NATURAL RUBBER LATEX FILLER MASTERBATCH BY SOAP SENSITISED COAGULATION- PREPARATION, PROCESSING AND EVALUATION

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Ph. D .Thesis

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Certificate

This is to certify that the thesis entitled "**Natural Rubber Latex Filler Masterbatch by Soap Sensitised Coagulation-Preparation, Processing and Evaluation**" which is being submitted by Mr. Sasidharan K.K., in partial fulfilment of the requirements of the degree of Doctor of Philosophy, to Cochin University of Science and Technology (CUSAT), Kochi, Kerala, India is a record of the bonafide research work carried out by him under our guidance and supervision.

Mr. Sasidharan has worked on the research problem for about eight years (part-time, 2005 - 2014) in the Rubber Research Institute of India, Kottayam and in the Department of Polymer Science and Rubber Technology of CUSAT, Kochi. In our opinion, the thesis has fulfilled all the requirements according to the regulations. The results embodied in this thesis have not been submitted for any other degree or diploma.

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Declaration

I hereby declare that the thesis entitled “**Natural Rubber Latex** tex **Filler Masterbatch by Soap Sensitised Coagulation - Preparation, Processing And Evaluation**” is the original research work carried out by me under the supervision of Dr. Thomas Kurian, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, India and Dr. (Mrs.) Rosamma Alex, Deputy Director, Rubber Technology Division, Rubber Research Institute of India, Kottayam, Kerala, India. No part of this thesis has been presented for any other degree from any other institution.

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Preface

Fillers when added to polymer systems are known to cause a considerable change in dynamic properties. This phenomenon has been investigated in-depth, especially in relation to rubber products. The level of dispersion of fillers like carbon black, silica and nanoclay in a rubber matrix is an important issue in a large variety of rubber products. Though carbon black could be easily dispersed in natural rubber by conventional mill mixing, there are issues like air pollution, material loss and higher energy consumption. Preparation of latex–carbon black masterbatch by the addition of carbon black as a slurry has been suggested as one of the methods to avoid some of these problems. In the case of fillers such as silica and nanoclay, it is extremely difficult to disperse these highly aggregate fillers in natural rubber using a mixing mill.

The mixing of filler in rubber includes stages like incorporation, distribution and dispersion. The first two processes are known to be energy intensive operations. Incorporation of fillers as dispersions in the latex stage followed by co-coagulation of the latex filler system is expected to be a less energy intensive process. The present study aims at standardisation of a method for quick coagulation of natural rubber latex, identification of a suitable form of the latex for the preparation latex-filler masterbatches, development of a protocol for the preparation of latex-dual filler masterbatches, preparation of masterbatches containing a nanofiller in addition to the conventional fillers and evaluation of the validity of natural rubber – filler masterbatches in blends of natural rubber with poly butadiene rubber.

The thesis consists of eight chapters. A concise introduction to the subject is presented in the first chapter. A review of literature and the objectives of the work are mentioned in this chapter. The second chapter describes the materials used and the various experimental procedures employed in the work. The third chapter describes fatty acid soap sensitised coagulation of fresh natural rubber latex. Fresh natural rubber (NR) latex coagulates immediately by sensitisation with fatty acid soaps.

Forth chapter reports the latex stage incorporation of fluffy carbon black (carbon black powder before pelletisation) in different forms of natural rubber latices like fresh latex, preserved latex, concentrated latex and a blend of preserved field latex and skim latex. The fifth chapter deals with carbon black / silica masterbatch from fresh natural rubber latex. A simple method for production of natural rubber latex - carbon black/silica masterbatches with enhanced mechanical properties is described.

The results of investigations on HAF/silica/nanoclay "ternary" masterbatch from fresh natural rubber latex is reported in chapter 6. A process for the production of carbon black/silica/nanoclay ternary filler masterbatch from fresh natural rubber latex was standardized. Chapter seven deals with blends of fresh natural rubber latex based masterbatch (dried) and polybutadiene rubber. The conclusion of the investigations is presented in the last chapter of the thesis.

Abstract

Sensitisation of natural rubber latex by addition of a small quantity of an anionic surfactant prior to the addition of a coacervant results in quick coagulation. The natural rubber prepared by the novel coagulation method shows improved raw rubber characteristics, better cure characteristics in gum and carbon black filled compounds and improved mechanical properties as compared to the conventionally coagulated natural rubber. Compounds based on dried masterbatches prepared by the incorporation of fluffy carbon black in different forms of soap sensitised natural rubber latices such as fresh latex, preserved field latex, centrifuged latex and a blend of preserved field latex and skim latex show improved cure characteristics and vucanizate properties as compared to an equivalent conventional dry rubber-fluffy carbon black based compound.

The latex masterbatch based vulcanizates show higher level of crosslinking and better dispersion of filler. Vulcanizates based on fresh natural rubber latex- dual filler masterbatches containing a blend of carbon black and silica prepared by the modified coagulation process shows very good mechanical and dynamic properties that could be correlated to a low rolling resistance. The carbon black/silica/nanoclay tri-filler - fresh natural rubber latex masterbatch based vulcanizates show improved mechanical properties as the proportion of nanoclay increased up to 5 phr.

The fresh natural rubber latex based carbon black-silica masterbatch/ polybutadiene blend vulcanizates show superior mechanical and dynamic properties as compared to the equivalent compound vulcanizates prepared from the dry natural rubber-filler (conventional dry mix)/polybutadiene blends.

Key words: carbon black masterbatch, coacervant, fresh natural rubber latex, surfactant, nanoclay, silica, polybutadiene rubber, quick coagulation

Contents

Chapter 3

Chapter 6

Chapter 7

Chapter 8

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Chapter 1

GENERAL INTRODUCTION

Contents

1.1 Introduction

Natural rubber latex is a colloid, the dispersed phase being predominantly rubber and the dispersion medium water. Fresh latex has a specific gravity of 0.96 to 0.98 and a pH in the range of 6.5 to 7.0. In addition to rubber and water, latex contains small quantities of proteins, resins including fats, fatty acids, other lipids, sterol and sterol esters, carbohydrates and mineral matter. Fresh latex is composed of rubber (30-40%), proteins (1-1.5%), resins (1.5-3%), mineral matter (0.7-0.9%), carbohydrates (0.8-1%) and water (55-60%) [1-4].

The size of the rubber particles range from 0.02 to 3.0 μm and their shape is mostly spherical. The particles are strongly protected by a film of adsorbed proteins and phospholipids [5-7]. The other particles in latex comprise lutoids and Frey-Wyssling particles. The lutoids are subcellular membrane bound bodies ranging in size from 2 to 5 µm, containing a fluid serum known as B-serum, which is a destabilizer for rubber particles. Frey-Wyssling particles are spherical, larger in size and are yellow coloured. Methyl-l-inositol (quebrachitol), sucrose and glucose are the major carbohydrates in latex. About 20% of the available proteins in latex is adsorbed on the rubber particles, an equal quantity is found in the B-serum and the remainder in the latex serum. The adsorbed proteins and phospholipids impart a negative charge on the rubber particles thereby improving the stability of the colloid [8-11]. The lipids associated with rubber and non-rubber particles play a key role in the stability and colloidal behaviour of latex. Latex also contains amino acid nucleotides and low molecular weight thiols. The nucleotides are co-factors and intermediates in the biosynthesis of rubber.

1.2 Processing of natural rubber latex

Fresh field latex is obtained from the bark of Hevea brasiliensis by a process of controlled wounding during which thin shavings of bark are removed. Generally latex accounts for about 80 % of the crop the rest being field coagulum. The fresh latex and the various forms of field coagulum are not suitable for storage and marketing as these are likely to deteriorate on storage. The presence of carbohydrates and other non-rubber constituents makes latex a suitable medium for the growth of micro-organisms such as bacteria and yeast. While bacteria cause conversion of carbohydrates into volatile fatty acids and proteins into simple compounds the yeast causes fermentation of the carbohydrates. These reactions cause spontaneous coagulation and putrefaction of latex [12, 13]. Thus fresh latex on keeping slowly undergoes thickening and ultimately coagulates into a lump. Putrefaction of proteins causes the formation of foul smelling gases such as hydrogen sulphide and sulphur dioxide. Fermentation leads to the production of large quantities of carbon dioxide which causes the coagulum to expand. Also prolonged storage of the wet coagula leads to deterioration of the rubber. Hence, both fresh latex as well as the field coagula have to be processed into forms suitable for long-term storage, marketing and further processing into a finished product. The process of conversion of fresh latex and field coagulum into a suitable marketable form of raw rubber is called primary processing as another stage of processing is necessary to convert the raw rubber into a finished product. The various marketable forms of raw rubber include preserved field latex and concentrated latex, ribbed smoked sheet (RSS) and air dried sheet (ADS), block or technically specified rubber (TSR), crepe rubber consisting of pale latex crepe (PLC) and estate brown crepe (EBC) and other low grade crepe made from field coagulum.

1.2.1 Preserved and concentrated latex

Preservation of latex aims at preventing bacterial activity and enhancing its stability. It is achieved by using preservatives such as ammonia. Apart from being a good bactericide, ammonia enhances the colloidal stability of latex and deactivates certain harmful metal ions. To be effective as preservative, ammonia is used at 0.7 to 1.0% by weight of latex. During storage, the higher fatty acid esters present in latex get hydrolysed into ammonium soaps, which improve the mechanical stability of latex. However, the pungent smell of ammonia, the low stability of latex in the presence of zinc oxide and longer gelling time of latex foam are disadvantages. Hence, many low ammonia preservative systems have been developed, in which the concentration of ammonia is reduced to around 0.2% and supplemented with secondary preservatives such as tetrmethyl thiuram disulphide (TMTD) - zinc oxide combination, zinc diethyl dithiocarbamate, boric acid etc. Of these, a combination of 0.2% ammonia, 0.0125% each of TMTD and zinc oxide and 0.05% of lauric acid (LATZ system) is the most promising [14, 15].

Concentration of latex is necessary on account of the preference by the latex products manufacturing industry for a latex with high dry rubber content (DRC) and for transport economy and purification of latex. Rubber products such as gloves, condoms, rubber bands, balloons, foam mattresses, elastic thread etc. are made directly from latex for which about 10% of the global production of NR is processed as preserved and concentrated latex.

The processes for concentration include evaporation, electrodecantation, creaming and centrifuging. Evaporation removes only water and hence the ratio of non-rubber constituents to rubber and the particle size distribution remain unchanged. However, the other three processes involve the partial removal of non-rubber materials and smaller rubber particles. Centrifuging and creaming are more popularly used for the production of concentrated latex. The principle of creaming and centrifuging involves the application of Stokes's Law [16, 17]. In any dispersion, the dispersed particle cream or sediment under the influence of gravity and the velocity of creaming depends on several factors and is stated mathematically as:

$$V = 2_g (Ds - Dr)\, r^2 / 9\acute{\eta} \text{ --- } (1.1)$$

Where V is the velocity of creaming (m/s)

g is the acceleration due to gravity (m/s^2)

Ds, Dr are the densities of serum and rubber particles, respectively (g/cm^3)

r is the effective radius of the particle (cm), and

$\acute{\eta}$ is the coefficient of viscosity of serum (centipoise)

In the creaming process, the creaming agent such as sodium alginate, forms an adsorbed layer over the rubber particles which reduces the Brownian movement and the intensity of the negative electric charge on the particle surface, thereby promoting temporary agglomeration of particles. Thus the effective size of the particle increases, favouring faster creaming. In the centrifugal process, when the latex enters the machine, rotating at a high speed of around 7000 rpm, the centrifugal force, which is several thousand times larger than the gravitational force causes rapid separation of the latex into cream and skim.

In creaming, the skim is almost clear serum and is therefore discarded. However, in the centrifugal process, the skim contains 2 – 8% rubber, which is recovered by coagulation using dilute sulphuric acid and processed as skim rubber, which is a low quality rubber. Concentrated natural rubber latex is marketed to strict technical specifications. The current ISO specifications for latex concentrates are given in Table 1.1[18]

Table 1.1 ISO 200e4: 1997 (E) (Specifications for concentrated natural rubber latex)

Characteristic	Type HA	Type LA	Type XA	Type HA creamed	Type LA creamed	Method of test
Total solids content[1], % (m/m), min.	61.5	61.5	61.5	66.0	66.0	ISO 124
Dry rubber content[1], % (m/m), min.	60.0	60.0	60.0	64.0	64.0	ISO 126
Non-rubber solids[2], % (m/m), max.	2.0	2.0	2.0	2.0	2.0	-
Alkalinity (asNH_3), % (m/m), calculated with respect to the latex concentrate	0.60 min	0.29max	0.30 min	0.55 min	0.35max	ISO 125
Mechanical stability, seconds, min.	650	650	650	650	650	ISO 35
Coagulum content, % (m/m), max.	0.05	0.05	0.05	0.05	0.05	ISO 706
Copper content, mg/kg of total solids, max.	8	8	8	8	8	ISO 8053
Manganese content, mg/kg of total solids, max.	8	8	8	8	8	ISO 7780
Sludge content, % (m/m), max.	0.10	0.10	0.10	0.10	0.10	ISO 2005
Volatile fatty acid (VFA) number, max.	0.20	0.20	0.20	0.20	0.20	ISO 506
KOH number, max.	1.0	1.0	1.0	1.0	1.0	ISO 127

[1]. The requirement is for either total solids content or dry rubber content.
[2]. The difference between the total solids content and dry rubber content.

1.2.2 Ribbed smoked sheet

This is the preferred form of processed natural rubber in small holdings in countries such as India and Thailand. The process is simple, relatively less expensive and is highly viable even when the quantity of available latex is small. Fresh field latex, after sieving to remove foreign matter and bulking to make it uniform in quality, is diluted to 12.5 to 15% DRC. Dilution improves the colour and transparency of the sheet and makes the sheeting operation easier, and allows denser impurities to sediment on standing for 10 – 15 min. Sodium bisulphite is added to latex at the rate of 1.2 g per kg DRC to prevent surface darkening on wet sheet caused by enzyme catalyzed oxidation of phenolic components in latex. The diluted latex is then transferred to coagulation tanks or pans and coagulated with dilute formic or acetic acid. These acids are preferred on account of their volatile and non-corrosive nature. After a few hours or the next day, the thick slab of coagulum is squeezed between a pair of steel or cast iron rollers to remove water and to make into a sheet of approximately 3 mm thickness. The final set of rollers is grooved to introduce ribbed markings on the sheets. These markings increase the surface area of sheet and hence facilitate drying. The wet sheets are soaked in a 0.1% solution of paranitrophenol (PNP) for a few minutes to prevent mould growth on dry sheets during storage. The sheets are then allowed to drip for a few hours before loading into the smoke house for drying.

Sheet rubber is ideally dried in smoke houses or hot air chambers and the dried sheet thus obtained are known as ribbed smoked sheet (RSS) or as air dried sheet (ADS) respectively. Partial drying in sun followed by smoke drying is widely practised in smallholdings. Several types of smoke houses such as those with furnace inside or outside the chamber, batch type or continuous type are in operation [19]. The temperature in the smoke house is maintained in the range of 40 – 60°C. The sheets are held on wooden or bamboo rods (beroties) placed on trolleys which move on a central rail track in a large tunnel type smoke house. In smaller type of smoke houses, the beroties are placed on a framework inside the chamber. Drying of sheets takes four to six days in smoke house. The dried sheets are visually examined and graded adopting the norms prescribed by the International Rubber Quality and Packing Conference under the Secretariat of the Rubber Manufacturers' Association (RMA) and described in the 'Green Book.' Grading is done on the basis of colour, transparency, presence of mould, oxidized spots, blisters, bubbles, dirt, sand and other foreign matter, degree of drying, tackiness, etc. There are six grades of sheet rubber which are designated as RMA or RSS 1X and RSS 1 to RSS 5. RSS 1X is the best and RSS 5 the least. Sheets of the same grade are packed together into a bale.

1.2.3 Pale latex crepe and sole crepe

These two are superior quality forms of natural rubber, prepared from fresh latex under controlled conditions. Both are light coloured and hence are produced from latex after either removing or bleaching the naturally occurring yellow carotenoid pigments. These forms of NR are preferred in products where light colour is important. Latex from certain selected clones such as PB 86 and RRIM 600, which give relatively white latex with minimum β-caroteins and are less susceptible to enzymic discolouration, is preferred for production of PLC. Pre-coagulation of latex is avoided preferably by the addition of sodium sulphite. The latex, after bulking is diluted to 20% DRC and the yellow pigments are bleached with 0.05% of tolyl mercpatan or its water souluble alkali metal salt [20]. Alternatively, the pigments are removed by fractional coagulation where about 1 g of acetic acid or oxalic acid is added to every kg DRC of latex followed by stirring and allowing to remain undisturbed for 1 to 2 hours. About 10% of the rubber coagulates along with bulk of the yellow pigments. The coagulum is removed and the remaining fraction of latex is fully coagulated and processed into crepe with thorough washing. The thin crepe, 1 – 2 mm thick, is dried in air at a maximum temperature of 35 °C for about two weeks. Very often, a combination of fractional coagulation and bleaching is used. Pale crepe is graded visually according to the Green Book as in the case of RSS. The main criterion is colour and the grades are PLC 1X, PLC 1, PLC 2 and PLC 3. Sole crepes are used in the footwear industry and are made by laminating plies of pale crepe to the required thickness and consolidating them by hand rolling and finally through even speed rollers.

1.2.4 Field coagulum crepe

Cup lump, tree lace and other forms of coagulated forms of the crop can be processed into crepe after soaking in water to make them soft and to remove surface contaminants. The soaked material is then passed through a battery of crepe rollers. Proper blending is carried out on the rollers to ensure uniformity. Simultaneously, thorough washing is done by providing running water in every crepe roller. The crepe is dried in drying sheds at ambient or slightly elevated temperature. Grading is done visually as per Green Book and the main criterion is again colour. Different grades are available in each type.

1.2.5 Technically specified rubber

With the availability of synthetic rubbers in compact bales and as per technical specifications, the disadvantages of sheet and crepe rubbers, available in irregularly shaped bales and with visual grading system, became very evident. Consequently new methods of processing and presentation were developed to market NR as technically specified rubber in compact bales, wrapped in polyethylene film. Technically specified rubber (TSR) is now produced in almost all NR producing countries and are marketed under different names such as Standard Malaysian Rubber (SMR), Standard Indonesian Rubber (SIR), Standard Thai Rubber (STR), Indian Standard Natural Rubber (ISNR), etc. The advantages of TSR include assurance of quality for important technical parameters, consistency in quality, minimum space for storage and clean and easy to handle packing. This method enables NR producers to process both latex and field coagulum using almost the same set of machinery and to minimise the processing time to less than 24 hours. Although different methods were developed to produce TSR, all these processes involve certain common steps such as coagulation of latex, soaking of field coagulum in water, size reduction, drying, baling, testing, grading and packing [21]. Differences among commercial processes exist in the method of coagulation or in the machinery used for crumbling the coagulum.

During the early stages of development, conventional machinery like creepers, macerators, etc. were used for the production of TSR. However, with the advancement of technology, as the demand for block rubber increased several fold, the industry started specific machines for various operations. The most important items of machinery are the machinery used for pre-cleaning and initial processing of latex or field coagulum, slab cutter, coagulum crusher, pre-breaker, macerator/crepe roller, granular/turbo mill and hammer mill. The machinery used for final size reduction are hammer mill, shredder and extruder. Another critical equipment used in TSR processing is drier.

Figure 1.1. Pre-breaker

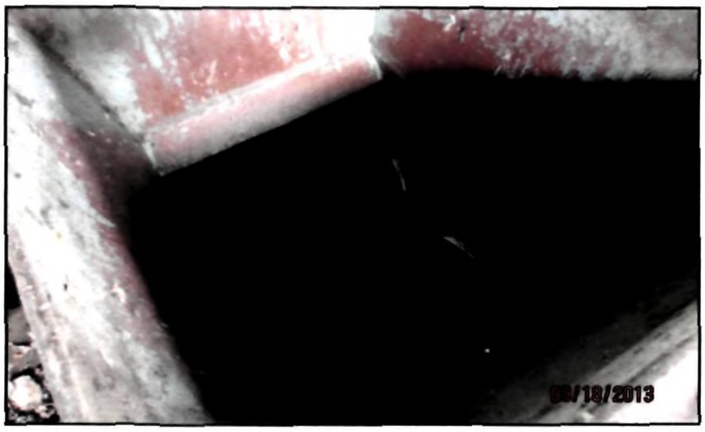


Figure1.2 Scrolls of the pre-breaker

Figure1. 3 Macerator/crepe

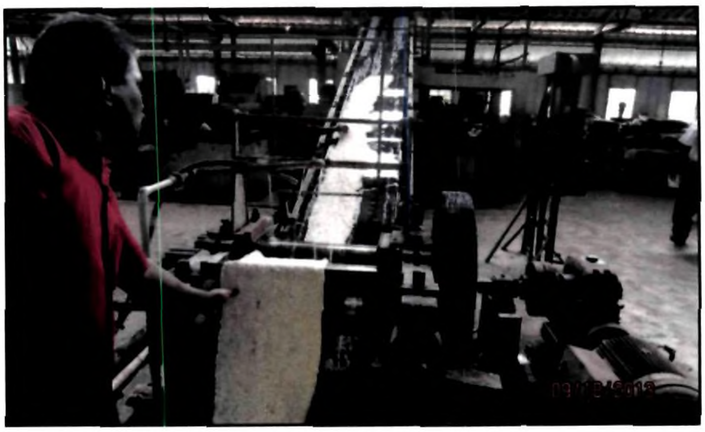


Figure1.4 Hammer mill / Shredder in operation

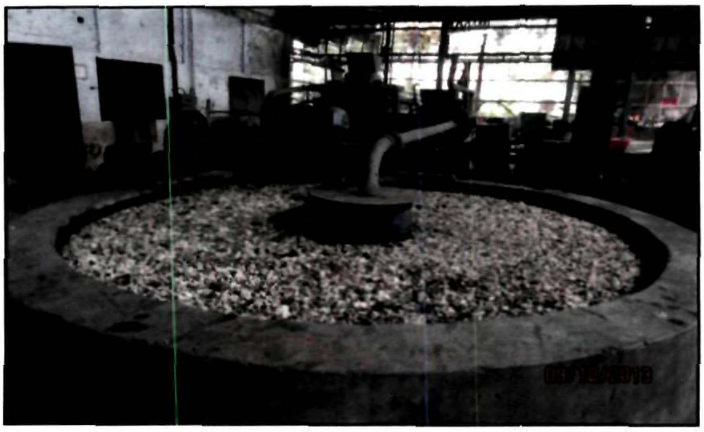


Figure 1.5 Crumbs collection tank

Figure1.6 Crumbs before loading in to dryer

Figure1.7 View of crumb drier

The objective is to accomplish uniform drying of the crumbs within the minimum possible time and to retain the intrinsic quality of natural rubber. The major components of driers are air circulation fans and heaters. Drying temperature of about 90 to 100 ^{0}C is maintained for field coagulum and around 100 to 110 ^{0}C for latex coagulum. The TSR is generally packed as 25 kg bales using baling press.

The major challenge in TSR processing is ensuring consistency in quality. Introduction of slab cutters or pre-breaker in the initial size reduction stage, use of macro-and micro-blending tanks, transfer of raw material from one tank to another by bucket elevator system and loading of final crumbs to the drier boxes with a slurry pump through a vibrating perforated screen and hopper are some of the recent developments in TSR production aimed at improving consistency in quality and reducing cost (Figures 1.1 – 1.7). The specifications for TSR have been revised several times depending upon the requirements of the consuming industry. The current ISO specifications for TSR are given in Table 1.2

Table 1.2 ISO 2000: 1989 (E) (Specifications for raw natural rubber) [18]

Characteristic	**Limits for rubber grades**						**Test method**
	CV	**L**	**5**	**10**	**20**	**50**	
	Colour code						
	Green	**Green**	**Green**	**Brown**	**Red**	**Yellow**	
Dirt content, %(m/m) retained on 45 μm sieve, max.	0.05	0. 05	0.05	0.10	0.20	0.50	ISO 249
Initial plasticity, min.	-	30	30	30	30	30	ISO 2007
Plasticity retention index (PRI), min.	60	60	60	50	40	30	ISO 2930
Nitrogen content, % (m/m), max.	0.60	0.60	0.60	0.60	0.60	0.60	ISO 1656
Volatile matter content, % (m/m), max.	0.80	0.80	0.80	0.80	0.80	0.80	ISO 248 (Oven method at100±5 °C)
Ash, % (m/m), max.	0.60	0.60	0.60	0.75	1.00	1.50	ISO 247
Colour index, max.	-	6	-	-	-	-	ISO 4660
Mooney viscosity, ML(1 + 4) 100 °C	60 ± 5						ISO 289

1.3 Properties of natural rubber

Natural rubber molecule is a linear, unsaturated, long chain aliphatic hydrocarbon polymer identified chemically as cis – 1, 4 polyisoprene. As in the case of other high polymers, natural rubber too is formed of molecules of different sizes with the weight average molecular weight ranging from 100,000 to about 10 million. A random blend of natural rubber shows a weight average molecular weight in the range of $1 - 1.5 \times 10^6$ and a number average molecular weight of $3 - 5 \times 10^5$. High molecular weight results in high viscosities. The Mooney viscosity of fresh dry natural rubber is in the range of 55 to 90. During storage the viscosity of natural rubber increases from 70 to 100 Mooney units depending on the length of the storage period. The natural storage hardening is believed to be due to the crosslinking reaction between aldehyde groups present in the rubber molecule with the amino groups of free amino acids and proteins [22, 23]. The aldehyde groups can be deactivated and storage hardening reaction can be inhibited by treating the rubber with 0.15% hydroxylamine salt. This is the technique used for the production of viscosity stabilized rubber grades, also known as constant viscosity (CV) rubbers.

Because of the high structural regularity, natural rubber crystallizes spontaneously when stored at low temperatures, or when it is stretched. Unstrained sample shows a maximum rate of crystallization at about -26 ^{0}C. Maximum degree of crystallinity attained is about 25 – 30 %. The un-stretched raw rubber shows a crystalline melting point (T_m) of +25 ^{0}C [24, 25].The strain induced crystallization behaviour gives natural rubber high tensile strength even in pure gum or vulcanizates filled with non-reinforcing fillers. Glass transition temperature of natural rubber is higher than that of cis-1, 4 polybutadiene. The density of natural rubber is about 0.913 g per cc., and its bulk density is about 0.85 g per cc. The rubber hydrocarbon content of raw natural rubber is about 94%. The presence of small quantities of non-rubber constituents such as proteins, fats, fatty acids, carbohydrates and mineral matter in natural rubber influences its physical and chemical properties.

A small percentage of rubber undergoes cross-linking even when present within the latex vessels of the tree. This is evident from the 5-10% gel content (microgel) in freshly prepared natural rubber. The gel content increases during storage and it is known as the macrogel. The macrogel is responsible for increased viscosity of natural rubber during storage. The macrogel breaks down almost completely during mastication of the rubber, and dissolves completely in aliphatic and aromatic solvents, chlorinated hydrocarbons, tetrahydrofuran and carbon disulphide. Coagulated and dried natural rubber is highly elastic at ambient temperature. On subjecting the dry rubber to intensive mechanical shearing it becomes progressively more plastic. This process is known as mastication. Masticated rubber is capable of flow, and therefore it can be shaped. The efficiency of mastication is temperature dependent and is minimum at about 100 ^{0}C [26]. Staudinger and Boundy [27] suggested that mastication involves the rupture of the rubber molecules due to the shearing forces. Efficiency of mastication can be improved by the addition of small quantities of chemicals known as peptizing agents (e.g. Zinc pentachlorothiophenate).

The high molecular weight, and the polymer chain entanglements make the dissolution of natural rubber in solvents difficult. The chemical reactivity of natural rubber is influenced by the presence of double bond in its molecular backbone. The presence of methyl group in the cis-1, 4-polyisoprene further enhances the reactivity of the double bond. Thus natural rubber is more reactive than polybutadiene, and poly styrene butadiene rubber to a number of chemicals, including the vulcanization chemicals.

1.4 Modified forms of natural rubber

As natural rubber is a product of nature, its properties are determined by the biochemical pathway by which the polymer is synthesized in the plant. In the case of natural rubber the polymerization process cannot be tailored like that of synthetic rubbers. The only option to modify natural rubber is after it has been harvested from the tree. Natural rubber can be modified by physical and chemical means. Rubber modified by physical means include oil extended natural rubber, latex stage compounds, latex carbon black masterbatch, polymer blends, deproteinised natural rubber and powdered rubber. Thermoplastic natural rubber prepared by blending natural rubber and polypropylene is also considered as a physically modified form of natural rubber.

The important chemically modified forms of natural rubber include hydrogenated natural rubber, chlorinated natural rubber, hydrohalogenated natural rubber, cyclized natural rubber, depolymerised liquid natural rubber, resin modified natural rubber, poly (methyl methacrylate) grafted natural rubber, poly (styrene) grafted natural rubber, and epoxidized natural rubber [28-30]. A few of the modified forms of natural rubber which have assumed commercial and/or scientific importance are detailed below.

1.4.1 Physically modified latex - filler masterbatch.

In the past several researchers have attempted the preparation of filler slurry incorporated natural rubber latex coagulum [31-35]. The preparation of carbon black masterbatch is carried out by mixing carbon black in water with latex and coagulating the latex carbon black mixture. However, the mismatch in the rate of coagulation of fresh field latex and carbon black slurry leads to poor dispersion of carbon black in rubber as well as significant loss of filler during the coagulation, making the process economically unviable [36-39]. Different forms of natural rubber latices like pre-vulcanized latex, modified latex and centrifuged latex were used for masterbatch preparation. US Patent 20080262123 describes a method to prepare pre-vulcanised latex coated carbon black powder [40-42]. In one of the methods coagulation was effected by high speed mixing of filler slurry and latex [43, 44]. Takashi *et al.* have patented a process in which the filler slurry is irradiated with high amplitude ultrasonic waves having amplitude of 80 μm or more and then mixed with concentrated natural rubber latex [45]. It was expected that the proteins adsorbed on rubber particles would interfere with polymer filler interactions and therefore in some methods the amide bonds in natural rubber latex were cleaved before preparing the masterbatch. However the expected benefit of reinforcement of rubber by fillers could not be realized by these attempts.

US Patent 2009/0088496 A1 [46] reports a process where rubber filler composite is obtained by jetting field latex of natural rubber in at high speed having a flow rate of 500 m/sec. or more into a mixing chamber, while supplying a filler slurry to the mixing chamber thereby separating and removing protein in the field latex and at the same time mixing the field latex and the filler slurry. US Patent 6841606 [47] reports a process wherein natural rubber masterbatch is prepared by mixing natural rubber latex having its amide linkage cleaved and an aqueous slurry having a filler dispersed in water and coagulating. US Patent 7960466 [48] discloses a method for latex stage incorporation of various types of fillers, like carbon black and silica along with surfactant, vulcanising agent and anti ageing agent.

1.4.2 Chemically modified forms of natural rubber

Hydrogenated natural rubber

Hydrogenation of natural rubber is still a scientific curiosity. Fully hydrogenated natural rubber, due to the removal of its unsaturation is unaffected by chemical reagents that normally attack unmodified natural rubber. However, the fully hydrogenated natural rubber cannot be vulcanized in the conventional manner. Platinum black was used as the catalyst for the production of hydrogenated rubber $(C_5H_{10})_x$ from dilute solutions of purified rubber. More recently Burfield et. al. [49] achieved complete hydrogenation in solution after one hour at 28 ^{0}C using homogeneous two component catalyst systems based on a variety of nickel and cobalt compounds in combination with tri-iosobutylaluminum. Potential applications considered for hydrogenated natural rubber are in cable industry, and for the preparation of adhesive compositions.

Chlorinated natural rubber

Chlorination of natural rubber in solution, in latex or in solid form results in substitution, addition and cyclization reactions. Kraus and Reynolds [50] have identified the following three distinct stages in the reaction of gaseous chlorine with natural rubber dissolved in carbon tetra chloride at 80^0C:

$$- C_{10} H_{16} - + 2Cl_2 \rightarrow - C_{10}H_{14}Cl_2 - + 2\,HCl \text{ --------------------}(1.2)$$

$$- C_{10}H_{14}Cl_2 - + 2Cl_2 \rightarrow - C_{10}H_{13}Cl_5 - + HCl \text{ ----------------}(1.3)$$

$$- C_{10}H_{13}Cl_5 - + 2Cl_2 \rightarrow - C_{10}H_{11}Cl_7 - + 2\,HCl \text{ -------------}(1.4)$$

The product after the first stage contains 35% chlorine, and is rubbery. The second stage product that contains 57% chlorine has no unsaturated groups. Further chlorination results in the final product containing 65.5% chlorine, with the empirical formula $-C_{10}H_{11}Cl_7-$. The final product of chlorination of natural rubber is a pale cream or off-white thermoplastic powder, which is inflammable and highly resistant to chemical attack.

It is also possible to chlorinate natural rubber in the latex stage [51]. The advantages of latex stage chlorination are the lower viscosity of the reaction system, better heat dissipation, and retention of high molecular mass in the product. In one of the methods for the chlorination of natural rubber in the latex stage proposed by van Amerongen [52] the latex is colloidially stabilized against acidification using 2 pphr of non-ionogenic ethoxylates, and 3-5 pphr cationic stabilizers of quaternary ammonium type. The stabilized latex is then strongly acidified with either concentrated hydrochloric acid or gaseous hydrogen chloride. Gaseous chlorine is then passed through the latex at a given temperature until the desired degree of chlorination has been attained. The main use of chlorinated natural rubber is for chemical and heat-resistant paints and coatings. It is also used in adhesive formulations, printing inks, paper coatings, and textile finishes.

Cyclized natural rubber

There are two main routes for the commercial production of cyclized natural rubber – by using sulphuric acid (or its derivatives such as p-toluene sulphonic acid), or by using chlorostannic acid. Cyclization reaction can be carried out in solution and in latex form [53, 54]. The applications of cyclized natural rubber are in printing inks, surface coatings (for chemical resistance), shoe soling, and for hard mouldings.

Graft copolymers based on natural rubber

Preparation of graft copolymers by polymerizing vinyl monomers either in natural rubber solution or in latex is a method for chemically modifying natural rubber. The common method to prepare a graft co-polymer is to polymerize an olefinic monomer by free radical mechanism within the latex of a polymer derived from another monomer. The result of polymerization is a graft copolymer which comprises the original polymer of the latex as the main chain component, and blocks derived from the added monomer as grafts [55-57]. Graft co-polymers of natural rubber with methyl methacrylate, styrene, and acrylonitrile [58] have been reported. The common methods of free radical polymerization to prepare the graft co-polymers based on natural rubber are: (i) by the use of peroxide based system, and (ii) irradiation with γ-rays.

Poly (methyl methacrylate) graft natural rubber

Poly (methyl methacrylate) grafted natural rubber has been commercially available since 1950 under the trade name Heveaplus. The popular commercial grades are Heveaplus MG 30, Heveaplus MG 40, and Heveaplus MG 49 where the numbers represent the percentage of methyl methacrylate in the grafted copolymer. Heveaplus MG 49 is the most popular grade. The major use of Heveaplus MG is in adhesives. It gives good bond strength for natural rubber to PVC and therefore, it is particularly useful in shoe manufacture. It is used as a compatibilizer in plastic-rubber blends. It is also used in applications such as automobile bumpers due to its self reinforcing nature [59].

Polystyrene graft natural rubber

Polystyrene can be grafted onto the natural rubber backbone by polymerizing styrene in natural rubber latex. The polystyrene grafted natural rubber is designated as SG rubber. A popular grade of the graft copolymer is SG50, where the number indicates the styrene content in the graft copolymer. The SG 50 graft copolymer is used in place of high styrene (SBR) rubber in rubber compounds for the manufacture of microcellular soling.

Epoxidised natural rubber

Epoxidised natural rubber (ENR) is an important modified form of natural rubber whose properties are close to those of special purpose synthetic rubbers. ENR is prepared by reacting natural rubber in latex form with performic acid formed *in situ* by the reaction of formic acid and hydrogen peroxide under controlled conditions [60, 61]. The double bonds of natural rubber react readily with peracids to yield epoxide groups. As shown in the reaction (Figure 1.8)

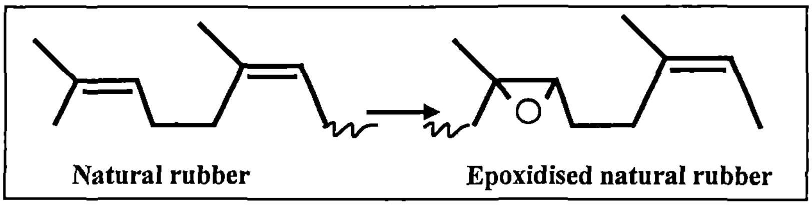


Figure 1.8 Formation of epoxidised natural rubber

Though any level of epoxidation can be achieved, only up to 50 mole percent is used in practice. 50, 25, and 10 mole% epoxidized products are termed ENR-50, ENR-25, and ENR-10. Studies using ^{13}C NMR have shown that the epoxide groups are randomly distributed along the natural rubber backbone [62].

Bulk epoxidised natural rubber can be vulcanised by heating with sulphur and conventional organic vulcanization accelerators, or by heating with peroxides. Baker, Gelling, and Newell [63] have studied the effect of epoxidation on ENR50, ENR 25, and ENR10. As the level of epoxidation is increased, the glass transition temperature (T_g) is raised by approximately 1 ^0C per mole percent epoxidation, and this results in a substantial drop in room temperature resilience for ENR 50, and increase in damping. Tg increases from -67 ^0C in the case of natural rubber to -47 ^0C for ENR 25, and -23 ^0C for ENR 50. Epoxidised natural rubber retains the cis-1, 4 configuration of natural rubber and hence undergoes strain crystallization and high tensile strength.

As compared to natural rubber, epoxidised grades of natural rubber shows improved reinforcement with silica without any coupling agent. Radial tyre tread prepared using formulations based on natural rubber with epoxide modification shows improved wet traction as compared to the tread based on unmodified natural rubber. Epoxidation of natural rubber reduces its gas permeability, making it suitable for applications such as tyre inner liner. The oil resistance of epoxidised natural rubber is superior to that of polychloroprene rubber [64], and it is almost equivalent to that of nitrile rubber with medium level of acrylonitrile content.

1.5 Rubber blends

Blending of rubbers is an easy method of getting tailor made properties for rubber for specific applications. The major problems of blending is the inherent incompatibility between polymers due to the difference in polarity, unequal distribution of curatives leading to inhomogeneous crosslinking and unequal distribution of fillers that may lead to poor mechanical properties. In many applications including tyres, rubbers are used in blends. The commercially used blends are based on, natural rubber, SBR, BR, NBR and EPDM.

Blends of natural rubber with thermoplastics

Raw natural rubber shows high green strength by virtue of strain-induced crystallization. Though natural rubber in the raw form is used in a few applications such as adhesives, binders and sole crepe, it is not truly thermoplastic, primarily due to its high molecular weight [65]. Mixing of natural rubber with polyolefin is one of the methods to prepare thermoplastic natural rubber (TPNR). TPNR behaves like vulcanized rubbers at ambient conditions, but at elevated temperatures they melt and flow like a thermoplastic material. Thus TPNR could be processed using conventional thermoplastic processing machinery without requiring vulcanization, and these materials could be reprocessed. Thus there is low level of wastage, as scrap too can be recycled.

Preparation of thermoplastic natural rubber

Thermoplastic natural rubber blends are prepared by blending natural rubber and polyolefins particularly polypropylene (PP) in an internal mixer. Immediately after dumping from the internal mixer the blend is sheeted on a two roll mill to a thickness of 4 to 8 mm. The mixing parameters include a temperature in the range of 175 to 185 °C and a total mixing time of about six minutes. Very high temperature of mixing is undesirable, as natural rubber may degrade at temperatures above 200 °C. The thermoplastic elastomeric nature of the blends is because of their two phase morphology. The hard phase that may be glassy or microcrystalline constitutes the pseudo-crosslinks or tie points, and these disappear upon heating. The elastic properties of the thermoplastic natural rubber blends are considerably improved if the rubber is partially cross-linked during blending. This process is known as dynamic cross-linking [66]. The popular cross-linking agents used in NR/PP blends include dicumyl peroxide and sulphur donor systems.

Properties and applications of TPNR

TPNR covers a wide range of material properties and has a correspondingly wide range of potential applications. TPNR in the 55 – 95 Shore A hardness range can be used to replace vulcanized rubbers, and flexible plastics for applications in footwear, sports goods, seals, mountings, and a wide range of moulded and extruded goods. Due to the presence of PP as a continuous phase, ozone resistance of TPNR is better than that of NR [67]. Grades of TPNR have been used for automotive bumpers, car radiator grills, floor tiles, castor wheels, handles and grips.

1.6 Manufacture of rubber products

Rubber has such remarkable and desirable properties that it is being put to many engineering applications like bearings, springs, and seals in addition to the manufacture of bulk products like tyres, tubes, belts hoses etc. Loads could be safely supported and misalignments accommodated by its ready elastic deformability. Resilience of rubber could be used to advantage in the production of efficient seals. In applications requiring exposure to adverse conditions like high temperature, exposure to oils, fuel solvents, ozone and other corrosive environments synthetic rubbers are preferred over natural rubber.

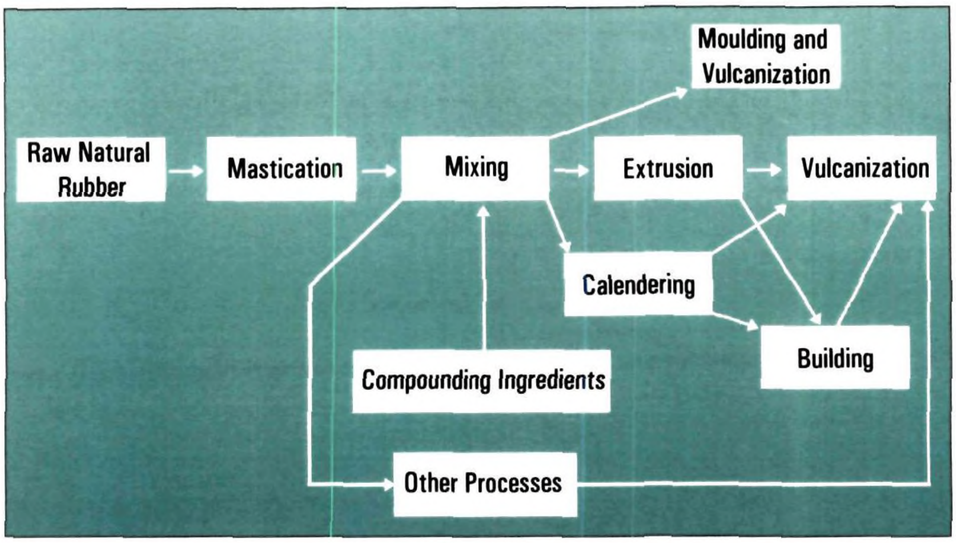


Figure 1.9 Basic steps in the manufacture of rubber products

A simplified flow diagram, which shows the basic steps in the manufacture of products from natural rubber, is shown in Fig 1.9 [18]. Starting with the raw rubber, the first step is usually mastication to soften the rubber by mechanical working and heat. The next step is the mixing or compounding of the softened raw rubber. This is also done in an open two roll mill or in an internal mixer. A wide variety of substances are frequently mixed with natural rubber. To develop a rubber compound the various ingredients to be used are compiled into a recipe. A recipe contains a number of components apart from the base rubber, each having a specific function during processing, vulcanization, or during service of the product. They are vulcanizing agents, accelerators, activators, fillers, processing aids, anti - degradants, and a number of special ingredients. The processing aids are generally liquids or resinous materials, which mix intimately with rubber and are used as softeners to permit incorporation of fillers, and to modify the flow behaviour of the rubber.

Fillers are classified into two groups: reinforcing and non-reinforcing. Reinforcing fillers are used for enhancement of properties like tear strength, abrasion resistance, and tensile strength. Examples of reinforcing fillers are carbon black, precipitated silica, and silicates. Non-reinforcing fillers are incorporated primarily to cheapen and stiffen the final product. Vulcanizing agents are substances which are added in order that cross-linking may occur subsequently, when the compounded rubber is heated to an appropriate temperature. Sulphur is the principal vulcanizing agent for natural rubber. Accelerators and activators are essential ingredients in the compound to achieve economic rates of vulcanization. A wide variety of organic accelerators are available today. The most widely used vulcanization activators are combinations of a metal oxide (e.g. zinc oxide) and a higher fatty acid (e.g. stearic acid). Anti-degradants are added in rubber compounds in order to increase the ability of the vulcanized products to resist the various deteriorative influences like oxygen, ozone, sunlight, etc., to which it may be subjected to during service.

1.7 Reinforcing fillers

Reinforcement of a rubber vulcanizate results in pronounced increase of tensile strength, improved tear strength and abrasion resistance as compared to the gum vulcanizate of the same rubber. The degree of reinforcement depands to a large extent on the molecular, chemical and rheological characteristics of the elastomer, filler characteristics, and the mixing process. The surface area of the filler particles together with the loading determines the effective contact between the filler and the polymer. For a significant reinforcement the filler particles must have high specific surface area [68-70]. Carbon black, silica and recently nanoclay too have attained great significance as reinforcing fillers in rubber industry. These fillers are popular for tyres due to the requirement of durability, fuel efficiency and improved safety [71-72]. The level of dispersion of fillers in a rubber matrix is a very important parameter that decides the mechanical and dynamic mechanical properties of a large variety of rubber products [73-74]. The mixing of filler and dry rubber includes stages like incorporation, distribution and dispersion. The mixing of dry rubber and reinforcing fillers is an energy intensive and environmentally harmful operation. The production of natural rubber latex – reinforcing filler masterbatch by the addition of suitable filler dispersion to the latex is a technique to avoid these problems [75].

1.8 Carbon black

In rubber industry carbon black is the most commonly used reinforcing filler. Its application plays a major role in elastomers, plastics, paints and inks. The beneficial effects in rubber applications include increase in strength-related parameters (tensile strength, tear and cut growth resistance), abrasion resistance, stiffness (hardness and modulus), energy absorption characteristics, and tyre traction [76, 77]. Well known detrimental side effects are increased hysteresis properties and poor fatigue resistance as the stiffness of the polymer-black mixture increases. About 90% of the worldwide production of carbon black is used by the rubber industry. Most of the reinforcing blacks are manufactured by the oil furnace process. Complete combustion of natural gas generates a very hot zone in the furnace [78]. An aromatic hydrocarbon feed stock continuously fed into the zone as a mist without air is thermally cracked in less than a microsecond to obtain carbon black nuclei(Figure1.10). The combustion of feed stock produces individual carbon particles that are still in a liquid state. They collide in the gas stream and form grape like clusters or aggregates [79]. Quenching determines the final aggregate configuration. Bag filters separate carbon black from the combustion gas to yield a fluffy black with a bulk density of about 30 kg/m^3. The palletizing process increases the bulk density to 300-640 kg/m^3 for ease of handling, economical transportation and safety [80].

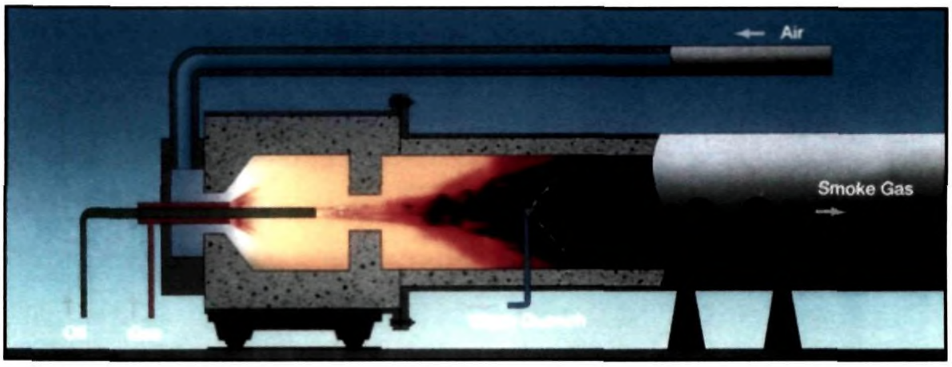


Figure 1.10 Furnace process for the production of carbon black [81]

Black with various structures can be obtained in a furnace process through the combination of feed stock and operating conditions such as, flow rate, gas rate, air rate, and quench position [82]. Compared to other types of carbon blacks furnace black has low oxygen content, neutral surface, and minimum retardation of cure in rubber compounds [83].

Practically all the blacks used by the rubber industry today are supplied in pellet form for ease of handling. Pellet hardness could affect carbon black dispersion in rubber. Pellets that are too hard will not break up during mixing of the rubber with the compounding ingredients causing a dispersion problem. Pellets that are too soft tend to break up during shipping and handling resulting in finer particles that are difficult to disperse [84, 85].

Although carbon black is mainly composed of carbon, they also contain small amounts of chemically combined functional groups such as carboxyl, phenol, quinone, and lactone that react with rubber molecules [86]. It has been found that the functional groups are primarily concentrated at the edge of the graphitic crystallites of the blacks and at the surface of the particles. The functional groups play a major role in the interaction between carbon black and the polymer. The oxygen content in the functional groups on the carbon black surface, reduce the pH that could significantly retard cure rate when mixed in the rubber compound [87, 88]. Other materials found on carbon black are small amount of sulphur, ash, and moisture [89-91].

Carbon black is classified in several ways. One way is to classify carbon black in accordance to their levels of abrasion resistance as super abrasion furnace (SAF), intermediate super abrasion furnace (ISAF), and high abrasion furnace (HAF). Extrusion rate is another way to classify carbon black, where fast extrusion furnace (FEF), and general purpose furnace black (GPF) are in that category. There are other classifications, but basically they all depend on their manufacturing process, structure and surface area. The American Society for Testing and Materials (ASTM) has designated numbers for rubber grade carbon blacks [92-95].

The primary morphological properties of the carbon black are determined in the reactor and can only be changed to a very minor extent later in the process. In the reaction zone, the gasified oil feedstock is subjected to very high temperatures of about 1900 ^{0}C. This causes the molecules to decompose into fragments. On loosing hydrogen, these fragments combine with other fragments until they have reached a size where they are spontaneously precipitated from the gas phase as nuclei. The higher the temperature, the higher the rate of pyrolysis and the more frequent the formation of such nuclei. As pyrolysis proceeds, the new molecular fragments precipitate on to existing nuclei which then continue to grow until all of the feedstock has been consumed. The higher the number of nuclei at any given amount of feedstock, the earlier the particles will stop growing since the amount of starting material is limited. [96]

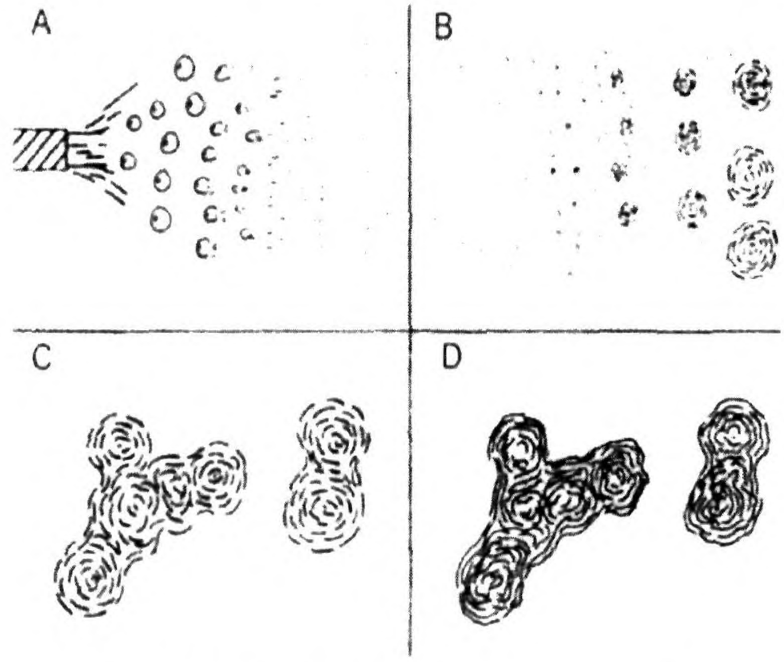


Figure 1.11 Carbon black formation steps [97]

Fig.1.11 gives a fairly good representation of different stages of carbon black formation from atomisation of feedstock through the formation of fairly spherical (semi-solid) particles and subsequent collisions to form the so-called aggregates of particles. Time - temperature parameters and raw material flow rates determine the size of the ultimate particles and the frequency of collisions of the particles under turbulent flow conditions determines the structure of the aggregates. Potassium salts may also be injected to reduce the level of structure formation. Small particle reinforcing blacks are produced at higher temperatures and short residence times in the order of 10 - 100 milliseconds. Large particle blacks are produced at lower temperatures and slower rates.

A carbon black contains a number of primary particles, also called nodules or nodes. A high structure black may consist of as many as 200 primary particles, while a low structure black may contain as low as 20 or 30. The aggregate is the primary reinforcing unit of the carbon black and is not easily broken down into smaller units. The aggregates are formed by collisions of semi-solid primary particles in the high temperature environment of the furnace. The aggregates in-turn combine readily with neighbouring aggregates to form agglomerates as secondary structure. The final pellet-form that is produced to facilitate handling and to reduce dust, is a condensed form consisting of many agglomerates.

1.8.1 Primary properties of carbon black

The properties of carbon black that determine its behaviour in a rubber vulcanizate are specific surface area, structure, size, and surface activity. The surface area is one of the main parameters used to characterise carbon black grades. Usually surface area measurements include molecular adsorption and this phenomenon is influenced by the surface activity and surface energy of carbon black, which is inhomogeneous across the surface, due to the turbostratic crystalline structure of graphitic layers mixed with amorphous carbon. The most widely accepted and commonly used measurement technique for surface area is the Brunauer, Emmet and Teller (BET) method (ASTM D3037 and D4820). Other commonly used and widely accepted methods are the surface area determination using cetyl trimethyl ammonium bromide (CTAB, ASTM D3765), and the iodine adsorption method (ASTM D1510).

The iodine-number is expressed in grams of iodine adsorbed per kilogram (g/kg) of carbon black and is not the true surface area. However, the concentration of the iodine solution has been adjusted so that the values are generally in good agreement with the nitrogen surface area for nonporous and non-oxidised carbon blacks. Surface impurities such as residual oil or oil used for beading depress the iodine number. The presence of high levels of surface oxygen functionality will also cause a severe reduction in the iodine number. The oxygen groups on the surface of the carbon black actually react with the potassium iodide in the test solution, thereby causing release of free iodine which makes the surface area to appear lower. But for routine production control or quality assurance testing of known grades, the iodine test is widely used. Structure is defined as the degree of aggregate irregularity or bulkiness of the carbon black. In general, high structure is associated with a large average number of primary particles per aggregate. This parameter characterises the empty space between randomly packed primary particles in aggregates. In the test: ASTM D 2414-08 (Oil absorption number) a moderately viscous liquid, di-butyl phthalate (DBP) is gradually added to dry carbon black in an internal mixer capable of measuring the torque as the mixing blades turn. An appreciable torque is not developed until the voids in the interstices between primary particles in the aggregates and agglomerates are filled with DBP. The rise to a predetermined torque is taken as the endpoint. The DBP absorption value is expressed as the number of grams of DBP absorbed per 100 grams of carbon black.

It is believed that surface activity plays a key role in the reinforcing capabilities of carbon black. Surface activity includes the surface roughness of small length scales, lower than the primary particle diameter, and the energy site distribution in relation to the primary particle microstructure and the specific reactivity of adsorption sites with a polymer.

1.8.2 Incorporation of carbon black into rubber

Carbon black is incorporated into rubber by shear forces experienced in an open mill or an internal mixer. In mixing a batch of rubber, a number of elementary steps are involved [98-101]. The steps are shown in Fig1.12. These steps are believed to be subdivision, incorporation, dispersion, distribution, and viscosity reduction. Subdivision results in the breaking of larger lumps or agglomerates to smaller ones, suitable for incorporation into the rubber. Incorporation of carbon black filler particles into rubber to forms a coherent mass. During incorporation, encapsulation and wetting take place as the polymer breaks into small pieces and seals in the carbon black. Without incorporation, the ingredients are tumbled around in the mixer with little energy being spent while practically no mixing takes place.

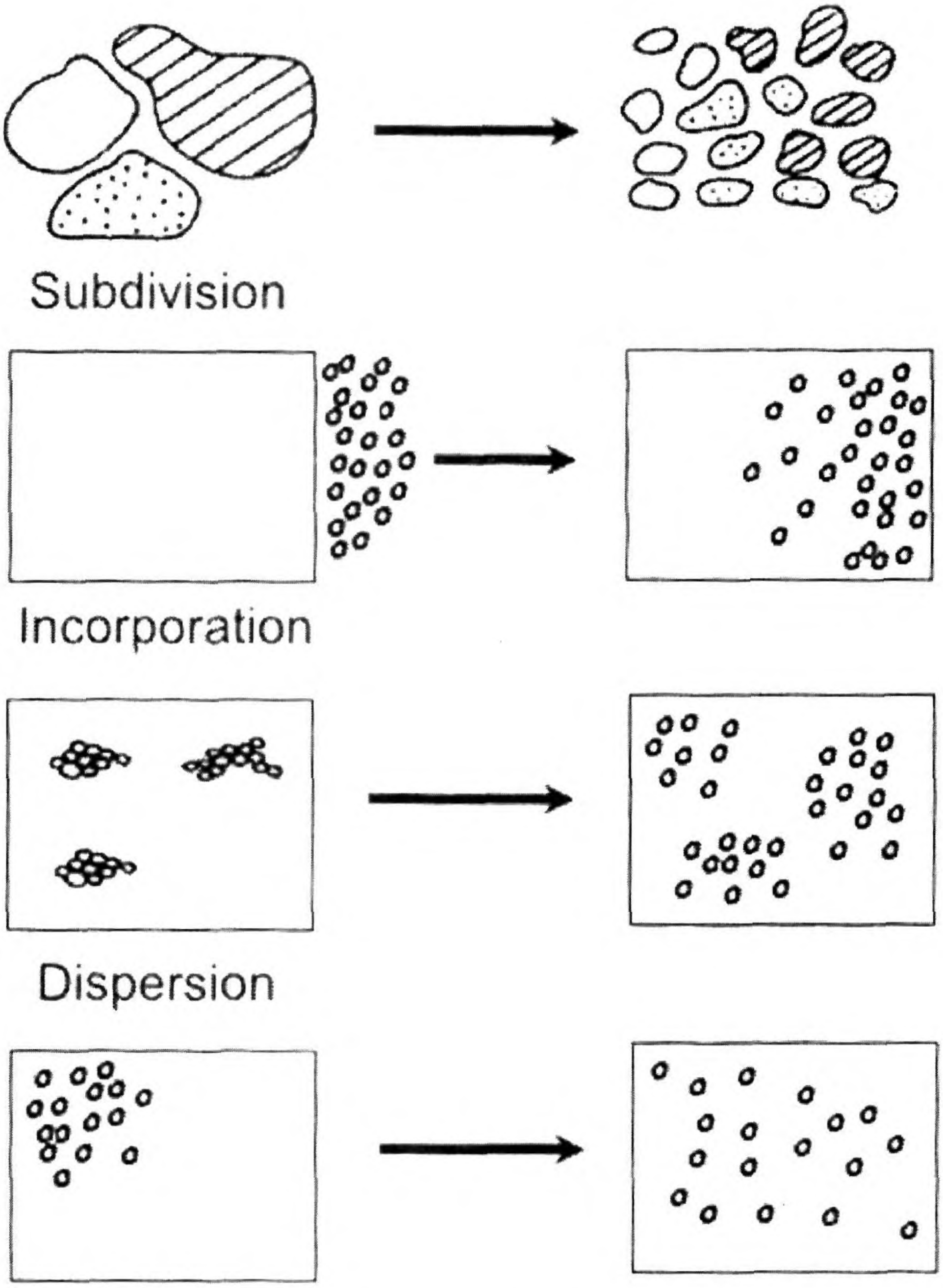


Figure 1.12 Various stages of rubber mixing [102]

Dispersion involves reduction of the size of agglomerates to their ultimate size: i.e., changing their physical state, while at the same time distributing the primary aggregates formed. This is of special importance when adding carbon black. This phase is also called dispersive or intensive mixing. Distribution involves the homogenisation of the mix by distributing the carbon black particles within the polymer matrix. This phase is also called simple mixing or extensive mixing. As the mixing proceeds viscosity reduction by mechano-chemical breakdown of the polymer occurs transforming it into a more easily deformable and less elastic mass. This process may be improved by the addition of rubber process oil.

1.9 Silica

Various forms of silica are commercially available. The important natural forms include silica (amorphous), silica (crystalline), silica diatomaceous (fossil origin) and microcrystalline silica. The important types of synthetic silica are precipitated, fumed (pyrogenic), aerogels, and hydrogels. The types of silica used for rubber reinforcement are precipitated, and fumed [103]. Precipitated silica is produced by acidification of alkali silicate solution under controlled conditions. Fumed silica is manufactured by the flame hydrolysis of silicon tetrachloride [104].

$$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4HCl \text{ ----------------------------(1.5)}$$

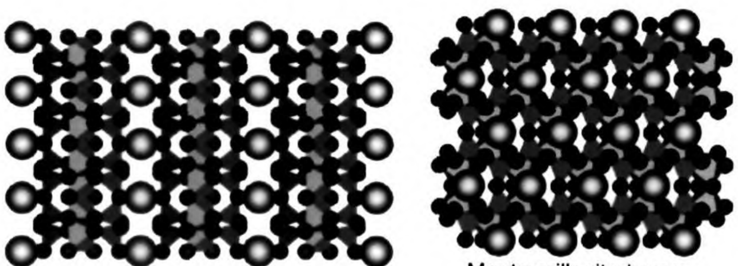
Precipitated silica is silicon dioxide containing about 10-14% water with particle size in the range 1-40 nm. They are reinforcing fillers giving high tensile strength, tear strength, abrasion resistance and hardness. Fumed silica is silicon dioxide containing less than 1.5% of adsorbed water [105].

High surface area of the filler results in a high level of reinforcement. Silica surface area values are higher than those of blacks of comparable particle size. Efficient reinforcing action, however, requires the presence of surface functional groups (surface activity) which provide a substantial bond of filler to elastomer. In contrast to the organic nature of the black surface, the silica surface is inorganic, and saturated with silanol (SiOH). These silanols are the reason for the hydrophilic reactivity of precipitated silica.

Silica without coupling agent is less reinforcing than carbon black. Coupling agents act as a connecting bridge between the silica and the rubber thereby enhancing the rubber reinforcement aspect of silica. Coupling agents are composed of a silane moiety which is capable of reacting with silica surface and also a part capable of reacting with rubber, particularly with sulpur vulcanizable rubber containing carbon-carbon double bonds [106]. Some of coupling agents of commercial importance are TESPT (bis(triethoxy silylpropyl) tetrasulphide), TESPD(bis (triethoxy silylpropyl) disulphide), TESPM (bis (triethoxy silylpropyl) monosulphide), and MTMO (mercapto propyl trimethoxy silane (A189)) [107,108].The main advantage of silica combined with a coupling agent over carbon black are improved tear resistance, abrasion resistance, heat resistance, flex stability, hardness, modulus, tack, and resilience [109,110]. The replacement of carbon black by silica fillers with the selection of a proper coupling agent in tyre tread formulations, results in significantly reduced rolling resistance of tyres and reduced fuel consumption of the vehicle, while keeping the wet traction and abrasion resistance on the same level. This environmental and economic incentive of silica technology is enough to overcome the higher production costs due to the difficult processing behavior and the higher raw material costs of these tyres [111, 112].

1.10 Nanofillers

Nanofillers are necessarily nanoscopic (at least one dimension in the nano-scale, < 100 nm) and have a high specific surface area [113, 114]. The specific surface area is one of the reasons why the reinforcement imparted by these materials in rubber vulcanizates even at very low filler loading (<10 phr) is very high. In typical rubber vulcanizates, the properties are dictated by the bulk properties of both matrix and filler. The interaction between the filler particles and the polymer decides the stiffening of the vulcanizates. In the case of the rubber vulcanizates filled with nanofillers the polymer filler interaction is concentrated at the interface [115,116]. The terms like "bound polymer" and "interface" have been used to describe the polymer at or near the interface. The interfacial structure is known to be different from bulk structure, and in polymers filled with nano-fillers possessing extremely high specific surface area, most of the polymer is present near the interface, in spite of the small weight fraction of filler. If the interaction at the interface is a strong one, or if the structure of the interfacial polymer is very different from the bulk, markedly different properties in the material as a whole can be observed. The changes have a fundamentally different origin than those found in the rubber vulcanizates filled with conventional fillers. The particle size and the aspect ratio of the fillers make another difference between conventional fillers and nano fillers [117]. Till date smectite group clays are most used nano-fillers in elastomers. Montmorillonite (MMT) is the most common smectite clay [118-128].



Montmorillonite layers (horizontal)

Montmorillonite layers (vertical)

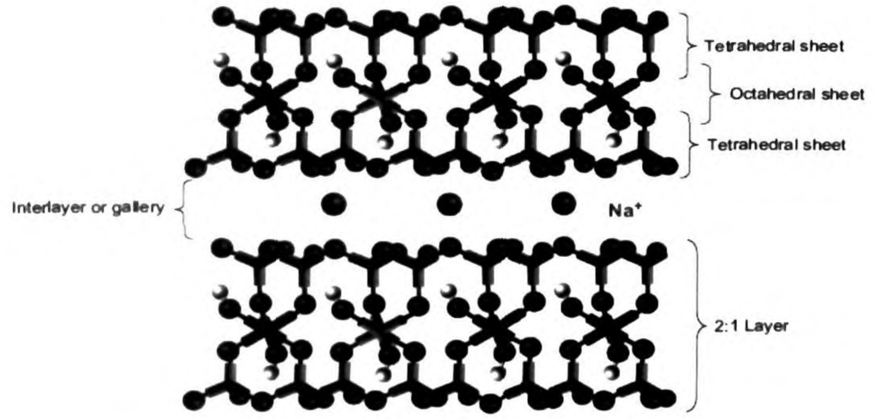


Figure 1.13 Structure of sodium montmorillonite [129 - 131]

1.11 Reinforcement

Properties of filler that influence rubber reinforcement are:

1) The particle size or specific surface area which together with loading determines the effective contact area between the filler and rubber matrix.

2) The structure or the degree of irregularity of the filler unit, which plays an essential role in the restrictive motion of elastomer chains under strain.

3) The surface activity, which is the predominant factor with regard to filler-filler and filler-polymer interaction.

Most of the elastomeric components are formed dynamically and required to have specified dynamic properties, therefore the effect of strain amplitude on the dynamic modulus was observed very intensively. Even in shear the modulus of filled rubber decreases with increasing applied strain, without regard to the dynamic or static nature of the deformation. A detailed study of the low frequency dynamic properties of filled natural rubber was carried out by Fletcher and Cent and was later extended by Payne. In cyclic strain tests the shear modulus can be simply expressed as a complex modulus G* [132-135]

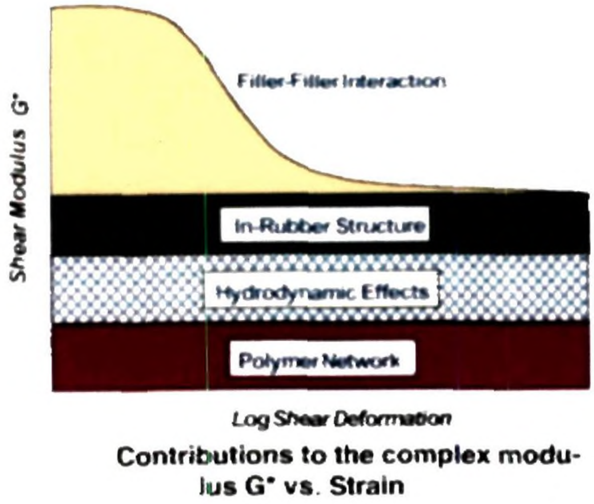


Figure 1.14 A schematic representation of various factors contributing towards reinforcement

$G^* = G' + G''$ ... (1.6) where G' is the in-phase modulus and G'' the out- of- phase modulus. The phase angle ∂ is given by

$\tan \partial = G''/G'$ .... (1..7)

The addition of fillers to rubber compounds has a strong impact on the static and dynamic behavior of rubber samples. Similar to the model of Payne, we see the strain-independent part of the modulus as a combination of the polymer network, the contribution from the hydrodynamic effect and the modulus resulting from the in-rubber structure (Figure 1.14). The polymer network contribution depends on the crosslink density of the matrix. The hydrodynamic effect in this model is nothing but the effect of strain amplification, resulting from the fact that the filler is the rigid phase, which cannot be deformed. As a consequence, the intrinsic strain of the polymer matrix is higher than the external strain yielding a strain independent contribution to the modulus

1.12 Objectives and scope of the present work

Development of new technologies to meet stringent requirements in rubber products like low heat build-up along with combination of excellent abrasion resistance, good road grip and low rolling resistance for tyre sector have given a great focus on rubber processing using different reinforcing nano fillers.

Fillers when added to polymer systems are known to cause a considerable change in mechanical and dynamic properties like modulus, strength and hysteresis. From a processing point of view mixing is the most critical process for rubber compounding. Along with basic physical changes of the materials, in some cases chemical reactions (e.g. reactions involving silane coupling agents) too take place during mixing. The primary functions of mixing are incorporation, dispersion and distribution of the filler and other ingredients in the polymer. Traditionally this is achieved by using batch mixing or continuous mixing of fillers and solid rubber or pellets, refereed to as dry mixing. Though carbon black could be easily dispersed in natural rubber by conventional mill mixing, there are issues like air pollution and higher energy consumption. In the case of inorganic fillers like silica and nanoclay, there is the problem of basic incompatibility and difficulty in filler dispersion as these are highly aggregated fillers.

Production of latex-carbon black masterbatch by the addition of carbon black as a slurry has been suggested as one of the methods to avoid some of the problems arising during filler incorporation. During the last few decades a great effort has been made to produce carbon black polymer masterbatches by mixing polymer latex with filler slurry and then coagulating the mixture physically or chemically. Masterbatch has been prepared from fresh latex, centrifuged preserved latex, modified latex, deproteinised latex and pre-vulcanized latex. Many of the methods reported earlier had drawbacks like longer coagulation time and hence poor filler dispersion and filler loss, reduction in mechanical properties, need for special mixing equipments, application of higher shear forces and use of modified latex. The full potential of carbon black masterbatch can be achieved if these problems are solved partially or fully. To be economically viable, fresh natural rubber latex obtained from the field should be used, the process has to be simple, filler loss should be minimum and the filler dispersion should be good and uniform with acceptable mechanical and dynamic properties. It will be highly useful if there exists a method for production of filler latex masterbatch using a simple latex coagulation process, with minimum filler loss, better filler dispersion and enhanced mechanical properties. This has not been fully realised in the methods reported earlier. Literature survey also depicts that there are no systematic reports on latex filler masterbatch prepared from fresh natural rubber latex using a simple process of modified coagulation with minimum process loss and enhanced mechanical and dynamic properties. Research reports in the literature that make use of a quick coagulation of fresh latex for latex stage incorporation of fillers are really scanty. The cited need for an environment friendly simple and effective process for latex filler masterbatch have lead to the foundation of this research work.

Objective of the present work

The main objectives of the present investigation are:

1) Standardisation of a method for modified coagulation of fresh natural rubber latex.
2) Identification of the most suitable form of natural rubber latex for preparing latex- carbon black masterbatch.
3) Standardisation of a protocol to prepare and evaluate latex dual filler masterbatch using commercially available carbon black and silica.
4) Improvement of the dynamic and mechanical properties of latex filler masterbatch using trifiller combination of commercially available carbon black, silica and nanoclay.
5) Evaluation of the validity of natural rubber latex filler masterbatch in blends of natural rubber with polybutadiene rubber.

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Chapter 2

EXPERIMENTAL TECHNIQUES AND MATERIALS USED

Contents

The materials used for the study and the experimental procedures are given in this chapter.

2.1 Materials

2.1.1 Polymers

2.1.1.1 Fresh natural rubber latex

Fresh natural rubber latex used in the investigation was collected from the plantation of the RRII, Kottayam. Properties of fresh latex used are given in Table 2.1

Table 2.1 Properties of fresh field latex

Properties	Value
Rubber content,%	40
Resin, %	1.5
Protein, %	2.2
Sugar,%	1
Ash,%	0.8
Water	54.5

2.1.1.2 Preserved field latex

Preserved natural rubber latex of dry rubber content (drc) 39 used in the investigation was collected from Central Experiment Station, Rubber Board, Chethackal, Ranni, Kerala.

2.1.1.3 Centrifuged natural rubber latex

The specifications of the centrifuged natural rubber latex (high ammonia (HA) type as per ASTM D 1076-2010) collected from Central Experiment Station, Rubber Board, Chethackal, Ranni, Kerala are given in Table 2.2

Table 2.2 Properties of centrifuged natural rubber

Properties	Value
Dry rubber content (% by mass)	60
Non rubber solids (% by mass)	1.0
Sludge content (% by mass)	0.04
Ammonia content (% by mass)	0.8
Potassium hydroxide number	0.5
Mechanical stability time (s)	1000
Volatile fatty acid number	0.01
Coagulum content (% by mass)	0.03
Copper content (ppm)	1
Manganese content	Traces

2.1.1.4 Skim latex

Skim latex is a protein rich byproduct obtained during the centrifugal concentration of natural rubber latex. Skim latex of drc 5 used in this study was collected from Central Experiment Station, Rubber Board, Chethackal, Ranni, Kerala.

2.1.1.5 Dry natural rubber

The dry natural rubber used in this study were RSS 1X grade, and ISNR-5 (Table.1.2 ISO 2000: 1989 (E) (Specifications for raw natural rubber), chapter 1 (1.2.5)) obtained from RRII, Kottayam.

2.1.1.6 Polybutadiene Rubber

Cis-1,4-polybutadiene rubber (Cisamer1220) was obtained from M/s Reliance Industries Ltd, Vadodara, Gujarat, India (Figure 2.1).

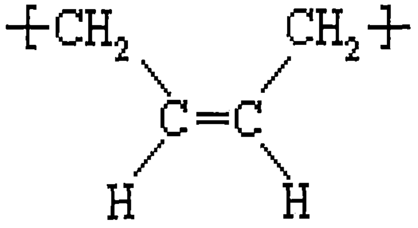


Figure 2.1 Chemical structure of polybutadiene

2.1.2 Fillers

2.1.2 1 Carbon black.

The carbon black used was high abrasion furnace (HAF) type; N330 grade (Table 2.3) supplied by M/s. Phillips Carbon Black Ltd, Kochi, India.

Table 2.3 Properties of carbon black (HAF), as per ASTM Designation: D1765-10

Parameter	ASTM	HAF (N330)
Iodine number, gm/kg	D1510	81.6
DBPA, cc/100gm	D2414	100.5
No.325 sieve residue, %	D1514	0.048
No.100 sieve residue, %	D1514	0.003
No.35 sieve residue,%	D1514	0.0004
Heat loss, %	D1509	0.4
Fines, %	D1508	0.8
Pour density, kg/m^3	D1513	380
Compressed DBP, cc/100 gm	D3439	89

2.1.2 .2 Precipitated silica

Precipitated silica used was Ultrasil VN3 (Table 2.4), manufactured by Degussa AG, Germany [1].

Table 2.4 Specifications of Ultrasil VN_3

Properties	Value
Specific surface area (N_2), m^2/g	175
p H	6.2
Heating loss,%	5.5
Tapped density, g/l	220
SiO_2 content, %	98

2.1.2.3 Nanoclay

Cloisite 93A (nanoclay) obtained from M/s, Southern Clay Products, Texas, USA was used for the study. Cloisite 93A (Table 2.5) is a natural montmorillonite with a quaternary ammonium salt [2].

Table 2.5 Specifications of Cloisite 93A (Natural montmorillonite modified with a ternary ammonium salt.)

Treatment/ Properties	**Organic Modifier (1)**	**Modifier Concentration**	**% Moisture**	**% Weight Loss on Ignition**
Cloisite® 93A	M2HT (1)	95 meq/100g clay	< 2%	39.5%

(1) M2HT: M2HT: methyl, dehydrogenated tallow ammonium

2.1.3 Other Chemicals

2.1.3.1 Ammonium laurate

20 % ammonium laurate was prepared in the laboratory.

2.1.3.2 Zinc oxide

Zinc oxide (Zn O) used in the study was supplied by M/s. Meta Zinc Ltd, Mumbai.

2.1.3.3 Stearic acid

Stearic acid (Table 2.6) used was supplied by M/s. Godrej soaps Pvt. Ltd, Mumbai.

Table 2.6 Specifications of stearic acid

Parameter	**Value**
Melting point	50-69 ^{0}C
Acid number	185-210
Iodine number, max	95
Specific gravity	85±0.01

2.1.3.4 Sulphur

Sulphur (Table 2.7) was supplied by M/s. Standard Chemical Company Pvt. Ltd, Chennai

Table 2.7 Specifications of sulphur

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

2.1.3.5 Other compounding ingredients

The materials such as antioxidants, rubber process oils and accelerators used in this study were rubber chemical grade.

2.2 Experimental Methods

2.2.1 Dry rubber content percent by mass (DRC)

DRC is defined as the mass in grams of rubber present in 100g of latex. The drc was determined using ISO 126 test method.

2.2.2 Total solids content (TSC)

The TSC was determined by ISO 124 test method. The TSC is defined as the mass in grams of total solids present in 100g of latex.

2.2.3 Approximate DRC determination

About 10g of fresh natural rubber latex was accurately weighed by difference method. About 0.8 to 1 ml ammonium laurate solution was added and mixed well. The latex was diluted to about 20-25% drc by addition of distilled water. The latex as coagulated by addition of 0.5% (v/v) sulphuric acid with stirring.

The coagulum was pressed into a thin sheet. Washed in running water and pressed with filter paper to remove moisture on the surface. The coagulum was dried in a microwave oven set at 360 watts for about 10-12 min. After about five minutes the sample was turned upside down. After drying the weight of the dry rubber was accurately noted. The experiment was conducted in duplicate to agree with results.

$$\text{DRC, \%} = (W1 / W2) \times 100) - C$$

Where, W1 = Weight of dry rubber in grams

W2 = Weight of NR latex in grams

C = 1.0 (C is the correction given due to addition of ammonium laurate solution)

2.2.4 Particle size measurement

The particle size of carbon black, silica, nanoclay in dispersions and natural rubber in latex was determined using dynamic light scattering technique (Figure 2.2) in Malvern Zetasizer, model Nano-S (U.K.) [3].

Figure 2.2. Malvern Zetasizer (Nano-S)

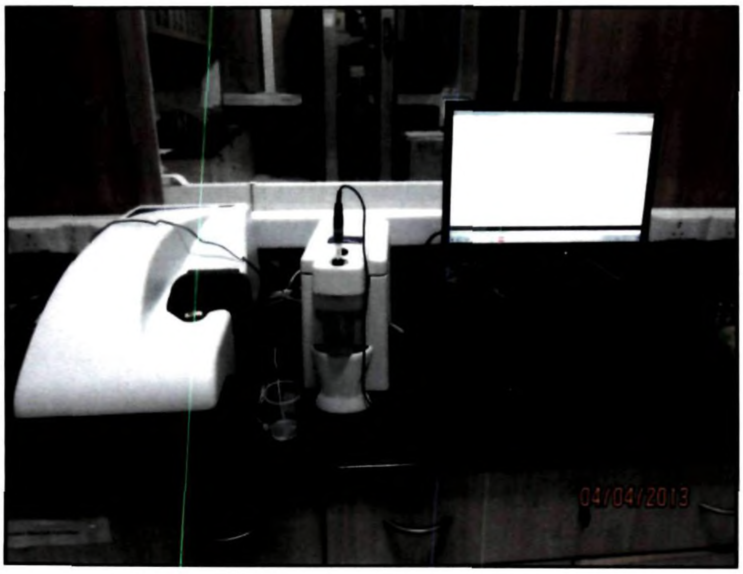


Figure 2.3 Malvern Zetasizer (Nano-Z)

2.2.5 Zeta potential measurement

Zeta potential was measured using Zeta potential analyser (Figure 2.3, Malvern Zetasizer (Nano-Z, U.K). The buffer solution in the pH range of 4 to 9 was freshly prepared for dispersing the natural rubber latex.

2.2.6 Volatile matter

Volatile matter percent mass was determined using the oven method at 100±5 °C as per ISO 248.

2.2.7 Acetone extract and acid value

Acetone extraction to remove non rubber constituents from rubber samples was done according to ASTM D 297-93 (2002).

The acid value was expressed as number of milligrams of caustic potash required to neutralize the acids present in the extract from 100 g of rubber. For this acetone extract from about 10 g of rubber was dissolved in 100 ml ethyl alcohol and titrated with 0.1 N KOH using phenolphthalein as indicator. Other tests were carried out as per relevant international standards.

2.2.8 Estimation of nitrogen content

The nitrogen content in the natural rubber samples were estimated using the Kjeldahl method as per ASTM D 3533-90.

2.2.9 Initial plasticity and plasticity retention index (PRI)

Plasticity retention index is a measure of the resistance of raw rubber to oxidation. The determination PRI of raw rubber samples were measured using a Wallace Rapid Plastimeter as per ASTM D 926 (2007).

2.2.10 Mooney Viscosity

The Mooney viscosity of the rubber samples were measured using Mooney Viscometer (Mooney MV 2000, ALPHA Technologies, Akron, USA), which is designed for measuring the shearing viscosity of polymers and compounds by a rotating disc in a cylindrical cavity set at 100 ^{0}C as per ASTM D1646 (2007). The results of samples were expressed as ML (1+4) 100 ^{0}C.

2.2.11 Bound rubber content

The fraction of the bound rubber in the masterbatches were calculated using the equation RB = Wfg -W [mf/ (mf +mp)] / W [mp / (mf + mp)] x 100 Where Wfg is the weight of filler and gel, mf the weight of filler in the compound, mp the weight of polymer in the compound and W the weight of the specimen [4].

2.2.12 Determination of volume fraction of rubber and crosslink density

Punched rubber vulcanizate samples of approximately 0.3g weight were allowed to swell in toluene till equilibrium swelling. The swollen samples were weighed quickly, solvent was removed in vacuum and samples were weighed again. The volume fraction of rubber (Vr) was calculated from the above measurement using the relation [5].

$$\mathrm{Vr} = \frac{(D - FT)\rho r^{-1}}{(D - FT)\rho r^{-1} + Ao\rho s^{-1}} \text{ -------------------------------- } (2\text{-}1)$$

Where T is the weight of the test specimen, D its deswollen weight, F the weight fraction of insoluble components and Ao is the weight of the absorbed solvent, corrected for the swelling increment, ρr and ρs are the densities of rubber and solvent respectively.

Crosslink density is calculated as per the Flory-Rehner equation given below [6].

$$v = -\frac{\ln(1-V_r)+V_r+\chi V_r^2}{Vs\,(V_r^{1/3}-0{,}5V_r)} \text{ ------------------------------------ } (2\text{-}2)$$

(v is crosslink density, Vr is volume fraction of rubber in equilibrium swelled vulcanizate sample, V_s is mole volume of used solvent, χ is Huggins parameter, n is the number of network chain segments bounded on both ends by crosslinks, n is the number of network chain segments bounded on both ends by crosslink).

2.2.13 Solvent resistance

Solvent resistance test was carried out using ASTM solvents C and E at room temperature by measurement of percent weight of fuel absorbed for various immersion periods at room temperature. A button was punched from moulded sheets. This was immersed in solvent. After specified time the sample was removed from the solvent, dried with a filter paper and put in a weighing bottle. The weight was taken immediately. The weight of solvent absorbed was determined using the following equation

% weight of solvent absorbed = (W2-W1) / W1 x 100

W1 = Initial wt of sample

W2 = Final wt after solvent absorption

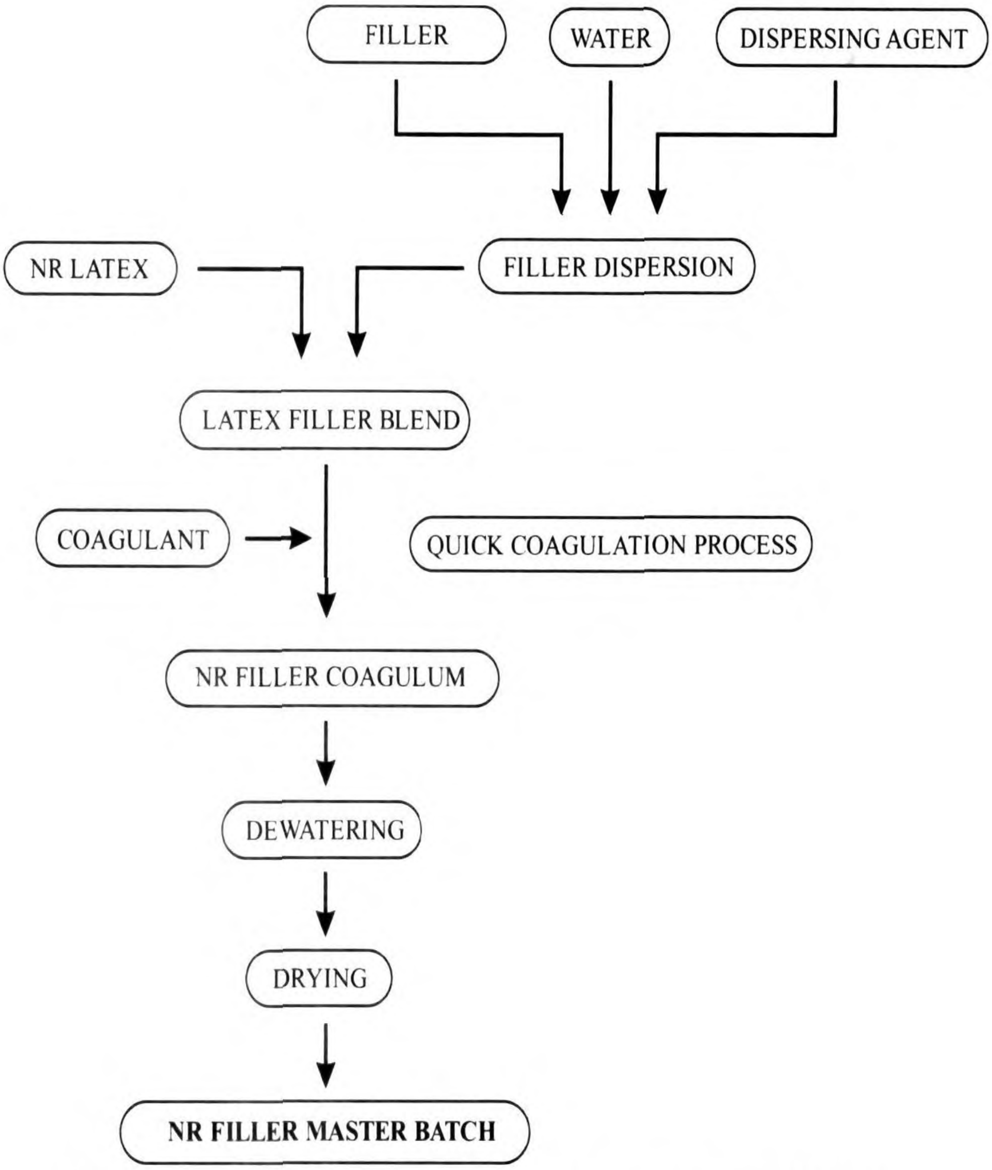
2.3 Preparation fluffy carbon black masterbatch using different forms of latex.

25 % dispersion of fluffy carbon black (Table 2.8) was prepared using a mechanical stirrer rotating at 400 rpm in presence of 20% ammonium laurate for 30 min and in the case of HAF pellets, 25 % dispersion was prepared by ball-milling for 24 h.

Table 2.8 Formulation for fluffy carbon black dispersion

Ingredients	Amount (g)
Fluffy Carbon black (HAF)	300
Water	890
20% surfactant	10

This dispersion was added slowly in to fresh natural rubber latex (which was sensitised for quick coagulation by adding the required quantity of fatty acid soap) under stirring and coagulated to produce latex carbon black masterbatch (Scheme 1). For coagulation, the latex-fluffy black mixture was poured into a tray and 0.5 % sulphuric acid was sprayed over this. This coagulum was pressed mechanically, to effect uniform coagulation of latex - fluffy black slurry. The coagulum was passed through rubber roller (Figure 2.4) to get thin sheets of wet masterbatch. This coagulum was washed well to remove the acid and dried in an air oven maintained at 70 ^{0}C to get the latex–filler masterbatch (Figure 2.5)



Scheme1. Flow chart showing preparation of latex filler masterbatch

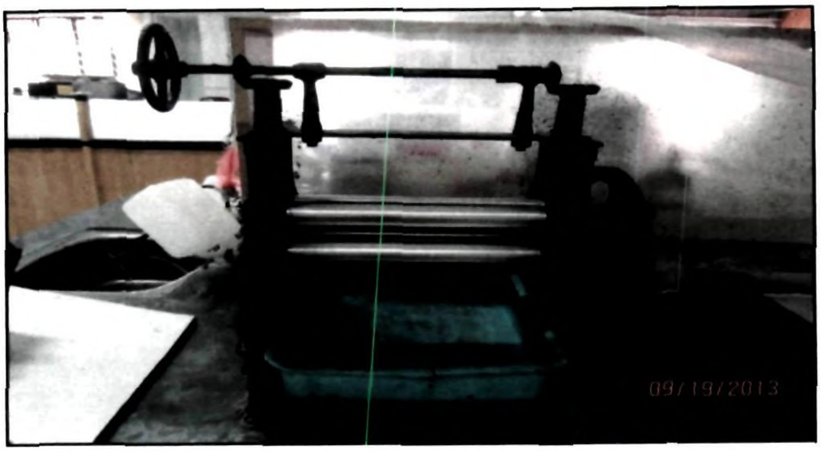


Figure 2.4 Roller for sheeting coagulum.

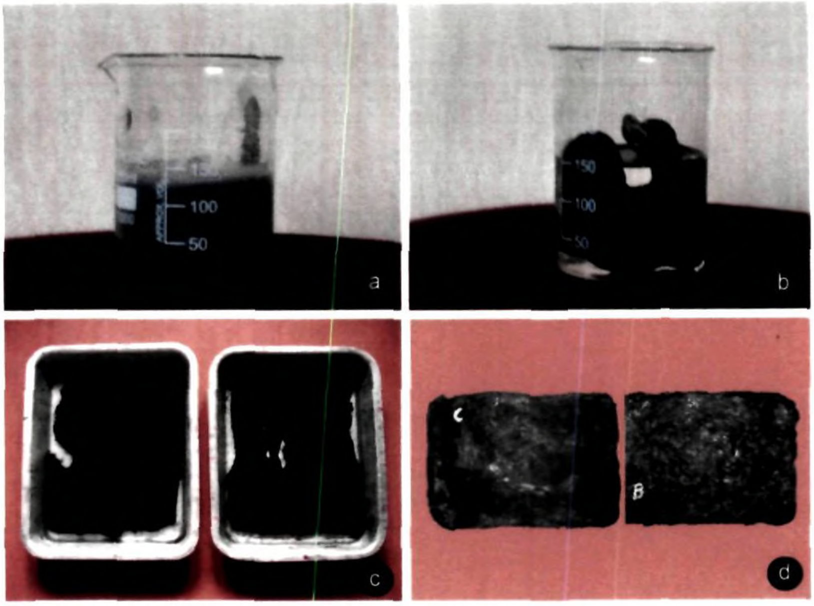


Figure 2.5 (a-d) Preparation of natural rubber latex carbon black masterbatch by quick coagulation and dried masterbatches

a- Fresh natural rubber latex / filler dispersion, b-Coagulum after quick coagulation using acid and clear serum (No loss of filler), c- More quantity of masterbatch coagulum after coagulation, d- Dried masterbatches

The same method was used to produce masterbatches using ammonia preserved natural rubber field latex, centrifuged natural rubber latex and skim latex with fluffy carbon black.

2.4 Preparation of carbon black, carbon black /silica and carbon black /silica/nanoclay masterbatches

The carbon black masterbatch, carbon black/silica dual masterbatch and carbon black/silica/nanoclay ternary masterbatch were prepared based on the quick coagulation process using the commercially available carbon black, silica and nanoclay. 25% dispersions of carbon black and silica were prepared separately by ball milling for 24 h (Table 2.9 to 2.10). 10% dispersion of nanoclay (Table 2.11) was prepared using mechanical stirrer at 400 rpm for 30min. The dispersion was added slowly in to fresh NR latex and coagulated by adding acid to produce the mixed filler masterbatch as described earlier (Scheme1).

Table 2.9 Formulation for Carbon black dispersion (Ball milled for 24h)

Ingredients	Amount (g)
HAF carbon black	300
Water	1200
20 % surfactant	5

Table 2.10 Formulation for Silica dispersion (Ball milled for 24h)

Ingredients	Amount (g)
Silica	300
Water	890
20 % surfactant	5
DEG	5

Table.2.11 Formulation for nanoclay dispersion (Mechanically stirred for 30 min at 400rpm)

Ingredients	Amount (g)
Nanoclay (Cloisite93A)	10
Water	85
20 % surfactant	5

2.5 Preparation of natural rubber latex carbon black/silica masterbatches and polybudadiene (BR) Blends

Natural rubber- filler masterbatch and polybutadiene were separately masticated and mixed with the required quantity of carbon black and silica on a mixing mill so as to have 25/25 phr carbon black / silica in 80/20 and 60/40 NR/BR blends. Rubber compounds were prepared in the conventional mill mixing process.

2.6 Determination of cure characteristics

The cure behaviour was determined using moving die Rheometer (MDR2000, ALPHA Technologies, Akron, USA) at 150 ^{0}C as per ASTM D 2084 (2007). The relevant data that could be taken from the torque–time graph are:

1) Minimum torque: Torque obtained by the mix after homogenizing at the test temperature before the onset of cure.
2) Maximum torque: Torque recorded after the complete curing of mix.
3) Scorch time (t_{10}): Time taken for attaining 10% of the maximum torque.
4) Optimum cure time (t_{90}): Time taken for attaining 90% of the maximum torque.

5) Cure rate: Cure rate was determined from the following equation.

Cure rate (Nm/min) = L_{max} - L_{min} / t_{90} - t_{10}. Where L_{max} and L_{min} are maximum torque and minimum torque and t_{90} and t_{10} the times corresponding to the optimum cure time and scorch time respectively.

2.7 Preparation of test specimens

The test specimens for the physical property determination were prepared by vulcanizing the blanks cut from un-vulcanized rubber compound sheets marked with mill direction, at a temperature of 150 ^{0}C by compression molding in an electrically heated hydraulic press. The molded samples after curing were quickly cooled and stored for 24 h before tests.

2.8 Mechanical properties

For the test described below five specimens per sample were tested for each property and mean values are reported.

The stress-strain properties were determined according to ASTM D412 (2006), Test Method A using dumbbell specimens on a Universal Testing Machine (Zwick Roell Z010, Germany). All the tests were carried out at ambient temperature. Samples were punched out from compression molded sheets along the mixing mill direction using a dumb-bell die. A thickness gauge was used to measure the thickness of the narrow portion. The sample was held tight by the two grips, the upper grip of which was fixed. The gauge length between the jaws at the start of each test was adjusted to 30 mm and the rate of separation of the power activated upper grip was fixed at 500 mm/min. The tensile strength, elongation at break and modulus were tested.

The tear strength of the samples were tested as per ASTM D 624 (2007) methods using unnicked 90^0 angle test pieces (die C) at ambient temperature at a cross-head speed of 500 mm/min using a Zwick Roell Z010 Universal Testing Machine.

The hardness (Shore A) of the moulded test specimens was measured using Zwick 3114 hardness tester according ASTM D 2240-05 (2010) [7].

The compression set of the samples (6.5mm thick and 18 mm diameter - in duplicate) were measured at 70 ^{0}C as per ASTM D 395(2008) [8].

The abrasion resistance of the samples was tested using a rotary drum Zwick abrasion tester as per ASTM D5963–04 (2010). The Goodrich flexometer (Model II - BF Goodrich, USA) conforming to ASTM D 623 (2007) was used for measuring the heat build-up [9] of the samples (2.5cm height and 1.9cm diameter). Rebound resilience of the samples were tested using a Dunlop Tripsometer (Model Bench R2/R2A, Wallace, England) as per ASTM D 2632-01 (2008).

2.9 Measurement of dispersion rating

Filler dispersion was studied using Dispergrader (Figure 2.6) model disper GRADER+, Tech Pro, USA, as per ISO 11345 method B. This technique is based on interferometric microscopy (IFM) and utilizes the interference fringes between in-phase light beams reflected from the rubber sample and a smooth reference surface to measure the three-dimensional surface topography.

Figure 2.6 Disper grader, model disper GRADER+

The peaks and valleys present on the fresh-cut surface are representative of the carbon black agglomerates and are used to characterize the dispersion. A set of ten image standards has been established for each of the different reference scales in the Dispergrader. For each of these reference images a numerical rating 1-10 (the x-value) has been assigned [10].

2.10 Scanning electron microscopic studies (SEM)

The fractured surfaces and the abraded surfaces where sputter coated with gold within 24 h of testing and examined under SEM. The study was conducted using a Hitachi SEM (model 2400) [11, 12].

2.11 X- ray diffraction analysis

The X- ray diffraction (XRD) analysis was used to determine the inter-spatial distance between the clay platelets. X-ray diffraction patterns were obtained by a model- D500 diffractometer, Siemens, Germany, using Ni-filtered Cu K_α radiation ($\lambda = 0.1542$ nm) [13].

2.12 Atomic force microscopy (AFM)

Atomic force microscopy studies were conducted at ambient conditions with a scanning probe microscope 5500 (Agilent Technologies, USA). Etched silicone probes with stiffness of 40 N/m were used in this study. Imaging was performed in oscillatory mode at different tip – samples forces by varying A_0 (amplitude of free oscillating probe) and A_{sp} (set point amplitude selected by the operator). In the oscillatory mode, the AFM probe is driven to oscillation at its resonant frequency and damping of the cantilever's amplitude due to tip-sample force interactions is employed for surface imaging. The change in cantilever amplitude from A_0 to A_{sp} is used for the feedback that tracks surface topography. Flat faces on the samples were prepared with an ultramicrotome RMC (Tucson, AZ). Cutting of the rubber sample was performed with a diamond knife at a temperature of -100 ^{0}C.Freshly prepared samples were used for imaging [14-16].

2.13 Dynamic mechanical analysis (DMA)

The dynamic mechanical properties were measured using Dynamic Mechanical Analyser, model 01dB- DMA50N, Metravib, France. The test was carried out at a constant amplitude of 10μm at a frequency of 1 Hz using specimens of dimensions 20 x 4 x 0.5 mm. The measurement was carried out over a temperature range of -100 ^{0}C to +100 ^{0}C. The Payne effect was studied by evaluating the storage modulus at dynamic strain varying from 0.0001 to 0.1 [17]

2.14 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were carried out in nitrogen and air at a heating rate of 20 ^{0}C/minute using a Parkin Elmer TGA model 4000. Thermograms were recorded from 0 ^{0}C to 800 ^{0}C. The temperature of onset of degradation, the temperature at which at the rate of weight loss is maximum (T_{max}) and the residual weight percentage were evaluated.

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Chapter 3

FATTY ACID SOAP SENSITISED COAGULATION OF FRESH NATURAL RUBBER LATEX*

Fresh natural rubber (NR) latex coagulates immediately by sensitisation with fatty acid soap. When soap is added to latex, the fatty acid ions displace a part of protein molecules and strongly adsorb on the rubber particles. These surface bound anions get converted to the corresponding unionized acid groups by reaction with acids during the process of coagulation. The fatty acids retained on rubber during coagulation play a major role on the cure characteristics and mechanical properties. Better raw rubber properties are obtained for natural rubber prepared by quick coagulation in comparison with the conventionally produced natural rubber. Carbon black filled vulcanizates give a higher modulus, tensile strength, hardness and abrasion resistance as compared with the conventional rubber vulcanizate. The compression set, tear strength and heat build-up characteristics are comparable with conventional rubber vulcanizate. A noticeably higher solvent resistance is also observed for carbon black filled NR prepared by the new process due to better interaction of filler with rubber.

*** Part of this work presentd in this chapter has been published as US Patent Pub. No.US 2013 / 0079444 A1 and Indian Patent application No.2564/ CHE/2011, dated 26/07/2011]**

3.1 Introduction

Natural rubber latex obtained from latex vessels of rubber tree (*Hevea brasiliensis)* is a colloidal dispersion of rubber particles in an aqueous medium. Along with rubber particles, latex contains non-rubber ingredients like proteins, phospholipids, carbohydrates, and inorganic cations [1-4]. The non-rubber constituents play a major role in the colloidal stability of latex and on the cure characteristics and mechanical properties of the dry rubber obtained from the latex. The composition of non-rubber constituents change after the latex leaves the tree and the obvious consequence of this is the spontaneous coagulation of latex within a few hours after tapping. Another change that takes place in latex at a later stage is putrefaction which is followed by development of bad odours. Normally rubber is recovered from latex by a slow coagulation process after addition of suitable coagulants. Earlier reports show that the process of spontaneous coagulation, which occurs in the absence of added coagulants, can be accelerated by addition of carboxylate soaps [5, 6]. The mechanism of this is believed to be due to displacement of protective layer of proteins by added carboxylate soap anions followed by their interaction with divalent metal ions which are either initially present or formed in latex. Hence sensitisation of latex with carboxylate soaps could reduce the time of coagulation of latex by the conventionally used coagulants like acids. By using suitable fatty acid soaps the non rubber constituents retained in rubber could also be adjusted so that rubber of improved cure characteristics and mechanical properties could be obtained.

This chapter presents the quality parameters and other characteristics of rubber recovered by fatty acid soap sensitised coagulation of fresh natural rubber latex. The effect of HAF black (N330) on the mechanical properties of the recovered rubber using conventional dry mixing is also presented.

3.2 Preparation of dry natural rubber obtained by fatty acid soap sensitised coagulation (NRSC)

The approximate DRC of fresh field latex was determined as per the method given in chapter2 (2.2.3). The latex was then sensitised to quick coagulation by addition of suitable quantity of surfactant (20 % ammonium laurate solution, Figure 3.1). The latex was then diluted to a DRC of 20 % and coagulated using 5 % formic acid.

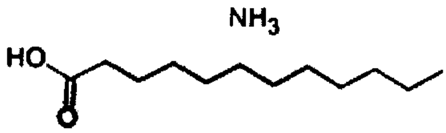

Figure 3.1 Ammonium laurate or dodecanoic acid

The freshly coagulated rubber was passed through creper mill and the crepe rubber was washed free of acid and dried at 70 °C in a laboratory oven. The control natural rubber (NRCV) was coagulated as per conventional method. Latex was diluted to a DRC of 12.5 %. 2 ml formic acid diluted to 400 ml with water was added to this, mixed well and left undisturbed for about six hours for coagulation. The coagulum obtained was washed thoroughly and passed through creper mills to obtain rubber in the crepe form. This crepe rubber was dried using a laboratory oven set at 70 ° C.

The dried rubber and carbon black filled mixes were processed in the conventional way as per ACSI ((American Chemical Society test recipe1) (Table 3.2and Table 3.4))

3.3 Effect of fatty acid soaps on coagulation of latex

It was observed that addition of long chain fatty acid soaps results in immediate coagulation of fresh latex within 3-5 seconds. Earlier reports show that spontaneous coagulation of latex was possible by different types of vegetable oil soaps [7, 8]. On addition of fatty acid soaps to latex they cause displacement of proteins and get strongly adsorbed on rubber particles. In this way the protein stabilised latex gets transformed into a soap stabilised system. On addition of acids to soap treated latex the adsorbed soap anions react with acid to form un-dissociated fatty acid, and deprive the latex particles of stabilisers. As a consequence, latex coagulates immediately [9-11]. Shortening of coagulation time has certain advantages which are realised during latex stage incorporation of fillers. Slow coagulation can lead to filler loss while quick coagulation can ensure homogeneous dispersion of fillers with minimum process loss. This process of quick coagulation of latex also improves the properties of rubber due to the presence of the surfactants incorporated during coagulation. This benefit cannot be achieved by addition of appropriate quantity of higher fatty acids during compounding of the rubber because during latex stage incorporation they are added as water soluble fatty acid soaps where it is expected that the dispersion is better.

3.4 Properties of raw rubber

The raw rubber obtained by surfactant sensitised coagulation (quick coagulation) shows a higher acetone extract, low initial plasticity (Po) and Mooney viscosity, lower plasticity retention index (PRI) and high acid value as compared to natural rubber prepared by conventional coagulation method (Table 3.1)

Table 3.1 Properties of rubber obtained from soap sensitised coagulation method (NRSC) and conventional method (NRCV)

Parameters	(NRSC)	(NRCV)
Volatile matter (%)	0.7	0.7
Acetone extract (%)	4.5	1.9
Acid number	714	144
Mooney viscosity (ML (1+4) 100 °C)	77	84
Initial plasticity (Po)	39	47
Aged plasticity (P30)	29	40
Plasticity retention index (PRI)	74	85

In this study PRI was found to be lower for natural rubber prepared by modified coagulation. It is reported that the carbonyl group of free fatty acids such as stearic, lauric, oleic and linoleic acids and their methyl esters are found to be of primary importance in increasing the rate of oxidation of polyisoprene. Lauric acid, oleic acid and linoleic acids exhibit synergistic pro-oxidant activity. It is expected that lauric acid and similar higher fatty acids are formed from the surfactant added to effect modified coagulation of latex and a lowering of PRI for this rubber as compared to conventionally prepared rubber is attributed to this [12]. The fatty acid or their salts formed by reaction with divalent ions present in latex get retained on rubber after coagulation. As the fatty acids are plasticizers of rubber they reduce Mooney viscosity and initial plasticity. Resins, quabrachitol and steroids along with organic acids, are known to be extracted by acetone [13, 14]. The acid number is high for the surfactant sensitised rubber (NRSC due to the presence of higher fatty acids.).

3.5 Cure characteristics

The formulations using natural rubber obtained by surfactant sensitised coagulation and conventional coagulation for determination of cure characteristics are given in Table 3. 2 and carbon black filled compounds in Table 3.4

As observed (Table.3.3 and 3.5) the rubber compound recovered by quick coagulation showed better overall cure characteristics higher level of cross-linking and higher cure time in comparison with conventionally coagulated rubber compound. A higher level of cross links could be due to a higher level of cure activation by the uniformly dispersed fatty acids retained on rubber [8]. A similar observation is shown by the carbon black filled compound.

Table 3.2 Formulations based on the soap sensitised natural rubber and conventionally coagulated natural rubber

Ingredients	Natural rubber obtained by soap sensitised coagulation (NRSC)	Natural rubber obtained by conventional method (NRCV)
Natural Rubber	100	100
Zinc oxide (phr)	6	6
Stearic acid (phr)	0.5	0.5
MBT (phr)	0.5	0.5
Sulphur (phr)	3.5	3.5

Table 3.3 Cure characteristics of soap sensitised natural rubber (NRSC) compound and conventionally coagulated natural rubber (NRCV) compound

Parameters	Soap sensitised natural rubber (NRSC) compound	Conventionally coagulated natural rubber (NRCV) compound
Torque Max (dN.m)	3.63	2.59
Torque Min (dN.m)	0.38	0.55
Optimum cure time (minute)	15.87	13.36
Scorch time T_{s2}, (minute)	4.41	4.23
Crosslink density, x 10^5 (moles/g rubber hydrocarbon)	3.783	3.058

Table 3.4 Formulation based on carbon black filled-natural rubber obtained by soap sensitised coagulation and carbon black filled dry natural rubber based compound (NRM and DRM).

Natural rubber obtained by soap sensitized coagulation	100	-
Natural rubber obtained by conventional coagulation method	-	100
Zinc oxide (phr)	5	5
Stearic acid (phr)	2	2
Antioxidant TDQ (phr)	1	1
HAF black (phr)	40	40
Aromatic oil (phr)	4	4
CBS (phr)	0.75	0.75
Sulphur (phr)	2.5	2.5

Table 3.5 Cure characteristics (NRM) and (DRM)

Parameters	Soap sensitised natural rubber filled carbon black compound (NRM)	Dry natural rubber (DRM) compound
Torque Max(dN.m)	14.93	10.15
Torque Min (dN.m)	0.77	0.62
Optimum cure time (minute)	11.05	11.0
Scorch time T_{s2} (minute)	2.77	2.67
Crosslink density, x 10^5 (moles/g rubber hydrocarbon)	2.965	2.624

3.6 Mechanical properties

Rubber prepared through a quick coagulation process (NRM vulcanizate) recorded a higher modulus, tensile strength and abrasion resistance. Heat-build up, tear strength and compression set were comparable to that of conventionally coagulated rubber based compound

(DRM) vulcanizate (Table3.6). The improvement in mechanical properties is attributed to the formation of higher level of cross links and better polymer-filler dispersion. In this study it is inferred that fatty acids soaps are formed during vulcanization from added surfactant and it acts as lubricant, reducing the abrasion loss [15, 16]. .

Table 3.6 Mechanical properties of vulcanizates

Parameter	Vulcanizates prepared from fatty acid soap sensitised natural rubber filled carbon black compound (NRM)	Vulcanizates prepared from conventionally coagulated natural rubber compound (DRM)
Modulus 100% (MPa)	2.25	2.05
Modulus 300% (MPa)	10.7	8.14
Tensile strength (MPa)	25.4	23.5
Elongation at break (%)	480	520
Hardness (Shore A)	61	57
Resilience (%)	71	73
Compression set (%)	21	20
Heat build-up, ΔT(°C)	20	20
Abrasion loss (mm^3)	102	116
Tear strength (kN/m)	66	64

3.7 Filler dispersion study using Disper Grader

The filler dispersion characteristics of the different vulcanizate are presented in Figure 3.2 and Table.3.7. A better dispersion and lower degree of aggregation is shown by the vulcanizates prepared from NRM as compared to the vulcanizate prepared from DRM. It is expected that there is better dispersion of carbon black when they are mixed in the modified coagulation process compared to mixing of carbon black in dry rubber using conventional mill mixing technique.

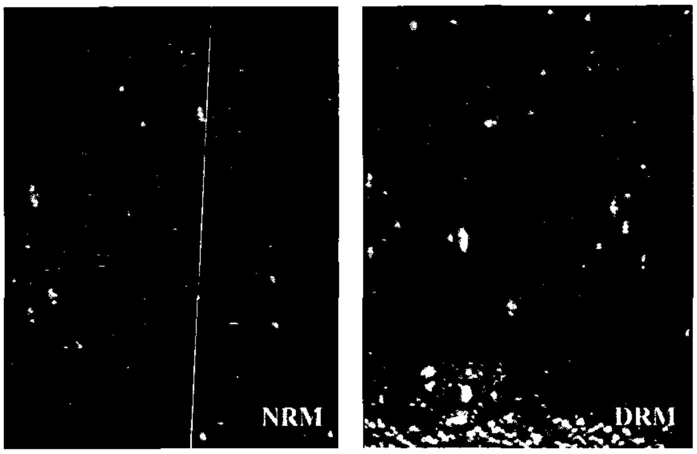

Figure 3.2 **Images of dispersion in carbon black filled natural rubber compound (NRM) vulcanisate and carbon black filled in conventionally coagulated natural rubber compound (DRM) vulcanizate as per rating in Table 3.7**

Table 3.7 Carbon black dispersion rating

Sample designation	Carbon black dispersion (X)	Agglomerate dispersion (Y)
NRM	7.2	7.8
DRM	6.3	7.0

3.8 Solvent resistance

Data on solvent resistance after immersion of samples in ASTM solvent C (The fuel used was ASTM D 471 Reference Fuel C which is a mixture of iso-octane and toluene, % by volume 50 and 50) for a duration of

15 days and in ASTM solvent E (The fuel used was ASTM D 471 Reference Fuel E which is toluene, 100 % by volume) for 60 h and15 days are shown in figures 3.3, 3.4, and 3.5. It is observed that the percentage solvent absorbed is much higher for conventionally coagulated natural rubber vulcanzates while it is lower for the soap sensitised coagulum natural rubber vulcanizate. A similar observation is seen in the case of the carbon black filled vulcanizates also. The improvement in solvent resistance is attributed to higher level of vulcanization and also to higher level of zinc soaps in the soap sensitised coagulum vulcanizate. The modified rubber contains fatty acids formed from the surfactants added during coagulation of latex. These are more polar in nature compared to the solvent used and this leads to a lower solvent uptake compared to the control natural rubber vulcanizates that have only much lesser proportion of higher fatty acids.

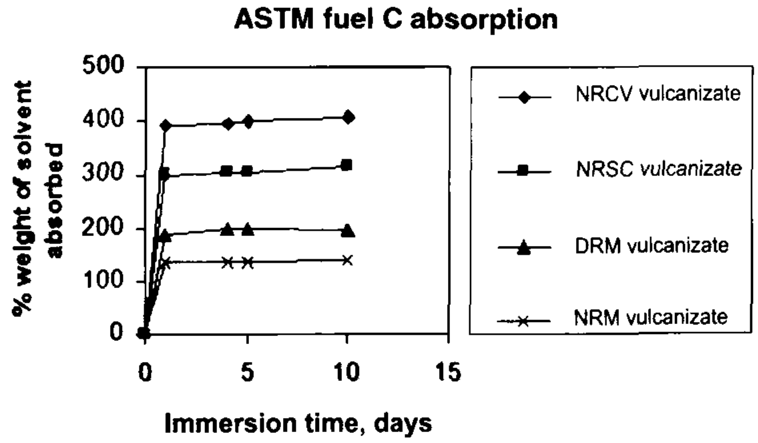

Figure 3.3 Solvent resistance in ASTM solvent C

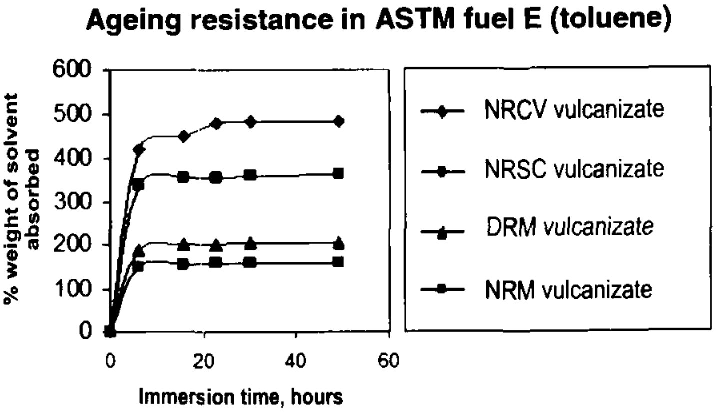

Figure 3.4 Solvent resistance in ASTM solvent E

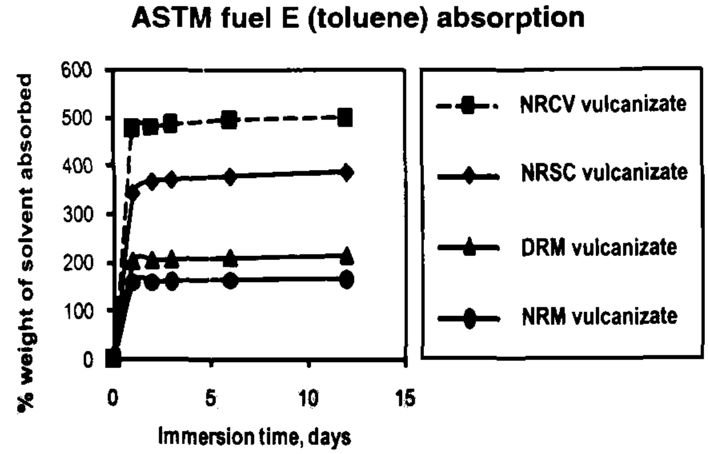

Figure 3.5 Solvent resistance in ASTM solvent E

3.9 Scanning electron microscopic (SEM) studies

The scanning electron microscopy data was taken to analyze the tensile fractured and abraded surface to understand the nature of the rubber matrix. The SEM photographs of the tensile fracture surfaces of NR vulcanizates prepared using rubber obtained by modified coagulation (NRM) and rubber obtained by conventional coagulation (DRM) at different magnifications of 200 x, 1000 x and 3000 x are shown in Figure 3.6. Both samples showed several broad fractured paths. At a low magnification 200 x, it is seen that the modified sample had shorter fracture paths which indicated fractured deviation while the conventional DRM had longer fracture paths and also smoother surface. An idea of nature of the surfaces is evident at higher magnifications. In 1000x and 3000x magnifications DRM appeared smoother and there were signs of material removal while the modified sample (NRM) showed a rougher surface. Earlier reports show that the presence of curved short tear lines and roughness on tensile fractured surfaces indicated rubber matrix of higher tensile strength [17]. The NRM had a higher tensile strength as shown in Table 3.6

The SEM photographs of the abraded surfaces of NR vulcanizates prepared using rubber obtained by modified coagulation (NRM) and rubber obtained by conventional coagulation (DRM) at different magnifications of 200 x, 1000 x and 3000 x are shown in Figure 3.7 At lower magnification it is evident that both samples showed ridge formation. More information about the ridges is observed at higher magnifications (1000 x and 3000 x.) The ridge pattern was comparatively wider for DRM. At high magnification (3000x) the presence of ridge was not observed on the abraded surface of rubber prepared in the conventional way while the rubber prepared by modified coagulation showed presence of ridges. Earlier reports show that during abrasion of rubber there is ridge formation, and the changes in the nature of ridges along with evidences of material removal could indicate the mechanism of abrasion resistance. Fine pattern for the ridges along with less material removal indicated higher abrasion resistance [18, 19]. Comparatively very high abrasion resistance was observed for NRM. (Table3.6). As discussed earlier fatty acid soaps can act as lubricant and reduce abrasion loss [15].

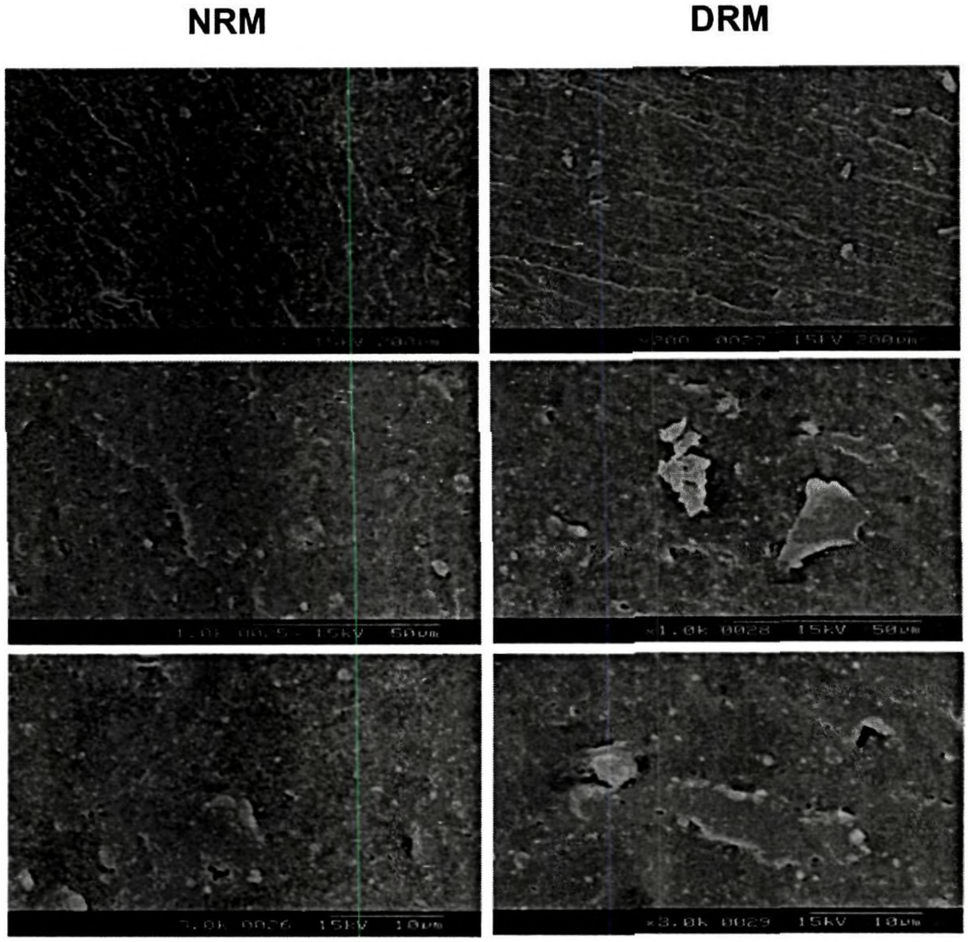

Figure 3.6 SEM photographs of tensile fractured surface of carbon black filled in soap sensitised natural rubber compound (NRM) vulcanizate and carbon black filled in conventionally coagulated natural rubber compound (DRM) vulcanizate

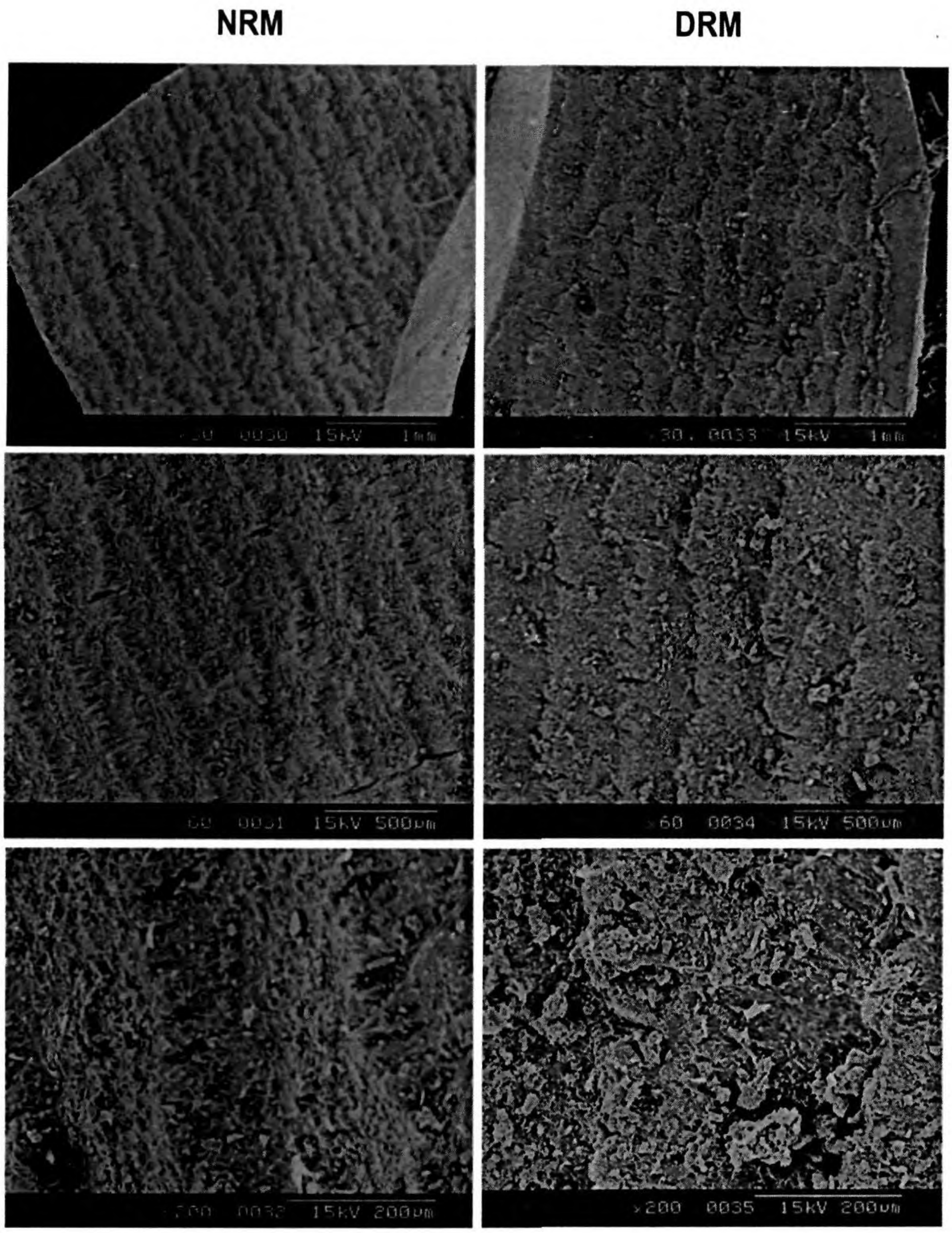

Figure 3.7 SEM photographs of abraded surface of carbon black filled in soap sensitised natural rubber compound (NRM) vulcanizate and carbon black filled in conventionally coagulated natural rubber compound (DRM) vulcanizate.

3.10 Atomic force microscopy (AFM) studies

The height and phase images of the surface of DRM (prepared from rubber obtained by conventional coagulation) and NRM (prepared from rubber obtained by modified coagulation) of the fresh faces of the samples obtained using an ultramicrotome are shown in Figures 3.8-3.10

As a general observation dispersion of carbon black as nanoparticles is observed for both samples. DRM contains little number of aggregates from topography images as marked. Phase images also show that there are aggregates which appear as lumps. Generally topography images account for differences in height and more information on fine features of the aggregates is obtained from phase images. It is known that during analysis, the AFM probe is driven to oscillation at its resonant frequency and damping of the cantilever's amplitude due to tip-sample force interactions is employed for surface phase imaging while the change in cantilever amplitude is used to track surface topography. The former gives more information on the nature of aggregates.

NRM also shows some level of aggregation as seen from topography image. In phase image as it highlights edges provides clearer observation on the edges of the aggregate. As observed from phase image edges appear less prominent, appear to be like a smear and seem to be distributed rather homogeneously. Low force imaging is known to give more relevant images and the small tip - sample contact area that accompanies low force imaging offer better image resolution. The low force AFM images of NRM also reveal homogeneous dispersion of carbon black in rubber matrix.

Thus on comparison it is observed that nature of aggregation of nanoparticles is more as lumps for DRM as compared to NRM. Earlier results show that AFM images could be used to determine the size of aggregates and diameter of single particles of carbon black [20, 21].

The plasticizers in general helps in the incorporation of fillers and they are likely to cause lower level of filler dispersion, caused by the lower shear forces experienced during mixing if the quantity used is high. From AFM studies it is observed that the filler aggregation is lower for rubber prepared by modified coagulation process. The hydrocarbon portion of the fatty acid soaps formed during vulcanization is soluble in rubber and it is expected that the degree of solubility of this portion is one of the factors that influence the mechanical properties of rubber. Wider molecular weight distribution of hydrocarbon chain of the surfactant processing additive results in a lowering of melting point and easy dispersion in rubber. High polarity functional groups tend to reduce the solubility in rubber somewhat and give the product more activity as a surface lubricant. But they have the advantage that they provide an attraction for polar fillers improving the dispersion of such fillers in the rubber compound. [12}.

Carbon blacks have functional groups such as hydroxyl, carboxyl, ketone and aldehyde on their surface and it is expected that there can be some interactions of filler with the polar groups of the surfactants added to latex.

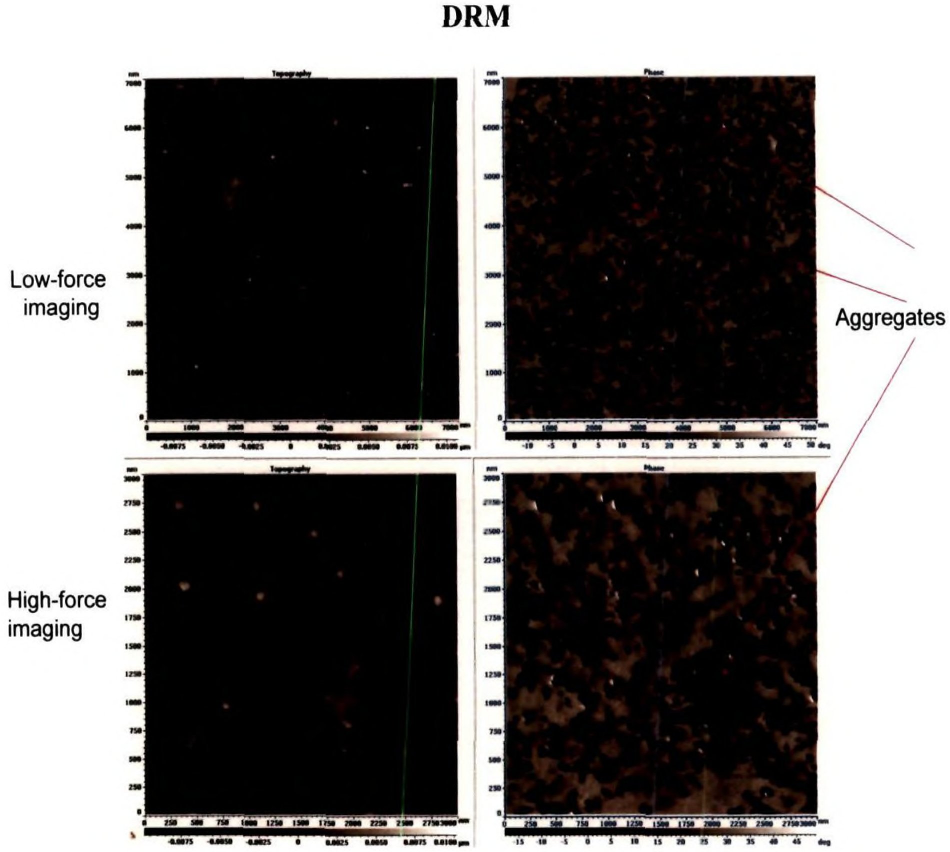

Figure 3.8 Low- force imaging and High force imaging topography and phase images of carbon black filled NR vulcanizates prepared using NR obtained through conventional coagulation (DRM) taken at two portions on microtomed sample

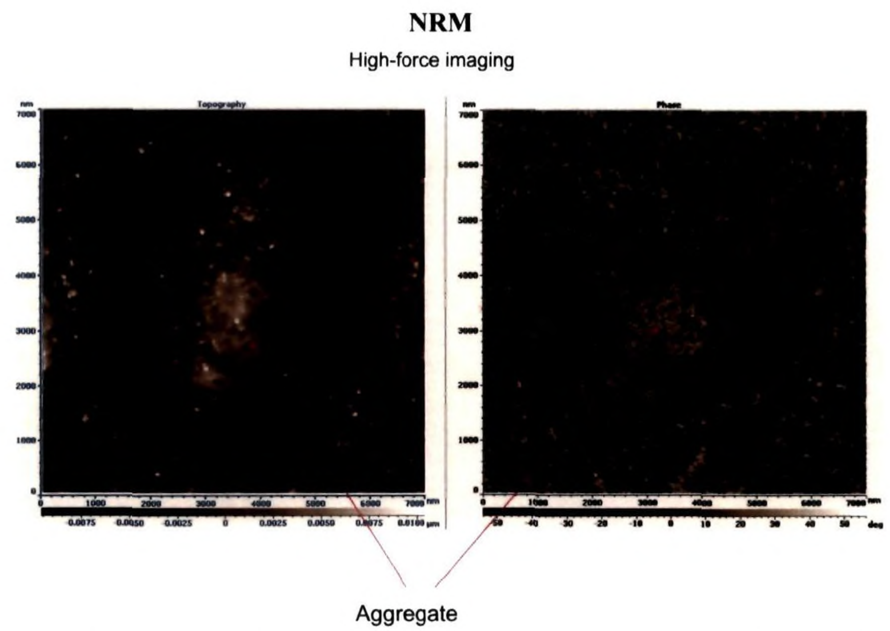

Figure 3.9 High force imaging topography and phase images of carbon black filled NR vulcanized prepared using NR obtained through modified coagulation (NRM).

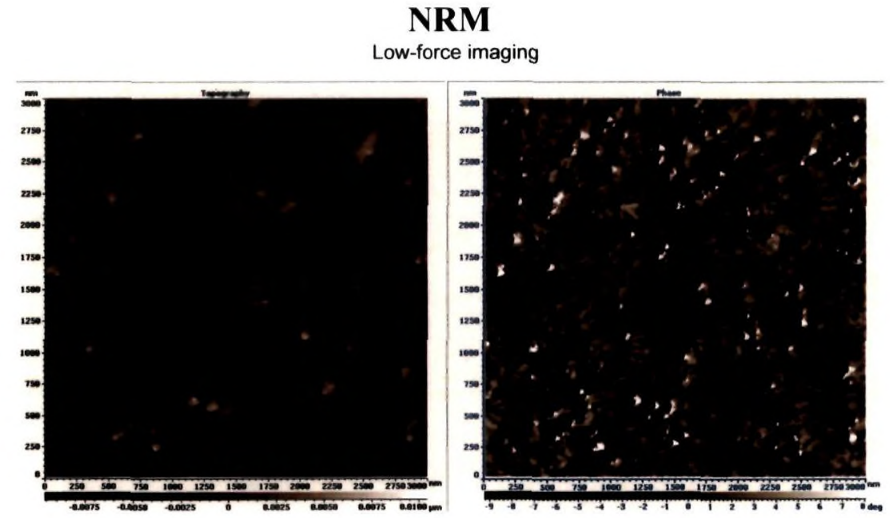

Figure 3.10 Low force topography and phase images of carbon black filled NR vulcanizates prepared using NR obtained through modified coagulation.

3.11 Conclusions

1) The coagulation of NR latex in presence of acids is accelerated by addition of small quantities of anionic surfactant.
2) A proportion of the surfactants added to latex gets adsorbed on rubber particles and are retained in rubber after coagulation.
3) The surfactants retained on rubber activate the vulcanization and enhance the filler dispersion thereby improving the mechanical and solvent ageing characteristics of recovered rubber.
4) The carbon black filled rubber vulcanizates based on rubber obtained by modified coagulation show significantly higher abrasion resistance mainly due to the lubricating action of the fatty acids formed in rubber.

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Chapter 4

LATEX STAGE INCORPORATION OF CARBON BLACK IN VARIOUS TYPES OF NATURAL RUBBER LATICES[*]

Contents

Different forms of natural rubber latices like fresh latex, preserved field latex and concentrated latex were used for producing carbon black masterbatch with fluffy carbon black. Factors like particle size, zeta potential, colloidal stability, rubber content, non-rubber ingredients, sensitivity to acid and raw rubber properties are different for these forms of latex. These parameters can affect the processing and quality aspects of the carbon black masterbatch. It was observed that the surfactant treated fresh natural rubber (NR) latex, preserved latex and latex concentrate containing filler dispersion coagulated to a consolidated mass quickly on addition of acid. A higher rheometric torque was observed for the masterbatches compared to the conventional dry mix. Within the masterbatches higher rheometric torque was recorded for dry rubber compounds based on fresh latex and preserved field latex (PFL) containing skim latex. This could be due to the presence of comparatively higher amount of surfactant in the latices. As compared to the control dry mixed vulcanizate, the masterbatches made from fresh latex show higher modulus, tensile strength, hardness, and tear strength. The masterbatches made from fresh latex show lower compression set, heat build-up and abrasion resistance. Better ageing resistance was also observed for the masterbatches. The overall mechanical properties shown by the vulcanizates prepared from the masterbatch based on fresh field latex was superior to others. The improvement in mechanical and ageing characteristics are attributed to the higher crosslinking and better dispersion of filler as observed from the filler dispersion data.

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4.1 Introduction

Concentration of latex is necessary for transport economy and purification of latex. Centrifuging is the most popular processes for concentration of natural rubber latex [1]. During concentration of latex by centrifuging process the comparatively bigger particles along with lower proportion of non rubber ingredients separate into the latex concentrate and smaller particles along with greater proportion of non-rubber ingredients separate as skim fraction [2]. Factors like particle size, zeta potential, colloidal stability, rubber content, non-rubber ingredients, sensitivity to coagulation by acids and raw rubber properties are different for the concentrated and the skim latices [3]. Latex stage mixing has been described as an energy saving method for preparing rubber compounds. Many early patents and reports described the use of latex stage incorporation of fillers for lower energy consumption, better filler dispersion and enhanced mechanical properties (4-8). There are several reports on production of carbon black masterbatch using preserved field latex (PFL), concentrated natural rubber latex, pre- vulcanized latex, and modified latex [9-11].

The carbon black used was either in the fluffy or pelletised form. In most of these methods, filler dispersion is prepared under suitable conditions, the dispersion is mixed with latex by applying high shear forces using special equipments and finally the latex-filler mixture is coagulated either physically or chemically. The coagulum is dried and processed in the conventional method. In all the reported methods the mixing process was energy intensive using specialised equipments, there was filler loss or the resulting material had inferior properties. So there exists a need to prepare latex filler masterbatch with enhanced dynamic and mechanical properties using a simple and economical process which is less energy intensive.

There has been no systematic reports on the influence on particle size and non rubber ingredients in the production of latex masterbatches. An attempt has been made to study the effect of these parameters using different types of natural rubber latices such as fresh field latex (FL), preserved field latex (PFL), centrifuged latex (LC) and skim latex - all obtained from the same source of natural rubber, for the production of latex fluffy carbon black masterbatch.

4.2 Features of various types of natural rubber latices

The size of rubber particles varies from about 80 to 5000 nm for fresh latex (FL), 85-5000 nm for preserved field latex (PFL), 100-6000 nm for latex concentrate (CL) and about 80-600 nm for skim latex is close to the values reported earlier [12,13] (Figure 4.1). A higher acetone extract and higher nitrogen content is observed for the skim rubber compared to rubber from fresh NR latex and concentrated latex. (Table 4.1) Rubber obtained from concentrated latex has the lowest nitrogen content.

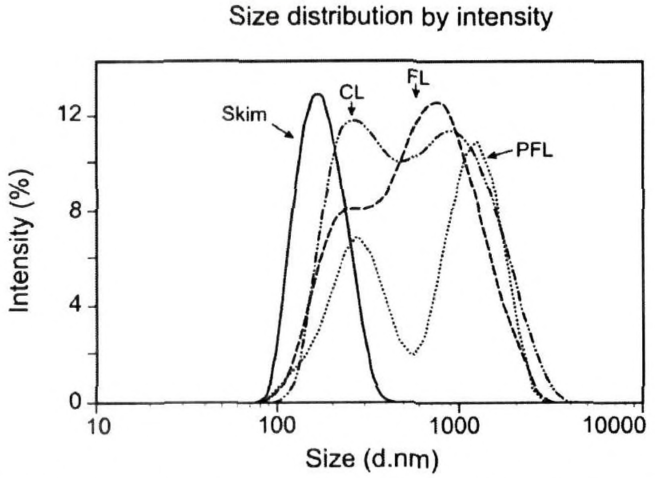

Figure 4.1 Particle size distribution of NR latex [fresh (FL), preserved (PFL), skim and centrifuged (CL)].

Table 4.1 Properties of latices

Parameters	Fresh latex	Latex concentrate	Skim latex
Acetone extract (%)	4.1	3.1	5.5
Nitrogen (%)	0.45	0.39	2.1

It is known that during centrifugal concentration a fraction of the rubber particles with wide variation of size distribution separate into skim fraction and cream fraction based on the size of rubber particles. While the latex is concentrated without the application of centrifugal force the rubber particles are subjected to three different forces: force due to gravity (Fg), force due to viscous drag (F_d) and force due to buoyancy (F_b). During the centrifugal concentration of latex the gravitational force is replaced by relative centrifugal force.

$$F_g = mg \quad \text{------} (4.1)$$

$$F_g = \rho_p 4/3 \Pi r^3 g \quad \text{------} (4.2)$$

$$Fd = 6 \Pi \eta r v \quad \text{------} (4.3)$$

$$Fb = 4/3 \Pi r^3 \rho_s g \quad \text{------} (4.4)$$

ρ_p is the density of rubber particle

ρ_s is the density of the serum

r is the radius of rubber particle

m is the mass of rubber particle

v is the velocity of the rubber particle

g is the acceleration due to gravity

In the equilibrium condition drag force balances the difference between gravitational force and force due to buoyancy. Considering (r = d/2 where d is the diameter) the equation governing concentration under gravitational force can be as follows

$$v = (\rho_s - \rho_p)\, g\, d^2/18\,\eta \text{ ------------------------------------ } (4.5)$$

Hence the particle size of skim fraction is comparatively low and the serum content is high. As the skim fraction has smaller particles and higher surface area it is expected that the quantity of the non rubber constituents adsorbed on the surface of the particles are higher. Consequently the proteinaceous materials are higher as revealed from higher nitrogen content and the surfactants retained on rubber are higher as shown by higher acetone extactable materials. Since bigger particles are separated in cream fraction, the acetone extractable materials and proteinaceous materials are comparatively lower for centrifuged latex.

The zeta potential of different natural rubber latices as a function of pH is shown in Figure 4.2 and the values for zeta potential at pH 9 are presented in Table 4.2. The zeta potential values are in the order fresh field latex > preserved field latex > centrifuged latex. The fresh natural rubber latex is composed of proteins, phospholipids, carbohydrates and metal ions.

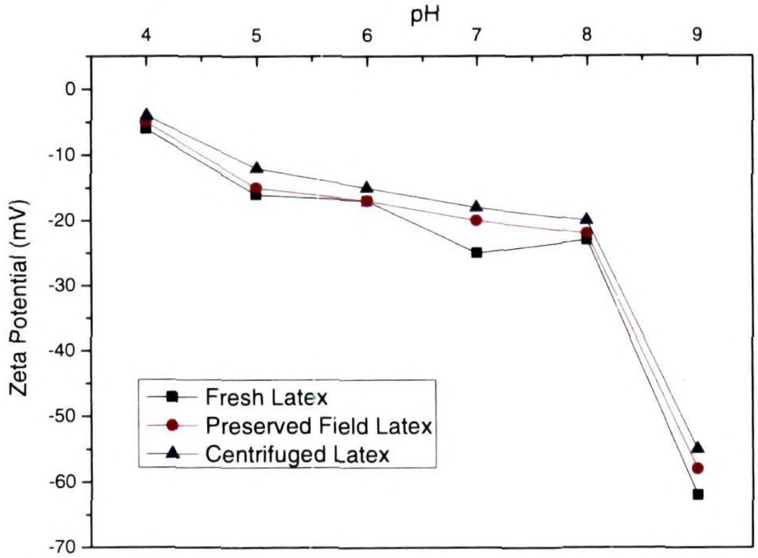

Figure 4.2 Zeta potential at different pH values

Table 4.2 Zeta potential value of natural rubber latices at pH 9

Samples	Zeta potential (mV)
Fresh latex	- 62
Preserved Field Latex	- 58
Centrifuged Latex	- 55

The negative value of zeta potential in all cases is attributed to the egatively charged ions adsorbed on rubber particles or the negative zeta otential value of rubber latex indicates a negative charge on rubber particle urface. Natural rubber latex centrifugation process removes proteins, hospholipids and metal ions resulting in lower negative zeta potential value 14]. A comparatively higher zeta potential shown by fresh latex can be due o the higher amount of adsorbed anions comprising of both proteins and fatty cid soaps [15]. In preserved and concentrated latex the adsorbed layer is predominantly of higher fatty acid soaps. Thus the type and amount of adsorbed anions are different for different forms of latex. It is known that zeta potential values decrease with the decrease of pH because at lower pH the latex reaches the isoelectric point when rubber particles have almost no charge.

4.3 Coagulation characteristics

4.3.1 Particle size of fluffy carbon black

Particle size of fluffy carbon black dispersion is shown in Figure 4.3. Comparatively small particle size varying from about 200 to 500 nm is recoded.

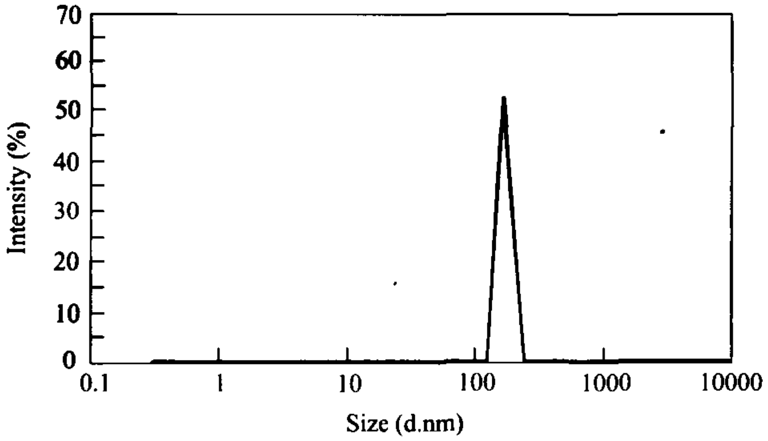

Figure 4.3 The size of the particles of the fluffy carbon black dispersion

Furnace blacks are obtained by burning liquid and gaseous hydrocarbons at very high temperature so the reaction is confined to a refractory–lined furnace and hence the name furnace black. After the carbon black is formed the reaction mixture is cooled by injecting water, and passing through heat exchanger for further cooling and then through filter bags. (Schematic diagram for production of carbon black is shown in

Figure 4.4.) Fluffy HAF black dispersion method is shown in Chapter 2 (Table 2.8)

Hence it is expected that when dispersion of fluffy black is prepared the particle size is low. However very small particles can get aggregated.

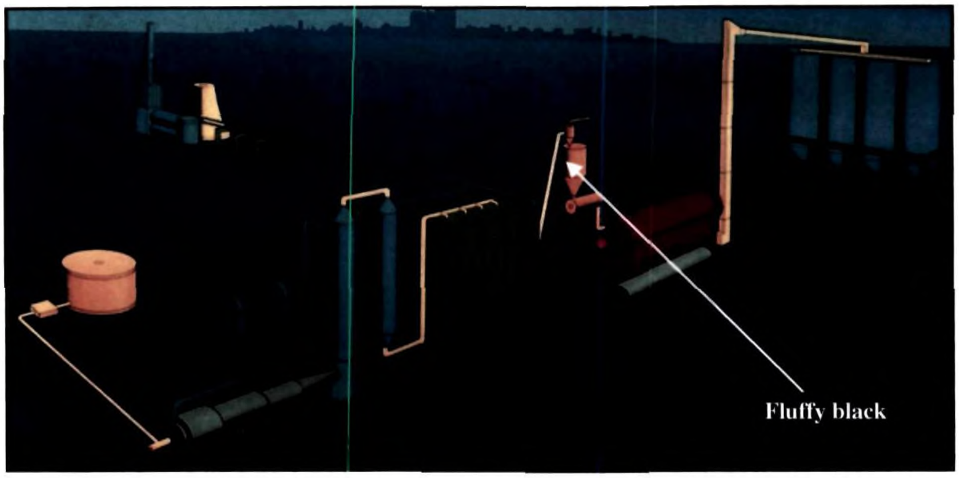

Figure 4.4 Furnace carbon black production unit

4.3.2 Coagulation characteristics of latex- fluffy carbon black masterbatches

It was observed that surfactant treated fresh latex, preserved latex and latex concentrate containing the filler dispersion (with particle size varying from 200 to 500 nm as shown Figure 4.3) coagulated to a consolidated mass quickly on addition of 0.5 % solution of sulphuric acid. However, it is observed that the coagulation was more uniform for fresh field latex compared to the other forms.

From the values of zeta potential, it is observed that fresh field latex had a higher zeta potential than other forms of latices. As explained earlier the type and amount of adsorbed anions are different for the different forms of latex and for concentrated latex the adsorbed ions are predominantly those of higher fatty acid soaps. In presence of added surfactants there is displacement of less active surfactants (proteins) by the more active ones (fatty acid soap anions) leading to an increased tendency for colloidal destabilization by coagulants [16]. The difference in the coagulation behaviour of the latex-fluffy black mixtures for the different forms of NR latex may be attributed to the varying type and amount of surfactants adsorbed on rubber particles.

Due to the increased sensitivity to coagulation by acids in all these forms of latex the well dispersed carbon black added to latex is expected to remain un-aggregated in the latex coagulum.

Table 4. 3 Composition of the masterbatches.

Sample designation	Composition of masterbatches
A	Fresh natural rubber latex + 30 phr fluffy HAF black
B	Preserved field latex +30 phr fluffy HAF black
C	Centrifuged latex + 30 phr fluffy HAF black
D	Preserved field latex (for75 parts rubber) + skim latex (for 25 parts rubber) +30 phr fluffy HAF black
E (control)	Dry rubber ((RSS-IX) + 30 phr fluffy HAF black

The different types natural rubber latex - fluffy (HAF) carbon black masterbatchs and the dry natural rubber (RSS-IX) - fluffy (HAF) carbon black masterbatch (control) shown in Table 4.3 were prepared as per the procedure described in Chapter 2.

The formulations based on the master batches are shown in Table 4.4

Table 4.4 Formulation based on fresh natural rubber latex - carbon black dried masterbatch rubber compounds and dry natural rubber based compounds

Ingredient	A	B	C	D	E
Dry natural rubber carbon black masterbatch	130	130	130	130	-
Natural rubber (RSS-I X)	-	-	-	-	100
Zinc oxide (phr)	5	5	5	5	5
Stearic acid (phr)	2	2	2	2	2
HAF carbon black (phr)	-	-	-	-	30
Naphthenic oil (phr)	1.5	1.5	1.5	1.5	1.5
Anioxidant TDQ (phr)	1	1	1	1	1
CBS (phr)	0.75	0.75	0.75	0.75	0.75
Sulphur (phr)	2.5	2.5	2.5	2.5	2.5

4.4 Mooney viscosity of the dry masterbatches and the control dry rubber

Mooney viscosity of the dry masterbatches and the control dry rubber is shown in Table 4.5. The masterbatch containing filler showed comparable Mooney viscosity values. The pure dry natural rubber without filler showed a lower Mooney viscosity. In skim latex the rubber molecules are believed to be linear without long chain branching whereas the non rubber ingredients are comparatively higher [17]. Both these factors affect the Mooney viscosity.

Table 4.5 Mooney viscosity of the dry samples

Samples	ML (1+4) 100 °C
A	99
B	101
C	102
D	99
Natural rubber (RSS-I X without filler)	78

4.5 Vulcanization characteristics

The masterbatch based mixes showed a higher level of vulcanization as obtained from a higher rheometric torque compared to the control. (Table.4.6)

Table 4.6 Vulcanization characteristics of the compounds based on the dry masterbatches and the control dry rubber

Parameters	A	B	C	D	E
Torque Min (dNm)	0.42	0.37	0.64	0.75	0.39
Torque Max (dNm)	17.6	16.0	15.5	18.0	10.2
Optimum cure time, t_{90} at 150^0 C (minutes)	9.17	9.49	9.28	9.48	8.52
Crosslink density,x 10^5 (moles/g rubber hydrocarbon)	2.662	2.585	2.638	2.615	2.341

The maximum rheometric torque for the compounds was in the order D > A > B > C > E. Comparatively higher crosslink density is also observed for the masterbatch compounds compared to the dry rubber compound.

Good level of cure is exhibited by fresh PFL and blends of PFL with skim latex in comparison with rubber from latex concentrate which is attributed to the proteins and fatty acids present in skim latex. (Table 4.1) In the case of fresh NR latex there is acceptable level of *in situ* formed fatty acids and proteinaceous materials (from the externally added surfactant) and this also help in the attainment of higher level of vulcanization. Comparatively lesser quantity of non rubber ingredients including fatty acid soaps and proteins are present in latex concentrate. The control compound showed a comparatively lower cure time and rheometric torque due to the presence of lower content of surfactants.

4.6 Mechanical properties

In general the vulcanizates prepared from the latex based masterbatches show higher modulus, tensile strength, hardness, tear strength, lower compression set, heat buildup and abrasion resistance as compared to the vulcanizate prepared from the control-dry rubber based vulcanizate. (Table.4.7). This is mainly attributed to the higher level of vulcanization and also better filler dispersion as will be explained later.

Table.4.7 Mechanical properties of masterbatch and dry mix.

Parameters	**A**	**B**	**C**	**D**	**E**
100% Modulus (MPa)	2.4	2.2	2.2	4.1	1.9
300% Modulus (MPa)	9.5	9.0	11.4	13.1	8.1
Elongation at break (%)	545	515	536	408	631
Tensile Strength (MPa)	25.5	24.2	25.0	19.0	23.1
Hardness (Shore A)	54	53	54	53	50
Compression set (%)	36	37	35	38	39
Heat build-up, ΔT (°C)	22	24	23	28	25
Abrasion loss (mm^3)	102	105	104	130	120
Resilience (%)	75	75	76	70	75
Tear strength (kN/m)	63	58	59	52	56

The higher modulus of vulcanizates containing skim rubber is due to presence of higher amount of proteins.

4.7 Filler dispersion study using Disper Grader

The filler dispersion data of vulcanizates containing 30 phr filler is given in Figure 4.5 and Table.4.8.

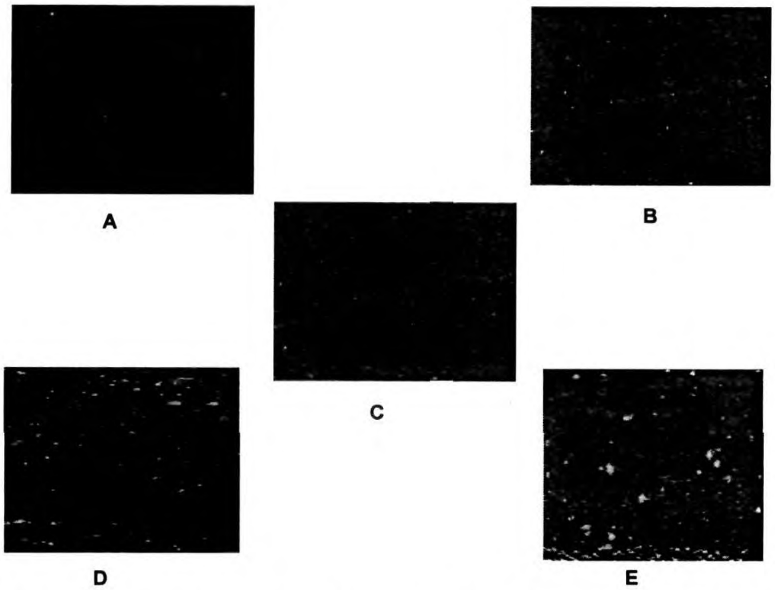

Figure 4.5 Images of carbon dispersion (A, B, C, D and E (Ref. Table 4.3)) as per rating in Table 8

Table 4.8 Carbon black dispersion rating

Sample designation	Carbon black dispersion (X)	Agglomerate dispersion (Y)
A	7.0	8.3
B	6.8	8.0
C	6.5	7.6
D	6.0	7.0
E	4.5	6.0

It is observed that the filler dispersion is better in the vulcanizates prepared from the latex based masterbatches as compared to the vulcanizate prepared from the control-dry rubber based mix. Dispersion was more uniform in the case of the vulcanizate prepared from the fresh field latex based masterbatch compared to the other samples. It is expected that there is better dispersion of fillers when they are mixed in the latex stage and coagulated quickly by a modified coagulation process compared to mixing of carbon black in dry rubber using conventional mill mixing technique. The in situ fatty acids which act also as plasticizers are also expected to help in better filler dispersion [18,19] .The improvement in mechanical properties for masterbatch prepared from fresh NR latex is attributed the better filler dispersion and higher level of vulcanisation.

4.8 Ageing Properties

The mechanical properties obtained after ageing the samples at 100 ^{0}C for three days are given in Table 4.9. The masterbatches prepared in the latex stage shows lower reduction in tensile strength and elongation at break as compared to the control dry rubber masterbatch even after exposing the samples to 100 ^{0}C for three days. This may be due to the higher level of crosslinking and better dispersion of filler in the masterbatches prepared in the latex stage [20, 21].

Table 4.9 Mechanical properties of the vulcanizates based on the dry masterbatches and the control dry rubber vulcanizate after ageing for three days at 100 ^{0}C.

Parameters	A	B	C	D	E
Modulus at 300% elongation (MPa)	10.8	10.3	12.5	14.4	10.5
Change in modulus (%)	+13.6	+14.4	+9.6	+9.9	+29.6
Elongation at break (%)	510	480	500	380	520
Change in elongation at break (%)	- 6.4	- 6.8	- 6.7	- 6.8	-17.6
Tensile strength (MPa)	23.5	21.7	22.4	18.1	20.5
Change in tensile strength (%)	- 7.8	- 10.3	- 10.4	- 5.0	- 11.3

4.9 Effect of fluffy carbon black on dry natural rubber prepared by latex stage masterbatching process

As evident from the results shown above the fresh natural rubber latex–fluffy carbon black (30 phr) masterbatch shows improved cure characteristics and vulcanizate properties as compared to the equivalent masterbatches prepared using centrifuged latex and preserved field latex as base materials. Table 4.10 shows the formulations of mixes prepared from the fresh natural rubber latex– fluffy carbon black masterbatches containg 10, 20, 30 and 40phr carbon black (e.g. : Fresh natural rubber latex - carbon black dried masterbatch = 100 parts natural rubber + 10 parts fluffy carbon black)

Table 4.10 Formulation based on fresh natural rubber latex - carbon black dried masterbatch rubber compounds and dry natural rubber based compounds (control)

Fresh natural rubber latex - carbon black dried masterbatch	110	120	130	140	-	-
Dry natural rubber (RSS-1 X)	-	-	-	-	100	100
Zinc oxide (phr)	5	5	5	5	5	5
Stearic acid (phr)	2	2	2	2	2	2
Naphthenic oil (phr)	1.5	1.5	1.5	1.5	1.5	1.5
HAF black (phr)	-	-	-	-	30	40
Antioxidant TDQ (phr)	1	1	1	1	1	1
CBS (phr)	0.75	0.75	0.75	0.75	0.75	0.75
Sulphur (phr)	2.5	2.5	2.5	2.5	2.5	2.5

The vulcanization characteristics of the compounds based on fresh natural rubber latex - carbon black dried masterbatch rubber compounds and dry natural rubber based compounds (control) are given in Table 4.11

Table 4.11 Vulcanization characteristics of the compounds based on fresh natural rubber latex - carbon black dried masterbatch rubber compounds and dry natural rubber based compounds (control)

Parameters	Fresh natural rubber latex - carbon black dried masterbatch rubber compounds				Dry natural rubber based compounds (control)	
Carbon black loading	10	20	30	40	30	40
Torque Min (dNm)	1.01	1.18	0.71	1.21	0.48	0.66
Torque Max (dNm)	9.0	9.82	10.56	12.99	9.47	12.37
Optimum cure time,t_{90} (min)	8.14	10.05	7.54	9.55	8.12	10.02
Crosslink density, x 10^5 (moles/g rubber hydrocarbon)	2.587	2.603	2.785	2.856	2.566	2.684

In the case of the latex stage masterbatches the maximum torque (T_{max}) increased as the dosage of the carbon black increased. The optimum cure time (t_{90}) too increased as the black loading increased. Similar results were obtained in the case of mixes prepared from dry rubber.

The bound rubber content values (Table 4.12) are found to be higher for masterbatches as compared to the dry mill mix samples. This proves that there is more rubber – filler interaction in the case of the master batches.

Table 4.12 Bound rubber contents in compounds based on fresh natural rubber latex - carbon black dried masterbatch and dry natural rubber

Samples	Bound rubber, %
Fresh natural rubber latex masterbatch vulcanizate with 30 phr HAF	57
Fresh natural rubber latex masterbatch vulcanizate with 40 phr HAF	60
Dry natural rubber based vulcanizates with 30 phr HAF	39
Dry natural rubber based vulcanizates with 40 phr HAF	41

The vulcanizates prepared from carbon black master batches by the new method shows higher tensile strength and a higher modulus, along with higher hardness, resilience and tear strength. The compression set, abrasion loss and heat build-up were found to be lower (Table 4.13).

Table 4.13 Mechanical properties of vulcanizates based on fresh natural rubber latex - carbon black dried masterbatch and dry natural rubber

Parameters	Vulcanizates prepared from fresh natural rubber latex-carbon black dried masterbatch rubber compounds				Vulcanizates prepared from dry natural rubber based compounds (control)	
Carbon black loading	10	20	30	40	30	40
Modulus at 100% (MPa)	1.2	1.3	1.9	2.2	1.50	2.1
Modulus at 300% (MPa)	2.8	3.5	7.8	9.8	5.7	8.8
Elongation at break (%)	742	640	549	526	627	606
Tensile strength (MPa)	26.0	26.3	26.5	28.4	24.0	26.7
Hardness (Shore A)	46	47	56	60	50	56
Compression set (%)	22	23	35	37	35	38
Heat buildup (°C)	16	17	23	24	24	25
Abrasion loss (mm^3)	142	131	105	103	120	114
Resilience (%)	82	80	75	72	76	74
Tear strength (kN/m)	44	52	57	65	53	63

4.10 Conclusions

Different types of natural rubber latics were used to prepare carbon black masterbatch. Fresh latex based masterbatch, has very good level of vulcanization and mechanical properties compared to masterbatches prepared from preserved field latex, latex concentrate or skim latex. This is attributed to a more uniform coagulation of fluffy carbon black latex mixture. The masterbatch mixes shows better dispersion of filler in the vulcanizates. Fresh latex based masterbatches with 30 phr and 40 phr fluffy HAF black show better mechanical properties.

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Chapter 5

CARBON BLACK / SILICA MASTERBATCH FROM FRESH NATURAL RUBBER LATEX*

Contents

A simple method for production of natural rubber latex - carbon black / silica masterbatches with enhanced mechanical properties is described. The main steps involved in the process are the preparation of filler dispersion, addition of the dispersions to the fresh natural rubber latex under stirring, coagulation of the mixture by the addition of acid, dewatering of the coagulum, and drying to obtain filler incorporated natural rubber (NR). The mechanical properties of the vulcanizates obtained from the latex stage and dry rubber incorporated mixes were evaluated and the filler interaction characteristics were studied. The masterbatch prepared by the new process showed a higher level of vulcanization as compared to the dry rubber mix. The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness were superior for the vulcanizates prepared by the new method. The heat build-up values were considerably low for the latex filler masterbatches. Slightly lower tan delta values were also observed for the latex filler masterbatches. The silica filled mixes showed comparatively very good mechanical properties in the absence of any coupling agent. The improvement in mechanical properties shown by the silica/carbon black masterbatches over the conventional mill mixed compounds could be attributed to better filler dispersion as evidenced by the results of filler dispersion data. A better polymer filler interaction was evident from the lower tan delta values observed by dynamic mechanical analysis.

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5.1 Introduction

Silica along with carbon black, have attained great significance in recent years as fillers especially for the tyre sector due to the requirement for increased durability, better fuel efficiency and improved safety [1, 2]. There are issues such as air pollution due to use of the fluffy fillers and higher energy consumption when reinforcing fillers are incorporated in dry rubber. The dispersion of these fillers in a rubber matrix is the crucial parameter that controls the resulting dynamic and mechanical properties [3-5]. In the case of carbon black and silica the production of natural rubber latex masterbatches by their addition as aqueous dispersion has been suggested as one of the methods to avoid some of the problems arising during filler incorporation [6-8]. The mixing of filler and rubber includes stages like incorporation, distribution and dispersion. The first two processes are known to be energy intensive operations. Incorporation of fillers as dispersions in the latex stage followed by co-coagulation of latex filler system is expected to be less energy intensive.

The results of the investigations reported in the previous chapters show that latex stage masterbatch process can produce well dispersed rubber-filler mixes. The Cabot Elastomer Composite is a natural rubber- carbon black masterbatch produced by a continuous liquid phase process [9-11]. Several techniques are described for the production of filler master batches from pre-vulcanized latex, modified latex or from centrifuged natural rubber latex [12- 15]. The preparation of latex carbon black/silica dual filler masterbatches from fresh natural rubber latex by a modified coagulation process, and the characterization of the masterbatches are discussed in this chapter.

5.2 Preparation of fresh natural rubber latex-carbon black/ silica masterbatches by quick coagulation method.

25% dispersions of carbon black and silica were prepared separately as per the recipes given in Tables 2.9 and 2.10 (Chapter 2) by ball milling for 24 hours. The dispersions were added slowly into fresh natural rubber latex containing 20% ammonium laurate (surfactant) under stirring at 50 rpm. The stirring was continued for 15 minutes and the masterbatch was coagulated by the addition of 0.5% dilute sulphuric acid. In this method the filler-latex mixture is coagulated within 3-5 seconds by the addition of acid. Since the soap sensitization of fresh latex ensured the simultaneous coagulation of latex and filler slurry, there was practically negligible or no loss of filler during coagulation. The coagulum was washed well to remove the acid and dried for 48 hours in an air oven maintained at 70 ^{0}C

The formulations (Tables 5.1 and 5.2) based on the dried masterbatches and the control dry rubber were prepared on a two- roll mixing mill.

Table 5.1 Formulations based on the latex based masterbatches

Dried masterbatches	NR + HAF/silica (Masterbatch)				
	100+10/30	100+20/20	100+0/40	100+25/25	100+30/30
Zinc oxide (phr)	5	5	5	5	5
Stearic acid (phr)	1.5	1.5	1.5	1.5	1.5
Anioxidant TDQ (phr)	1	1	1	1	1
DEG (phr)	0.8	0.8	0.8	0.8	0.8
MBTS (phr)	1.0	1.0	1.0	1.0	1.0
DPG (phr)	0.2	0.2	0.2	0.2	0.2
Sulphur (phr)	2.5	2.5	2.5	2.5	2.5

Table 5.2 Formulations based on dry natural rubber (control)

Natural rubber (RSS-I X)	100	100	100	100	100
Zinc oxide (phr)	5	5	5	5	5
Stearic acid (phr)	1.5	1.5	1.5	1.5	1.5
HAF/silica (phr)	10 / 30	20 /20	0 /40	25 /25	30 /30
Anioxidant TDQ (phr)	1	1	1	1	1
DEG (phr)	0.8	0.8	0.8	0.8	0.8
MBTS (phr)	1.0	1.0	1.0	1.0	1.0
DPG (phr)	0.2	0.2	0.2	0.2	0.2
Sulphur (phr)	2.5	2.5	2.5	2.5	2.5

5.3 Coagulation characteristics

The particle size distributions in the dispersions of carbon black and silica are shown in Figures 5.1a and 5.1b. Particle size of carbon black varies from 150 nm to 290 nm and that of silica varies from 150 to 220 nm. It is expected that these dispersions mix uniformly with latex as the particle sizes of dispersions, and the sizes of the rubber particles in the latex are almost similar.

In the presence of added surfactants there is a displacement of proteins from the rubber particle surface which make the latex more sensitive to coagulation and help in better dispersion of fillers. On addition of acids to surfactant containing latex, the latex become more sensitive to coagulation by acids. As a consequence, latex coagulates immediately. Due to quick coagulation it is expected that the uniformly mixed fillers remain un-aggregated during coagulation and further processing [16, 17].

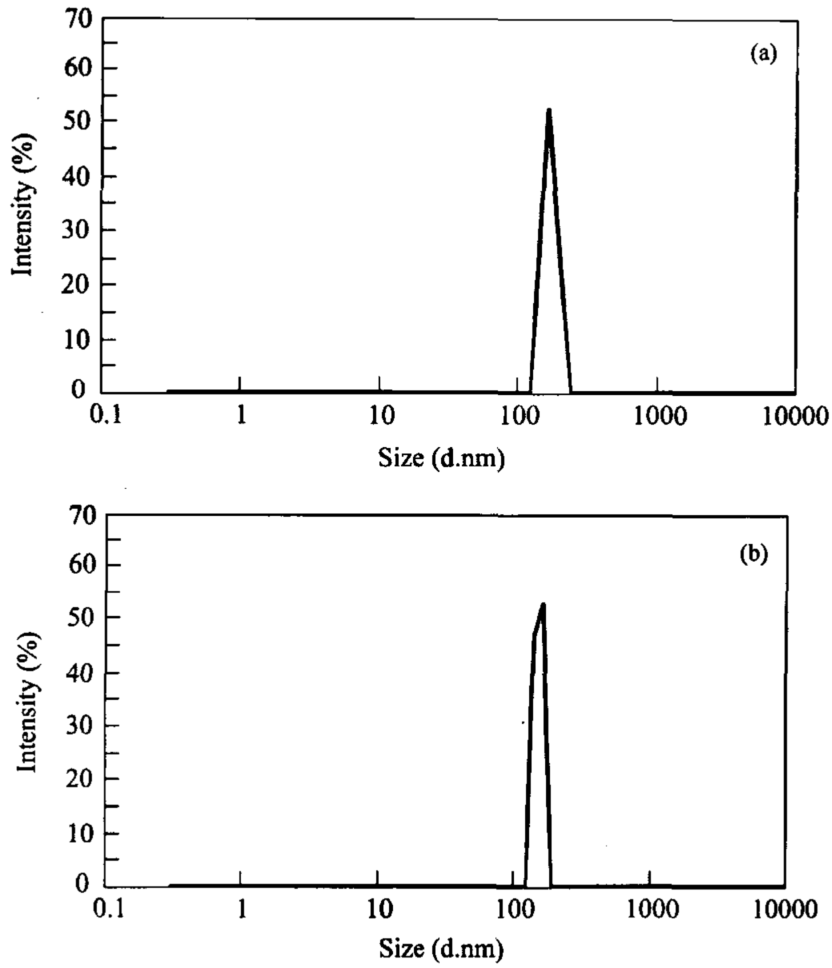


Figure 5.1 Sizes of Particles in (a) carbon black dispersion, and (b) silica dispersion

5.4 Cure characteristics

The cure characteristics of the compounds prepared from fresh natural rubber latex based masterbatches and the control dry rubber based compounds are shown in Tables 5.3. In the masterbatch mixes containing 40 phr of silica/carbon black dual fillers a comparatively higher torque is recorded when the carbon black content is higher. For the silica filled compounds a lower minimum torque and lower scorch time is recorded for the masterbatch as compared to the mill mixed compounds. For same filler loadings, the masterbatch based mixes recorded a higher rheometric torque and lower cure time as compared to the compounds based on dry rubber. Similar results were observed in the case of the compounds containing higher dosages of the fillers (50phr and 60phr). During the preparation of masterbatches, the filler-latex mixture co-coagulates along with a portion of the surfactant that apparently got converted into the corresponding fatty acid. This helps in better vulcanization characteristics of rubber as fatty acids are activators of vulcanization [18, 19].

Table 5.3 Cure characteristics at 150 ^{0}C of compounds prepared from fresh natural rubber latex based masterbatches and dry rubber based compounds

Parameter	Compounds prepared from fresh natural rubber latex based masterbatches					Dry rubber based compounds				
Dosage of carbon black/silica (phr)	10/30	20/20	0/40	25/25	30/30	10/30	20/20	0/40	25/25	30/30
Torque $_{max}$ (dNm)	19.4	20.1	23.5	22.7	24.1	15.0	16.5	19.0	21.3	21.4
Torque $_{min}$ (dNm)	1.7	1.6	1.5	2.4	2.2	1.1	1.4	3.9	2.4	2.2
Optimum cure time t_{90} (minutes)	6.19	7.31	7.0	9.39	5.40	6.47	7.5	8.54	9.86	6.27
Scorch time, ts_2 (minutes)	1.0	1.29	1.39	1.41	1.09	1.01	1.75	2.08	2.06	1.19
Crosslink density, x 10^5 (moles/g rubber hydrocarbon)	2.980	3.085	3.140	3.215	3.308	2.754	2.885	2.516	3.045	3.220

5.5 Mooney viscosity

The Mooney viscosities of masterbatches are given in Table 5.4. The masterbatches recorded a higher Mooney viscosity as compared to the raw natural rubber. This observation is in conformity with the earlier reports [20]. However the Mooney viscosity of the masterbatch is not very high as expected. It is assumed that the presence of fatty acid soaps in the masterbatch results in a good filler dispersion and comparatively low Mooney viscosity by lubrication at molecular level. Fatty acid soaps have been shown to improve the processability of natural rubber compounds [22].

Table 5.4 Mooney viscosity ML (1+4) 100 ^{0}C of fresh natural rubber latex based dried masterbatches and dry rubber (NR).

Parameters	**Dry rubber (NR)**	**Fresh natural rubber latex based dried masterbatches**				
Dosage of carbon black /silica (phr)	0/0	10/30	20/20	25/25	30/30	0/40
Mooney viscosity (ML (1+4) 100 ^{0}C)	78	101	104	110	116	102

5.6 Mechanical properties

The vulcanizates prepared from the masterbatches by the new method shows higher tensile strength, modulus, hardness and tear strength along with lower heat build-up and abrasion loss (Table 5.5). The improvement in mechanical properties is attributed to better filler dispersion and a higher level of vulcanization. The filler dispersion characteristics are presented in Figure 5.2 and Table 5.6. A comparatively better dispersion and lower degree of aggregation is shown by the vulcanizates prepared from fresh natural rubber based masterbatches as compared to the vulcanizate prepared from dry natural rubber based compounds.

Table 5.5 Mechanical properties of the vulcanizates prepared from fresh natural rubber latex based masterbatches and dry rubber based vulcanizates

Parameter	Vulcanizates prepared from fresh natural rubber latex based masterbatches					Dry rubber based vulcanizates				
Dosage of carbon black/silica (phr)	10/30	20/20	0/40	25/25	30/30	10/30	20/20	0/40	25/25	30/3
Modulus at 300% elongation (MPa)	12.0	14.0	4.22	10.8	14.8	10.8	10.5	3.0	7.2	12.
Tensile strength (MPa)	26.4	28.2	27.6	27.3	26.6	25.6	26.2	21.5	24.5	24.
Elongation at break (%)	500	560	680	570	460	550	580	600	620	48
Tear Strength (kN/m)	66.0	70.0	70.0	103	107	50.0	60	53.0	88	95
Hardness (Shore A)	60.0	64.0	58.0	66.0	68.0	55.0	56.0	54.0	58.0	64.
Heat Build-up, $\Delta T(^0C)$	14.0	13.0	12.0	16.0	17.0	17.0	18.0	18.0	21.0	22.
Abrasion loss (mm^3)	120	118	153	107	113	130	140	270	143	13

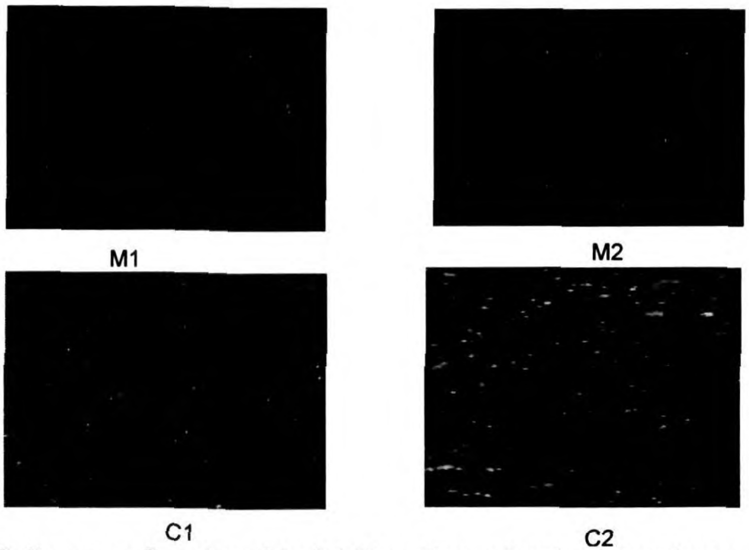


Figure 5.2 Images of carbon black/silica dispersion in vulcanizates prepared from the: masterbatches based on fresh natural rubber latex (M1-silica/carbon black 25/25, and M2- silica/carbon black 30/30), and Dry natural rubber based vulcanizates (C1-silica /carbon black -25/25, and C2 silica /carbon black -30/30)

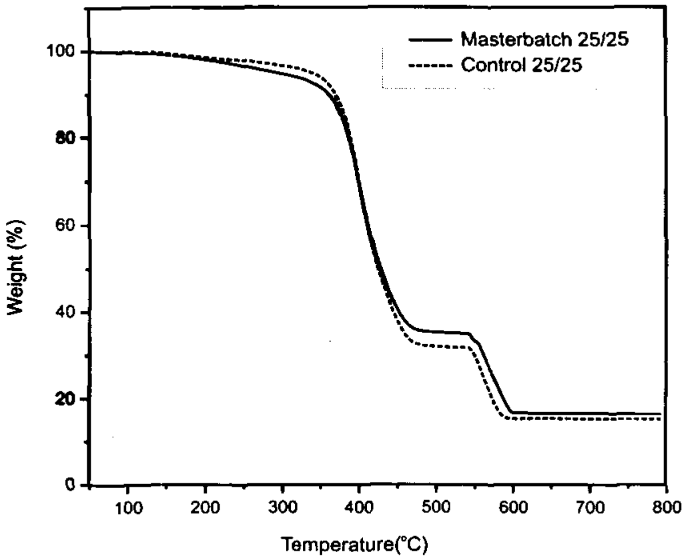
Table 5.6 Results of filler dispersion

Sample name	Fillers dispersion(X)	Agglomerate dispersion(Y)
Masterbatch based vulcanizate on fresh natural rubber latex (M1-silica/carbon black 25/25)	8.2	9.0
Masterbatch based vulcanizate on fresh natural rubber latex (M2-silica/carbon black 30/30)	8.0	8.7
Dry natural rubber based vulcanizate (C1-silica/carbon black -25/25	7.1	7.6
Dry natural rubber based vulcanizate (C2-silica/carbon black -30/30)	7.0	7.4

5.7 Thermogravimetric analysis (TGA)

The thermograms of the vulcanizates prepared from the fresh natural rubber latex based masterbatch and dry rubber based vulcanizate are shown in

Figure 5. 3. The results are tabulated in Table 5.7. The results show that the thermal stability of vulcanizates prepared from the fresh natural rubber latex based masterbatch and the dry rubber based vulcanizate is almost similar.



Figur 5.3 **Thermograms of the masterbatch based on fresh natural rubber latex (M1-silica/carbon black 25/25) and Dry natural rubber based vulcanizate (C1-silica/carbon black – control 25/25).**

Table 5.7 **Data from Thermogravimetric Analyzer for the masterbatch vulcanizate based on fresh natural rubber latex (M1- silica/carbon black 25/25) and Dry natural rubber based vulcanizate (C1-silica/carbon black – control 25/25).**

Sample	Temperature of onset of degradation (^{0}C)	Temperature at which the rate of weight loss is maximum (^{0}C)	Residual weight (%)
Masterbatch vulcanizate based on fresh natural rubber latex (M1- silica/carbon black 25/25)	314.7	401.34	17.77
Dry natural rubber based vulcanizate (C1-silica/carbon black – control 25/25).	315.15	401.34	18.33

5.8 Dynamic mechanical properties

Damping characteristics from -90 to +100 ^{0}C for the the vulcanizates prepared from the fresh natural rubber latex based masterbatch and dry natural rubber based vulcanizate containing 50 phr fillers are given in Figure 5.4. For masterbatch vulcanizates there is a lowering of the tan delta peak height compared to the dry rubber vulcanizates indicating stiffening as a result of better polymer filler interaction for the masterbatch as compared to the dry rubber based vulcanizates.

It is also observed that the temperature at which the tan delta value is maximum is marginally lower for the vulcanizates prepared from the fresh natural rubber latex based masterbatch than for dry natural rubber based vulcanizates. This may be due to the higher chain flexibility due to lower filler-filler interactions. Ideal compounds for tyre tread are those which possess high polymer–filler and low filler–filler interactions [23]. It is observed that a lower tan delta at 60 ^{0}C (Figure 5.5) is obtained for the masterbatch compared to the control. It is well known that the tan delta at 60 ^{0}C is a measure of the degree of rolling resistance [23]. It is inferred that there is lower rolling resistance for the masterbatch compared to a conventional mix.

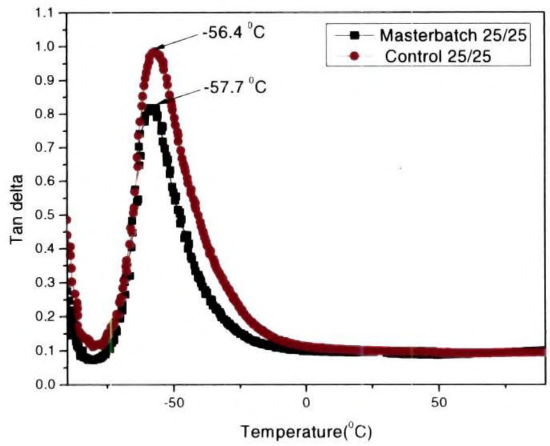


Figure 5.4 Tan delta versus temperature plot for the for the masterbatch vulcanizate based on fresh natural rubber latex containing 25/25 silica/carbon black and the dry natural rubber based vulcanizate (control) containing 25/25 silica/carbon black

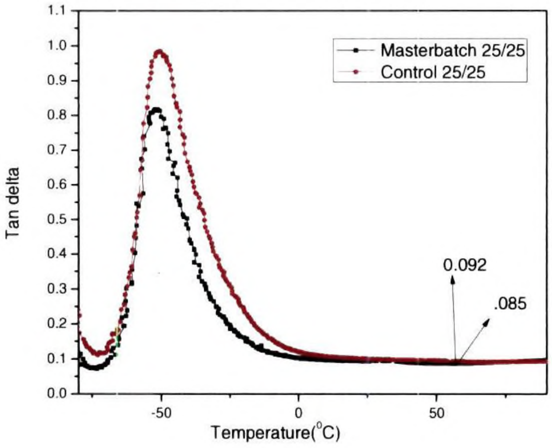


Figure 5.5 Plots of tan delta versus temperature for the masterbatch containing 25/25 silica/carbon black, and conventional dry mix containing 25/25 silica/carbon black at 60 °C.

5.9 Conclusions

Modified coagulation process of natural rubber latex provides a method to produce fresh natural rubber latex/carbon black/silica masterbatches with very good mechanical and dynamic properties. The filler masterbatch prepared by this method shows a higher level of vulcanization along with better filler dispersion compared to conventionally prepared mixes. Due to this, a comparatively low tan delta value at 60 ^{0}C that correlates to a lower rolling resistance is observed for the masterbatch vulcanizates.

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Chapter 6

HAF/SILICA/NANOCLAY "TERNARY" MASTERBATCH FROM FRESH NATURAL RUBBER LATEX[*]

A process for production of carbon black/silica/nanoclay ternary filler masterbatch from fresh natural rubber (NR) latex was standardized. The fillers were incorporated in fresh NR latex by a modified coagulation process. The latex mixed with the filler dispersions was coagulated immediately on addition of acids. The coagulum containing fillers was dried at 70 ^{0}C in an air oven to get latex- filler masterbatch which was processed further in the conventional way. The masterbatch compounds containing only silica/carbon black shows higher level of vulcanization as compared to the corresponding dry mixes. The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness increased with the proportion of nanoclay in the mixes up to 5 phr. The improvement in mechanical properties of the vulcanizates was very meagre on further addition of the nanofiller. Lower tan delta values were observed for all the masterbatches containing nanoclay in the ranges 3-10 phr compared to the control dry mix containing 25/25 carbon black/silica. The improvement in mechanical properties and dynamic properties shown by the masterbatches over the conventional mill mixed compounds could be attributed to the factors related to improved filler dispersion as evident from the data from Dispersion analyzer images and X-Ray diffractograms.

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[*] **Part of the work presented in this chapter has been accepted for publication in Rubber Chemistry and Technology (in press)**

6.1 Introduction

The key factors for reinforcement by fillers like silica and carbon black are smaller particle size, better polymer filler interaction and good dispersions [1, 2]. Carbon black has remained as the most prominent filler in the tyre sector for over hundred years. Silica gained importance in tire sector due to the lower hysteresis in the presence of a silane coupling agent [3-5]. Mixing of rubber with carbon black, silica, and nanoclay are highly energy consuming process. Mill mixing of these fillers with rubber pollutes the ambient air due to flying of the particles. In the case of silica and nanoclay, it is extremely difficult to disperse these highly aggregate fillers in natural rubber by mill mixing [6, 7]. In the case of carbon black, preparation of latex-carbon black masterbatch by the addition of carbon black as a slurry has been suggested as one of the methods to avoid the problems of mixing filler and to give vulcanizates with enhanced properties [8-16]. Masterbatch has been prepared from fresh latex, and centrifuged preserved latex as described in the chapters 3-5. This chapter presents the preparation of latex carbon black/silica/nanoclay triple filler masterbatches from fresh natural rubber followed by a modified coagulation process.

6.2 Preparation of carbon black /silica / nanocly dispersions

25% dispersions of carbon black and silica based on the recipes given in Tables 2.9 and 2.10 were prepared separately by ball milling for 24 hours. 10% dispersion of nanoclay as per the recipe given in Table 2.11 was prepared by stirring at 400 rpm for 30 minutes (Chapter 2). The calculated quantities of the dispersions were added to the drc estimated fresh natural rubber latex slowly in the order nanoclay, silica and carbon black. The latex after the addition of dispersions is coagulated immediately by the addition of 0.5% sulphuric acid with stirring (Chapter 2.4). The formulations of carbon black/silica/nanocly masterbatches from latex based and dry natural rubber based compounds are shown in Tables 6.1 and 6.2

Table 6.1 Formulations based on the dry natural rubber prepared from fresh latex carbon black/silica/nanocly masterbatches

Natural rubber + HAF/silica/ nanoclay (Dried masterbatch)	**100+25/25/0 (M1)**	**100+25/25/3 (M2)**	**100+25/25/5 (M3)**	**100+25/25/10 (M4)**	**100+30/30/0 (M5)**
Zinc oxide (phr)	5	5	5	5	5
Stearic acid (phr)	1.5	1.5	1.5	1.5	1.5
Anioxidant TDQ (phr)	1	1	1	1	1
DEG (phr)	0.8	0.8	0.8	0.8	0.8
MBTS (phr)	1.0	1.0	1.0	1.0	1.0
DPG (phr)	0.2	0.2	0.2	0.2	0.2
Sulphur (phr)	2.5	2.5	2.5	2.5	2.5

Table 6.2 Formulations based on dry natural rubber (control)

Natural rubber (RSS-I X)	**100 (C1)**	**100 (C2)**	**100 (C5)**
Zinc oxide (phr)	5	5	5
Stearic acid (phr)	1.5	1.5	1.5
HAF/silica/nanoclay (phr)	25/25/0	25 /25/3	30 /30
Anioxidant TDQ (phr)	1	1	1
DEG (phr)	0.8	0.8	0.8
MBTS (phr)	1.0	1.0	1.0
DPG (phr)	0.2	0.2	0.2
Sulphur (phr)	2.5	2.5	2.5

6.3 Coagulation characteristics

The particle size distribution in the dispersions of nanoclay, carbon black and silica are shown in the Figure 6.1 (a, b, and c).

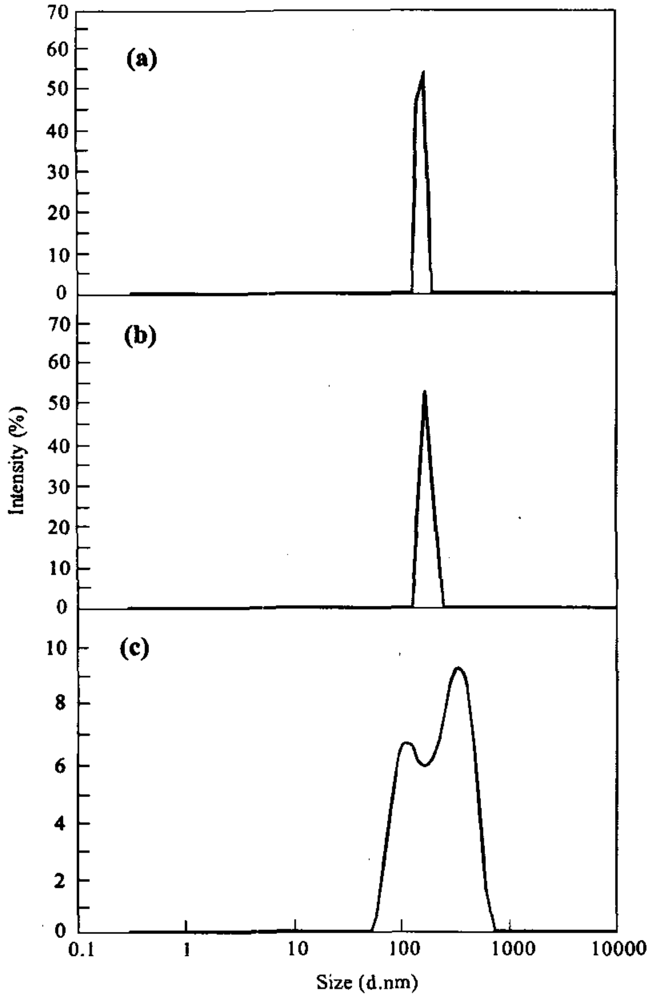

Figure 6.1 Particle size distribution in the dispersions of (a) carbon black (b) silica and (c) nanoclay.

Particle size of carbon black in the dispersion varies from 150 nm to 290 nm, and that of silica dispersion varies from 150 to 220 nm. Nanoclay dispersion has wide variation in particle size. The size varies from 70 to 700 nm.

It is expected that these dispersions mix uniformly with latex as particle size of dispersions is comparable to the size of the rubber particles in latex. On quick coagulation of the masterbatch by the addition of dilute sulphuric acid an almost clear serum separated (chapter 4.3). Apparently the uniformly mixed fillers remained un-aggregated during the quick coagulation [17, 18].

6.4 Vulcanization characteristics

The vulcanization characteristics of compounds prepared from dried fresh natural rubber latex based masterbatches and dry rubber based compounds are shown in Table 6.3.

Table 6.3 Vulcanization characteristics at 150^{0}C of compounds prepared from dried fresh natural rubber latex based masterbatches and dry rubber based compounds.

Parameter	Compounds prepared from fresh natural rubber latex based dried masterbatches					Dry rubber based compounds		
Dosage of carbon black/silica/ nanoclay (phr)	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	25/25/3 (C2)	30/30/0 (C5)
Torque$_{max,}$ (dNm)	22.7	23.0	25.3	25.5	24.1	21.0	22.4	21.4
Torque$_{min}$ (dNm)	2.4	2.4	2.8	2.1	2.2	2.3	2.34	2.18
Optimum cure time t_{90} (minutes)	9.39	9.0	9.01	9.19	5.40	9.06	9.5	6.27
Scorch time, ts_2 (minutes)	1.41	2.13	2.04	2.02	1.09	2.06	1.98	1.19
Crosslink density, x 10^5(moles/g rubber hydrocarbon)	2.905	2.915	2.990	3.140	3.308	2.845	2.884	3.120

The cure time and scorch time were comparable for the masterbatches and control mixes. The incorporation of nanoclay did not adversely affect cure characteristics like cure time and scorch time. The masterbatch mixes containing 25/25 and 30/30 carbon black/silica fillers (M1 and M5) recorded higher rheometric torque compared to the corresponding dry mixes (C1 and C5). The masterbatch mixes containing nanoclay (M1, M2, M3 and M4) recorded higher rheometric torque compared to dry mixes that contain only carbon black/silica. During the preparation of masterbatches, the filler-latex mixture might have co-coagulated along with a portion of the surfactant that got converted into the corresponding fatty acid. This may be the reason for better vulcanization characteristics of rubber as fatty acids are activators of vulcanization [19].

6.5 Mooney viscosity

Mooney viscosity of the masterbatches after drying was measured using Mooney viscometer and the data is given in Table 6.4

Table 6.4 Mooney viscosity ML (1+4)100 °C of dried masterbatches prepared from fresh natural rubber latex and dry natural rubber.

Parameters	Dry rubber (NR)	Dried masterbatches prepared from fresh natural rubber latex				
Dosage of silica/carbon/nanoclay	0/0	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)
Mooney viscosity (ML (1+4) 100 °C)	78	110	112	115	120	116

The Mooney viscosity of the dried masterbatches prepared from fresh natural rubber latex increased as the dosage of filler increased. Incorporation of nanocly improves the Mooney viscosity. The Mooney viscosity increased as the dosage of nanoclay increased [3]. The presence of fatty acid soap in the masterbatch apparently improves the filler dispersion and lubrication at the molecular level thus preventing abrupt increase of Mooney viscosity. Fatty acid soaps have been shown to improve the processability of natural rubber masterbatch compounds [20].

6.6 Filler dispersion characteristics

a) Dispersion grading by using disper grader

The filler dispersion images are presented in Figure 6.2 and the rating is given in Table 6.5. Comparatively better dispersion and lower aggregation of the filler particles is shown by masterbatch vulcanizates as compared to dry rubber vulcanizates.

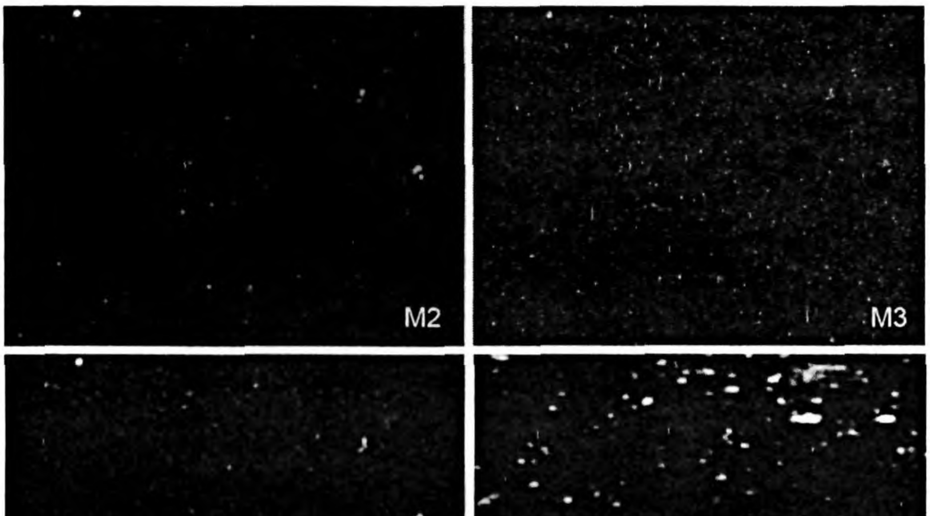

Figure 6.2. Disper grader images showing the dispersion of carbon black/silica/nanoclay in the vulcanizates prepared from masterbatches based on dried fresh natural rubber latex: (M2-silica/carbon black/nanoclay 25/25/3, M3-silica/carbon black/nanoclay (25/25/5), M4- silica/carbon black/ nanoclay (25/25/10) and dry natural rubber based vulcanizates: (C1-silica /carbon black/nanoclay - 25/25/0).

Table 6.5 Results of dispersion ratings of fillers

Sample name	Filler dispersion(X)	Agglomerate dispersion(Y)
Vulcanizate prepared from the masterbatch based on dried fresh natural rubber latex (M2- silica/carbon black/nanoclay 25/25/3)	9.2	9.5
Vulcanizate prepared from the masterbatch based on dried fresh natural rubber latex (M3- silica/carbon black/nanoclay 25/25/5)	9.8	9.9
Vulcanizate prepared from the masterbatch based on dried fresh natural rubber latex (M4- silica/carbon black/nanoclay 25/25/10)	8.7	9.4
Dry natural rubber based vulcanizate (C1-silica/carbonblack/nanoclay-25/25/0)	7.4	7.9

b) X-ray diffraction studies

X-ray diffraction patterns of nanoclay and dried natural rubber latex based carbon black/silica/nanoclay masterbatch vulcanizates are shown in Figure 6.3.

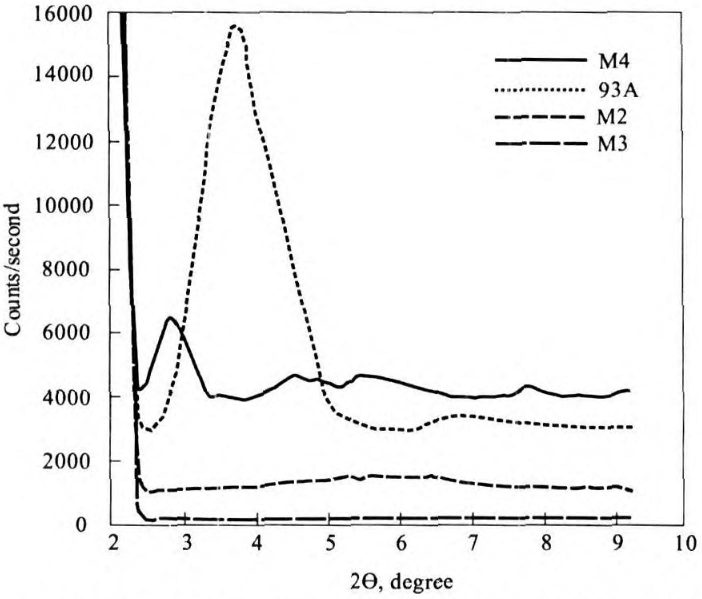

Figure 6.3. X-ray diffraction patterns of masterbatch vulcanizates (M2, M3, M4) and the nanoclay (Cloisite 93A).

X-ray diffraction patterns of cloisite 93A contains sharp peak at 2θ = 3.697° corresponding to a basal spacing of 23.88 Å. In the vulcanizates prepared from the dried fresh natural rubber latex masterbatch M4 (containing the filler dosage silica/carbon black/nanoclay - 25/25/10) the peak corresponding to the nanoclay shifted to a lower 2θ angle of 2.809°, suggesting a basal spacing corresponding to the clay basal spacing of 31.43 Å. The above result implies that the cloisite 93A is intercalated in this vulcanizate. The characteristic X-ray diffraction peak of the clay cannot be seen in samples M2 (silica/carbon black/nanoclay - 25/25/3) and M3 (silica/carbon black/nanoclay 25/25/5). This may be due to the exfoliation of the nanoclay in these vulcanizates.

6.7 Mechanical properties

The HAF/silica/nanoclay "ternary" natural rubber latex stage masterbatch (dried) based vulcanizates showed significantly improved properties like modulus, tear strength, abrasion resistance and heat build-up (Table.6.6), compared to the similar formulations based on dry natural rubber (control). The results show considerable improvement in mechanical properties in the vulcanizates on addition of nanoclay (3-10 phr).

Table 6.6. Mechanical properties of the vulcanizates prepared from fresh natural rubber latex based masterbatches (dried) and dry rubber based vulcanizates.

Parameter	Vulcanizates prepared from fresh natural rubber latex based dried masterbatches					Dry rubber based vulcanizates		
Dosage of carbon black/silica/nanoclay (phr)	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	25/25/3 (C2)	30/30/0 (C5)
Modulus at 300% elongation (MPa)	10.80	11.69	14.85	12.10	14.80	7.20	10.25	12.70
Tensile strength (MPa)	25.30	25.74	25.85	25.40	25.60	24.50	24.80	24.70
Elongation at break (%)	570	553	471	527	460	620	580	484
Tear Strength, (kN/m)	103	105	106	104	105	88	89	95
Hardness (Shore A)	66	68	74	70	68	58	60	64
Heat build-up, ΔT (^0C)	16	13	16	16	17	21	20	22
Abrasion loss (mm^3)	107	97	87	92	113	143	126	132

The elongation at break and modulus at 300% elongation of the vulcanizate loaded with 5 phr nanoclay was 471% and 14.85MPa. The corresponding values of the parameters in the case of the formulations containing 10 phr and 3 phr nanocly (keeping similar dosage for all other ingredients) were 527%, 553%, 12.1 MPa, and 11.69 MPa. The specific surface area is one of the reasons for the considerable reinforcement imparted by the nano-material (<10 phr) [22]. In rubber vulcanizates, the properties are dictated by the bulk properties of both matrix and filler. The interaction between the filler particles and the polymer decides the stiffening of the vulcanizates. In the case of the rubber vulcanizates filled with nanofillers the polymer filler interaction is concentrated at the interface. The terms like "bound polymer" and "interface" have been used to describe the polymer at or near the interface. The interfacial structure is known to be different from bulk structure. In polymers filled with nano-fillers possessing extremely high specific surface area, most of the polymer is present near the interface, in spite of the small weight fraction of filler. If the interaction at the interface is a strong, or if the structure of the interfacial polymer is very different from the bulk, markedly different properties in the material as a whole can be observed. The changes have a fundamentally different origin than those found in the rubber vulcanizates filled with conventional fillers [3, 23]. The mechanical properties obtained after ageing the samples at100 ^{0}C for three days are given in Table 6.7.

Table 6.7 Comparison of mechanical properties of the vulcanizates prepared from the fresh natural rubber latex based masterbatches (dried) and dry rubber based vulcanizates after ageing (100 ^{0}C for 3 days)

Parameter	Vulcanizates prepared from fresh natural rubber latex based dried masterbatches					Dry rubber based vulcanizates		
Dosage of carbon black/silica/nanoclay (phr)	25/25/0 (M1)	25/25/3 (M2)	25/25/5 (M3)	25/25/10 (M4)	30/30/0 (M5)	25/25/0 (C1)	25/25/3 (C2)	30/30/0 (C5)
Modulus at 300% elongation (MPa)	11.58	12.46	16.0	14.07	15.8	9.05	12.50	14.5
Change in modulus (%)	+7.2	+6.6	+7.7	+16.2	+6.8	+25	+21.9	+14.2
Tensile strength (MPa)	22.0	24.28	23.8	23.9	23.5	21.78	22.80	23.0
Change in tensile strength (%)	-13	-5.7	-7.9	-5.9	-8.4	-11.1	-8.0	-6.8
Elongation at break (%)	525	541	415	472	445	590	480	412
Change in elongation at break (%)	-7.9	-2.1	-11.9	-10.4	-3.2	-4.8	-17.2	-14.9

The retention of the mechanical properties were better in the case of the masterbatch based vulcanizates compared to dry rubber based (control) vulcanizates. The enhancement in mechanical properties and ageing behaviours may be attributed to better filler dispersion along with higher level of cross linking.

6.8 Dynamic mechanical properties

Damping characteristics from -90 to +100 ^{0}C for the vulcanizates based on the ternary filler-fresh natural rubber latex masterbatches and a control dry rubber based vulcanizate are given in Figure 6.4. The masterbatches show lower tan delta peak height compared to the control showing that there is better polymer filler interaction in the masterbatches compared to the control. In the case of the vulcanizates containing various dosages of the nanofiller the reinforcement was in the order 5 phr > 3 phr > 10 phr.

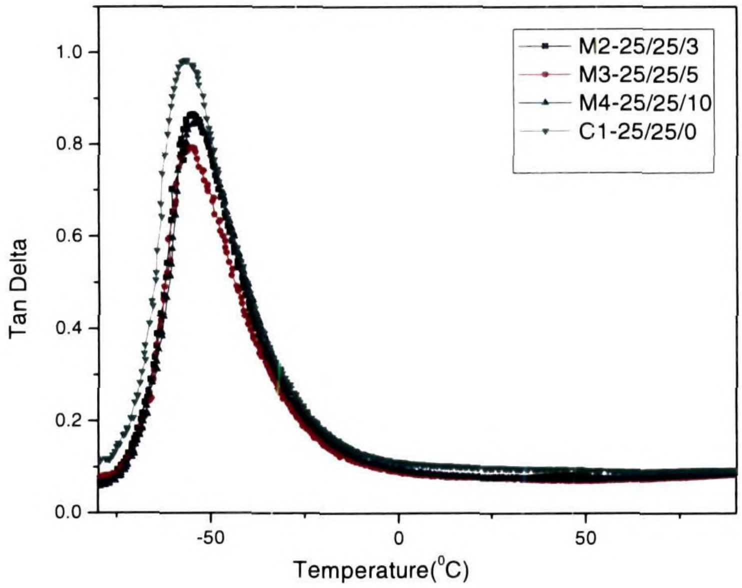

Figure 6.4 Damping characteristics of fresh natural rubber latex masterbatches (dried) vulcanizates and dry rubber vulcanizates containing carbon black/silica/nanoclay (M2, M3, M4 and C1).

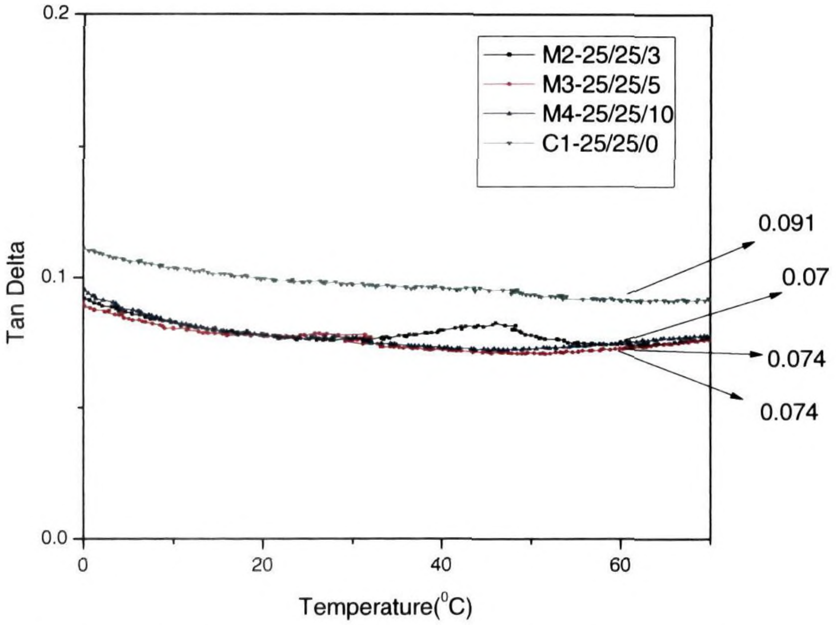

Figure6.5. The tan delta values for the masterbatch and dry rubber vulcanizates containing carbon black/silica/nanoclay (M2, M3, M4 and C1) at 60 ⁰C

However at higher loading the tan delta peak height increases but it is lower than dual filler dry rubber system. The storage modulus and loss modulus are also higher for the masterbatch vulcanizates compared to the dry rubber vulcanizate. This is in line with the observations on tensile properties. Ideal filler for tyre tread compounds are those which possess high polymer–filler and low filler–filler interactions. The former ensures higher abrasion resistance and the latter is necessary for lower rolling resistance or lower tan delta [24-26]. The tan delta values for the masterbatch and dry rubber vulcanizates at 60 ^{0}C are shown in Figure 6.5. It is observed that a lower tan delta at 60 ^{0}C is obtained for the masterbatch compared to the dry rubber, showing a lower rolling resistance for the masterbatch vulcanizates.

6.9 Thermogravimetric analysis

The thermograms of the vulcanizates prepared from fresh natural rubber latex based masterbatches (dried) and dry rubber based vulcanizates are given in Figure 6.6 and the data is presented in Table 6.8.

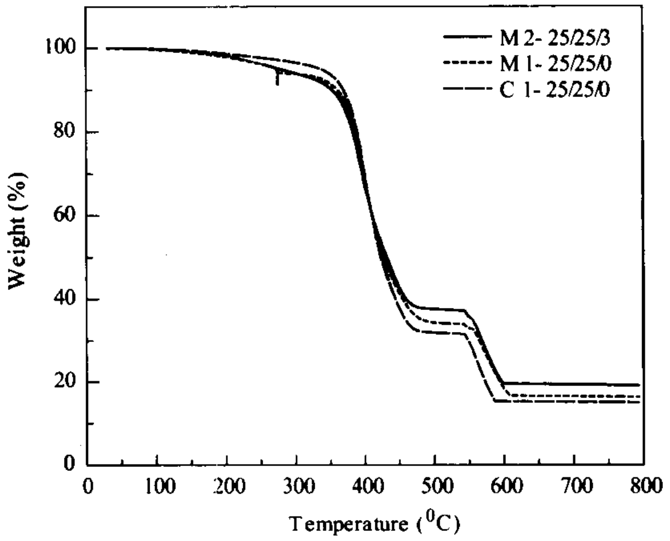

Figure 6.6. Thermograms of fresh natural rubber latex based masterbatches (dried) (M1, M2) and dry rubber based vulcanizate (C1)

Table 6.8 Data from thermogravimetric analysis for the vulcanizates prepared from fresh natural rubber latex based dried masterbatches and dry rubber based vulcanizates

Sample	Temperature of onset of degradation (^{0}C)	Temperature at which the rate of weight loss is maximum (^{0}C)	Residual weight (%)
Masterbatch vulcanizate based on fresh natural rubber latex (M1- silica/ carbon black 25/25)	314.7	401.34	17.7
Masterbatch vulcanizate based on fresh natural rubber latex (M2- silica/ carbon black 25/25/3)	315.15	396.14	20
Dry natural rubber based vulcanizate (C1-silica/ carbon black – control 25/25).	315.15	401.34	18.33

Although the peak decomposition temperature for the nanoclay compound (M2) is a bit lesser than that of the masterbatch (M1), the percentage retention is more here. That is the rate of decomposition is slower in the nanoclay vulcanizate. This is further supported by the fact that the final dissociation temperature (also time) for the nanoclay filled vulcanizate is more than that of masterbatch M1 and dry rubber based vulcanizate C1.

6.10 Conclusions

A novel method of preparing natural rubber based masterbatch containing carbon black/silica/nanoclay tri-filler system from fresh natural rubber latex has been developed. The properties of the nanoclay containing masterbatch vulcanizates prepared by latex stage showed excellent improvement in abrasion resistance, lowering of heat build-up and lower tan delta at 60 ^{0}C compared to a conventional dry rubber vulcanizates.

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Chapter 7

BLENDS OF FRESH NATURAL RUBBER LATEX BASED MASTERBATCH (DRIED) AND POLYBUTADIENE RUBBER*

Contents

Carbon black and silica were incorporated into fresh natural rubber latex and coagulated by quick coagulation process. The coagulum containing the fillers was dried to get dried masterbatches. Natural rubber/polybutadiene rubber (NR/BR) blend compounds were prepared by mixing the dried masterbatch with the required quantity of BR and other compounding ingredients. The compounds were vulcanized and characterized for mechanical and dynamic properties. It was observed that blends prepared from masterbatches had better mechanical properties like tensile strength, modulus, tear strength, abrasion resistance, hardness and lower heat build-up compared to the blends prepared using conventional dry rubber mixing technique. As the proportion of BR in the blend increased abrasion loss reduced while hardness and heat build-up increased due to the unique micro structure of cis-1, 4-polybutadiene rubber. There was reduced filler-filler interaction on blending natural rubber with polybutadiene rubber for the blends based on the masterbatches. Filler dispersion data indicated that the filler dispersion was not adversely affected on blending. Plots of tan δ versus temperature shows a lowering of tan δ peak height in the case of the materbatches indicating better polymer-filler interaction compared to the dry rubber compound vulcanizates. The tan δ value at 60 °C and hence the rolling resistance was lower for the 80/20 NR/BR blend prepared with the masterbatches.

*** Part of the work presented in this chapter has been published in Rubber Science, 25(2): 297-306, 2012.**

7.1 Introduction

Blends based on natural rubber and polybutadiene rubber are extensively used in tyre industry due to their favourable properties such as low heat build-up, better abrasion resistance and low rolling resistance. Silica as a reinforcing filler along with carbon black, has attained great significance in recent years especially in tyre sector due to the requirement for increased durability, better fuel efficiency and improved road safety [1-2]. Due to filler-filler interactions of the reinforcing fillers it is difficult to disperse them uniformly in rubber matrix - either single or in blends. The dispersion of the fillers is the crucial parameter that controls the dynamic and mechanical properties of rubber vulcanizates [3-5].

Many attempts have been made in the past to add filler as a slurry to natural rubber latex and then coagulate the latex–filler mixture to get filler incorporated dry coagulum. However the expected benefit was not realized in the methods standardized earlier [6-15].

Filler distribution in blends is influenced by the method of addition of the filler, mixing method, surface polarity of filler and other factors like un-saturation, viscosity and polarity of blend components. The incorporation of carbon black in 50/50 elastomer pre-blends indicated that the affinity for carbon black decreased in the order, ploybutadiene rubber (BR) > styrene-butadiene rubber (SBR) > polychloroprene rubber (CR) > nitrile rubber (NBR) > natural rubber (NR) > ethylene propylene diene rubber (EPDM) > butyl rubber (IIR) [16,17].

This chapter presents the preparation and characterization of blends of fresh natural rubber latex- carbon black/silica masterbatch (dried) and polybutadiene rubber.

7.2 Preparation of fresh natural rubber latex- carbon black/silica masterbatch and blends with polybutdiene rubber

Fresh natural rubber latex - carbon black/silica masterbatches were prepared as per the procedure given in chapter 2. The dried masterbatches and polybutadiene rubber was separately masticated and mixed with the required quantity of carbon black and silica (based on the quantity of polybutadiene in the blend) on a mixing mill so as to have 25 phr each of carbon black and silica in 100:0, 80:20 and 60:40 natural rubber/ polybutadiene blends. The code of the blend samples and the details are given below in Table.7.1

Table 7.1 Composition of the masterbatches.

Sample designation	Composition of masterbatches
MB 100	Fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch : polybutadiene rubber (100:0)
MB 80	Fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch : polybutadiene rubber (80:20)
MB 60	Fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch : polybutadiene rubber (60:40)
DB 100	Dry natural rubber: polybutadiene ruber (100:0)
DB 80	Dry natural rubber : polybutadiene ruber (80:20)
DB 60	Dry natural rubber : polybutadiene ruber (60:40)

Rubber compounds were prepared as per the formulations given in Table 7.2

Table7.2. Formulations based on fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch/polybutadiene rubber compounds and dry natural rubber/poly butadiene rubber based compounds (control).

Fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch : polybutadiene rubber (Cisamer 1220)	150:0 (MB 100)	120:20 (MB 80)	90:40 (MB 60)	-	-	-
Dry natural rubber (ISNR5): polybutadiene rubber (Cisamer 1220)	-	-	-	100:0 (DB 100)	80:20 (DB 80)	60:40 (DB 60)
Zinc oxide (phr)	5	5	5	5	5	5
Stearic acid (phr)	1.5	1.5	1.5	2	2	2
HAF black (phr)	0	5	10	25	25	25
Silica (phr)	0	5	10	25	25	25
Antioxidant TDQ (phr)	1	1	1	1	1	1
MBTS (phr)	1.4	1.5	1.6	1.4	1.5	1.6
DPG (phr)	0.25	0.25	0.25	0,25	0.25	0.25
Sulphur (phr)	2.5	2.5	2.5	2.5	2.5	2.5

7.3 Cure characteristics

The cure characteristics are shown in Table 7.3 The fresh natural rubber latex-carbon black/silica (25/25) dried masterbatch/polybutadiene rubber compounds recorded a higher rheometric torque, lower cure time and lower scorch time compared to dry natural rubber/poly butadiene rubber based compounds (control). This is due to the better filler dispersion and higher level of vulcanization in the fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch/polybutadiene rubber compounds as compared to the conventional dry natural rubber/poly butadiene rubber based compounds [18-20].

Table7.3. Cure characteristics of fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch/polybutadiene rubber compounds and dry natural rubber/poly butadiene rubber based compounds (control) at 150 ^{0}C.

Fresh natural rubber based carbon black-silica (25/25) dried masterbatch: polybutadiene rubber	100:0 (MB100)	80:20 (MB 80)	60:40 (MB 60)	-	-	-
Dry natural rubber : polybutadiene ruber (control)	-	-	-	100:0 (DB 100)	80:20 (DB 80)	60:40 (DB 60)
Torque Min (dNm)	1.27	1.61	2.55	1.39	1.98	2.2
Torque Max (dNm)	20.52	22.8	23.07	18.88	13.17	13.9
Δ Torque (dNm)	19.25	21.19	20.52	16.49	11.85	12.0
Optimum cure time,t_{90}, (minute)	12.5	9.75	9.45	12.9	12.75	12.8
Scorch time,ts_2 (minute)	2.2	2.2	2.6	3.9	4.0	4.1

7.4 Mechanical Properties

The fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch/polybutadiene rubber vulcanizates showed a higher tensile strength, higher modulus, higher hardness and higher tear strength along with lower heat build-up and abrasion loss compared to the dry natural rubber/poly butadiene rubber based compounds (control). In all the blends as the proportion of polybutadiene increased there was a decrease in modulus, tear strength and tensile strength along with decrease in heat build- up. The abrasion resistance improved as the polybutadiene content increased (Table7.4). These are attributed to the unique micro structure of cis-1, 4-polybutadiene rubber like molecular weight and branching. It is well known that addition of small quantity of cis-1, 4- polybutadiene rubber improves the abrasion resistance of the compound due to the inherent high elasticity on account of the very low glass transition temperature which is lower than that of natural rubber.

The filler dispersion characteristics are presented in Figure 7.1 and Table 7.5. Comparatively better dispersion and lower aggregation is shown by fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch /polybutadiene rubber vulcanizates and dry natural rubber/poly butadiene rubber based vulcanizates (control).

Filler dispersion characteristics do not show much variation on blending with polybutadiene rubber in both 80/20 and 60/40 proportions for the vulcanizates based on masterbatches. It is inferred that the filler distribution is not adversely affected on blending though carbon black has a tendency to migrate to polybutadine rubber phase and silica to natural rubber phase [17]. During the masterbatch preparation both silica and carbon black are incorporated in the natural rubber phase. So migration to butadiene phase on mixing with polybutadiene rubber is expected to be low and the molecular weight also does not reduce as in the case of the control dry rubber as larger portion of the fillers is incorporated in the latex stage that does not involve high shear rate. The better mechanical properties in the case of the fresh natural rubber latex-carbon black/silica (25/25) dried masterbatch/polybutadiene rubber vulcanizates is attributed to better filler dispersion and higher level of vulcanization.

Table7.4. Mechanical properties of the fresh natural rubber based carbon black-silica (25/25) dried masterbatch/polybutadiene rubber vulcanizates and dry natural rubber/ polybutadiene rubber based vulcanizates (control)

Fresh natural rubber based carbon black-silica (25/25) dried masterbatch: polybutadiene	100:0 (MB100)	80:20 (MB 80)	60:40 (MB-60)	-	-	-
Dry natural rubber : polybutadiene ruber (control)	-	-	-	100:0 (DB 100)	80:20 (DB 80)	60:40 (DB 60)
Modulus at 300% (MPa)	10.8	8.0	7.8	7.2	5.3	5.2
Tensile strength (MPa)	27.3	28	24.7	24.5	20.0	18.8
Elongation at break (%)	540	625	680	620	700	660
Tear strength (kN/m)	100	94	77	88	68	60
Hardness (Shore A)	66	69	68	58	60	65
Heat Build-up, ΔT (^{0}C)	16	15	14	21	18	16
Abrasion loss (mm^3)	107	93	88	143	99	95

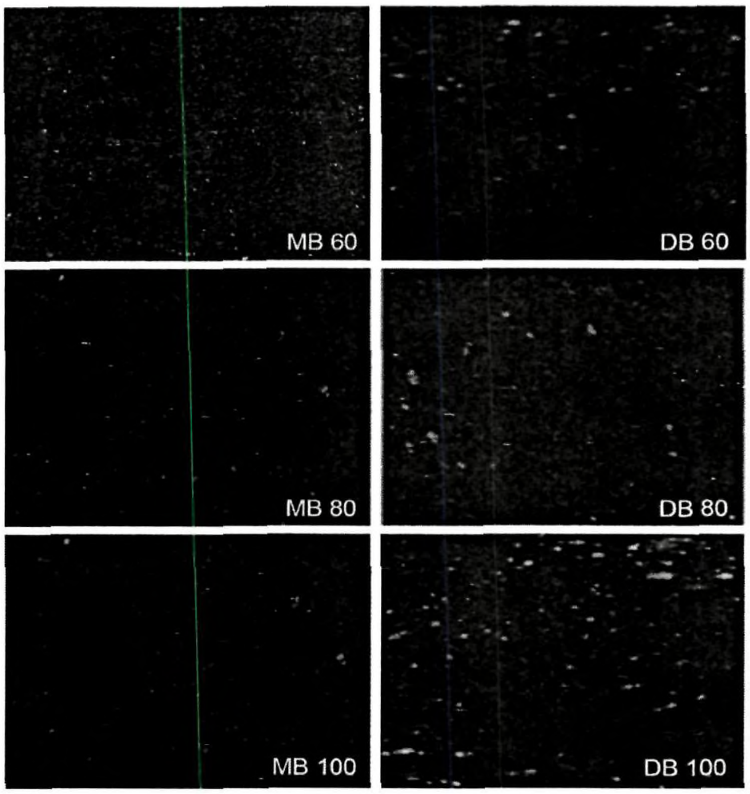

Figure 7.1 Disper grader images showing the dispersion of fillers in natural rubber latex carbon black/silica (25/25) dried masterbatches/ polybutadiene blend vulcanizates and dry rubber/polybutadiene blend vulcanizates.

Table7.5 Results of dispersion ratings of fresh natural rubber based carbon black- silica (25/25) dried masterbatch/polybutadiene rubber vulcanizates and dry natural rubber/ polybutadiene rubber based vulcanizates (control).

Sample name	Carbon black/silica dispersion(X)	Carbon black/silica agglomerate dispersion (Y)
Fresh natural rubber based carbon black- silica (25/25) dried masterbatch: polybutadiene vulcanzate (MB 80)	8.9	9.3
Fresh natural rubber based carbon black- silica (25/25) dried masterbatch: polybutadiene vulcanzate (MB 60)	9.0	9.5
Fresh natural rubber based carbon black- silica (25/25) dried masterbatch: polybutadiene vulcanzate (MB 100)	8.8	9.3
Dry natural rubber: polybutadiene rubber vulcanzate (DB 80)	7.2	8.4
Dry natural rubber: polybutadiene rubber vulcanzate (DB 60)	7.5	8.5
Dry natural rubber: polybutadiene rubber vulcanzate (DB 100)	7.0	7.8

7.5 Dynamic mechanical properties

The filler–filler interactions can be evaluated from the strain dependence of elastic modulus. Generally for filled vulcanizates the elastic modulus decreases with strain amplitude and this phenomenon is known as Payne effect [21, 22]. The plots of storage modulus versus strain amplitude for the blends prepared from latex masterbatches is shown in Figure 7.2. It is observed that Payne effect is not increasing on blending. Though there is a decrease in the modulus, the Payne effect also decreases as the proportion of polybutadiene in the blend increase. This shows that the filler-filler interaction is reduced on blending with polybutadiene. This result is in conformity with the good tensile properties obtained for fresh natural rubber latex - carbon black/silica (25/25) dried masterbatch/polybutadiene rubber vulcanizates compared to the latex - carbon black/silica (25/25) dried masterbatch.

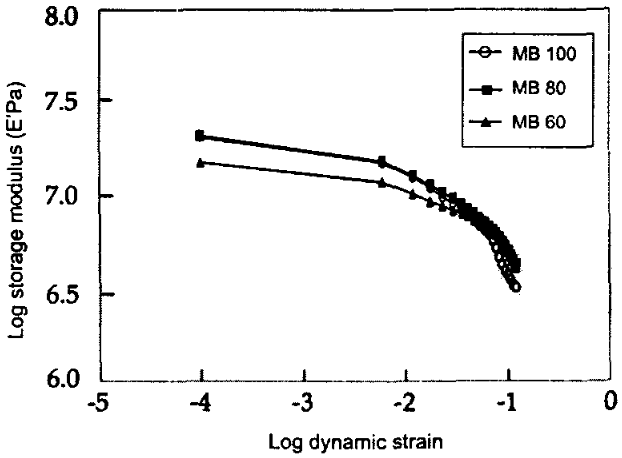

Figure 7.2 Strain dependence of storage modulus of fresh natural rubber based carbon black- silica (25/25) dried masterbatch:polybutadiene rubber vulcanizates, 100:0 (MB 100), 80:20 (MB 80), 60 :40 (MB60).

Damping characteristics from -80 to +100 ^{0}C for the fresh natural rubber based carbon black- silica (25/25) dried masterbatch, fresh natural rubber based carbon black- silica (25/25) dried masterbatch:polybutadiene rubber vulcanizates and, control vulcanizates are given in Figure7.3 and 7.4. For the masterbatches there is a lowering of tan delta peak height compared to the control showing that there is better polymer filler interaction in the masterbatch-vulcanizates as compare to the control vulcanizates. Fresh natural rubber based carbon black- silica (25/25) dried masterbatch: polybutadiene (MB 80) shows a lower tan delta at 60^{0}C compared to the control. These observations reveal that there is higher chain flexibility for the masterbatch vulcanizates. This is possibly due to factors like preserving the higher molecular weight of rubber in the latex in the dried rubber, better filler dispersion and more uniform mixing of the two rubbers [23]. Higher chain flexibility is known to correlate with higher abrasion resistance and lower heat build-up characteristics [23]. Ideal filler for tyre tread compounds are those which possess high polymer–filler and low filler–filler interactions. The former ensures higher abrasion resistance and the latter is necessary for lower rolling resistance or lower tan delta [23]. It is well known that the tan delta at 60 ^{0}C is a measure of the degree of rolling resistance [24]. It is clearly inferred that there is lower rolling resistance for the masterbatch vulcanizates compared to the dry rubber (control) vulcanizates

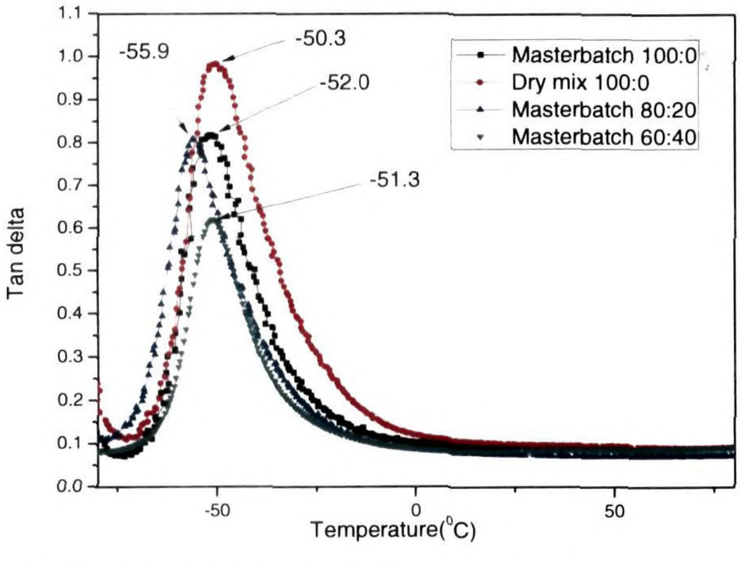

Figure 7.3 Plots of tan delta versus temperature of fresh natural rubber based carbon black-silica (25/25) dried masterbatch: polybutadiene blend vulcanizates,100:0 (MB 100), 80:20 (MB 80), 60:40 (MB 60) and dry natural rubber: polybutadiene blend vulcanizates 100:0 (DM 100).

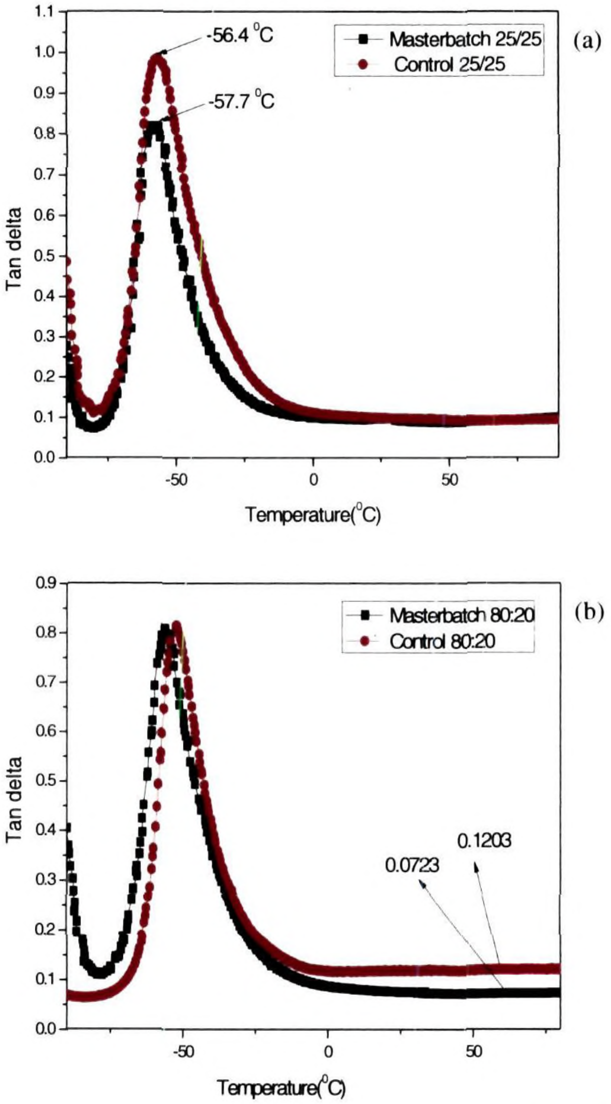

Figure 7.4 (a) Plots of tan delta versus temperature for (a) fresh natural rubber based carbon black-silica dried masterbatch vulcanizate (MB 100) and dry natural rubber vulcanizate (DB100), 7.4 (b) Plots of tan delta versus temperature for fresh natural rubber based carbon black-silica (25/25) dried masterbatch: polybutadiene blend vulcanizate 80:20 (MB 80) and dry natural rubber: polybutadiene vulcanzate (DB 80).

7.6 Thermogravimetric analysis

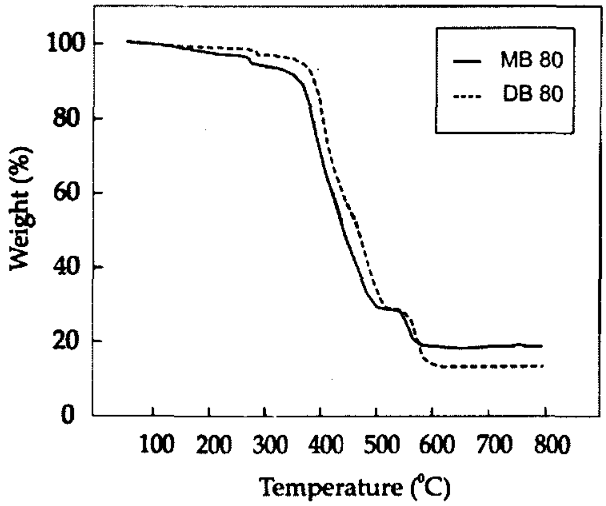

Figure 7.5 Thermograms of fresh natural rubber based carbon black- silica (25/25) dried masterbatch : polybutadiene blend vulcanizate 80:20 (MB80) and dry natural rubber: polybutadiene blend vulcanizate 80:20 (DM 80).

Table 7.6 Data from thermogravimetric analyzer for the vulcanizates prepared from dried fresh natural rubber latex based carbon black-silica masterbatch/ polybutadiene blend and dry natural rubber / polybutadiene based vulcanizate

Sample	Temperature of onset of degradation (°C)	Temperature at which the rate of weight loss is maximum (°C)	Residual weight (%)
Fresh natural rubber based carbon black-silica (25/25) masterbatch: polybutadiene 80:20 vulcanizate (MB 80)	315.15	401.34	23.3
Dry natural rubber: polybutadiene 80:20 vulcanizate (DB 80)	439.4	479.38	15.5

The thermograms of the vulcanizates prepared from dried fresh natural rubber latex based carbon black-silica masterbatch/polybutadiene blend 80:20 (MB 80) and dry natural rubber / polybutadiene 80:20 (DB 80) based vulcanizates are given in Figure 7.5 and the data in Table 7.6 It is inferred that thermal stability of carbon black /silica polybutdiene rubber blend masterbatch and the dry rubber blend vulcanizates were almost same.

7.7 Conclusions

Latex-filler masterbatches can be prepared by latex stage incorporation of filler and using a modified coagulation process. The masterbatches offer precise advantages in blends with polybutadiene rubber. The latex - filler masterbatche based blends show very good polymer-filler interaction, lower filler-filler interaction and high level of vulcanization. The fresh natural rubber latex based carbon black-silica masterbatch/polybutadiene blend vulcanizates show superior mechanical and dynamic properties as compared to the equivalent compound vulcanizates prepared from the dry natural rubber-filler (conventional dry mix) / polybutadiene blends.

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Chapter 8

CONCLUSIONS

A novel route is attempted for preparing latex stage masterbatches using different types of natural rubber latex with HAF (N330), fluffy carbon black (carbon black powder before pelletisation), silica and nanocly either alone or in combination. The effect of masterbatching on natural rubber/polybutadiene rubber (NR/BR) blend compounds prepared by mixing the dried masterbatches with the required quantity of BR and other compounding ingredients was also investigated.

Mixing of carbon black, silica and nanoclay with dry rubber is a highly energy consuming process and is accompanied by pollution of the surrounding air due to flying of the particles to the atmosphere. Silica and nanoclay is extremely difficult to disperse in dry natural rubber using a two roll mixing mill. The concept utilised in the present work to minimize air pollution and minimize energy consumption results in enhancement in filler dispersion in the vulcanizates and enhanced properties.

Fresh natural rubber (NR) latex coagulates immediately by sensitisation with fatty acid soaps. Though the basic objective of the new process was to shorten the coagulation time, the use of surfactants plays a major role in improving cure characteristics and mechanical properties. Shortening of coagulation time is advantageous in the latex stage incorporation of fillers. The conventional slow coagulation leads to filler loss whereas the soap sensitised quick coagulation ensures homogeneous dispersion of fillers with minimum loss. This benefit cannot be achieved by addition of appropriate quantity of higher fatty acids during the dry compounding of the rubber. The coagulation of natural rubber latex in presence of acids is accelerated by addition of small quantities of an anionic surfactant. A proportion of the surfactants added to latex gets adsorbed on rubber particles and are retained in rubber after coagulation. The surfactants retained on rubber activate the vulcanization and enhance the filler dispersion thereby improving the mechanical and solvent ageing characteristics of recovered rubber. The carbon black filled rubber vulcanizates based on natural rubber obtained by modified coagulation show significantly higher abrasion resistance mainly due to the lubricating action of the fatty acids formed in rubber.

Carbon black masterbatches prepared with different forms of natural rubber latices like fresh latex, preserved filed latex (PFL) and concentrated latex with fluffy carbon black show higher rheometric torque. The cure time observed for the masterbatches was comparable to the conventional dry rubber compound. As compared to the control dry rubber vulcanizate, the masterbatch vulcanizates made from fresh latex show higher modulus, tensile strength, hardness, and tear strength. The masterbatch vulcanizates prepared from fresh latex show lower compression set, heat build-up and abrasion resistance. The ageing resistance too was superior for vulcanizates prepared from the latex based masterbatches. This is attributed to a uniform dispersion of fluffy carbon black in rubber in the latex based masterbatches.

For the silica filled compounds a lower minimum torque and lower scorch time is recorded for the latex based masterbatches as compared to the mill mixed dry rubber compounds. For same filler loadings, the master batch based mixes recorded a higher rheometric torque and lower cure time as compared to the compounds based on dry rubber. Similar results were observed in the case of the compounds containing higher dosages of the fillers (50phr and 60phr) also. During the preparation of masterbatches, the filler-latex mixture co- coagulates along with a portion of the surfactant that apparently got converted into the corresponding fatty acid. This helps in better vulcanization characteristics of rubber as fatty acids are activators of vulcanization.

In the case of these latex based vulcanizates too the mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness were superior as compared to the conventional dry rubber vulcanizates. The heat build–up values were considerably low for the latex filler masterbatch based vulcanizates. Slightly lower tan delta values were also observed for the latex filler masterbatches. The silica filled mixes showed comparatively very good mechanical properties in the absence of any coupling agent. The filler masterbatches prepared by this method shows a higher level of vulcanization along with better filler dispersion compared to conventionally prepared mixes. Due to this, a comparatively low tan delta value at 60 ^{0}C that correlates to a lower rolling resistance is observed for the masterbatch vulcanizates.

A process for production of carbon black/silica/nanoclay ternary filler masterbatches from fresh natural rubber (NR) latex was standardized.

The masterbatch compounds containing 25/25 and 30/30 carbon black/silica fillers recorded higher rheometric torque compared to the corresponding dry rubber compounds. The masterbatch compounds containing 25/25/3, 25/25/5, 25/25/10 carbon black/silica/nanoclay recorded higher rheometric torque compared to dry rubber compounds that contain only carbon black/silica.

The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness increased with proportion of nanoclay in the masterbatch vulcanizates up to 5 phr and with further amount the change was only marginal. Lower tan delta values were observed for all the masterbatch vulcanizates containing nanoclay in the ranges 3-10 phr compared to the dry rubber vulcanizate containing 25/25 carbon black/silica. The improvement in mechanical properties and dynamic properties shown by the masterbatch vulcanizates over the conventional dry rubber vulcanizates was attributed to factors related to filler dispersion as evidenced from the data of Dispersion Analyzer images and X-ray diffractograms, and higher level of vulcanization. The vulcanizate properties of the nanoclay containing masterbatches prepared by latex stage mixing show excellent improvement in abrasion resistance, lowering of heat build-up and lower tan delta at 60 ^{0}C compared to a conventional dry rubber. These compounds can be used to manufacture tyre treads with better fuel efficiency and improved wear resistance.

Fresh natural rubber latex - carbon black/silica masterbatches were prepared. The dried masterbatches and polybutadiene rubber(BR) was separately masticated and mixed with the required quantity of carbon black and silica (based on the quantity of polybutadiene in the blend) on a mixing mill so as to have 25 phr each of carbon black and silica in 100:0, 80:20

and 60:40 natural rubber/ polybutadiene blends. The compounds were vulcanized and characterized for mechanical and dynamic properties.

The fresh natural rubber latex based carbon black-silica masterbatch and polybutadiene blend compound vulcanizates shows better mechanical properties like tensile strength, modulus, tear strength, abrasion resistance, hardness and lower heat build-up compared to the blends prepared using conventional dry rubber vulcanizates. As the proportion of BR in the blend increased abrasion loss reduced while hardness and heat build-up increased due to the unique micro structure of cis-1, 4-polybutadiene rubber.

There was reduced filler-filler interaction on blending natural rubber with polybutadiene rubber for the blends based on the masterbatch vulcanizates. Filler dispersion data indicated that dispersion was not adversely affected on blending. Plots of tan δ versus temperature show a lowering of tan δ peak height in the case of the materbatch vulcanizates indicating better polymer-filler interaction compared to the dry rubber vulcanizates. The tan δ value at 60 °C show lower and hence the rolling resistance was lower for the 80/20 NR/BR blend prepared with the masterbatch vulcanizates.

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Abbreviations and Symbols

Å - Angstrom
λ - Wavelength
δ - Phase angle
α - Extension ratio
γ - Shear rate
ε - Strain
η - Viscosity
$\acute{\eta}$ - Coefficient of viscosity
χ - Interaction parameter
τ - Shear stress
σ - Stress
τ_0 - Yield stress
k - Viscosity index
α - Extension ratio
d - Interlamellar spacing
ν - Crosslink density
n - Pseudoplastic index
F - Weight fraction of the filler
q - Swelling index
σ - Surface charge density
$\acute{\eta}$ - Coefficient of viscosity
g - Acceleration due to gravity (m/s^2)
V - Velocity of creaming (m/s)
r - Effective radius of the particle (cm)
V_r - Volume fraction of rubber
ρ_r - Specific gravity of rubber (0.92)
ρ_s - Specific gravity of solvent (0.86)
δ_p - Solubility parameter of polymer
η_o - Zero shear viscosity
Φ_1 - Volume fraction of component 1
Φ_2 - Volume fraction of component 2

Fg	Force due to gravity
F_d	Force due to viscous drag
F_b	Force due to buoyancy
nm	Nanometer
μm	Micrometer
ADS	Air dried sheet
AFM	Atomic force microscopy
ASTM	American Society for Testing and Materials
BET	Brunauer, Emmet and Teller
BIS	Bureau of Indian Standards
BR	Poly butadiene rubber
CBS	N-Cyclohexyl 2 – benzothiazole sulphonamide
CR	Polychloroprene rubber
CRI	Cure rate index
CTAB	Cetyl trimethyl ammonium bromide
CV	Constant viscosity
DMA	Dynamic mechanical analysis
DRC	Dry rubber content
DPNR	Dproteinized natural rubber
DBP	Dibutyl phthalate
DEG	Diethylene glycol
EBC	Estate brown crepe
ENR	Epoxidised natural rubber
EPDM	Ethylene propylene diene rubber
HAF	High abrasion furnace
IIR	Butyl rubber
ISNR	Indian standard natural rubber
MBTS	Mercaptobenzthiazole
MMT	Montmorillonite
MTMO	Mercapto propyl trimethoxy silane
NR	Natural rubber
OCT	Optimum cure time
Po	Initial plasticity

Phr	-	Parts per hundered rubber
PLC	-	Pale latex crepe
PNP	-	Paranitrophenol
PP	-	Polypropylene
ppm	-	Parts per million
PRI	-	Plasticity retention index
RMA	-	Rubber Manufacturers' Association
RSS	-	Rribbed smoked sheet
SBR	-	Styrene-butadiene rubber
SEM	-	Scanning electron micrograph
SIR,	-	Standard Indonesian Rubber
SMR	-	Standard Malaysian Rubber
STR	-	Standard Thai Rubber
TDQ	-	2, 2, 4-trimethyl-1, 2-dihydroquinoline
TESPD	-	Bis (triethoxy silylpropyl) disulphide),
TESPM	-	Bis (triethoxy silylpropyl)
TESPT	-	Bis (triethoxy silylpropyl) tetrasulphide
TGA	-	Thermogravimetric analysis
TPNR	-	Thermoplastic natural rubber
TSR	-	Technically specified rubber
XRD	-	X- ray diffraction
ZDC	-	Zinc diethyl dithiocarbamate
ZnO	-	Zinc oxide

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List of Publications

International Journals

[1] **Sasidharan K.K**, Rosamma Alex and Thomas Kurian, HAF/silica/ nanoclay "ternary" masterbatch andHAF/silica binary masterbatch from fresh natural rubber latex, ***Rubber Chemistry and Technology*** (in press).

[2] Rosamma Alex, **Sasidharan K.K**, Thomas Kurian and Arup K Chandra, Carbon black masterbatch from fresh natural rubber latex, ***Plastics, Rubber Composites,*** Vol. 40, No. 8: 420 - 424 (2011).

[3] **Sasidharan K.K,** Rosamma Alex, Blends of polybutadiene with natural rubber latex masterbatch, ***Rubber Science,*** 25 (2): 297-306 (2012).

[4] **Sasidharan K.K**, Rosamma Alex and Thomas Kurian, Carbon black masterbatch using different forms of natural rubber latex, ***Rubber Science*** 26 (1): 158-165 (2013).

[5] Rosamma Alex and **Sasidharan K.K**, Mechanical properties of rubber obtained by surfactant sensitised coagulation of fresh natural rubber latex, ***Rubber Science*** 26 (2): 323-333(2013)

International/ National Conferences

[1] **Sasidharan K.K**, Rosamma Alex and Thomas Kurian, Carbon black masterbatch from fresh natural rubber latex, ***International Conference on Advances in Polymer Technology***, Kochi, (September, 25-27 (2008).

[2] **Sasidharan K.K**, Rosamma Alex , Jacob K Varkey and Benny George, A method for producing carbon black/silica masterbatches, ***International Rubber Research and Development Board (IRRDB) - International Rubber Conference (IRC)***, 14-17, December 2011 Chiangmai, Thailand (2011).

[3] **Sasidharan K.K**, Rosamma Alex , Arup K Chandra, Thomas Kurian and James Jacob, Carbon black / silica masterbatch from fresh natural rubber latex, 21st***Rubber Conference of the Indian Rubber Manufacturers Research Association (IRMRA,*** Govt. of India affiliated) held at Imperial Palace, Mumbai, during 20-21 January, 2012, ***Best Technical Paper Award (2012).***

[4] **Sasidharan K.K**, Rosamma Alex and Thomas Kurian A Method for producing carbon black/silica/ nanoclay masterbatches from fresh natural rubber latexat, ***International Rubber Conference (IRC),***29 October to 02 November 2012, Kovalam, Kerala, India (2012).

Patents

[1] R. Alex, **Sasidharan K.K** and James Jacob ***U.S. Patent Application Publication No. US 2013/0079444 AI.*** Pub. Date: Mar. 28, 2013. Novel process for the preparation of carbon black/silica/nanoclay masterbatch from fresh natural rubber latex.

[2] R. Alex, **Sasidharan KK** and James Jacob, ***Indian Patent Application No.2564/ CHE/2011,*** Novel Process for the preparation of carbon black/silica/nanoclay masterbatch from fresh natural rubber latex final deposited the specification and abstract dated 26/07/2011.

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Curriculum Vitae

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Religion	:	Hindu.
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Educational qualifications

Qualifications	**Board/University**	**Year**
M. Tech (Polymer Technology)	Cochin University of Science and Technology, Kochi	2002
B. Tech (Polymer Science & Rubber Technology)	Cochin University of Science and Technology .Kochi	1999
Diploma in Polymer Technology	State Board of Technical Education, Kerala Govt. Polytechnic College, Kottayam	1981
SSLC	Board of Public Exams, Kerala	1975

Professional experience:

Post held	Institution	Period	
		From	**To**
Chemist (R&D)	Carbon and Chemicals India Ltd, Kochi SRCC, Texas Collaborated (M/s. Philips Carbon Black Ltd)	01-03-1983	16-09-1986
Instructor, Polymer Technology	Govt. Polytechnic College, Kottayam, Kerala, India	22-09-1986	24-09-1997
Asst.Rubber Technologist	Technical consultancy Division, Rubber Research Institute of India, Kottayam, Kerala, Indian Rubber Board	25-09-1997	Continuing

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