Natural Rubber : Agromanagement and Crop Processing
Editors : P.J. George and C. Kuruvilla Jacob

Chapter 25

Modified forms of natural rubber

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1. INTRODUCTION

With the development of synthetic rubbers during and after the second World War, the monopoly till then enjoyed by natural rubber (NR) in the elastomer market was broken. Subsequently, a complex balance of technical properties and cost emerged as the decisive factor in NR usage. The traditional visually-graded sheet and crepe rubbers were not considered adequate enough to face the stiff competition from the synthetics. Attempts to improve its presentation and quality have finally resulted in the evolution of technically specified rubber (TSR) which, on a global scale, accounts for around 50 per cent of the NR processed. Also different special forms of NR have been developed to make it suitable for certain specific processes and applications. Even before the war, NR was found suitable for different types of chemical modification, leading to the production of a number of polymeric materials of very interesting properties. Although many such materials lost their significance consequent to the development of totally synthetic counterparts, some are still technologically important. Moreover, the limited availability of petroleum-based feed stocks and the increasing awareness of the relevance of renewable and environment-friendly resources such as NR, have caused renewed interest in the development of modified forms of NR (Baker, 1988; Gelling and Porter, 1988; Subramaniam, 1988; Campbell, 1992).

Natural rubber can be modified by physical and/or chemical means. Figure 1 gives most of the different types of modification of NR. Some of these such as viscosity-stabilized rubber, superior processing rubber, thermoplastic natural rubber, graft co-polymers, chlorinated rubber, *etc.* have already been produced commercially. The commercial significance of the others depends mostly on emerging market forces.

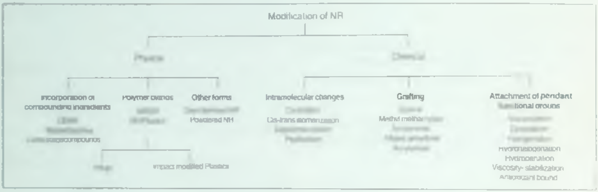

Fig. 1. Types of modification of NR

2. PHYSICAL MODIFICATION

Physical methods involve incorporation of additives which do not react chemically with the rubber.

2.1 Incorporation of compounding ingredients

Oil-extended NR, latex-carbon black masterbatches and latex stage compounds are made by incorporating various ingredients.

2.1.1 Oil-extended natural rubber

Use of petroleum oil in rubber, either as a process aid or as an extender is very old. Depending on the quantity, it functions either as a plasticizer (process aid) for improving processability and filler incorporation or as an extender for lowering the cost of a rubber compound while retaining adequate properties for the particular end use. Usually when an oil is used in concentrations below 10 parts per hundred rubber (phr), it is referred to as a plasticizer or process aid. Above this level, the oil functions as an extender for cheapening the product and the mixture is referred to as oil-extended rubber. In oil-extended rubbers the concentration of the oil is usually in the range of 20 to 40 phr. Although some properties may be impaired by extenders, others may be well maintained or improved. In general, increasing oil content reduces tensile strength and resilience, but the compounds retain good tear resistance and have very high wear resistance when blended with polybutadiene rubber. It also shows high skid resistance on wet surfaces when used in tyre tread compounds.

Oil-extension of NR can be carried out either in the latex stage (Thomas *et al.*, 1983) or in the dry rubber stage (Grosch and Swift, 1966) with naphthenic or aromatic types of hydrocarbon oil. Extension at the latex stage is effected by adding an aqueous emulsion of the required quantity of the selected oil into the latex and coagulating the mixture using an acid.

Mixing is carried out at an alkaline pH (8.0 - 8.5) to avoid destabilization. The coagulum is then processed in a manner similar to block rubber production. In dry stage mixing, the oil and rubber are mixed in a specially-modified extruder.

Tyre treads based on oil-extended natural rubber (OENR) have better grip on snow and ice and good resistance to skidding on wet roads. In addition, they have adequate resistance to wear and groove cracking. Hence they provide an economic alternative to oil-extended styrene butadiene rubber (OESBR) treads. On icy roads below 0°C, OENR is considerably superior to the OESBR (Jones *et al.*, 1988). The wear performance is improved by blending with polybutadiene. Through oil-extension and blending with polybutadiene, compounds have been developed with improved overall performance under a wide variety of road conditions. Such compounds have gained considerable acceptance as winter car treads in European countries.

2.1.2 Latex-carbon black masterbatches

The preparation of latex-carbon black masterbatch is carried out by mixing carbon black dispersed in water with latex and coagulating the latex-carbon black mixture (Janssen and Weinstock, 1961; Gopalakrishnan *et al.*, 1976).

Production of latex-black masterbatch in solid block form involves four steps, *viz.* preparation of carbon black dispersion, blending of the black dispersion with latex, coagulation of the blend followed by further processing and drying.

The composition of rubber : carbon black : oil in the masterbatch is maintained at 100 : 50 : 7.5. A 20 per cent dispersion of carbon black is prepared by ball-milling carbon black in an aqueous medium dispersed with one per cent of an anionic dispersing agent for 18 h. The carbon black dispersion is then added under high speed stirring to field latex containing the oil and mixed for about 45 s before coagulation with two per cent acetic acid. Dispersant-free carbon black masterbatch is prepared by adding high abrasion furnace (HAF) black to field latex, containing emulsion of the oil, under high speed stirring (3000 rpm) and mixing for about 45 s followed by coagulation with two per cent acetic acid. The coagulum is macerated and hammer-milled. The crumbs are dried at 90 - 100°C for 5 - 6 h before pressing into bales.

The dried latex-carbon black masterbatch retains over 96 per cent of carbon black. Batch to batch variation in Mooney viscosity ranges from 104 to 138. The vulcanizate properties of the compound are similar to those of mill-mixed samples.

2.1.3 Latex stage compounds

The production of latex stage compounds (Rajammal *et al.*, 1980) involves mixing of rubber and compounding ingredients in the latex stage followed by coagulation, drying and packing into standard bales. The compounding ingredients like accelerators and antioxidants are added as 50 per cent dispersions. Fillers are incorporated as 50 per cent dispersions or slurries. Oils are added as emulsions. Homogenized latex is mixed with a stabilizer and slowly stirred. Dispersions and emulsions of compounding ingredients, in the required quantity based on DRC of latex, are added to the stabilized latex. After mixing the latex compound well, it is coagulated by the addition of formic acid. Sulphur is usually not added in the latex stage to avoid scorch problem. The coagulum size is reduced and the wet crumb is dried at 100°C and finally pressed in a suitable press to form a loose bale of rubber compound.

2.2 Blending

2.2.1 Thermoplastic natural rubber

Thermoplastic elastomers (TPE) are a new class of materials which possess the processing characteristics of thermoplastics and behaviour of vulcanized rubbers at room temperature. Thus TPE soften reversibly and flow at elevated temperatures, but, unlike thermoplastics, have a considerable amount of resilience and flexibility which is normally associated with vulcanized rubber. They have commercially important advantages compared with conventional elastomers.

TPE are, therefore, finding markets previously held by vulcanized rubbers especially in products where high resilience and strength are not essential. At the same time they are being utilized by the plastic industry for products with better performance than those obtained with general purpose thermoplastics, such as polyvinyl chloride (PVC) and polyethylene. Thermoplastic natural rubber (TPNR) blends are prepared by blending NR and polyolefine, particularly polypropylene (PP), in varying proportions. As the composition of the blend varies, materials with a wide range of properties are obtained. At high rubber content, the blends are thermoplastic elastomers, whilst semi-rigid rubber-modified plastics are obtained at low rubber content. The mechanical properties of elastomer-thermoplastic blends depend on the proportion of elastomer and thermoplastic components. In order to get reasonably good mechanical properties, the hard phase must be continuous. The soft phase which provides elastic properties, need not be continuous provided the dispersed NR particles are sufficiently small and adhere to the matrix under stress.

The elastic properties of TPNR are considerably increased if the rubber is partially cross-linked during blending, a process termed as 'dynamic vulcanization'. Cross-linking of the elastomer phase in TPNR increases its hardness, modulus, strength and set properties. The effect is more noticeable in fairly soft blends.

2.2.1.1 Production of TPNR blends

Mixing of NR with polypropylene is normally carried out in internal mixers at 175 to 185°C. The total time taken for mixing a partially cross-linked TPNR is only about 6 min as shown below

0 min : Mix NR, PP and filler (if used)
2 - 3 min : Add cross-linking agent
5 min : Add antioxidant
6 min : Dump

After dumping, the blend is immediately sheeted in a two-roll mill to a thickness of 4 to 8 mm.

2.2.1.2 Typical properties

In comparison with general purpose NR vulcanizates, TPNR blends are remarkably resistant to heat ageing. The ozone resistance of TPNR is also excellent (Elliott, 1982).

The hard grades of TPNR are rubber-toughened forms of polypropylene. The rubber content usually ranges from 10 to 20 per cent. The key property of these materials is impact strength, particularly at low temperatures. The factors affecting impact strength are composition, phase morphology, interfacial adhesion and cohesive strength of the rubber phase. The last two factors can substantially be improved by the addition of 0.5 phr of m-phenyienebismaleimide (HVA-2, Du Pont) or 1 phr of phenolformaldehyde resin and 0.5 phr of ZnO, which in turn, will give a substantial increase in the low temperature impact strength (Mathew and Tinker, 1986; Elliott and Tinker, 1988). These additives, however, do not significantly affect the processability of the material.

2.2.1.3 Applications

Soft grades of TPNR can be used to replace vulcanized rubbers and flexible plastics for application in footwear, sports goods, seals and mountings and a wide range of moulded and extruded goods. The automotive sector is the largest potential market for the hard grades of TPNR in applications such as bumpers and body protection strips. They can also be used in products requiring a high impact strength such as floor tiles, railway sleeper pads, handles and grips and bump impellers. Car radiator grills and underground pipe closures use NR/PP blends containing 15 per cent NR.

An effective way to establish the use of TPNR in a NR-producing country like India would be in the competitive field of general mouldings where its attractive price and capability of giving high production rates could lead to increased profitability. Electric plugs, closures, handle bar and pedal bar are just some of the possibilities.

2.2.2 Superior processing natural rubber

Superior processing (SP) consists of an intimate mixture of vulcanized and unvulcanized rubber obtained by mixing vulcanized latex with field latex in different proportions before coagulation (Fletcher and Baker, 1957). It can be compounded in a manner similar to ordinary grades of NR with little loss of physical properties of the final vulcanizates. Improved processing characteristics and ability to retain dimensional stability make it an ideal material for calendered and extruded products.

The superior processing rubber that contains 20 parts of vulcanized and 80 parts of unvulcanized NR is termed as SP 20 and is generally used to replace completely the rubber in a formulation. Superior processing rubber is available in two forms (1) crepe and sheet (like SP crepe, SP air-dried sheet, SP smoked sheet and SP brown crepe) and (2) masterbatches (like PA 80 and PA 57). PA 80 contains 80 parts of vulcanized rubber and 20 parts of unvulcanized rubber. When one part of PA 80 is blended with three parts of NR, the resultant material is equivalent to the regular SP types. PA 57 is an oil-extended form of PA 80. PA 57 contains 57 parts of cross-linked rubber and is obtained by mixing, in latex stage, 80 parts of cross-linked rubber with 20 parts of unvulcanized rubber to which is added 40 parts of light-coloured, non-staining oil (O'Connel *et al.*, 1965). It is specifically designed for fast and easy dispersion without pre-mastication in many types of elastomers.

2.2.2.1 Production

Production of SP rubber involves preparation of a dispersion of the vulcanizing agent, vulcanization of latex, blending of vulcanized latex with ammonia-preserved field latex, coagulation of the blend and processing of the coagulum (Drake, 1960).

The field latex to be vulcanized is sieved through 60-mesh and ammoniated to 0.3 per cent (w/w on latex). Dry rubber content of the latex is then determined and an amount of 8.2 phr of vulcanizing dispersion is added. The composition for the vulcanizing dispersion is given in Table 1.

Table 1. Composition for vulcanizing dispersion

Dispersing chemicals	Concentration in phr (on DRC)
Sulphur	2.00
Zinc oxide (ZnO)	0.75
Zinc diethyldithiocarbamate (ZDC)	0.20
Mercaptobenzthiazole (MBT)	0.40
Dispersing agent	0.02
Water	4.85

The latex is steam-heated to 80 to 85°C for 1 h and held at this temperature for 2 h under gentle stirring (35 rpm). To test the completion of vulcanization, a sample is withdrawn and coagulated with chloroform. Reaction is complete if the coagulum is powdery and dispersible when rubbed between fingers. The vulcanized latex is brought to room temperature and its total solids content determined. SP 20 is prepared by mixing field latex and vulcanized latex in the ratio 4:1 based on the DRC of field latex and total solids content of vulcanized latex. It is then stirred and coagulated with two per cent (w/w) formic acid. For the preparation of PA 80, vulcanized latex is first diluted to 20 per cent total solids content. This is then mixed with fresh field latex in the ratio of 4:1 based on the total solids content of vulcanized latex and DRC of field latex. Blending time shall be as short as possible. The blended latex is then sieved through a 60-mesh sieve and coagulated immediately with five per cent sulphuric acid. The serum is then removed and coagulum soaked in water for 30 min. The coagulum is then made into crepe, crumbled and soaked again in water for 1 h. It is then dried at 70°C for 4 to 5 h and pressed into bales. In the preparation of PA 57, the required amount of oil is added in the form of a stable emulsion to the correct blend of vulcanized and unvulcanized latex before coagulation.

2.2.2.2 Advantages

Superior processing rubbers can be used with great advantage in extrusion processes, especially at lower filler loading, due to its (1) low die swell, less affected by extrusion conditions and better surface finish and (2) higher stock viscosities permitting easier handling and better open-steam curing characteristics (resistance to watermarking). It also allows wider range of extrusion temperatures and roll speeds for smooth extrusion leading to increased productivity. The superior processing quality (Baker and Stokes, 1960) and better extrudate properties of SP rubbers can also be imparted to several synthetic rubbers like SBR, polychloroprene and ethylene propylene diene monomer (EPDM) by blending in suitable proportions (Nair *et al.*, 1992).

2.2.3 Tyre rubber

The tyre industry prefers generally lower grades of TSR, reflecting the industry's basic requirement of a material which is available in large quantities at lower cost and which can provide satisfactory technological properties to the end product. However, a major portion of the TSR happens to be of higher quality derived from latex. These grades, though suitable for use in tyres, are too highly priced to be attractive to the industry. This has led to the production of tyre rubber which is a blend of high quality latex grade rubber and field coagulum. It is prepared from a blend of three types of raw materials and a plasticizer (Table 2).

Table 2. Composition of tyre rubber

Raw material	Weight(%)
Latex (as dry rubber)	30
Unsmoked sheet	30
Field coagulum	30
Plasticizer (mineral oil)	10

The field coagulum is made into a blanket. Dirt content of the blanket shall be less than 0.12 per cent by weight. The unsmoked sheets are also milled into a blanket. The two blankets are then blended and crumbled with the aid of castor oil. The crumbs are then spread evenly in the coagulation trough. A 10 per cent formic acid solution is sprayed onto the crumbs and excess acid recovered for further use. The required quantity of aromatic oil is emulsified and then mixed with the pre-determined quantity of latex. The pH of the latex-oil mixture is adjusted to be between 7.0 and 7.5 and the mixture is poured into the coagulation trough. The mixture flows easily through the mass of crumbs before it coagulates. The coagulum is then processed and dried as if it were a whole-latex coagulum. The typical properties of tyre rubber are listed in Table 3.

Table 3. Raw rubber properties of tyre rubber

Property	Values
Mooney viscosity, ML(1+4) 100°C	55-65
Plasticity retention index, PRI	81
Dirt content (% by weight)	0.04
Nitrogen content (% by weight)	0.38
Ash content (% by weight)	0.33
Acetone extract (% by weight)	13.01

Apart from economic advantages,tyre rubber has many desirable technological qualities. It has excellent resistance to low temperature crystallization.Its low Mooney viscosity makes pre-mastication unnecessary. In compounds containing 10 phr plasticizer, the use of tyre rubber to replace pre-masticated natural rubber and oil could lead to improved vulcanizate properties such as strength, flex cracking resistance and lower heat build up.

2.3 Other forms

2.3.1 Deproteinized natural rubber

Deproteinized natural rubber (DPNR) is a highly purified form of NR with very low nitrogen and ash contents. It is suitable for electrical and engineering applications where reduced creep and stress relaxation, superior dynamic properties and consistency in stiffness are required.

The naturally occurring proteins in latex can stiffen rubber to a similar extent as an equivalent volume of fast extrusion furnace black (N 550 black). However, the proteins and other hydrophilic non-rubbers can absorb moisture which lead to reduction in stiffening action thereby reducing the modulus. This leads to increased stress relaxation and creep in NR vulcanizates which can lead to inferior physical properties. Absorption of water by unvulcanized rubber can affect its degree of cross-linking and other cure characteristics. Deproteinization of NR reduces moisture sensitivity thereby increasing consistency in stiffness.

2.3.1.1 Production

The general method of preparing DPNR involves treating the latex with an enzyme preparation and diluting the treated latex to three per cent total solids content before coagulation. This enzyme hydrolyses the proteinaceous non-rubber materials into water soluble forms which are then washed away during subsequent processing.

In a typical method, concentrated latex is treated with 0.4 phr of ammonium or potassium naphthenate and 0.25 phr 'superase' for 20 h. It is then diluted to three per cent total solids content and coagulated with two per cent phosphoric acid. The coagulum is processed as crepe, treated with castor oil and crumbled. The crumbs are then treated with 0.2 per cent thiourea solution and dried (Chin *et al.*, 1974).

In another method (Rajammal and Thomas, 1978), ammonia-preserved concentrated latex is first stabilized with 1 phr non-ionic stabilizer and the pH adjusted to six by adding five per cent boric acid solution. It is then treated with 1 phr of 'anilozyme P-10' and kept for 20 h at 50°C. It is then diluted to three per cent total solids and coagulated by heating the latex to 85 to 90°C followed by addition of 2.5 phr of potassium oleate (as 10% solution) and 0.7 phr of sulphuric acid (as 4% solution). The coagulum is macerated and hammer-milled. The resulting crumbs are dipped in one per cent phosphoric acid and dried.

DPNR of constant viscosity can be prepared from field latex (Khoo *et al.*, 1987). Bulked field latex is ammoniated to 0.3 per cent level in an aluminium tank and 1.5 phr of a non-ionic surfactant and 0.15 phr of hydroxylamine neutral sulphate are added as 10 per cent solutions. An enzyme solution is added at 0.2 phr level and stirred for uniform distribution. Stirring is then stopped and the latex allowed to undergo enzymic hydrolysis for 40 to 42 h. When the hydrolysis is over, the latex is pumped into a neutralization-cum-holding tank. Dilute formic acid is gradually added to it as two per cent solution with gentle stirring until pH 6 is reached. The latex is then coagulated using a continuous steam column coagulator. The coagulum is allowed to mature overnight, macerated and treated with castor oil and hammer-milled. The resulting crumbs are dipped in 0.5 per cent thiourea solution for improving PRI and dried at 100°C for 4 to 5 h. The dried crumbs are then baled and packed.

The lower nitrogen content of the DPNR produced by this method is attributed to the use of a non-ionic stabilizer, the higher pH of the latex during steam coagulation and the higher temperature at which coagulation is carried out. All these factors enhance the solubility of the protein hydrolysate.

2.3.2 Powdered natural rubber

Powdered rubber or granulated rubber offers alternative processing routes to those normally used for mixing bale rubber in internal mixers. As the name implies, powdered rubber is rubber in free-flowing powdered form with a particle size range of 0.5 to 1.6 mm which can be loosely mixed in a relatively cheap,low shear, low temperature (30°C), one stage mixing process in a powder blender with all the compounding ingredients including sulphur and accelerators. The resulting loose powder blend is thoroughly mixed in special extruders or on two roll-mills or in internal mixers into homogeneous rubber compounds which can be moulded in the conventional way. Direct extrusion and injection moulding of the powder blend have been shown to be possible, thus avoiding use of heavy and capital intensive machines (Evans, 1988; Wheelans, 1988).

Commonly-used methods for powdered rubber production are spray drying of latex and mechanical grinding of latex coagula and bale rubber. Addition of partitioning agents is necessary to prevent reagglomeration of the rubber particles during storage and transport. Satisfactory partitioning agents include talc, silica, whiting, clay, carbon black and starch. However, high quantities of partitionig agents tend to spoil the physical properties of rubber.

Production, packaging, storage and transport of powdered rubber, which is considerably large in volume, increase its cost in comparison with bale rubber. The success of powder process and any financial advantages are dependent on whether the mixing and subsequent processing advantages exceed the premium on powdered rubber or the cost of granulating.

3. CHEMICAL MODIFICATION

Chemical modification of NR depends on the chemical activity of the rubber molecule. Being unsaturated, it is highly reactive and several chemical reactions could be carried out on NR resulting in materials having entirely different properties. These reactions could be divided broadly into (1) attachment of pendant functional group (2) grafting of a different polymer at one or more points along the NR molecule and (3) intramolecular changes without the introduction of a new chemical group.

3.1 Attachment of pendant functional groups

3.1.1 Chlorinated rubber

Chlorinated rubber is one of the first forms of chemically-modified NR which finds commercial application. Chlorination of NR is carried out either in solution or in latex by passing chlorine gas. Whether carried out in solution or in latex, the reaction involves substitution and cyclization along with addition of chlorine.

3.1.1.1 Production

Chlorinated rubber is commonly produced by treating a dilute solution of rubber with gaseous chlorine. Masticated rubber is dissolved in carbon tetrachloride to get a four to five per cent solution. Chlorine gas from a cylinder, after being bubbled through sulphuric acid, is passed into the rubber solution. The temperature is maintained at 70 to 80°C. At the end of the reaction, the chlorinated rubber is precipitated by adding the solution into excess of alcohol. It is also possible to recover the product from solution by steam distillation or by evaporation of the solution. The chlorine content of the product is about 65 per cent. Use of depolymerized natural rubber as a starting material for the production of chlorinated rubber has also been reported (Veeralakshmanan *et al.*, 1995). The main advantage is that a solution of higher concentration could be used for the process, resulting in higher yield.

The alternative method is by passing gaseous chlorine through stabilized and strongly-acidified NR latex. In a typical process, 30 per cent latex stabilized with a non-ionic stabilizer (2 - 5% on rubber content) is acidified with concentrated HCl to have an acidity equal to 8 N in the aqueous phase. The temperature is maintained at 20 to 30°C and gaseous chlorine is passed for 20 to 25 h. The chlorine content of the product thus obtained will be 60 per cent. In order to raise the chlorine content to 65 per cent, the chlorinated rubber latex is swelled in carbon tetrachloride emulsion for one day and further chlorinated by passing gaseous chlorine. The chlorinated rubber is precipitated by methanol or by warming the latex while adding sodium chloride. It is then dried to a fine white powder.

Technical advantages of chlorinating rubber in latex, compared to that in solution, are the much higher rubber concentration which can be used and the ease of cooling the less viscous latex during the reaction. Moreover, stable chlorinated latex is obtained which can be used as such and in some uses it is advantagous to have the original high molecular weight of the polymer.

3.1.1.2 Uses

Chlorinated rubber with 65 per cent chlorine is available commercially. It is a pale cream-coloured thermoplastic powder, which is non-flammable and highly resistant to chemicals. Hence it is used in anticorrosive and heat resistant paints and coatings. Such paints usually contain about 10 to 12 per cent chlorinated rubber which can be applied to the surface by brush or spray. Chlorinated rubber is also used in adhesives, printing inks, paper coatings and textile finishes.

3.1.2 Epoxidized natural rubber

Though the mechanical properties of NR are superior to those of most synthetic rubbers, it cannot compete with the speciality synthetic elastomers with regard to such properties as gas permeability and resistance to hydrocarbon oils. Latex stage epoxidation of NR under controlled conditions gives a chemically-modified form of NR, called epoxidized natural rubber (ENR) with improved resistance to hydrocarbon oils, low air permeability, increased damping and good bonding properties while retaining the high strength properties of NR (Baker *et al.*, 1985; Gelling, 1985). Improvement in these properties depends on the degree of epoxidation. Consequently two grades of ENR, ENR 25 and ENR 50 with 25 and 50 mole per cent of epoxidation respectively, have attained commercial importance.

3.1.2.1 Production

ENR is produced from NR latex by performic acid formed *in situ* by the reaction of formic acid with hydrogen peroxide (Gelling, 1985; George *et al.*, 1992). The reaction is carried out under carefully controlled conditions to avoid secondary ring opening reactions. NR latex is first stabilized against acid coagulation by the addition of non-ionic surfactant and the epoxidation carried out at 55 to 65°C for a pre-determined time. At the end of the reaction, ENR latex is neutralized with ammonia and coagulated with salt and heat. It is washed thoroughly and processed into bales in a manner similar to that of TSR.

3.1.2.2 Properties

The epoxide groups are randomly distributed along the NR backbone and ENR retains the stereoregular cis-1,4-configuration of NR. Therefore, ENR can undergo strain crystallization resulting in high tensile strength and tear properties for the vulcanizates.

Epoxidation of NR leads to a systematic increase in polarity and glass transition temperature (Tg). For every one mole per cent of epoxidation, Tg increases by approximately 1°C. Thus Tg increases from –67°C for NR to –47°C for ENR 25 and -23°C for ENR 50. The effect of this change in Tg is clearly reflected in the vulcanizate properties of these materials.

The resistance of ENR to hydrocarbon oils increases with increase in epoxide content. The volume swelling value of ENR 50 in ASTM oils approaches that of medium acrylonitrile NBR and is superior to that of polychloroprene rubber (Baker *et al.*, 1986). Hence ENR 50 can find potential use in areas where NBR is presently being used.

Epoxidation also leads to substantial decrease in air permeability (Gelling, 1985). The permeability of ENR 50 is quite comparable to that of butyl rubber and, therefore, it can find application in inner tubes.

Another distinctive feature of ENR is the high degree of reinforcement achieved with silica fillers without the addition of a silane coupling agent (Baker *et al.*, 1986; Alex *et al.*, 1989). Silica reinforces ENR 25 and ENR 50 to an extent equivalent to that obtained with carbon black.

3.1.2.3 Applications

With increasing levels of epoxidation, hysteresis also increases and this is reflected in increased wet grip and lower resilience at ambient temperatures. Wet grip and rolling resistance ratings of tyre retreaded with ENR 25 compounds show that these tread compounds have a wet grip superior to an oil-extended SBR and a rolling resistance equivalent to that of NR (Baker, 1988). The wear properties of ENR 25 black and black/silica (35:15) filled compounds are comparable with NR tread stock. By blending with polybutadiene rubber (BR), improvements in wear can also be obtained (Gelling and Porter, 1988).

ENR has considerable potential in both conventional adhesives and sealants. It can be used as a bonding agent to improve adhesion between component parts of rubber products (*e.g.* the liner and cover compounds of oil hose). It can also be used as cover compound for PVC core conveyor belting (Gelling and Porter, 1988).

A wide range of general rubber applications can be envisaged for ENR, like milking inflations, pharmaceutical and food contact applications, oil hose, conveyor belting, shoe soles, floor coverings and high damping engine mountings. ENR 50 or its blends with suitable rubbers can find application in inner tubes for bicycles, motorcycles and light agricultural vehicles.

3.1.3 Constant viscosity and low viscosity natural rubber

Natural rubber undergoes hardening or increase in viscosity during primary processing and subsequent storage under ambient conditions. This process is termed storage hardening and is greatly enhanced by low relative humidity. The increase in viscosity is caused by a cross-linking reaction involving the randomly distributed carbonyl groups on the main rubber chain and the amino acids present among the non-rubber constituents (Sekhar, 1960). The cross-linking reactions leading to hardening of rubber can effectively be inhibited by the addition of a small amount of hydroxylamine hydrochloride or hydroxylamine neutral sulphate or semicarbazide to the latex before coagulation. These chemicals effectively block the carbonyl groups and preserve the Mooney viscosity of the rubber at the level at which the treatment is made. The rubber so treated retains its original viscosity for a long time and is graded as constant viscocity (CV) rubber. The controlled and stable Mooney viscosity provides easy and uniform processing. Pre-mastication can be reduced or even eliminated.

Viscosity-stabilized rubber is technically specified and is available in two forms: ISNR 5CV and ISNR 5LV. The CV and LV forms are stabilized in the same manner, but LV differs from CV in having an added 4 phr of a non-staining naphthenic process oil. The largest proportion of production falls within the Mooney viscosity range of 60 to 65 for CV and 50±5 for LV.

3.1.3.1 Production of CV rubber

Properly blended, bulked and diluted latex is ammoniated to 0.01 to 0.1 per cent by weight of latex. The latex is treated with five per cent solution of sodium metabisulphite (0.04 phr on DRC) to prevent enzymic discolouration. Hydroxylamine neutral sulphate is added (0.15 phr on DRC) as 10 per cent aqueous solution under stirring. Stirring is continued for 3 to 5 min and the latex coagulated and processed in the usual manner.

3.1.3.2 Processing into LV rubber

Naphthenic oil (4 phr on DRC of latex) is added to the latex treated with hydroxylamine neutral sulphate in the form of an emulsion in water. The latex is then coagulated and processed.

3.1.3.3 Testing of CV and LV rubber

Three parameters have to be satisfied to classify the viscosity stabilized rubber to CV or LV grades in addition to the ISNR specifications . (1) The Mooney viscosity shall be within the designated range. The test for this has to be carried out on homogenized samples, (2) Effective stabilization of viscosity as evaluated by an accelerated storage hardening test, which involves heating initial plasticity test pellets for 24 h at 60°C in an atmosphere dried by phosphorus pentoxide. The increase in initial plasticity must be less than eight units. Rubbers which pass this test have been shown not to harden by more than two units during transport and storage, (3) The correct amount of mineral oil is added in the case of LV rubbers. The level of oil is estimated by acetone extraction. LV rubbers must have an acetone extract content of six to eight per cent.

3.2 Grafting

Natural rubber can chemically be modified to graft co-polymers by polymerizing vinyl monomers either in latex or in solution. Methyl methacrylate (MMA), styrene and acrylonitrile (Claramma *et al.*, 1984; Claramma *et al.*, 1989) are the prominent monomers used for grafting onto NR. Among the NR-based graft co-polymers, poly (methyl-methacrylate) graft NR (PMMA-g-NR) is the most popular and has been commercialized since mid-1950s in Malaysia under the trade name Heveaplus MG. During polymerization, a substantial portion of the vinyl polymer gets chemically bonded to the NR backbone while some amount of vinyl polymer remains free.

Generally, grafting can be achieved using free radical initiation by two methods *viz.* by use of chemicals and by irradiation with γ rays. Benzoyl peroxide, potassium persulphate, polyamine-peroxide redox combination and cumene hydroperoxide with tetra ethylene pentamine (TEP) activator are the commonly-used free radical initiators.

3.2.1 Poly (methyl-methacrylate) graft natural rubber

It is produced by reacting methyl methacrylate monomer in NR latex with cumene hydroperoxide which acts as initiator (Muthurajah, 1964) or by the irradiation method (George *et al.*, 1987). Methyl methacrylate, made free of inhibitor by washing with 10 per cent sodium hydroxide solution and then with water, is made into an emulsion containing cumene hydroperoxide (0.35% on DRC) with ammonium oleate as emulsifying agent.

The required amount of field latex (ammoniated to 0.5% w/v) is charged into the reaction tank and diluted with an equal volume of water. The methyl methacrylate emulsion is then added to the latex under stirring and the stirring continued for 30 min at 50 to 60 rpm. A solution of TEP activator in water (10% v/v) is added to the latex at a rate of 0.3 per cent by weight on rubber and stirred for a few more minutes. When the contents are thoroughly mixed, stirring is stopped and the reaction allowed to continue overnight. Then the latex is coagulated by running it to an equal volume of boiling water containing 12 per cent formic acid. The coagulum is washed and milled into crepe and dried at 80°C.

A wide range of products is possible depending upon the amount of MMA monomer used for grafting. Three grades of Heveaplus MG are generally prepared, MG 30, MG 40 and MG 49 where the numbers represent the percentage of methyl methacrylate content in the grafted rubber. Heveaplus MG 49 is the most commonly used one.

3.2.1.1 Properties and uses of Heveaplus MG

Poly (methyl-methacrylate) is a hard plastic and when grafted onto NR it increases the modulus of rubber. The increase in modulus depends on the percentage of poly (methyl-methacrylate) grafted to NR. The main commercial interest of Heveaplus MG lies in its ability to produce self-reinforced vulcanizates. It can also act as a reinforcing agent for NR with which it is compatible in all proportions. Heveaplus MG or its blends with NR can be compounded and vulcanized in much the same way as rubber, the incorporation of the vulcanizing agents being carried out in internal mixers or two-roll mills. The vulcanizates have excellent physical properties at high hardness levels with good hardness retention at higher temperatures, excellent flow properties and good electrical properties.

The major use of Heveaplus MG is in adhesives. It gives exceptionally good bond strength for NR onto PVC which can be particularly useful in shoe industry. The adhesive property can also be used in tyre cord dipping. Developments in automotive field have created a demand for hard, flexible materials based on NR in applications such as sight shields, soft fronts, rear ends, rubbing strips and bumpers where the blends of Heveaplus MG 49 with NR can be used (Wheelans, 1977). It can also find use as a compatibilizer in plastic rubber blends.

3.2.2 Polystyrene graft natural rubber

Polystyrene can be grafted onto NR backbone by polymerizing styrene in NR latex. Various levels of modification can be achieved according to the proportion of grafted polystyrene. They are designated as SG rubbers. Styrene, washed free of inhibitor and containing cumene hydroperoxide (0.25 parts per 100 parts of dry rubber) is emulsified in water using non-ionic stabilizer (Vulcastab VL) as the emulsifying agent. The emulsion is then added to the field latex diluted with an equal amount of water under stirring. When a homogeneous dispersion is obtained, a 10 per cent solution of tetraethylenepentamine (2 parts per 100 parts of dry rubber) is added and heated to 55°C. The reaction is allowed to continue for 6 to 7 h. The latex is then coagulated by slowly pouring into boiling water containing 0.5 per cent formic acid. It is then washed, milled into crepe and dried at 80°C. It can be blended with NR, compounded and vulcanized in the usual manner. SG 50 can find application in microcellular solings in place of high styrene resin grade of SBR.

3.3 Intramolecular changes

3.3.1 Liquid natural rubber

Extensive size reduction of molecular chains of NR by depolymerization leads to the formation of liquid NR. Depolymerization can be achieved by chemical means or by the application of a combination of thermal and mechanical energy or by high energy radiation. The process can be carried out in latex stage as well as in dry rubber stage.

3.3.1.1 Production

Liquid natural rubber (LNR) is prepared either by thermal or by chemical depolymerization of NR. Thermal depolymerization involves heating of the masticated rubber at 220 to 240°C for a predetermined time under stirring while chemical depolymerization involves an oxidation-reduction reaction using phenylhydrazine and air. In both methods, the liquid NR retains the linear structure of the natural cis-1, 4 polyisoprene molecule.

In thermal depolymerization, rubber with 0.2 to 0.6 phr of a peptizer is first masticated in a two-roll mill to a Mooney viscosity of 25 to 30 and then loaded into the depolymerizing apparatus. It is then heated to 220 to 240°C under stirring for 3 to 7 h. Liquid NR with a viscosity average molecular weight (Mv) ranging from 5000 to 20000 can be prepared depending on the amount of peptizer and time of heating (Claramma *et al.*, 1991).

Chemical depolymerization is carried out in the latex stage by a redox reaction involving phenylhydrazine and air (UNIDO, 1985). The mechanism of depolymerization involves the oxidation of phenylhydrazine by air to give phenyl radical, which through addition or transfer reactions, initiates the formation of hydroperoxides. These peroxides lead, by chain breakage, to liquid NR with molecular weight range 6000 to 20000, depending on the quantity of reagent used. The process involves four steps :

(1) Stabilization : Stabilization of ammonia-preserved latex is achieved through addition of 1 phr of an anionic stabilizer (sodium di-isobutylsulphonate) and 0.2 phr of NaOH, until a pH of 10 is obtained. The latex is then deammoniated by mechanical stirring at room temperature for 24 to 48 h.

(2) Depolymerization : The latex is then heated up to 65°C and air-bubbled to ensure good oxygenation. A hot water dispersion of phenylhydrazine is slowly added over a few hours while stirring the latex. Stirring, heating and air-bubbling are carried out for 12 to 24 h.

(3) Coagulation and washing : Coagulation of LNR is made by adding formic acid (pH 4.8). After separation from the serum, the coagulum is washed three times with water.

(4) Drying : The washed coagulum is dried in a thin layer continuous dryer at 160 to 200°C.

LNR can be vulcanized to get very low hardness vulcanizates. The ingredients may be added as dispersions in plasticizer for uniform distribution. Large amounts of plasticizer are required in the case of the filled compounds. The vulcanizates have much inferior physical properties when compared with those made from conventional dry rubber (Claramma *et al.*, 1991). Addition of fillers does not improve the physical properties of LNR vulcanizates.

3.3.1.2 Applications

Various industrial and art work require cheap and elastic moulds. Some of them are made from synthetic liquid elastomers, especially fluid silicones. LNR can be used in their place with economic advantage. The printing industry requires very low hardness rubber goods and LNR gum vulcanizates can be used for the same. Due to excellent tack properties, LNR can also be used as a binder in grinding wheels. Another potential field of application is the use of LNR as a reactive plasticizer, where it acts as a processing aid during compounding, but on heating covulcanizes into the rubber network, and hence becomes advantageous (Nair *et al.*, 1989). LNR can also be used as bulk viscosity modifiers in rubber compounds (Nair *et al.*, 1997).

3.3.2 Cyclized natural rubber

Cyclized rubber is a hard brittle thermoplastic derivative of NR, obtained by treating natural rubber with acidic catalysts such as sulphuric acid, aromatic sulphonic acids and Lewis acids such as stannic chloride, titanium tetrachloride and boron trifluoride (Coomarasamy *et al.*, 1978). Cyclized rubber prepared from sulphuric acid or its derivatives are more resinous in nature, varying from brownish black to light-coloured transparent resins of comparatively low molecular weight. The low molecular weight product is readily soluble in many solvents and is compatible with a range of resins, oils and plasticizers. Cyclized rubber prepared from chlorostannic acid is tougher and has higher physical strength.

3.3.2.1 Preparation

Cyclized rubber can be prepared from rubber solutions, solid rubber or from latex and these involve different methods of manufacture. The simplest method of preparation is by mixing 100 parts of NR with 8 parts of paratoluene sulphonic acid and heating the resulting mixture at 140°C (Narangoda, 1973) Removal of proteins present in NR increases efficiency of cyclization. Cyclized rubber can be prepared commercially from DPNR (Coomarasamy *et al.*, 1981). DPNR is milled with 10 parts of paratoluene sulphonic acid for about 30 to 45 min until rubber crumbles into pieces. The crumbs are then milled into loose sheets and kept in aluminium trays for autocyclization to take place. During this process, rubber is converted into a molten liquid which solidifies to a dark brittle resin on cooling. For preparation of solution grade cyclized rubber either xylyl mercaptan or tolyl mercaptan is added before the deproteinization process.

Chlorostannic acid-catalysed cyclized rubber is prepared from dry rubber by milling in 10 per cent of the hydratyed chlorostannic acid for 2 to 5 h at 130 to 150°C depending on the degree of cyclization required, or by refluxing a solution of masticated rubber in benzene with chlorostannic acid. A process of cyclization involving cyclization of NR in liquid phase using tin salts is also reported (Tillekeratne, 1993).

3.3.2.2 Uses

Cyclization results in reduced unsaturation, loss of elastic behaviour and increase in density of NR and gives a product inert to thermal, chemical and atmospheric degradation. Cyclized rubber of low molecular weight is soluble in many solvents and is compatible with a range of resins including rubber seed oil alkyds, and finds application in paints, printing inks and surface coatings especially where resistance to chemicals is required. The advantages of using cyclized rubber as a binder in road marking paints include its quick drying characteristics and abrasion resistance. Cyclized rubber, depending on the extent of cyclization, finds use as reinforcing resin, adhesive and bonding agent. A high degree of cyclization of over 70 per cent is required for use of cyclized rubber as a reinforcing resin. As a reinforcing filler, cyclized rubber can be used in the manufacture of shock resistant paints. A typical compound would consist of 70 parts of cyclized rubber and 30 parts of rubber as a plasticizer to decrease the brittle point with the normal amount of fillers and vulcanizing agents. Cyclized rubber, when properly mixed in rubber compounds, imparts good physical properties by its reinforcing action and hence finds application in shoe soles, hard mouldings and non-black heavy duty industrial rollers.

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