STUDIES ON NR/NBR BLENDS VIA NEW ROUTE USING SKIM NR LATEX

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CERTIFICATE

Certified that this **Project Report** entitled "**Studies on NR/NBR blends via new route using skim NR latex**" is the bonafide record of work done by **Anagha Sasidharan V.K** in partial fulfilment 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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CERTIFICATE

This is to certify that the thesis titled *"Studies on NR/NBR blends via new route using skim NR latex"* being submitted by Kum. Anagha Sasidharan V.K. 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. Anagha Sasidharan V.K has worked on her research topic from April to June 2009, under my supervision. The results included in this report have not been submitted for the award of any other degree.

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CONTENTS

CHAPTER 1

Introduction

1. Natural rubber
1.1 Different marketable forms of Natural rubber
    1.1.1 Sheet rubber
    1.1.2 Crepe rubber
    1.1.3 Technically specified Rubber (TSR)
1.2 Preserved field latex
1.3 Concentration of latex
    1.3.1 Evaporation
    1.3.2 Electro decantation
    1.3.3 Creaming process
    1.3.4 Centrifuging process
1.4 Skim latex
1.5 Improved skim rubber
1.6 Use of skim rubber
1.7 Acrylonitrile butadiene rubber
1.7.1 Manufacture of nitrile rubber
1.7.2 Properties of NBR
1.7.3 Uses
1.8 Blending of Rubbers
1.8.1 Factors affecting blend properties
1.8.2 Blends based on NR and NBR

1.10 Selection of ingredients
    1.10.1 Polymer or rubber (Blend of polymers)
    1.10.2 Crosslinking agents
    1.10.3 Accelerators for crosslinking reaction
    1.10.4 Acceleration modifiers (activators or retarders)
    1.10.5 Reinforcing fillers
    1.10.6 Antidegradents
    1.10.7Antiozonants
    1.10.8 Processing aids
    1.10.9 Special additives
1.11 Mastication and mixing
1.12 Vulcanization
1.12.1 Sulphur vulcanization
1.13 Scope and objective of the present study
CHAPTER 2
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 compounds
2.5 Testing for vulcanizate properties
CHAPTER 3
3.Results and discussion
3.1 coagulation characteristics
3.2 Cure characteristics
3.3 Mechanical properties

3.4 Ageing characteristics
3.5 Solvent/ Fuel ageing
CHAPTER 4
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* and *Taraxacum koksaghyz*. The modern age of natural rubber started during the 1870 s when the British transported *Hevea* seeds for planting in India [2].

The main crop from the tree is latex, a milky white dispersion of rubber in water which is harvested by the process of tapping. NR from rubber tree is collected as latex which contains about 30-40 % dry rubber and the rest 33-25 % crop in the form of field coagulum. The proportion of field latex to field coagulum varies depending on the age of trees, tapping season, climatic conditions and clonal variation. All forms of coagulated rubber obtained from the field are collectively known as field coagulum.

The fundamental changes in the properties of NR through vulcanization removed most of its susceptibility to climatic conditions and its limitation as a raw material for mechanical applications. Natural rubber forms the raw material for a large number of rubber products like tyres, footwear, hoses, beltings, foam, mattresses 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. Different marketable forms of natural rubber

1.1.1. Sheet Rubber

Sheet rubber holds the predominant share in the Indian natural rubber market. Raw rubber sheet are of various types like ribbed smoked sheets (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 lattices in a common tank called bulking tank. For getting sheets of uniform quality, it is essential that the lattices from different fields are blended together. This is done by mixing latex uniformly in bulking tank.

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 sodiumbisulphite to latex prevents the discoloration by preferential reaction with oxygen, getting itself 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 and formic acids 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 plane rollers and a pair of 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 through 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 to 3mm.

Drying

Freshly machined and dripped sheets contain 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[3]. 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 sheets is due to the enzymic action on the non rubber constituents present in latex and can be controlled by using sodium bisulphite. Rust is a brownish deposit or more usually thin an invisible film on rubber sheets which can be formed by prolonged dripping of the wet sheet before being taken into 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 favourable 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 Inter National 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, RSS2, RSS3, RSS4 and RSS5. All ribbed smoked sheets shall be packed in rubber covered bales of about 50kg.

1.1.2. 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, retreading materials etc.

1.1.3. 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 1.1 and 1.2.

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

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.

1.2. Preserved field latex

NR latex is a colloid, like milk. The dispersed phase is mainly rubber and the dispersion medium (serum) water. In addition to rubber (30-40%) and water (55-65%), latex contains small quantities of proteins (1.0-1.5%) , resins including fats, fatty acids, other lipids, sterols, sterol esters(1.0-1.25%), carbohydrates(1.0%) and mineral mater. A major part of these non rubber constituents is associated with the rubber particles while the remaining part is distributed between the non rubber particles and the serum. The proteins and the phospholipids are primarily responsible for making the otherwise hydrophobic rubber particles hydrophilic by forming a thin layer over its surface. They also help in the acquisition of negative charge to the particle, which further promotes the stability of latex. For all applications of latex rubber, it is essential to maintain its colloidal character. This could be achieved through preservation. In addition to this preservation aims at prevention of bacterial activity by adding chemicals having bactericidal activity. Usually the preservative used is ammonia.

1.3. 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.

1.3.1. 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.*

1.3.2. 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.

1.3.3. 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-sludged 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.

1.3.4. 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.

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.

1.4. 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 Table1. 3.

1.5. Improved Skim Rubber

Several methods have been suggested for improving the quality of skim rubber and enzymic deproteinization of skim latex followed by coagulation is one of them. Under the influence of the enzyme, the proteins are hydrolyzed into water soluble product and are thus removed from rubber. In a typical process trypsin, a protein splitting enzyme preparation, allowed to act on skim latex for 24hrs in wax-lined tanks. Enzyme preparations like papain and anilozyme p-10 are available in India which could be used in place of trypsin. Creaming of skim latex using tamarind seed powder followed by coagulation also improves the quality of skim rubber[13-14]. In yet another process, skim latex is treated with Sodium meta bisulphate before acid coagulation.

1.6. Use of skim rubber

The main application of skim rubber is in compound with higher hardness such as solings. The preparation of high styrene resin used solings could be reduced to a certain extent by using skim rubber.

1.7. Acrylonitrile butadiene rubber (NBR)

Nitrile rubber is defined as a copolymer of a diene and an unsaturated nitrile .The majority of the nitrile elastomers produced today are copolymers of acrylonitrile and butadiene. The basic polymer reaction may be shown as follows.

$$CH_2{=}CH\text{-}CH{=}HC_2 + CH_2{=}CH\text{-}CN \longrightarrow (CH_2\text{-}CH{=}CH\text{-}CH_2.CH_2\text{-}CH\text{-}CN)$$

Butadiene Acrylonitrile Copolymer unit

(Depending on the ratio of acrylo nitrile to butadiene)

Acrylonitrile content (ACN) is one of the primary criteria for defining every NBR. ACN level due to polarity determines several basic properties such as oil and solvent resistance, low temperature flexibility, glass transition temperature and abrasion resistance.

1.7.1. Manufacture of nitrile rubber

1. Preparation of monomers

Butadiene monomer:- Ethyl alcohol is dehydrogenated to acetaldehyde

$$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_3CHO+H_2$$

Acetaldehyde and ethyl alcohol are passed over dehydrating catalyst to produce butadiene monomer.

$$CH_3CHO+CH_3CH_2OH \rightarrow CH_2=CH\text{-}CH=CH_2+H_2O$$

2. Polymerisation

Acrylonitrile and butadiene monomers are made to copolymerize under strictly controlled conditions of pressure and temperature using emulsion polymerization. The polymerization temperature which is very critical during the process is controlled at approximately 50 C for cold rubbers. The conversion of monomer is not carried out to completion for the reaction is stopped at predetermined intermediate stage to obtain the desired properties in the finished rubbers.

1.7.2. Properties of NBR

The important properties are as follows:

1. Oil, fuel and grease resistance
2. Good abrasion resistance
3. Good hot air resistance
4. Good processing characteristics
5. Low gas permeability
6. Moderate ozone resistance

The properties of NBR depends on the acrylonitrile content as shown in Table 1.4

1.7.3 .Uses

1. In rubber goods as molded technical goods, hoses and tubes

2. In printing rollers, brake linings and clutches. cellular goods coated fabrics, special foot wear rollers, cables and wires and sealing materials.

1.8. Blending of Rubbers

Polymer blends are often referred to as poly blends and physical blending or 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 vulcanizing 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 compatible. A blend is compatible when it does not exhibit gross symptoms of phase segregation. The aspects of polymer –polymer miscibility and the properties and applications of polymer blends have been reviewed by several authors.

1.8.1. Factors affecting blend properties

The above factors may be summarised as

1. Polymer ratios
2. Phase morphology
3. Interfacial adhesion /cross linking
4. Distribution of filler between the elastomers
5. Disrtribution of plasticizer between the elastomers
6. Distribution of crosslinks between the elastomer

1. Polymer ratio

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

2. Phase morphology

Phase morphology has two aspects viz type size. Whilst type of phase morphology as its simplest whether one phase is dispersed within another or whether both are continuous is largely governed 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 attained and some same elastomers undergo scission during mixing and there can be an optimum degree of mixing before phase size increases again.

3. 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 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 elastomers at the interface, the opportunity for crosslinking between the two are reduced and this can cause a weakness at the interface.

4. Distribution of filler between the elastomer

In 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

1. Degree of saturation of polymer
2. Viscosity of polymer
3. Polarities of the polymer
4. Type of amount of filler and
5. Mixing method

Distribution of carbon black is generally readily controllable by preparing well mixed master batches of each elastomer 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 .

5. Distribution of Plasticizer between the elastomers

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

6. Distribution of cross-links between the elastomers

It is important that the vulcanisate network structure formed is uniform throughout. Sulphur and accelerators more soluble in unsaturated elastomers. Accelerators have greater affinity for polar elastomers. These curatives have tendency to migrate to low viscosity phase since it tends to occupy the outer regions of flow and usually to low viscosity phase forms the continuous phase. If there is a great difference in the solubility of the curatives in the two phases, the cross linking density of final vulcanizate will be heterogeneous. Rate of vulcanization varies for different elastomers in the blend depletion of curatives 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.

1.8.1Blends based on NR and NBR

NR has very good mechanical properties but the ageing properties are very poor. These properties can be improved by blending with an oil resistant polymer like NBR. However it is very difficult to blend these rubbers due to the wide variation in polarity. Generally compatibilisers like chloroprene rubber, acrylonitrile grafted NR and methyl methacrylate grafted NR are used to to solve this problem of incompatibility[15].

1.9. 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. Antidegradants (Antioxidants, antiozonant, inhibitors of mineral catalyzed oxidation, protective waxes)
8. Diluents(Inter mineral fillers, organic materials and extending oils)
9. Special additives(Blowing agent)

1.10. Selection of ingredients

1.10.1. 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.

1.10.2. Crosslinking 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.

1.10.3. 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.

1.10.4. 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

1.10.5. 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.

1.10.6. Antidegradants

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.

1.10.7. Antioxidants

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

1.10.8. 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 hysterisis.

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.

Eg. 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. Some pigments used in compounding is given in Table 1.5

1.10.9. 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 Dinitrosopentamethylenetetramine, benzenesulphone hydroxide, azonitrates etc.

1.11. 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 ratio1:1.1to1:1.5 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.

1.12. 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[16]. 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[17]. 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[18]. 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[19].

1.12.1. Sulphur vulcanization[20]

Sulphur vulcanizing systems usually contained sulphur in amounts of 2.5 to 3 pphr and accelerator in amounts of 0.5 to 1.0 pphr. 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.

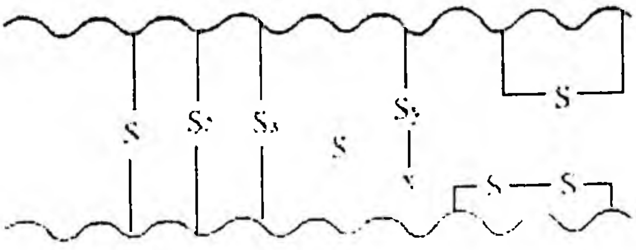
Conventional systems give vulcanizates which possesses excellent initial properties like strength, resilience and resistance to fatigue and abrasion and are satisfactory for many applications. However their heat ageing resistance, creep and stress relaxation properties are less satisfactory. For good 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 [21]

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.



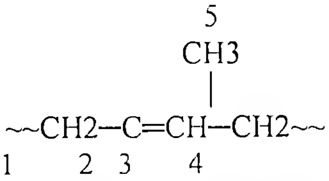
Scheme 1

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 nonsulphur 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.

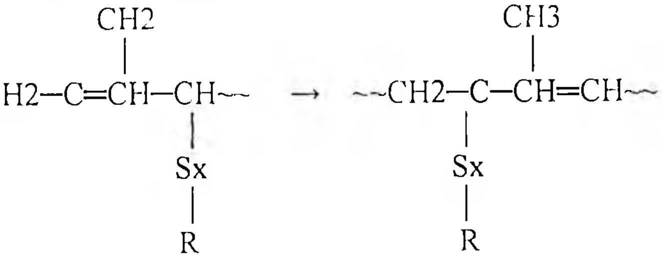


$$\sim\sim\underset{1}{CH2}-\underset{2}{C}=\underset{3}{\overset{\begin{array}{c}5\\CH3\\|\end{array}}{CH}}-\underset{4}{CH2}\sim\sim$$

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

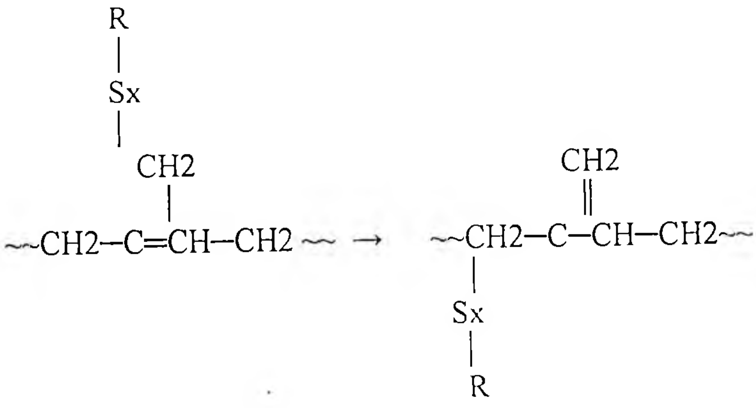
$$XSxR + RH \rightarrow RSx\text{-}1R + XSH$$

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.



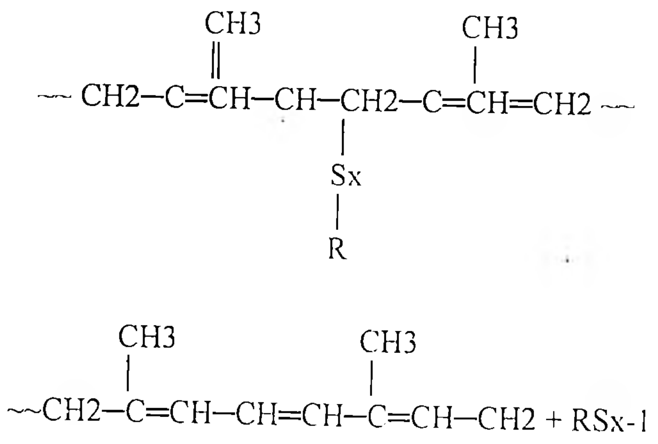
$$H2-\overset{\begin{array}{c}CH2\\|\end{array}}{C}=CH-\underset{\begin{array}{c}|\\Sx\\|\\R\end{array}}{CH}\sim\sim \rightarrow \sim\sim CH2-\underset{\begin{array}{c}|\\Sx\\|\\R\end{array}}{C}-\overset{\begin{array}{c}CH3\\|\end{array}}{CH}=CH\sim\sim$$

And



$$\sim\sim CH2-C=\overset{\begin{array}{c}R\\|\\Sx\\|\\CH2\\|\end{array}}{CH}-CH2\sim\sim \rightarrow \sim\sim\underset{\begin{array}{c}|\\Sx\\|\\R\end{array}}{CH2}-C-\overset{\begin{array}{c}CH2\\\|\end{array}}{CH}-CH2\sim\sim$$

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



$$\sim CH_2-\overset{\overset{CH_3}{\|}}{C}=CH-CH-\underset{\underset{\underset{R}{|}}{\underset{Sx}{|}}}{CH_2}-\overset{\overset{CH_3}{|}}{C}=CH=CH_2 \sim$$

$$\sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH=CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2 + RS_{x-1}$$

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.

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[22]. 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-sulpher-carbon- bonds from sulpher 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.

1.13. Scope and objective of the present study

For several decades the properties of natural rubber had been improved either blending with synthetic rubbers or by chemical modification .Acrylo nitrile - co –butadiene rubber is a material of immense interest due to its excellent oil /solvent resistance ,easy processability and moderate cost .Extensive work has been carried out in blends of NR with specialty rubbers such as NBR and EPDM[15] .But in most cases ,best combination of properties have not been achieved as there were problems related to unequal crosslinking and filler migration .Blends of NR and NBR expected to be highly useful in a variety of automobile gaskets and sieves and also in dairy applications ,where materials is required to be capable of resistant to swelling by butter ,fat oil etc yet have the strength required by the service condition.

Skim latex is produced in large quantities in latex centrifuging factories and it is environmentally desirable to process it . It is well known that the rubber recovered from skim latex has good mechanical properties comparable to conventional grades of rubber . Though the protein content is higher the potential of skim latex as a good source of NR is yet to receive appropriate attention and there are only few reports on the use of skim latex in blends with NBR for production of NR/NBR blends . In this report a new route for the production of NBR /NR blends from a comparatively cheap source of NR by latex stage blending process is presented.

Chart 1.1 Flow diagram for processing latex into technically specified rubber

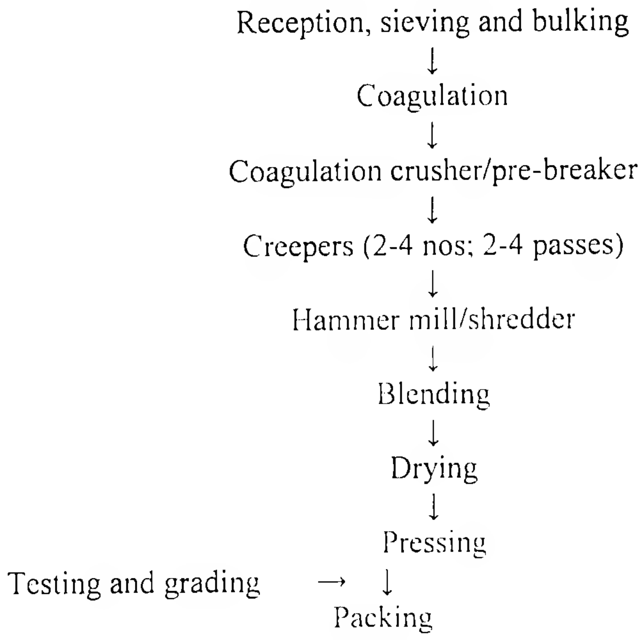


Chart 1.2. Flow diagram for processing field coagulum into technically specified rubber

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 requirement 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
Colour (*Lovibond* scale, max)	-	6.0	-	-	-	
Mooney viscosity, ML(1+4)100°C	60±5	-	-	-	-	
Accelerated storage hardening(max)	8	-	-	-	-	-
Colour code	black	black	green	brown	red	yellow

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

Table 1.3 . Main Characteristics of skim rubber

Colour	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 behaviour	Variable

Table1.4 . Property trends influenced by the percent of acrylo nitrile in a nitrile rubber

	% Acrylo nitrile (15 ⟶ 50)
Oil resistance improves	→
Fuel resistance increases	→
Tensile strength increases	→
Hardness and Heat resistance increases	→
Abrasion resistance improves	→
Gas permeability increases	→
Low temperature flexibility improves	←
Resilience improves	←
Plasticizer compatibility increases	←
Compression set decreases	←

Table 1.5 Pigments used for imparting colour to rubber compounds

White pigments	Lithopone, ZnO, and TiO_2
Red pigments	Iron oxide
Yellow pigments	Cadmium lithopone
Green pigment	Chromium oxide
Blue pigment	Ultra marine

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 20, skim rubber, Deproteinized skim rubber (DPSR) and Deproteinized skim latex (DPSL) were obtained from Rubber Research Institute of India. Skim NR latex as per specification given in Table 2.1 was obtained from Pilot Latex Processing Centre, Chethackal, Kerala. NBR and NBR latex of high acrylonitrile content as per specification in Table 2.1 were obtained Eliokem Industries, 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 ,% = $W_1/W_2 \times 100$

W_1 is the weight of dried film

W_2 is the weight of latex taken

Observations and calculations

DRC of the cenex (%) =59.65

Total weight of skim latex and cenex =28.5855

Dry weight =4.4684

DRC of the blend =15.6317

28.5855 g of the blend contain 22.4803g skim latex and 6.1052g of cenex

Thus DRC of skim latex

$$22.4803 \times X + 6.1052 \times 59.65 = 28.5855 \times 15.6319$$

$$22.4803X = 446.8399 - 364.1752$$

$$X = 3.677$$

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 (%) $=(W3 - W1 \quad W2 - W1) \cdot 100$

W1 =Weight of Petri dish

W2 =Weight of petridish + sample

W3 =Weight of petridish + 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.

$$\text{Nitrogen \% by weight} = \frac{V \times N \times 1.4}{W}$$

N = Normality of HCL

V = Volume of the sample required for distillation

W = weight in gram of sample used

Results are given in tables 2 and 3

Acrylo nitrile content of NBR can be estimated by multiplying the nitrogen content by 3.9

2.3. Preparation of blends

2.3.1.Latex blends

Skim NR latex, Deproteinised skim latex and NBR latex were mixed as per formulation in Table 2.2.The blended latex was treated with 5 % sulphuric acid so as to coagulate the latex to a consolidated mass. The wet coagulum was washed well to remove acid and dried at 70 ^{0} C to get rubber blends.

.2.4. 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.

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.

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

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.

2.5. 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,

$$T = F/A$$

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 10N. 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.

$$V = (\Delta m/\rho) \times 100$$

V = Abrasion loss, mm^3

Δm = (m1-m2), weight loss, g

ρ = density of the sample.

D. Rebound Resilience (ASTM D 1054-02)

Rebound resilience is the property of a material to return the applied energy usefully after an impact. 'Dunlop Tripsometer' was used to measure rebound resilience. The equipment consists of a pendulum made of solid steel disc of 41.9±0.13 cm in diameter. The disc carries a bracket which hold a steel ball 4±0.04mm in diameter with its centre 20±0.05cm from the centre of the disc, the ball and bracket together adding an unbalanced mass of 60±0.2g.

The sample was loaded in the test piece holder and held in position by vacuum. The disc was rotated in an anti-clockwise direction at an angle of 45° and clamped. The disc is allowed to fall six times from the horizontal position on the specimen and caught each time before it strikes the sample once more. The first of the three blows constitutes the mechanical conditioning of the specimen. The rebound angle is read on the 4th, 5th and 6th strokes. The average of the three readings is used for the calculation.

The rebound resilience was calculated as follows

$$RB = \frac{1 - \cos \theta_2}{1 - \cos \theta_1} \times 100$$

Where RB = Rebound Resilience (%)

θ_2 = Angle of rebound

θ_1 = Original angle, i.e., 45° in all tests

E. 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.

F. Hardness (ASTM D 2240-05)

Hardness measures the elastic modulus of the rubber by determining its resistance to a rigid indentor 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 indentor 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 indentor at least 12mm from the edge of the specimen. Measurements were taken as the hardness value.

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/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:

$M = M2-M1/M1 * 100$

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.Thermogravimetric Analysis(TGA)

Thermal Analysis involves the measurement of property of polymer as a function of temperature. Experimental plot of weight loss versus temperature is called thermogram. Thermogravimetry is the technique which records the weight of a substance in an environment heated or cooled at a controlled rate as a function of time or temperature. A thermal Analyser (TA 2100 with 951 TG Module) was used for thermal characterization of sample in nitrogen atmosphere (flow rate 60 ml /min). A sample mass of 10 ± 1 mg, was scanned from 30 -55 ^{0} C at a heating rate of 10 ^{0} C/min and TGA traces were obtained.

Table 2.1 Specification of the raw material

Parameter	Skim latex	DPSL	NBR latex	NBR
DRC, %	4.02	8.04	-	-
TSC, %	7.7	14.5	17.09	-
Nitrogen content, %	3.43	0.70	10.69	10.89
Acrylonitrile content , %	-	-	40.62	41.38

Table 2.2 Formulation of latex blends

Rubber	SL/NBRL	DPSL/NBRL
Skim NR latex, ml	1600	-
Deproteinised skim latex, ml	-	800
NBR latex, ml	3000	3000

Table2.3 .Formulation of mixes

Ingredients	Mix designation				
	Skim NR	DPSR	NBR	SL/NBRL	DPSL/NBRL	NR/NBR
Skim rubber	100	-	-	-	-	-
Deproteinized skim rubber	-	100	-	-	-	-
NBR of high acrylonitrile content	-	-	100	-	-	-
70:30 (NBR:skim NR)latex blend	-	-	-	100	-	-
70:30(NBR:DPSL)latex blend	-	-	-	-	100	
70:30(NBR:ISNR20)	-	-	-	-	-	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	1	2	2	2
HAF black	30	30	30	30	30	30
DOP[1]	-	-	3	-	-	-
TMTD[2]	-	-	0.20	-	-	0.20
CBS[3]	0.7	0.7	1.0	-	-	-
MBS[4]	-	-	-	2.48	2.48	2.48
MBTS[5]			-	0.32	0.32	0.32
Sulphur	2.5	2.5	1.5	2.6	2.6	2.6

[1] Di Octyl Phthalate

[2] Tetramethylthiuram disulphide

[3] Cyclohexyl benz thiazyl sulphenamide

[4] Morpholino benz thiazyl sulphenamide

[5] Di benzthiazyl di sulphide

CHAPTER 3

RESULTS AND DISCUSSION

Chapter 3

Results and discussion

3. Results and discussion

3.1. Coagulation characteristics

It is very difficult to coagulate normal skim latex and pure NBR latex. However on blending skim latex with NBR latex in 30:70 proportions, the latex coagulates to a consolidated mass. A large proportion of the proteins and fatty acid soaps of NR latex separate into skim fraction during centrifugation. Though the stabilizers are high in skim latex, the DRC is low as seen in Table 2.1, due to which skim latex does not coagulate easily to a consolidated mass on addition of fatty acids. It is well known that synthetic latex contains higher proportion of stabilizers[23] and hence does not coagulate by dilute acids easily. On blending there is an interchange of stabilizers, that is replacement of less active ones by more active ones.[24,25]

3.2. Cure characteristics

Cure characteristics of the mixes at 150 ^{0} C are given in Table 3.1 and the rheographs at 150°C of latex (SL/NBRL) and dry rubber blended(NR/NBR) mixes are given in Figures 3.1 and 3.2 .

High level of torque is shown by conventional skim rubber and NBR. The blends recorded a comparatively lower torque. Within the blends, latex blended mixes showed higher torque and higher scorch time as compared to dry blend. Both deproteinised skim latex and normal skim latex contains some fatty acids and proteins which help in attainment of higher level of vulcanization. However higher proportion of fatty acids like stearic acid , oleic acids lower the rate of vulcanization [26]

3.3 .Mechanical properties

Properties of skim rubber, deproteinized skim rubber, NBR of high acrylonitrile content and NR/NBR blends prepared by latex stage blending and dry rubber blending using ISNR-20 is given in Table 3.2. Conventionally prepared skim rubber showed a comparable tensile strength ,lower elongation at break, higher tear strength, higher resilience and lower heat build up as compared to pure NBR. Deproteinised skim rubber (DPSR) recorded a higher strength, lower modulus ,higher elongation at break .lower hardness ,higher resilience and lower heat build up and higher abrasion resistance as compared to conventionally prepared skim rubber .NR has high elasticity as compared to NBR and hence has better dynamic mechanical properties. Natural rubber recovered from skim rubber contains higher proportion of proteins which are known to affect adversely the dynamic properties.

On replacing NBR with 30 parts of NR either skim NR or ISNR-20, there is enhancement in modulus and hardness. NR/ NBR blends prepared from latex stage blending showed a higher modulus, lower elongation at break, higher tear strength, and higher hardness as compared to dry rubber blend. The enhancement in these properties is attributed to higher homogeneity in mixing of the two rubbers by latex blending and attainment of a higher level of cure as shown in Table 3.1. Comparatively higher resilience, higher abrasion resistance and lower heat buildup were recorded by NR/NBR blend prepared by dry rubber mixing as compared to latex mixed blend. A slightly higher tensile strength and modulus were recorded for latex blends using normal skim latex. Thus NR/NBR blends prepared by latex blending had comparatively good mechanical properties though dynamic properties were inferior as compared to dry rubber blends

During latex stage blending the mixing of the two rubbers is expected to be more uniform Skim NR latex contains higher proportion of proteins and fatty acids [9], that can adversely affect dynamic properties depending on their concentration. The variation in properties shown by latex stage and dry rubber mixed vulcanizates is attributed these factors.

3.4. Ageing characteristics

Ageing properties (100^0C /3 days) of blends along with pure NBR and NR are given in Table 3.3. A higher tensile strength and modulus along with a higher percent retention of tensile strength and elongation at break were shown by NBR as compared to NR. Blends prepared by latex blending showed a higher modulus, tensile strength and also higher retention of tensile strength and elongation at break as compared to blend prepared from dry blending. Comparable ageing resistance is observed for the two latex blended samples. Thus NR /NBR blends prepared using skim latex had better air ageing resistance as compared to blend prepared by dry blending. Skim latex contains higher proportion of proteins as compared to ISNR 20. Amines which are hydrolytic products of proteins are expected to act as antioxidants in rubber [20].As the proportion of skim latex incorporated in the blend is low the adverse effect due to higher content of non rubbers is not reflected in these blends. Pure NBR has lesser double bonds on the main chain as compared to NR and is more polar due to acrylonitrile content. Hence the air ageing resistance and fuel ageing resistance is expected to be higher for NBR.

3.5 Solvent/Fuel ageing

Percent weight of n heptane absorbed versus square root of time for all the vulcanizates are given in Figure 3.3 Percent weight of solvent absorbed is very high for NR while it is very low for NBR. Solvent absorption recorded by blends is lower than NR but higher than NBR. The solvent absorption follows the order

DPSL>SL >DPSL/NBRL > SL/NBRL>NR/NBR >NBR

Percent weight of solvent absorbed after immersion in isooctane for 1 h 24 h and 48 h is shown m Figure 3.4. Solvent absorption follows a similar pattern as observed for n heptane. NBR is highly polar in nature and this polarity confers solvent resistance to it compared to ISNR 20. Skim rubber contains higher proportion of proteins hence solvent absorption is lesser for blends containing skim latex. Thus NR/NBR blends prepared using skim latex showed a higher solvent resistance as compared to dry rubber blends.

The enhancement in ageing resistance of SL as compared to conventional skim NR (ISNR 20) is supported by TGA shown in Figure 3.5 and Table 3.4. A lower percent weight loss is recorded by skim NR as compared to ISNR 20. This is attributed to the hydrolytic products of protein present in skim latex that act as antioxidants.

Table 3.1 Cure characteristics of the mixes

Parameters	Mix Numbers					
	Skim NR	**DPSR**	**NBR**	**SL/NBRL**	**DPSL/NBRL**	**NR/NBR**
Minimum torque ,dN .m	2.18	0.75	1.81	2.40	1.81	2.05
Maximum torque ,dN .m	30.8	21.44	29.92	26	25	23.06
Δ ,Rheometric torque,dN.m	28.04	20.69	28.11	23.6	23.2	21.01
Optimum cure time at 150^0C , min (t90)	11.93	15.58	7.98	11.85	14.46	3.14
Scorch time (Ts_2) at 150^0C, min	2.48	2.93	2.83	2.61	2.90	1.33
Cure rate index dN .m/min	10.58	7.90	31.93	10.83	8.65	55.40

Table 3.2.Mechanical properties

Parameters	Skim NR	DPSR	NBR	SL/NBRL	DPSL/NBRL	NR/NBR
Modulus,100% MPa	3.38	2.24	3.16	5.32	4.44	4.06
Modulus,200% MPa	7.18	5.18	8.33	11.57	9.51	9.76
Modulus,300% MPa	11.91	9.71	15.48	18.41	14.02	16.62
Tensile Strength, MPa	19.43	25.0	19.94	19.60	14.70	19.60
Elongation at break %	455	440	360	305	330	340
Tear strength,kN/m	76	74	34.08	32.2	32.4	26.92
Hardness, Shore A	74	64	69	75	74	70
Resilience,%	50	60	45	36	39	51
Heat build up,ΔT^0C	24	14	25	28	27	28
Abrasion lose,cc/mm^3	168	147	120	153	144	145

Table 3.3 . Ageing characteristics of pure NR/NBR blends after ageing at 100^0C, 3days

Parameter	Mix numbers					
	Skim NR	DPSR	NBR	SL/NBRL	DPSL/ NBRL	NR/NBR
100% Modulus, MPa	2.91	3.34	4.61	8.71	7.44	7.22
200% Modulus, MPa	-	4.54	16.20	-	9.85	-
Tensile strength, MPa	3.83	6.85	16.20	15.70	13.05	12.80
% retention of tensile properties						
Tensile strength, %	19.09	24.18	84.25	85.27	88.77	81.09
Elongation at break, %	25.82	33.96	77.77	56.32	58.99	55.85

Table 3.4 Thermogravimetric analysis of skim NR, DPSR and NR (ISNR 20)

Sample	Temperature at which maximum degradation occurs, ^{0} C	Percent weight loss at maximum degradation temperature, %
Skim NR	373	51.51
DPSR	373	55.19
ISNR 20	373	58.07

CHAPTER 4

SUMMARY AND CONCLUSION

Chapter 4

Summary and Conclusion

Acrylonitrile-co-butadiene rubber is a material of immense interest due to its excellent oil/solvent resistance, easy processability and moderate cost. Blends of NR and NBR expected to be highly useful in a variety of automobile gaskets and seals and also in dairy applications, where materials are required to be capable of resistant to swelling by butter, fat, oil etc yet have the strength required by the service condition.

Skim latex is produced in large quantities in latex centrifuging factories. The rubber recovered from skim latex has good mechanical properties comparable to conventional grades of rubber. Though the protein content is higher the potential of skim latex as a good source of NR is yet to receive appropriate attention and there are only few reports on the use of skim latex in blends with NBR for production of NR/NBR blends. A new route for the production of NBR /NR blends from a comparatively cheap source of NR by latex stage blending process is carried out.

Cure behaviour and technological properties of mixes were determined. Higher level of torque is shown by conventional skim rubber and NBR compared with NR/NBR blends. Within the blends, latex blended mixes showed higher torques and lower cure time as compared to dry blends.

On replacing NBR with 30 parts of NR, either skim NR or ISNR-20, there was enhancement in modulus and hardness. NR/ NBR blends prepared from latex stage blending using skim latex showed a higher modulus, lower elongation at break, higher tear strength, higher hardness as compared to dry rubber blends. Comparatively higher resilience, higher abrasion resistance and lower heat buildup were recorded by NR/NBR blend prepared by dry rubber mixing. Thus NR/NBR blends prepared by latex blending had comparatively good mechanical properties though dynamic properties were inferior as compared to dry rubber blends. Retention of tensile properties after ageing was better for the latex blend as compared to dry rubber blend. NR/NBR blends prepared using skim latex showed a higher solvent resistance as compared to dry rubber blends.

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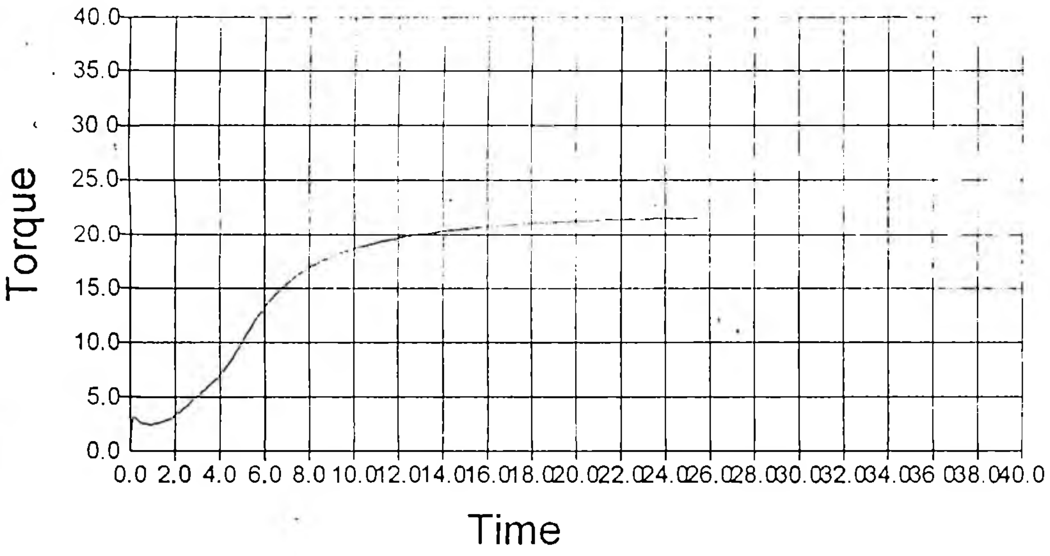


Figure 3.1 Rheograph of 30/70 SL/NBRL blend mix at 150 ⁰ C

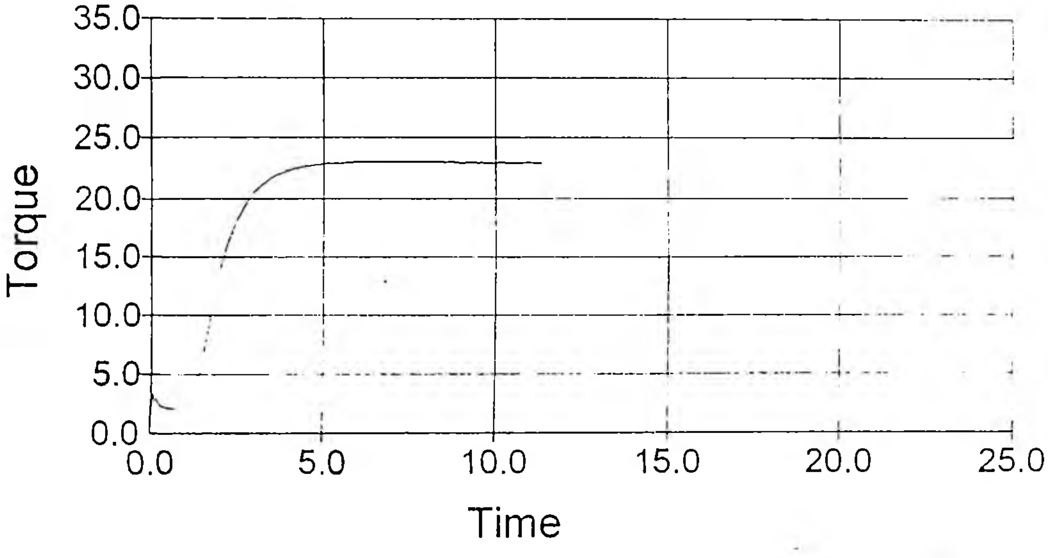


Figure 3.2 Rheograph of 30/70 NR/NBR blend mix at 150 ⁰ C

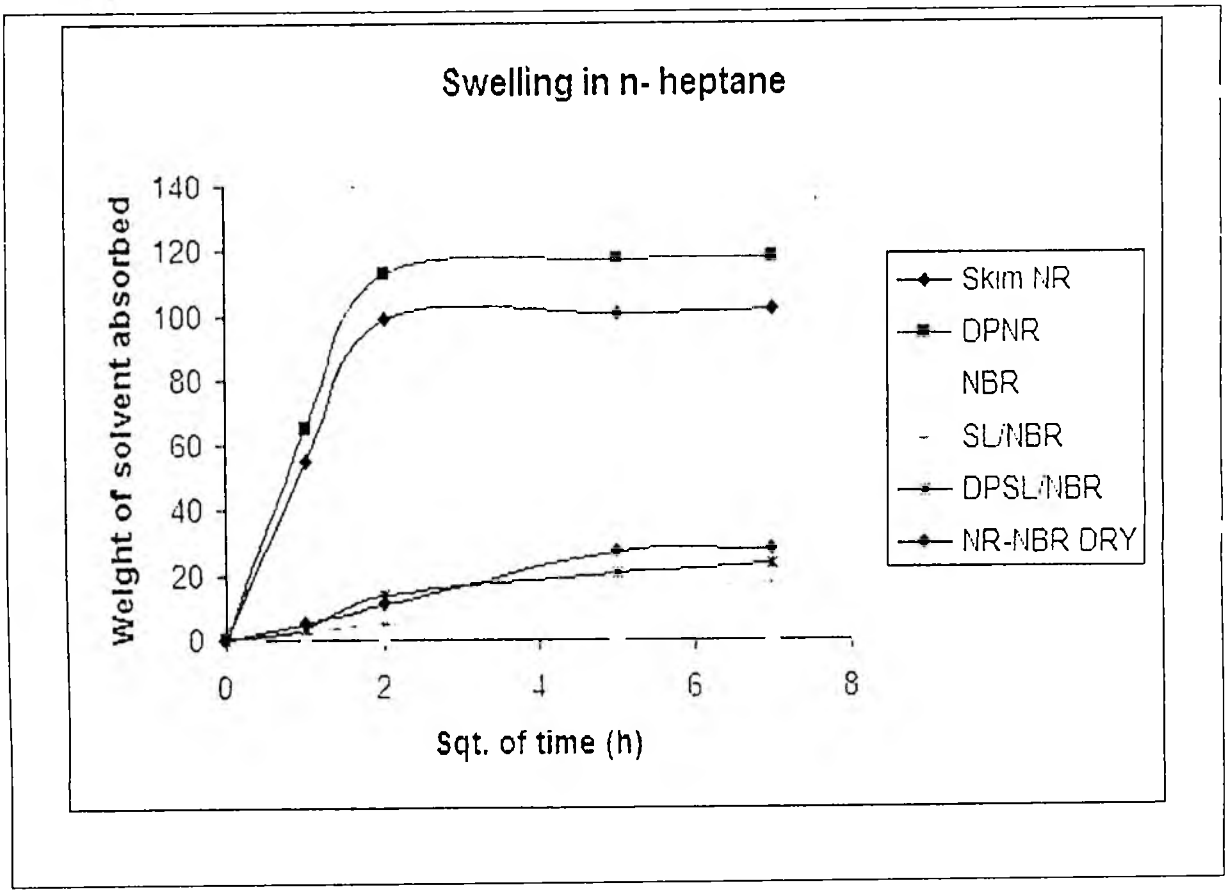


Figure 3.3 Percent weigt of n heptanc absorbed versus square root of time for NR/NBR blends in comparison with skim NR, DPNR and NBR

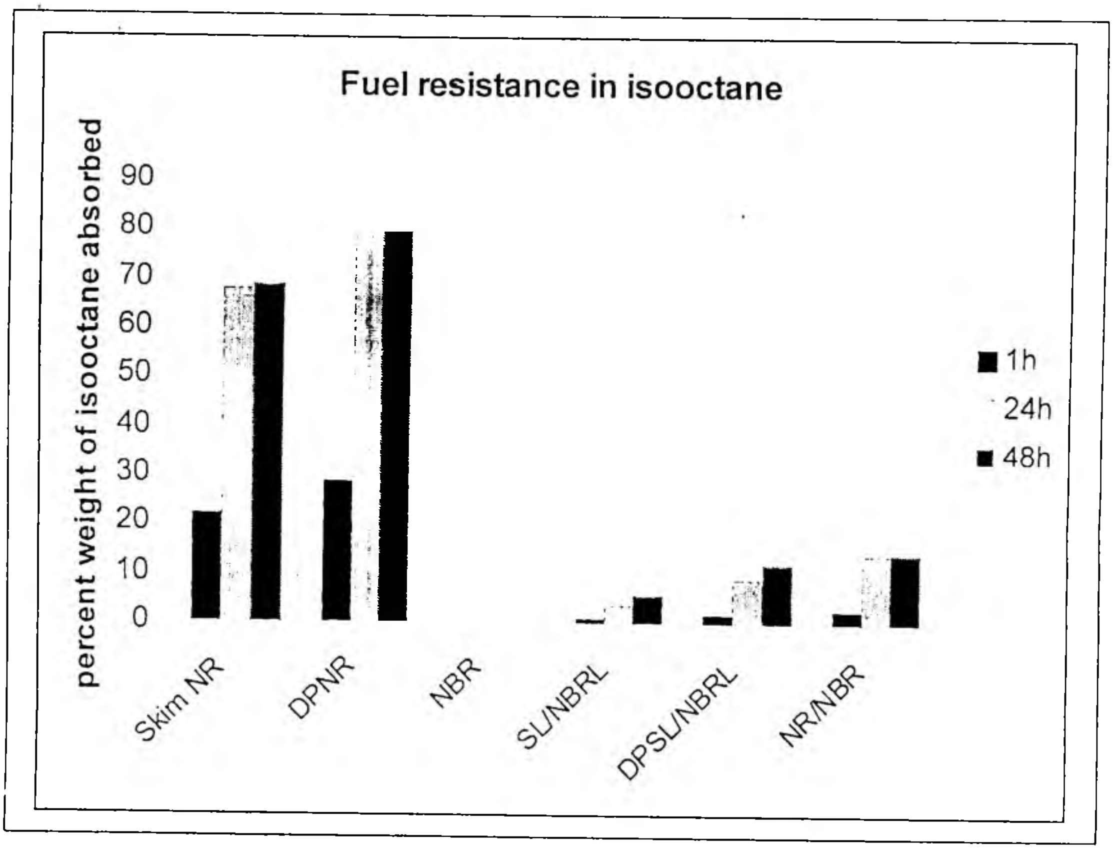
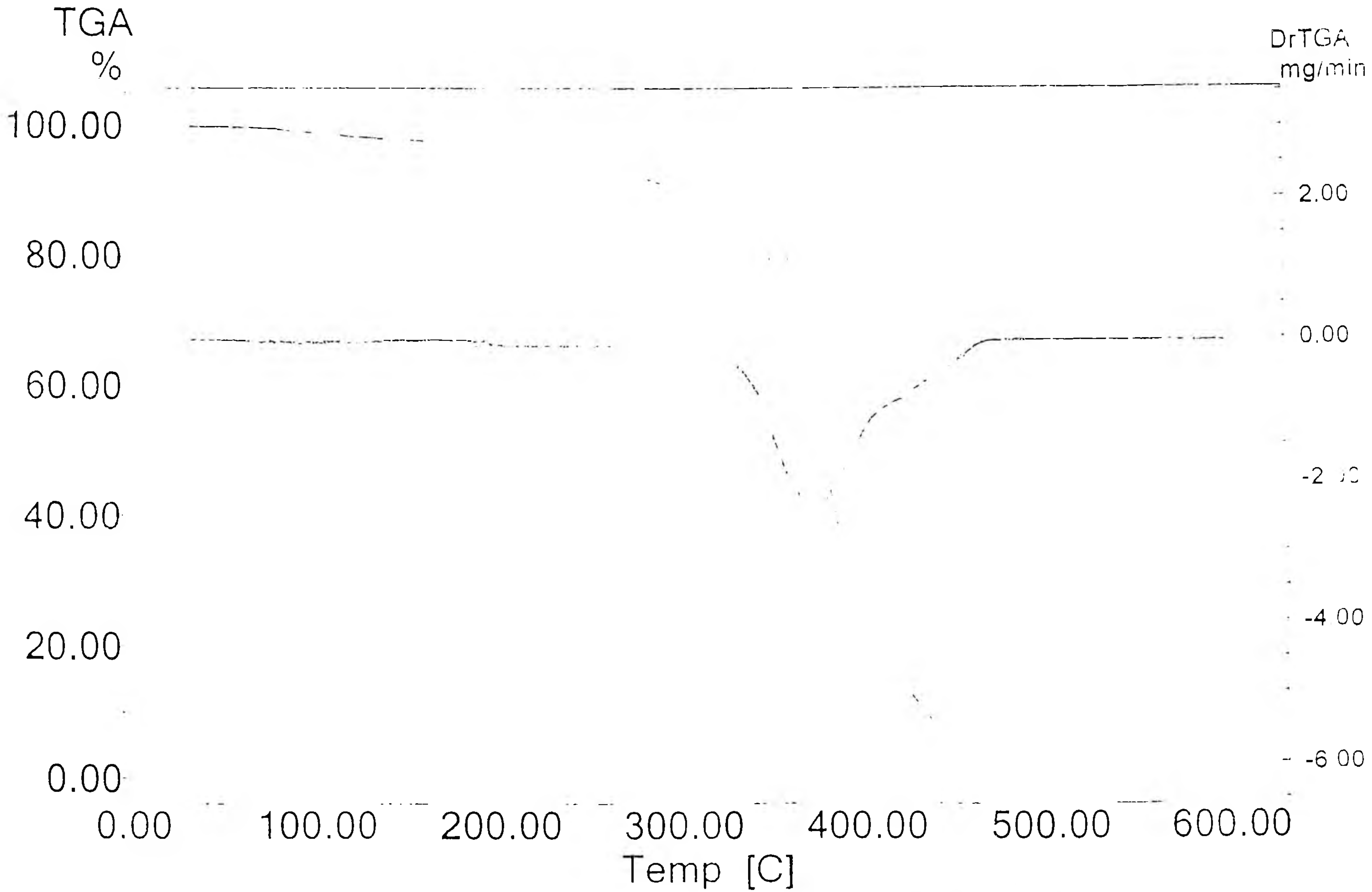


Figure 3.4 Percent weight of isooctane absorbed versus time or NR/NBR blends, skim NR , DPSR and NBR


TGA
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