EFFECT OF DIFFERENT FORMS OF NATURAL RUBBER ON REINFORCEMENT CHARACTERISTICS USING SILICA AND ISAF BLACK FILLER

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
IN
APPLIED CHEMISTRY
BY
DHANYA C

UNDER THE GUIDANCE OF
Mrs. K. MARIAMMA GEORGE
SCIENTIST C, RUBBER RESEARCH INSTITUTE OF INDIA
KOTTAYAM

Department of chemistry
University of Calicut
2011

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT

Grams: UNICAL
Phone: 0494 401144
Etn.: Office-413
H.D -414
Email: che@unical.ac.in

CALICUT UNIVERSITY P.O
673635, KERALA, INDIA

22/06/11

Ref. No.

CERTIFICATE

Certified that this Project Report entitled "**EFFECT** OF DIFFERENT FORMS OF NATURAL RUBBER ON REINFORCEMENT CHARACTERISTICS USING SILICA AND ISAF BLACK" is the bonafide record of work done by DHANYA C in a partial fulfillment of the requirements for the award of the degree of Master of Science in Applied Chemistry, Department of Chemistry, University of Calicut..

Guided by

Mrs. K. MARIAMMA GEORGE

Dr. Prof. T. Ganga Devi
Head of the Department

भारतीय रबड़ गवेषण संस्थान
रबड़ बोर्ड, वाणिज्य एवं उद्योग मंत्रालय, भारत सरकार
The Rubber Research Institute of India
Rubber Board, Ministry of Commerce and Industry, Govt. of India

Ref: RT/RES/Proj/1 22-06-11

CERTIFICATE

This is to certify that the thesis titled “Effect of different forms of natural rubber on reinforcement characteristics using silica and ISAF black” being submitted by Ms. Dhanya C to the Department of Chemistry, University of Calicut, for the award of the Degree of Master of Science in Applied Chemistry is a record of bonafide research work carried out by her. Ms. Dhanya has worked on her research topic from March to June 2011, under my supervision. The results included in this report have not been submitted for the award of any other degree.

Mrs. K. Mariamma George
Scientist C
Rubber Technology Division
Rubber Research Institute of India
Kottayam

Rubber Board P.O, Kottayam – 686 009, Kerala, INDIA
रबड़ बोर्ड पी. ओ., कोट्टयम, ६८६००९, केरल, भारत
दूरभाष/Tele Phone: 91- 481- 2353311 to 2353320 फैक्स/ Fax: 91- 481- 2353327
ई मेल/E-mail: rrii@rubberboard.org.in वेबसाइट/ Website: www.rubberboard.org.in

Acknowledgement

I express my deep sense of gratitude to Mrs. K. Mariamma George, ScientistC, Rubber Technology Division, Rubber Research Institute of India, Kottayam for her guidance and valuable suggestions during the course of this work.

I am grateful to Dr. James Jacob, Director of Research, Dr. K.T. Thomas, Joint Director and also to Dr. Rosamma Alex, Deputy Director, Rubber Technology Division, Rubber Research Institute of India, Kottayam for allowing me to do the project at RRII and also providing me the necessary facilities for the completion of the work.

I gratefully acknowledge to Dr. T Gangadevi,, Head of the department of chemistry, University of Calicut, Calicut for the support and encouragement for doing this work at RRII, Kottayam.

I express my sincere thanks to all the staff of RT Division especially to Mr. S.N. Sajeev, Mrs. Susamma Joseph, Mrs. Valsa George, Mrs. Treesa Cherian, Dr. Geethakumary Amma and Mr. Manoj Jacob Varghese for their assistance at various stages of the project. I would also acknowledge with thanks the service rendered by the RRII Library.

Dhanya C

Contents

CHAPTER 1
Introduction
1. Natural rubber
1.1 Composition of latex
1.2 Processing of latex
1.3 Different marketable forms of Natural rubber
1.3.1 Sheet rubber
1.3.2 Crepe rubber
1.3.3 Technically specified Rubber (TSR)
1.3.4 Preserved field latex
1.3.5 Concentration of latex
1.3.5.1 Evaporation
1.3.5.2 Electro decantation
1.3.5.3 Creaming process
1.3.5.4 Centrifuging process
1.3.6 Skim latex
1.3.7 Modified forms of rubber
1.3.7.1 Physical modification
1.3.7.1.1 Incorporation of compounding ingredients
1.3.7.1.2 Deproteinised rubber
1.3.7.2 Chemical modification
1.3.7.2.1 Grafting
1.4 Compounding of rubbers

1.5 Selection of ingredients
  1.5.1 Polymer or rubber (Blend of polymers)
  1.5.2 Crosslinking agents
  1.5.3 Accelerators for crosslinking reaction
  1.5.4 Acceleration modifiers (activators or retarders)
  1.5.5 Reinforcing fillers
  1.5.6 Antidegradents
  1.5.7Antiozonants
  1.5.8 Processing aids
  1.5.9 Special additives
1.6 Mastication and mixing
1.7 Vulcanization
  1.7.1 Sulphur vulcanization
  1.7.2 Peroxide vulcanization
  1.7.3 Radiation vulcanisation
1.8 Scope and objective of the present study

CHAPTER 2

Materials and Experimental techniques

2.1 Materials used
2.2 Methods
2.3 Preparation of blends
  2.3.1 Latex blends
2.4 Preparation of rubber compounds
2.5 Testing for vulcanizate properties

CHAPTER 3

Results and discussion

- **3.1 Latex properties**
  - **3.1.1 Particle size distribution of latex**
  - **3.1.2 Raw rubber properties**
  - **3.1.3 Viscosity and molecular weight**
  - **3.1.4 Flow characteristics**
  - **3.1.5 FTIR studies**
- **3.2 Dry mix**
  - **3.2.1 Cure characteristics**
  - **3.2.2 Mechanical properties**
  - **3.2.3 Aeging properties**
- **3.3 Effect of latex stage incorporation of fillers**
  - **3.3.1 Cure characteristics**
  - **3.3.2 Technological properties**
- **3.4 Solvent swelling**

CHAPTER 4

Summary and conclusion

References

CHAPTER 1

INTRODUCTION

Chapter 1

Introduction

1. Natural Rubber

Hevea brasiliensis, [1]the only major commercial source of natural rubber is one of the most recently domesticated crops species in the world which produces 99 % of the world's natural rubber. Natural rubber however has been found in latex of over 2000 species of plants belonging to 311 genera of 77 families. The minor source of natural rubber is *Manihot glaziovii, Ficus elastica, Parthenium argentatum* etc.

Hevea brasiliensis is a native of the Amazon River basin of South America. It was introduced to tropical Asia in 1876 through Kew Garden in the UK with the seeds brought from Brazil by Sir Henry Wickham. The tree is now grown in the tropical regions of Asia, Africa and America.

Christopher Columbus is considered to be the first European to discover natural rubber. The term "rubber" was coined by John Priestly in 1770, when he found that the material could erase pencil mark.

The rubber tree is sturdy, quick growing and tall. It grows on many types of soils, provided they are deep and well drained. A warm humid equable climate and a fairly distributed annual rainfall of not less than 200 cm are necessary for the optimum growth. Rubber trees have a well developed taproot and laterals.

Latex is the main crop from *Hevea brasiliensis,* which is white or a slightly yellowish opaque liquid with a specific gravity which varies between 0.974 and 0.986.The latex is obtained from the bark of the rubber tree by tapping. Tapping is a process of controlled wounding during which thin shavings of bark are removed. The aim of tapping is to cut open the latex vessels in the case of trees tapped for the first time or to remove the coagulum which blocks the cut end of the latex vessels in the case of trees under regular tapping. The latex just collected is called field latex.

The fundamental changes in the properties of natural rubber (NR) through vulcanization removed most of its susceptibility to climatic conditions and its limitations as a raw material for mechanical applications. NR forms the raw material for a large number of rubber products like tyres, footwear, hoses, belting, foam, mattress etc. This is because of the important properties like high resilience, high shock absorbing quality and excellent dynamic mechanical properties. A disadvantage as compared to synthetic rubber is that it has poor ageing resistance towards oil, fuel, oxygen, ozone and high temperature.

1.1 Composition of latex

Hevea latex in the latex vessels of tapped trees contains 30-40% rubber in the form of particles. Latex is a hydrosol in which the dispersed particles are protected by a complex film. It contains more than one disperse phase. Besides rubber, the latex contains certain other particles also, namely lutoids and Frey Wyssling particles. Lutoids are associated with the process of latex vessel plugging which stops the flow of latex a few hours after tapping.

The latex is a weak lyophilic colloidal system of spherical or pear shaped rubber globules suspended in an aqueous serum. The rubber globule is surrounded by a protective layer of proteins and phospholipids which impart the lyophilic colloidal nature to latex and the stability of latex is due to the negative charge present on the protective layer. Also it contains a variety of non rubber constituents both organic and inorganic, in addition to rubber. The proportion of these constituents may vary with clones, nutrition, climate etc.

Fresh latex, as it comes out from the tree is slightly alkaline or natural. It becomes acidic rapidly due to bacterial action. The formation of organic acids neutralises the negative charge on rubber particles and the latex gradually thickens and gets coagulated on keeping. Therefore, fresh latex cannot be kept for long without coagulation.

Intensive tapping reduces the rubber content in latex. The latex from daily tapped trees or slaughter tapped trees may have a rubber content as low as 20% or below.

Typical composition of fresh natural rubber latex

Rubber - 30-40%

Resin - 1-2 %

Protein - 2- 2.5 %

Sugar - 1-1.5%

Ash - 0.7 – 0.9 %

Water - 55 – 65 %

1.2. Processing of latex

About 3 – 4 hrs after tapping, the latex is collected from tree, treated with an anti coagulant (if necessary) to prevent premature coagulation and brought to factory. Ammonia is the most common anticoagulant used though others such as sodium sulphite and formalin are also still in use. About 80 – 85% of the crop is collected as latex

Latex continues to flow slowly for several hours after the initial collection. This latex is not collected but coagulates spontaneously in the collection cup .This is known as cup lump. A small amount of latex coagulates as thin film on the tapping cut to form tree lace. Some latex also drips to the ground to form earth scrap. The coagulated materials known as field coagulum rubbers constitute about 15 – 20% of the total crop.

1.3. Different marketable forms of natural rubber

1. Sheet rubbers
2. Crepe rubbers
3. Preserved field latex and latex concentrates
4. Block rubber

1.3.1. Sheet Rubber

Sheet rubber holds the predominant share in the Indian natural rubber market. Raw rubber sheets are of various types like ribbed smoked sheet (RSS), air dried sheets (ADS) and sun dried sheets, depending on the method adopted for drying.

The processing procedure for making sheet rubbers includes sieving, bulking, standardization of latex, addition of chemicals, coagulation, sheeting, dripping and drying.

Sieving and bulking

Latex collected from the field is liable to contamination with small clots of rubber coagulum or extraneous impurities like sand particles. For removing these, it is sieved first through a 40 mesh and then 60 mesh sieve. For providing uniformity, it is necessary to bulk all the latex in a common tank called bulking tank. For getting sheets of uniform quality, it is essential that the latex from different fields is blended together. This is done by mixing latex uniformly in bulking tanks.

Standardization of latex

The bulked latex is to be diluted to a standard DRC of 12.5 % before it is coagulated. Dilution helps in obtaining a softer coagulum which can be easily sheeted.

Addition of chemicals before coagulation

Addition of sodium bisulphite to latex prevents the discoloration by preferential reaction with oxygen, getting it converted into sodium bisulphate in the process.

Coagulation

Coagulation is the process of destabilization of latex by some means with a view to recovering rubber from it. There are several methods for coagulation like coagulation by addition of chemicals, natural coagulation. In the chemical method several coagulants like acids, metallic salts and alcohols are used. Among these the popular coagulants are acetic acid and formic acid. Dilute acetic acid and formic acid produced slow and uniform coagulation and are easily removed by washing the coagulum during sheeting. Formic acid is preferred as its action is quick and acid possesses light and septic properties. Natural coagulation is a result of production of acid by micro organisms at the expense of non rubber constituents in latex. Acid coagulation of latex by the addition of acid is due to neutralization of charge on the protective layer of proteins surrounding the rubber particles. The latex proteins which surround the rubber particles and which may carry the negative charge have an isoelectric point near 4.7. The acid requirement for latex coagulation is given in Table 1.1. The required quantity of diluted acid is added to latex and mixed thoroughly by stirring. The froth formed is then skimmed off by glass plate.

Sheeting and dripping

After draining out the serum, the coagulum is washed with water before sheeting. The sheeting rollers consist of a pair of plain rollers and a pair grooved rollers. The nip of the rollers can be adjusted in such a way that the sheets will have a final thickness of 2.5-3 mm after 3 or 4 passes trough the plane and one through the grooved rollers. After the final pass through the grooved rollers once, the thickness of the coagulum is reduced to 2.5-3mm.

Drying

Freshly machined and dripped sheet contained about 20% moisture. For the preparation of RSS, these sheets are dried in smoke houses. Defects in sheets may be caused either by microbial attack or by other reasons. Sheets produced under unhygienic conditions or stored in an improper way are subjected to defects of microbial origin, which includes pinhead bubble, rust, discoloration and mould growth[2]. Bubbles of bacterial origin in sheet rubber are in the form of pinhead and clusters all over the sheets. The presence of gas forming bacteria and acid coagulation above pH 4.8, which favors the multiplication of bacteria are the reasons for this. The discoloration in the sheet is due to the enzymatic action on the non rubber constituents present in latex and can be control by using sodium bisulphate. Rust is a brownish deposit or more usually a thin film on rubber sheets which can be formed by prolonged dripping of the wet sheet before being taken in to the smoke house. Mould growth occurs when the moisture content of the rubber sheets are high. Relative humidity above 75% and air temperatures of 37-40°C are favorable for fungal growth. Addition of PNP to latex or soaking of sheeted coagulum in PNP solution is helpful in preventing mould growth. Defects due to other reasons may arise out of excessive use of certain chemicals, contamination with foreign matter or faulty conditions of drying. These defects are usually tackiness, blisters, reaper marks and case hardening of tar drops.

After drying sheets in smoke houses, they are visually examined by holding them against clear light to see any speck or impurity remaining inside. The grading and packing of smoked sheet rubber is carried out as described in the International Standards of quality and packing for natural rubber grades- The Green Book. According to the green book specification the 6 grades are RSS 1X, RSS 1, RSS 2, RSS 3, RSS 4 and RSS 5. All ribbed smoked sheets shall be packed in rubber covered bales of about 50 kg.

1.3.2. Crepe rubbers

When coagulum from latex any other forms of field coagulum or RSS cuttings, after preliminary treatment is passed through a set of crepe making machines, crinkly, lace-like rubber is obtained. This, when dried is called crepe rubbers. Based on the raw materials used crepe rubbers are classified into two. They are crepes produced from latex, i.e. pale latex crepe (PLC) and sole crepe and those produced from field coagulum. The latex crepe is of better quality when compared to that of field coagulum. Different grades of PLC are used for high quality products like pharmaceutical articles, light coloured and transparent goods, adhesives, tapes, tubings and derivatives such as chlorinated rubber. Sole crepe is used primarily for the production of translucent shoe soling material. Process involved in the production of latex crepes includes sieving, and bulking, standardization of latex, addition of chemicals, removal of pigments, coagulation, crepe making and drying. The grading pale latex crepe and sole crepe is done by examining factors like colour, presence of dirt and variation from thickness and weight specified.

The crepes prepared from field coagulum materials fall into 5 types-thin estate brown crepe, thin brown crepe, thick blanket crepe, flat bark crepe and pure smoked blanket crepe. Processing into crepe rubber was one of the method to upgrade low quality field coagulum such as earth scrap, shell scrap, tree lace etc. Through soaking, agitation, cleaning, creping operation and drying are required to produce good quality field coagulum materials. Crepes are graded by examining parameters like colour, strength and thickness. There are three grades 1X, 2X and 3X. The field coagulum crepes are used for the manufacture of tires, footwear, re-treading materials etc.

1.3.3. Technically Specified Rubber (TSR)

TSR is a modern form of marketable rubber and can be produced from latex, field coagulum or blend of both. The production of TSR started during 1960's. Natural rubber marketed as RSS or crepe form, is graded only by visual methods. The inadequacies of the visual grading system made gradual reduction in the marketing of NR. Consequently new methods of processing and presentation were developed to attain the market for NR in compact, medium sized blocks wrapped in polyethylene and adopting a grading system on specifications. These are called technically specified rubbers. In India the standards for specification of NR are laid down by the Indian Standards Institution (ISI) in 1968. In 1974, ISI revised the technical specifications and introduced new grades with general name Indian Standard Natural Rubber (ISNR).

Conventional forms of NR such as RSS and crepe can be processed and graded into TSR in accordance with technical specifications, only if the processing methods are standardized. The process required proper blending, size reduction, dirt removal etc, to improve the quality of the product. The process involves re-milling of the ungraded and lower grade sheets, size reduction of the resultant crepe on a shredder or hammer mill and drying to obtain TSR. The processes which have received commercial acceptance are *Decan Grana*[4] process, *Hevea*[5] crump process, granulation process, *Dynat* process and extraction drying process.

Both latex and field coagulum is used for the production of TSR. The former offers greater uniformity of the raw material and consequently higher grade product. When field latex is used as the raw material, the processing includes operations like bulking, preservation, sieving, coagulation, dewatering, size reduction, drying, bailing, and grading.

When field coagulum is used the essential unit operations for processing them include dry blending, soaking, pre cleaning, macro blending(creping) and dirt removal, size reduction and dirt removal, drying, bailing and grading. Flow diagrams for processing latex and field coagulum into technically specified rubber are shown in Charts 1 and 2.

Soaking the crumbs in 1% solution of phosphoric acid or oxalic acid for 15-20 min may improve PRI by about 5-8 units. Air drying of crepe for a week may also give the same results. Smoking of field coagulum improves the P0 and PRI of the product.

The major rubber producing countries like Thailand, Indonesia, and Malaysia export block rubber. Each block weighing 33.33kg after marking the grade, is put in LDPE bag and then packed in wooden pallet crates. Each pallet contains 30 blocks.

With the commercial production of block rubber in India in 1973, the ISI revised the previous three grades, i.e. Grade-A, Grade-B, Grade-C, into 5 grades of Indian Standard Natural Rubber (ISNR). They were ISNR5 special, ISNR5, ISNR10, ISNR20and ISNR50.These grades and their specifications were subsequently revised. In the meantime, ISNR5 special were replaced by ISNR 3L and ISNR 3CV (a constant viscosity version). The specification as per the latest revisions adopted by BIS [6] is given in Table 1.2.

Advantages of TSR are quality assurance with respect to important technical parameters[7], consistency in quality, clean and easy to handle packing, minimum storage space and reduction in processing time[8].

The main advantages of TSR are that, (1) it is available in 6 different grades with technical specifications and consumer can choose the grades according to requirements, (2) as it is processed in bulk quantities adopting latest technology, variations in properties within the same grade is minimum, (3) impurities in the rubber can be assessed as the content of foreign material and volatile matter and (4) being marketed in compact PE wrapped bales, contamination on storage, handling and transportation is avoided.

1.3.4. Preserved Field Latex

To keep latex for longer period's bacterial activity should be suppressed so as to prevent coagulation. This can be accomplished by addition of preservatives. Such latex is called preserved field latex.

Preservation of latex

Shortly after latex is obtained from rubber tree, bacterial action begins and in order to preserve latex in an un-coagulated condition for more than a few hours after tapping, it is necessary that some preservatives be added. Ammonia is the most popular latex preservative. Preservatives should be added as soon after tapping as possible.

Why preservation is necessary

Natural rubber latex is a negatively charged colloidal dispersion of rubber particles in an aqueous serum. The presence of non rubber constituents like proteins, carbohydrates etc in latex make it a suitable medium for growth of microorganisms. Because of the proliferation of micro organisms organic acids are produced and these decrease the stability of latex and eventually coagulate it. This is called spontaneous coagulation that takes place with in a period of 6 – 12 hrs. Hence if latex is to be kept for longer periods, bacterial activity should be suppressed. This is accomplished by the addition of preservatives.

Preservatives

Various chemicals are used as preservatives among which ammonia is of prime importance. Other chemicals used along with ammonia are known as secondary preservatives.

Attributes of preservatives

1. It should destroy or inactivate microorganisms

2. It should contribute positively to the colloidal stability of latex by increasing the charge on the particles and the potential of the rubber – ser um interface
3. It should deactivate or remove traces of metal ions present in latex
4. It should not be harmful to people
5. It should not have adverse reaction on rubber or containers of latex
6. It should be cheap ,readily available and convenient to handle

Importance of ammonia as a preservative

Ammonia is the most widely used preservative. Ammonia at a concentration of 0.7 – 1 % by weight of latex is added for preservation. This treatment preservers latex and maintains it in a stable colloidal condition almost in definitely. Also during storage the higher fatty acid esters present in latex get hydrolyzed in to ammonium soaps, which improve the mechanical stability of latex[3].

As a bactericide, ammonia is effective at concentration above 0.35%, being an alkali it imparts an alkaline reaction to latex there by enhancing the magnitude of negative charge on the particles and the potential at the rubber-serum interface, thus improving the stability.

1.3.5. Concentration of latex

It is the process of removal of a substantial quantity of serum (water and water soluble materials) from field latex, thus making latex richer in rubber. Concentration of latex is necessary because of reasons such as preference for high DRC by the consuming industry, economy in transportation and higher degree of purity.

Various process used for concentrating latex are evaporation, electro decantation, creaming and centrifuging. In India, only centrifuging and creaming are commercially used for the production of concentrated latex.

1.3.5.1. Evaporation

In a typical process, latex is circulated through a tubular heat exchanger and then passed to a chamber where evaporation occurs under reduced pressure. Three types of evaporated latex are standard Revertex, LCS revertex and Trevertex.

1.3.5.2. Electro decantation

In this process, application of potential difference between two electrodes of an electrolyte causes the negatively charged rubber particles to move towards the anode. They are intercepted by a semi permeable membrane and provided the potential gradient is not excessive, they get deposited at the membrane in an essentially reversible condition. The particles tend to form loose agglomerates in the region of the membrane surface and those agglomerates cream rapidly. A layer of concentrate thus forms at the surface of the containing vessel.

1.3.5.3. Creaming Process

Latex is collected and ammoniated to 1.0-1.2% by weight and kept for a few weeks for ageing. The creaming agent solution (3%) and soap solution (10%) are prepared and sieved. The preserved and de-sludge latex is taken in the creaming tank. The required quantity of soap solution is added so as to get a concentration of 0.05% soap on latex. Then the required quantity of creaming agent solution is added to the latex slowly with stirring. The creaming agent used usually are sodium alginate, ammonium alginate and tamarind seed powder. After complete addition of creaming agent solution, stirring has to be continued for one hour. Since the creaming agent solution is very viscous, thorough mixing is necessary for uniform distribution. The creaming tank is closed and the latex is allowed to remain undisturbed till the desired level of creaming is obtained.

After the creaming agent is added, there is an induction period of several hours before any creaming is visible. For the first 24-40 hours, creaming is rather rapid and then it becomes slow. When the desired level of separation is obtained, the skim layer is drained off through the outlet valve at the bottom. The concentrate obtained is homogenized by stirring, the DRC and ammonia content adjusted and the latex packed.

1.3.5.4. Centrifuging process

Ammoniated field latex is usually transported to the factory in tankers and fed by gravitational flow into field latex storage tank. From these tanks, the latex is fed to the centrifuging machines.

De-Laval Latex Centrifuging Machine

The machine consists of a rotating bowl in which a set of concentric conical metallic separator discs are enclosed. Latex enters the bowl through a central feed tube and passes to the bottom of the bowl through a distributor. A series of small holes on a separator discs, positioned at definite distance from the center, allow the latex to get distributed and broken up into a number of thin conical shells within the bowl which rotates at a speed of around 6000 rpm. By maintaining a very small clearance between successive conical shells, the maximum distance which a particle has to traverse in order to pass from the skim to the cream is made very small.

Minimum required quantity of ammonia shall be added to latex before centrifuging. Most of the ammonia added to the field latex goes into the skim which makes coagulation of the skim more difficult. Usually latex is to be ammoniated and kept overnight before being centrifuged, thus giving time for the sludge to settle down. During the working of machines, the centrifuge inverts to the axis of rotation and then empties from the bowl through the holes into a stationary gully. The cream is separately collected in bulking tank, its ammonia content estimated and adjusted to a minimum of 0.6% on latex and packed in drums.

Efficiency of centrifuging process is defined as the proportion of total rubber recovered as concentrate. The important factors which affect the efficiency are feed rate, angular velocity of machine, length of regulating screws and DRC of field latex. The shorter screw increases the DRC of the cream but reduces the efficiency, since the proportion by volume of input which emerges as skim increases. Non rubber content in the cream will be less.

1.3.6. Skim latex

When field latex is centrifuged, in addition to the concentrate containing most of the rubber, a large volume of serum containing very small proportion of rubber is also obtained. This is known as skim latex. As the normal efficiency of centrifuging process is only 85-95% about 10-15% of the incoming rubber goes into the skim. Hence, on economic grounds it is essential to recover the rubber present in the skim latex.

Normally, the rubber content of the skim latex varies between 3 and 8 %. The average size of the rubber particles is smaller than that of field latex, since larger particles separate more readily into the concentrate fraction. In addition to the water soluble substances in the serum, latex contains proteins which are mainly distributed as an adsorbed film on the surface of the rubber particles and as the particles are small, the protein content per unit weight of rubber is more in the case of skim latex. This not only renders coagulation more difficult, but also has a marked effect on the properties of the skim rubber. Skim latex also contains comparatively higher level of fatty acid soaps.[9] Skim also contains ammonia which adds to the cost and difficulty of acid coagulation. With increasing efficiency in concentration, the DRC of skim fraction decreases and the difficulty and cost of any recovery process are increased.

The usual method of recovery of skim rubber is by spontaneous coagulation or by acid coagulation. Coagulation by surface active quaternary ammonium compounds is also reported[10]. In spontaneous coagulation, the skim latex is de-ammoniated by bubbling air through it and then kept in tanks for few days for coagulation to occur by fermentation. In the other method, coagulation of skim latex is done in batches by the addition of dilute sulphuric acid (20-50%). About 1kg of sulphuric acid is required for recovering 4-5kg of skim rubber. Ammonium stearate when added to skim latex can accelerate the formation of a firm skim coagulum after acid addition[11]. In either case, the coagulum obtained is processed into crepe by conventional means, taking special care to give thorough washing. Due to the presence of high serum solid and protein content, the rubber made from skim has inferior properties. Blending of skim rubber with other forms of rubber causes much trouble to rubber product manufacturers owing to its abnormal properties, particularly a tendency to scorch. Ageing[12] resistance of vulcanizates prepared from skim rubber is poor, as the rubber contains higher level of metallic pro-oxidants, such as copper. The main characteristics of skim rubber are in Table 1. 3.

1.3.7. Modified forms of natural rubber

Though NR has very high rubbery characteristics it cannot be used in applications that required high heat and oil resistance. These are mainly obtained by modification of rubber. There are two methods of modifications, physical and chemical. Physical modification includes incorporation of compounding ingredients like latex carbon black master batches, oil extended natural rubber and latex stage compounding. Polymer blends includes blends with other rubbers and plastics. There are other physically modified forms like deproteinised natural rubber and powdered natural rubber. Chemical modification includes intramolecular changes like cyclisation and de-polymerisation. Another type of chemical modification is through grafting of monomers like styrene, methyl methacrylate, acrylonitrile etc into NR. A third type of chemical modification is by attachment of pendent functional group, eg. In the production of constant viscosity rubber the carbonyl group present on natural rubber chains react with hydroxyl amine. Vulcanisation also is a chemical modification in which sulphur is attached to the NR molecules. There are other reactions like epoxidation and halogenation where epoxy group and halogen is introduced in the main chain.

1.3.7.1. Physical modifications

1.3.7.1.1. Incorporation of compounding ingredients

a. Latex carbon black master batch

Latex carbon black master batch become popular in the early seventies and it was mainly to avoid the problems of environmental pollution by carbon black dust. This was available in forms which could readily be used in tyre industry. However, this did not get popularity due to the loss of carbon black during master batching. In the conventional process oil emulsion and carbon black slurry are added to NR or SBR latex and then it is coagulated using a coagulant. The rubber is dried well and packed in bales of 25 kg. The disadvantage with method is the long coagulation time and the loss of carbon black during the process. A process of continuous mixing and coagulation of NR latex with carbon black slurry was developed by Cabot Corporation, USA through an energy intensing process of coagulation.

b. Polymer blends

The commonly used blends of NR are with SBR, Br, NBR and EPDM. The basic problem with the blending of rubbers is the polarity difference between two rubbers, un-equal distribution of fillers and compounding ingredients. To get good mechanical properties, use of compatabilisers and judicial choice of compounding ingredients were attained.

1.3.7.1.2. Deproteinised rubber

Deproteinisation can be carried out by using proteolytic enzyme or by exposure using gamma radiation. During chemical treatment and exposure to radiation proteins hydrolyse to low molecular fractions and become soluble in the serum.

1.3.7.2. Chemical modifications

1.3.7.2.1. Grafting

Grafting reactions are achieved by chemicals like peroxides which initiate the formation of grafting by forming free radicals or by exposure to gamma radiation where free radicals are formed by removal of electrons from natural rubber molecules by high energy radiation.

1.4. Compounding of rubber

The art of making a compound by mixing rubber and compounding ingredients in order to make a product is known as compounding of rubber. When designing a mixing formulation for a specific end use the compounder takes into account two factors 1.vulcanizate properties, and 2.cost of raw materials involved in the production process which transforms these raw materials into product. The principal task of compounding is to acquire a balance between the final vulcanizate properties, price and processability.

In a rubber product number of ingredients other than the rubber may be present. They are usually,

1. Polymer or rubber(blend of rubber)
2. Cross linking agents, usually sulphur
3. Accelerators for crosslinking reaction
4. Accelerator modifiers
5. Aids to processing(chemical peptizers for polymers, softeners, plasticizers, dispersing acids, tackifiers, and lubricants)

6. Reinforcing fillers(Black, mineral and organic)
7. Antidegradents (Antioxidants, antiozonant, inhibitors of mineral catalyzed oxidation, protective waxes)
8. Diluents (Inter mineral fillers, organic materials and extending oils)
9. Special additives (Blowing agent)

1.5. Selection of Ingredients

1.5.1. Polymer or rubber (blend of polymer)

Most important component of a rubber compound is the polymer. It may be natural, synthetic or reclaimed rubber, mixture of these or a mixture of rubber and a thermoplastic material. This polymer should be of lowest price and should have required properties to provide adequate service, and also it should offer ease of mixing.

1.5.2. Cross linking agent

Sulphur is the most popular crosslinking agent used by the industry. By the use of crosslinking agent the rubber becomes less plastic, resistant to swelling in organic liquids and at the same time the elastic properties are improved. The crosslinking agent reacts with active sites in the polymer to form crosslinks between the chains. Vulcanization system without the involvement of sulphur donors are less commonly used and involved peroxides, urethanes, metal oxides, resins, electron beams and radiation.

1.5.3. Accelerators for crosslinking reaction

Accelerators are materials added to make a rubber compound to increase the rate of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiencies. They can also decrease the quantity of sulphur necessary for vulcanization and considerably improve the physical and technological properties of the vulcanizate.

Accelerators have been classified arbitrarily as low, medium-fast, fast, semi-ultra and as having direct or delayed action accelerators. Again it is classified into organic and inorganic. Organic in turn is divided into two, acidic and basic.

1.5.4. Acceleration modifiers (activators or retardant)

They are materials or mixture of materials to an accelerated vulcanizing system to realize its full potential. The activators used most commonly are ZnO and stearic acid. Increase in fatty acid usually shows the rate of cure increase but result in a higher concentration of more tightly cured and thermally stable network. The additions of ZnO produce a significant change and produce a well cured stock.

1.5.5. Reinforcing fillers

Reinforcing fillers are most particulate constituent of a compound added in large quantities to the rubber to improve the physical properties or to decrease the volume cost. According to their effectiveness they are graded as reinforcing and non-reinforcing. Reinforcing fillers include carbon blacks, fine light coloured fillers, and synthetic reinforcing resins. Non-reinforcing fillers include diluents, coloured pigments, white pigments and also fillers are activators (e.g., ZnO, MgO, Magnesium carbonate) litharge, red lead and $Ca(OH)_2$.

Reinforcing fillers enhance compound properties like hardness tensile strength, modulus, and tear strength and abrasion resistance of a compound. They are sub divided into black and non black fillers. Black fillers are various grades of carbon black and non black fillers include silica, clay, talc etc.

1.5.5.1. Reinforcement with carbon black

Fillers may be either reinforcing or non-reinforcing or extended. Generally non black fillers like clay, whiting and barites are inert fillers which have very little effect on physical properties while fillers like carbon black and silica enhance the mechanical properties like modulus, tensile strength, tear strength and abrasion resistance. They are generally called reinforcing fillers. Reinforcing effect of fillers depends on its nature, particle size, type and amounts of fillers.

Carbon black is the most important filler in rubber formulation, its loading can vary from 30 to70 phr. Carbon black consist of elemental carbon (90-99%) along with hydrogen and oxygen and is present in active group like lactones or ketone, carbonyl etc. Commercially carbon black classifieds into furnace black, thermal black, channel black and lamp black, according to the process by which they are manufactured. Furnace black is the oldest type of carbon black. Channel black is the highly reinforcing type of carbon black, but they retard vulcanization due to the acidic nature. Furnace and thermal black are used in wide range of applications. Different types of carbon black are ISAF, SAF, HAF, GPF, SRF etc. The particles of carbon black are not discrete but are fused or cluster of individual particles. Carbon black surface contain functional group capable of reacting with polymer molecules to form grafts during processing and vulcanization. When carbon black is incorporated to rubber matrix, the strength related properties (modulus, Mooney viscosity, rebound and abrasion resistance) of the rubber largely improved, depending on the nature of the carbon black particle size, structure, surface area and surface activity.

In general, the reinforcement imparted to elastomers increases as the particle size of the carbon black decrease. The specifications of different types of carbon black are given in table 1.4. The blackness of carbon black is generally runs parallel to its particle size. The smaller it is the blacker the color.

The term structure of carbon black refers to the joining together of carbon particles in to long chains and tangled three-dimensional aggregates of a carbon black. The more irregular the shape of aggregates resulted in less aggregates capable of packing together. The higher the structure, in turn, the greater it's reinforcing potential.

1.5.6. Antidegradents

They are substances when add to rubber in a small quantity retards ageing and protect rubber from internal and external influences in deterioration. These are classified according to the type of protection.

1. Retard to prevent atmospheric oxidation and its effects(oxidation)
2. Retard or prevent the formation of tears caused by ozone attack, under static or dynamic stress (antiozonants)
3. Protect against special type of ageing(special additives)

Antioxidants are of two types, chain breaking and preventive antioxidants according to their function. Some of the commonly used oxidants are 2, 2, 4-trimethyl-1, 2-dihydroquinoline (TDQ), substituted phenols etc.

1.5.7. Antioxidants

They are amorphous and microcrystalline waxes which migrate to the surface and form a physical protective surface layer. E.g. N, N-Diphenyl-p-phenylenediamine.

1.5.8. Processing aids

a. Softeners or processing oils

Mineral oils are used to increase the plasticity of the compounds, facilitates the dispersion of fillers, improve processability and act as diluents. These are called processing oils. These are classified according to their chemical composition into three main groups. Paraffinic, naphthenic, and aromatic oil gives the best low temperature properties and good ageing and low hystersis.

b. Chemical peptizers

Chemicals which act as mastication aids, reclaiming agent, enabling mixing time to be reduced, plasticity increased, and the viscosity of the solution reduced. They act as oxygen carriers and thus increase the oxidative decomposition of gel structure of rubber. Peptizer has no effect on the hardness of vulcanizate.

E.g. Xylyl mercaptan

c. Plasticizers

A material which may be added to rubber to improve flexibility, particularly at low temperature is called a plasticizer.

d. Diluents

They include inert mineral fillers, extending oils, etc which have been explained already.

E. Colouring agents and pigments

They are dye stuffs for colouring the rubber to the required shade. These can be grouped into inorganic dyes, organic dyes and lacquers. Inorganic dyes include lithopone, titanium dioxide, iron oxide, chromium etc. Organic dyes include a vast range of shades. Among the many types of filler, carbon black act as a powerful pigment.

1.5.9. Special additives

These are substances which decompose into gaseous products at high temperature or which evolve gases and thus causes rubber compounds to expand before vulcanization, used for the production of cellular rubber articles and hollow articles. They must be well dispersed to obtain an even cell structure, they should not produce any toxic products on decomposition and should have a minimal effect on vulcanization. Blowing agent today in use are Dinitroso pentamethylene tetramine, benzene sulphone hydroxide, azonitrates etc.

1.6. Mastication and mixing

The raw rubber natural and synthetic can be softened either by mechanical work termed mastication or by heat or peptizers. The mastication by peptisers is used only when it is necessary as there can be considerable molecular weight reduction in its presence which is generally undesirable. An internal mixer like Banbury mixer is an efficient machine for mastication, generally for NR.

Mixing mill is a machine having two hollow rolls which contain cooling or heating systems and are placed in a frame in horizontal for diagonal positions. The rolls move in opposite directions at different speeds in the ratio 1:1.1 to 1:1.5 the second roll is the one moves at a faster speed. The gap between the rolls may be altered. The raw rubber is processed between the rolls by mechanical friction and plasticized. The degree of mastication is greater on cold rolls than warm rolls. The rubber is formed as a band around the front roll, thickness of the band depending on the gap between the rolls while superfluous rubber lies between the rolls as a bank when degree of mastication is reached. The fillers and vulcanizing agents are added on the rolls and the compounded rubber is taken out the rolls by cutting.

Internal mixer consists of two parallel kneading rotors each rotating within the corresponding region of the mixing chamber is constituted by a ram or heating weight which is V-shaped at the bottom. Discharge is through the bottom which is an inverted V-section in the term of a hinged W drop door operating hydraulically. The ram can be lowered or raised with a hollow vertical shaft, thus providing a chaining entry when in raised position and sealing the mixing chamber when lowered. The capacity of the mixer is 1L and the mixing was done at 90% volume loading.

1.7. Vulcanization

Vulcanization is a chemical process of inter linking of rubber molecules to change the predominantly plastic properties to elastic properties. Vulcanization is the conversion of rubber molecules into a network by the formation of cross links. These vulcanizing agents are mostly sulphur, peroxide, other special vulcanizing agents or high energy irradiation. Vulcanization is an intermolecular reaction which increases the reactive force and reduces the amount of permanent deformation remaining after removal of the deforming force. According to the theory of rubber elasticity the reactive force resulting from a deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer[13]. Vulcanization usually produces network junctures by the insertion of chemical cross links between polymer chains. The cross links may be formed through chains of sulphur atoms, single sulphur atoms or carbon-carbon bonds. The vulcanizate properties are not functions of cross link density only they are affected by the type of cross link, nature of polymer, type and amount of fillers etc[14]. The most widely used vulcanization procedure even today is merely elaborations of the original method of heating rubber with sulphur discovered by Charles Goodyear in 1839 and by Thomas Hancock in 1843[15]. The introduction of organic accelerator in the vulcanization of rubber which began more than 75 years ago led to revolutionary changes in the manufacturing of rubber products. The accelerators enabled vulcanization time to be reduced. The proportion of sulphur required for optimum physical properties could be reduced thus improving the resistance of rubber goods to ageing and preventing blooming of sulphur[16].

1.7.1. Sulphur vulcanization[17]

Sulphur vulcanizing systems usually contained sulphur in amounts of 2.5 to 3 phr and accelerator in amounts of 0.5 to 1.0 phr. The accelerated sulphur vulcanization system can be classified into 3 types.

1. Conventional system (CV) containing high sulphur /accelerator ratios
2. Efficient systems (EV) containing high accelerator/sulphur ratios
3. Semi EV systems that is intermediate between 1 and 2

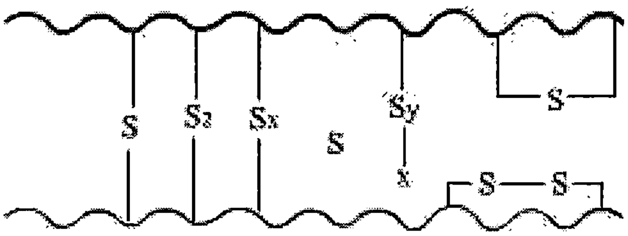
Conventional systems give vulcanizates which possesses excellent initial properties like strength, resilience and resistance to fatigue and abrasion and are satisfactory for many applications. However their heat ageing resistance, creep and stress relaxation properties are less satisfactory. For good ageing resistance and low compression set an EV system is essential or a semi EV system may be chosen as a compromise between cost/performance.

Soluble EV and semi EV systems are zinc-2-ethyl hexanote rather than stearic acid, the latter leading to insoluble zinc stearate formation in the vulcanizates and affects properties. Sulphur is limited to 0.8 phr. Soluble EV system overcomes some of the problems of EV systems such as high physical creep and low resilience. They are ideal for use in engineering components that require low compression set, low creep, low stress relaxation and high reproducibility in modulus and strength.

Theory of sulphur vulcanization [18]

The chemistry of sulphur vulcanization is so complex. In sulphur vulcanization sulphur is combined in the vulcanization network in a number of ways. As cross links it may be present as monosulphide, disulphide or polysulphide, but it may also be present as pendent sulphides or cyclic monosulphides and disulphides.

A diagrammatic representation of the network structure is given in Scheme 1.



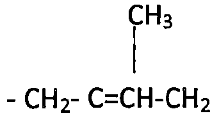
Scheme 1

An estimate of the no. of sulphur atoms for each crosslink formed has been made. An unaccelerated rubber sulphur vulcanizate may give a figure of 40-45 whilst in conventional accelerated sulphur vulcanizates this "inefficiency" figure may drop to 10-15, special efficient vulcanizing systems can reduce it still further to 4or 5 but for even lower values the so called non sulphur vulcanizing systems must be used.

The initial step in vulcanization is the reaction of sulphur with the zinc perthiosalt Xsx ZnSxX, where X is a group derived from the accelerator (e.g. thio carbomate or benzthiozyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber bound intermediate.

X SxZn SxX + RH → X Sx R + ZnS + HSx-1X

And a perthio-accelerator group which with further ZnO will form a zinc perthio-salt of lower sulphur content this may again be an active sulphurating agent forming intermediates Xsx-1R. The hydrogen atom which is removed is likely to be attached to a methylene group in the X-position to the double bond, i.e., in natural rubber the hydrogen atoms at positions 4 and 5 the most liable in this type of reaction.

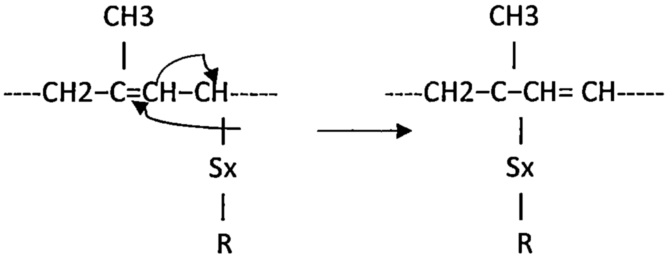


$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2 \text{-------------- (1)}$$

The intermediate XSxR then react with a molecule of rubber hydrocarbons RH to give a crosslink and more accelerators is regenerated.

XSxR + RH → RSx-1R + XSH---------------- (2)

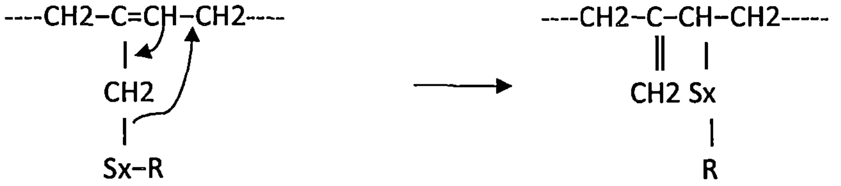
It is evident that the cross links which were initially at positions 4 and 5 undergo an allylic shift, with the result that new configuration appear.



$$\text{----}CH2-\overset{\overset{\displaystyle CH3}{|}}{C}=CH-\underset{\underset{\underset{\displaystyle R}{|}}{Sx}}{\underset{|}{CH}}\text{-----} \longrightarrow \text{----}CH2-\underset{\underset{\underset{\underset{\displaystyle R}{|}}{Sx}}{|}}{\overset{\overset{\displaystyle CH3}{|}}{C}}-CH=CH\text{-----}$$

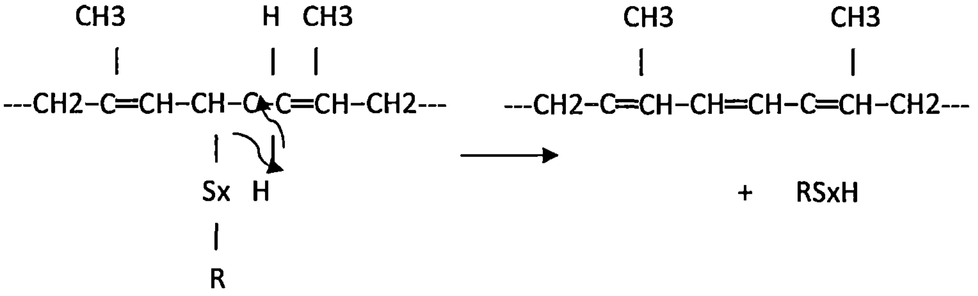
------------------ (3)

And



$$----CH_2-\underset{\underset{\underset{Sx-R}{|}}{\underset{CH_2}{|}}}{C}=CH-CH_2---- \longrightarrow ----CH_2-\underset{\underset{CH_2}{\|}}{C}-\underset{\underset{\underset{R}{|}}{Sx}}{\underset{|}{CH}}-CH_2----- \quad -------------- (4)$$

At the same time, disappearance of crosslinks of the disulphide and polysulphide type occurs with formations of conjugated trienes.



$$---CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\underset{\underset{\underset{R}{|}}{Sx}}{\underset{|}{\overset{\overset{H}{|}}{CH}}}-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-C=CH-CH_2--- \longrightarrow ---CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH=CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2--- + RSxH \quad ---------- (5)$$

A consideration of above reaction leads to the conclusion that, if proceeds as in the case of the final network will be highly crosslinked with mainly monosulphidic bonds, and there will be relatively few modifications of the cyclic sulphide or conjugated such a network is termed efficiently crosslinked.

1.7.2. Peroxide vulcanization

In peroxide vulcanization, direct carbon-carbon crosslinks are formed between elastomer molecules. The peroxide decomposes under vulcanization conditions forming free radicals on the polymer chains, leading to direct crosslink formation. Peroxides can be used to crosslink a wide variety of both saturated and unsaturated elastomers where as sulphur vulcanization will occur only in unsaturated species.

Peroxides, which cure elastomers through free radical process, have been established as the best known non-sulphur crosslinking agent[19]. Peroxides are widely accepted today and are used in many areas of the rubber industry. A peroxide that may be used for the vulcanization of elastomers falls into two basic types.

a) Peroxides with carboxylic acid groups. E.g., Benzoyl peroxide

b) Peroxide without carboxylic acid groups. E.g., Dicumyl peroxide.

In general carbon-carbon bonds from peroxides initiated crosslinks are more stable than the carbon-sulphur-carbon- bonds from sulphur vulcanization. Thus peroxides initiated cures often give superior ageing properties in the rubber products. However peroxide initiated cures often give superior ageing properties in the rubber processing.

A wide variety of organic peroxides are available including products such as benzoyl peroxide class must take into account its stability, activity, intended cure temperature and effect on processing properties. Carbon-carbon crosslinks can also be initiated by gamma, or X-radiation these presently find limited application.

1.7.3. Radiation vulcanization

Latex can be crosslinked by exposure to gamma radiation by doses of about 15 kGy. At low doses and in the absence of sensitisers the level of vulcanization is very low. In the presence of monomers like n-Butyl acrylate, the level of crosslinking is faster. The level of cross linking that obtained by sulphur and accelerators can be achieved by gamma radiation.

1.8 Scope and objective of the present study

Natural rubber is used in a large number of rubber products. About 60% of the rubber produced in our country is used in tyre sector. Few of the properties required for the tyre are high mileage (good abrasion resistance), low rolling resistance (higher resilience and low heat build-up) and good grip on the road. These properties are generally met by adding both silica and carbon black to the rubber matrix. Mixing of carbon black to rubber is an energy consuming process and there is flying of carbon black dust in the mixing area which is hazardous to people working there. Similar problems are there for silica but there is an additional difficulty that silica has poor compatibility with rubber matrix. It is expected that a low amount of gel content can help in application of higher shear forces during mixing process and hence better polymer-filler interaction. Further by incorporation of fillers in the latex stage, it is possible to reduce the health hazardous due to the flying of particles into the surrounding atmosphere.

Since carbon black and silica are two fillers which are indispensable for the tyre sector, it is required that there should be an easier and efficient method to disperse these fillers in rubber. In this work an attempt is made to disperse silica and carbon black (SAF) in natural rubber, so as to obtain better mechanical properties. Better filler dispersion is attempted by use of natural rubber with higher gel content and filler addition by conventional mill mixing and latex stage incorporation.

Chart 1 Flow diagram for processing latex into technically specified rubber

Reception, sieving and bulking
↓
Coagulation
↓
Coagulation crusher/pre-breaker
↓
Creepers (2-4 nos; 2-4 passes)
↓
Hammer mill/shredder
↓
Blending
↓
Drying
↓
Pressing
Testing and grading → ↓
Packing

Chart 2. Flow diagram for processing field coagulum into technically specified rubber

Field coagulum
↓
Sorting and blending
↓
Soaking
↓
Slab cutter/pre-breaker
↓
Blending
↓
Creepers (2-3 nos., 2-4 passes)
↓
Hammer mill
↓
Blending
↓
Creepers (3-4 no.s, 6-8 passes)
↓
Hammer mill/shredder
↓
Blending
↓
Drying
↓
Pressing
↓
Testing and grading
↓
Packing

Table 1.1 Acid requirements for coagulation of latex containing 1Kg dry rubber

Sheet time	Acetic acid	Formic acid
Next day	6 ml diluted to 600 ml with water	3 ml diluted to 600 ml with water
Same day	8 ml diluted to 800 ml with water	4 ml diluted to 800 ml with water

Table 1.2 Specification for raw natural rubber

Property	**ISNR 3CV**	**ISNR 3L**	**ISNR 5**	**ISNR 10**	**ISNR 20**	**ISNR 50**
Dirt retained on 44-micron aperture(%max)	0.03	0.03	0.05	0.10	0.20	0.50
Ash(%max)	0.50	0.50	0.60	0.75	1.00	1.50
Nitrogen(%max)	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter(%max)	0.80	0.80	0.80	0.80	0.80	0.80
Initial plasticity,P0(min)	**	30	30	30	30	30
Plasticity retention index, PRI(%min)	60	60	60	50	40	30
Color (*Lovibond* scale, max)	-	6.0	-	-	-	
Mooney viscosity, ML(1+4)100°C	60±5	-	-	-	-	
Accelerated storage hardening(max)	8	-	-	-	-	-
Color code	black	black	green	brown	red	yellow

Source: BIS, 1992 **as agreed by purchaser and supplier.

Table 1.3 Main Characteristics of skim rubber

Color : Light
Dirt content : Very low
Non-rubber content : Up to 30%
Copper content : 4-20ppm
Acetone extract : 3-5%
Mill breakdown : Normal
Power consumption : Slightly high
Mill shrinkage : Less than normal
Cure rate : Fast, giving scorched compound
Hardness : High
Modulus : High
Resilience : Low
Ageing behavior : Variable

Table 1.4 Specifications of different types of carbon black

Type code	ASTM D 1765	Iodine absorption	Mean particle diameter	Structure(ASTM D 2414),
SAF-LS	-	140	22	90
SAF	N-110	140	22	115
SAF-HS	-	140	22	135
ISAF-LS	N-219	120	28	80
ISAF-LM	N-231	120	28	90
ISAF	N-220	120	28	115
ISAF-HS	N-242	120	28	130
HAF-LS-SC	S-315	80	32	70
HAF-LS	N-326	80	32	70
HAF	N-330	80	32	105
HAF-HS	N-347	80	32	125

CHAPTER 2

EXPERIMENTAL TECHNIQUES

Chapter 2

Materials and Experimental Techniques

The materials used and the experimental procedure adopted are described in this chapter.

2.1. Materials used

ISNR 5 and rubber of higher gel content obtained by irradiation to different doses were obtained from Rubber Research Institute of India. The other ingredients used were of commercial grade.

2.2. Methods

A. Determination of dry rubber content (DRC)

Principle

Weighing the dried coagulum obtained after coagulating latex by addition of acid at a definite dilution gives the dry rubber content.

Reagent: 2% solution of acetic acid

Procedure

Weighed about 10g of the well mixed sample accurately into a 250 ml beaker from a stoppered conical flask. Added water until total solids content of latex was about 20%. Added about 2 ml of 2% acetic acid per gram of sample by gentle stirring. Kept the solution undisturbed for about 15minutes in a water bath. If serum remained milky added about 0.5 ml of rectified spirit / g of the sample and gently stirred. When the serum was clear filtered the serum through Whatman No.1 filter paper. Collected any small particle of coagulum .The thickness of the coagulum was reduced to about 2mm either by hand roller or mechanical roller .Collected all small particles of coagulum by rubbing with main bulk .Washed the coagulum with running water or at least with six changes of water until neutral to litmus .The rolled coagulum was dried in a hot air circulating oven at 70^0 C ,cooled in a dessicator and weighed .For the determination of the DRC of skim latex , first determine the DRC of the cenex sample (centrifuged latex) then found out the DRC of the blend of cenex sample and skim latex ..

Dry rubber content, % = $W_1/W_2 \times 100$ --------------(1)

W_1 is the weight of dried film

W_2 is the weight of latex taken

B. Determination of Total solids content (TSC)

Principle

Drying of a definite quantity of latex and measurement of the residue gives the total solids content.

Procedure

Taken 5- 10g of well mixed sample in a stoppered conical flask .Poured about 2g of the sample into a previously weighed Petri dish of about 60mm diameter and weighed to obtain weight of latex added by difference .Swirled the Petri dish gently to ensure that latex covered the bottom of the dish . Dried the test portion in a hot air circulating oven at a temperature of 70^0C .Cooled in a desicator and weighed .Repeated the drying operation until the loss in weight is less than 1mg.

Total solid content (%) = $(W3 - W1/W2 - W1) \times 100$ ------------------ (2)

W1 =Weight of Petri dish

W2 =Weight of Petri dish + sample

W3 =Weight of Petri dish + dry film

C. Determination of Nitrogen (ASTM D 3533-90)

The determination of nitrogen in natural rubber is used for the estimation of protein content.

Apparatus

Micro-Kjeldahl digestion and distillation apparatus

Reagents

1. Boric acid solution
2. Catalytic mixture of potassium sulphate, cupric sulphate and selenium powder.
3. Indicator: ethyl Red- Bromo cresol Green.
4. 60% sodium hydroxide solution.
5. Concentrated sulphuric acid.
6. 0.01 N HCL

Procedure

Weighed about 0.1 gm of the sample into a micro Kjeldahl flask. Added about 0.6 gm of catalytic mixture and 3 ml concentrated H_2SO_4. Boiled gently by electrical heating and continued boiling for about 30 minutes after the digest had become a clear green colour with no yellow tint. Cooled the digest and transferred the solution to the distillation apparatus.

About 5 ml of boric acid solution was taken in the receiving flask. Added two drops of the indicator and placed the receiver so that the end of the condenser dips below the surface of boric acid solution. Added about 100ml of 60% NaOH solution to the digestion flask and washed it with water. Passed steam from the steam generating flask through the distillation apparatus until the total volume of the solution in the receiver was about 50 ml. Lowered the receiver until the condenser tip was well above the solution and continued distilling for 1 minute. Washed the end of the condenser with water.

Titrated the distillate with standardized 0.01N hydrochloric acid. Carried a blank determination through the entire procedure using all of the reagents but omitting the sample.

$$\text{Nitrogen \% by weight} = \frac{V \times N \times 1.4}{W} \quad \text{-------------------- (3)}$$

N = Normality of HCL

V = Volume of the sample required for distillation

W = weight in gram of sample used

D. Determination of Initial plasticity and plasticity retention index (ASTM D 3194-04)

The test was done using Wallace Plastimeter. The platen of the Plastimeter should come to equilibrium at 100 ± 1°C for 15 min before taking the measurement. Placed two pieces of tissue paper between the heated platens and set the thickness measuring device to zero when the platens were closed. Inserted a pellet sample at room temperature between two pieces of tissue paper and placed the whole assembly centrally between the heated platens. The machine lever was put into operation. After 10 sec conditioning period the timing device automatically released a spring which applied a load of 98 N to compress the specimen. This load period is automatically adjusted exactly 15 sec duration and the load was removed automatically. Recorded the measured thickness from the dial micrometer. Repeated for three times and the medium value was taken as the initial plasticity (Po).

Repeated the same with the aged specimen (140°C, 30 min) and the reading was taken as the plasticity of the aged specimen. PRI was calculated as, PRI = Plasticity aged / Plasticity original x 100 -------------------- (4)

E. Acetone extract of the dried rubber (ASTM D 297-93)

Approximately 5 gm of the sample was wrapped in a filter paper is placed in the extraction apparatus and sufficient acetone was added to fill the extraction vessel. Assemble the apparatus and adjust the heating rate so that the quantity of the distilled solvent fillers the extraction up to 10 to 20 times per hour and extract for 16 ± 1 hr. After the extraction period is over, recover the combined acetone from the extraction flask by distillation. The contents of the flask were dried in an air oven at 65°C for about I hr to remove the last trace of acetone.

Solvent extract percentage by weight = $W_1 / W_2 \times 100$ --------------- (5)

W_1 = weight in gm of matter extracted

W_2 = weight in gm of tested portion

F. Molecular weight determination by viscosity measurements

The weight average molecular weight Mw was measured using an Ostwald viscometer. A known quantity of the rubber was dissolved in toluene and different dilutions were prepared from the same. Using the Ostwald viscometer, the flow time of the solutions were found. And from the flow time the relative viscosity was calculated using the expression t_s/t_0 ,where t_s is the flow time of the rubber solution and t_0 is the flow time of the solvent. The intrinsic viscosity can be obtained as

$$\eta = K M^a \quad \text{-------------------- (6)}$$

Where M =Average molecular weight

K,a = Constants for the solvent-polymer system,

For NR-toluene system $K=50.2 \times 10^5$, a= .667

η can be obtained experimentally from

$$\eta = \mathrm{Lim}_{c\to 0}\,[\;\eta_{sp}/c]$$

Where η_{sp} = Specific viscosity, $\eta_{sp} = \eta_{r} - 1$

Where $\eta_{r} = t_s/t_0$

G. Viscosity measurements (Haake viscometer)

The viscosity of the solution was determined by concentric disc viscometer. About 10cc of rubber solution of different concentration was prepared and introduced in the cylinder. The rotter is fixed and rotated at different rpm corresponding to different shear rate from 1 to 200. The machine automatically record the shear stress required for the particular shear rate. The concentrations of the rubber solution prepared were about 0.3%.

2.3. Preparation of rubber compounds

The rubber compounds were prepared as per formulation in Table 2.3 using a laboratory model two roll mixing mill. The mixes were vulcanized to their optimum cure time using Rheo Tech MD plus at 150 ^{0}C.

Table 1 Formulation of mixes (dry mix*)

Ingredients	Mix designation		
	0 kGy	**5 kGy**	**10 kGy**
Rubber	100	100	100
Zno	5	5	5
Stearic acid	1.5	1.5	1.5
Anti oxidant	1	1	1
MBTS	1	1	1
DPG	0.2	0.2	0.2
DEG	1	1	1
Precipitated silica	25	25	25
SAF black	25	25	25
Sulphur	2.5	2.5	2.5

* Rubber is obtained by soap sensitized coagulation

A. Determination of cure characteristics (ASTM D 5289-96)

Cure time is the time for the torque to reach a given percentage of full cure. The most commonly used percentage is 50 and 90. Cure characteristics of the compounds were determined using rheo TECH MD+ at 150 °C according to ASTM D 5289 procedure.

The rheometer test can be tested where a rubber specimen is stretched to a given distance (strain) then relaxed by oscillation of the lower die at a specified speed. The test is performed while the specimen is confined in a heat chamber at curing temperature under pressure. The stiffness of the sample increases as vulcanization proceeds and reaches maximum and remains same. The force required to stretch the rubber (stress) is directly proportional to stiffness of the rubber.

The optimum cure time corresponds to the time to achieve 90 % of the cure was represented by the torque attained. It was calculated from the equation optimum cure time.

$$t_{90} = 90/100 \times (M_{max}-M_{min}) + Mmin \qquad \text{-----------------} (7)$$

Where M_{max} = Maximum torque

M_{min} = Minimum torque

B. Moulding

Test samples were prepared by compression moulding method. The compounded rubber was placed between the cavities of the mould heated to 150 °C and pressure of about 1600 Psi was applied by a hydraulic press by placing this mould between the heated platens of the press. To ensure complete filling a slight excess of compounded rubber was placed in the mould. After curing the pressure was released, the mould was taken out from it and the sample was cooled.

2.4. Testing for vulcanizate properties

Technological properties

A. Tensile properties (modulus, tensile strength and elongation) ASTM D 412-06)

The three parameters were determined according to the ASTM standards, using dumb bell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die, along the mill grain direction of the vulcanized sheets. The thickness was measured using a dial gauge. The tests were carried out in a Zwick Universal Testing Machine (UTM) model 1474 at 25±2 °C. The dumb bell specimen was placed in the grip of the testing machine taking care to adjust the specimen symmetrically to distribute tension uniformly over the cross-section. The rate of the grip separator shall be 500 mm/min. The force at the elongation specified for the test and at the time of rupture was recorded to the nearest 10%. Tensile stress at any specified elongation be given as,

$$T = F/A \qquad \text{-------------} (8)$$

Where T = Tensile stress at % elongation MPa

F = Force at specified elongation MN

A = Cross section area of specimen m^2

The modulus at 100%, 200%, 300% and elongation at break were also noted.

B. Tear Resistance (ASTM D 624-02)

The test was carried out as per ASTM standards. Samples were punched out from the sheets parallel to the grain direction. This test was carried out on the tensile testing machine. The test sample was mounted on the testing machine. A steadily increasing traction force was applied at 500±50 mm/min until the test piece was completely ruptured. The tear strength values are reported in N/mm.

C. Abrasion Resistance (ASTM D 5963-04)

Abrasion resistances of the samples were measured using a DIN abrader. It consists of a drum on to which a standard abrasion paper is fixed. The drum rotates at a speed of 40 rpm and the total abrasion length is 42 m. Discs of test pieces having dimensions of 16 mm diameter and 6 mm height were used. The test piece was traversed in sample holder, across the rotating drum. The test piece was pressed against the drum with a vertical force of 10 N. Initially a pre-run was given for the test sample for a definite distance and it was weighed (m1). Then the test run was conducted. The sample was weighed (m2) after the final run. Abrasion loss is calculated from the formula.

$$V = (\Delta m/\rho) \times 100 \qquad \text{-------------------} (9)$$

V = Abrasion loss, mm^3

Δm = (m1-m2), weight loss, g

ρ = density of the sample.

D. Heat Build Up (ASTM D 623-07)

Heat build up of the samples were measured as per ASTM standards. Cylindrical test specimen with diameter of 17.8±0.1 mm and height of 25±0.5 mm were used. The test piece was subjected to rapidly oscillating compressive stresses in Goodrich flexometer at 1800 cycles per min, at an initial chamber temperature of 50 °C. A constant initial compressive load was applied to the specimen through a level having high inertia and imposing on the specimen and an additional high frequency cyclic compression of definite amplitude. The stroke given was 4.45 mm. The increase in temperature at the base of the test specimen was measured with a thermocouple which provided indication of the heat generated in flexing the specimen.

E. Hardness (ASTM D 2240-05)

Hardness measures the elastic modulus of the rubber by determining its resistance to a rigid indenter to which a force is applied.

The hardness of the samples were measured as per ASTM standards using a shore A type durometer having a pressure foot, and indenter and a scale reading from 0 to 100. The specimen was placed on a hard horizontal surface. Hold the durometer in a vertical position with point of the indenter at least 12mm from the edge of the specimen. Measurements were taken as the hardness value.

F. Compression set (ASTM D-395B)

The test was done as per ASTM D-395-71. The samples were compressed in the compression set apparatus to give 25 per cent compression. It was then kept in air oven at 700C for 22 hours. After the heating period, the samples were removed, cooled to 28 ± 10 C for half an hour and final thickness was noted. The compression set was calculated as follows.

$$\text{Compression set (\%)} = \frac{(t_0 - t_1)}{(t_0 - t_s)} \times 100 \qquad \text{-----------} (10)$$

Where t_0 and t_1 are the initial and final thickness of the specimen and ts is the thickness of the space bar used.

G. Thermal aging

Thermal ageing refers to ageing under the influence of oil or air at high temperature. Air ageing was carried out by measuring the tensile properties after ageing in an air oven at 100 ^{0}C for 3 days. Solvent and fuel ageing was done as per ASTM D 573-04. Solvent ageing was done by immersing samples of dimension 1 cm diameter and 3mm thickness into n heptane and measuring the percent weight of solvent absorbed after 1 ,4, 24 and 48 hours at room temperature. Fuel ageing was carried out by immersing samples of dimension about 1 cm diameter and 3 mm thickness into isooctane and measuring the percent weight of fuel absorbed after 1,24 and 48 hours at room temperature.

The percent weight of solvent /fuel absorbed was calculated as follows:

$$M = M2-M1/M1 * 100 \qquad \text{-----------} (11)$$

Where M is the percent weight of solvent/fuel absorbed

M1 = initial mass of specimen in air , g

M2 = Mass of specimen in air after immersion, g

H. Demattia flexing (ASTM D 813-07)

This test method covers the determination of crack growth of vulcanized rubber when subjected to repeated bending strain or flexing. A molded test specimen with a pierced groove is repeatedly flexed on a De- mattia type machine with the flexing (blending) axis parallel to the groove. After adjustment of the apparatus and specimens, start the machine to record the k/cycles. Take frequent readings during the test. Stop the machine after 1000, 3000, and 5000 cycles' periods. Observe the specimens and measure the k/cycles at the time of initiation of crack and complete failure.

I. Swelling studies in toluene (ASTM D 471-98)

Test pieces weighing about 0.2g were punched out from vulcanized sheets of about 2mm thick and it was immersed in toluene in a squadish for 28hrs. the specimen were removed blot tightly with filter paper, place them immediately in a stoppered weighing bottle and determined the weight.

$$\Delta m = M_2 - M_1 / M_1 \times 100 \qquad \text{----------------------------} \; (12)$$

Δm = change in mass, %

M_1 = initial mass of the specimen, gm

M_2 = final mass of the specimen, gm

CHAPTER 3

REULTS AND DISCUSSION

Chapter 3

Results and discussion

3. Results and discussion

3.1. Latex properties

3.1.1 Particle size distribution of latex

The particle size distribution of ammonia preserved NR latex before and after irradiation is shown in Fig. 1. The particle size varies from about 100 nm 3000 nm for un-irradiated sample and that after irradiation is from about 100 nm to 2000 nm and a small number of particles in the range 5000 -6000 nm. The bimodal distribution is unchanged but the amount of bigger sized particles increase after irradiation. During irradiation it is possible that some chemical

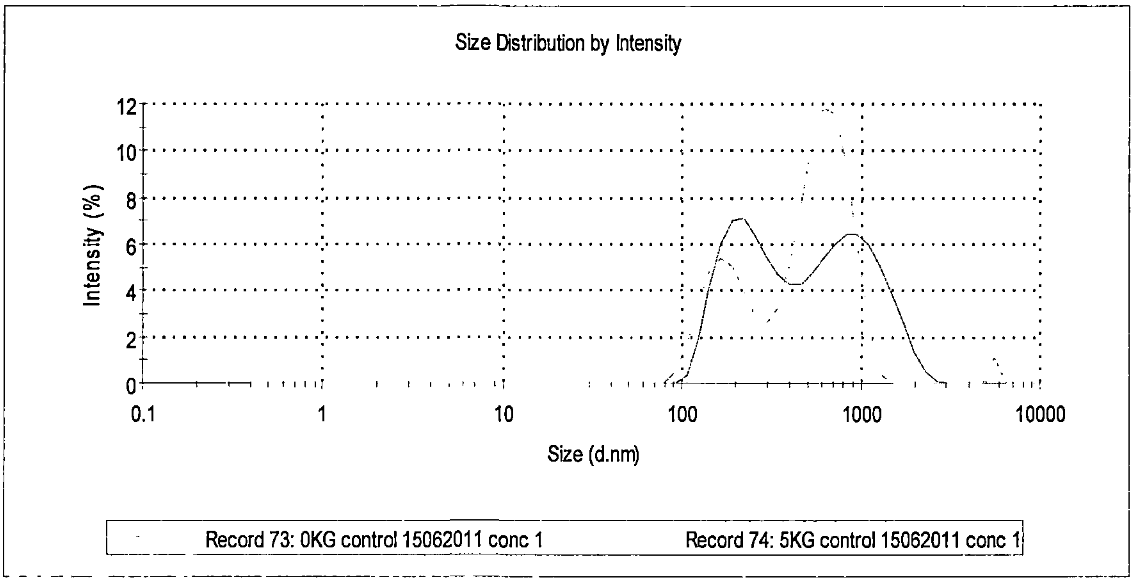


Figure 1 Particle size distribution of NR latex before and after irradiation

changes take place for the pertinacious materials and there can be antiparticle interactions that lead to a type of week agglomerations.

3.1.2 Raw rubber properties

The raw rubber properties of rubber obtained by irradiation of latex to different irradiation dose are given in Table 1.

Table 1. Raw Rubber Properties

Property		**Radiation dose**				
	ISNR 5	**0**	**1**	**3**	**5**	**10**
Nitrogen content, %	0.37	0.33	0.31	0.35	0.34	0.38
Po	42	29	30	30	33	39
PRI	50	7	7	10	9	5
Acetone extractable, %	2.65	3.87	5.29	5.92	5.95	2.09
Gel content, %	12	2	8	20	36	52

It is observed that the nitrogen content remains almost same while the Po increases with irradiation. The irradiated samples recorded higher PRI and acetone extractable compared to_unirradiated rubber up to a level of 5 kGy. It is also noted that on exposure of fresh NR latex to gamma radiation gel content increases with irradiation dose (Fig. 2) (Photograph 1).

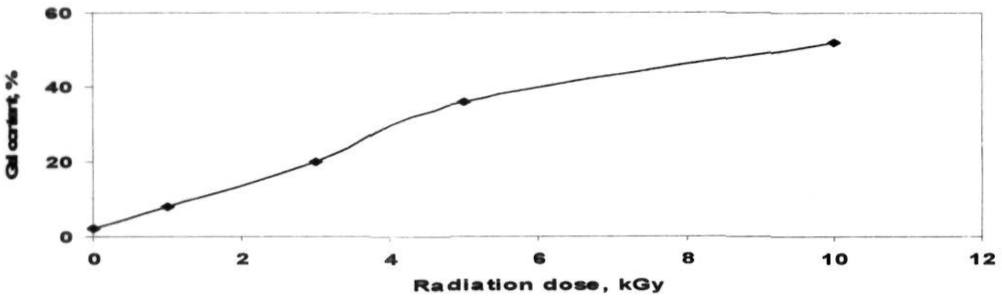


Figure 2. Gel content versus irradiation dose

Photograph 1

It is expected that there can be slight cross linking involving proteins leading to gel formation. An increase in Po and PRI for irradiated samples can be due to formation of gel during irradiation. A slight cross linking between rubber chains also contribute to increase in Po and PRI. Due to the chemical changes in the non rubber ingredients there is an increase in acetone extractable. Earlier reports show that proteins get degraded on exposure to radiation [20]

3.1.3 Viscosity and molecular weight

The data on flow characteristics using a viscometer is given in Table 2.

Table 2 Molecular weight determination by viscosity method

Dose of radiation	Conc. Of solution	Flow time	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity	Molecular weight*10^5
0	.3108	427	3.45	2.45	7.88	2.75	3.92
	.2082	289	2.34	1.34	6.43		
	.1041	180	1.46	.46	4.42		
1	.2951	480	3.90	2.90	9.82	3.5	5.78
	.1977	315	2.56	1.56	7.89		
	.0988	191	1.55	.55	5.56		
3	.2553	480	3.90	2.90	11.35	4.8	9.30
	.1787	328	2.67	1.67	9.35		
	.0983	210	1.71	.71	7.22		
5	.2067	324	2.63	1.63	7.89	4.9	9.58
	.1581	261	2.12	1.12	7.08		
	.0888	189	1.54	.54	6.07		
10	.1528	196	1.59	.59	3.82	3.58	5.98
	.1200	181	1.47	.47	3.82		
	.0837	161	1.31	31	3.70		

From the table it is observed that the intrinsic viscosity increases with irradiation. From plots of reduced viscosity versus concentration (Figs. 3 – 7), intrinsic viscosity is obtained and from which molecular weight is calculated[21].

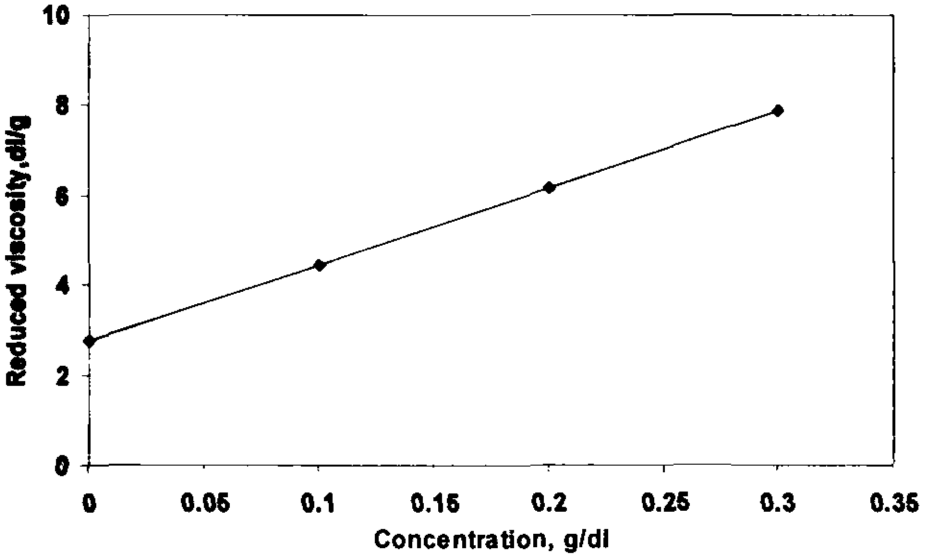


Figure 3 Concentration versus reduced viscosity (0 kGy)

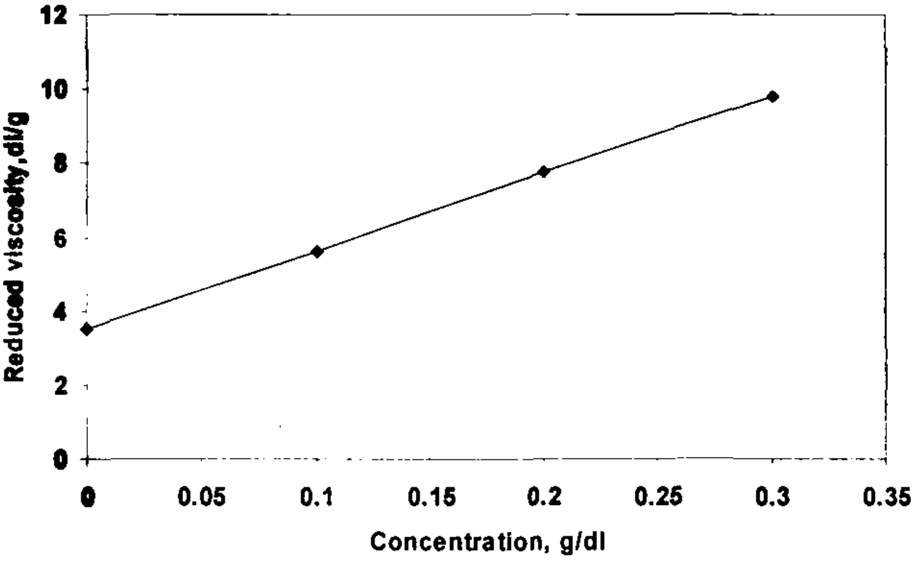


Figure 4 Concentration versus reduced viscosity (1 kGy)

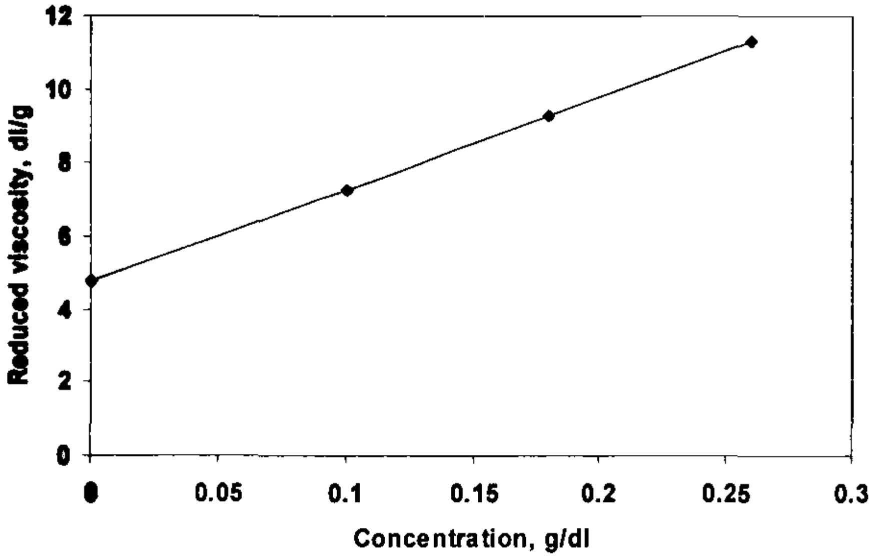


Figure 5 Concentration versus reduced viscosity (3 kGy)

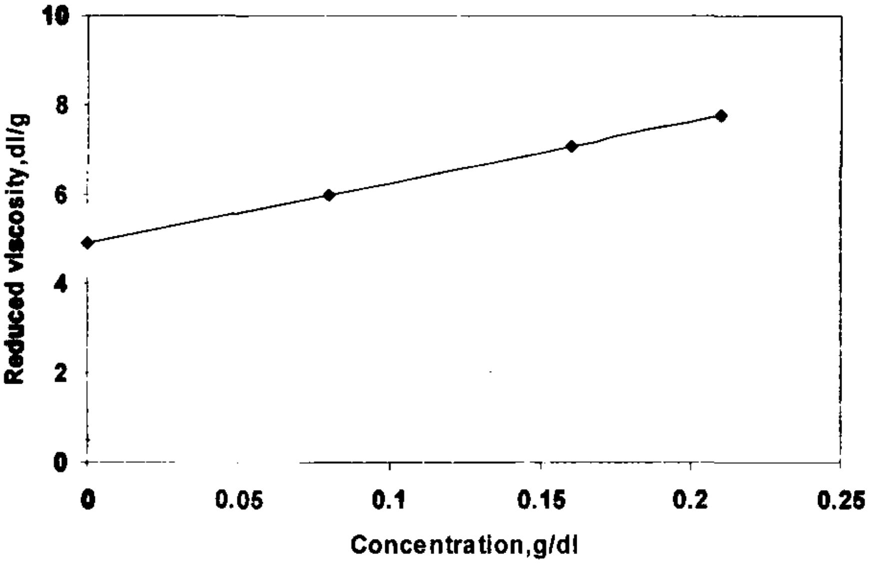


Figure 6 Concentration versus reduced viscosity (5 kGy)

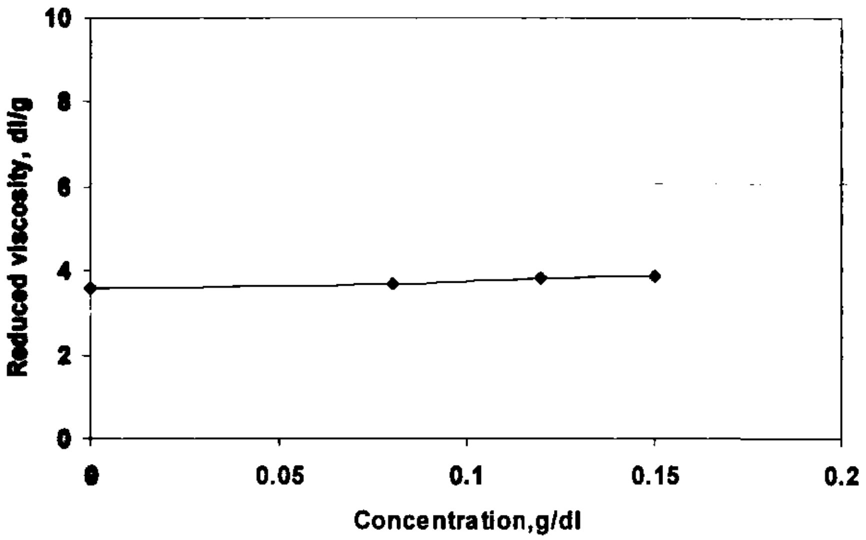


Figure 7 Concentration versus reduced viscosity (10 kGy)

Molecular weight calculated from intrinsic viscosity for the un-irradiated and irradiated rubber samples are given in Fig. 8. It is observed that the molecular weight increases with the irradiation dose up to 5 kGy and then decreases. The increase in molecular weight can be attributed to chain entanglements and light cross linking.

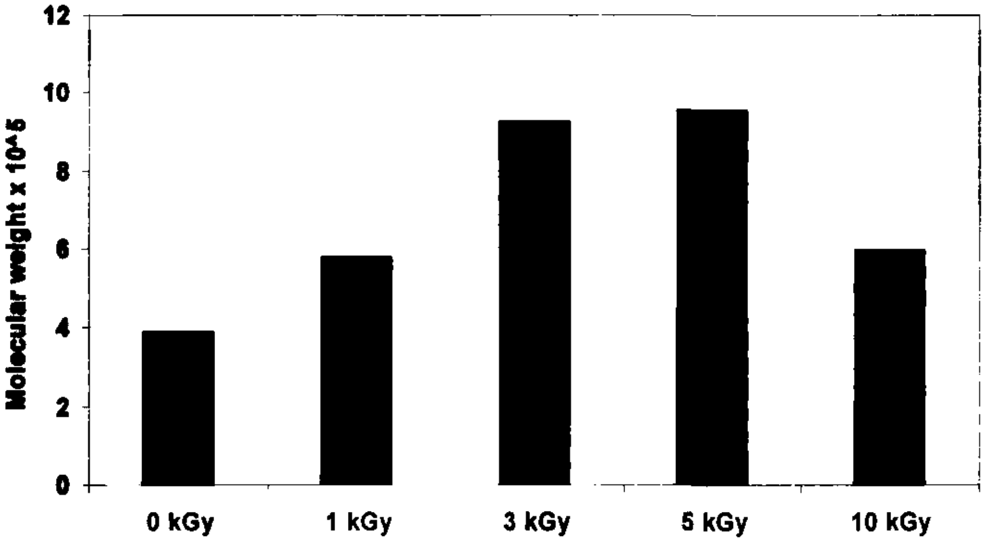


Figure 8 Molecular weight versus irradiation dose

3.1.4 Flow characteristics (Haake viscometer)

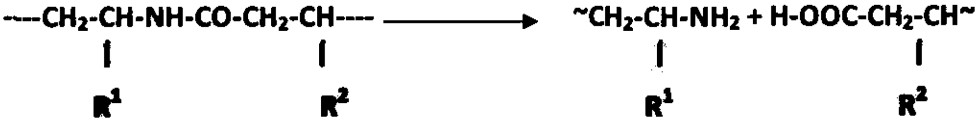
The flow characteristics as plots of viscosity versus shear rate of the rubber solution are given in Figs 9-10 and Table 3. It is seen that the flow is non-Newtonian as noted earlier [22]. The viscosity decreases as shear rate increases. It is also noted that the viscosity increases after irradiation.

Table 3 Viscosity versus shear rate

Shear rate / sec	Viscosity, mPa s			
	0	1	5	10
60	3.5	5	5.5	15
120	3	3.5	4.5	10
180	2.5	2	3.5	5

3.1.5 FTIR Studies

The IR spectra of irradiated and un-irradiated samples are shown in Figures 11 and 12. It is observed that the absorption due to amine at 3600 – due to OH stretching and at 1615 cm -1 due to amines increases as the radiation dose increases. Proteins contain CO-NH linkage which on hydrolysis produces – CO NH2 as shown below (Eqn 1)



$$\text{---}CH_2\text{-}\underset{R^1}{CH}\text{-}NH\text{-}CO\text{-}CH_2\text{-}\underset{R^2}{CH}\text{----} \longrightarrow \text{~}CH_2\text{-}\underset{R^1}{CH}\text{-}NH_2 + H\text{-}OOC\text{-}CH_2\text{-}\underset{R^2}{CH}\text{~} \quad \text{.......(1)}$$

Though it is expected that proteins undergo hydrolysis to low molecular weight fractions, and separated in serum this is not reflected in the nitrogen content as there is no substantial change in nitrogen content of rubber after irradiation. . It is possible that these lower molecular weight fractions are also retained on rubber during coagulation. On exposure to gamma radiation several chemical changes can take place in latex.

1. The proteins present in latex can undergo hydrolysis to lower molecular weight fractions

2. The rubber chains can undergo cross linking

In ammonia preservation process the phospholipids hydrolyses to form long chain fatty acids that combine with ammonia to form fatty acid soaps. The change in raw rubber properties is attributed to these chemical changes.

3.2 Dry mix

3.2.1 Cure characteristics

Cure characteristics of the dry mixed samples are given in Table 4. It is observed that rubber obtained through soap sensitized coagulation showed higher level of vulcanization and so recorded a higher rheometric torque as compared to conventional ISNR. However the scorch time and cure time is not changed significantly. Within the irradiated mixes prepared through soap sensitized coagulation, the cross linking as measured from rheometric torque increases as radiation dose increases up to 5 kGy and then decreases for 10 kGy irradiation . It is expected that soaps formed in latex get converted to fatty acids during coagulation. This fatty acid act as vulcanization activator and hence gives higher level of vulcanization.

Table 4. Cure characteristics - Silica and ISAF (Dry mix)

Parameter		**Irradiation dose, kGy**		
	ISNR 5	**0**	**5**	**10**
Mini. torque, dN.m	20.0	21.1	16.9	22.2
Max. torque, dN.m	83.5	86.8	100.1	92.7
Δ, Rheometric torque, dN.m	63.5	65.5	83.2	70.6
Optimum cure time (t_{90}) at 150°C, min	10.0	15.7	14.4	14.0
Scorch time (ts_2) at 150°C, min	2.0	2.1	2.9	2.8

3.2.2 Mechanical properties

Mechanical properties of the mixes are given in Table 5. The mechanical properties of rubber obtained through soap sensitized coagulation have higher modulus, lower heat build up and abrasion resistance compared to conventional rubber. The properties were further enhanced after irradiation to 5 kGy. The mechanical properties like modulus, tensile strength, tear strength, abrasion resistance increase with irradiation up to 5 kg and then the change is not significant. The compression set and elongation at break decreases with irradiation dose.

Table 5. Technological properties Silica and ISAF (Dry-Mix)

Properties		***Irradiation dose, kGy**		
	ISNR 5	**0**	**5**	**10**
100 % Modulus, MPa	1.6	1.73	2.5	2.2
200 % Modulus, MPa	2.8	3.11	5.6	4.9
300 % Modulus, MPa	4.4	5.01	5.65	5.1
Tensile strength, MPa	25.8	22.65	24.3	25.4
Elongation at break, %	948	873	534	570
Tear strength, N/mm	102	98	92	109
Hardness, Shore A	60	58	58	56
Abrasion loss, mm3	159	139	124	136
Heat build-up, ΔT°C	19	14	13	14
Compression set, %	51	47	46	47

*soap sensitized coagulated rubber

3.2.3 Ageing studies

Ageing was done at 100°C for3 days. Due to the high temperature the rubber underwent oxidation to a higher level and so elongation at break and tensile strength deteriorated. Within the unirradiated and irradiated ones the latter showed better air ageing characteristics (Table 6)

Table 6. Ageing characteristics after ageing at 100°C, 3days

Properties	ISNR 5	Irradiation dose, kGy		
		0	5	10
Tensile strength, MPa	2.9	3.1	3.7	2.8
Elongation at break, %	42	59	60	54

3.3 Effect of latex stage incorporation of fillers

3.3.1 Cure characteristics

Cure characteristics and mechanical properties of the latex stage blended samples are given in Tables 7 and 8 respectively. It is observed that the cure characteristics and mechanical properties are improved for the latex stage incorporated samples as compared to dry mixes which is further improved with irradiation dose.

Table 7. Cure characteristics - Silica and ISAF (Latex mix)

Parameters	ISNR 5	Irradiation dose, kGy			
		0	1	3	5
Mini. torque, dN.m	20.0	14.1	15	17.9	18
Max. torque, dN.m	83.5	86.4	122.9	113.7	103
Δ, Rheometric torque, dN.m	63.5	72.3	80	83	85
Optimum cure time (t90) at 150°C, min	10	14.4	13.1	14.3	13.7
Scorch time (ts2) at 150°C, min	2.0	2.7	2.1	2.2	2.3

3.3.2 Technological properties

The latex stage incorporated mix showed higher modulus, higher tensile strength, lower elongation at break, lower heat build-up and lower abrasion loss as compared to dry mix (ISNR 5). On latex stage incorporation, latex exposed to gamma radiation gave vulcanizates with higher modulus, higher tensile strength, higher hardness, lower abrasion loss, lower compression set and lower heat build-up. The improvement in mechanical properties is attributed to the better filler dispersion and higher level of vulcanization due to the in situ formed fatty acids that act as cure activators.

The rubber recovered after exposure to gamma radiation to which filler is incorporated by conventional mill mixing technique showed a considerably lower heat build-up than the similar rubber in which the filler is incorporated in the latex stage. However the modulus obtained by latex stage incorporated mix is higher.

Heat build-up follows the order 5 kGy dry mix < 5 kGy latex incorporated mix < ISNR 5

Modulus follows the order 5 kGy latex incorporated mix > 5 kGy dry mix > ISNR 5

Abrasion resistance follows the order 5 kGy dry mix > 5 kGy latex incorporated mix >> ISNR 5

Table 8. Mechanical properties - Silica and ISAF (Latex mix)

Parameter	Irradiation dose, kGy			
	0	1	3	5
100 % Modulus, MPa	1.4	1.5	1.9	2.1
200 % Modulus, MPa	2.3	3.1	3.8	4.3
300 % Modulus, MPa	4.1	5	7	8.1
Tensile strength, MPa	20.3	20.9	21.4	21.7
Elongation at break, %	471	398	463	451
Tear strength, N/mm	78	80	82	79
Hardness, Shore A	70	77	70	71
Abrasion loss, mm3	131	124	129	127
Heat build-up, ΔT°C	22	22	19	18
Compression set, %	59	58.9	61.7	56.8

3.4 Solvent swelling

The solvent swelling resistance of dry and latex mixes is given in Figs. 13 and 14 respectively. The solvent swelling resistance increases with soap sensitization and the resistance further increased with irradiation. On latex stage incorporation the solvent resistance further increases.

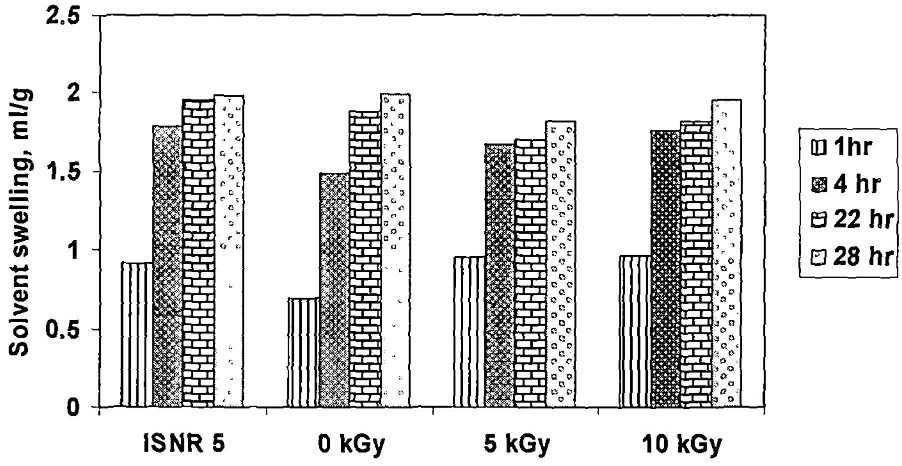


Figure 13 Solvent swelling versus irradiation dose (Dry mix)

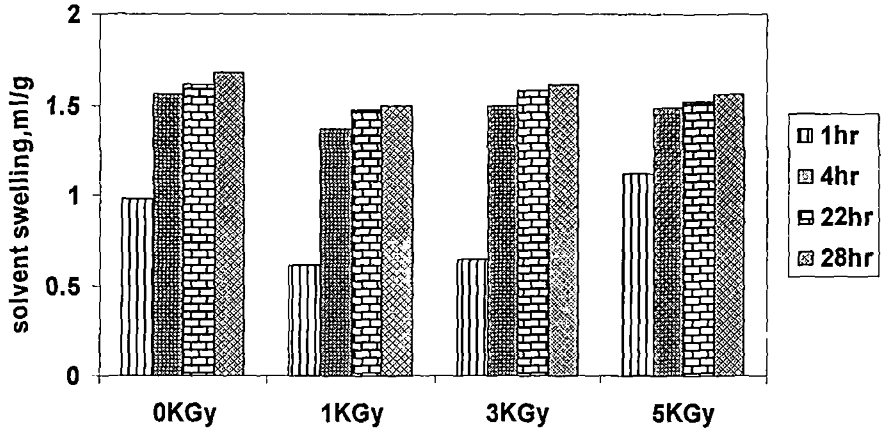


Figure 14 Solvent swelling versus irradiation dose (Latex mix)

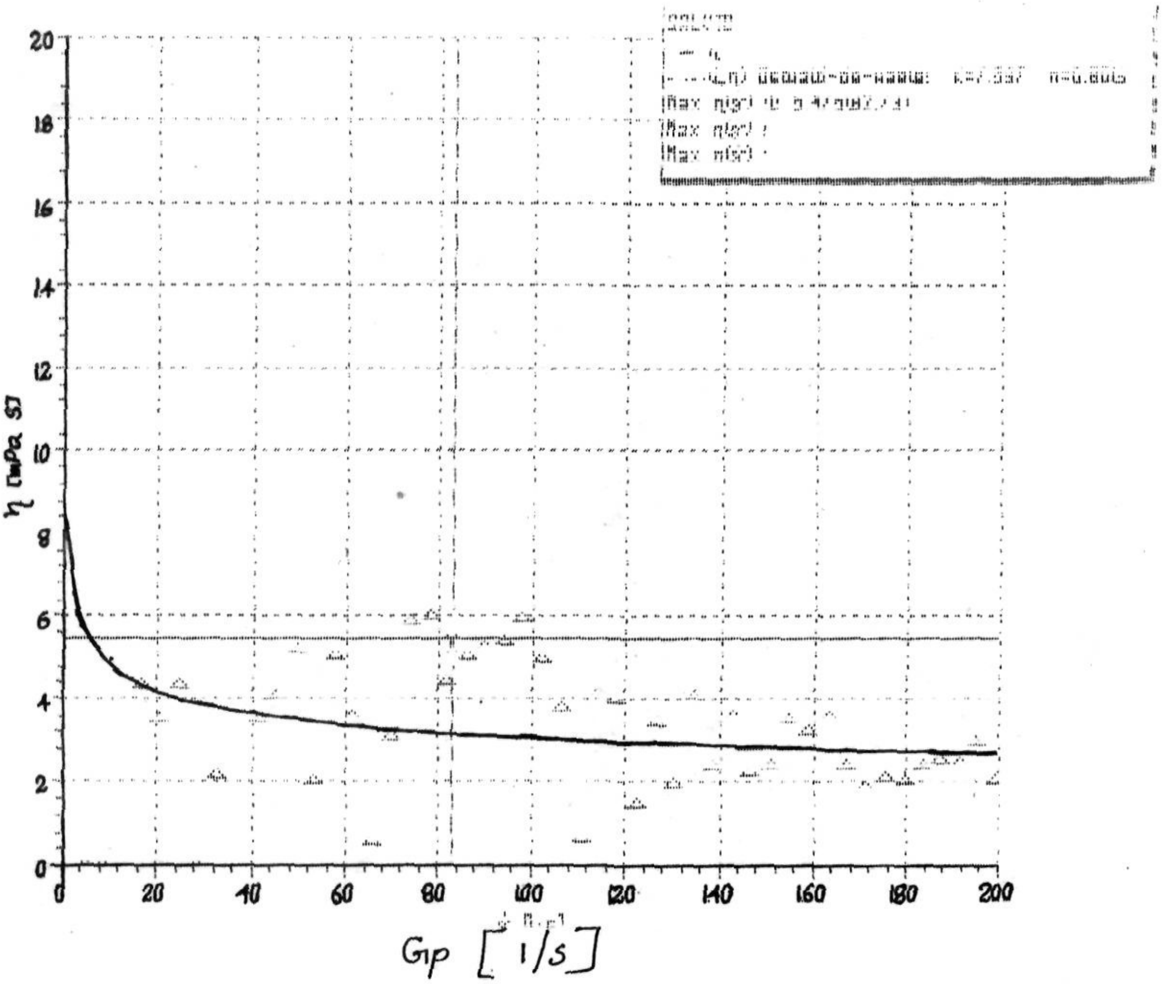


Figure 9. Viscosity versus shear rate of the rubber solution (okbry of 0.3% concentration)

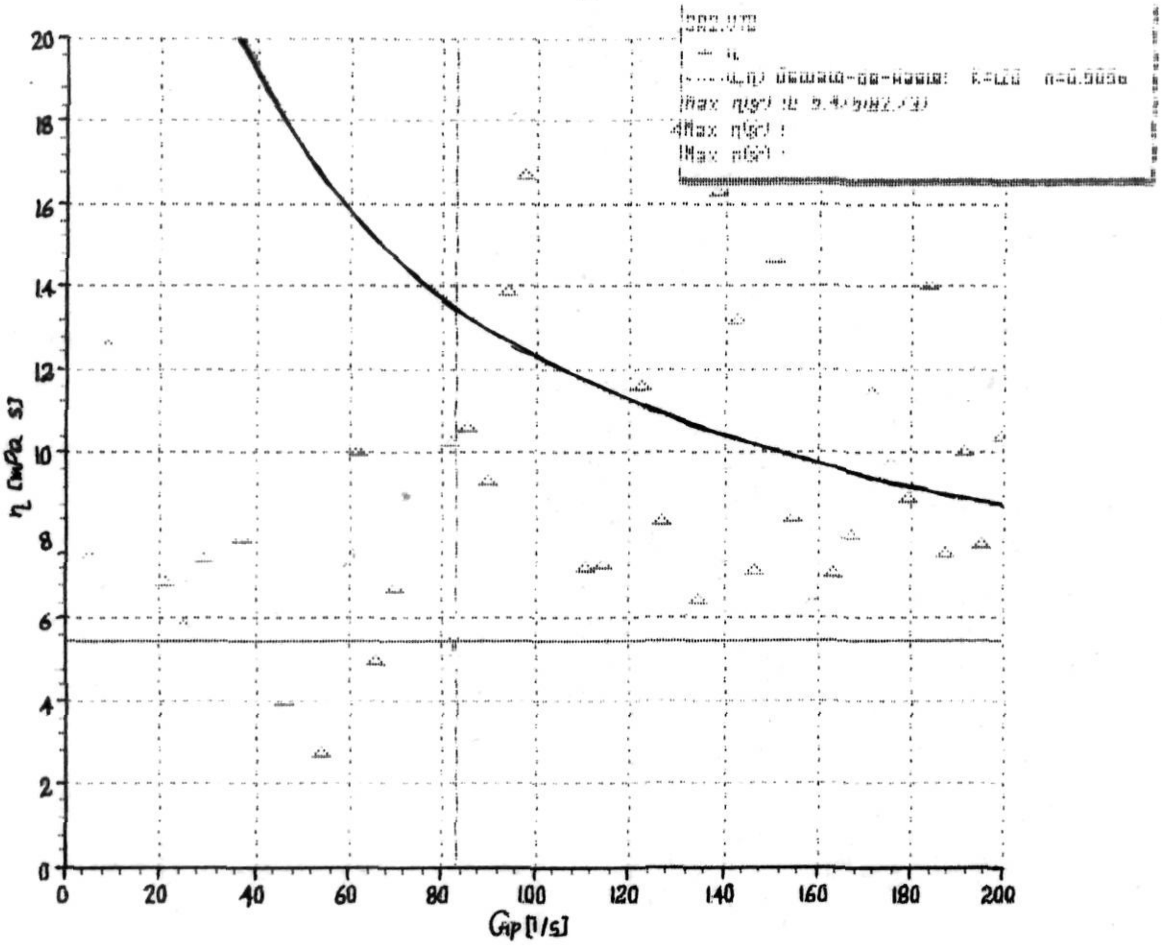


Figure 10. Viscosity versus shear rate of the rubber solution
(5kGy of 0.3 % concentration)

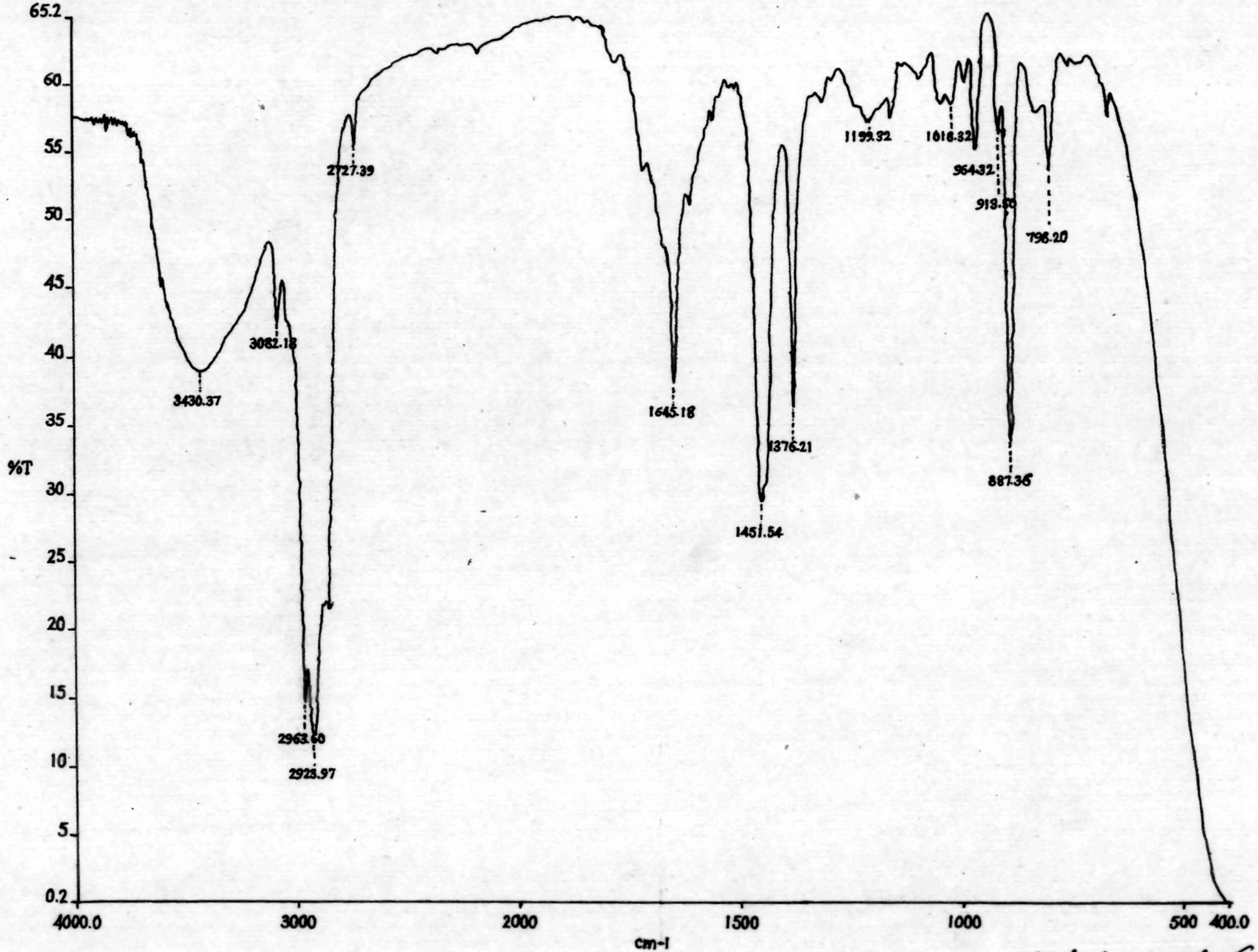


Figure 11. IR Spectra of un-irradiated sample (0 kGy)

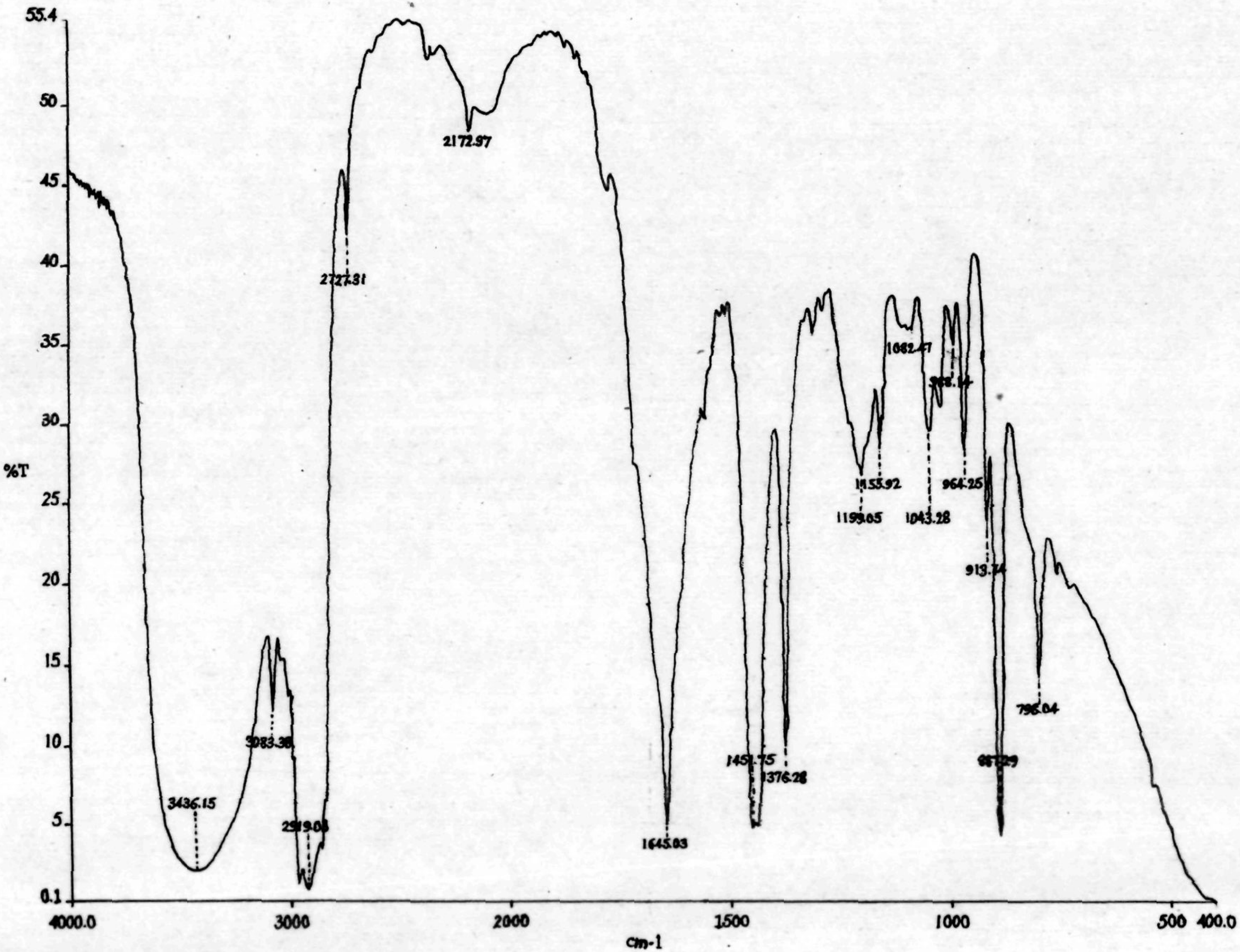


Figure 12. IR Spectra of irradiated sample (5k Gy)

CHAPTER 4

SUMMARY AND CONCLUSION

Chapter 4

Summary and Conclusion

4 Summary and Conclusion

Rubber of higher gel content was obtained by exposing fresh NR latex to gamma radiation of doses varying from 1-10 kGy. It was observed that NR latex when exposed to 5 kGy shows the best curing characteristics and mechanical properties. ISAF black and silica fillers together were used at a level of 50 phr in 1:1 ratio. The fillers were incorporated to the dry mix and also in the latex stage. The latex containing fillers were coagulated by acids, dried and processed in the conventional way. The cure characteristics and mechanical properties were found and the following conclusions were made.

1. Rubber prepared by soap sensitized coagulation has a higher modulus as compared to conventional NR.
2. The mechanical properties can be improved by exposure of latex to gamma radiation, followed by conversion into dry rubber and further processing.
3. Latex stage incorporation gives vulcanizates with superior mechanical properties that is further improved by prior exposure of latex to low doses of gamma radiation.

The rubber recovered after exposure to gamma radiation to which filler is incorporated by conventional mill mixing technique showed a considerably lower heat build-up than the similar rubber in which the filler is incorporated in the latex stage. However the modulus obtained by latex stage incorporated mix is higher.

Heat build-up follows the order 5 kGy dry mix < 5 kGy latex incorporated mix < ISNR 5

Modulus follows the order 5 kGy latex incorporated mix > 5 kGy dry mix > ISNR 5

Abrasion resistance follows the order 5 kGy dry mix > 5 kGy latex incorporated mix >> ISNR 5

It is observed that due to the presence of surfactants formed during irradiation in latex, the level of vulcanization is higher and mechanical properties are also better. Such advantages are not obtained by conventional mill mixing method.

References

1. Markham, C.R.(1976), Journal of Society of Arts (473-482).
2. Wiltshire,J.L. (1932), Journal of Rubber Research Institute of Malaya, 4 (2), (94-103).
3. Blackley, D.C, Polymer Latices, Vol. 1,2 & 3.
4. Gyss, P.R. and Fluerot, M. (1969), Five Years of Natural Rubbers, Journal of Rubber Research Institute of Malaya, 22 (1): 70-77.
5. Johnston, J.P. (1966), Planters' Bulletin, 105: 299-305.
6. BIS (1992), Indian Standard 4588(1986), Bureau of Indian Standards, New Delhi.
7. ASTM (1996) D 2227-96, American Society for Testing and Materials.
8. Bekeman, N.P. (1969), Consumer appraisals of natural rubber, Journal of Rubber Research Institute of Malaysia, 22 (1): 1-13.
9. Crop processing and Agromanagement, 2000, P.J.George and Kuruvilla Jacob (Eds), Rubber Research Institute of India.
10. Ng, C.S. (1983), Quaternary Ammonium Surfactants as Alternative Coagulants by Skim Latex- A laboratory study, Journal of Rubber Research Institute of Malaysia, 31 (1): 49-59.
11. Khoo. T.C., Ong, C.D. and Rais, A.R. (1991), A New Process for Skim Rubber Production, Proceedings, Rubber Research Institute of Malaysia, Rubber Growers Conference, 1991, Kuala Lumpur, Malaysia, pp: 495-509.
12. Morris, J.E. (1954), Proceedings of the Third Rubber Technology

Conference, 1954, London, U.K, pp: 13-37.

13. Coran, A.Y. (1978), Science and Technology of Rubber (291-335).

14. Dogadkin, B.A., Tara Sorer, Z.N. and golberg (1962), Proceedings 4th Rubber Technology Conference, London, IRI, 65-67.

15 Bateman, L., Moor, C.G. Porter and Saville, B. (1963), The Chemistry and Physics of Rubber - Like Substances (451-561).

16. Chapman, A.V. and Porter, M. (1988), Natural Rubber Science and Technology (511-601).

17. Blow, C.M (1971), Rubber Technology and Manufacture, Chapter-5, The Chemistry and Technology of Vulcanization (148-153).

18. Gelling, I.R. and Morison, N.J. (1985) Vol.58, Sulphur Vulcanization and Oxidative Ageing of Epoxidised Natural Rubber (256-259).

19. Banja, J. (2000), The Rubber International Magazine 2 (19), (79-85).

20. Minoura, Y. and Asao, M. (1961), Studies on the γ-irradiation of natural rubber latex. Journal of Applied Polymer Science, 5: 233–239. doi: 10.1002/app.1961.070051416.

21. Billmayer F.W. ,Text book of polymer science,3rd edition, Wiley-inter science, New York, 1984.

22. F. Patat and G. Spott Non-Newtonian Flow of Polymer Solutions Rubber Chem. Technol. 39, 1411 (1966).