Figure 3.4.3 shows variation of cure time for the mixes A-F. On addition of reclaim to the nitrile rubber cure time decreases regularly. This may due to the presence of curatives in the reclaim. In a similar pattern scorch time also decreases with reclaim loading. (Figure 3.4.4) However it is observed that there is no significant increase in the cure rate, which was due to the less availability of reactive sites for cross-link formation with increase in reclaim. (Figure 3.4.5)

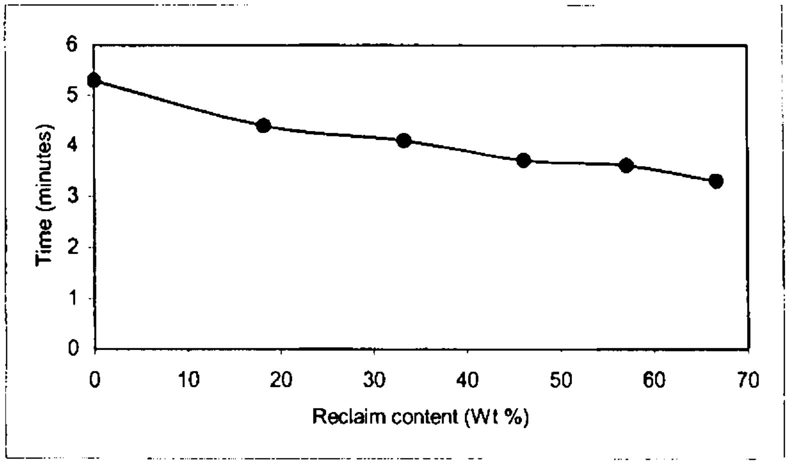


Figure 3.4.3 Variation of cure time with reclaim loading

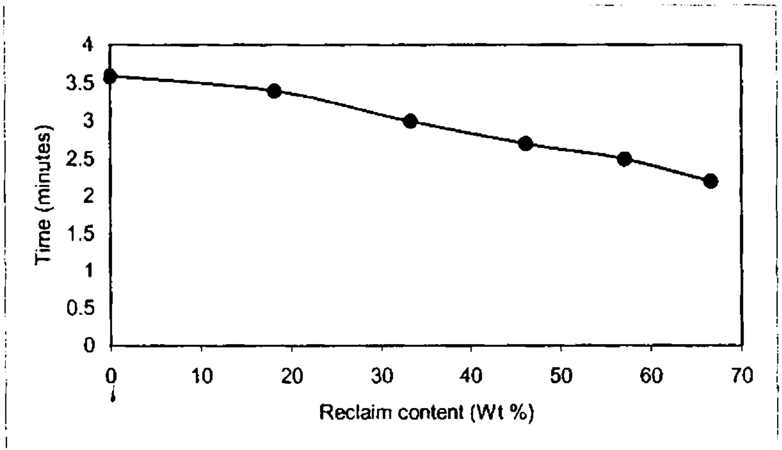


Figure 3.4.4. Variation of Scorch time with reclaim loading

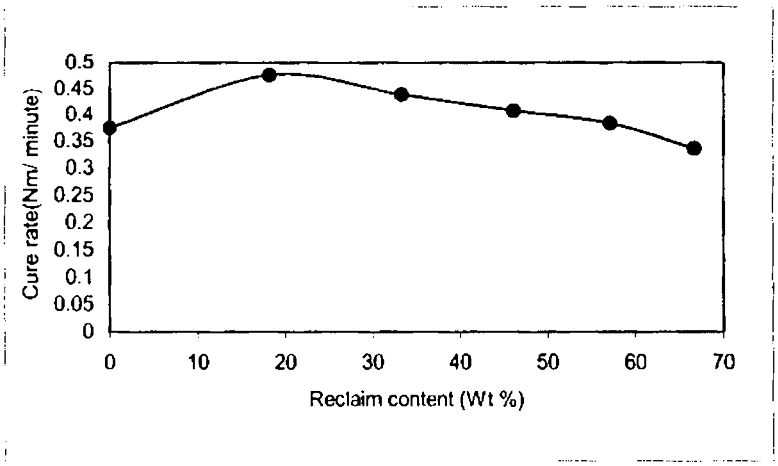


Figure 3.4.5. Variation of cure rate with reclaim loading

3.4.3.Mechanical Properties

Figure 3.4.6 shows the variation of tensile strength with reclaim loading. Tensile strength shows almost a linear increase from 2.0 MPa to 7.2 MPa at 66.6- weight percentage of reclaim. The increase in tensile strength may be attributed to the presence of reinforcing filler, carbon black, in the reclaim. (section2.1.1.f.)

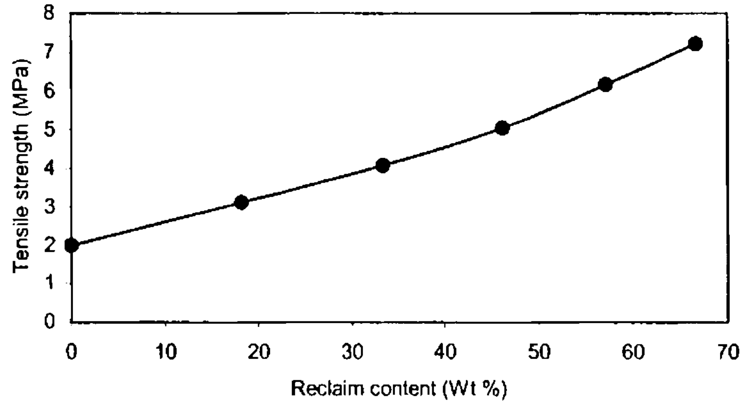


Figure 3.4.6 Variation of tensile strength with reclaim loading

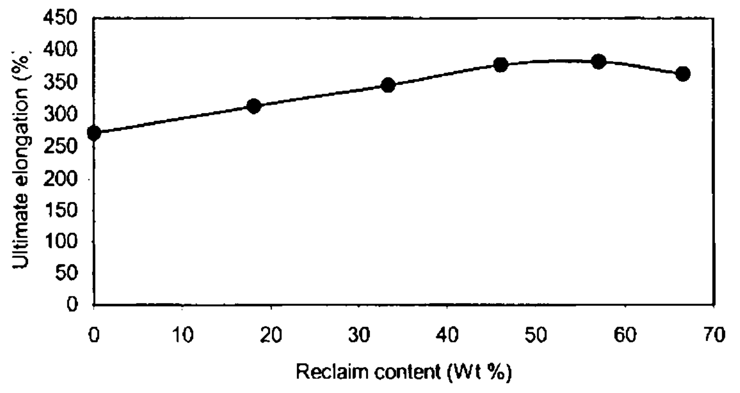


Figure 3.4.7 Variation of ultimate elongation with reclaim loading

Figure 3.4.7 gives a plot of ultimate elongation versus reclaim loading. The tensile strength measurements ultimate elongation also shows a linear increase with the increase in reclaim content. This is due the extensibility of the matrix due to the presence of about 15% plasticizer in the reclaim rubber. (2.1.1.f.)

Figure 3.4.8 shows variation of tear strength with the increase in reclaim loading. Tear strength increases with increase in reclaim loading. Increased tear strength in the case of blends again conforms the reinforcing capacity of the reclaim arising from the presence of carbon black filler. Rate of improvement of tear strength decreases after 57 weights percent. This may attribute for the dilution effect produced by low molecular weight reclaimed rubber.

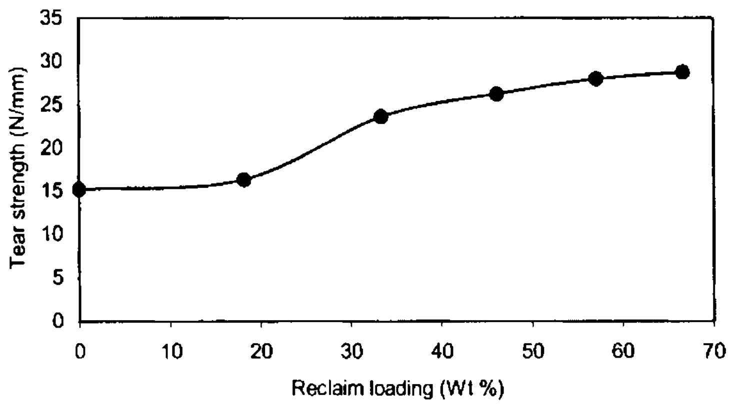


Figure 3.4.8 Variation of tear resistance with reclaim loading

Figure 3.4.9 shows a plot of abrasion loss versus reclaim loading. There is an increase in the abrasion loss with the reclaim loading. The abrasion is a phenomenon involving tear and hysteresis. Though the tear resistance is improved, the hysteresis is adversely affected with the increase in reclaim loading. The result is manifested as improved abrasion resistance. Similar results have been reported by Phadke et al ⁽²⁾

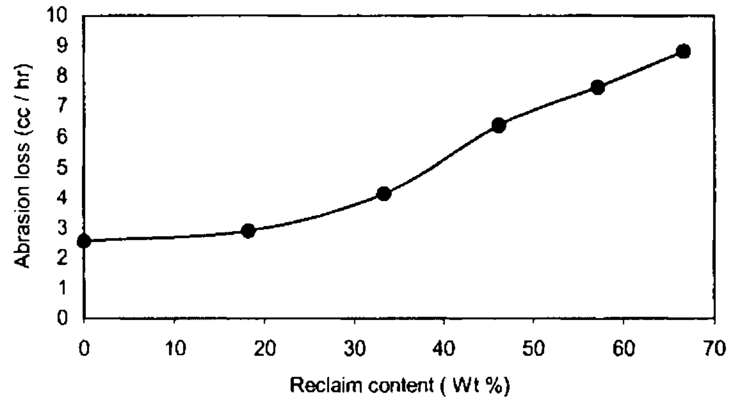


Figure 3.4.9 Variation of abrasion resistance with reclaim loading

Figure 3.4.10 shows the variation of compression set with reclaim loading. Set increases with the incorporation of the reclaim to the nitrile rubber. This is in agreement with increase in hysteresis loss and decrease in resilience with the reclaim loading. This marked increase in the set at higher reclaim loading may be resulting from the combined effect of filler, plasticizer and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values. Similar results have been reported by Phadke et.al (2)

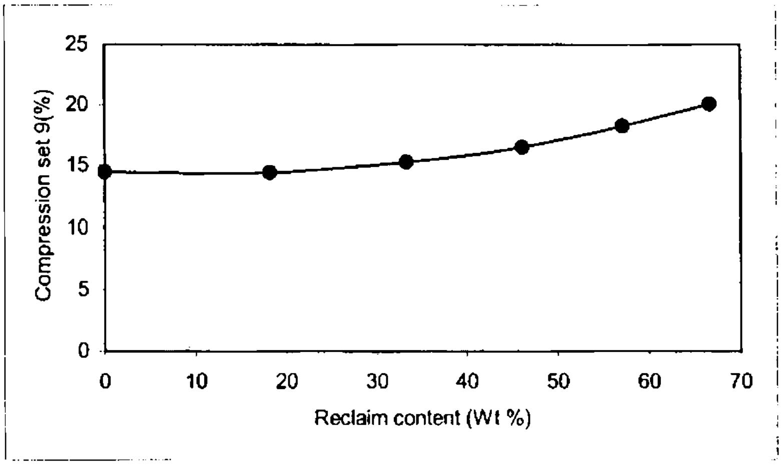


Figure 3.4.10 Variation of compression set with reclaim loading

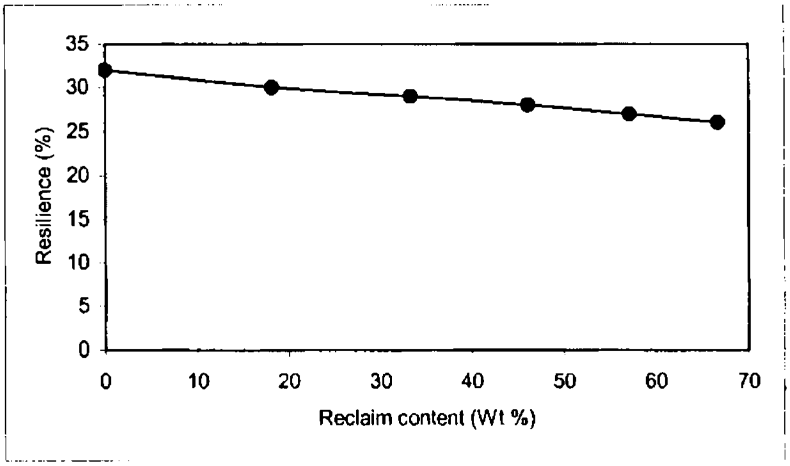


Figure 3.4.11 Variation of resilience with reclaim loading

The reduced elasticity is also evident from figure 3.4.11, which is a plot of resilience versus reclaim loading. This decrease in resilience value is in agreement with the observed compression set values.

Figure 3.4.12. shows heat build up in a mixes A-F. There is a gradual increase in heat build up with the increase in WTR loading. Higher the concentration of filler, higher is the chances of energy dissipation as heat. The energy dissipation can be through filler – matrix interface, friction between the chains and breakdown of filler structure.

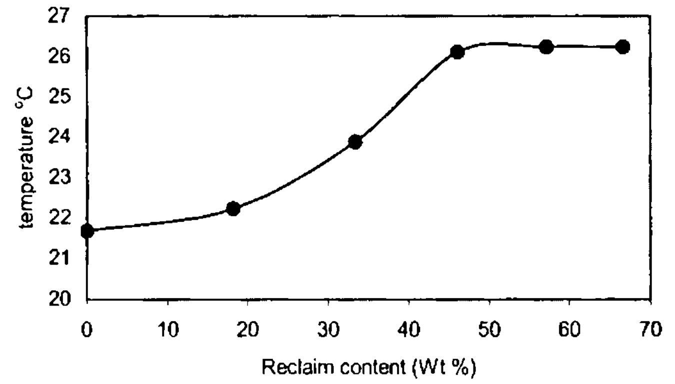


Figure 3.4.12. Variation of heat build up with reclaim loading

3.4.4. Ageing Resistance

Table 3.4.2 shows the tensile strength of the blends before and after ageing. In all the cases, the aged samples show higher tensile strength. The percentage of retention shows a gradual reduction from 120 to 111 at a reclaim content of 66.6 weight percent. This shows that the state of cure is improved while ageing. However in the presence reclaim, there is some degradation. This may be attributed to the fact that the reclaim mainly consists of natural rubber and it is more prone to degradation under elevated temperature.

Table 3.4.2. Tensile strength of mixes before and after the ageing

Mix No.	Tensile strength (MPa)		Percentage retention
	Before ageing	After ageing	
A	2.0	2.4	120
B	3.3	3.5	109
C	4.1	4.3	106
D	5.1	5.7	112
E	6.2	6.8	110
F	7.2	8.0	111

Table 3.1.3 Tear resistance of mixes before and after the ageing

Mix No.	Tear resistance (N/mm)		Percentage retention
	Before ageing	After ageing	
A	15.2	15.2	100
B	16.4	16.2	98
C	23.6	23.2	98
D	25.3	25.4	99
E	28.0	27.6	98
F	29.7	27.6	99

Table 3.4.3. shows that tear strength of aged sample is lesser than that of unaged sample. This indicates that tear strength is better when the compound is slightly under cured.

Table 3.4.4. shows the retention of ultimate elongation of the mixes A-F. Ultimate elongation of the aged sample is lower than that of the unaged sample.

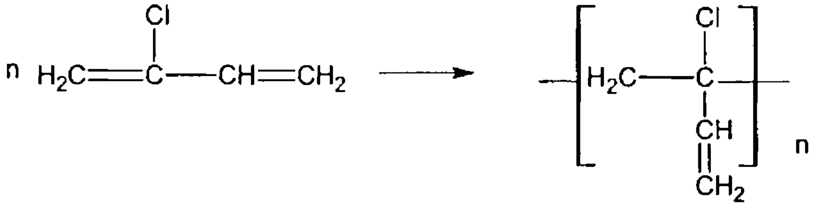
Table. 3.4.4 Ultimate elongation of mixes before and after the ageing

Mix No.	Ultimate elongation (%)		Percentage retention
	Before ageing	After ageing	
A	272	271	100
B	313	308	98
C	333	322	97
D	377	352	93
E	406	398	98
F	363	355	98

PART 5

3.5. Chloroprene Rubber (CR)/ Whole tyre reclaimed rubber (WTR) blend*

Polychloroprene or Neoprene is a synthetic elastomer available in solid form or latex. Solid chloroprene is available in different grades. Of these W type has more uniform distribution of molecular weight. It is vulcanised with metallic oxides rather than sulphur. Chloroprene is resistant to oils, oxygen, ozone and electric discharge. Isocyanate-modified form of chloroprene has high flame resistance. Chloroprene is chemically polymer of 2 chloro 1,3 butadiene and it can be represented as



$$n\ H_2C{=}C(Cl){-}CH{=}CH_2 \longrightarrow \left[-H_2C{-}C(Cl)(CH{=}CH_2)-\right]_n$$

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[*] Results of this chapter is communicated to *Int. J. Polymer Materials*

3.5.1.Preparation of blends

Formulation of the mixes is given in the table 3.5.1. Samples preparation and various test method employed are given in the chapter 2

Table 3.5.1. Formulation of the mixes

Ingredient	Mix. No					
	A	B	C	D	E	F
CR	100	90	80	70	60	50
WTR	---	20	40	60	80	100

Note:- CR- Chloroprene, WTR - whole tyre reclaim, weight of whole tyre reclaim is adjusted so as to get 100 grams rubber hydrocarbon. ZnO –5 g, MgO-4 g, Stearic acid – 0.5 g, 4020 -1 g NA22 (ethylene thio urea) 0.5 g are common to all mixes

Vulcanization of polychloroprene is considerably different from that of natural rubber and other synthetic rubbers. The vulcanization of chloroprene compounds is carried out using metal oxide. The cross linking agent is usually zinc oxide in combination with magnesium oxide. (6) The details of metal oxide curing is available in the books. (7,8,9,10,11)

3.5. 2.Cure Characteristics

Figure 3.5.1 shows the variation of minimum torque with reclaim loading. Minimum torque, a measure of the stock viscosity, shows a gradual reduction with respect to reclaim loading. This increased flowability of the mixes can be attributed to the plasticizer present in the matrix. The reclaim contains 15 % plasticizer. Increasing reclaim loading increases plastizicer content of the mixes, and hence the minimum torque decreases.

Figure 3.5.2. shows variation of (maximum – minimum) torque (Δt) of mixes A -F. The (max – min) torque value shows a reduction with the addition of reclaim. The (Δt) value is a measure of cross-links that are formed during the vulcanization reaction. The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is

already partially cross linked matrix and it is not further cross linked with the metal oxide cure system used.

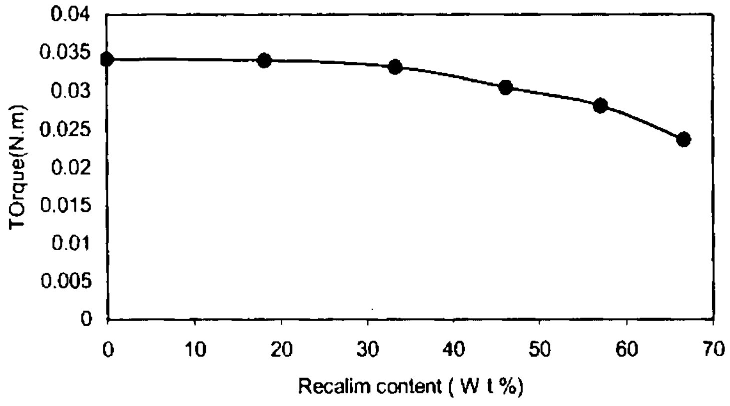


Figure 3.5.1 Variation of minimum torque with reclaim loading

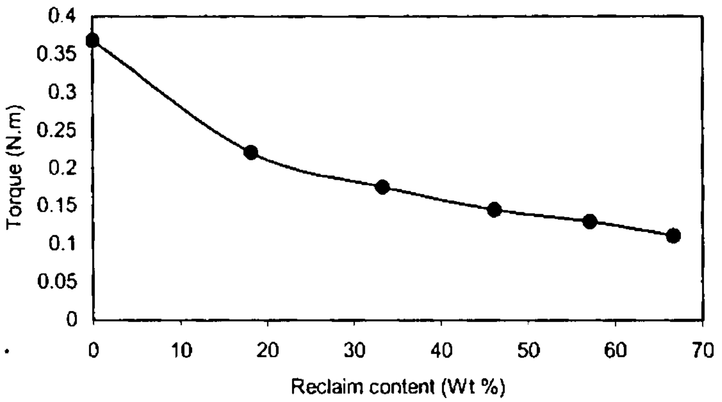


Figure 3.5.2 Variation of (max –min) torque with reclaim loading

Figure 3.5.3 gives a plot of cure time versus reclaim loading. The cure time is increased gradually from 18.5 minutes to 22 minute at 66.6 weight percent of reclaim loading. The cure rate is reduced correspondingly. (Figure 3.5.5.) The scorch time (Figure 3.5.4.) shows only a marginal reduction. This indicates that the reclaimed rubber adversely affects the cure reaction of chloroprene rubber.

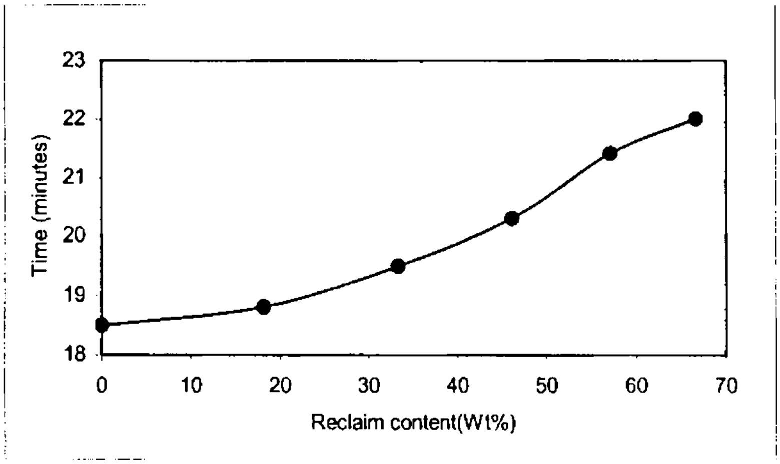


Figure 3.5.3 Variation of cure time with reclaim loading

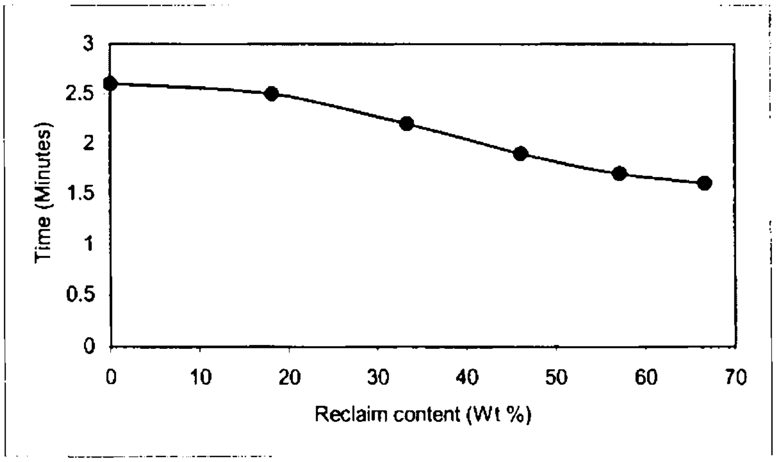


Figure 3.5.4 Variation of Scorch time with reclaim loading

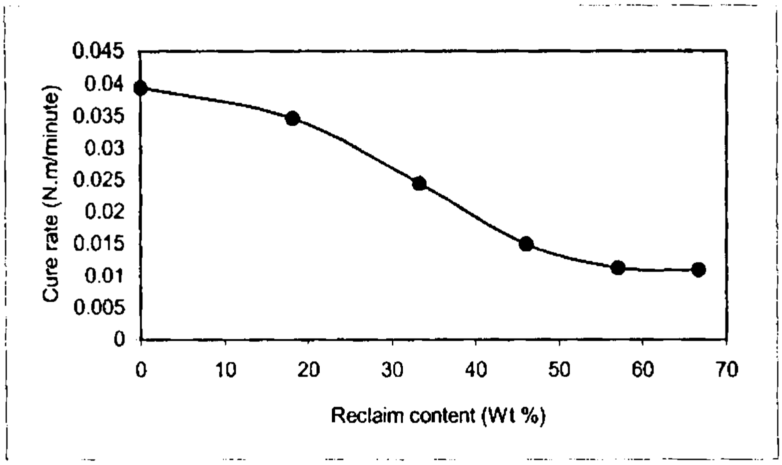
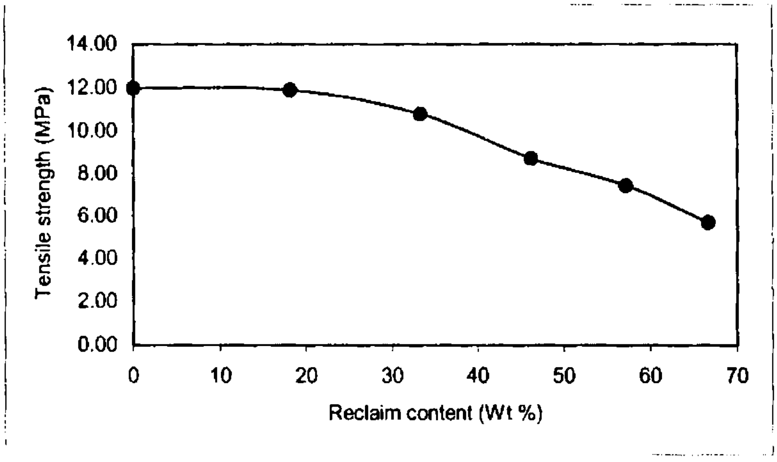


Figure 3.5.5 Variation of cure rate with reclaim loading

3.5.3. Mechanical Properties

Figure 3.5.6 shows the variation of tensile strength with reclaim loading. Tensile strength changes from 12.0 MPa to 5.7 at 66 weight percent of reclaim loading. The Chloroprene rubber, like natural rubber, shows high gum tensile strength compared to styrene butadiene rubber or acrylonitrile butadiene rubber.



Compatible? –

Figure 3.3.6. Variation of tensile strength with reclaim loading

Addition of reclaimed rubber to the chloroprene matrix reduces the tensile strength gradually. This may be attributed to the lower level of cross links formed and the dilution effect generated by the low molecular weight reclaim rubber. This is in agreement with the lower (Δt) values of the blend. (Figure 3.5.2).

These fillers also cause increased in homogeneity in the matrix and result in the low ultimate elongation values (Figure 3.5.7).

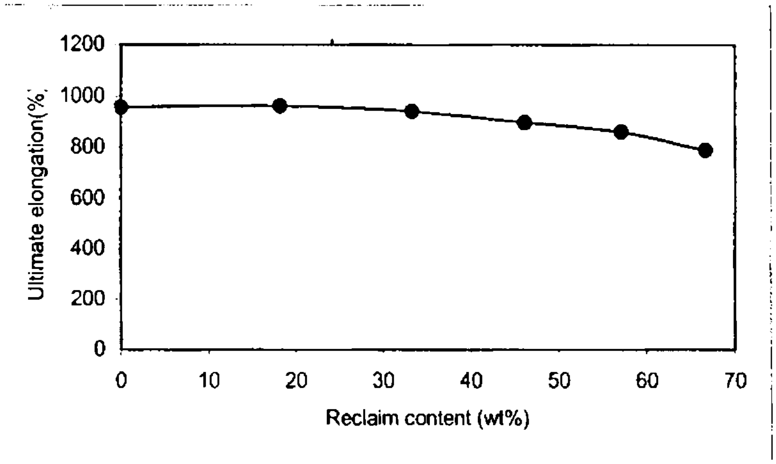


Figure 3.5.7.Variation of ultimate elongation with reclaim loading

Figure 3.5.8. shows variation of tear resistance with reclaim loading. Tear strength is unaffected by the addition of reclaimed rubber to be matrix up to 46 weight percentage of reclaim and is reduced beyond this concentration (Figure 3.5.8.). For the gum CR, the higher tear resistance may be attributed to the strain crystallisibility of the matrix.

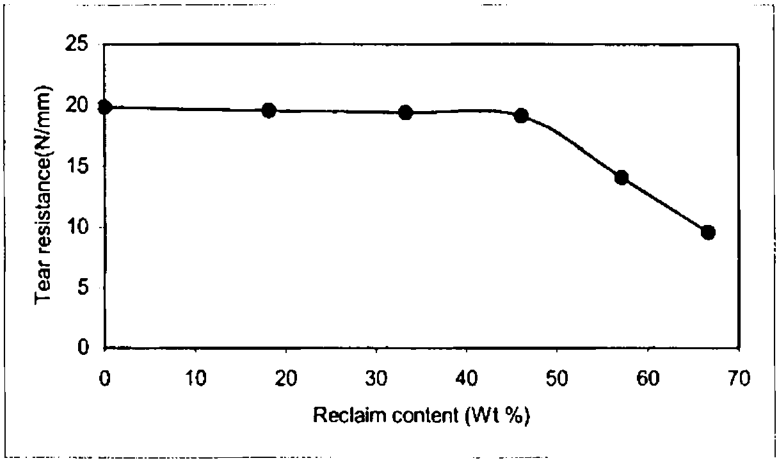


Figure 3.5.8 Variation of Tear resistance with reclaim loading

At higher reclaim loading, the presence of a second component in the blend reduces this possibility and hence the tear strength is lower. As the blend composition changes from low to high reclaim content, the CR matrix is both diluted and reinforced due the presence of the black filler. At lower levels these two tend to equalize and there is no net change. At higher loading the dilution effect becomes prominent and the tear resistance decreases.

Figure 3.5.9 shows a plot of abrasion loss versus reclaim loading. There is a significant increase in abrasion loss beyond 33 weight percent of reclaim loading. The abrasion process involves both hysteresis and tear resistance and both are adversely affected beyond 33 weight percent of reclaim loading resulting in higher abrasion loss.

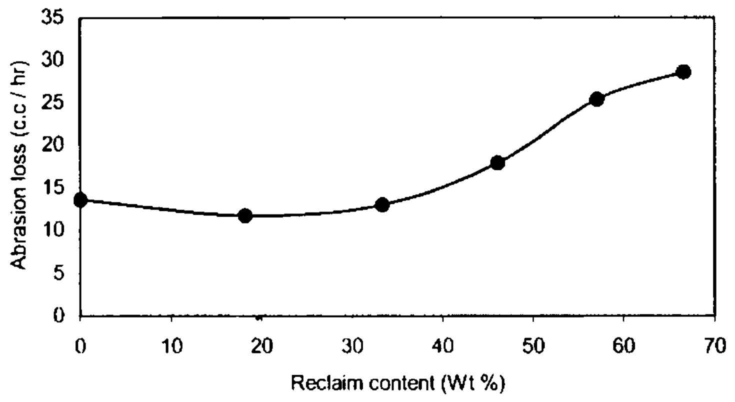


Figure 3.5.9 Variation of abrasion resistance with reclaim loading

The reduced elasticity is also evident from figure 3.5.10. which is a plot of resilience versus reclaim loading for the mixes A - F. As expected, the resilience decreases with the addition of the reclaim.

Figure 3.5.11 shows the variation of compression set with reclaim loading. This marked increase in the set values at higher reclaim loading may be resulting from combined effect of filler, plasticizer and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values. Similar results have been reported by Phadke et al (2)

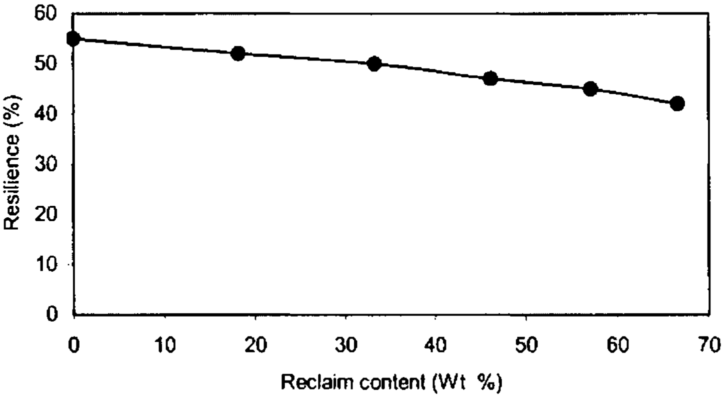


Figure 3.5.10 Variation of resilience with reclaim loading

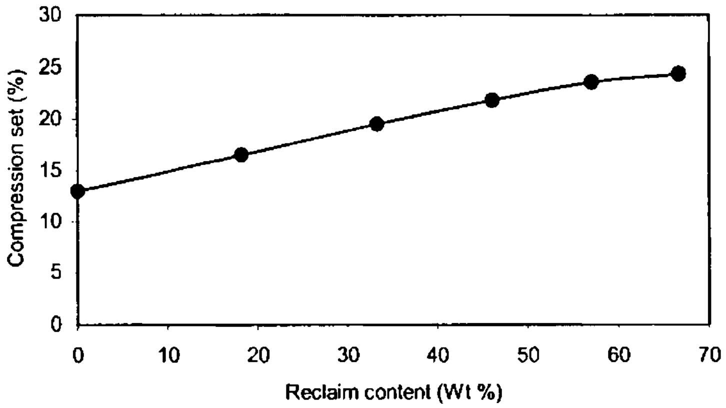


Figure 3.5.11 Variation of compression set with reclaim loading

Figure 3.5.12 shows increase in heat build up with the reclaim loading. The increase in heat build is again due to the presence of reinforcing filler present in the reclaim matrix. The filler - matrix interface is an area of energy dissipation. More is the filler, more is the interface area and hence more is the dissipation of energy by heat due to friction.

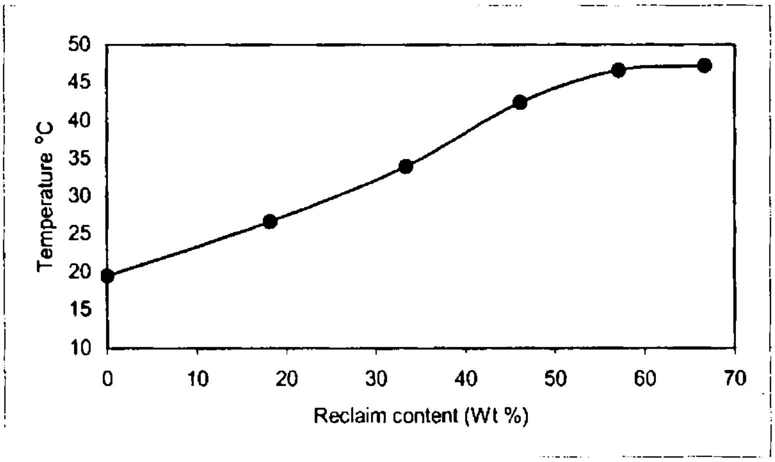


Figure 3.5.12. Variation of heat build up with reclaim loading

3.5.4.Ageing Resistance

The percentage retention of tensile strength shows that chloroprene rubber retains its properties after aging. Incorporation of reclaimed rubber to the chloroprene rubber does not adversely affected the ageing properties of the blend. Similar trends are observed in tear and ultimate elongation results, indicating higher aging resistance of the chloroprene /reclaim blend. (Table 3.5.2 to 3.5.4)

Table 3.5.2 Tensile strength of mixes before and after the ageing

Mix No.	Tensile strength in MPa		Percentage retention
	Before ageing	After ageing	
A	12.0	12.1	100
B	12.9	12.7	107
C	10.8	11.7	108
D	8.7	9.6	107
E	7.4	7.9	106
F	5.7	5.8	101

Table 3.5.3 Tear resistance of mixes before and after the ageing

Mix No.	Tear resistance N/mm		Percentage retention
	Before ageing	After ageing	
A	19.8	22.4	113
B	19.5	22.8	116
C	19.3	23.2	120
D	19.1	23.2	121
E	14.1	16.6	117
F	9.6	11.0	114

Table.3.5.4 Ultimate elongation of mixes before and after the ageing

Mix No.	Ultimate elongation (%)		Percentage retention
	Before ageing	After ageing	
A	890	957	108
B	901	960	107
C	920	939	102
D	988	896	91
E	851	861	101
F	700	789	113

Table.3.5.4 shows the retention of ultimate elongation of the aged and un aged sample. Ultimate elongation values of the aged sample are greater than that of the unaged sample.

3.6.Conclusions

Whole tyre reclaim (WTR) is a good compounding ingredient, which can contribute rubber hydrocarbon and carbon black to the rubber compounds. When WTR was used as a compounding ingredient easy processibility of the blend is observed due to the presence of plastizicer in the reclaim. The presence of plasticizer in the reclaim is reflected in the lower minimum torque of the blends.

Cure time of blends of whole tyre reclaim with NBR, SBR, and BR show a reduction with respect to increasing in whole tyre reclaim concentration. In the Chloroprene rubber addition of reclaim increases the cure time since accelerator relics present in the reclaim does not favour metal oxide cure of the chloroprene system. Scorch time is reduced in all the blends of whole tyre with the natural rubber, acrylonitrile rubber, styrene butadiene rubber, butadiene rubber and chloroprene rubber.

In the Nitrile rubber, Styrene butadiene rubber and Butadiene rubber addition of whole tyre reclaimed rubber increases the tensile strength which, may be accounted for increased reinforcing capacity of the carbon black in the whole tyre reclaim. Natural rubber and Chloroprene rubber, which have high degree of crystallinity, show high tensile strength in the gum vulcanizate itself. When whole tyre reclaim is added to these rubbers results in decrease in tensile strength.

Tear strength of the blends of whole tyre reclaim increases with the addition of whole tyre reclaim in NBR, SBR and BR matrixes. This may be due to the reinforcing character of carbon black filler in the WTR.

Abrasion resistance is decreased with the addition of whole tyre reclaim to the rubber. This may be attributed to the low molecular weight of WTR. But in the case of blends of butadiene rubber with WTR abrasion resistance is increased with the incorporation of WTR. Compression set is increased with the addition of whole tyre reclaim to the NBR, SBR, CR, BR and NR. Resilience is decreased in all blends of whole tyre reclaim. Heat build up is increased with the increasing reclaim loading.

Proceeding date?

3.7.Reference

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CHAPTER 4

EFFECT OF GRAFTING MALEIC ANHYDRIDE ON TO WHOLE TYRE RECLAIM

Improvements in mechanical and dynamic properties of a blend can be achieved by surface treatments such as grafting of functional groups on one of the blend components or activation by the application of a coating of a polymer to one of the blend components.

This chapter deals with the influence of grafting of Maleic anhydride on to WTR on the properties of its blends with Acrylonitrile butadiene rubber, Styrene butadiene rubber and Chloroprene rubber. Grafting of maleic anhydride provides a means for making WTR more polar so that it can be more compatible with polar rubbers such as NBR and CR. Good compatibility of the blend call for the similarity in their structure in terms of polarity apart from similarity in molecular weight.

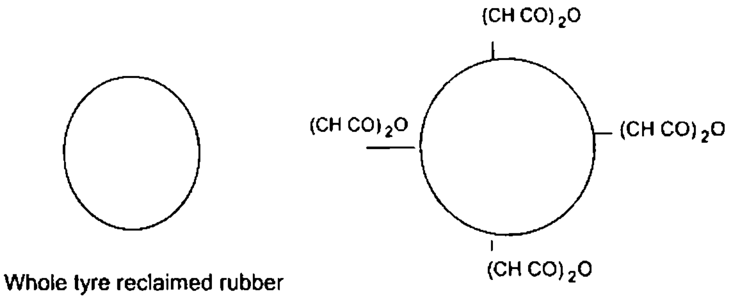


Figure 4 A.1. Representation of grafting reaction in a polymer.

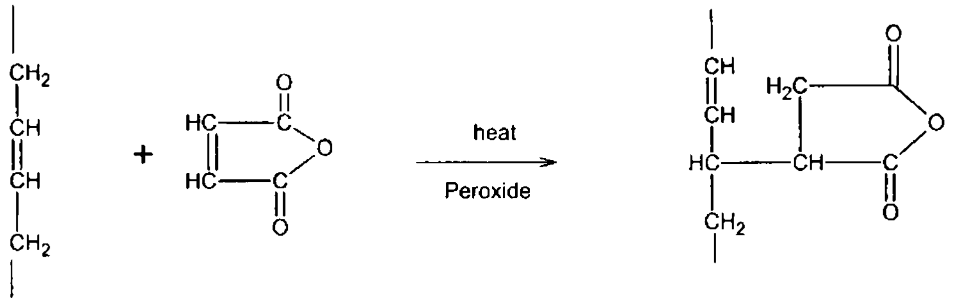
Chapter 4 is consists of three parts. First part deals with the cure characteristics and mechanical properties of MA-g-WTR /NBR blends.

Second part deals with influence of maleic anhydride grafting on whole tyre reclaim on cure characteristics and mechanical properties of MA-g-

WTR/CR blends. For comparison blends with SBR also prepared and cure characteristics and mechanical properties are reported in the part 3.

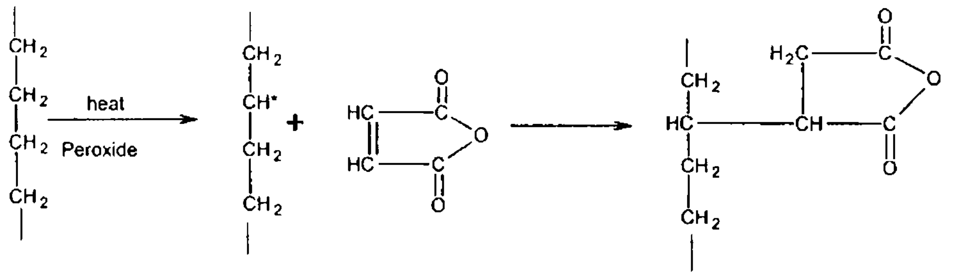
4.A. Grafting of Maleic anhydride on reclaimed rubber.

Maleic anhydride (MA) is frequently used to functionalise polymers in presence of peroxide. Free radical chemistry of MA has been reviewed by a number of researchers. (1,2) Farmer and Wheeler patented the modification of rubbers with maleic anhydride. (3) Grafting of maleic anhydride on rubber gives a new product with a high Mooney Viscosity and easy processibility. (4) Grafting of maleic anhydride on rubber hydrocarbon can be schematically represented as



Reaction of maleic anhydride with rubber containing unsaturated backbone (5,6,7)

It has been reported that saturated hydrocarbon polymers can also be functionalized with maleic anhydride. Exposing the polymer to sufficiently high temperature or the use of organic peroxides to form polymeric free radicals will cause the addition of maleic anhydride to the polymeric chain as represented below.



Reactions of maleic anhydride with polymers containing saturated backbone

Preparation and characterization of MA-g-WTR is discussed in detail in chapter 2. FTIR spectrum of unmodified and modified reclaimed rubber (MA-g- WTR) is given in the figure 4.A.2. and 4.A.3, respectively. An additional peak appearing at 1783 cm^{-1} in the figure 4.A.3 corresponds to carbonyl group vibration. This confirms that maleic anhydride has been grafted to the whole tyre reclaim.

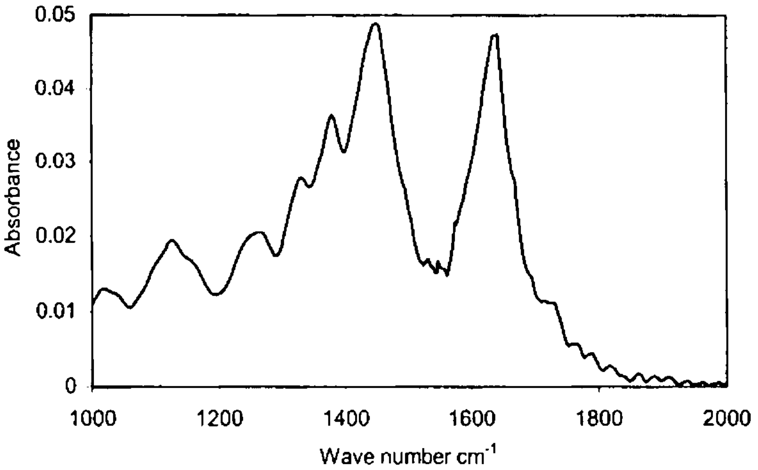


Figure 4.A.1. FTIR spectrum of WTR

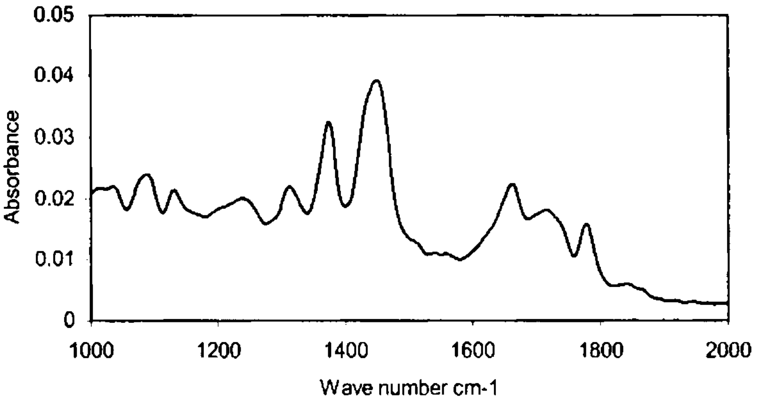


Figure 4.A.2. FTIR spectrum of MA-g-WTR

PART 1

Acrylonitrile butadiene rubber (NBR)/ MA-g- WTR blends*

This section discusses the preparation and properties of NBR/MA-g-WTR blends. Cure characteristics and mechanical properties of the blend are studied in detail.

4.1.1 Preparation of blends

Formulation of the mixes are given in table 4.1.1. Method of preparation of the blends is discussed in detail in chapter 2.

Table 4.1.1 Formulation of the Mixes

Ingredient	Mix. No										
	A	B	C	D	E	F	G	H	I	J	K
NBR	100	90	80	70	60	50	90	80	70	60	50
WTR	---	20	40	60	80	100					
MA-g- WTR							20	40	60	80	100

Note: NBR - Nitrile rubber. WTR -whole tyre reclaim, MA-g- WTR – Maleic anhydride grafted whole tyre reclaim. ZnO -5 g, Stearic acid–2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g are common to all mixes. Amount of WTR and MA-g- WTR is adjusted so as to get a total rubber hydrocarbon content of 100.

4.1.2 Cure Characteristics

Figure 4.1.1. shows the variation of minimum torque of the blends containing modified and unmodified WTR. The blends with the modified WTR shows consistently higher torque values indicating a more viscous matrix. This may be resulting from improved polar interaction of NBR with the grafted WTR. However, with increased loading of maleic anhydride grafted whole tyre reclaim (MA-g -WTR), the decrease in the minimum torque is not prominent as in the case of blends with unmodified WTR. This may be attributed to the increased viscosity of the matrix due to the grafting

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* Results of this part (1) is published in Progress in Rubber, Plastics and Recycling Technology **19** (3) (2003)

reaction [4]. The reclaim rubber contains 15% plasitcizer in addition to rubber hydrocarbon and filler (2.1.1.f.). Increasing the proportion of WTR also increases plastizicer content of the blends, which results in the net reduction of the initial viscosity.

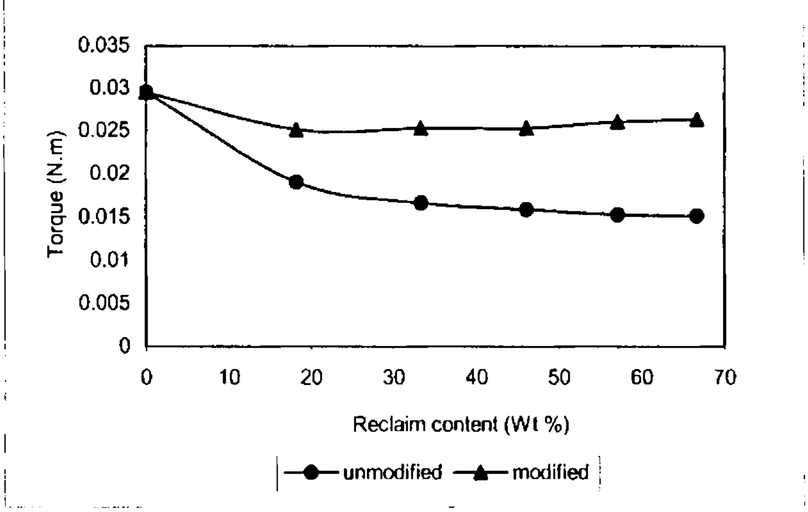


Figure 4.1.1. Variation of minimum torque with MA-g- WTR loading

Figure 4.1.2. shows the variation of (maximum – minimum) torque (Δt). In all the cases the (Δt) of the blends containing MA-g-WTR is higher than that of the unmodified blends, indicating a relatively more restrained matrix resulting from the combined effect of higher interaction between blend components and higher levels of cross links formed.

With increasing reclaim content in the blends, the (Δt) is found to be gradually decreased, the effect being less significant in the case of MA-g-WTR blends. The lower level of cross-links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross-linked matrix and hence there is relatively less reaction sites available for further cross linking. However the improved matrix interaction compensates for this and hence observed higher (Δt) for the modified blends. The higher cross-link density in the case of modified blends (Table 4.1.2) also contributes to difference in behaviour of the modified and unmodified blends.

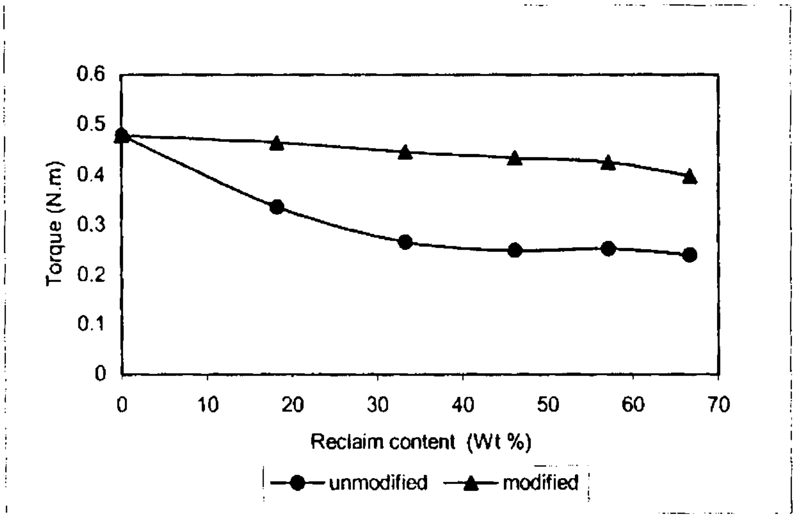


Figure 4.1.2. Variation of (max-min) torque with MA-g- WTR loading

Table 4.1.2. Cross-link density of blends

Cross link density in m. mole / Kg of rubber hydrocarbon	
Unmodified blend (mix C)	Modified blend (mix H)
23	26

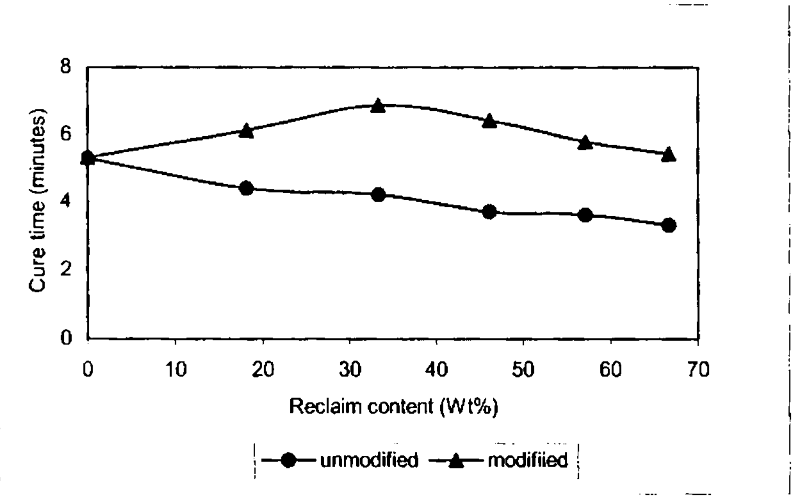


Figure 4.1.3. Variation of cure time with MA-g- WTR loading

Figure 4.1.3 gives a plot of cure time versus reclaim loading. The blends containing modified WTR show higher cure time in all the blend ratios. This may be attributed to the fact that the grafting introduces anhydride group on the WTR and the anhydrides are known cure retarders. The anhydride not only delays the onset of cure reaction but also reduces the cure rate resulting in higher cure times. The observed scorch times and cure rates (Figure 4.1.4 and 4.1.5) are in agreement with this view. In all the cases the variation with increasing grafted reclaim loading is similar to the blends containing unmodified WTR

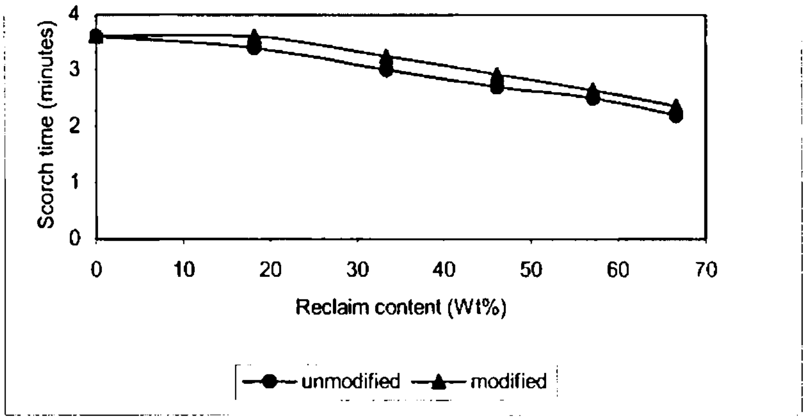
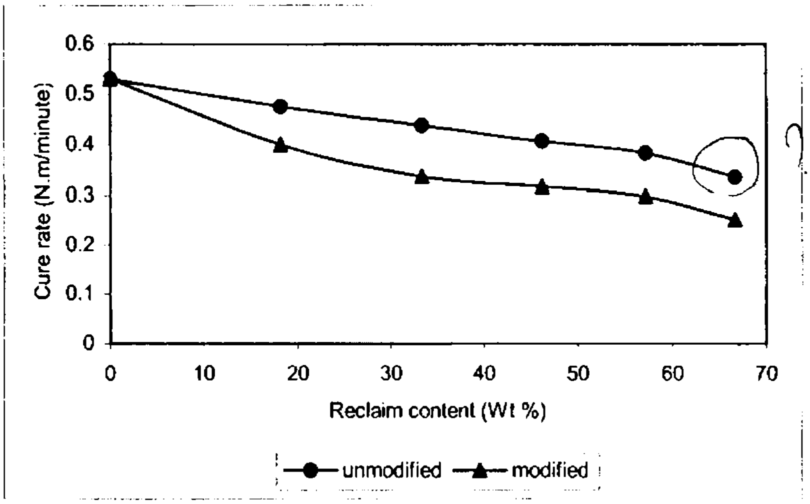


Figure 4.1.4. Variation of scorch time with MA-g- WTR loading



Pl. see fig. 3.4.5
Cure rate increa
then decrease
why is it different
here?

Figure 4.1.5. Variation of cure rate with MA-g- WTR loading

4.1.3. Mechanical Properties

Figure 4.1.6 shows the tensile strength of mixes A-K. In all the cases the tensile strength increases with reclaim content. This may be attributed to the reinforcing fillers present in the WTR. The tensile strength of the blends containing MA-g-WTR is higher than that of the blends with unmodified WTR at all blend ratios.

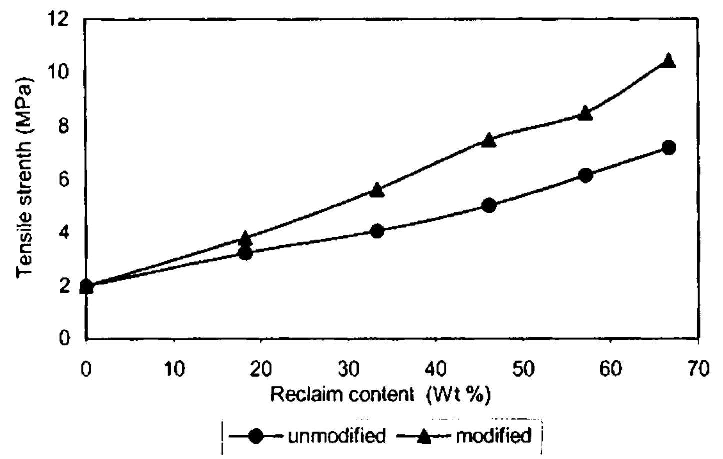


Figure 4.1.6. Variation of tensile strength with MA-g- WTR loading

At 66 weights percentage of MA-g-WTR loading the tensile strength is 10 MPa while at the same loading of the unmodified WTR tensile strength is only 7.2 MPa. This may be attributed to the possibility of improved polar – polar interaction between the blend components and the filler particles.

The variation of elongation at the break with increasing reclaim loading is shown in figure 4.1.7. Blends with higher reclaim contents show higher elongation at break values. This may be attributed to the presence of plasticizers in the WTR (2.1.1.f.). The blends containing grafted WTR show marginally higher elongation.

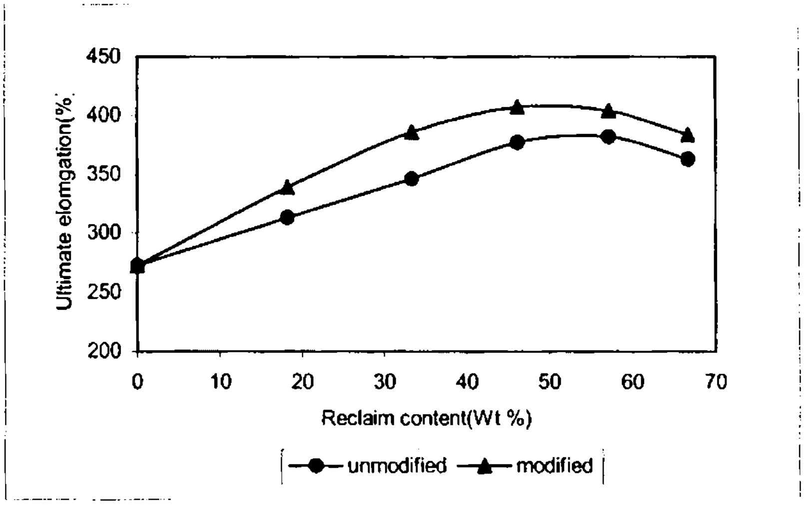


Figure 4.1.7. Variation of ultimate elongation with MA-g- WTR loading

Figure 4.1.8. shows comparison of tear strength with reclaim loading. The tear strength of the blends with modified and unmodified WTR show the same pattern with increasing reclaim content. Both the blends show the improved tear resistance at higher reclaim loading. The improved resistance to tear can be attributed to the presence of reinforcing filler in the WTR matrix. However, the grafting of the WTR does not seem to have significant effect on the tear strength of the blends. This may be attributed to the difference in mechanism of failure in tensile and tear modes.

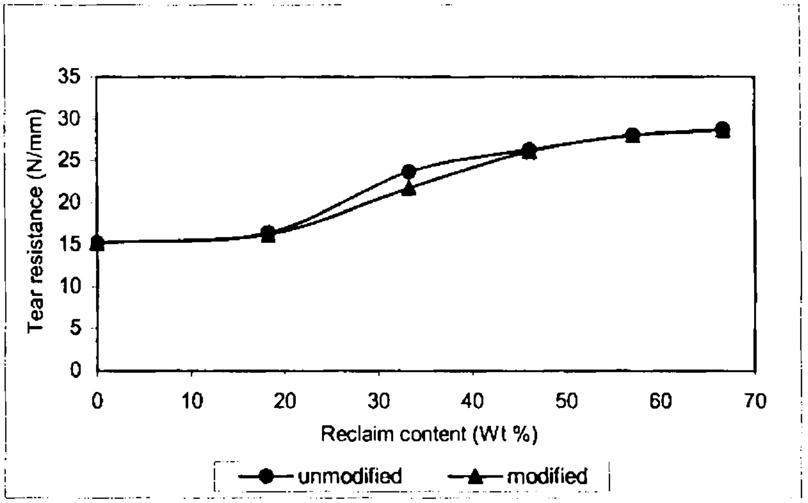


Figure 4.1.8. Variation of tear strength with MA-g- WTR loading

Figure 4.1.9. shows a plot of abrasion loss versus reclaim loading. Modified reclaim blend shows a low abrasion loss and hence better abrasion resistance than the unmodified reclaim blend. The low abrasion loss in the case of modified blend can be explained as due to the improved matrix-matrix and matrix- filler interaction. A better interface interaction restrains the matrix better, resulting in better abrasion resistance of the modified blends.

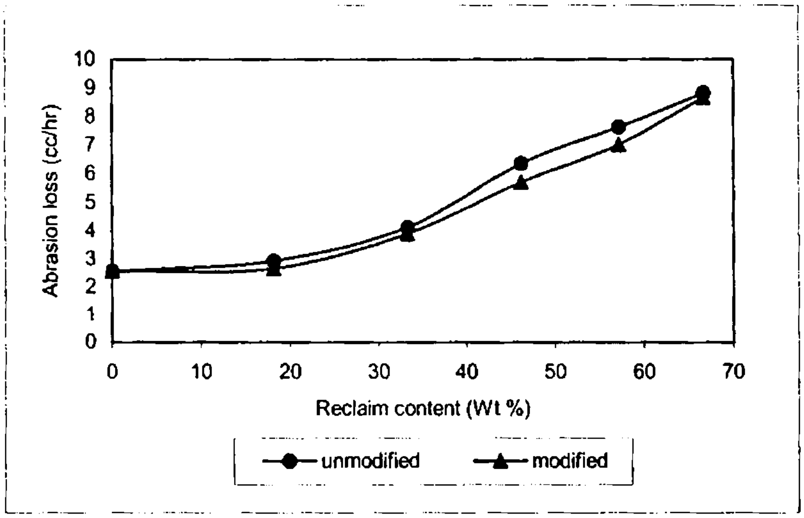


Figure 4.1.9. Variation of abrasion loss with MA-g- WTR loading

Figure 4.1.10. shows the comparison of compression set with reclaim loading. Compression set values of the modified reclaim blends are found to be lower than the unmodified reclaim blend. The reduced compression set values also indicates a more restrained matrix. This also supports the view that the grafting improves the interaction between the blend components. The increased set values at higher reclaim loading may be resulting from combined effect of filler, plasitcizer and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values. Increase in compression set values with reclaim loading in natural rubber has been reported by Phadke(8).

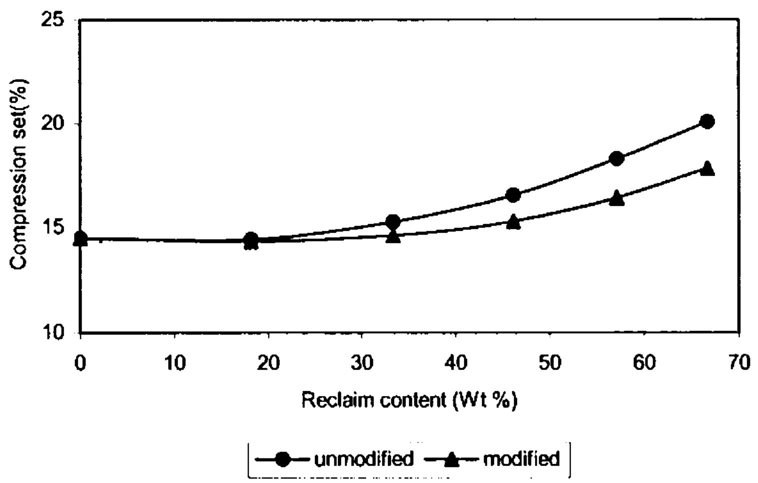


Figure 4.1.10. Variation of compression set with MA-g- WTR loading

The increased elasticity is also evident from figure 4.1.11, which is a plot of resilience values of modified and unmodified reclaim blends against the reclaim content. The resilience of the modified blend increases with reclaim loading in contrast to the blends containing unmodified blends where the resilience is decreases with the increase in reclaim loading.

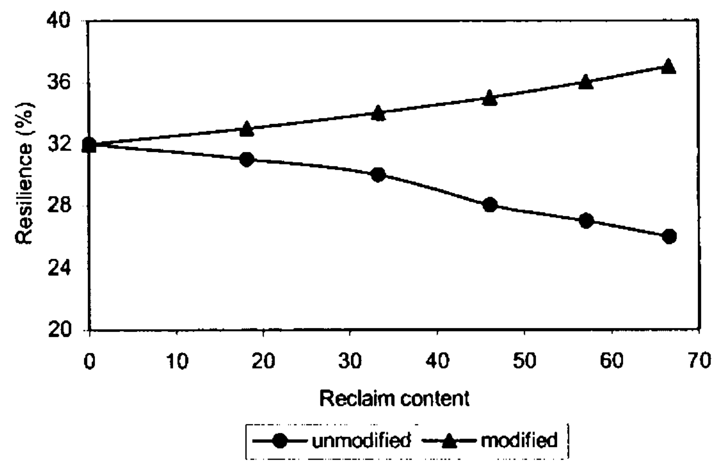


Figure 4.1.11. Variation of resilience with MA-g- WTR loading

The apparent difference may be attributed to the better reinforcing effect of the fillers through the improved polar interactions in the case of modified blends. The matrix undergoes relatively more elastics deformation under low strains as a consequence of better reinforcement of the matrix. In the case of the unmodified blends there is more chance of energy dissipation at filler –matrix interface due to the relatively weak interfacial bonds and hence the lower resilience values.

Figure 4.1.12. shows comparison of heat build up with the modified and unmodified reclaim loading. The heat generation under dynamic loading is higher at higher reclaim loading in the case of modified and unmodified blends. The modified blends show higher hysteresis loss at higher reclaim loading. This is in contrast to the observed resilience values. The difference can mainly be attributed to the difference in the level of strains. In the heat build up test the sample is strained to a larger extent than in the case of the resilience test. At higher strains, the chance of the energy loss by interfacial bond breakage is more and hence the higher heat generation.

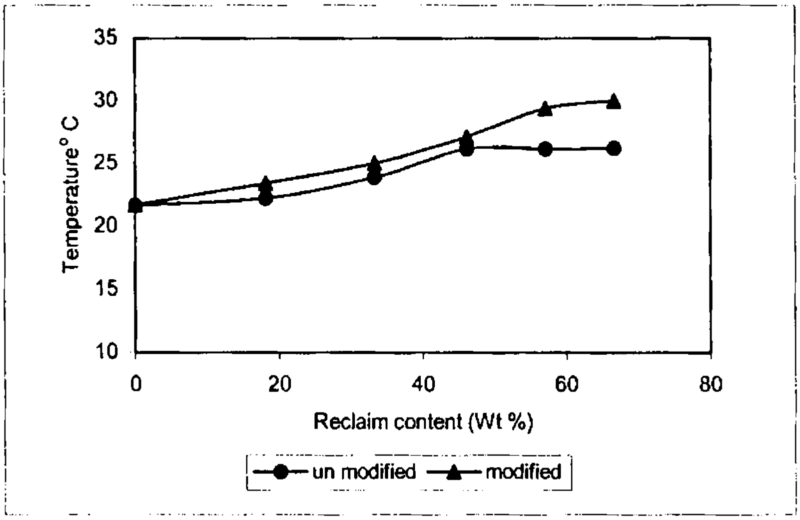


Figure 4.1.12. Variation of heat build up with MA-g- WTR loading

4.1.4. Ageing Resistance

Table 4.1.3 shows the tensile strength of the blends before and after ageing. The percentage retention calculated as the ratio of tensile strength after and before ageing, shows a gradual reduction with increasing reclaim loading. As synthetic matrix with better resistance to degradation, the NBR gum compound (mix A) gives percentage retention of 120. Whereas in the blends, the presences of reclaim which is relatively more prone to degradation, lowers the retention values. In all the cases modified blend shows lower retention.

Table 4.1.3. Tensile strength of mixes before and after the ageing.

Tensile strength (M Pa)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	2.0	2.4	120	-	-	-	-
B	3.2	3.5	109	G	3.8	3.4	88
C	4.1	4.3	106	H	5.6	5.5	97
D	5.1	5.7	112	I	7.5	7.2	96
E	6.2	6.8	110	J	8.5	8.5	100
F	7.2	8.0	111	K	10.4	10.4	99

A similar trend is also observed in the case of tear retention on ageing. (Table 4.1.4) The retention of the modified blends is marginally lower than that of the unmodified blends.

Table 4.1.4. Tear strength of mixes before and after the ageing

Tear resistance (N/mm)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	15.2	15.2	100	-	-	-	-
B	16.4	16.2	97	G	16.0	15.8	97
C	23.6	23.2	98	H	23.2	21.2	91
D	25.3	25.6	99	I	25.1	25.2	92
E	28.0	27.6	98	J	27.9	25.0	90
F	29.7	27.6	99	K	29.6	24.6	83

Table 4.1.5. shows the retention of ultimate elongation of the modified and unmodified sample. Ultimate elongation of the aged sample is lower than that of the unaged sample. Percentage retention of the modified reclaim blend is again marginally less than the unmodified reclaim blend.

Table. 4.1.5. Ultimate elongation of mixes before and after the ageing

Ultimate elongation (%)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	272	271	100	-	-	-	-
B	313	308	98	G	339	291	86
C	333	322	97	H	386	339	88
D	377	352	93	I	407	345	85
E	382	362	95	J	404	349	86
F	363	355	99	K	392	368	94

PART 2

Chloroprene rubber (CR) /MA-g-WTR blends*

This chapter deals with cure characteristics and mechanical properties of chloroprene /maleic anhydride grafted whole tyre reclaim blends. The properties are compared with that of the blends containing unmodified WTR.

4.2.1. Preparation of the blends

Preparation of the blends and the details of the various test methods are discussed in the chapter 2. Formulation of the mixes are given in the table 4.2.1

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* Results of this of this Part 2 have been accepted for publication in Journal of Applied Polymer Science

Table 4.2.1 Formulation of the mixes

Ingredient	Mix. No										
	A	B	C	D	E	F	G	H	I	J	K
Chloroprene Rubber	100	90	80	70	60	50	90	80	70	60	50
WTR	---	20	40	60	80	100					
MA-g-WTR							20	40	60	80	100

Note: CR-Chloroprene rubber, WTR whole tyre reclaim, MA-g-WTR- Maleic anhydride grafted reclaimed rubber. -ZnO - 5 g, MgO - 4 g, Stearic acid-0.5 g, 4020-1 g, NA22 (ethylene thiourea) 0.5 g are common to all mixes. Amount of WTR and MA-g-WTR is adjusted so as to get a total of rubber hydrocarbon concentration 100.

4.2.2.Cure Characteristics

Figure 4.2.1 shows the variation of minimum torque of the blends containing modified and unmodified WTR. The blends containing modified WTR show consistently higher torque value indicating a more viscous matrix.(4)

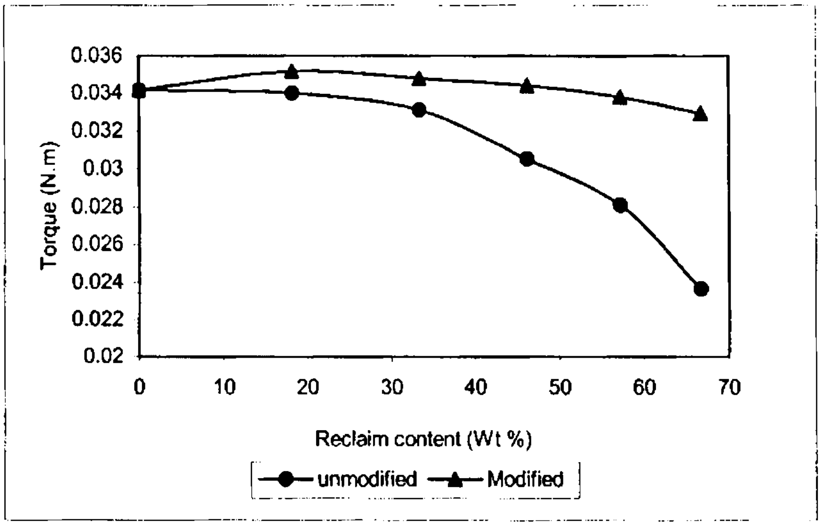

Figure 4.2.1.Variation of minimum torque with MA-g- WTR loading

This may be resulting from improved polar interaction of chloroprene rubber with the grafted WTR. While the torque falls from 0.03428 N m to 0.02368 N m for unmodified blend at 66.6 weight percent of reclaim loading, the drop is only to 0.03292 N m in the case of modified blend.

Figure 4.2.2 shows the variation of (maximum – minimum) torque (Δt) with reclaim loading. The (Δt) decreases from 0.36816 to 0.27685 and 0.36816 to 0.11108, for modified and unmodified blends respectively at 66 weight percent of reclaim loading. In all the cases the (Δt) of the blends containing modified WTR is higher than that of the unmodified blends, indicating a relatively more restrained matrix resulting from the combined effect of higher interaction between blend components and higher levels of cross links formed. (Table 4.2.1) With increasing reclaim content in the blends, the (Δt) is found to be gradually decreased.

Table 4.2.2. Cross-link density of the mixes C and H

Cross link density in m. mole / Kg of rubber hydrocarbon	
Unmodified blend (mix C)	Modified blend (mix H)
30.55	36.86

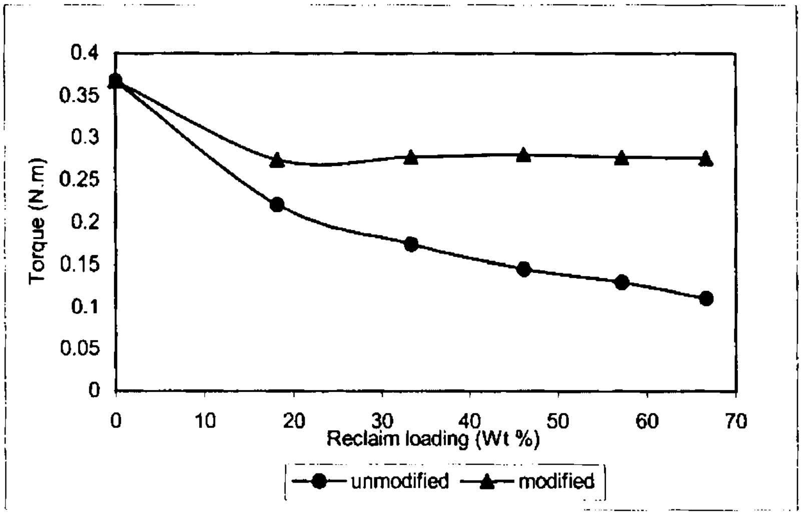

Figure 4.2.2. Variation of (max- min) torque with MA-g- WTR loading

The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking. However, the improved matrix interaction compensates for this and hence the observed higher (Δt) for the modified blends.

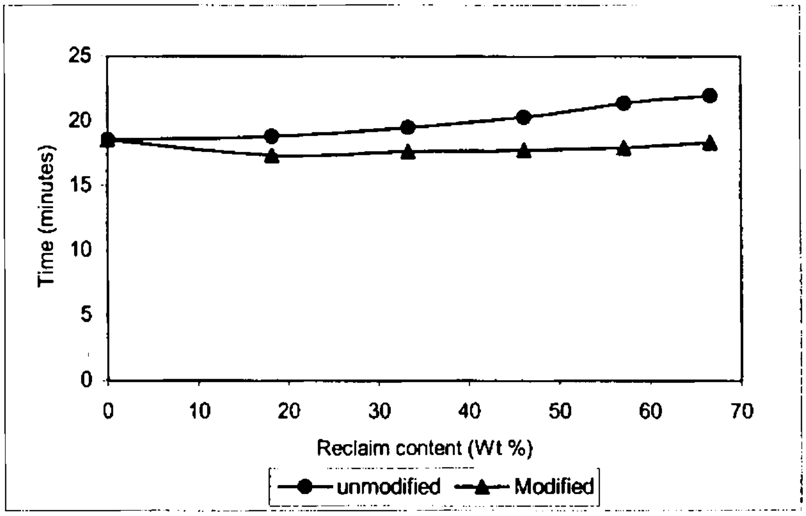

Figure 4.2.3.Variation of cure time with MA-g- WTR loading

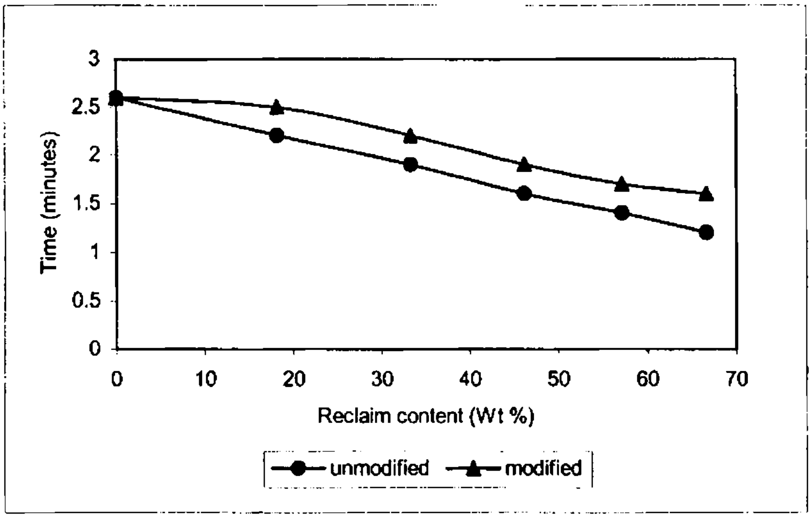

Figure 4.2.4. Variation of scorch time with MA-g- WTR loading

Figure 4.2.3 gives a plot of cure time versus reclaim loading. While the cure time increases marginally from 18.5 to 22 minutes in the case of unmodified blends, it remains more or less constant in the case of modified blends. At all blend ratios, the modified blends have lower cure time than the unmodified blends. They also show lower scorch time and higher cure rates (Figure 4.2.4 and 4.2.5). These indicate that the functionalisation of the WTR with maleic anhydride promotes the cure reaction of the blends.

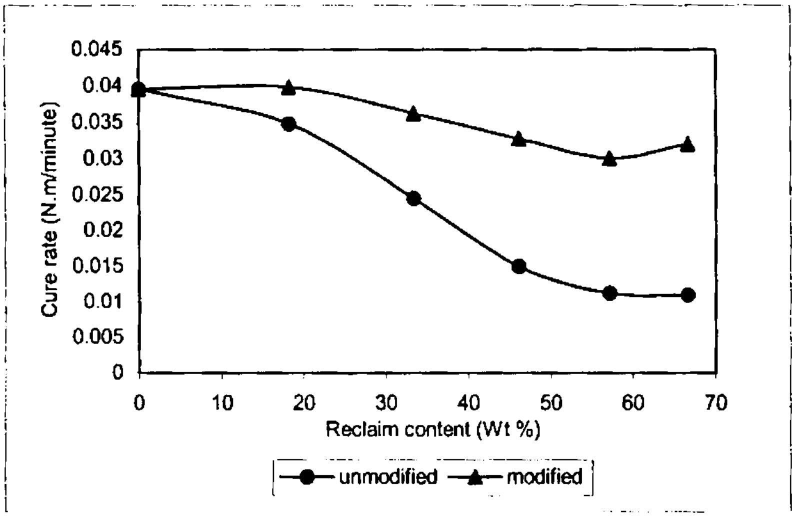

Figure 4.2.5.Variation of cure rate with MA-g- WTR loading

4.2.3.Mechanical Properties

Figure 4.2.6. shows the comparison of tensile strength with reclaim loading. In all mix ratios, the modified blend shows higher tensile strength compared to that of unmodified blend, resulting from improved inter component interaction. In the modified WTR blend, the tensile strength value changes from 12.0 MPa to 10.4 MPa at 66-weight percentage of reclaim loading and in the case of unmodified blend it falls to 5.7 MPa. In both the cases tensile strength value shows a marginal increase at 18 weight percentage of reclaim loading. This is in agreement with the higher (Δt) values shown by the modified blend. (Figure 4.2.2)

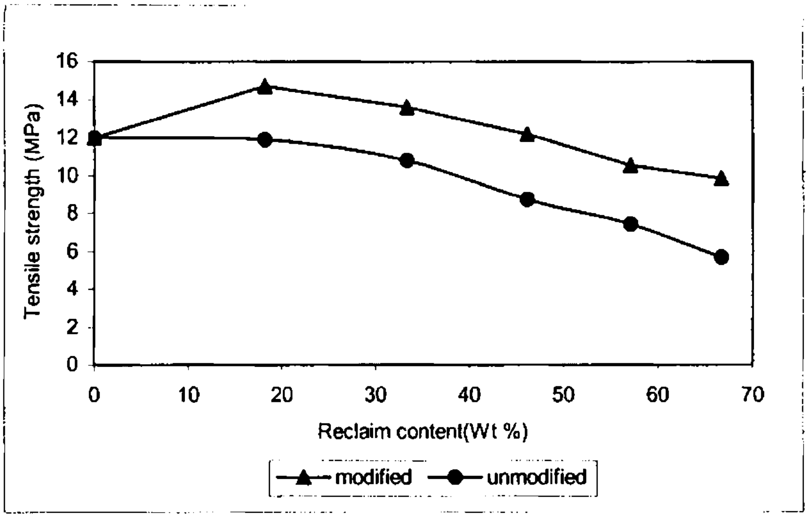

Figure 4.2.6.Variation of tensile strength with MA-g- WTR loading

Figure 4.2.7. gives a plot of ultimate elongation versus reclaim loading. The ultimate elongation of the modified and unmodified blends remains almost constant up to 55 weight percent. However at 66 weight percent, while the modified blend retains the ultimate elongation, the unmodified blend registers a drastic drop. This may be attributed to improved inter action between the blend components in the modified blend.

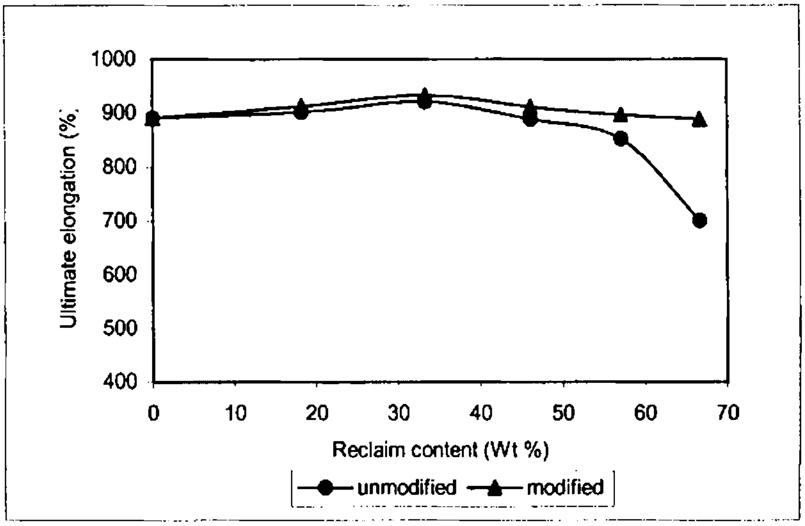

Figure 4.2.7. Variation of ultimate elongation with MA-g- WTR loading

Figure 4.2.8 shows comparison of tear strength with reclaim loading. Up to 46- weight percentage of WTR the tear strength remains constant beyond which it shows a drastic reduction in the case of unmodified blends. However the modified blends show a very significant improvement in the tear strength in this range. This may be attributed to better polar-polar interaction between the blend components. In the absence of strong interaction between CR and WTR, higher loading of WTR only dilutes the matrix resulting in lower tear strength values.

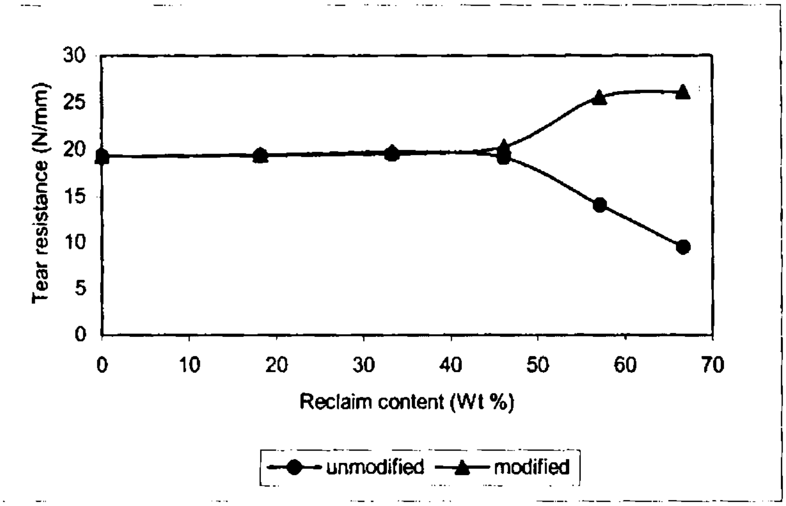

Figure 4.2.8. Variation of tear resistance with MA-g- WTR loading

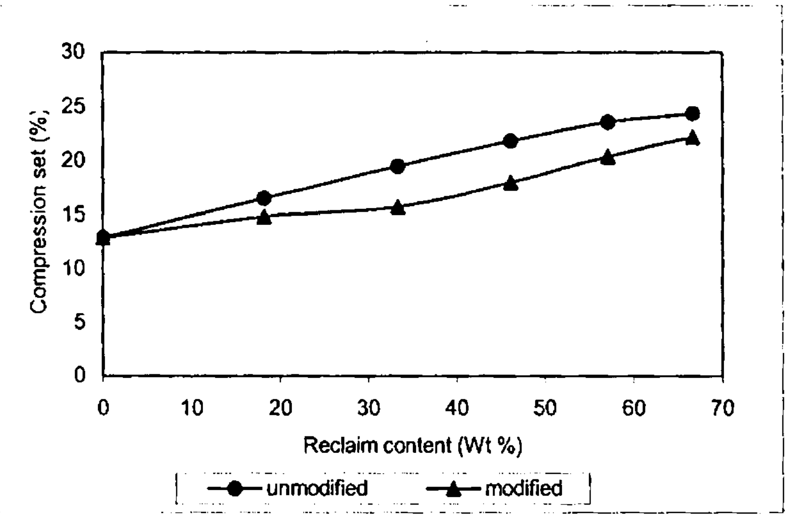

Figure 4.2.9. Variation of compression set with MA-g- WTR loading

Figure 4.2.9 shows the comparison of compression set with reclaim loading. Compression set values of the modified reclaim blends are found to be lower than the unmodified reclaim blend. The reduced compression set values indicate a more restrained matrix. This also supports the view that the grafting improves the interaction between the blend components. The increased set values at higher reclaim loading may be resulting from combined effect of filler, plasitcizer and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrix facilitates irreversible flow under stress, resulting in higher set values, as explained in the chapter 3.

Figure 4.2.10 shows a plot of abrasion loss versus reclaim loading. Modified reclaim blends show lower abrasion loss and hence better abrasion resistance than the unmodified reclaim blend. Increased loading of reclaimed rubber increases the abrasion loss. This may be due to the low molecular mass of the WTR (9). The low abrasion loss in the case of modified blend can be explained as due to the improved matrix-matrix and matrix-filler interaction. A better interface interaction restrains the matrix better, resulting in better abrasion resistance.

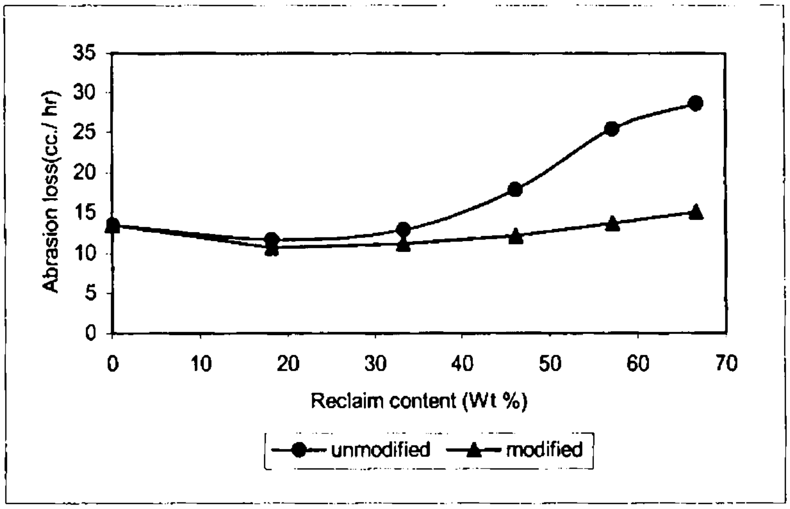

Figure 4.2.10. Variation of abrasion loss with MA-g- WTR loading

Figure 4.2.11. shows the comparison of heat build up of modified and unmodified blends with reclaim loading. With increase in WTR loading, in both the cases the heat build up is increasing. This increase in hysteresis

loss may be attributed to higher energy loss at filler matrix interface. Higher is the filler content, more is the interface area and hence more is the dissipation energy as heat. The heat generation of the modified blends is lower than that of the unmodified blends at all blend ratios. The reduced heat build up in the case of modified reclaim blend is due to the efficient polar interaction and hence, stronger inter component interface.

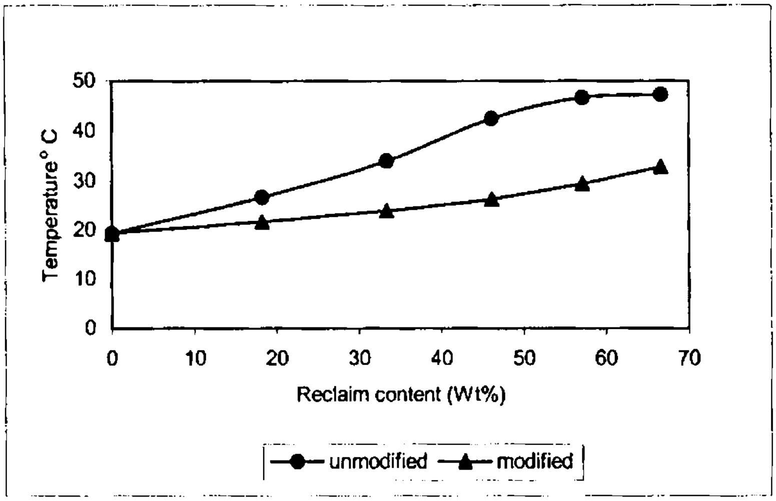

Figure 4.2.11. Variation of heat build up with MA-g- WTR loading

The increased elasticity in the case of modified blend is also evident from figure 4.2.12, which is a plot of resilience values of modified and unmodified reclaim blends against reclaim loading. The resilience decreases with increasing WTR content in the case of modified and unmodified blends. Introduction of more filler by the way of adding more WTR increases chance of energy loss at the interfaces. In the case of modified blends, the resilience is lower than that of unmodified blend at all blend ratios. This is in contrast to the improvement observed in the hysteresis and compression set. That the improved inter component interaction is not reflected as improved resilience in the case of modified blends may be attributed to the extent of strain involved. The level of strain on sample is subjected to in a resilience test is very small compared to that in hysteresis or compression set tests.

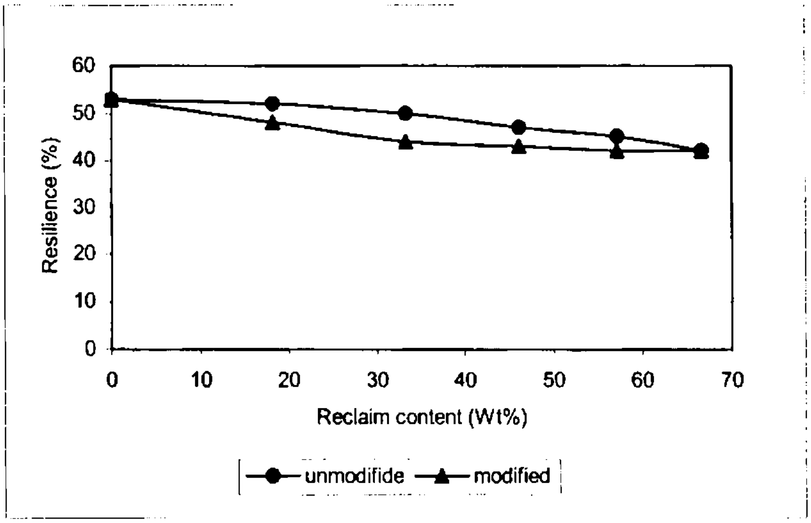

Figure 4.2.12. Variation of resilience with MA-g- WTR loading

4.2.4.Ageing Resistance

Table 4.2.3. shows the tensile strength of the blends before and after ageing. The percentage retention calculated as the ratio of tensile strength after and before ageing, shows a gradual reduction. A similar trend is also observed in the case of tear resistance on ageing. (Table 4.2.4.) Modified blends gives lower retention for tensile strength and tear strength

Table 4.2.3. Tensile strength of mixes before and after the ageing

Tensile strength (M Pa)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	12.0	12.0	100	-	-	-	-
B	11.9	12.7	107	G	14.7	13.2	90
C	10.8	11.7	108	H	13.0	12.9	100
D	8.7	9.6	110	I	12.2	11.5	94
E	7.5	7.9	107	J	10.6	11.1	105
F	5.7	5.9	103	K	9.9	10.4	105

Table 4.2.4 Tear strength of mixes before and after the ageing.

Tear strength (N/mm)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	19.3	21.5	111	-	-	-	-
B	19.5	22.9	117	G	19.3	23.0	98
C	19.4	23.2	120	H	19.7	23.3	91
D	19.1	23.2	121	I	20.3	24.7	92
E	14.1	16.6	118	J	25.5	30.0	91
F	9.6	11.0	116	K	26.1	30.3	89

Table 4.2.5 Ultimate elongation of mixes before and after the ageing.

Ultimate elongation (%)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	890	957	108	-	-	-	-
B	901	960	107	G	912	901	99
C	920	939	102	H	932	908	97
D	888	896	100	I	911	894	98
E	851	861	101	J	896	873	97
F	700	789	113	K	888	842	95

Table 4.2.5 shows the retention of ultimate elongation of the modified and unmodified sample. Ultimate elongation values of the aged samples are

lower than that of the unaged samples. Modified blends gives better retention for ultimate elongation.

PART 3

Styrene butadiene rubber (SBR) /MA-g-WTR blends*

This chapter deals with the properties of Maleic anhydride grafted whole tyre reclaim /Styrene butadiene rubber blends. Cure characteristics and mechanical properties are discussed in detail.

4.3.1. Preparation of the blends

Preparation of the blends and various mechanical testing are discussed in the chapter 2. Formulation of the mixes is given in the table 4.3.1.

Table 4.3.1 Formulation of the Mixes

Ingredient	Mix. No										
	A	B	C	D	E	F	G	H	I	J	K
SBR	100	90	80	70	60	50	90	80	70	60	50
WTR	---	20	40	60	80	100					
MA-g- WTR							20	40	60	80	100

Note: SBR - Styrene butadiene rubber, WTR whole tyre reclaim; MA-g-WTR - Maleic anhydride grafted Whole tyre reclaimed rubber. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g, are common to all mixes. Amount of WTR and MA-g-WTR are adjusted so as to get total rubber hydrocarbon concentration of 100.

4.3.2. Cure Characteristics

Figure 4.3.1. shows the variation of minimum torque of the blends containing modified and unmodified WTR. The blends containing modified WTR show consistently higher torque values indicating a more viscous matrix. This may be resulting from improved polar interaction of SBR with the grafted WTR (4) With increasing loading of maleic anhydride grafted WTR (MA-g-WTR), decrease in the minimum torque value is also marginal due to the

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* Results of this part (3) is has been accepted for publication in Journal of Polymer Plastics Technology and Engineering (in Press)

improved inter component interaction within the blend. The change of minimum torque values in the unmodified and modified reclaim blend is 0.02954 to 0.01514, and 0.02954 to 0.0264 N.m., respectively. The reclaimed rubber contains 15 % plasticizer (section 2.1.1.f) in addition to rubber hydrocarbon and filler. Increasing proportion of WTR also increases plasticizer content of the blends, which results in the reduction of the initial viscosity.

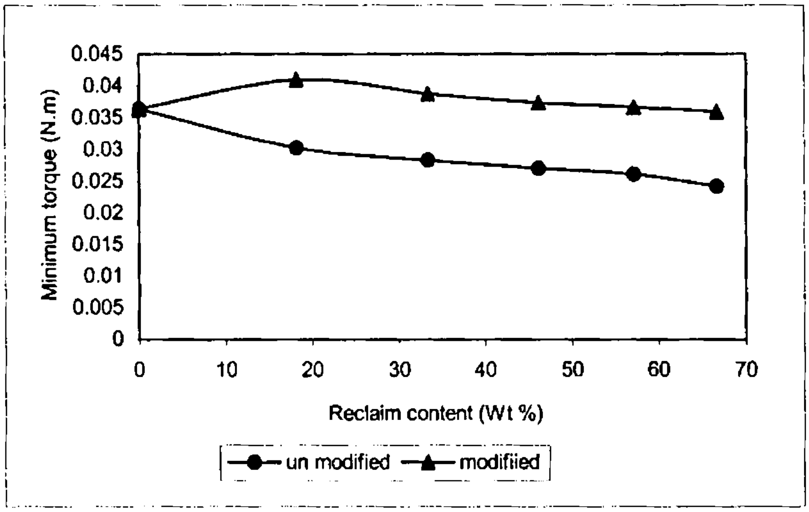

Figure 4.3.1. Variation of minimum torque with MA-g-WTR loading

Figure 4.3.2 shows the variation of (maximum – minimum) torque (Δt). In all the cases (Δt) of the blends containing modified WTR is higher than that of the unmodified blends, indicating a relatively more restrained matrix in MA-g-WTR blends resulting from the combined effect of higher interaction between blend components and higher levels of cross links formed (Table 4.3.2). With increasing reclaim content in the blends, the (Δt) is found to be gradually decreased, the effect being less significant in the case of MA-g-WTR blends. In the unmodified and modified blends, the (max – min) torque value changes from 0.4783 to 0.2407 and 0.4783 to 0.3989 respectively at 66-weight percentage of reclaim loading. The lower level of cross links at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking. However the improved matrix interaction compensates for this and hence the observed higher (Δt) for the modified blends.

Table 4.3.2 Cross-link density of SBR/MA-g- WTR blends

Cross link density in m. mole / Kg of rubber hydrocarbon	
Unmodified blend (mix C)	Modified blend (mix H)
38.8	48.2

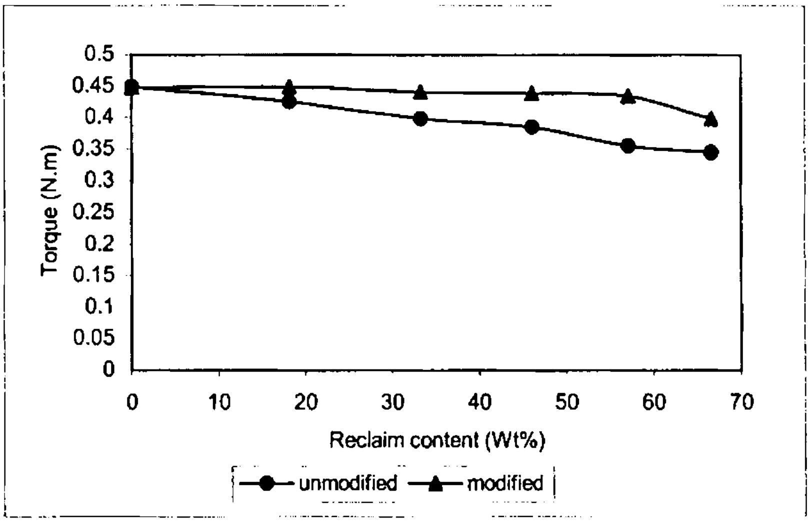

Figure 4.3.2 Variation of (max- min) torque with MA-g-WTR loading

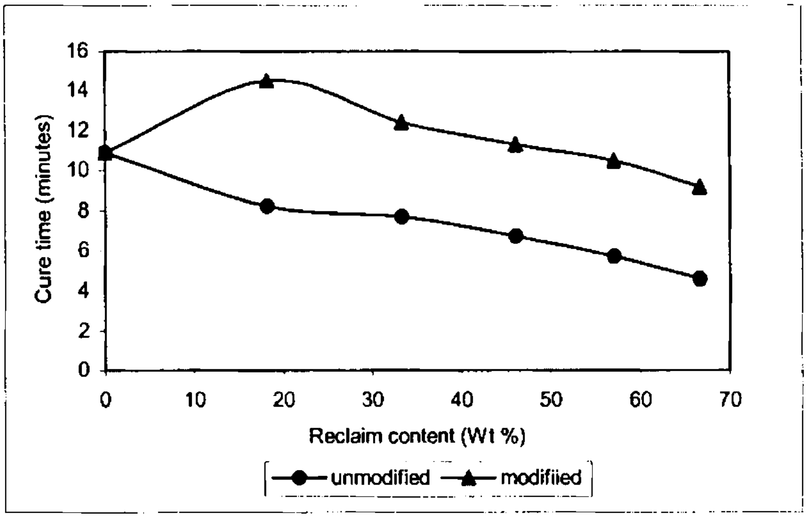

Figure 4.3.3 Variation of cure time with MA-g-WTR loading

Figure 4 3.3. gives a plot of cure time versus reclaim loading. Addition of reclaimed rubber to styrene butadiene matrix reduces the cure time. This may be attributed to the accelerator relics present in the WTR. The cure time decreases from 10.9 to 4.6 minutes at 66-weight percentage of unmodified reclaim loading, while it is reduced only to 9.2 minutes only in the case of blends containing grafted WTR.

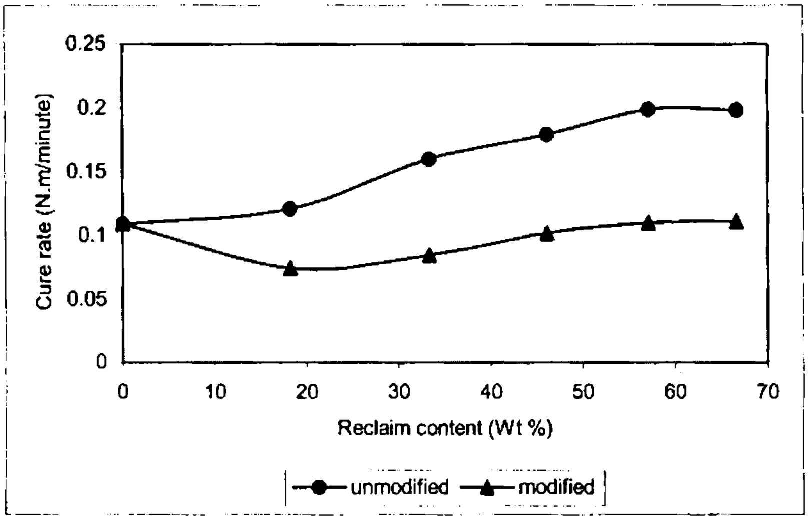

Figure 4.3.4 Variation of cure rate with MA-g-WTR loading

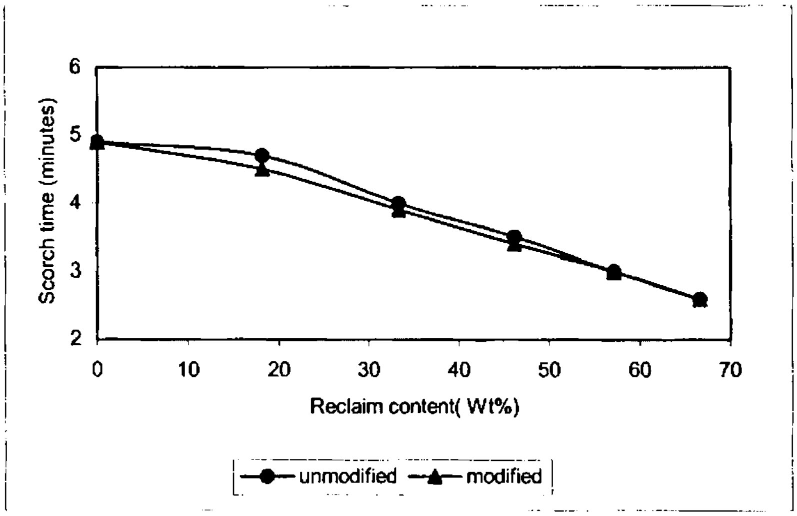

Figure 4.3.5 Variation of scorch time with MA-g-WTR loading

At all blend ratios, the modified blend show longer cure time. The increased cure time is also accompanied by a reduction in cure rate in all mix ratios. (Figure 4.3.4) This may be attributed to the presence of cure retarders- the anhydride groups - on WTR. Scorch time is reduced from 5 minutes to 2.5 minutes. (Figure 4.3.5).

4.3.3. Mechanical Properties

Figure 4.3.6. shows the tensile strength of mixes A-K. In all the cases the tensile strength increases with reclaim content. This may be attributed to the reinforcing fillers present in the WTR. The tensile strength of the blends containing MA-g-WTR is higher than that of the blends with unmodified WTR at all blend ratios.

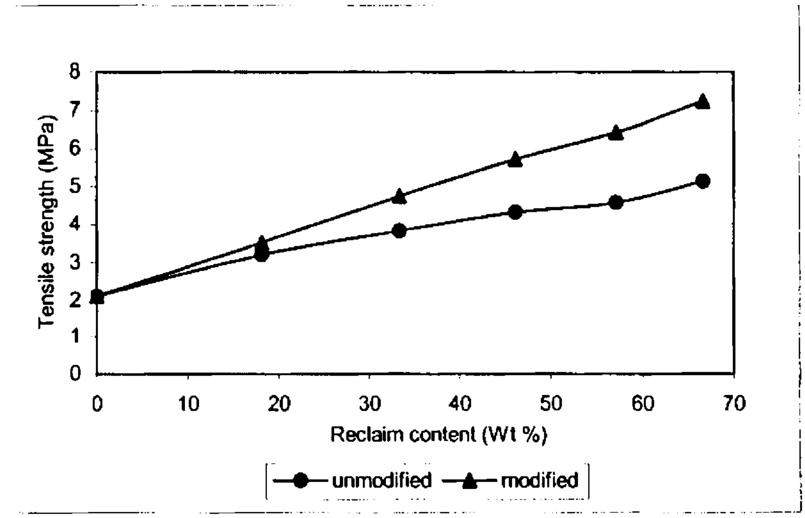

Figure 4.3.6. Variation of tensile strength with MA-g-WTR loading

Tensile strength changes from 2.1 MPa to 5.1 at 66-weight percentage of WTR where as in the case of MA-g-WTR blends the tensile strength is 7.2 MPa at the same concentration. This may be attributed to the possibility of the improved polar –polar interaction between the blend components and the filler particles.

Figure 4.3.7. gives a plot of ultimate elongation versus reclaim loading. The ultimate elongation of the modified blend is higher at all blend

ratios. This indicates that the polar interaction brought about by the anhydride group is not effective under high strains.

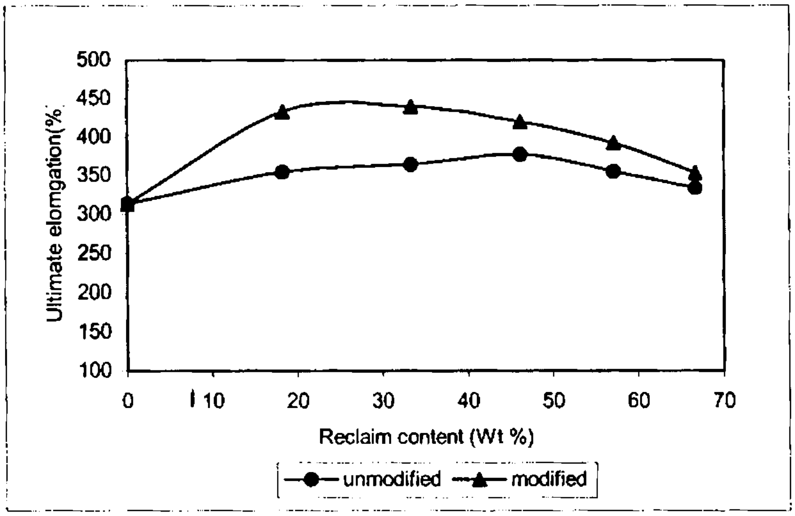

Figure 4.3.7. Variation of ultimate elongation with MA-g-WTR loading

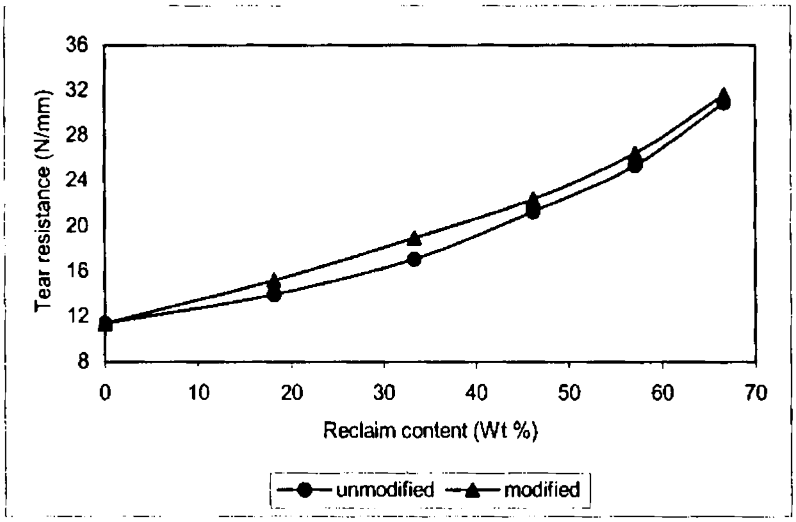

Figure 4.3.8 variation of tear strength with MA-g-WTR loading

Figure 4.3.8 shows comparison of tear strength with reclaim loading. The tear strength of the blends with modified and unmodified WTR shows the same pattern with increasing reclaim content. Both the blends show improved tear resistance at higher reclaim loading. The improved resistance to tear can be attributed to the presence of reinforcing filler in the WTR matrix.[9] Tear strength of the modified blends is higher than that of the unmodified at all mix ratio, again resulting from better interaction between the blend components.

Figure 4.3.9. shows a plot of abrasion loss versus reclaim loading. Modified reclaim blend shows a low abrasion loss and hence better abrasion resistance than the unmodified reclaim blend. The low abrasion loss in the case of modified blend also indicates improved matrix - filler interaction. A better interface interaction restrains the matrix better, resulting in better abrasion resistance.

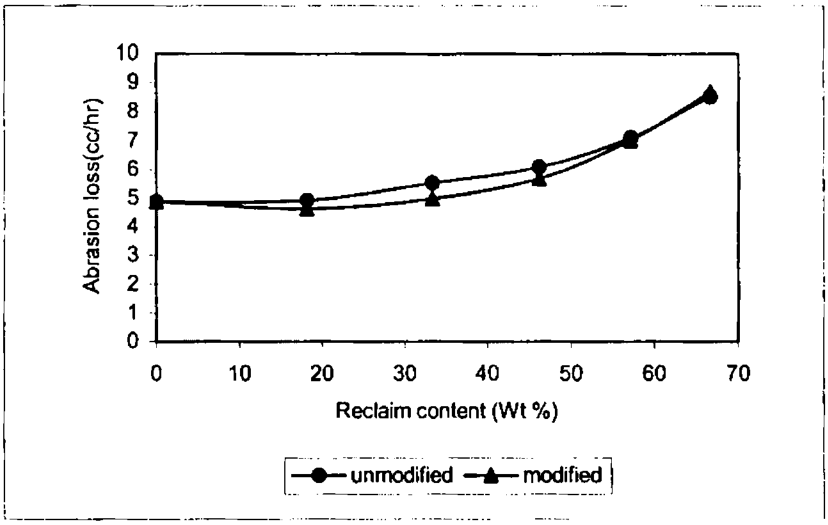

Figure 4.3.9. Variation of abrasion loss with MA-g-WTR loading

Figure 4.3.10 shows the comparison of compression set with reclaim loading. Compression set values of the unmodified blends is increasing with the reclaimed rubber. This is accounted for as due to the combined effect of filler, plasitcizer and elevated temperature, all of which reduce the elasticity of the matrix as explained in the chapter 3. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values. In the modified reclaim blend set value is lower at all mix ratios compared to unmodified blend. The reduced compression set values indicate a more restrained matrix. In the modified blends, the compression set is minimum at higher reclaim loading. This may be due to the fact that at higher grafted reclaim loading, there is more chance for inter component interaction.

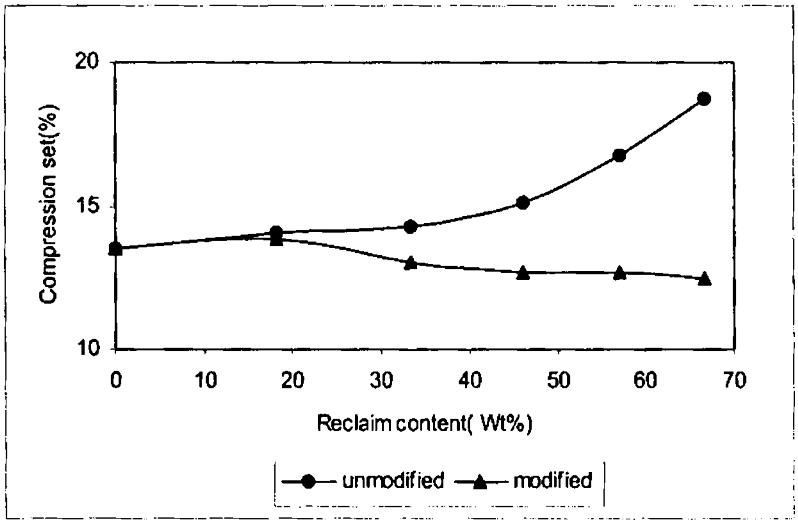

Figure 4.3.10. Variation of compression set with MA-g-WTR loading

The increased elasticity is also evident from Figure 4.3.11, which is a plot of resilience values of modified and unmodified reclaim blends versus reclaim loading. The resilience of the modified blend and unmodified blends decreases with reclaim loading. The modified reclaim blends show marginally higher resilience values.

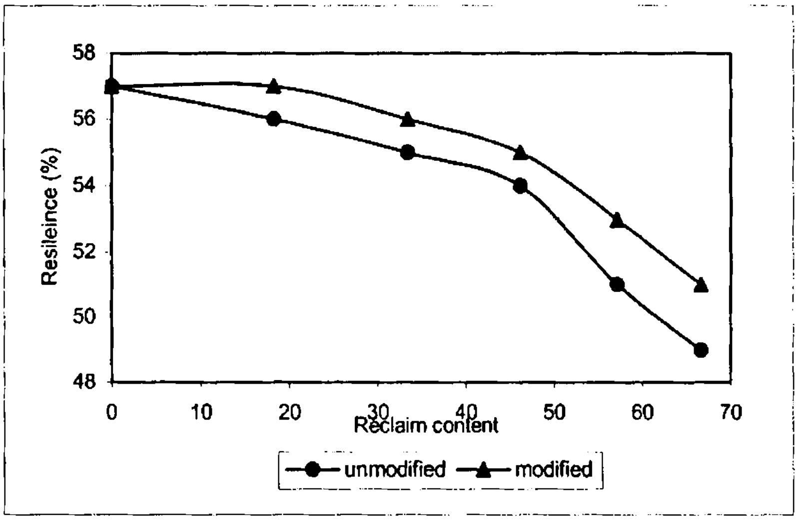

Figure 4.3.11. Variation of resilience with MA-g-WTR loading

Figure 4.3.12 shows comparison of heat build up with the modified and unmodified reclaim loading. The heat generation under dynamic loading is higher at higher reclaim loading in the case of modified and unmodified blends. This is in contrast to the observed resilience values. The difference can mainly be attributed to the difference in the level of strains, as explained in the chapter 3.

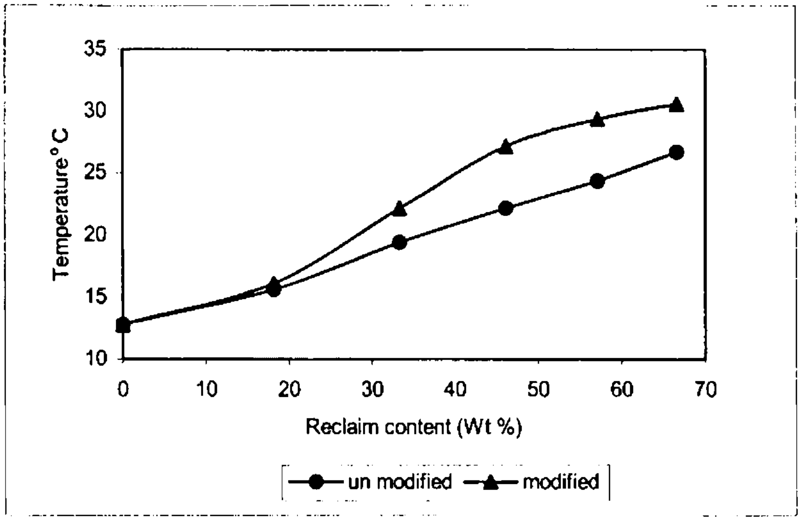

Figure 4.3.12. Variation of heat build up with MA-g-WTR loading

At higher strains, the chance of the energy loss by interfacial bond breakage is more and hence the higher heat generation. The higher hysteresis loss in the case of modified blends indicates that the polar interaction introduced by grafting is not very strong and energy loss occurs at these points under dynamic loading.

4.3.4. Ageing Resistance

Table 4.3.3 shows the tensile strength of the blends before and after ageing. In all the cases the tensile strength is found to be increased by the grafting of maleic anhydride on the reclaimed rubber. The percentage of retention, calculated as the ratio of tensile strength after and before ageing shows a gradual reduction. As synthetic matrix with better resistance to degradation, the SBR gum compound (mix A) gives percentage retention of 114. Where as in the blends, the presence of reclaim which relatively more prone to degradation lowers the retention values. Percentage retention of tensile strength increases with ageing in modified blend. Table 4.3.4 shows tear resistance of the unmodified and modified blends before and after the ageing. In all the cases the tear retention is higher for modified blend.

Table 4.3.3 Tensile strength of mixes before and after the ageing.

Tensile strength (MPa)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	2.1	2.4	114	-	-	-	-
B	3.2	3.4	106	G	3.5	3.8	108
C	3.8	3.9	103	H	4.7	5.0	106
D	4.3	4.3	100	I	5.7	6.5	114
E	4.6	4.5	98	J	6.4	7.4	115
F	5.1	5.2	102	K	7.2	7.8	108

Table 4.3.4 Tear resistance of mixes before and after the ageing

Tear resistance (N/mm)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	11.4	10.2	89	-	-	-	-
B	13.9	13.3	96	G	15.2	17.3	114
C	17.0	15.9	94	H	18.9	23.2	123
D	21.3	19.1	90	I	22.4	27.3	122
E	25.4	22.6	89	J	26.4	29.7	113
F	30.9	28.3	92	K	31.6	31.6	100

Table 4.3.5. shows the retention of ultimate elongation of the modified and unmodified sample. Ultimate elongation of the aged sample is lower than that of the unaged sample. The percentage retention values of the modified reclaim blends are almost similar. The values show that the ageing resistance of the modified reclaim blend is higher than that of unmodified reclaim blend.

Table. 4.3.5. Ultimate elongation of mixes before and after the ageing

Ultimate elongation (%)							
Unmodified				Modified			
Mix No.	Before ageing	After ageing	Percentage retention	Mix No.	Before ageing	After ageing	Percentage retention
A	313	252	81	-	-	-	-
B	355	359	73	G	433	369	85
C	364	266	73	H	440	377	88
D	378	276	73	I	420	403	96
E	355	287	81	J	392	363	93
F	334	322	96	K	353	330	93

4.4.Conclusion

Chapter 4 is an attempt to improve the compatibility of otherwise incompatible blends of whole tyre reclaim with NBR and CR by grafting maleic anhydride on the WTR For comparison blends of modified WTR with SBR was also prepared and evaluated. The effect of modification is manifested as improved mechanical properties in general though to different extent in different matrices.

The results can be summarized below

Cure rate of the blend decreased with the modification in NBR and SBR blends, where as in the case of chloroprene blends cure rate is higher for the modified blends.

Minimum torque of the blends is higher than the control mix for all matrices. The (max-min) torque of the modified blends is higher than the control mix due to higher levels of cross-linking. Cross-link density of the blends with grafted WTR is higher than the unmodified blends.

Mechanical properties of the blends are improved by using grafted WTR. In all matrices tensile strength and tear strength are improved by grafting. Abrasion resistance is higher for the modified blends. Compression set values of the modified blends is lower than the control mixes. Resilience and heat build up are higher for the modified blends. Ageing studies show lower ageing resistance for the modified blend compared to that of unmodified blends.

4.5. Reference:

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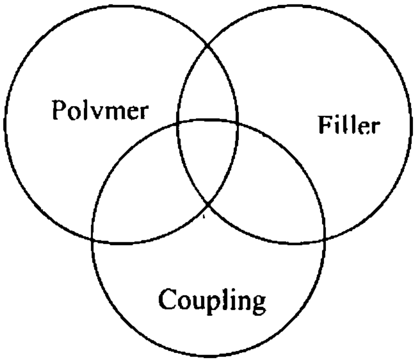
CHAPTER 5

EFFECT OF COUPLING AGENT ON WHOLE TYRE RECLAIM BLENDS

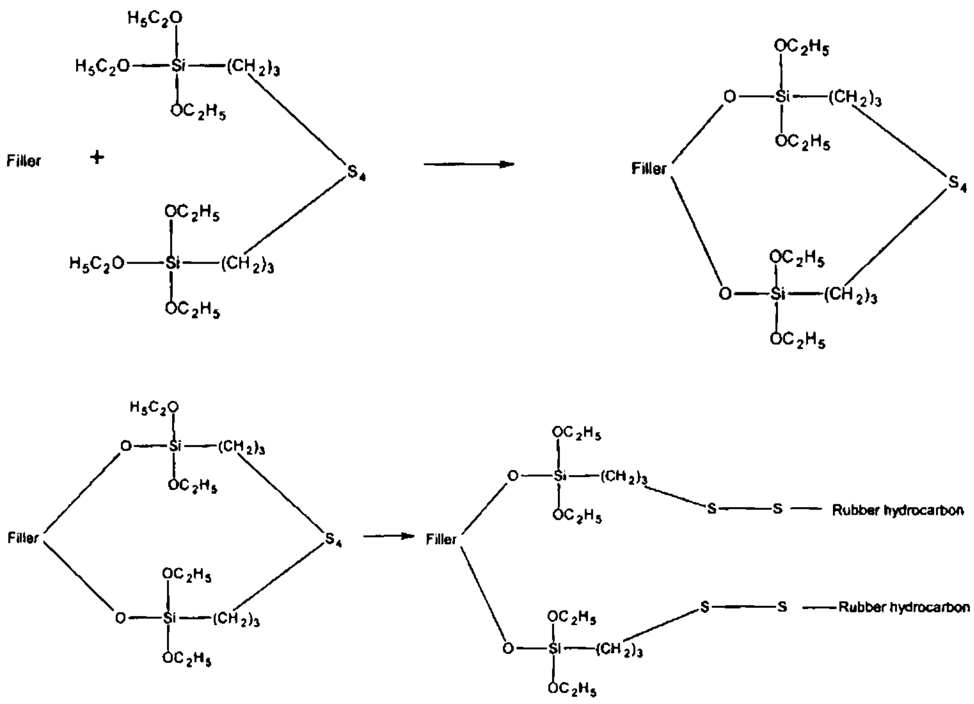
This chapter deals with the influence of silane coupling agent, Si69 (Bis(3-triethoxysilylpropyl) tetrasulphide) on the blends of whole tyre reclaim (WTR) blends with Acrylonitrile butadiene rubber, Styrene butadiene rubber and Chloroprene rubber. The presence of compatibilising agent permits the blending of other wise incompatible polymers to yield poly blend with unique properties, generally not attained from the individual components. The compatibilising agent acts as a polymeric surfactant lowering surface tension and promoting interfacial adhesion between the dispersed and matrix polymer phases in a polyblend.

Silanes are a group of organo functional compounds that have the ability to bond inorganic materials such as glass, mineral fillers, metals and metallic oxides to organic matrix. The silanes react chemically and promote adhesion between non-polar base polymer and polar fillers or vice versa in the vulcanised rubber compounds. The $Si(OR)_3$ portion reacts with the polar components while the organo functional (vinyl-, amino-, epoxy-, etc.) group reacts with the non polar matrix. It is expected that Si 69 can also improve interaction between polar and non-polar matrix. Schematic representation of role of coupling agent in a blend is given below (1)



Scheme 5.1 Schematic representation of role of coupling agent in a blend.

A large number of workers explored the (Si 69) (Bis (3-triethoxysilylpropyl)tetrasulphide) as coupling agent and curing agent$^{(2-9)}$. Mechanism of coupling reaction can be represented below.$^{(10)}$



PART 1

Effect of silane coupling agent on NBR/ WTR blends*

This chapter gives a study of cure characteristics and mechanical properties of blends of acrylonitrile butadiene rubber with whole tyre reclaimed rubber in presence of silane coupling agent. The amount of silane coupling agent used in this study varies from zero to 4 phr.

5.1.1. Preparation of the blend

Formulation of the mixes is given in the table 5.1.1. Method of preparation and procedure adopted for the determination of cure characteristics and mechanical properties of the blend are given in the chapter 2.

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* Results of this part is accepted for publication in Progress in Rubber, Plastics and Recycling Technology (in press)

Table 5.1.1 Formulation of the Mixes

MixNo	A	B	C	D	E	A_1	B_1	C_1	D_1	E_1	A_2	B_2	C_2	D_2	E_2	A_3	B_3	C_3	D_3	E_3	A_4	B_4	C_4	D_4	E_4
NBR	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50
WTR	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
Si69	-	-	-	-	-	1	1	1	1	1	2	2	2	2	2	3	3	3	3	3	4	4	4	4	4

All mixes contain ZnO 5 g, Stearic acid 2 g, Sulphur 2 g, MBTS 0.8 g, TMTD 0.4 g and Antioxidant 4020 1 g. Amount of WTR was adjusted so as to get total rubber hydrocarbon concentration of 100

5.1.2. Cure Characteristics

Figure 5.1.1. shows the minimum torque values of the mixes A to E_4 containing different levels of silane coupling agent. All the blends containing silane-coupling agent show higher minimum torque, indicating higher viscosity of the blends. This can be attributed to improved interaction between the matrix and filler particles in the blend. The effect of silane coupling agent on the stock viscosity is best reflected at higher reclaim content.

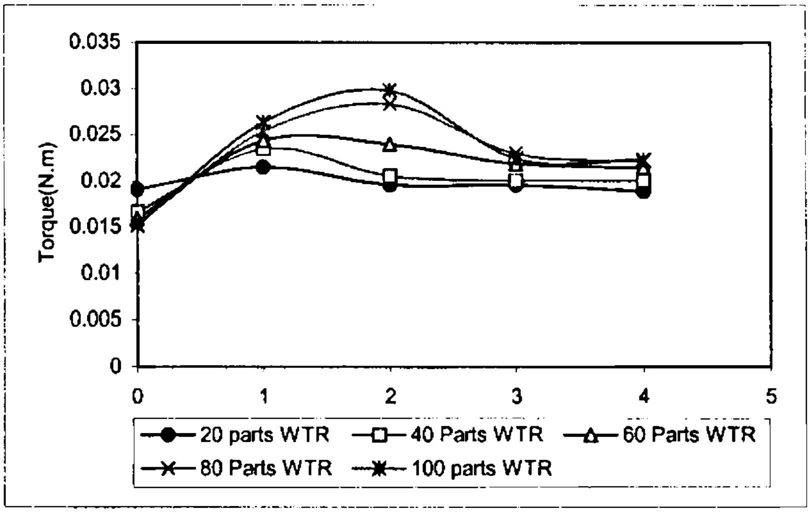


Figure 5.1.1.Variation of minimum torque with silane loading

This is because at higher WTR loading higher is the filler content and hence higher is the chance of matrix -filler interactions. In the 40-60 parts

WTR loading range, mixes containing 1 phr of silane coupling agent show higher viscosity. However, in the 80-100 range the higher viscosity is obtained with 2 phr of silane coupling agent. At 3 and 4 phr of silane loading, the viscosity remains more or less constant for all mixes.

Figure 5.1.2. shows the variation of (maximum- minimum) torque (Δt) for the mixes A to E_4. In all the cases the blends containing silane coupling agent show higher torque values compared to that of the control compound (A,B,C,D and E) indicating a relatively more restrained matrix resulting from the combined effect of higher interaction between blend components and higher levels of cross links formed. Table 5.1.2 shows that the cross-link density is higher at higher loading of coupling agent. Accordingly, all blends containing 4 parts of Si69 show the highest torque values.

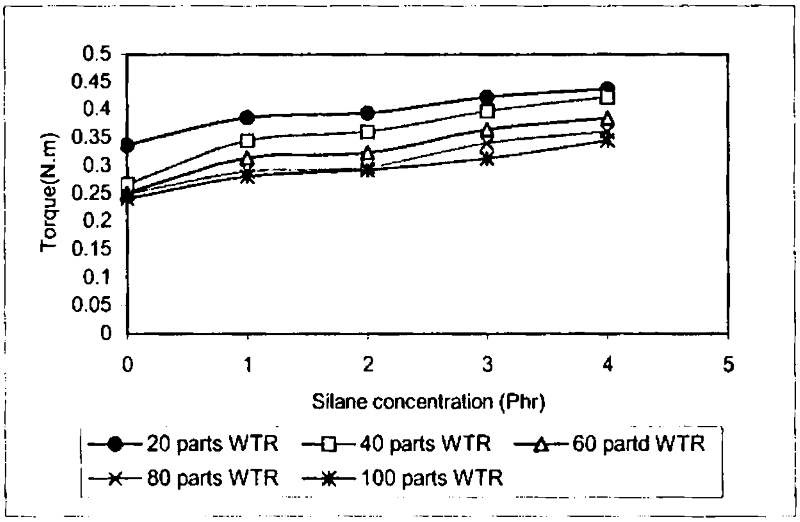


Figure 5.1.2.Variation of (max-min) torque with silane loading

With increasing reclaim content in the blends, the (Δt) is found to be gradually decreased, the effect being less significant in the presence of silane coupling agent. The lower level of cross-link at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking. However, the improved matrix interaction compensates for this and hence (Δt) for the blends containing silane-coupling agent is higher.

Table 5.1.2. Cross-link density of reclaim blends (mixes B, B_1, B_2,B_3,B_4)

No	Blend ratio NBR:WTR	Silane coupling agent in phr	Cross link density in m. mole/kg of rubber hydrocarbon
1	80:20	0	23.0
2	80:20	1	29.7
3	80:20	2	30.5
4	80:20	3	31.6
5	80:20	4	37.6

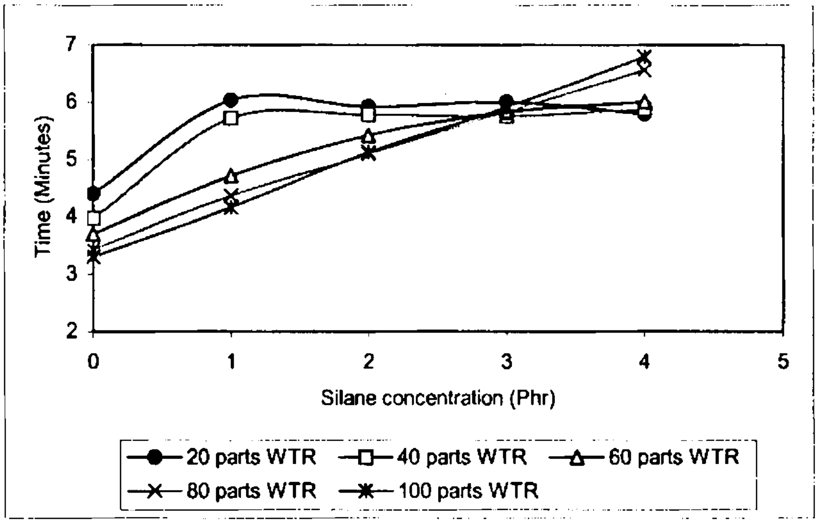


Figure 5.1.3 Variation of cure time with silane loading

Figure 5.1.3. shows the variation of cure time with silane loading of different mixes. (A to E_4) The effect of Si 69 loading on the cure time is dependant on the blend composition. At low WTR level, the cure time is almost the same at all loading of Si69. Where as at higher blend ratios, the Si69 content seems to have very marked effect on the cure time. From zero to 4 phr of Si69 there is a gradual increase in cure time, suggesting an adverse effect on the rate of cure.

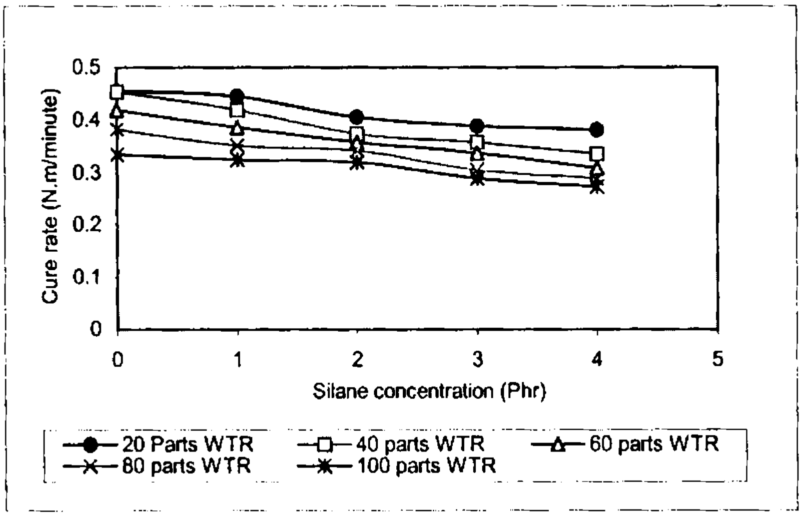


Figure 5.1.4.Variation of cure rate with silane loading

Figure 5.1.4 shows there indeed is a drop in cure rate at higher WTR and Si69 loadings. The relatively lower scorch time (Figure 5.1.5) coupled with higher (max-min) torque (figure 5.1.2) for Si69 containing samples indicates that the delay in completion of cure is only temporary and complete cure does take place within the extended cure time.

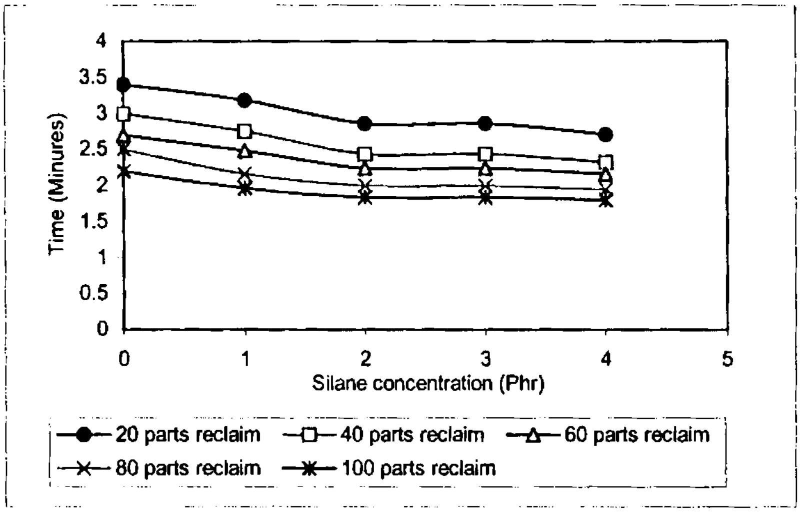


Figure 5.1.5.Variation of scorch time with silane loading

5.1.3.Mechanical Properties

Figure 5.1.6 shows variation of tensile strength of blends containing zero to 4 phr of Si 69. With increasing WTR content the tensile strength is found to increase for all the blends. This may be attributed to the presence of reinforcing filler contained in the WTR. Table 2.1.1.f shows that WTR contains about 30 percent carbon black filler. All the blends containing Si69 show improved tensile strength, the effect being more pronounced at higher WTR content. At 40 parts of WTR, incorporation of more than 1 phr of Si69 does not have a much effect on the tensile strength. At 60 parts of WTR the optimum loading of the coupling agent is 3 phr. At still higher WTR loading again there is not much difference in the tensile strength of the samples containing different levels of coupling agent. The improved tensile strength of the blends in the presence of Si69 may be attributed to the improved interaction between the blend components and filler apart from the higher extent of cure (Table 5.1.2) of the modified blends.

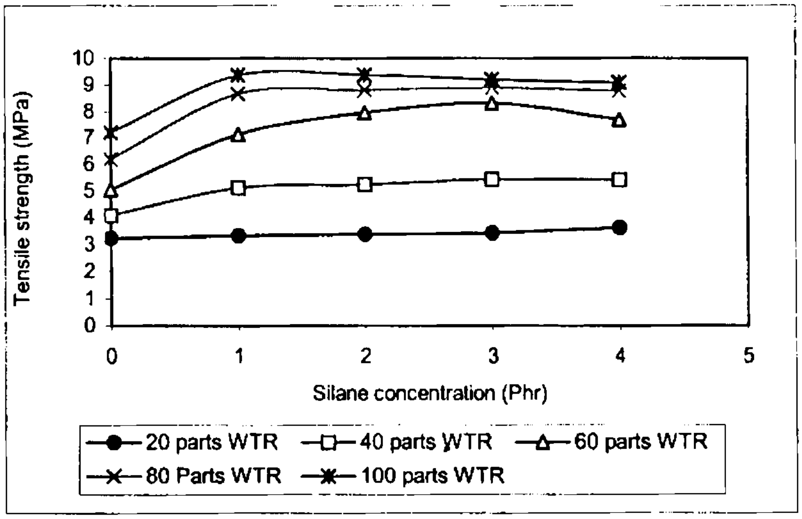


Figure 5.1.6.Variation of tensile strength with silane loading

Figure 5.1.7. shows the ultimate elongation values of the blends at different Si 69 loadings. All the blends containing coupling agent show higher elongation than the blends without coupling agent. The maximum elongation is obtained for the blend containing 80 parts of WTR with 3 phr of coupling

agent. The higher elongation of the samples containing coupling agent indicates that the coupling agent has a plasticizing effect also on the blends.

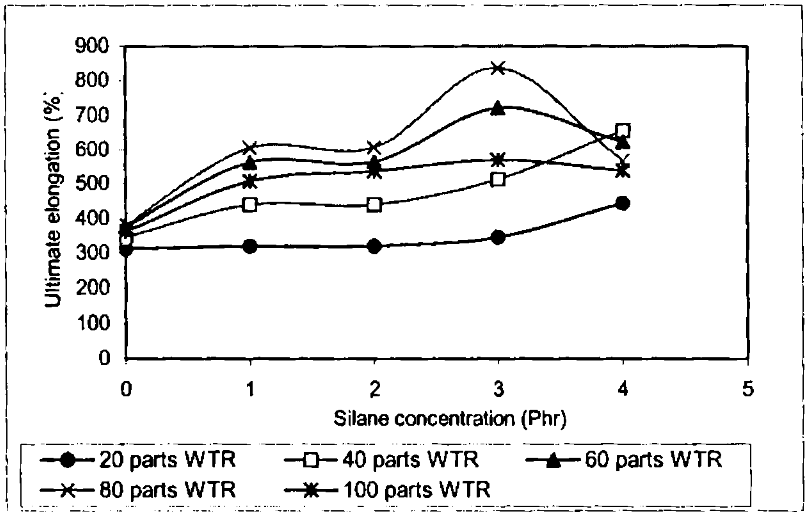


Figure 5.1.7.Variation of ultimate elongation with silane loading

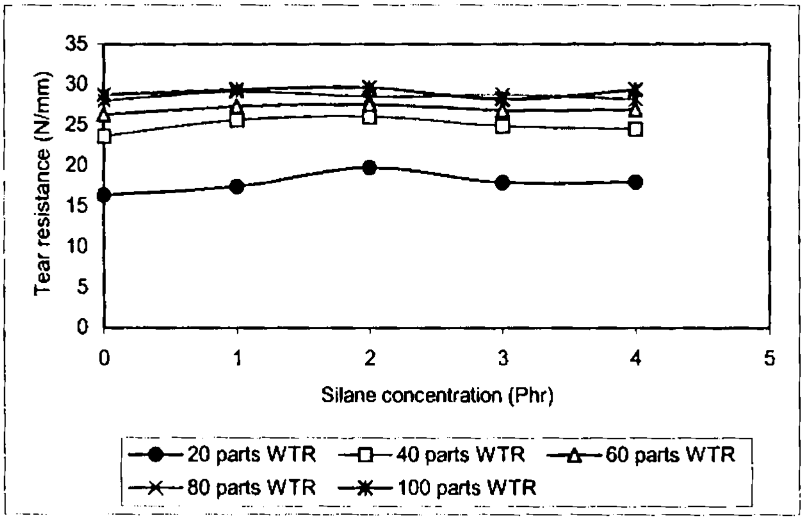


Figure 5.1.8.Variation of tear resistance with silane loading

Figure 5.1.8. shows tear strength of the blends at different loading of the coupling agent. All the blends show similar trend with a marked improvement in the tear strength beyond 30 parts of WTR. This may be attributed to the reinforcing effect of the filler present in WTR. (Table

2.1.1.f) In the presence of the coupling agent, the tear strength is only marginally affected.

Figure 5.1.9. shows the variation of compression set of the blends containing different levels of the coupling agent. The compression set is found to increase with the WTR content. This may be attributed to the poor strength of the low molecular weight WTR(11). At the test temperature under load, the blends containing higher WTR flow more resulting in higher compression set. With increasing coupling agent loading, compression set is also found to be more. This may be arising from the type of additional cross links that are formed in the presence of Si69. The higher compression set values indicate that the cross links formed are predominately poly sulphidic which are prone to break down and rearrangement under elevated stress and temperature.

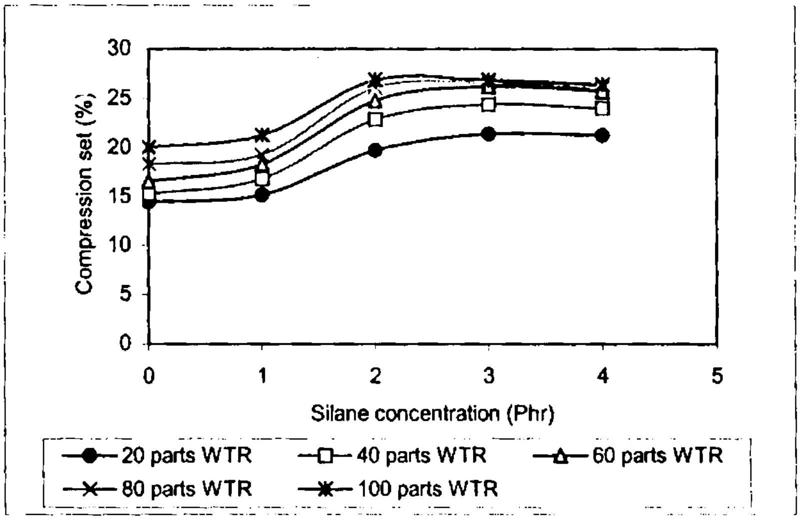


Figure 5.1.9.Variation of tear resistance with silane loading

Figure 5.1.10. represents variation of abrasion loss with silane loading in NBR/WTR blend. In the absence of coupling agent, blends containing higher level of WTR show higher abrasion loss.

In presence of coupling agent all the blends containing different levels of WTR show significantly lower abrasion loss. The detrimental effect of WTR on the abrasion resistance of the blends seems to be compensated for by the improved filler –matrix interaction in the presence of coupling agent resulting in almost constant abrasion resistance of all the blends.

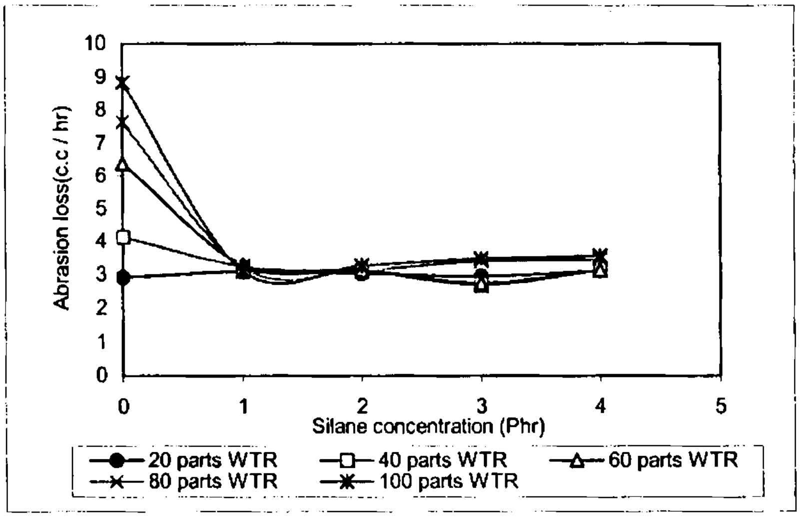
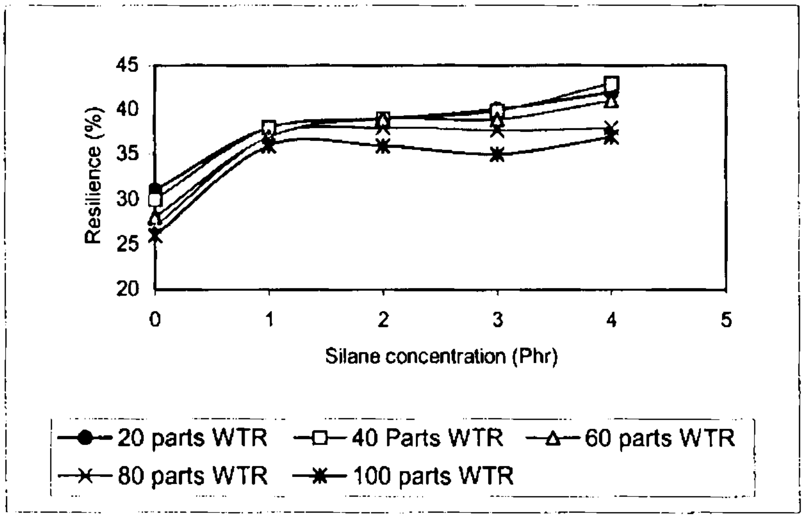


Figure 5.1.10.Variation of abrasion loss with silane loading



The adverse effect of WTR is reflected in the resilience of the blends containing no coupling agent. (Figure 5.1.11.) Higher the WTR content, lower is the resilience. With coupling agent all the blends show remarkable improvements in the resilience. This again suggests improved matrix-filler interaction and formation of additional poly sulphidic cross-links in the presence of coupling agent.

5.1.4. Ageing studies

The percentage retention of tensile strength, ultimate elongation and tear resistance was calculated as the ratio of the aged property to the unaged property. (Table 5.1.3. and 5.1.4.) In the absence of coupling agent, the retention is marginally higher than 100%. In the presence of coupling agent, the ageing resistance is relatively lower. This may be attributed to the presence of more poly sulphidic cross links in these blends.

Table 5.1.3 Retention of tensile strength and ultimate elongation after ageing

Tensile strength (MPa)				Ultimate elongation (%)			
Mix no	Before ageing	After ageing	Retention (%)	Mix no	Before ageing	After ageing	Retention (%)
A	3.3	3.5	109	A	313	308	98
B	4.1	4.3	106	B	346	322	93
C	5.1	5.7	112	C	377	352	93
D	6.2	6.8	110	D	382	358	94
E	7.2	8.0	111	E	363	340	93
A_1	3.0	3.4	111	A_1	320	301	94
B_1	5.1	5.3	103	B_1	440	400	91
C_1	7.1	7.5	105	C_1	564	530	94
D_1	8.7	8.7	100	D_1	607	565	93
E_1	9.4	9.3	99	E_1	509	482	95
A_2	3.0	3.6	117	A_2	320	318	95
B_2	5.2	5.8	111	B_2	440	406	92
C_2	8.0	7.9	99	C_2	565	510	90
D_2	8.8	8.7	99	D_2	608	551	91
E_2	9.4	8.5	91	E_2	538	501	93
A_3	3.4	3.8	112	A_3	345	328	95
B_3	5.4	5.3	98	B_3	514	480	93
C_3	8.3	7.0	85	C_3	722	593	95
D_3	8.9	8.6	97	D_3	632	593	94
E_3	9.2	8.8	95	E_3	571	508	89
A_4	3.6	3.2	88	A_4	443	302	84
B_4	6.5	4.9	75	B_4	526	465	88
C_4	7.7	7.1	92	C_4	625	526	84
D_4	7.7	7.6	98	D_4	570	487	86
E_4	8.5	7.4	86	E_4	540	442	82

Table 5.1.4 Retention of tear strength after ageing

Tear strength (N/mm)			
Mix no	Before ageing	After ageing	Retention (%)
A	16.4	16.0	98
B	23.6	23.2	98
C	26.3	25.1	95
D	28.0	27.5	98
E	28.7	28.0	97
A_1	17.4	16.7	96
B_1	25.6	24.2	94
C_1	27.3	24.8	91
D_1	29.1	25.9	89
E_1	29.4	26.7	91
A_2	19.7	18.8	95
B_2	26.0	23.7	91
C_2	27.5	24.5.	92
D_2	28.5	26.2	92
E_2	29.6	26.5	89
A_3	19.9	16.9	94
B_3	24.9	22.9	92
C_3	26.8	24.3	90
D_3	28.7	25.6	89
E_3	28.2	26.2	92
A_4	18.0	17.8	98
B_4	24.5	22.8	93
C_4	26.9	24.6	92
D_4	28.2	25.6	91
E_4	29.4	25.6	87

PART 2

Effect of silane coupling agent on CR / WTR blends[*]

The properties of chloroprene rubber/whole tyre reclaim blends containing varying amount of silane coupling agent are discussed in this chapter. Amount of Si69 varies from zero to 4 Phr.

5.2.1 Preparation of the blend

Formulation of the mixes is given in the table 5.3.1. Method of preparation and procedure adopted for the determination of cure characteristics and mechanical properties of the blend are given in chapter 2.

Table 5.2.1 Formulation of mixes

MixNo	A	B	C	D	E	A_1	B_1	C_1	D_1	E_1	A_2	B_2	C_2	D_2	E_2	A_3	B_3	C_3	D_3	E_3	A_4	B_4	C_4	D_4	E_4
Chloroprene	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50
WTR	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
Si69	-	-	-	-	-	1	1	1	1	1	2	2	2	2	2	3	3	3	3	3	4	4	4	4	4

All mixes A to E_4 contain ZnO 5 g, MgO 4 g, Stearic acid 0.5 g, NA 22 0.5 g, and Antioxidant 4020 1 g. Amount of WTR is adjusted so as to get total hydrocarbon concentration is 100

5.2.2 Cure Characteristics

Figure 5.2.1 shows the minimum torque values of the mixes containing different levels of silane coupling agent. All the blends containing silane-coupling agent show higher minimum torque, indicating higher viscosity of the blends. This can be attributed to the improved interaction between the matrix and filler in presence of coupling agent. The improvement in stock viscosity is found to be more pronounced in blends containing higher proportions of WTR. This may be attributed to the fact that at higher WTR levels, the blend contains higher filler concentration

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[*] Results of this part is accepted for publication in Polymer-Plastics-Technology-Engineering

and hence better chance of interaction. There also seems to be a leveling off beyond 2-3 phr of Si 69.

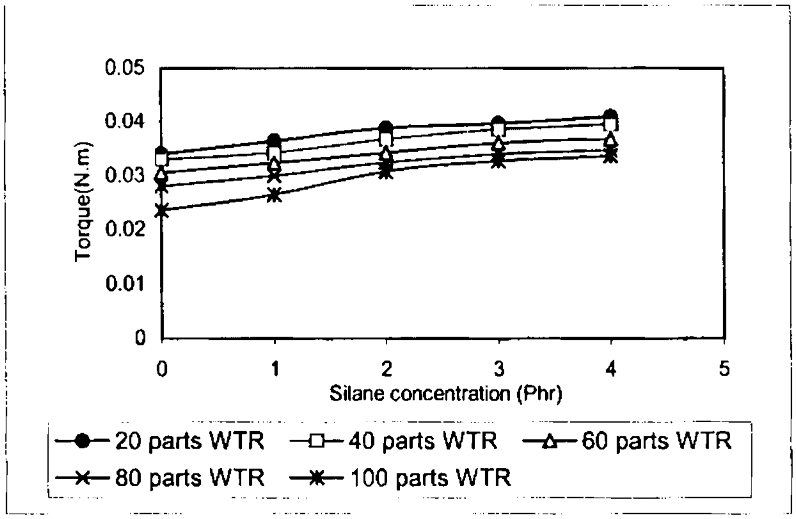

Figure 5.2.1.Variation of minimum torque with silane loading

The Figure 5.2.2. shows the variation of (maximum- minimum) torque (Δt). In all the cases the (Δt) gradually increases with the increase in concentration of silane coupling agent, indicating a relatively more restrained matrix resulting from improved interaction between the blend components.

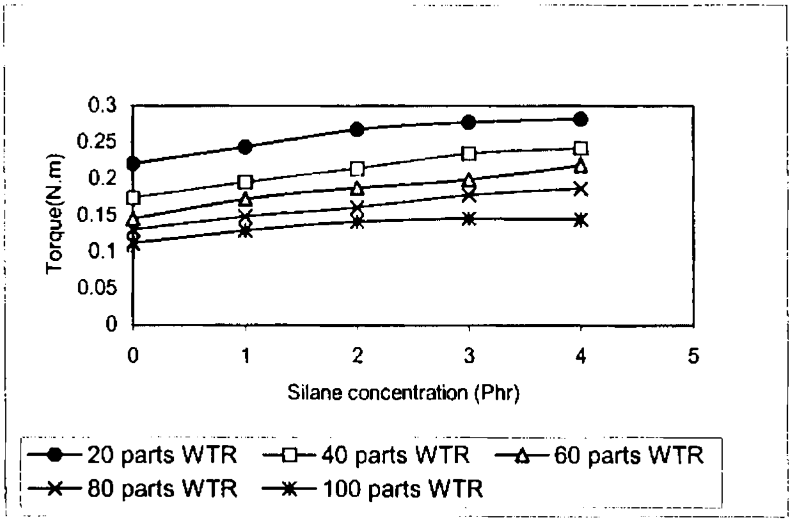

Figure 5.2.2.Variation of (max- min) torque with silane loading

The improved interaction between the blend components is also indicated by the increase in cross-link density of the matrix (Table 5.2.2). It is observed that after 3-phr silane concentration there is no significant improvement in the (Δt). There is also a decrease in (Δt) values with increasing the WTR content. The lower level of cross linking at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking. However, the improved matrix interaction compensates for this and hence (Δt) for the blends containing silane-coupling agent is higher.

Table 5.2.2 Cross-link density of reclaim blends (mixes B, B_1, B_2,B_3,B_4)

No	Blend ratio CR:WTR	Silane coupling agent in phr	Cross link density in m. mole/kg of rubber hydrocarbon
1	80:40	0	30.6
2	80:40	1	40.9
3	80:40	2	42.8
4	80:40	3	44.6
5	80:40	4	44.1

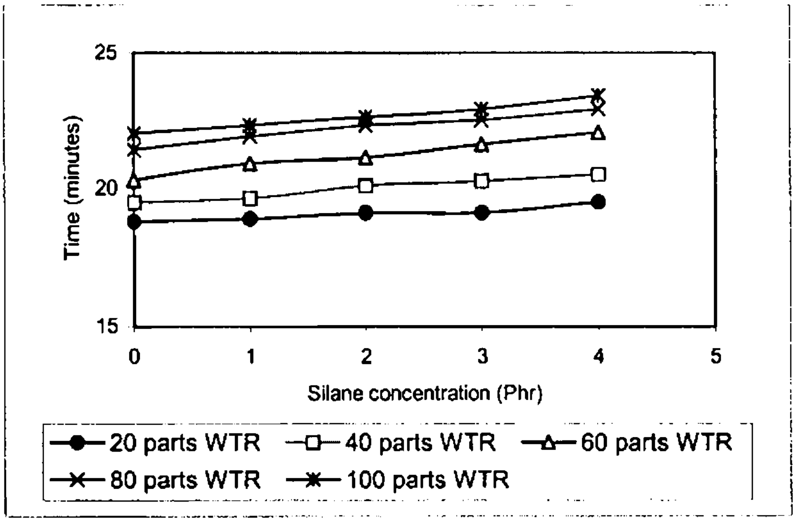

Figure 5.2.3. Variation of cure time with silane loading

Figure 5.2.3 shows variation of cure time in the presence of different levels of silane coupling agent. The cure time registers a gradual increase with increasing silane loading. Figure 5.2.4 shows that there is also a corresponding delay in the onset of cure. The more or less constant cure rate of all the blends (Figure 5.2.5) indicate that the delay in the start of the reaction is only temporary and the reaction precedes to full cure.

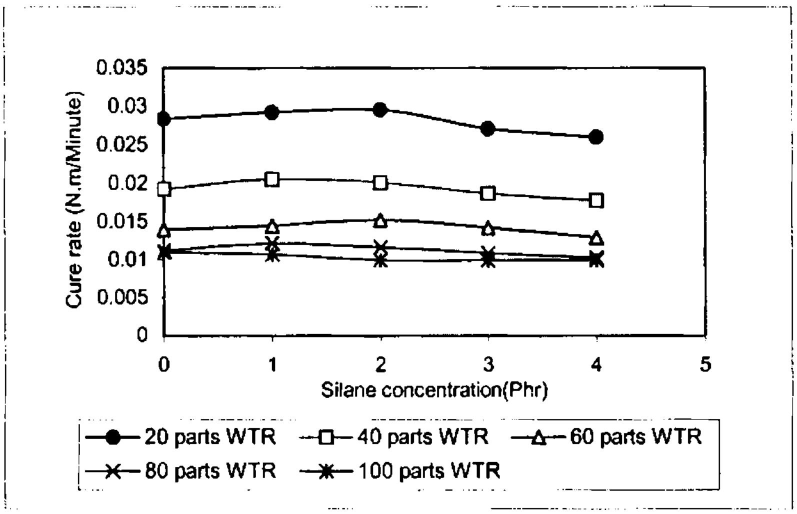

Figure 5.2.4. Variation of cure rate with silane loading

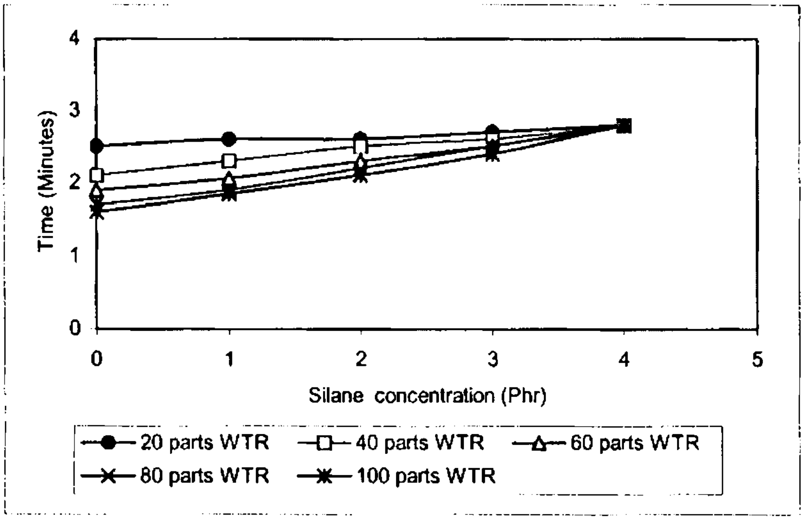

Figure 5.2.5.Variation of scorch time with silane loading

5.2.3. Mechanical Properties

Figure 5.2.6. shows the tensile strength of different blends containing zero to 4 phr of Si 69. It is observed that tensile strength is gradually increased by the addition of silane coupling agent.

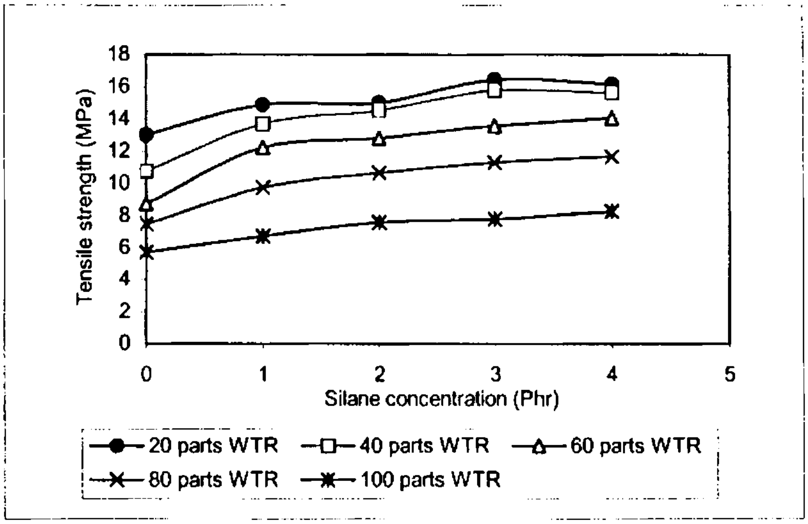

Figure 5.2.6.Variation of tensile strength with silane loading

The increase in tensile strength is accounted for on the basis of increased interaction between the blend components in presence of the coupling agent. At any silane concentration increase in reclaim content reduces the tensile strength. It may be attributed to the dilution effect produced by the addition of reclaim to the chloroprene matrix. Since the whole tyre reclaim is predominately natural rubber, addition of reclaim to the chloroprene reduces the crystallisability of the matrix and hence results in lower tensile strength.

Figure 5.2.7. shows the variation of ultimate elongation with the silane-coupling agent. The ultimate elongation increases with the addition of Si 69 and level off beyond 1 phr. The increased extensibility of the matrix in the presence of the coupling agent points to its minor plasticizing effect. Similar reports have been reported by Ismail H. et al ([12]).

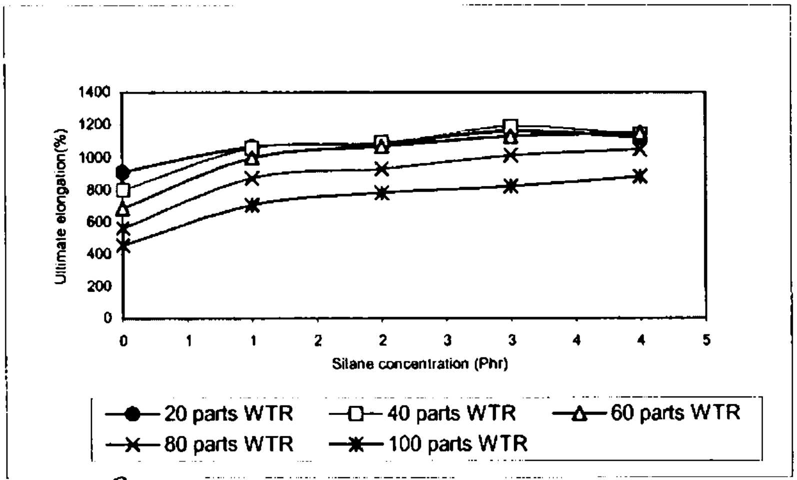

Figure 5.3.7.Variation of ultimate elongation with silane loading

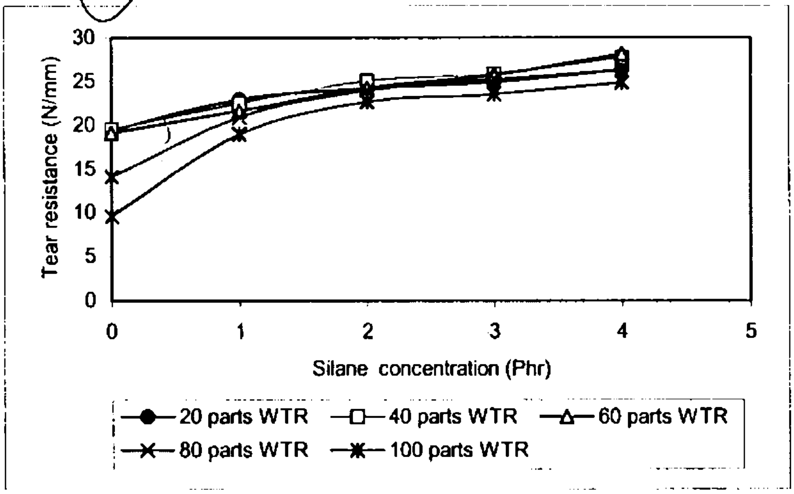

Figure 5.2.8.Variation of tear strength with silane loading

Figure 5.2.8 shows comparison of tear strength with the addition of coupling agent in mixes A to E_4. In the chloroprene /reclaim blend without coupling agent, with the increase in reclaim concentration the tear strength decreases. But in presence of coupling agent the tear strength increases significantly. This may be attributed to the increased inter-component interaction in the blend in the presence of Si69. The improvement in the tear strength is more pronounced in blends containing higher WTR. At higher reclaim loading more is the filler and hence more is the chance of coupling interaction between carbon black filler present in the reclaimed rubber and chloroprene matrix.

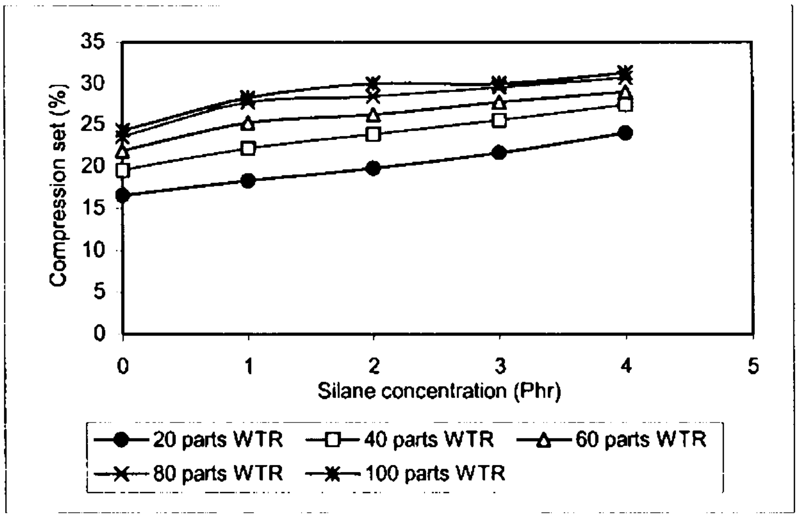

Figure 5.2.9 Variation of compression set with silane loading

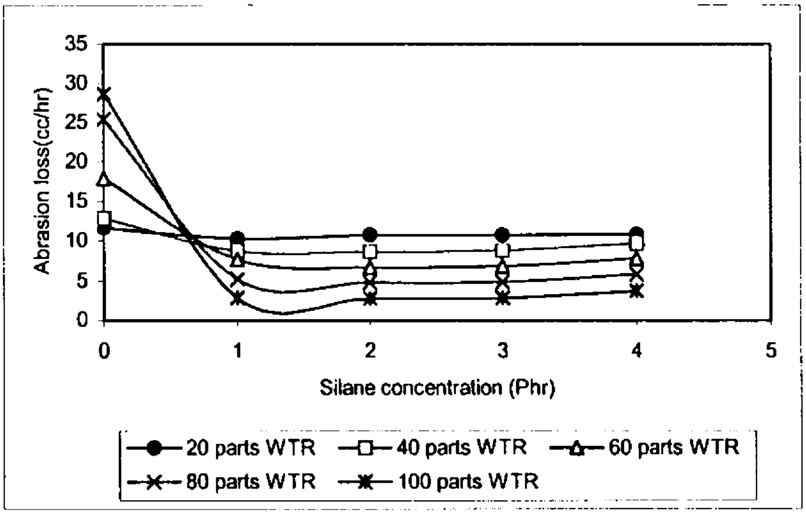

Figure 5.2.10.Variation of abrasion loss with silane loading

Figure 5.2.9. shows the variations of compression set of the blends containing different levels of the coupling agent. The compression set is found to increase with the increase in concentration of silane coupling agent. At the test temperature under load, the blends containing higher

WTR flows more, resulting in higher compression set, as explained in the chapter 3. The possible breakage of additional polysulphidic cross links formed in the presence of Si69 also might be contributing to this.

Fig. 5.2.10

Figure 5.3.10 shows the variation of abrasion loss with increase in concentration of silane coupling agent in mixes A to E_4. It is observed that abrasion loss decreases with the addition of silane coupling agent. Decreased abrasion loss i.e increased abrasion resistance in the presence of coupling agent may be attributed to improved interaction between the blend components. The effect is more predominant at higher reclaim concentration.

Figure 5.2.11 shows the variation of resilience with the addition of coupling agent in mixes A to E_4. The resilience decreases with the addition of Si69 the effect being more prominent at higher reclaim loading. Introduction of more filler by the way of adding more WTR increases chances of energy loss at the interfaces leading to the lower resilience (13).

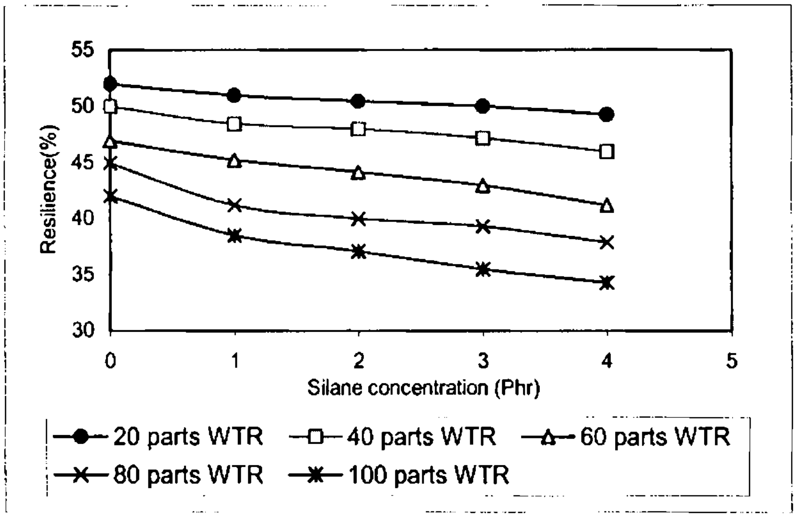

Figure 5.2.11.Variation of resilience with silane loading

The improved inter component interaction is not reflected as improved resilience in the case of blends containing coupling agent. This may be attributed to the extent of strain involved. The level of strain the sample is subjected to in a resilience test is very small compared to that a compression set tests.

5.2.4. Ageing studies

The percentage retention of tensile strength, ultimate elongation and tear resistance were calculated as the ratio of the aged property to the unaged property.

Table 5.2. 4 Retention of tensile strength and ultimate elongation after ageing

Tensile strength (MPa)				Ultimate elongation (%)			
Mix no	Before ageing	After ageing	Retention (%)	Mix no	Before ageing	After ageing	Retention (%)
A	13.0	13.7	106	A	912.	877.	96
B	10.8	11.7	108	B	802	750	94
C	8.7	9.6	110	C	684	750	91
D	7.5	7.9	107	D	566	462	82
E	5.7	5.9	103	E	456	437	96
A_1	14.9	14.5	97	A_1	1064	1045	98
B_1	13.7	13.7	100	B_1	1056	1000	95
C_1	12.2	11.6	94	C_1	1000	980	98
D_1	9.7	9.6	98	D_1	785	820	94
E_1	6.7	6.5	97	E_1	726	623	88
A_2	15.0	14.2	95	A_2	1088	1075	99
B_2	14.5	14.4	99	B_2	1094	1080	99
C_2	12.8	12.5	97	C_2	1069	993	93
D_2	10.7	9.9	93	D_2	931	848	91
E_2	7.6	7.0	92	E_2	783	685	87
A_3	16.5	13.8	84	A_3	1160	1046	90
B_3	15.8	14.9	94	B_3	1188	1029	87
C_3	13.6	10.8	80	C_3	1131	990	88
D_3	11.3	9.3	82	D_3	1013	862	85
E_3	7.8	7.7	99	E_3	825	788	96
A_4	16.2	14.7	91	A_4	1120	963	86
B_4	15.6	14.6	94	B_4	1143	923	81
C_4	14.1	11.5	82	C_4	1150	920	80
D_4	11.7	9.9	85	D_4	1150	887	84
E_4	8.3	7.3	88	E_4	883	768	87

(Tables 5.3.4 and 5.3.5) In the case of tensile strength control mixes show marginally higher retention compared to blends containing coupling agent. For mixes A to E_4 the retention of ultimate elongation is less than 100%. Tear measurements of mixes A to E_4 shows lower retention for blends containing Si69.

Table 5.2.4. Retention of tear strength after ageing

Tear strength (N/mm)			
Mix no	Before ageing	After ageing	Retention (%)
A	19.3	22.4	116
B	19.4	22.9	118
C	19.5	23.2	119
D	19.1	23.2	121
E	14.1	16.6	118
A_1	19.6	22.1	113
B_1	21.9	26.5	115
C_1	22.5	24.6	109
D_1	21.6	24.3	112
E_1	20.9	22.2	106
A_2	19.0	19.6	103
B_2	24.2	26.2	108
C_2	24.1	25.9	103
D_2	24.3	25.9	107
E_2	23.9	24.6	103
A_3	22.6	24.4	108
B_3	24.9	27.5	111
C_3	25.9	28.6	111
D_3	25.7	27.6	107
E_3	25.2	24.2	104
A_4	23.5	24.2	103
B_4	23.6	27.8	106
C_4	27.8	28.2	101
D_4	28.2	29.1	103
E_4	22.3	27.3	104

PART 3

Effect of silane coupling agent on SBR/WTR blends*

This chapter discusses on the cure characteristics and mechanical properties of styrene butadiene rubber with whole tyre reclaim blends in presence of silane coupling agent. The Si 69 concentration changes from zero to 4 Phr

5.3.1.Preparation of blends

Formulation of the mixes is given in table 5.3.1. Method of preparation of the blends and the details of the test methods are discussed in the chapter 2.

Table 5.3.1 Formulation of the Mixes

Mix No	A	B	C	D	E	A_1	B_1	C_1	D_1	E_1	A_2	B_2	C_2	D_2	E_2	A_3	B_3	C_3	D_3	E_3	A_4	B_4	C_4	D_4	E_4
SBR	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50
WTR	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
Si 69	-	-	-	-	-	1	1	1	1	1	2	2	2	2	2	3	3	3	3	3	4	4	4	4	4

All mixes contain CR- Chloroprene, WTR - whole tyre reclaim, weight of whole tyre reclaim is adjusted so as to get 100 grams rubber hydrocarbon. ZnO -5 g, MgO-4 g, Stearic acid – 0.5 g, 4020 -1 g NA22 (ethylene thio urea) 0.5 g are common to all mixes

5.3.1.Cure Characteristics

Figure 5.2.1. shows the minimum torque values of the mixes A to E_4 containing different levels of silane coupling agent. It is observed that with the increase in concentration of coupling agent the minimum torque increases gradually, at all reclaim concentration indicating higher stock viscosity resulting from improved filler matrix interaction. At 4- phr silane loading there is a drop in the minimum torque, the effect being more prominent at lower WTR content. At lower WTR content where filler

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* Results of this part is communicated to Int. J .Polymer Materials (in press)

content is lower, 4 phr of the coupling agent is slightly excess and this results in the lower stock viscosity.

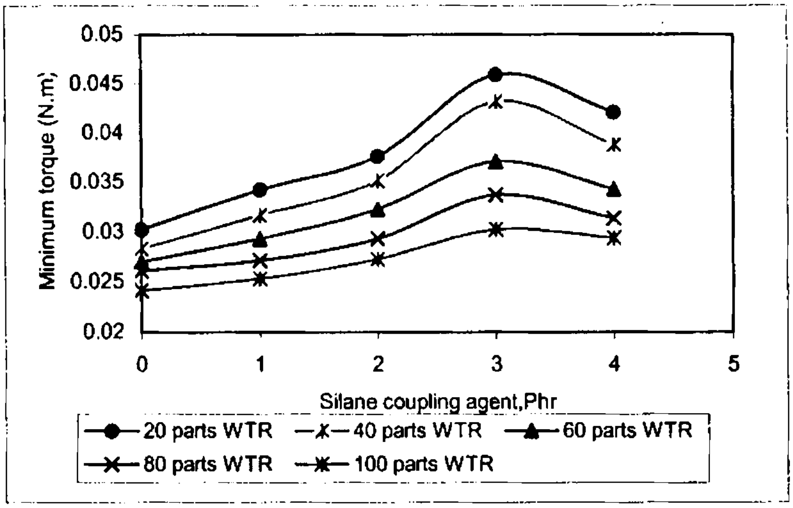

Figure 5.3.1 Variation of minimum torque with of silane coupling

Figure 5.3.2. shows the variation of (maximum – minimum) torque (Δt). From the figure it is clear that (Δt) of the blends increases with increase in silane concentration and attains a maximum value at 2-3 phr silane concentrations.

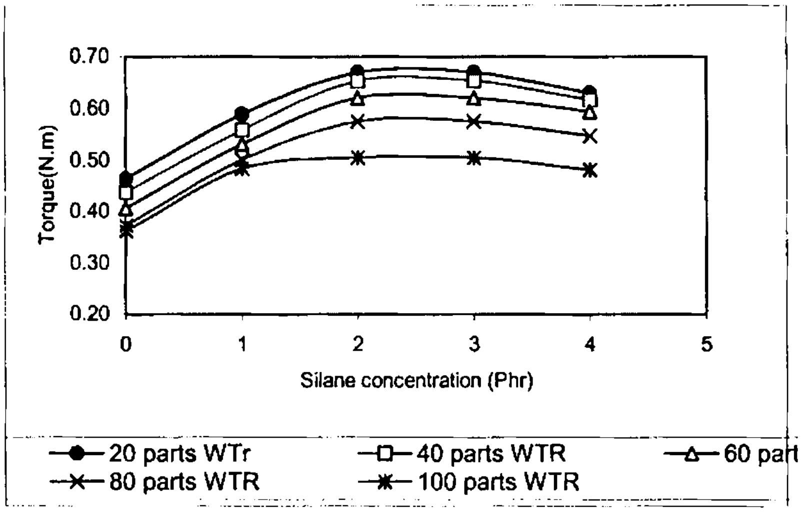

Figure 5.3.2 Variation of (max-min) torque with of silane coupling

The increase in (max-min) torque indicates increased cross-link density of the system in the presence of Si69. Si69 contains four sulphur atoms per molecule, which can get involved in the cure reaction. The cross-link density measurements (Table 5.3.2.) show that there is an increase in the cross-link density in the presence of Si69.

Table 5.3.2 Cross-link density of the mixes B, B_1, B_2, B_3 and B_4.

No	Blend ratio SBR: WTR	Silane coupling agent in phr	Cross link density in m. mole/kg of rubber hydrocarbon
1	80:40	0	38.8
2	80:40	1	49.3
3	80:40	2	65.3
4	80:40	3	62.8
5	80:40	4	61.6

At higher silane content there is a marginal drop in (Δt) for mixes containing lower levels of WTR. For mixes containing higher WTR levels, the (Δt) is stabilized beyond 2-3 phr of Si69. This may be arising from the fact that at lower WTR levels there is less filler available for interaction with the coupling agent and the excess Si69 then acts as plasticizer.

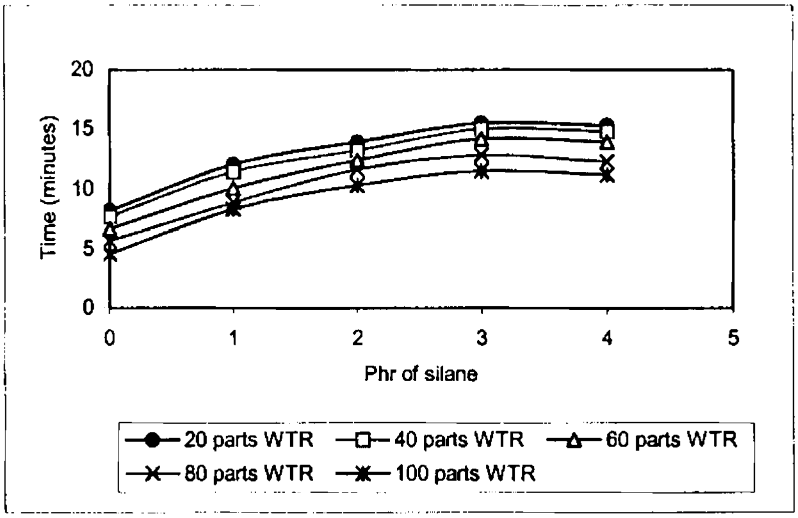

Figure 5.3.3 Variation of cure time with silane coupling agent

Figure 5.3.3 shows the variation of cure time at different loadings of Si69. The cure time gradually increases with the addition of coupling agent. Beyond 3 Phr of the coupling agent cure time is almost constant. Delayed completion of cure in presence of the coupling agent indicates an adverse effect it has on the sulphur accelerator cure of the blend.

Figure 5.3.4 shows change in scorch time with silane coupling agent loading. Scorch time of the mixes A to E_4 decreases with the silane coupling agent concentration. Delayed completion of cure coupled with reduced scorch time and almost constant cure rate (Figure 5.2.5) indicates the formation of higher number of cross links during the vulcanization in the presence of Si69. The measured cross link density values are in agreement with this. (Table 5.2.2)

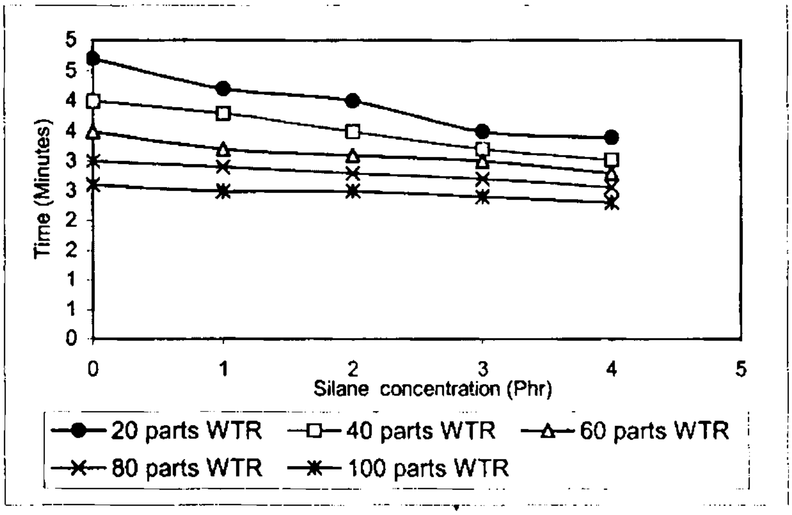

Figure 5.3.4. Variation of scorch time with silane coupling agent

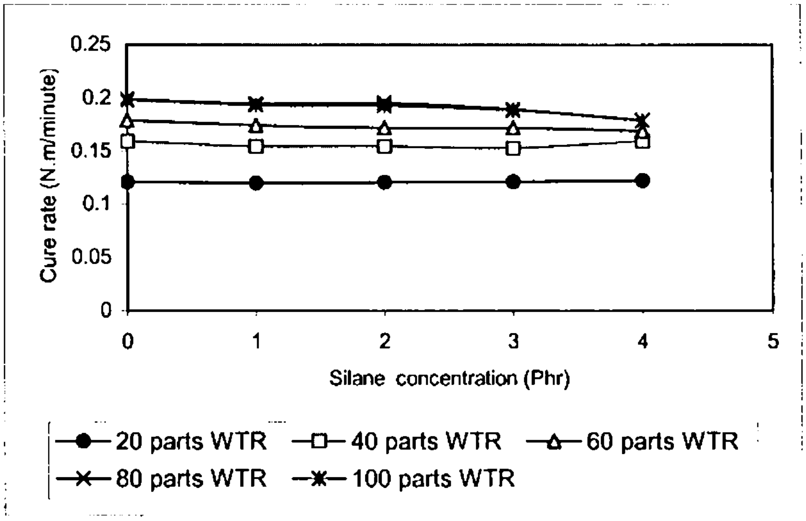

Figure 5.3.5 Variation of cure rate with silane coupling agent

5.3.3 Mechanical Properties

Figure 5.3.6. shows variation of tensile strength of blends containing different amounts of Si69. The effect of Si69 is a function of WTR content of the blends. At lower WTR levels (20 parts) there is no significant improvement in tensile strength. For blends containing higher WTR loading the tensile strength registers marked improvements at lower silane concentration.

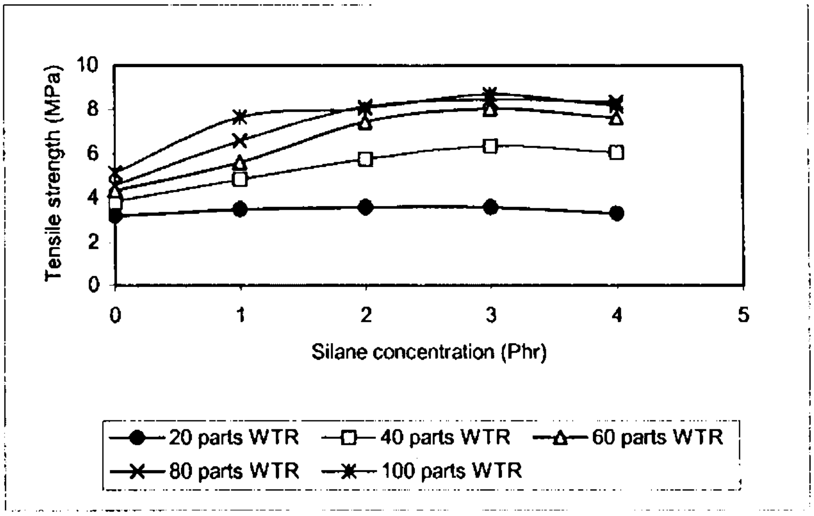

Figure 5.3.6 Variation of tensile strength with silane coupling agent

For 40 parts of WTR, 2-3 parts of silane coupling agent is found to be optimum while for 60 and 80 parts the improvement in tensile strength is obtained at 1-2 parts of Si69. At 100 parts of WTR level, 1 phr of Si69 is sufficient to bring improvements in tensile strength. This indicates that at higher WTR content, higher levels of Si69 gives a plasticizing effect resulting in lower tensile strength. Similar results have been reported in natural rubber /bamboo fiber composites by Ismail H. et al. (12)

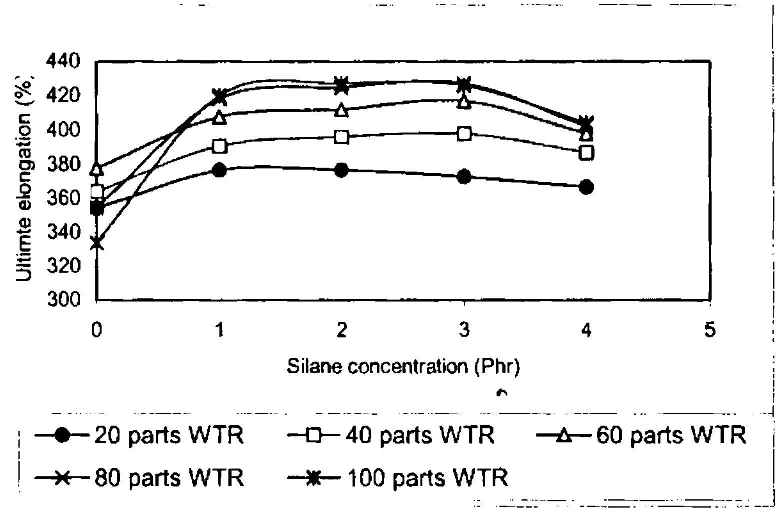

Figure 5.3.7 Variation of ultimate elongation with silane coupling agent

Figure 5.3.7. shows the ultimate elongation values of the blends containing different amounts of Si69. Addition of silane coupling agent increases the ultimate elongation value of the blends. For blends containing 20 to 60 parts of reclaim, the influence of the coupling agent is only marginal. But at 80 and 100 parts of reclaim concentration, even at 1 phr concentration of the coupling agent a significant improvement in the ultimate elongation is obtained. This also supports that Si69 has a plasticizing effect in the blend.

Figure 5.3.8 shows tear strength of the blends A to E_4 at different loading of the coupling agent. Addition of coupling agent increases the tear strength. Increase of tear strength is accounted for on the basis of improved interaction between the carbon black filler present in the WTR and the matrix in presence of coupling agent. For blends containing 20 to 60 parts of reclaim there is significant improvement in tear strength. But at 80 and 100 parts of reclaim the change is only marginal.

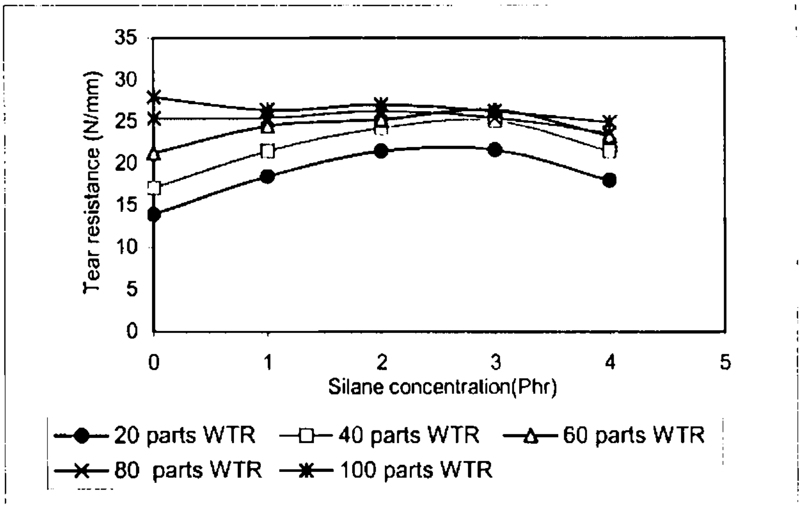

Figure 5.3.8 Variation of tear resistance with silane coupling

Figure 5.3.9. shows the variation of compression set of the blends containing different levels of the coupling agent. The compression set is found to increase with increased concentration of coupling agent and also increase with the increase in whole tyre reclaim concentration at any fixed silane concentration. Similar results have been reported by Phadke et al (13). This may be arising from the type of additional cross links formed in the presence of Si69. The higher compression set values indicate that the cross link formed is predominately polysulphidic which are prone to break down and rearrangement under elevated temperature and stress. Increased set value to higher reclaim concentration may be attributed to the poor strength of the low molecular weight WTR. At the test temperature under load, the blends containing higher WTR flow more, resulting in higher compression set.

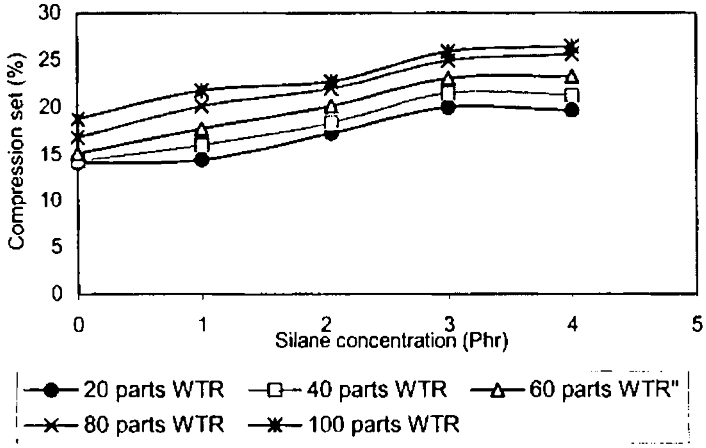

Figure 5.3.9 Variation of compression set with silane coupling agent

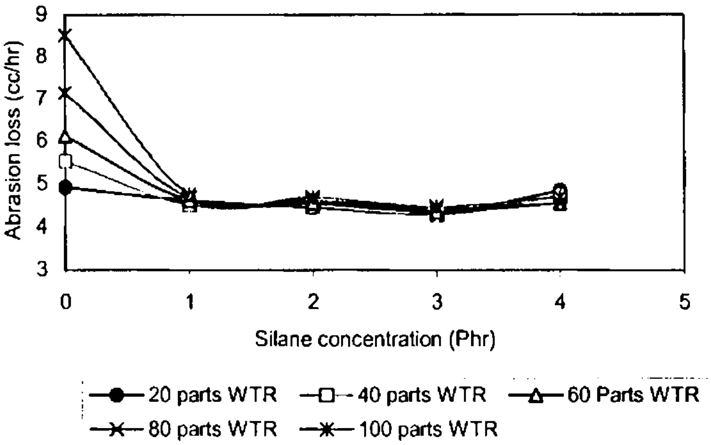

Figure 5.3.10 Variation of abrasion loss with silane coupling agent

The abrasion loss is decreased with coupling agent loading Figure 5.3.10. In the presence of coupling agent, all the blends containing different levels of WTR show significantly lower abrasion loss. The detrimental effect of WTR on the abrasion resistance of the blends seems to be compensated for by the improved filler -matrix interaction in the presence of coupling agent resulting in almost constant abrasion resistance of all the blends. Improvement in abrasion resistance of the blends is more significant at higher reclaim concentration.

The advantage of the coupling agents is also reflected in the resilience. (Figure 5.3.11) Though the resilience is almost constant with increasing silane concentration at lower WTR loading, there is definite improvement at 80 and 100 parts of WTR.

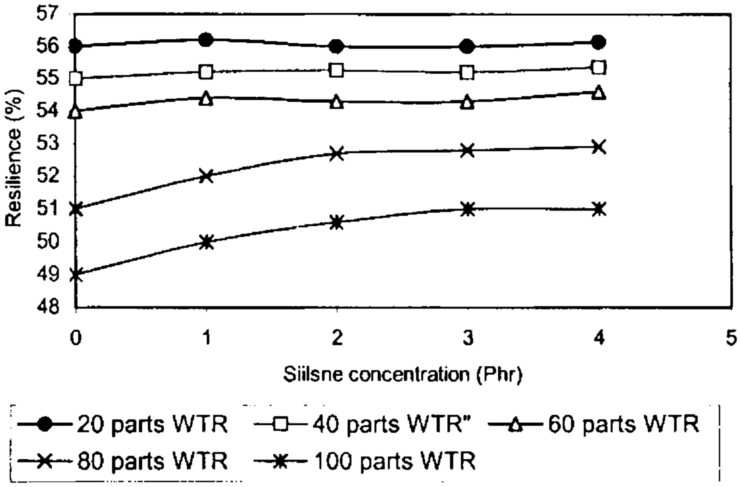

Figure 5.2.11 Variation of resilience with silane coupling agent

5.3.4 Ageing studies

The percentage retention of tensile strength, ultimate elongation and tear resistance was calculated as the ratio of the aged property to the unaged property. (Tables 5.3.3 and 5.3.4) In the presence of coupling agent, retention of tensile strength, ultimate elongation showed improvement while tear resistance retention is decreased.

Table 5.3.3 Retention of tensile strength and ultimate elongation after ageing.

Tensile strength (MPa)				Ultimate elongation (%)			
Mix no	Before ageing	After ageing	Retention (%)	Mix no	Before ageing	After ageing	Retention (%)
A	3.2	3.4	106	A	355	259	73
B	3.8	3.9	103	B	364	266	73
C	4.3	4.4	102	C	378	276	73
D	4.6	4.6	100	D	355	287	81
E	5.1	5.2	102	E	334	322	96
A_1	3.5	3.8	108	A_1	377	321	85
B_1	4.8	5.3	109	B_1	391	323	83
C_1	5.6	6.1	108	C_1	408	349	86
D_1	6.6	7.2	110	D_1	418	367	88
E_1	7.7	9.0	118	E_1	420	372	89
A_2	3.6	3.8	107	A_2	377	323	86
B_2	5.8	6.6	113	B_2	396	344	87
C_2	7.4	8.7	117	C_2	412	368	89
D_2	8.1	8.4	104	D_2	425	381	90
E_2	8.0	8.7	108	E_2	427	383	89
A_3	3.6	4.0	113	A_3	373	333	89
B_3	6.3	6.7	105	B_3	398	362	91
C_3	8.0	8.7	109	C_3	416	379	91
D_3	8.4	8.9	106	D_3	426	386	91
E_3	8.7	9.7	111	E_3	427	392	92
A_4	3.3	3.4	101	A_4	367	335	91
B_4	6.0	6.4	105	B_4	387	351	91
C_4	7.6	7.9	104	C_4	398	351	90
D_4	8.0	8.2	102	D_4	402	343	85
E_4	8.2	8.4	103	E_4	404	356	88

Table 5.3.4. Retention of tear strength

Tear strength (N/mm)			
Mix no	Before ageing	After ageing	Retention (%)
A	16.4	16.0	97
B	23.6	23.2	98
C	26.3	25.1	95
D	28.0	27.5	98
E	27.9	26.3	94
A_1	18.5	16.3	88
B_1	25.6	24.3	95
C_1	27.3	25.8	94
D_1	27.5	24.6	89
E_1	29.4	27.2	92
A_2	21.5	18.0	86
B_2	26.0	23.7	91
C_2	27.5	25.4	92
D_2	28.5	24.0	91
E_2	29.6	27.5	93
A_3	21.6	19.7	91
B_3	25.1	23.3	93
C_3	26.4	24.4	92
D_3	25.5	22.6	89
E_3	26.3	23.9	92
A_4	18.0	16.1	89
B_4	21.5	20.1	93
C_4	23.2	20.9	90
D_4	23.6	21.0	89
E_4	24.9	22.0	88

5.4 Conclusion

The Si69 can be used to improve properties of blends of WTR with acrylonitrile rubber, chloroprene rubber and Styrene butadiene rubber. This is reflected in the mechanical properties of the blends. Increase in viscosity, indicated by increase minimum torque and (max-min) torque, shows improvement in compatibility. Cross-link density is higher for blends containing silane-coupling agent compared to control mix. Optimum concentration of Si69 in the blend is depended on composition.

Introduction of coupling agent to the acrylonitrile butadiene /whole tyre reclaim blend shows a significant improvement in mechanical properties such as tensile strength and abrasion resistance. Compression set of the blends containing silane-coupling agent is higher than the unmodified blend. Tear strength measurements has no such improvements in presence of coupling agent. In the presence of coupling agent cure time is found to be higher where as scorch time and cure rate are found to be lesser than the control mix. Cross-link density is increased in presence of coupling agent.

Introduction of Si69 coupling agent to the CR/ WTR blend increase the cure time and reduce scorch time and cure rate. Addition of Si69 improves the mechanical properties such as tensile strength, ultimate elongation, tear resistance and abrasion resistance. Cross-link density is improved in presence of coupling agent. Resilience of the blend decreases with the increase in silane concentration.

In the SBR/WTR blends (min) torque and (max-min) torque are increased in presence of coupling agent. The tensile strength and abrasion resistance registers marked improvements in the presence of silane coupling agent. Tear resistance and resilience is improved only at higher WTR concentration. A higher level of cross-link density is obtained for SBR/WTR blends containing coupling agent. Cure time is higher for blends containing coupling agent.

In the NBR/WTR blend and CR/WTR blend ageing studies shows that retention of property is lower than that blends without coupling agent. In the case of SBR/WTR blend ageing not significantly affect the properties.

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CHAPTER 6

THERMAL STUDIES OF BLENDS OF WHOLE TYRE RUBBER WITH NATURAL RUBBER AND SYNTHETIC RUBBERS

In the previous chapters utilisation of reclaimed rubber (WTR) in different blends is discussed. It is found that blending of whole tyre reclaim with virgin rubber results in improvement in mechanical properties and cure characteristics. In this chapter thermal property of the blends of WTR with natural rubber, butadiene rubber, acrylonitrile rubber and styrene butadiene rubber is discussed.

PART 1

Thermal analysis of blends of whole tyre reclaim with Natural rubber and Butadiene rubber

61.1.Preparation of blends

In this experiment blends of whole tyre reclaim with natural rubber and butadiene rubber are prepared and its thermal stability is evaluated using Thermogravimetric analysis. The formulation of the mixes is given in the table 6.1.1. Sample preparation and test method employed are given in the chapter 2.

Table 6.1.1. Formulation of the mixes

Ingredient	Mix No			
	A	B	C	D
NR	100	80	-	-
BR	-	-	100	80
WTR	-	40	-	40
Sulphur	2.5	2.5	2.0	2.0
MBTS	0.5	0.5	0.8	0.8
TMTD	0.2	0.2	0.4	0.4

Note: NR - Natural rubber, BR- butadiene rubber, WTR- whole tyre reclaim ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g are common to all mixes. Weight of the reclaimed rubber is adjusted so as to get rubber hydrocarbon of 100.

Thermal Analysis

The thermal degradation of the blends was studied by Universal V3 . 2B T A Instrument. All the analyses were carried out using 10 mg samples on platinum pan in an atmosphere of nitrogen. The heating rate of was 10° C/ minute.

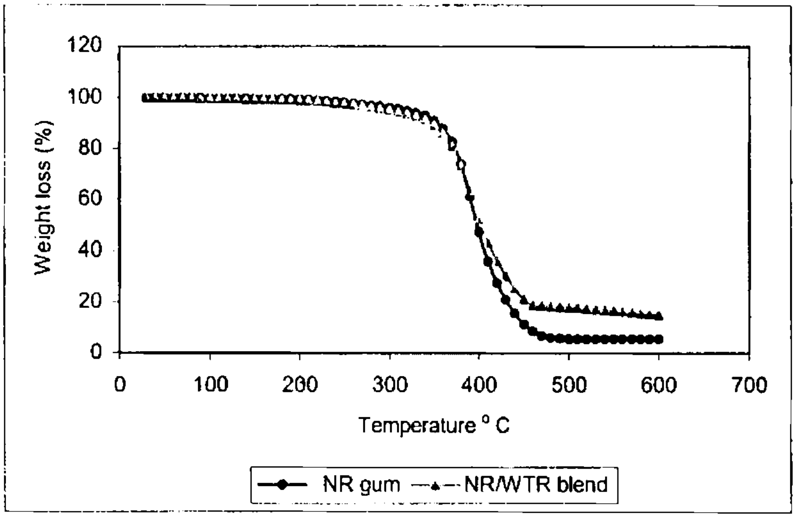

Figure 6.1.1 TGA curve of NR gum and NR/ WTR blend

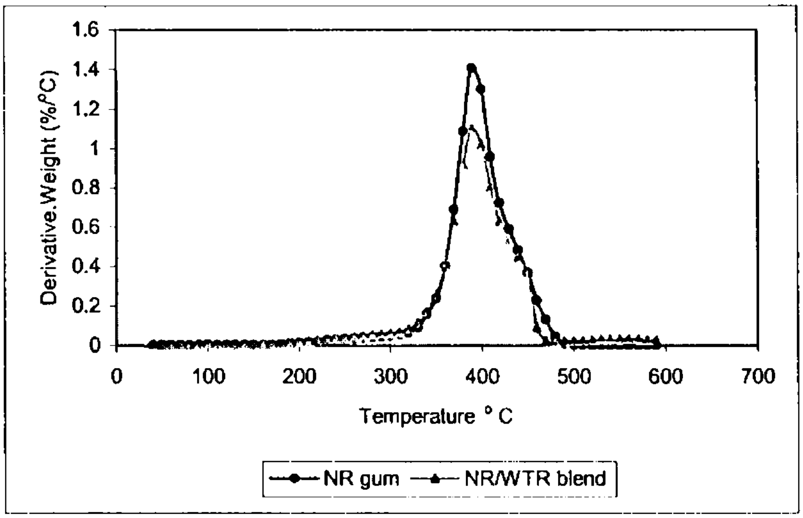

Figure 6.1.2 DTA of NR/WTR blend

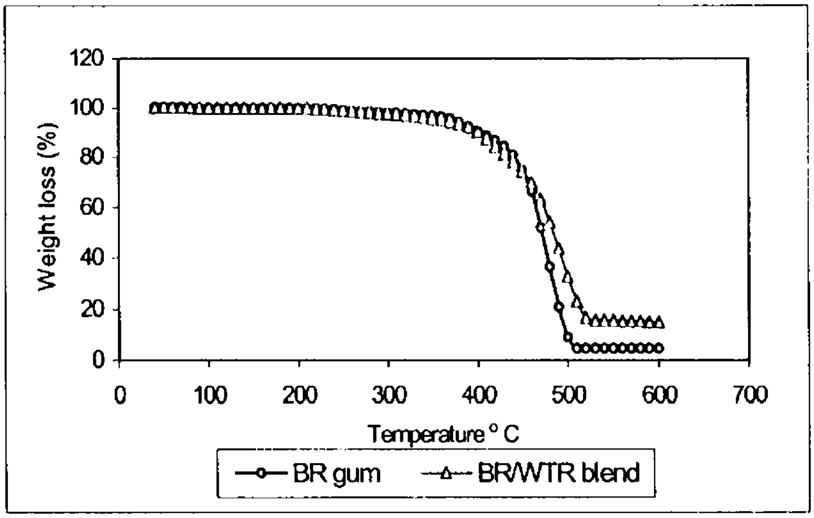

Figure 6.1.3. TGA curve of BR gum and BR/ WTR blend

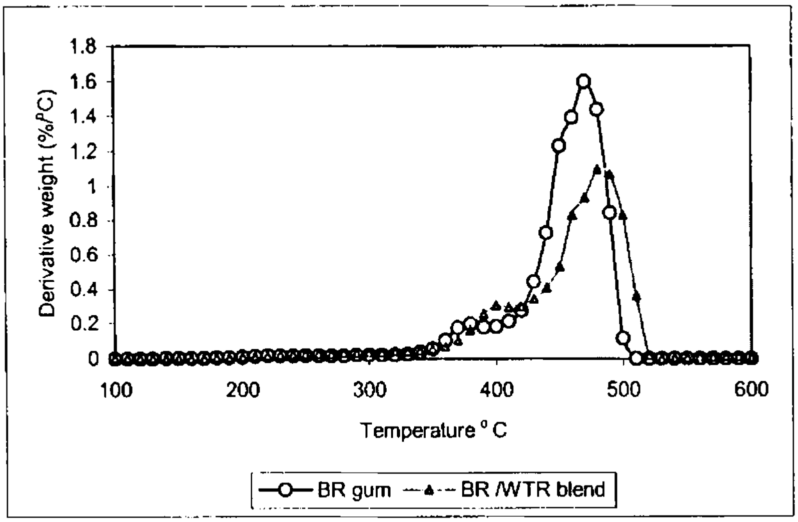

Table 6.1.4. DTA of BR/WTR blend

Figure 6.1.1 to figure 6.1.4 represent TGA curves of the mixes A to D. Percentage of mass loss of the substance is plotted against temperature. The following characteristics were noted from the thermogravimetric curves: the temperature of onset of degradation (T_i), temperature at which the rate of decomposition is maximum (T_{max}) and the weight of residue at 600 °C and are tabulated in the table 6.1.2

Table 6.1.2 Degradation characteristics of WTR blends

Mix No	T_i °C	T_{max} (°C)	Residue (%)	Peak rate of decomposition
Mix A	343.62	430	6.20	1.4
Mix B	341.98	431	10.31	1.1
Mix C	357.07	509	5.13	1.6
Mix D	356.83	515	12.46	1.1

From 6.1.1 and 6.1.2 it is clear that the degradation pattern of NR is not significantly altered by the presence of WTR. Both the mixes A and B have the almost similar temperature of initiation of degradation and the temperature of peak rate of degradation (T_{max}). This may be arising from the fact that the WTR predominantly consists of natural rubber. The rate of

degradation at (T_{max}) is however higher for the NR gum compound. The lower rate of degradation for the WTR blend may be attributed to the WTR contains only about 50 % of rubber hydrocarbon that is involved in the degradation reaction. The actual rubber hydrocarbon in the blend is about 83 % and the observed rate of degradation of the blend is approximately 80 % of the virgin natural rubber. The weight of residue at 600 °C is higher for mix B. The 6.2 % of the residue for the mix A is mainly due to the presence of 5 % of zinc oxide included in the recipe. The higher residue of the blend may be attributed to the presence of inorganic fillers in the WTR.

Figure 6.1.3 and 6.2.4 show he thermal degradation of Butadiene and its blends with WTR. Though the overall pattern of degradation is the same, there is marked improvement in the thermal stability of the BR in the presence of WTR. While the T_i is shifted from 357.07 ° C to 356.83 °C, the peak degradation is temperature is shifted from 509.69 °C to 515.26 °C in the case of mix containing WTR. The improved thermal stability of the blend may be attributed to the combined effect of reinforcing filler in WTR and the higher cross-link density. The rate of degradation is lower in the case of butadiene blend also. The residue at 600 °C is higher for the blend.

The order of the degradation reaction was calculated by the Freeman- Carroll(1) method using the equation

$$(\Delta \log \frac{dW}{dt}) = n. \Delta \log Wr - (\Delta E/2.3.R) (\Delta \frac{1}{T}) \qquad (1)$$

where dW/dt is the rate of reaction, n is the order of reaction, R is the gas constant and T is the absolute temperature and Wr is proportional to the amount of reactant remaining.

The above equation can be rearranged to

$$\frac{(\Delta \log dW/dt)}{\Delta \log Wr} = \frac{n - (\Delta E/2.3\ R)\, \Delta (1/T)}{\Delta \log Wr} \qquad (2)$$

The order and activation energy can be obtained from the intercept and gradient of the plots of the left side of the equation (2) versus Δ (1/T)/ Δ log Wr. Figure 6.1.5 and 6.1.6 represents plot of (Δ log dW/dt)/

Δ log Wr against Δ (1/T) / Δ log Wr of NR gum and NR/WTR blend respectively. Intercepts shows the degradation reaction follows first order reaction mechanism. Similarly Figure 6.1.7 and 6.1.8 represents plots of (Δ log dW/dt)/Δ log Wr against Δ (1/T) / Δ log Wr of BR gum and BR/WTR blend respectively. Intercepts of the plot indicates that the degradation reaction follows first order mechanism.

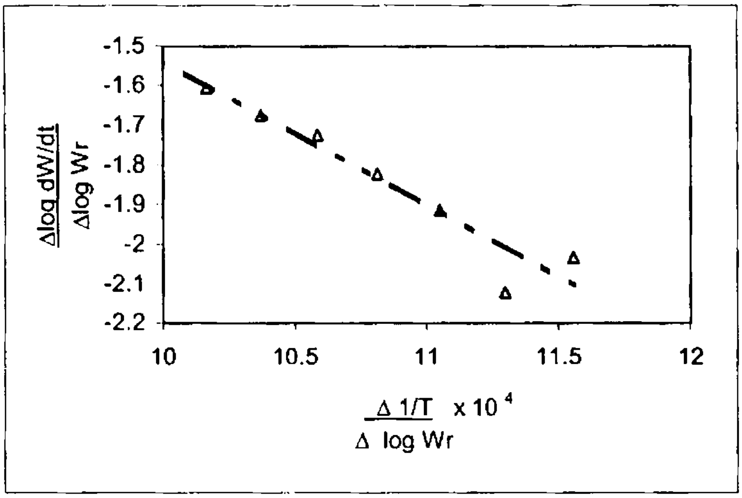

Figure 6.1.5 Freeman -Carroll plot for NR gum

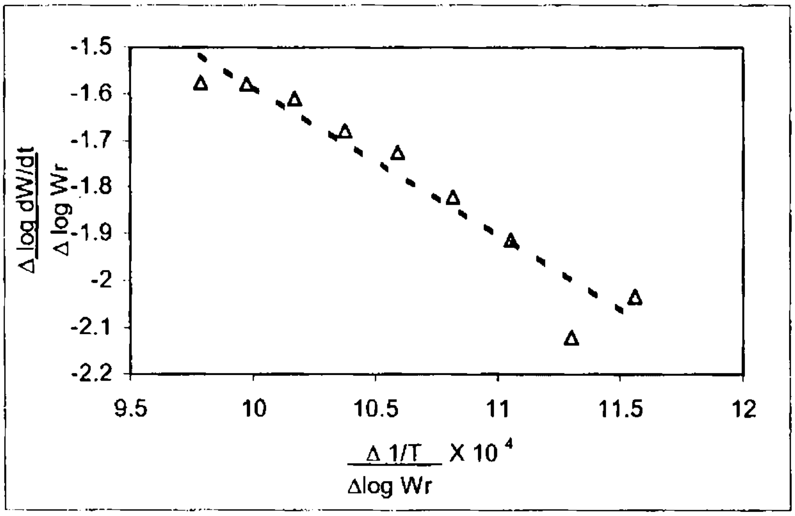

Figure 6.1.6 Freeman -Carroll plot for NR blend

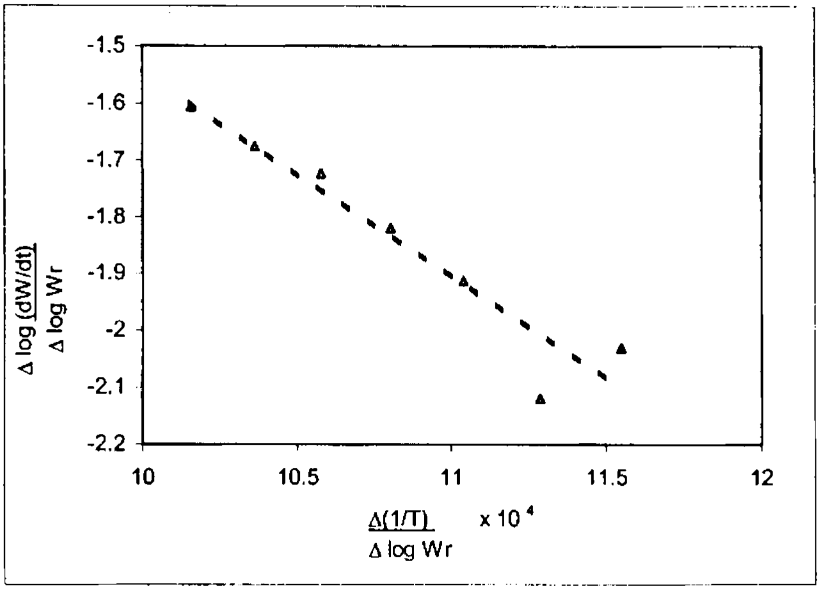

Figure 6.2.7 Freeman -Carroll plot for BR gum

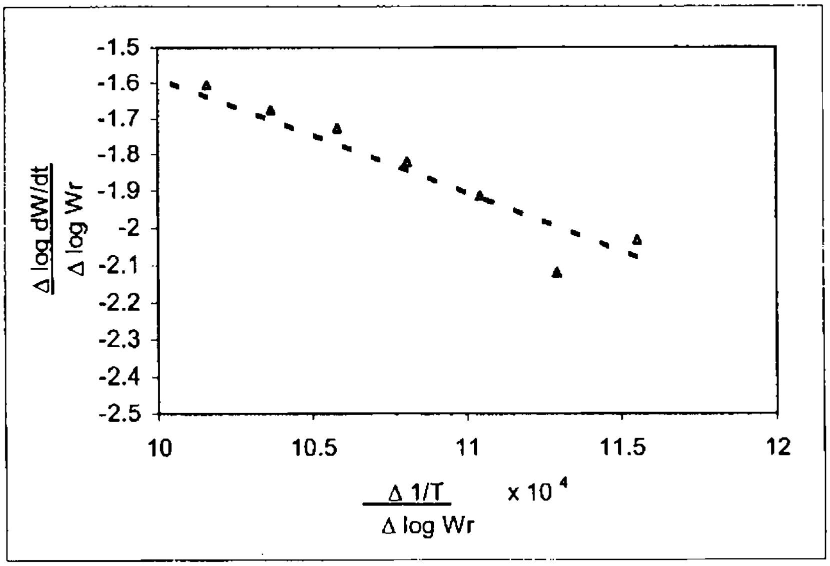

Figure 6.2.8 Freeman -Carroll plot for BR blend

PART 2

Effect of silane coupling agent and Maleic anhydride on thermal stability

In this section the thermal degradation of WTR/NBR and WTR/SBR blends are discussed. The effect of grafting of maleic anhydride and use of coupling agent on the thermal stability of the blend is also discussed.

6. 2.1.Preparation of blends

Blends of NBR and SBR with WTR were prepared in a blend ratio 80:40 Formulation of the mixes is given in the table 6.2.2. Sample preparation and test method employed are given in the chapter 2.

Table 6.2.1. Formulation of the mixes

Ingredient	Mix. No							
	A	B	C	D	E	F	G	H
NBR	100	80	80	80	---	---	---	---
SBR	---	---	---	40	100	80	80	80
WTR	---	40	---	---	---	40	---	40
WTR MA-g- WTR	---	---	40	---	---	---	40	---
Si 69	---			2	---	---	---	2

Note: NBR - Acrylonitrile butadiene rubber. WTR whole tyre reclaim SBR- styrene butadiene rubber. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g are common to all mixes. Amount of WTR was adjusted so as to get 100 grams of rubber hydrocarbon

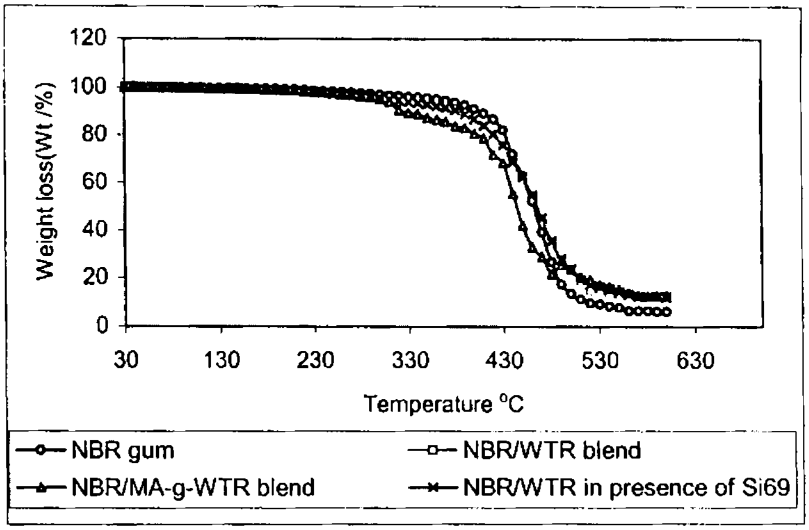

Figure 6.2.1. TGA curve of different blends of NBR blends with WTR

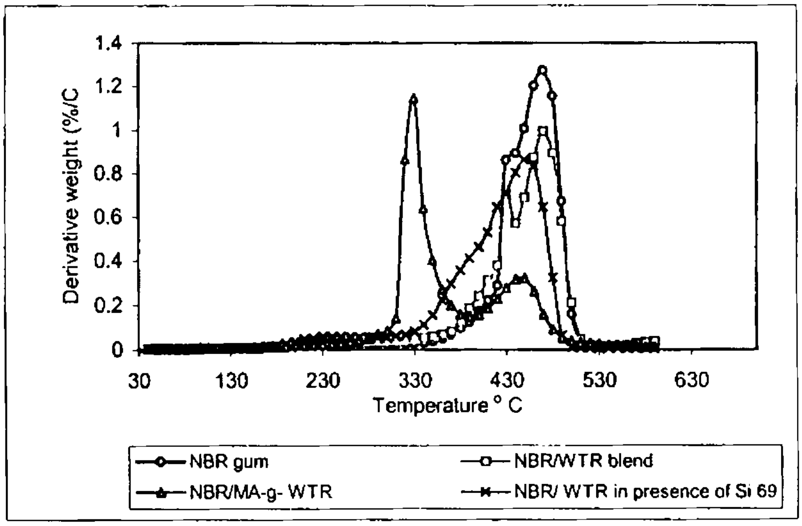

Figure 6.2. 2 DTA of NBR/WTR blend

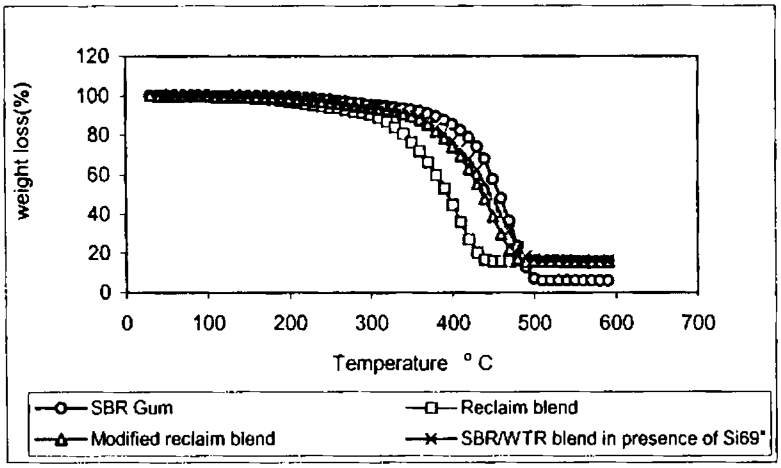

Figure 6.2.3. TGA curve of different blends of SBR blends with WTR

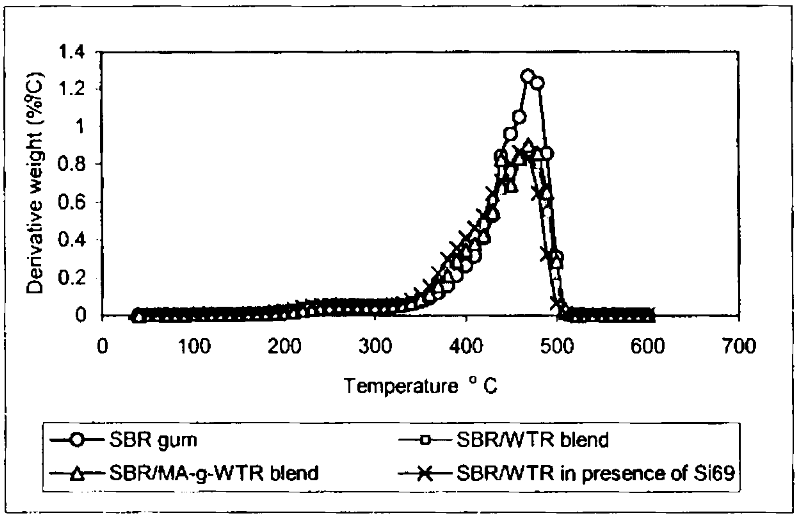

Figure 6.2. 4 DTA of SBR/WTR blends

Figure 6.2.1 to 6.2.4 represent TGA curve of blends of whole tyre reclaim with acrylonitrile butadiene rubber and styrene butadiene rubber (mixes A to H). Percentage of mass loss of the substance is plotted against temperature. The temperature of onset of the weight loss, temperature peak rate of degradation, the higher rate of degradation and the weight of residue are given in the table 6.2.2.

Table 6.2.2 Degradation characteristics of NBR/WTR and SBR/WTR blends

Material	T_i ° C	T_{max} ° C	Higher rate of degradation	Residue (%)
Mix A	377	497	1.25	6.28
Mix B	376	496	0.988	12.02
Mix C	310	465	0.85	12.38
Mix D	379	495	1.17	12.49
Mix E	385	490	1.325	6.05
Mix F	363	503	0.875	15.11
Mix G	342	463	0.825	15.58
Mix H	373	503	0.903	16.46

Figure 6.2.1 and 6.2.2 represent TGA of different compounds of nitrile rubber (mix A to D). The figure 6.2.2 shows nitrile rubber whole tyre reclaim blend-containing MA-g-WTR shows lower onset temperature. All other mix has almost same onset temperature. The major degradation reaction occurs around 496 for first three mixes. The blend with coupling agent shows lower T_{max} showing low thermal stability. Rate of degradation is maximum for gum compounds. Since WTR contain only 50 % of rubber hydrocarbon addition of whole tyre reclaim to the NBR matrix normally reduce amount of rubber hydrocarbon and thus reduces the rate of degradation. As in the case of blends of whole tyre reclaim with natural rubber and butadiene rubber ash content of the blend of nitrile rubber also higher than the gum compound.

In the case of SBR/WTR blends TGA pattern is almost identical (Figure 6.2.3 to 6.2.4) in all cases. Onset temperature of the blends decreases with the addition of reclaim to styrene butadiene matrix. Blend contains MA-g-WTR show relatively low onset temperature. T_{max} increases with the addition of reclaim to the styrene butadiene matrix indicating higher thermal stability. But blend with MA-g-WTR shows lower T_{max}. Like NBR compounds, rate of degradation of SBR gum compound is higher compared to the blend. This may be attributed to the presence of lower quantity of the rubber hydrocarbon in the blend. In the styrene butadiene blend also higher amount of ash content is obtained, due to the presence of other inorganic filler in the reclaim.

Figure 6.2.5 and 6.2.6 represent Freeman Carroll plots for different blends of acrylonitrile rubber and styrene butadiene with whole tyre reclaim. As in the case of natural rubber and butadiene rubber order of the degradation reaction can be evaluated from the plots of (Δ log dW/dt)/ Δ log Wr against Δ (1/T) / Δ log Wr . The order and activation energy can be obtained from the intercept and gradient. Intercepts of the plot indicate that the degradation reaction follows first order mechanism.

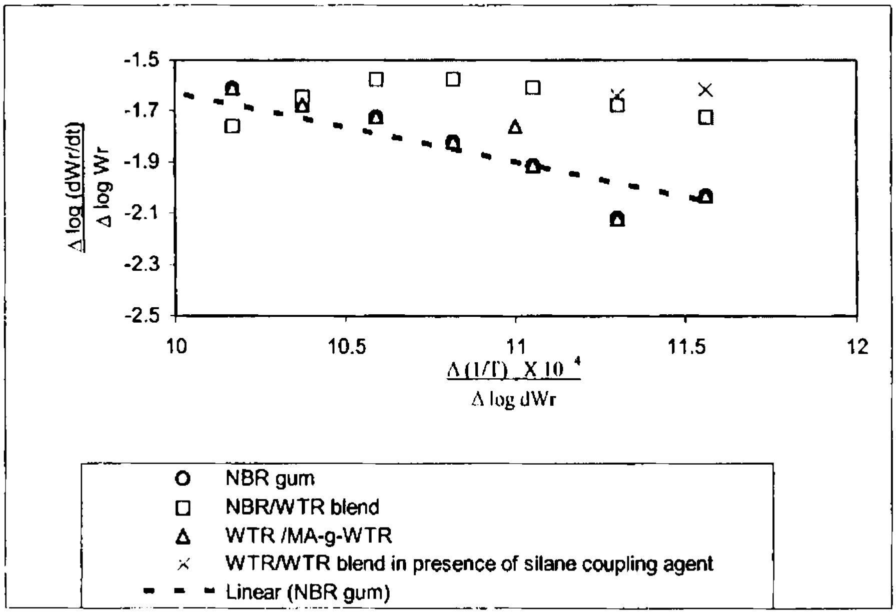

Figure 6.2.4 Freeman -Carroll plot for NBR compounds

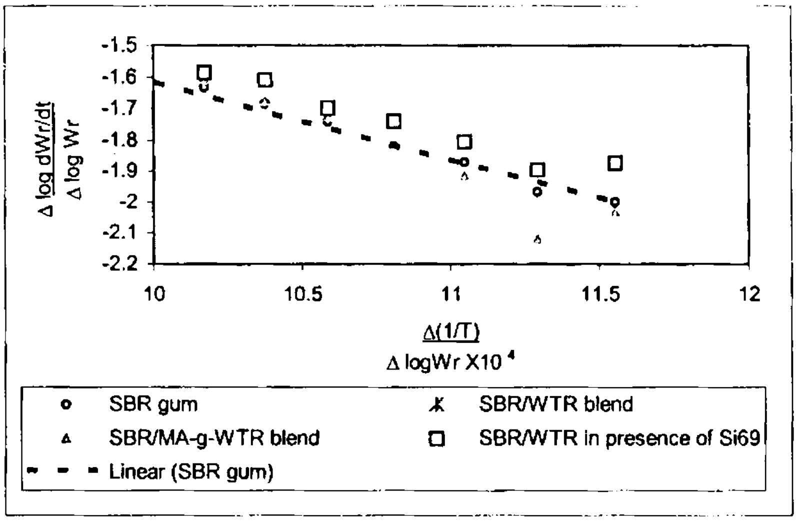

Figure 6.2.5 Freeman -Carroll plot for SBR compounds

6.4. Conclusion

Thermal stability of the blends of whole tyre reclaim with various rubbers such as Natural rubber, Butadiene rubber, Acrylonitrile butadiene rubber and Styrene butadiene rubber were evaluated thermogravimetrically. The incorporation of WTR into these rubbers does not alter the temperature of onset degradation. However, peak degradation temperature is increased in the case of NR, BR and SBR showing higher thermal stability. No significant change in T_{max} occurred in the NBR compounds on WTR blending.. The modification of by maleic anhydride grafting decreases the thermal stability indicated by the lower peak degradation temperature. Use of silane coupling agent results in higher T_{max}. This shows that use of silane coupling agent is a better choice in this regard. Kinetic study shows that the degradation reaction follows first order kinetics.

6.5. Reference

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CHAPTER 7

SUMMARY AND CONCLUSION

Whole tyre reclaim can be used to substitute partially virgin rubber in rubber compounds. Being a rich source of rubber hydrocarbon and carbon black filler, the WTR can be advantageously used in non polar rubber matrix such as Natural rubber (NR),Butadiene matrix(BR) and styrene butadiene matrix(SBR). In polar rubbers like NBR and CR the use of WTR calls for some modification such as grafting of polar groups onto WTR or use of a coupling agent. The effect of WTR in blends is matrix and blend ratio dependant. Apart from the mechanical properties the thermal studies of the blends are also affected by the WTR. The concise conclusions of the study are summarized below.

The conclusions are presented in four parts. The first part discusses the preparation ,cure characteristics ,mechanical properties and ageing study of blends of whole tyre reclaim with natural rubber, butadiene rubber, styrene butadiene rubber, acrylonitrile rubber and chloroprene rubber. In all the cases, there is significant improvement in mechanical properties and state of cure. Optimum loading of reclaim in different virgin rubbers was found to be property dependant.

The second part deals on improvement of properties of the blends by grafting maleic anhydride on whole tyre reclaim in the case of NBR, CR and SBR.

The third part discusses on influence of coupling agent, Si69 on the properties of the blends of whole tyre reclaim with NBR, CR and SBR.

The fourth part discusses the thermal stability of the blends at higher temperature and kinetics of the thermal degradation.

Addition of whole tyre reclaim to natural rubber reduces the chance of strain-induced crystallization, resulting in blends with lower strength. The rate and state of cure is improved in the case of blends. Reinforcing effect of carbon black filler in the WTR is reflected in the improvement in tear strength. Heat build up, compression set, abrasion resistance and resilience are adversely affected by the addition of the reclaim to the natural rubber matrix.

In the blends of butadiene rubber and whole tyre reclaim state of cure and mechanical properties are improved by the addition of WTR. Reinforcing capacity of the carbon black filler present in the reclaim is reflected in the improvements in mechanical properties like tensile strength, tear resistance and abrasion resistance. Resilience, compression set and heat build up are adversely affected by the addition of reclaim to the butadiene matrix.

Cure characteristics and mechanical properties of the styrene butadiene rubber/whole tyre reclaim blends are almost comparable to acrylonitrile rubber/whole tyre reclaim blends. State of cure is improved with the addition of reclaim to the styrene butadiene matrix. While the mechanical properties like tensile strength, ultimate elongation and tear resistance are improved, abrasion resistance, compression set, heat build up and resilience are adversely affected.

In the acrylonitrile butadiene rubber addition of WTR results in improved state of cure, low cure time and higher cure rate. Mechanical properties such as tensile strength, ultimate elongation and tear strength are improved by the addition of WTR. Heat build up, compression set, abrasion resistance and resilience are adversely affected by the addition of reclaim.

Cure characteristics and mechanical properties of chloroprene rubber are affected by the incorporation of the reclaim. Addition of whole tyre reclaim to a crystalline chloroprene matrix adversely affected the cure characteristics indicated by higher cure time and low cure rate. As expected from the difference in crystallinity, addition of whole tyre reclaim to the chloroprene matrix not contributed higher improvements in mechanical properties.

Maleic anhydride can be grafted on to the WTR to increase its polarity so that it can be more compatible with polar rubbers such as NBR and CR. Chapter 4 discusses the method of grafting maleic anhydride on WTR in presence of dicumyl peroxide and its influence on cure characteristics and mechanical properties of the blends of NBR, CR and SBR.

In the blends of acrylonitrile butadiene rubber and whole tyre reclaim mechanical properties are improved by grafting of maleic anhydride on WTR. The completion of cure is delayed in the presence of modified WTR. While the tensile strength, ultimate elongation, abrasion resistance and compression set are improved; the heat build up is adversely affected when MA-g-WTR is used in NBR.

When MA-g-WTR is blended with chloroprene rubber state of cure is improved. Cross-link density of the modified blend is higher compared to control mix. Mechanical properties of the modified blends are higher compared to unmodified blend, even though adverse effect is produced by the addition of reclaim to the chloroprene matrix.

The effect of maleic anhydride on cure characteristics and mechanical properties of the blend is almost in the same pattern as acrylonitrile butadiene rubber/MA-g-WTR blend. Cross-link density of the modified blend is higher compared to unmodified blend. The tensile strength, ultimate elongation, abrasion resistance, resilience and compression set are improved by maleic anhydride grafting. Tear resistance is marginally lower than the unmodified blend. Heat build up also adversely affected by maleic anhydride grafting.

Chapter 5 discusses silane-coupling agent Si69 [Bis (3-(triethoxysilyl)propyl) tetrasulphide]in a blend of WTR with other rubbers.

In the NBR/WTR blends, the mechanical properties are improved by silane coupling agent. Introduction of coupling agent leads to marginally higher cure time and lower cure rate of the blends. Mechanical properties like tensile strength, ultimate elongation, and resilience and abrasion resistance are improved by the presence of coupling agent. Tear resistance is marginally improved by the presence of coupling agent. The coupling agent adversely affects compression set. Cross-link density of the blends is higher in presence of coupling agent.

Silane coupling agent also influence both cure characteristics and mechanical properties of the chloroprene/WTR blends. Cure time increases in the presence of silane coupling agent. Cure rate is less constant with the silane loading. Cross-link density of the blend is increased and is maximum at 3 Phr of Si69. The coupling agent improves mechanical properties of the blends. Tensile strength, ultimate elongation, tear resistance and abrasion resistance are in the presence of the coupling agent. The coupling agent adversely affects compression set and resilience.

In the case of SBR/WTR blends with the increase in concentration of silane coupling agent cure time is increased and cure rate is decreased The tensile strength, ultimate elongation, tear resistance and abrasion resistance are improved with the increase in silane concentration and attains a maximum value at 3 Phr silane concentration . The coupling agent adversely affects resilience and compression set.

Ageing resistance of the blends of WTR with all the rubbers studied is marginally lower than the respective gum compounds. The modification of WTR by grafting maleic anhydride and the use of Si69 coupling agent in the blends further reduce the ageing resistance.

Chapter 6 discuss the thermal stability of the blends of whole tyre reclaim with various rubbers such as Natural rubber, Butadiene rubber, Acrylonitrile butadiene rubber and Styrene butadiene rubber were evaluated thermogravimetrically. The incorporation of WTR into these rubbers does not alter the temperature of onset degradation. However, peak degradation temperature is increased in the case of NR, BR and SBR showing higher thermal stability. The modification of by maleic anhydride grafting decreases the thermal stability indicated by the lower peak degradation temperature. Use of silane coupling agent results in higher T_{max}. This shows that use of silane coupling agent is a better choice in this regard. Kinetic study shows that the degradation reaction follows first order mechanism.

The list of publications from this work is included at the end of the thesis.

PUBLICATIONS

1. **"Cure characteristics and mechanical properties of Butadiene Rubber /Whole tyre reclaimed rubber blends"** P.A.Nelson and S.K.N. Kutty *Progress in Rubber, Plastics and Recycling Technology,* **18** (2),85 (2002)
2. **"Studies on Maleic anhydride grafted reclaimed rubber/ Acrylonitrile butadiene rubber blends."** P.A. Nelson and S.K.N. Kutty *Progress in Rubber, Plastics and Recycling Technology,* **19** (3) 171 (2003)
3. **"Cure characteristics and mechanical properties of Maleic anhydride grafted reclaimed rubber/ Styrene butadiene rubber blends.**"P.A. Nelson and S.K.N. Kutty *Polymer –Plastics Technology and Engineering* (in press)
4. **"Studies on Neoprene / Reclaimed rubber blends"** P.A. Nelson and S.K.N. Kutty *Int. J .Polymer Materials* (Communicated)
5. **"Cure characteristics and mechanical Properties of Maleic anhydride grafted reclaimed rubber/ Chloroprene blends."** P.A.Nelson and S.K.N Kutty *Journal of Applied Polymer Science.* (Accepted)
6. **"Effect of Silane coupling agent on cure characteristics and mechanical properties of Nitrile rubber /Reclaimed rubber blend".** P.A.Nelson and S.K.N Kutty *Progress in Rubber, Plastics and Recycling Technology* (in press)
7. **"Effect of Silane coupling agent on cure characteristics and mechanical properties of Chloroprene rubber /Reclaimed rubber blend."** P.A. Nelson and S.K.N. Kutty *Polymer –Plastics –Technology -Engineering*(communicated)
8. **"Optimisation of silane coupling agent in Styrene butadiene rubber whole tyre reclaim blends"** P.A. Nelson and S.K.N. Kutty *Int. J .Polymer Materials* (communicated)

9. **"Thermal degradation of styrene butadiene rubber /whole tyre reclaim blends."** P.A. Nelson and S.K.N. Kutty *Polymer Degradation and Stability* (Communicated)
10. **"Studies on Thermal degradation of Acrylonitrile butadiene rubber /whole tyre reclaim blends".** P.A. Nelson and S.K.N. *Kutty Progress in Rubber, Plastics and Recycling Technology* (Communicated)
11. **"Studies on thermal degradation of NR /WTR and BR/WTR blends."** P.A. Nelson and S.K.N. Kutty *Polymer –Plastics Technology and Engineering (Communicated)*

Paper presentation in Conferences

1. **"Studies on Styrene butadiene rubber / Maleic anhydride grafted reclaimed rubber blends."** P.A.Nelson. S.K.N.Kutty International seminar on Advances in Polymer Technology conducted by Department of Polymer Science and Rubber Technology Cochin University of Science and Technology on 12-14 (December 2002)
2. **"Studies on Butadiene Rubber/Reclaimed rubber Blends."** P.A. Nelson S.K.N. Kutty Proceedings of fourteenth Kerala Science Congress 29-31 Cochin p544 (January 2002)
3. **"Cure characteristics and Mechanical Properties of Reclaimed rubber/ Neoprene blends."** P.A. Nelson S.K.N. Kutty Proceedings of fourteenth Kerala Science Congress 27-30 Trivandrum p 671 January (2003)