QUALITY IMPROVEMENT OF RVNRL BY BLENDING WITH HIGH STYRENE , STYRENE BUTADIENE RUBBER LATEX

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE

REQUREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN APPLIED CHEMISTRY

BY

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UNDER THE GIIDANCE OF

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1955-2005
Golden Jubilee

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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/3 29/6/2012

CERTIFICATE

This is to certify that the thesis titled “Quality improvement of RVNRL by blending with high styrene, styrene butadiene rubber latex ” being submitted by Kum. Subina C.B., 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. Kum. Subina C.B., has worked on her research topic from April 2012 to June 2012, under my supervision. The results included in this report have not been submitted for the award of any other degree.

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Certified that this Project Report entitled "**QUALITY IMPROVEMENT OF RVNRL BY BLENDING WITH STYRENE,HIGH STYRENS BUTADIENE RUBBER LATEX**" is the bonafide record of work done by SUBINA C.B 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..

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ACKNOWLEDGEMENT

I express my deep sense of gratitude to Dr. Rosamma Alex, Dy. Director, 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. Abdul mujeeb 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 Mrs. Susamma Joseph, Mrs. Valsa George, Mrs. Treesa Cherian, Mr.madhusudhanan for their assistance at various stages of the project.Igreatefully aknowledge the full co-operation and immense help from Mr.John Britto,Radiological safety officer,RRII Kottayam,during my all stages of work. I would also acknowledge with thanks the service rendered by the RRII Library.
I would like to thank my parents and my friends for their encouragement and valuable helps.

Subina C.B

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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 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 Marketable Forms of Natural Rubber

These marketable forms of rubber form the raw material for the very large number of rubber products in both tyre & non tyre sector. About 10% of the total crop is converted in to latex concentrated. And these forms the raw material for the different latex based product like gloves ,balloons, catheters etc.

- Sheet Rubber
- TSR
- Crepe Rubber
- PFL& Latex concentration

1.2.1 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 are 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. 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.

1.2.2 Technically Specified Rubber

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.

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).

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

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.

1.2.3 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.

1.2.4 PFL& Latex Concentration

To keep latex for longer periods 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

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.

1.2.4.1 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.

1.2.4.2 PRESERVATION OF LATEX

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

It should destroy or inactivate microorganisms.

It should contribute positively to the colloidal stability of latex by increasing the charge on the particles and the potential at the rubber –serum interface.

It should deactivate or remove traces of metal ions present in latex.

It should not be harmful to people.

It should not have adverse reaction on rubber or containers of latex.

It should be cheap, readily available and convenient to handle.

1.2.4.3 Importance of Ammonia as a Preservative

Use of ammonia was described in 1853. Now ammonia is the most widely used preservative. Ammonia at a concentration of 0.7-1.0% by weight of latex is added for preservation. This treatment preservers latex and maintains it in a stable colloidal *condition almost indefinitely.* Also *during storage the higher fatty acid esters present in* latex get hydrolyzed into ammonium soaps, which improve the mechanical stability of latex

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

1.2.4.4 LATEX CONCENTRATES.

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.

1.2.4.4.1 Centrifugation

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.

1.2.4.4.2 Evapouration

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.

1.2.4.4.3 Electrodecantation

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.

1.2.4.4.4 Creaming

Creaming of latex is done with the use of materials known as creaming agents. This process is simple and involves only simple machinery and low power consumption. Hence small scale latex goods manufacturers can produce concentrated latex by this technique.

Principles of creaming

Rubber latex is a dispersion of rubber particles in an aqueous serum. In any dispersion, the dispersed particles cream or sediment under the influence of gravity. Rubber particles being lighter than serum tend to cream up. The velocity of creaming depends up on number of factors and it can be mathematically stated as,

$$v = \frac{2g(Ds - Dr)\, r^2}{9\eta}$$

When creaming is done with the help of creaming agents, the effective size of latex particles increased and this enhances the velocity of creaming.

One mechanism suggested for creaming is that the creaming agent is absorbed on to the surface of rubber particles and this is some way favors the agglomeration of the particles to form relatively large groups.

When ammonia preserved field latex which contains creaming agent is allowed to stand, a slowly increasing volume of serum separates at the bottom in the form of a lower layer. The boundary separating serum and cream gradually moves upwards, so that the volume of cream falls progressively while its rubber content increase. The serum that separates at the bottom 2-3% by wt of rubber, when the desired level of creaming is obtained, serum is drain off.

Creaming agents

A large number of vegetable gums and gelatinous materials as well as many synthetic substances have been tried as creaming agents. But on the basis of cost, efficiency and availability only a few have been found to be satisfactory. These are sodium alginate, ammonium alginate and tamarind seed powder. As tamarind seed powder readily available in cheap rate, it is the most widely used creaming agent in India.

All creaming agents have certain properties in common. They swell in water and form viscous solutions in water at lower concentrations.

Creaming process

1. Preparation of creaming agent solution

Creaming agents are generally added to latex as a 3% solution in water. Sodium and ammonium alginates are fully soluble in water and hence their solution can be prepared by adding the chemical in to the required quantity of hot water, preferably at 50-60degC, and stirring the same until a clear solution is obtained. This solution is then sieved through voil cloth and allowed to cool to room temperature before adding in to latex.

Tamarind seed powder is not soluble in cool water. Its solution is prepared by first allowing the powder to swell in water for some time and then making it in to slurry. The slurry is then boiled for one hour and the loss in volume during boiling is made up by adding the required quantity of water. It is then sieved through voil cloth to remove uncooked materials. The total solid content of this solution is determined before adding in to latex if necessary.

The dosage of creaming agent generally 0.2 parts for 100 parts by weight of latex, that is 400gms of creaming agent for 200 liters. Sodium and ammonium alginates are added as per this rate, but for tamarind seed powder a higher quality, 0.25 parts for 100 parts of latex by weight is required, since there will be some loss of uncooked material during sieving. That means for each barrel of latex, about 500gms of tamarind seed powder is required.

2. Preparation of soap solution

Small concentrations of fatty acid soaps in latex increase the efficiency of creaming. Hence soap solutions are added to latex during creaming. Soap such as potassium oleates, ammonium oleates, etc can be used. Commercially, washing soaps are also being used. Soap is prepared by dissolve it in the required quantity of water.

The dosage of soap during creaming is 0.05 parts for 100 parts by weight of latex. For 200 liters of latex 100gms of soap is required.

3. Creaming process

Latex is collected and ammoniated to 1-1.2 percent by weight on latex and kept for a few (about 70) days for ageing. The creaming agent solution at 3% concentration is prepared as describe. The preserved latex is transferred to creaming tanks, without disturbing the sludge content at the bottom. Calculated quantity of creaming agent solution, sufficient quantity of 10% solution of soap is added so as to get a final concentration 0.05% soap on latex. The latex is then thoroughly stirred for one hour. Since creaming agent solution is viscous, it will mix with latex only if it is thoroughly stirred. Otherwise, the unmixed portion drops to the bottom of the tanks and its value is lost. Therefore, complete dissolution of the creaming agent and thorough mixing of solution in latex are very important. After stirring, the latex is allowed to remain undisturbed till the desired level of creaming is obtained.

4. Equipment

The essential equipment for creaming latex is one or more vertical tanks of proper size depending on the amount of latex to be handled. The height diameter ratio of the tank should be preferably more than two in order facilitate separation of the serum. It should preferably have a conical or slopping bottom with an outlet valve at the lowest point. This valve shall preferably be a gate for easy flow of latex

1.2.5 COMPOUNDING OF LATEX

The main process involved in the production of latex based rubber goods is compounding. This is the process in which various chemicals are mixed to latex Some of the important compound ingredients added are

1. The chemicals that helps in vulcanization
2. Fillers that improve the modulus & strength of rubber

The most common vulcanizing agent is sulphur and the common accerlerators are ,zinc diethyl dithiocarbamate, Zinc mercapto benzothiazole, Tetramethyl thiuram disulphide and xanthates. The cure activator is zinc oxide. The commonly used filers are clay , silica and mica.

. By compounding there is very large improvement in physical properties of rubber. There is improvement in strength and ageing resistance after compounding and vulcanization.

1.2.5.1 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

1.2.5.2. Sulphur vulcanization

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

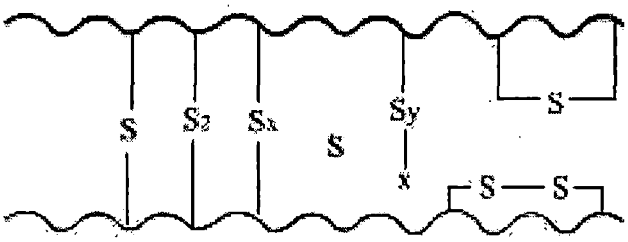
Conventional systems give vulcanizates which possesses excellent initial properties like strength, resilience and resistance to fatigue and abrasion and are satisfactory for many applications. However their heat ageing resistance, creep and stress relaxation properties are less satisfactory. For good 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

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.



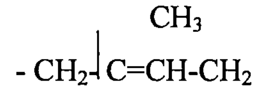
An estimate of the no. of sulphur atoms for each crosslink formed has been made. An unaccelerated rubber sulphur vulcanizate may give a figure of 40-45 whilst in conventional accelerated sulphur vulcanizates this "inefficiency" figure may drop to 10-

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 (eg. thio carbomate or benzthiozyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber bound intermediate.

$X\,SxZn\,SxX + RH \rightarrow X\,Sx\,R + ZnS + HSx\text{-}1X$

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.

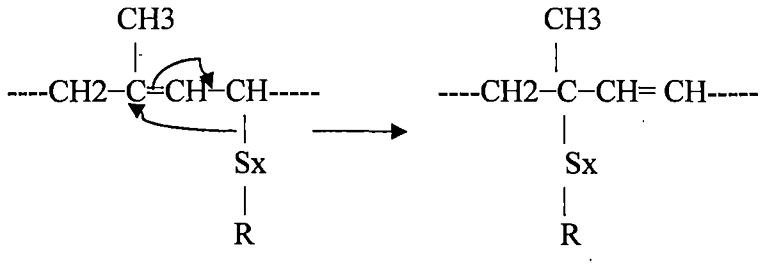


$-CH_2-\overset{CH_3}{C}=CH-CH_2$

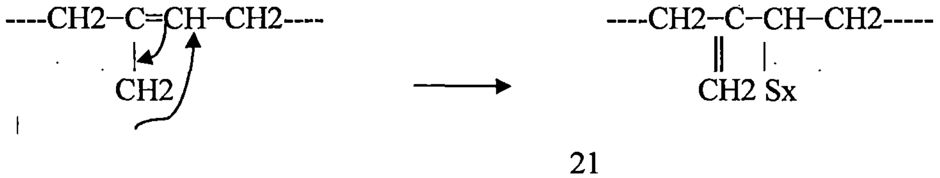
The intermediate XSxR then react with a molecule of rubber hydrocarbons RH to give a crosslink and more accelerators is regenerated.

$XSxR + RH \rightarrow RSx\text{-}1R + XSH$

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.

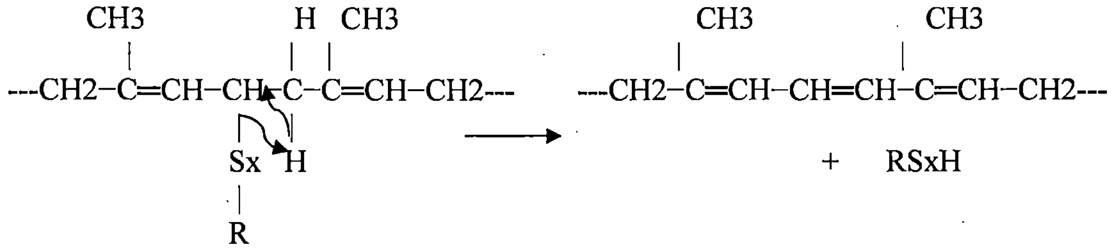


And



$$\underset{\text{Sx–R}}{|} \qquad\qquad\qquad \underset{\text{R}}{|}$$

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



$$\text{---CH2–}\overset{\text{CH3}}{\overset{|}{\text{C}}}\text{=CH–}\underset{\underset{\underset{\text{R}}{|}}{\text{Sx}}}{\text{CH}}\text{–}\overset{\text{H}}{\overset{|}{\underset{\underset{\text{H}}{|}}{\text{C}}}}\text{–}\overset{\text{CH3}}{\overset{|}{\text{C}}}\text{=CH–CH2---} \longrightarrow \text{---CH2–}\overset{\text{CH3}}{\overset{|}{\text{C}}}\text{=CH–CH=CH–}\overset{\text{CH3}}{\overset{|}{\text{C}}}\text{=CH–CH2---} + \text{RSxH}$$

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

DRAWBACKS OF SULPHUR VULCUNIZATION

It is reported that SVNRL (Sulphur Vulcanized Natural Rubber Latex) products like examination gloves, surgical gloves, catheters etc, may cause health problems in some of the users. This is due to the residual traces of accelerators or chemicals, which causes allergy (Type IV). The residual proteins causes allergy (Type 1).Moreover, nitrosamines are produced in the latex products by this nitrosation reaction of secondary amines generated from antioxidants or accelerators. These accelerators are carcinogenic. Hence it becomes necessary to develop a new technology to vulcanize NR latex to avoid the above health problems.

1.2.5.3 RADIATION VULCANIZATION

The radiation vulcanization of natural rubber latex has been investigated for a long time since early 1960's. The technique was not been used in industries due to the high cost of irradiation, low quality products and ambiguous advantages of the products. But recently, significant progress has been made in cost reduction and quality improvement in support of

International Atomic Energy Agency (IAEA) and United Nations development program known as Regional Co- operative Agreement (RCA).

In RVNRL, the cross – linking of rubber particles in natural rubber latex is brought about by Gamma radiation coming from a Co-60 source..

Nature of latex used for radiation vulcanization

Latex collected from plantation will have a rubber content of 30-40%. For industrial uses, this latex is concentrated to 60% rubber content and this concentrated latex is used for RVNRL production.

Source of irradiation

Generally, the source of radiation is Co-60. It is a radioactive isotope of cobalt with an atomic weight of 60. It does not exist in nature. It is produced by bombarding a suitable nucleus of Co-59 with a neutron in nuclear reactor.

The reaction is as follows.

$_{27}\mathrm{Co}^{59} + {}_{0}n^{1} \rightarrow {}_{27}\mathrm{Co}^{60}$

This Co-60nucleus being unstable emits energy in the form of gamma rays and beta rays. But these beta rays are recaptured by the source itself.

$_{27}\mathrm{Co}^{60} \rightarrow \gamma\text{-ray} + \beta\text{-ray} + {}_{28}\mathrm{Ni}^{60}$

Production of Soluble Protein free latex by radiation process.

During irradiation of NR latex for vulcanization, the latex proteins undergo disintegration, which lives high soluble protein content. In order to follow up the effects of radiation on NR protein, field latex was irradiated with gamma rays and the soluble protein concentration in the rubber phase and the scrum phase where analyzed. It was found that the water solubility of proteins in the latex increases with increasing dose. In the soluble protein content in the cream face (rubber) decreased whereas that in the serum phase increased with radiation dose SDS-PAGE analysis revealed that the 27 KD protein together with 14KD appear in the radiation vulcanized latex up to a radiation dose of 160 KGY and at 320 KGY in the disappear due to disintegration by radiation. A new process for the preparation of protein-free latex has been developed (3).

In the new process the radiation pre vulcanized centrifuged latex is subjected to dilution and then centrifuged in the case of field latex, it is irradiated first and then centrifuged after dilution. The new process results in prevulcanized latex almost free from solid protein. Tensile strength of the sample produced from the new process is comparable to that from the conventional radiation process

SENZITIZERS.

Radiation vulcanization of natural rubber latex can be obtained by irradiating NRL without using Senzitizer. But the vulcanization dose (DV-the dose at which the maximum tensile property of irritated latex is found) needed will be about 200-300 KGY. This is too high to be used for industrial application. So it become necessary to degrees the dust to a considerable extent which is active by adding a suitable senitizer. n- BA is selected as the suitable sensitizer for RVNRL because it can be easily removed by drying owing to its high vapour pressure. But the addition of n-BA increases the viscosity of NRL, sometimes causing coagulation. To stabilize NRL against n-BA, KOH is added as stabilizer. In practice, phr KOH is enough to stabilize the latex containing 5 phr of n-BA.

In order to decreases the doe to a considerable extent, it is necessary to add a suitable sensitizer. Requirements of a sensitizer are:

- Non-toxic
- Easy availability and low cost
- Easy removal of uncreated part

The commonly used sensitizer are n-BA(n-butylate acrylate) . The sensitizing action of n-BA

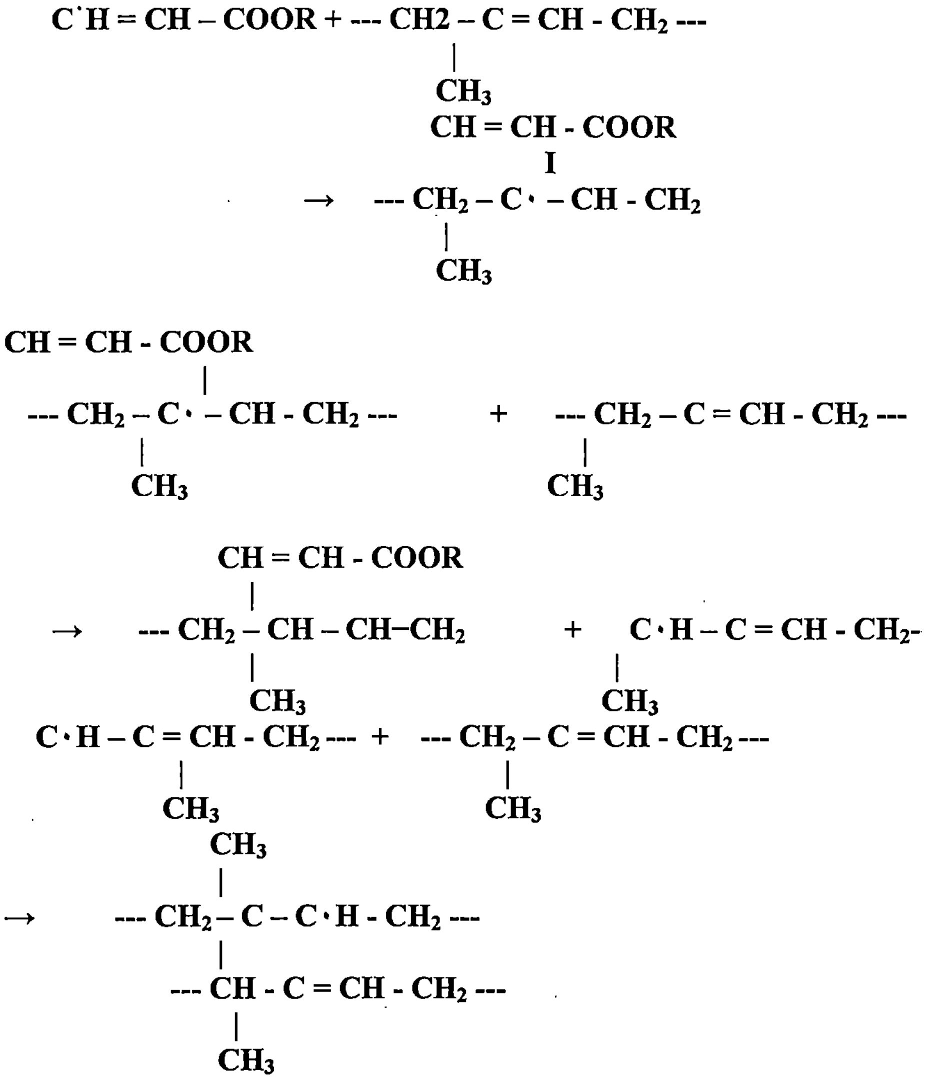
SENZITIZING MECHANISM OF n-BA

The mechanism of sensitizing action of MFA can be represented in the following manner.

$$CH_2 = CH - COOR \xrightarrow{\gamma rays} C^{\cdot}H = CH - COOR + H^{\cdot}$$

(Acrylate radical)

As acrylate radical formed more mobile than the rubber chain; it attacks a double bond in the adjacent chain.



$$C^{\cdot}H = CH - COOR + \text{---}\,CH2 - \underset{\substack{|\\ CH_3}}{C} = CH - CH_2\,\text{---}$$

$$\rightarrow \text{---}\,CH_2 - \underset{\substack{|\\ CH_3}}{C^{\bullet}} - \overset{\substack{CH = CH - COOR\\ I}}{CH} - CH_2$$

$$\text{---}\,CH_2 - \underset{\substack{|\\ CH_3}}{\overset{\substack{CH = CH - COOR\\ |}}{C^{\bullet}}} - CH - CH_2\,\text{---} \quad + \quad \text{---}\,CH_2 - \underset{\substack{|\\ CH_3}}{C} = CH - CH_2\,\text{---}$$

$$\rightarrow \text{---}\,CH_2 - \underset{\substack{|\\ CH_3}}{\overset{\substack{CH = CH - COOR\\ |}}{CH}} - CH - CH_2 \quad + \quad \underset{\substack{|\\ CH_3}}{C^{\bullet}H} - C = CH - CH_2 -$$

$$\underset{\substack{|\\ CH_3}}{C^{\bullet}H} - C = CH - CH_2\,\text{---} \; + \; \text{---}\,CH_2 - \underset{\substack{|\\ CH_3}}{C} = CH - CH_2\,\text{---}$$

$$\rightarrow \begin{array}{l} \text{---}\,CH_2 - \underset{\substack{|}}{\overset{\substack{CH_3\\ |}}{C}} - C^{\bullet}H - CH_2\,\text{---} \\ \text{---}\,\underset{\substack{|\\ CH_3}}{CH} - C = CH - CH_2\,\text{---} \end{array}$$

(Cross linked structure)

Addition of antioxidants:

The effective way of improving the thermal oxidative degradation radiation vulcanizate by using anti oxidant.The anti oxidant also decreases the gel fraction.The anti oxidant, selected for RVNRL is TNPP(tris-nonylated phenyl phosphate). The necessary requirement for a antioxidant is that it should not cause any allergic reactions or generate any nitrosamines.

A) **TNPP**(tris –nonylated phenyl phosphate)

RVNRL films ,containing 2phr TNPPas anti oxidant shows very good ageing behaviour.Actual effect of TNPP on ageing property RVNRL films were examined as measured by the retention of Tb and Eb of vulcanizite aged at 100^0 c for 20 hrs. The Tb & Eb of the vulcanizite before ageingwere 30 Mpa and 10 -20% respectively .With 2 Phr of TNPP 99% of Tb retention was achieved.The appearance of the aged film containing TNPP is better .Eg; Better transparency& lower decolourtaion consequently,TNPP was selected as the suitable anti oxidant for RVNRL

B) Antiox SNF-50

It is a synergetic blend of hinderd phenol and thio ester.Hinderd phenol consists of butylated adduct of di cyclo penta diene / Para cresol.Antiox SNF -50 is non staining non discolouring anti oxidant and provide highly efficient protection against oxidation as well as stabilization.Infact the protection is better than the hinderd phenol is by it delt.

Antiox SNF -50 is recommended in SBR and NR latex at 0.25 to 1.25 Phr. It is Exellent or use in carpet backing as well as thin walled dipped goods like balloon and condoms.

Dose of irradiation

Dose can be defined as the energy absorbed per unit mass of the irradiated material at the place of intercept. Its unit is 'rad' (radiation absorbed dose)

1 rad = 100erg/g

SI unit of dose id J/Kg and is called 'Gray'. The symbol is Gy.

100rads = 1Gy

When 1Kg of matter absorbs 1J of energy, then this material is said to have received a dose of 1Gray. When 1Kg matter absorbs 1000J of energy, it is said to have received a dose of 1Kgy.

Irradiation time

Irradiation time is calculated using the formula
Irradiation time = Dose / Dose rates
The value of dose rate changes from day today, which is obtained from the table. The dose rate decreases day to day due to the disintegration of Co-60.

Advantages of radiation vulcanization

Latex producers and product manufacturers were compelled to develop a new vulcanization method for overcoming problems of allergy and nitrosamine base toxicity. RVNRL is completely free from toxic chemicals and it is non-allergic. The chemicals used are KOH and n-BA. KOH is removed completely by leaching. N-BA itself polymerizes and the residue will be removed on drying due to high vapour pressure. The antioxidant added is tris nonylated phenyl phosphite (TNPP), which gives a transparent appearance to the RVNRL film. The other advantages are the following:

- Longer shelf-life period
- Lower modulus
- Biodegradability
- Less extractable protein content
- Low emission of sulphur dioxide
- Lower ash content
- No problem associated with zinc contamination in the effluent generated
- No problem associated with chemical stability or zinc oxide thickening

Application of RVNRL

a) Examination Gloves
b) Condoms
c) Toy Balloon
d) Catheter
e) Other medical and pharmaceutical products

Features of Pilot for the Radiation Vulcanization of Latex

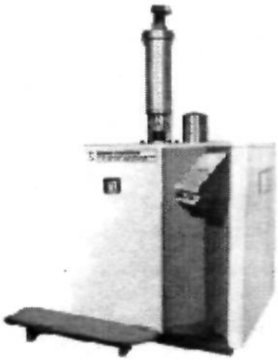
The completion of the latex irradiator at Kottayam has marked the beginning of "Radiation Induced Vulcanization" as an industrial process in India. This pilot plant is the result of the collaborated efforts of BARC, the multi-disciplinary research center and the Rubber Board, the prime organization promoting the rubber industry in India.

The basic requirements of an irradiator are:-

* A source for irradiating the product
* Biological shielding for protecting the plant personnel during irradiation
* A shielding to the source when not in use

The source used for the latex irradiator is Co-60 and the biological shielding is by concrete. The gamma source is stored and shielded under water and is brought up for irradiation. It is a batch process where the latex is irradiated in a vessel with stirrers.

GAMMA CHAMBER 5000



Description:

Gamma chamber 5000 is a compact self-shield cobalt-60 gamma irradiator providing an irradiation
volume of 5000 cc.Gamma chamber can also be used in many other research applications which require
irradiation of materials with ionizing radiations to varying doses.

Specifications of gamma chamber 5000

Maximum Co-60 source capacity : 444 TBq(12000 Ci)
Dose rate at maximum capacity : 0.9 Mega Rad/hr at the center of sample chamber
Dose rate uniformity : +25% or better radially-25% or better radially
Irradiation volume : 5000 cc
Size of sample chamber : 17.2 cm (dia) X 20.5 cm(ht)
Shielding material : Lead and stainless steel
Weight of the unit : 5600 kg
Size of unit : 125 cm X 106.5 cm X 150 cm
Timer range : 6 sec onwards

1.2.6 LATEX DIPPING PROCESS(production of rubber products)

•

Latex dipping is the process in which thin walled rubber products are produced by first immersing a former in latex which has been suitably compounded and then subsequently slowly with drawing the former from the latex in such a way as to leave a uniform deposit up on the former. The thickness of the deposite can be increased if desired by repetition of the process.

A) CLASSIFICATION OF LATEX DIPPING PROCESS

- Simple or straight dipping
- Coagulant dipping
- Heat sensitizer dipping
- Electron deposition

If no colloid destabilization agencies are used in the formation of a polymer deposite up on the former then the process is known as simple or straight dipping. If adirect coaservent is used to promot the formation of the deposite,the process is known as coagulant dipping. If the latex compound is formulated in such a way as to be heat sensitive and the formation of deposite is facilitated by heating the former prior to immersion in the latex is known as heat sensitized dipping.In electrone deposition process the formation of deposite is facilitated by the application of electric field in the latex which cause the particles to accumulate in the vicinityof the former

B) COAGULANT DIPPING

The general principle underlying is followes.

The main body of the latex film is provided by first coating the former with coaservent.The former is then immersed in the latex compound and allowed to remain dwell for a specified period .during this period, The latex in the vicinity of the former surface should become sufficiently collidly destabilized to form a gelled layer around the former .The end of the dwell period the former is slowly withdrawn from the latex, and the deposite then subjected to further processing. The film which coats the former at the withdrawel stage is usully partially gelledThe outer layer being still more or less fluid. The principle advantage of coagulant dipping is that considerably thicker depposite can be obtained as the result of single dipp than by simple dipping.

The coaservent may be a liquid such as acetic acid ,formic acid in which case the process is known as wet coagulant dipping or a solid such as calcium chloride in which case the process is known as dry coagulant dipping.Of this later is widely used by coagulant process,the coagulant is initially dissolved in the suitable solvent to facilitate the coating of the former.Before immersion in the latex compound solvent is compleately removed by evapouratoin. Dry coaservant are usually calcium salt which readly soluble in the mixture of water and common water insoluble organic solvent.

1.2.7 BLENDING OF RUBBERS

Polymer blends are often refered to as poly blends and physical blending are mixing of two or more existing polymers yield polymer blends.Blending of rubber is important in view of the properties that can be achieved by blend composition, choice of additives, blending techniques and vulcanization condition. Polymer miscibility refers to the intimate mixing of two or more rubbers.based on the degree of miscibility blends are classified as compatible, incompatible and partially compatable. A blend is compatible when it does not exhibit gross symptoms of phase segregation . The aspect of polymer –polymer miscibility and theproperties and applications of polymer blends have been reviewed by several authors.

Factors affecting blend properties

The above factors may be summerised as

- ✓ Polymer ratios
- ✓ Phase mormhology
- ✓ Interfacial adhesion/cross linking

- ✓ Distribution of filler between the elastomers
- ✓ Distribution of plasticizer between the elastomer
- ✓ Distribution of cross links between elastomer

a) Polymer ratio

Polymer ratio is the relative amount of each elastomer used for blending. It is readly controlled and often dictated by the end use.

b)Phase mormhology.

Phase morphology has two aspects viz type size . whilst type of phase morphology as itssimplest whether one phase is dispersed or with in another or whether both are continuous is largely govern by the polymer volume ratio, other factors such as the relative viscosity of the two elastomers can play a role.

Phase size mainly depends on the conditions of preparation of the blend.In general, the higher the shear used in mixing the smaller the phase size attaned and some same elastomers undergo scission during mixing and there can be and optimum degree of mixing before phase size increases again

c)Interfacial tension

When there is a large difference in solubility parameters between the two elastomers, There is high interfacial tension and hence the two elastomers do not mix uniformly . To alleviate this problem suitable compatibilizers are in incorporated in the blends. Interfacial tension also plays a role in the control of interfacial adhesion and crosslinking between the two elastomers at the interface. If there is a little mixing of the two elastomer at the interface, the opportunity for crosslinking between the two are reduced and this can cause a weakness at the interface.

d)Distribution of filler between the elastomers

Elastomers blends it is difficult to distribute fillers uniformly in the two phases,particularly for carbon black. The factor that dominated the dispersion of carbon black are

- Degree of saturation of polymer
- Viscosity of polymer
- Polarities of the polymer
- Type of amount of filler
- Mixing method

Distribution of carbon black is generally readily controllable by preparing well mixed master batches of each customer containing the desired loading of black.The better interaction of the elastomer with the surface of carbon black, forming the so called bound rubber, ensures that there is little transfer of filler between the two elastomers on cross blending of master batches

e) Distribution of plasticizer between the elastomers

Distribution of plasticizer has not been considered extensively as many compounds do not contain large quantites of plastizer.However when substantial quantites of plasticizers are used,there can be migration of plasticizer to one of the components.

f) Distribution of cross-links between the elastomer

It is important that the vulcanisate network structure formed is uniform throughout .Sulpher and accelerators more soluble in unsaturated elastomers.Accelerators have great affinity for polar elastomers.These curatives have tendency to migrate to low viscosity phase since it tends to occupy the outer regions of low and usually to low viscosity phase forms the continous phase.If there is a great difference in the solubility of the curatives in the two phase,The cross linking density of final vulcunizate will be heterogeneous.Rate of vulcanization varies for different elastomers in the blend depletion of curtives in the faster curing component also cause curative negative loss and hence cure imbalance.Thus the use of combination of properties is achieved when the two elastomers are similar in respect of polarity, saturation level and Mooney viscosity

1.2.8 SCOPE OF THE PRESENT WORK

In sulphur vulcanization there are some drawbacks.in the conventional vulcanization of latex using sulphur& accelerators toxic product like products like Nitrosamines during product manufacturing & during service life of rubber products.Different international regulations like REACH (Registration,Evaluation,AuthorisationRestriction of Chemicals) are being enforced now.And it is atmost important that the chemical used in rubber products are safe.Latex prepared by radiation vulcanization can be considered almost chemical free as only sensitizer which is non toxic is used in its production. NR latex has high strength due to the specific micro structure consisting of cis-1,4 poly isoprene unit. Some of these rubber molecules due to some specific groups undergo long chain branching. Due to these two factors, NR has very high strength if absence of any filler and due to this that NR latex is used to produce products like gloves, balloons, catheters etc. NR has poor ageing properties with reference to oil, fuels& high temperatures. These can be overcome by blending NR latex with other latice that have higher resistance to different ageing condition .One such synthetic latex is,styrene butadiene rubber . synthetic rubbers are eg SBR Latex,CR Latex etc prepared by emulsion polymerization technique they are available in latex form. The advantage of this is that such latex can be used either alone or in combination to prepare latex based products.

The basic problem with HSBRL is that the rubbery nature is low. So it is preferred that it is used in Blends with NR latex to get high strength and rubbery nature. There are only few products on RVNRL with Blends. An aattempt is made to prepared urinary cathedral ,finger caps using RVNRLBlend with HSBRL

CHAPTER 2

2. MATERIALS & EXPERIMENTAL TECHNIQUE

2.1 NR latex

High ammonia preserved field latex was obtained from PCRF RRII. The latex was subjected to a creaming process using ammonium alginate.
Styrene butadiene rubber latex with a TSC of 50.3 was

2.2 MATERIAL CHARACTERIZATION & TEST METHOD

2.2.1 Raw rubber& latex properties

2.2.1.1 Particle size Analysis

Latex of varying particle size distribution of the latex samples were determined using Malvern Zetasizer Nano series (Nano S) particle size analyzer.

2.2.1.2 DRC

The quantity of rubber present in latex is calculated from its dry rubber content (DRC). This is defined as the quantity in grams present in 100gms of latex. The DRC of latex falls in the range 30-40.
method: **Procedure:**
Standard laboratory
About 10 – 15gms of representative sample is taken in a container from a stopped conical flaskThe latex is coagulated with sufficient 2% acetic acid and heated overaa steam bath until a clear serum is obtained. The coagulum is thoroughly washed, rolled to a thin film of around 2mm and placed in a thermostatically controlled over about 70^0 C for 16 hours. The dried rubber obtained is cooled in a
desiccator and weighed in a chemical balance.

$$\text{DRC}(\%) = \frac{\text{Weight of rubber} \times 100}{\text{Weight of latex}}$$

$$= g/w \times 100$$

2.2.1.3 TSC

It is defined as the amount in grams of total solids present in 100 g of latex.

Procedure:

Weighed correctly a clean petridish (w1 grams). Add about 2 gms of latex into a petridish and again weight correctly (w2 grams). Gently swirl the dish so that the latex is distributed over the bottom of the dish and dry the specimen in an oven at 70 ± 2^0 C for 16 hours or 2 hours at 100 ± 2^0 C. Cool the sample to room temperature and weighed again (w3gm). The total solid content is calculated as,

$$\text{TSC}(\%) \quad = \quad W3 - W1/W2 - W1 \times 100$$

W1 - weight of Petri dish
W2 - weight of Petri dish + sample
W3 - weight of Petri dish + decide sample

2.2.1.4 Nitrogen content

Determination of nitrogen content by 'kjeidhal method'

Reagents:

0.1g sample
Conc: H_2SO_4
60% NaOH
Catalyst mixture (15g K_2SO_4 +2g $Cu(SO_4)_2$) +1g Selenium)

2% boric acid

Indicator (methyl red –methylene blue)

Apparatus:

Semi–micro kjeldahl digestion and distillation apparatus

Procedure:

A small amount of the sample was digested by mixing sample,. catalyst mixture, and Conc: H_2SO_4 in a beaker when the mixture is clear, the sample is digested. Transfer digested sample to a distillation flask. Add 10ml of 60% NaOH solution and distill. The distillates are collected in a conical flask containing 10ml of 2% boric acid and titrate against 0.1N H_2SO_4. Indicator used is methyl red –
methylene blue.

$$\text{Nitrogen Content (\%)} = 1.4 \times N \times V \backslash W$$

2.2.1.5 Acetone extraction

Approximately 5 gm of the sample was wraped 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 filles 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.

\Acetonet extract percentage by weight = $W_1 / W_2 \times 100$

W_1 = weight in gm of matter extracted

W_2 = weight in gm of tested portion

2.2.6 Gel content

Take 100 ml toluene and 0.3gm sample in a dried beaker and kept in room temperature for 48 hrs . then filtered using already weighed wiregause and dried in an oven. The difference in weight is calculated.

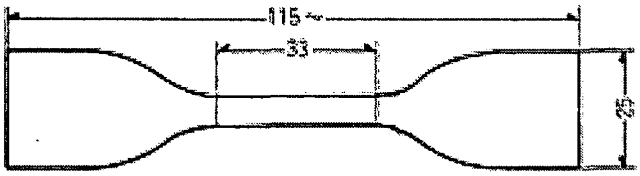
Percentage weight of gel content = difference in weight / original weight ×100

PREPARATION OF FILMS TO DETERMINE TESILE STRENGTH

The films are prepared by pouring the irradiated latex on a leveld glass plate of 10×10 dimension. After spreading the latex, the execess latex is poured out and the glass plate containing latex is kept overnight for drying. The films are taken out from the glass plate by dusting. The film is dusted to prevent adhesion to itself and to other articles. Tile was used for dusting and then leached in co,d water for 4hrs,dried at RT till transparent and again dried at 70^0c for 4 hrs in hot air oven.after that it is taken out and kept in a decicator. The film to be tested is cut in to dumbbell strips. The physical properties of casted filme were determined in each case using UTM (Universal Testing Machine)

2.2.1.7 Tensile strength

The tensile properties where determined from dumb-bell samples. The samples were conditioned at room temperature and tested on a Universal Testing Machine. The modulus, elongation at break and tensile strength were recorded. A dumb-bell specimen is shown below.



A= overall length;
B= width of end;
C=Length of narrow parallel portion;
D= Width of narrow parallel portion,
R = Large radius,
r= Small radius.

Tensile Strength

The tensile stress requires stretching the test pier to the breaking point, the conditions of being such that the stress is substantially uniform over the cross section.

Principle method

In this test the dumb-bells are stretched in a tensile testing machine at a constant rate of transverse of the driven grip. Reading of load and elongation are taken as required during the uninterrupted stretching of test piece and when it breaks.

The experiment was conducted on RVNRL. The required dumb-bell samples were cut out and subjected to test.

- **Temperature of the test; the test was carried out at 27+2c**

Experiment: - The dumb- bell was inserted into the grip of the testing machine, with the samples arranged symmetrically so that the tension will be uniform over the cross section. The machine was started and the distance between the centers of the reference lines was measured until the test piece breaks.

2.2.1.8 SWELLING STUDIES

Test pieces weighing about 0.2g were punched out from vulcanized sheets of about 2mm thickness and it was immersed in toluene and methyl ethyl ketone separately in a squadish for 25 hrs. The specimen were taken out, blot lightly with filter paper, placed d immediately in a stoppered weighing bottle and determine the weight.Percent weight of solvent absorbed was calculated as,

$$\Delta m = \frac{M_2 - M_1}{M_1} \times 100$$

Δm _ change in mass, %
M_1 _ initial mass of specimen in air,
M_2 _ mass of specimen in air after immersion,

2.2.1.9 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

$$\eta = K M^a$$

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

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

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

Where $\eta_r = t_s/t_0$

2.3 PROCESSING OF RVNRL

2.3.1 CREAMING

Fresh latex was colleced and preserved with 1% ammonia .small portion of latex was exposed to gamma radiation of low doses. Both un irradiated and pre irradiated latex was subjected to creaming process.the creaming is carried by adding creaming agents and secondary ceaming agents.

The formulation used for creaming is given table.1

Latex	4L
Ammonoum alginate3%	10 gm/340mL
Ammonium laurate20%	200 mL
Water	3L

Chemicals were added to the latex was stirred for 1 hr using a mechanical stirrer with 60 rpm speed. After that it is poured into an asperater tanks and kept undisturbed for two days

2.3.2.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.making RVNRL 5 phr n- BA&0.3phr KOH are added.

The following chart gives a brief picture of radiation vulcanization of NR Latex.

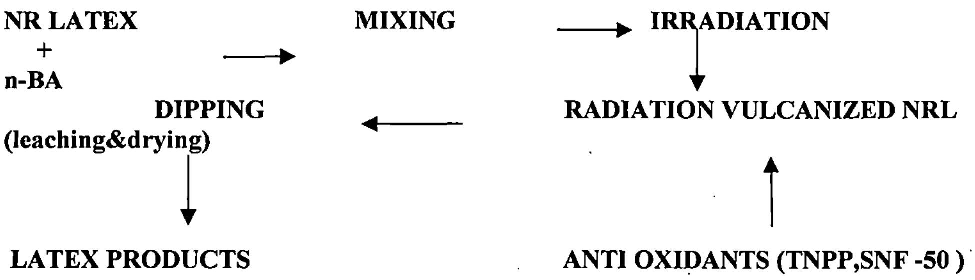


Table 2 For preparing RVNRL, latex was compounded as per table given below

INGREDIENTS	QUANTITY
Latex CDRC?39·(.	755 g(dry weight)
n-BA 5 phr	38g
KOH 0.3phr	2.5g
H_2O	2.5g

TNPP (50%) 2 phr	3.2g
SNF -50 (50%) 1 phr	0.8g

The ingredients are added was stirred using mechanical stirrer and kept for one day. Then the sample is exposed to 15KGY to effect vulcanization.After the latex was mixed required quantities

Antioxidants TNPPor SNF-50 stirred for half an hour using magnetic stirrer. And the latex kept undisturbed for overnight.

2.3.4 SULPHUR VULCANIZATION

Table-3 The latex was compounded as per formulation in the given table.

Ingredients	dry weight(g)	Wet weight (g)
60% con. Latex	100	167
10% potassium laurate	0.1	1
ZnO 50%	0.5	1
Znes 50%	1.0	2
Anti oxidant 50%	0.5	1

2.4 BLENDING OF LATEX

Latex blends were prepared by blending NRL and HSBRL so as to have dry rubber content in the ratio 90/10, 80/20.

CHAPTER 3

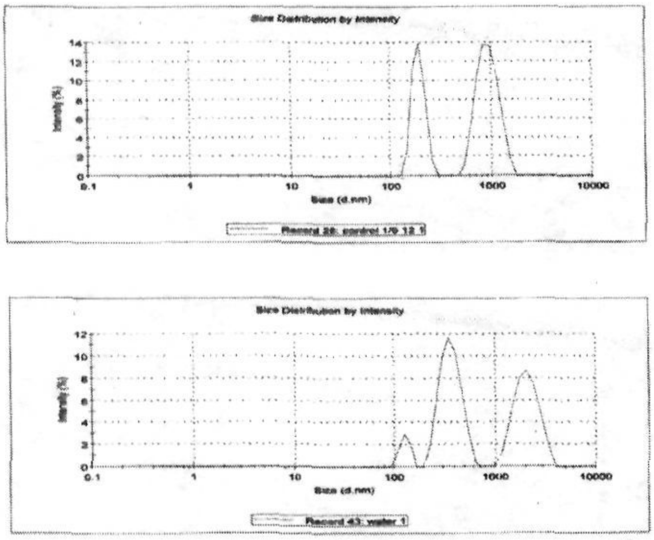
RESULTS AND DISCUSSIONS

3.1. *PARTICLE SIZE DISTRIBUTION OF LATEX*

a) Creamed PFL b)Pre irradiated creamed PFL

The particle size distribution of fresh creamed PFL and creamed latex exposed to low doses of radiation are given in Fig 1a. an1 b. The particle size varies about 200 to 2000 nm.for fresh creamed latex. There is a bimodal distribution for the particle size. For pre irradiated creamed latex Fig 1 b. the particle size varies from 100 to 5000 nm. The distribution is very close to bimodal distribution.

Fig 1 particle size distribution of creamed latex,a. fresh creamed latex,b. pre irradiated creamed latex



After pre irradiation there is an increased in lower sized particles and higher sized particle.During irradiation one important chemical change that occurs is partial hydrolysis of high molecular weight proteins to low molecular weight water soluble forms. The reduction in particle size can be attributed to partial removal of proteins There is also a possibility for particle aggregation Due to these two reasons the particle size distribution varies after pre irradiation.

3.2. RAW RUBBER PROPERTIES

The nitrogen content before and after creaming is shown in Table 1. After pre irradiation and creaming there is a decrease in nitrogen content and increase in gel content.

Table- 1 raw rubber properties before and after creaming

Parameter	Control(un-irradiated)		Samples(pre irradiated)5KGY	
	Before creaming	After creaming	Before creaming	After creaming
Nitrogen content%	0.48	0.46	0.47	0.18
Gel content	2	5.03	25.89	30.15

3.3

STRENGTH OF RVNRL FILMS

Creamed latex was used to prepare RVNRL as discussed in experimental section.The films was tested for properties like tensile strength,modulus etc. given in table 2

3.3.1 Mechanical properties of RVNRL &BLEND

Table 2. Mechanical properties of RVNRL

Properties	Control (Creamed PFL)	Sample (pre-irradiated Creamed PFL)
Gum strength, MPa	1.54	3.0
Modulus 300%, MPa	0.85	1.1
Modulus 500%, MPa	1.14	1.6
Tensile strength, MPa	22.0	25.32
Elongation at break,%	1379	1283
Solvent swelling, % (after 24 hours)	230	170
Tension set after 1 hour at 300 % elongation	10	6

The better mechanical properties are higher for pre irradiated creamed sample than the creamed PFL.

A comparatively higher storage modulus is shown by RVNRL prepared using pre-irradiated latex compared to the control. A similar observation is seen for the blends. At a strain amplitude of .01 % very high elastic modulus of about $7*10^6$ Pa is shown by the 80/20 blend based on pre-irradiated latex while in the same proportion RVNRL blend from fresh creamed NR latex showed storage modulus of $3*10^6$ Pa. The storage modulus decreases to a small extend at higher strain amplitudes for the pure RVNRL samples and to a comparatively higher extend for the blend samples. The decrease in modulus with strain amplitude was higher for blends obtained from pre-irradiated latex compared to the control.

In NR molecules there is the possibility of cross linking by intermolecular hydrogen bonding as explained earlier. During production of RVNRL there is some grafting of the n butyl acrylate chains on NR molecules . This can lead to more entanglement when mixed with HSBL as the polarity of NR chains increase. Both intermolecular hydrogen bonding and entanglements lead to higher molecular interactions. Due to these interactions the elastic modulus decreases as strain amplitude increases

3.3.2 Mechanical properties of blend

Table 3. Mechanical properties of the blend

Parameter	Control RVNRL/HSBL(based on drc*)		Sample RVNRL/HSBL(based on drc)	
	90/10	80/20	90/10	80/20
Modulus 300%, MPa	1.83	2.564	2.08	3.25
Modulus 500%, MPa	3,64	5.02	4.24	6.51
Modulus 700%, ,MPa	8.18	9.72	9.14	12.45
Tensile strength, MPa	18.18	12.89	25.51	16.62
Elongation at break, %	910	805	1055	800

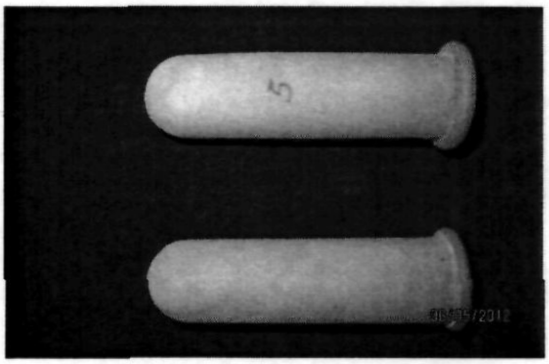
On blending RVNRL with HSBL (90/10 based on dry rubber content) the modulus increased significantly (Table 3). Further improvement in modulus was obtained after pre-irradiation. The tensile strength was only marginally reduced by adding HSBL. When the proportion of HSBL was increased from 10 to 20 , the modulus increased sharply and the vulcanizate became hard and more plastic natured. The increase in modulus is mainly due to the rigidity of the styrene butadiene copolymer. So using these latex catheters,finger caps can be prepared

3.4.2 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		

Molecular weight of latex increases when latex exposed to different doses of radiation.This is due to on irradiation the molecules undergo aggregation.Also the viscosity of the solution increases.

4. LATEX DIPPED PRODUCTS



The blended latex shows good mechanical properties.So this latex is used for making dipped products.

5. CONCLUSION

The green strength of NR latex increase after exposing fresh latex to low doses of gamma radiation and is attributed to gel formation. RVNRL prepared from latex of higher gel content has a higher tensile strength and modulus along with better dynamic properties like higher elastic modulus , lower hysterisis loss and lower permanent set. The flow characteristics of the latex change after blending RVNRL with low proportion of HSBL and the latter becomes more non Newtonian. The tensile strength and modulus of RVNRL films increase significantly after blending RVNRL prepared from latex exposed to small doses of gamma radiation ,with 10 parts of high styrene content styrene butadiene copolymer latex (HSBL).

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