

**IMPROVEMENT OF QUALITY AND STORAGE STABILITY
OF PRE-VULCANIZED NATURAL RUBBER LATEX
CONCENTRATES**

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**Affectionately
Dedicated**

To

My Parents & Teachers

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ABSTRACT

State of vulcanization is quite important in pre-vulcanized lattices. But excess compounding ingredients which may retain after pre-vulcanization cause further formation of primary linkages between the latex particles and such lattices would become unsuitable for product manufacture. Hence a safer and an advanced technology is essential to prepare pre-vulcanized latex with long term storage stability. This study describes developments made to prevent over vulcanization and thereby improve storage stability of pre-vulcanized latex.

Three different processing methodologies were used in the preparation of pre-vulcanized lattices with a view to achieve long term storage stability. Latex quality parameters and tensile properties of the films were evaluated. The results revealed that one of the method, i.e. technique 1 which contain 40% of field latex and 60% of pre-vulcanized latex yield the best stability compared to the others and this technique exhibited good tensile strength in comparison to the other methods.

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LIST OF ABBREVIATIONS

Natural Rubber	NR
Mechanical Stability Time	MST
Volatile Fatty Acid	VFA
Total Solid Content	TSC
Dry Rubber Content	DRC
Zinc diethyldithiocarbamate	ZDEC
Tetraramethylthiuramdisulphide	TMTD
Diammoniumhydrogenphosphate	DAHP

CHAPTER 1

INTRODUCTION

1.1 Background

Polymer lattices can be pre-vulcanized in the latex stage itself. Pre-vulcanization of natural rubber latex or other lattices is the cross-linking of rubber particles in the latex stage without prior coagulation. The possibility of vulcanizing the dispersed phase of latex without affecting the colloidal stability was first investigated by Schidrowitz (Schidrowitz and Goldbrough 1915). Pre-vulcanized latex can be widely used for the manufacture of several latex products. The lattices are usually pre-vulcanized by heating with dispersions of sulphur, accelerator such as zinc diethyldithiocarbamate to 50°C – 80°C. The reaction proceeds much more rapidly than the vulcanization of dry rubber compounds containing the vulcanizing ingredients at the same temperature (Balow 1988). Properties of pre-vulcanized and post vulcanized natural rubber (NR) latex films have been studied in the past by Porter, 1989 (Ranimol et.al. 2006).

Sulphur pre-vulcanization of the compounded lattices and their blends have been carried out at 70°C for 2 hours using a water bath. Different theories have been proposed to explain the mechanism of pre-vulcanization (Blackley 1966). Some researchers have reported that the reaction takes place as a result of direct contact between particles of reactants and rubber. Few scientists reported that the reactants must dissolve in the aqueous phase before diffusing into the rubber particles. Porter and co-workers reported the chemistry behind the pre-vulcanization of latex. They suggested that the pre-vulcanization takes place as a result of the dissolution of accelerator and sulphur in the aqueous serum of latex followed by migration into the rubber phase. It then diffuses into the rubber phase and cross-links it. There are two possibilities for the pre-vulcanization of latex. One possibility is the diffusion of vulcanizing ingredients to the surface followed by cross-linking. The other possibility is that cross-linking takes place faster than diffusion. Homogenously cross-linked rubber particles are formed in the latter case, whilst in the former only the surface gets cross-linked. If the latex is homogenously cross-linked, the particles will coalesce well and form a film with good ultimate properties. According to Hu et al., the rate of cross-linking is much greater than the rate of diffusion (Elliot and Tidd 1975).

Pre-vulcanized latex has the attraction that the product made out of it does not require vulcanization. Drying of the latex article made from it is sufficient to achieve a vulcanized product with physical properties that are satisfactory for many purposes. However, due to the residual vulcanizing ingredients and other factors such as temperature, poor stability results during storage (Ranimol et.al. 2006).

Hence a safer and advanced technology is essential to prepare pre-vulcanized latex with long term storage stability. Storage stability means preventing over-vulcanization of the latex during storage. Therefore, excess vulcanizing ingredients can be minimized by centrifuging the pre-vulcanized latex. The objective of the research is to develop an advanced technology to prevent over vulcanization and thereby improve the quality and storage stability of pre-vulcanized latex (Elliot and Tidd 1975).

1.2. Objectives

1.2.1 Overall Objective

Improvement of quality and storage stability of pre-vulcanized natural rubber latex concentrates

1.2.2 Specific Objectives

- To determine quality parameters
- To determine tensile properties

CHAPTER 2

REVIEW OF LITERATURE

2.1 Natural Rubber Tree

2.1.1 History of natural rubber tree

The Para rubber tree initially grew only in the Amazon Rainforest. Increasing demand and the discovery of the vulcanization procedure in 1839 led to the rubber boom in that region, enriching the cities of Belem and Manaus. The name of the tree derives from Para, the second largest Brazilian state, whose capital is Belem.

There had been an attempt made, in 1873, to grow rubber outside Brazil. After some effort, twelve seedlings were germinated at the Royal Botanic Gardens, Kew. These were sent to India for cultivation, but died. A second attempt was then made, some 70,000 seeds being sent to Kew in 1875. About 4% of these germinated, and in 1876 about 2000 seedlings were sent, in Wardian cases, to Ceylon, and 22 sent to the Botanic Gardens in Singapore. Once established outside its native country, rubber was extensively propagated in the British colonies. Rubber trees were brought to the botanical gardens at Buitenzorg, Java in 1883. By 1898, a rubber plantation had been established in Malaya, and today most rubber tree plantations are in South and Southeast Asia and some also in tropical West Africa.

In India commercial cultivation of natural rubber was introduced by the British Planters, although the experimental efforts to grow rubber on a commercial scale in India were initiated as early as 1873 at the Botanical Gardens, Kolkata. The first commercial *Hevea* plantations in India were established at Thattekadu in Kerala in 1902 (<http://en.wikipedia.org/wiki/Rubber>).

2.1.2 Scientific classification and description

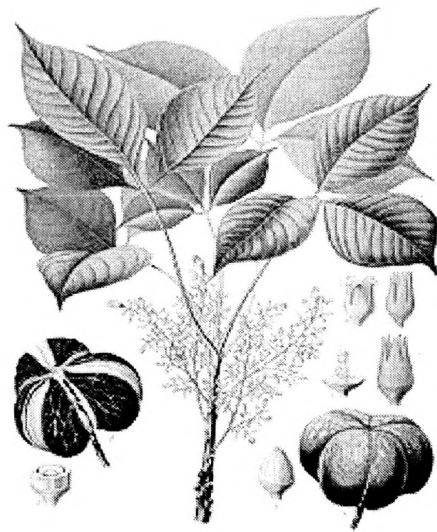


Figure 2.1 Parts of rubber tree (<http://en.wikipedia.org/wiki/Rubber>)

Kingdom: Plantae

Division: Magnoliophyta

Class: Magnoliopsida

Order: Malpighiales

Family: Euphorbiaceae

Subfamily: Crotonoideae

Tribe: Micrandreae

Subtribe: Heveinae

Genus: *Hevea*

Species: *Hevea brasiliensis*

The “Para rubber tree” (*Hevea brasiliensis*), often simply called rubber tree, is a tree belonging to the family Euphorbiaceae and the most economically important member of the genus *Hevea*. It is of major economic importance because its sap-like extract (known as latex) can be collected and is the primary source of natural rubber.

In the wild, the tree can reach a height of up to 144ft (44m). The white or yellow latex occurs in latex vessels in the bark, mostly outside the phloem. These vessels spiral up the tree in a right-handed helix which forms an angle of about 30 degrees with the horizontal. It Can grow as high as 45 ft. In plantations, the trees are kept smaller, up to 78ft (24m) tall, so as to use most of the available carbon dioxide for latex production (<http://en.wikipedia.org/wiki/Rubber>).

2.1.3 Cultivation of natural rubber tree

Rubber latex is extracted from Rubber trees. The economic life period of rubber trees in plantations is around 32 years and up to 7 years of immature phase and about 25 years of productive phase.

The soil requirement of the plant is generally well-drained weathered soil consisting of laterite, lateritic types, sedimentary types, nonlateritic red or alluvial soils.

The climatic conditions for optimum growth of Rubber tree consist of, rainfall of around 2500mm evenly distributed without any marked dry season and with at least 100 rainy days per annum, temperature range of about 20°C to 34°C with a monthly mean of 25°C to 28°C, high atmospheric humidity of around 80%, bright sunshine amounting to about 2000 hours per annum at the rate of 6 hours per day throughout the year and absence of strong winds.

Many high-yielding clones have been developed for commercial planting. These clones yield more than 2,000 kilograms of dry Rubber per hectare per annum, when grown under ideal conditions (<http://www.irrdb.com/IRRDB/NaturalRubber/Default.htm>).

2.2 Harvest of Natural rubber latex

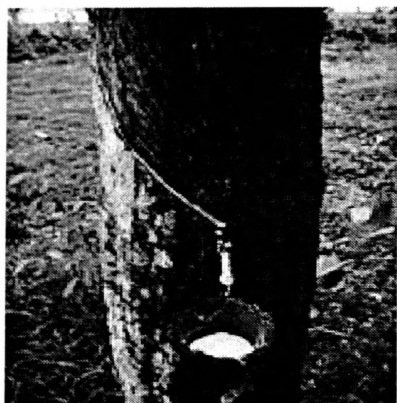


Figure 2.2 Latex being collected from an incised rubber tree

Once the trees are 5-6 years old, the harvest can begin: incisions are made orthogonal to the latex vessels, just deep enough to tap the vessels without harming the trees growth, and the sap is collected in small buckets. This process is known as rubber tapping. Older trees yield more latex (<http://en.wikipedia.org/wiki/Rubber>).

2.2.1 Tapping of latex

In places like Kerala, where coconuts are in abundance, the shell of half a coconut is used as the collection container for the latex but glazed pottery or aluminium cups are more common elsewhere. The cups are supported by a wire that encircles the tree. This wire incorporates a spring so that it can stretch as the tree grows. The latex is led into the cup by a galvanised "spout" that has been knocked into the bark. Tapping normally takes place early in the morning when the internal pressure of the tree is highest. A good tapper can tap a tree every 20 seconds on a standard half-spiral system and a common daily "task" size is between 450 and 650 trees. Trees are usually tapped alternate or third daily although there are many variations in timing, length and number of cuts. The latex, which contains 25 - 40% dry rubber, is in the bark so the tapper must avoid cutting right through to the wood or the growing cambial layer will be damaged and the renewing bark will be badly deformed making later tapping difficult. It is usually tap a panel at least twice, sometimes three times, during the trees life. The economic life of the tree depends on how well the tapping is carried out as the critical factor is bark consumption. A standard for alternate daily tapping is 25cm

(vertical) bark consumption per annum. The latex tubes in the bark ascend in a spiral to the right. For this reason, tapping cuts usually ascend to the left to cut more tubes (<http://www.irrdb.com/IRRDB/NaturalRubber/Default.htm>).

2.2.2 Collection of latex

The trees will drip latex for about four hours, stopping as latex coagulates naturally on the tapping cut thus blocking the latex tubes in the bark. Tappers usually start collecting the latex at about midday. Some trees will continue to drip after the collection and this leads to a small amount of cup lump which is collected at the next tapping. The latex that coagulates on the cut is also collected as tree lace. Tree lace and cup lump together account for 10.- 20% of the dry rubber produced.

The latex can be collected in its liquid state. It is sometimes necessary to add a few drops of ammonia solution to the cup, or to the transport tank, to prevent pre-coagulation of the latex before it reaches the factory. It can also be left in the cup to coagulate naturally into cup lump for collection before the next tapping, although this will produce a lower grade of product.

Latex is generally processed into either latex concentrate for manufacture of dipped goods or it can be coagulated under controlled, clean conditions using formic acid. The coagulated latex can then be processed into the higher grade technically specified block rubbers (<http://en.wikipedia.org/wiki/Rubber>).

2.2.3 Properties of natural rubber latex

Rubber latex is term used to cover a range of colloids having macro molecular substances the dispersed phase and water as the dispersion medium. Most important latex used in rubber industry is natural rubber (NR) latex. This is an aqueous dispersion of *cis*-1, 4 polyisoprene in water containing dissolved serum substances.

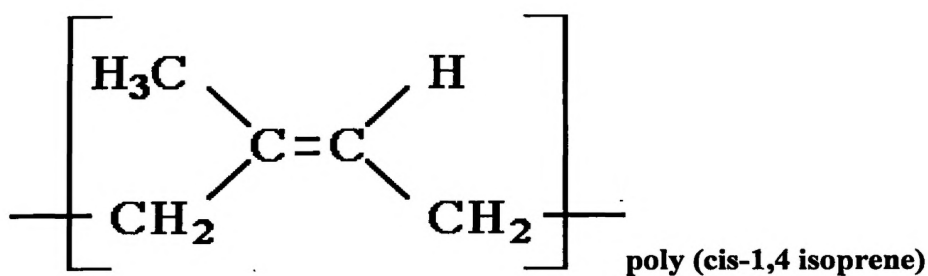


Figure 2.3 Repeating unit of rubber chain (<http://en.wikipedia.org/wiki/Rubber>)

2.2.4 Composition of NR latex

The composition of NR latex varies depending on many factors such as clone, season, soil condition, tapping method and tapping frequency, the age of the tree, etc.

Table 2.1 Composition of NR latex (Blow 1998)

Component	% by weight of latex
Dry rubber	30-35
Pertinacious substances	1-1.5
Lipids	1-2.5
sugar	1
Inorganic ions	1
water	60-65

It is believed that a rubber particle in fresh NR latex comprises a sphere of mainly rubber hydrocarbon, surrounded by two layers, the inner of phospholipids and the outer of proteins (<http://en.wikipedia.org/wiki/Rubber>).

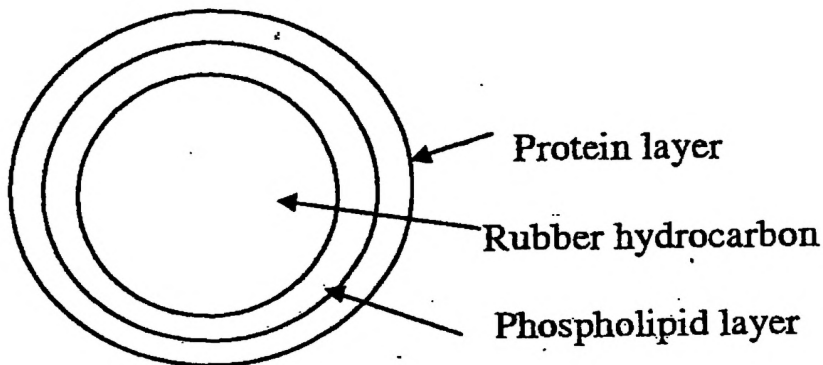
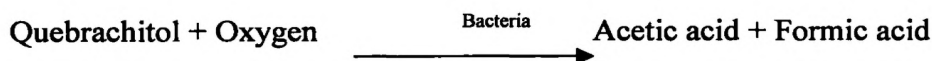


Figure 2.4 The structure of a natural rubber particle (<http://en.wikipedia.org/wiki/Rubber>)

2.2.5 Natural destabilization of NR latex

It is a well-known fact that NR latex undergoes pre-coagulation, due to the formation of formic and acetic acids, resulting from the microbial action on the sugars, such as quebrachitol, present in NR latex.



These acids are capable of coagulating the latex and this process is referred to as pre-coagulation of latex. In addition to this process, bacteria can act on proteins and produce fatty acids, which thereafter partially replace the protein layer. These fatty acids can react with Mg^{2+} ions available in the medium and form insoluble Magnesium soaps, which facilitate coagulation of latex.

Therefore, prevention of pre-coagulation is vital in the NR latex industry and preservatives are used for this purpose (Akiba and Hashim, 1997).

2.2.6 Some latex properties

The properties of polymer lattices are of interested for there separate kinds of reasons. First they may be investigated in a sprit of enquiry, the motive being to gain thereby a better understanding of the physical and chemical nature of the latex. Secondly, certain properties may be evaluated because it is thought that they can be used to assess the fitness of latex for a particular application. Thirdly, certain properties may be used for the purpose of quality control. In this latter category it may well be that some of the tests selected may appear to have little relevance to any end-use to which the latex is put. The justification for carrying out such procedure is that, over the years, the results have been found to be useful indices of quality and to correlate well with subsequent behavior (Barlow 1988).

2.2.6.1 Mechanical stability time

The mechanical stability of latex is defined as its resistance to destabilization by mechanical agitation on shear forces. During concentration, pumping to the containers and transportation and compounding and processing mechanical forces are applied. Due to these forces rubber particles collide rapidly and it causes destruction of stabilizing layer on the rubber particle, so the coagulation is the result.

The general procedure for mechanical stability determination is to stir a definite amount of latex under given conditions of dilution, temperature and speed of stirring, and to measure the time which elapse before signs of incipient coacervation appear. The mechanical stability is expressed in seconds.

In its simplest terms, the mechanical stability test involves the increasing of the translational kinetic energy of the particles to such an extent that any electrical and mechanical hindrances to coacervation are speedily overcome. It may be readily calculated that the peripheral speed of the specified disc, rotating at 14,000 rpm, is almost exactly $1,500 \text{ cm sec}^{-1}$ (Barlow 1988).

2.2.6.2 Volatile fatty acid number

There are two types of fatty acid that are associated with the natural rubber latex.

- 1) Volatile fatty acids such as formic, acetic and propionic.
- 2) Non volatile acids such as stearic, oleic, amino acids, polypeptides and proteins.

The effects upon latex of these two types of ammonium salts are quite distinct. The former tend to reduce the stability of the latex by increasing the ionic strength of the serum; the latter increase stability by virtue of their surface-activity. Clearly, what is required is a procedure which will separate the anions into these two categories, and this is what the Volatile fatty acid (VFA) number test seeks to do.

The general method is to separate the serum from a known weight of latex, and then to subject the strongly acidified serum to steam distillation. The steam-volatile acids are then assayed by titration (Barlow 1988).

2.2.6.3 Viscosity

Viscosity is an important property of the latex, and it is inversely proportional to the mechanical stability time. Effect of latex depends upon concentration of polymer which it contains. At low concentration the effect is slight but become increasingly pronounced as the concentration rises.

In general, with most fluids, lattices become less viscous as the temperature is increased. This is due primarily to the reduction in the viscosity of the dispersion medium (Barlow 1988).

2.2.6.4 Total solid content

The total solid content of latex is defined as the percentage by weight of the whole which is non-volatile at a defined temperature in an open atmosphere. The term is something of a misnomer since not all the components of the non-volatile residue are necessarily solid at room temperature. It is useful chiefly as a measure of the percentage of volatiles, the principle volatile being, of course, water (Barlow 1988).

2.2.7 Preservation of NR latex

A preservative is a chemical or mixture of chemicals which when added to latex can prevent bacterial action in it and at the same time stabilizes it. The common preservative for centrifuged concentrated latex is ammonia and depending upon the ammonia content the lattices can be high ammonia (HA) or low ammonia (LA). HA lattices contain only ammonia,

whereas the LA lattices in addition to ammonia contain secondary preservatives used. Secondary preservatives can be boric acid, tetramethylthiuram disulphide/Zinc oxide (TMTD/ZnO), etc. Table 2.2 gives common preservative systems for centrifuged latex. Formaldehyde and KOH can also be used as preservatives for concentrated NR latex (Blow 1998).

Table 2.2 Preservative systems for centrifuged latex (Blow 1998)

Type	Preservative system
1. High ammonia (HA)	0.7% ammonia
2. Low ammonia (LA)	
a. LA-BA	0.2% ammonia + 0.2%boric acid + 0.05% lauric acid
b. LA-ZDC	0.2% ammonia + 0.1% Zinc diethyldithiocarbamate + 0.05%lauric acid
c. LA-TMTD/ZnO (LATZ)	0.2% ammonia + 0.013%tetramethylthiuramdisulphide + 0.013%Zinc oxide + 0.05%lauric acid

2.2.8 Concentrated NR latex

NR latex is a dispersion of rubber particles in water having *ca.*30% (w/w) of dry rubber content (DRC). However, field latex could not be directly used for product manufacturing due to the low level of DRC. Therefore latex concentrate method must be employed to increase the DRC in latex. This concentration makes it an attractive proposition for latex-based industries such as production of dipped goods, rubber thread, latex foam, cast products, and also in applications such as carpet backing, rubberized coir, adhesives, etc (Akiba and Hashim 1997).

2.2.8.1 Latex concentration by evaporation

In this method the latex is stabilized with protective colloids and alkalies and evaporated to remove part of the water (Akiba and Hashim 1997).

2.2.8.2 Latex concentration by creaming

The processing of latex into creamed concentrates involves the mixing of a creaming agent solution such as ammonium alginate or tamarind seed powder with properly preserved field latex and allowing the latex to separate into two layers, an upper layer of concentrated latex and lower layer of serum containing very little rubber. The lower layer of serum (skim latex) is removed; leaving the latex concentrates which is then tested, packed.

Though this method of processing latex into concentrates has been superseded by the centrifugal concentration method, it can still be employed with advantage for producing latex concentrate, because the equipments required for a creaming factory can be fabricated locally unlike the machines required for a factory producing latex concentrates by centrifugation (Akiba and Hashim 1997).

2.2.8.3 Latex concentration by centrifugation

Adequately preserved field latex is transferred from the settling tanks to the centrifuges where separation of rubber particles from the watery serum takes place.

In a centrifuge rotating at 7000-10,000rpm, a force of about 8000 times that of gravity is generated, enabling fast separation of rubber particles. A latex centrifuge is made up of a large of cones of stainless steel arranged one on top of the other. The latex is first fed to a feed cup on top of the centrifuge where the liquid level is held constant by means of a float. The latex flows by gravity through the feed tube into the centre of the rotating bowl where the centrifugal action forces it through a series of distribution tubes in the distributor, into the disk stack. When the latex flows upwards through the holes in the disk stack, it is split into two fractions. The heavier particles are forced outward and the lighter particles inward. Thus, at the top of the centrifuge the output runs into two streams, one consisting of rubber (average volume = 45% from the total throughput and DRC = 60%) and the other of serum containing so called non rubber substances rich skim rubber (average volume = 55% from the total throughput and DRC=3-6%) (Akiba and Hashim 1997).

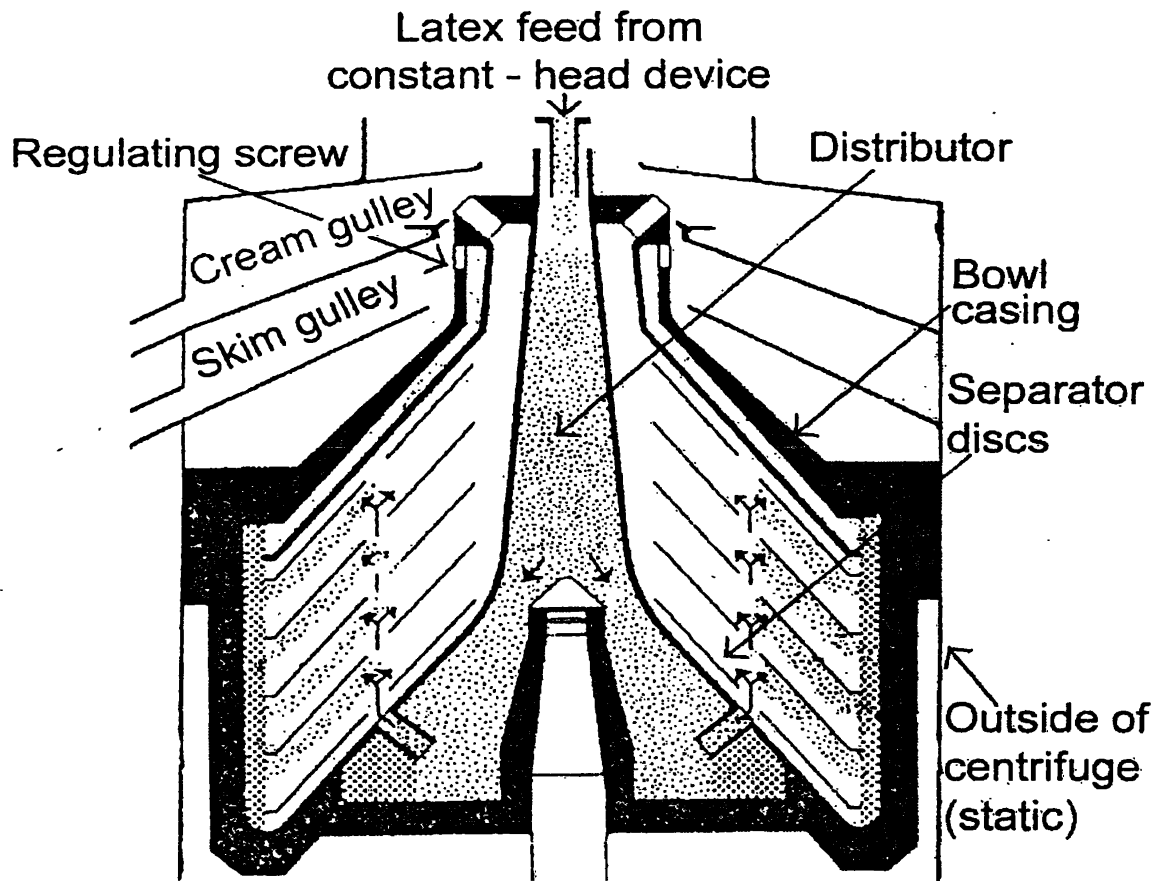


Figure 2.5 Longitudinal section through bowl and upper part of the machine (Akiba and Hashim 1997)

2.3 Sulphur pre-vulcanization of natural rubber latex

2.3.1 History of sulphur-prevulcanization of natural rubber latex

The possibility of vulcanizing the disperse phase of natural rubber latex without any concomitant colloidal destabilization was first investigated by Schidrowitz in the early years of this century. His interest was in making a cellular rubber directly from natural rubber latex. He had the idea that the production time would be significantly reduced if the initial latex were a dispersion of particles of vulcanized rubber. In this way, the requirement for subsequent vulcanization would be obviated. It has subsequently been recognized that pre-vulcanized natural rubber latex is not a suitable material for the production of latex foam

rubber; it has never been widely used for this purpose. Thus, although Schidrowitz did succeed in pre-vulcanizing natural rubber latex, he did not achieve his principal objective. The method of pre-vulcanizing natural rubber latex disclosed in the first of his patents was to heat the latex with sodium polysulphide, sulphur and Zinc Oxide at 145 °C for *ca.* 30-45 minutes. At the conclusion of the process, it was necessary to reduce the steam pressure very slowly to prevent the latex from boiling over. Relatively high vulcanization temperatures were necessary because very active organic accelerators of sulphur-vulcanization were not available at first. Subsequently, water-soluble accelerators of high activity became available. By their use, it was possible to reduce the intensity of the vulcanization conditions to, say, 60 minutes at 70-80 °C, preceded by a 1 hour rise to that temperature. In the years since the experiment of Schidrowitz, pre-vulcanized natural rubber latex has become widely used industrially. It has become available commercially as such for users who do not wish to prepare their own pre-vulcanized latex (Blackley 1966).

2.3.2 Kinetics and mechanism of sulphur pre-vulcanization of natural rubber latex

Before proceeding to discuss the kinetics and mechanism of the sulphur pre-vulcanization reaction, it is desirable to form a clear picture of the reaction system. The initial stage of the reaction system is illustrated schematically in figure 2.6. The vulcanizing ingredients are dispersed as sparingly soluble particles in the aqueous phase of the latex, together with the rubber particles. It seems likely that the vulcanizing ingredients become absorbed into the rubber particles via the aqueous phase, and not by direct contact between the rubber particles and those of the vulcanizing ingredients. As the pre-vulcanization reaction proceeds, it appears that the sulphur and organic accelerator become converted to forms which do not cause opacity in films deposited from the latex. The obvious interpretation of the observations in this respect made by that these ingredients have become almost entirely absorbed within the rubber particles in forms which are rubber-soluble (Blackley 1966).

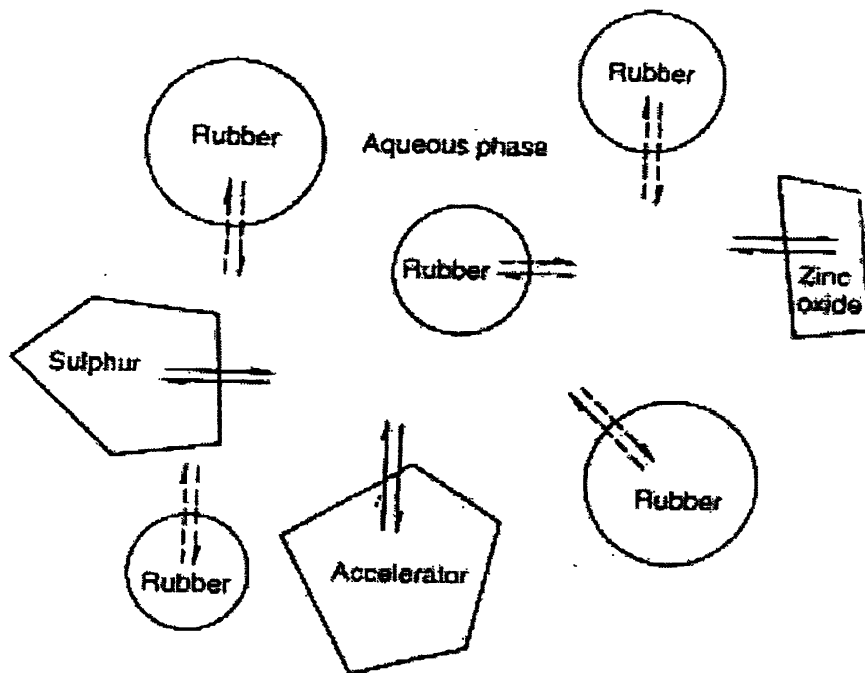


Figure 2.6 Schematic illustration of sulphur pre-vulcanization reaction system (Blackley 1966)

In addition to consistency with the observed kinetics of the reaction, the more obvious requirements which any satisfactory theory of the mechanism of the sulphur pre-vulcanization reaction must fulfill are as follows:

1. It must be consistent with the reaction mechanisms which are generally accepted for the vulcanization of solid natural rubber using sulphur and organic vulcanization accelerators. This requirement implies that the sequence of reactions which is postulated to occur within the rubber particles must be of a similar nature to that which is believed to bring about sulphur-vulcanization in dry natural rubber.
2. It must explain the process by which vulcanizing reagents which are initially confined entirely to the aqueous phase of the latex rapidly become present in the rubber particles in a form in which they are able to effect cross-linking of the rubber macromolecules by sulphur bridges.
3. It must explain the facility with which the reaction can occur at relatively low temperatures (Blackley 1966).

2.3.3 Properties of films derived from sulphur pre-vulcanized natural rubber latex

Films which have been dried down from sulphur pre-vulcanized natural rubber latex closely resemble films which have been cast from an equivalent compounded un-vulcanized natural rubber latex and then post-vulcanized. However, in making comparisons between the two types of film, it must be recognized that difference between them tend to be minimized if, as is usual industrial practice, films from sulphur pre-vulcanized latex are subjected to subsequent post vulcanization. If precautions are taken to avoid post-vulcanization, implying the use of relatively low drying temperatures, then tensile strengths tend to be rather low, being typically *ca.* 10-15 MPa. Extension at break are *ca.* 700-800%. If, as is usual, the drying conditions are such that significant post-vulcanization occurs after the particles of the film have integrated.

The tensile stress-strain curve for films from sulphur pre-vulcanized natural rubber latex formed under conditions which preclude significant post-vulcanization are intermediate in character between those for un-vulcanized latex film and those for post-vulcanized latex film. At low extensions (up to *ca.* 500%), the curve for pre-vulcanized film resembles that for the un-vulcanized film, having a modulus somewhat higher than that for un-vulcanized film but lower than that for post-vulcanized film. Furthermore, at low extensions, the tensile stress-strain curve for pre-vulcanized film is rather flat, as is that for un-vulcanized film. Then, at extension exceeding *ca.* 500%, the modulus increases sharply in the same way as for a post-vulcanized film. The tensile strength of vulcanized films depends upon the conditions under which the film was dried, but is always considerably greater than that of un-vulcanized films (Blackley 1966).

2.3.4 Preparation of sulphur pre-vulcanized natural rubber latex

Sulphur pre-vulcanized natural rubber latex is invariably prepared by allowing the rubber molecules in the particles to react with sulphur under the influence of one or more organic accelerators, and possibly of an inorganic vulcanization activator as well. These reagents are present in the aqueous phase of the latex. It is not usual to allow sulphur pre-vulcanization to proceed to the maximum extent which is possible. What is usually sought is an optimum balance between, on the one hand, the convenience of effecting as much as possible of the total vulcanization of the final product at the pre-vulcanization stage, and on the other, maximum desirable mechanical properties of the final product. It is common practice to achieve this optimum balance by partially pre-vulcanizing the latex, and then completing the

vulcanization of the rubber after the final product has been formed from the latex. It may be necessary to add further vulcanizing ingredients to the latex after pre-vulcanization and before the final processing in order to achieve the desired degree of vulcanization in the final product (Blackley 1966).

The inorganic vulcanization activator is usually a sparingly-soluble metal compound, and thus has to be added to the latex as an aqueous dispersion. The substance most commonly used for this purpose is zinc oxide; zinc carbonate is an alternative sometimes used. An important function of the zinc compound is to regenerate the accelerator as the reaction proceeds. Occasionally, water-soluble zinc salts, such as zinc acetate, have been used as vulcanization activators. However, it is to be expected that the presence of such compounds would drastically reduce the colloid stability of the latex. The use of water-soluble activators might be advantageous if maximum optical clarity is required in the eventual rubber film, because much of the zinc compound should then be removed during water-leaching. The presence of zinc oxide or zinc carbonate in the eventual rubber film is, of course, detrimental to optical clarity (Blackley 1966).

There are several features of the process which are subjected to variation. These include:

1. The level of sulphur;
2. Whether the vulcanization accelerators are to be water soluble or water insoluble, or a combination;
3. The natures and levels of the accelerators;
4. The particle size of the sulphur dispersion;
5. The particle size of dispersions of any water-insoluble accelerators which are used;
6. Whether or not to use an inorganic activator, and if so, the type and amount;
7. The temperature – time profile which is imposed for the reaction;
8. The extent to which the reaction is allowed to continue.

It is clear from this list that many variants of the sulphur pre-vulcanization process are possible. The effects of some of these variables upon the pre-vulcanized latex itself, and upon films obtained from the latex, will become apparent in what follows.

In a variant of this process, the latex is heated with the minimum amounts of vulcanizing ingredients required to attain the desired degree of pre-vulcanization. If they are water-

insoluble, the vulcanizing ingredients are added to the latex as fine dispersions of the type commonly used for compounding lattices with water-insoluble powders. This method depends upon the assumption that a high proportion of the vulcanizing ingredients will be consumed during the vulcanization reaction. Separation of unreacted vulcanizing ingredients is therefore unnecessary. Having these ingredients present as fine dispersions ensures that, in comparison with coarse dispersions, availability for reaction is increased and tendency to sediment is reduced (Blackley 1966).

It has become increasingly realized in recent years that, to effect satisfactory pre-vulcanization of natural rubber latex, there is no necessity to heat the compounded latex to the high temperatures which have previously been regarded as essential. It has been found possible to produce satisfactorily pre-vulcanized natural rubber latex by allowing the compounded latex to stand for a long period at warm ambient temperature, such as is normal in tropical regions, provided that one of the more active zinc dialkyldithiocarbamates, such as zinc di-n-butyldithiocarbamate, is used as the principal accelerator (Blackley 1966).

2.3.5 Measuring the degree of vulcanization

It might be thought that the determination of unreacted (or free) sulphur in the vulcanizate would also provide an indication of the degree of vulcanization of pre-vulcanized natural rubber latex. This property is certainly of considerable interest in its own right. It is also broadly true that, for a given type of sulphur-vulcanization system, the degree of vulcanization tends to increase as the concentration of unreacted sulphur in the rubber decreases. However free sulphur content is not a good index of degree of vulcanization, because it provides information relating only to the disappearance of sulphur, it is silent as to the fate of the sulphur. Combined sulphur can in principle be present in various forms in a vulcanizate. Even that which is combined with the rubber can be present in forms other than cross-links between rubber molecules. Even the proportion which is combined in the form of cross-links provides no satisfactory index of the concentration of cross-links, because the important matter of the average number of sulphur atoms per crosslink remains unclear. Of the test methods listed below, only the chloroform coagulation test is peculiar to pre-vulcanized natural rubber latex, in that it is a test which is applied to the latex itself, and not to films dried down from the latex. The other three tests are applied to films from the latex, and are in principle applicable to any elastomeric films, including post vulcanized films derived from rubber lattices (Blackley 1966).

2.3.6 Methods for assessing the degree of vulcanization of pre-vulcanized natural rubber latex

There are four principal types of test which are commonly used to assess the degree of vulcanization of pre-vulcanized natural rubber latex. They are:

1. Chloroform coagulation test- in Which the latex is stirred with a fixed proportion of chloroform, and the degree of vulcanization judged from the appearance of the coagulum which forms;
2. Equilibrium swelling test- in which the degree of vulcanization is judged from the extent of equilibrium swelling of films dried down from the latex, the swelling being carried out under controlled conditions using a suitable rubber solvent;
3. The relaxed modulus test-in which the degree of vulcanization is judged from the relaxed modulus at 100% extension (MR 100) of films dried down from the latex
4. Pre-vulcanize relaxed modulus (PRM) test- in which the degree of vulcanization is again judged from the relaxed modulus at 100%extension (MR 100) of films dried down from the latex.

The chloroform-coagulation test provides a very simple, rapid semi-quantitative procedure for assessing degree of vulcanization in pre-vulcanized natural rubber latex. A small volume (typically 10 cm³) of the latex is mixed with an equal volume of chloroform, and the mixture stirred until coagulation occurs as a consequence of the latex particles having absorbed much of the chloroform. The physical character of the coagulum is then examined; it depends upon the degree of vulcanization of the latex particles. The more highly cross-linked are the particles, the less readily do they coalesce together to form a coherent coagulum. As the degree of vulcanization increases, so the coagulum changes from a soft, plastic well-integrated mass to a crumbly material. The state of vulcanization can therefore be judged from the appearance of the coagulum. An arbitrary number, known as the chloroform number, is assigned to the latex on the basis of the appearance. Four stages of pre-vulcanization are usually distinguished by this test, and are assigned chloroform numbers as follows, the perceived degree of vulcanization increasing with increasing chloroform number:

1. Chloroform number 1: the coagulum is a tacky mass, breaking in a stringy manner when stretched;
2. Chloroform number 2: the coagulum is a weak lump which breaks short when stretched;
3. Chloroform number 3: the coagulum has the form of non-tacky agglomerates;
4. Chloroform number 4: the coagulum has the form of small dry crumbs (Blackley 1966).

2.3.7 Comparison between sulphur-prevulcanization of natural rubber latex and Sulphur-vulcanization of dry natural rubber

The sulphur-prevulcanization reaction in natural rubber latex occurs at much lower temperatures, and is generally more facile, than would be expected from experience with the vulcanization of dry natural rubber with sulphur and organic accelerators. Figures 2.7 (a) and (b), which are based upon results obtained by Loh, illustrate clearly that sulphur-prevulcanization occurs much more rapidly than does the vulcanization of the solid natural rubber at the same temperature using the same vulcanizing ingredients.

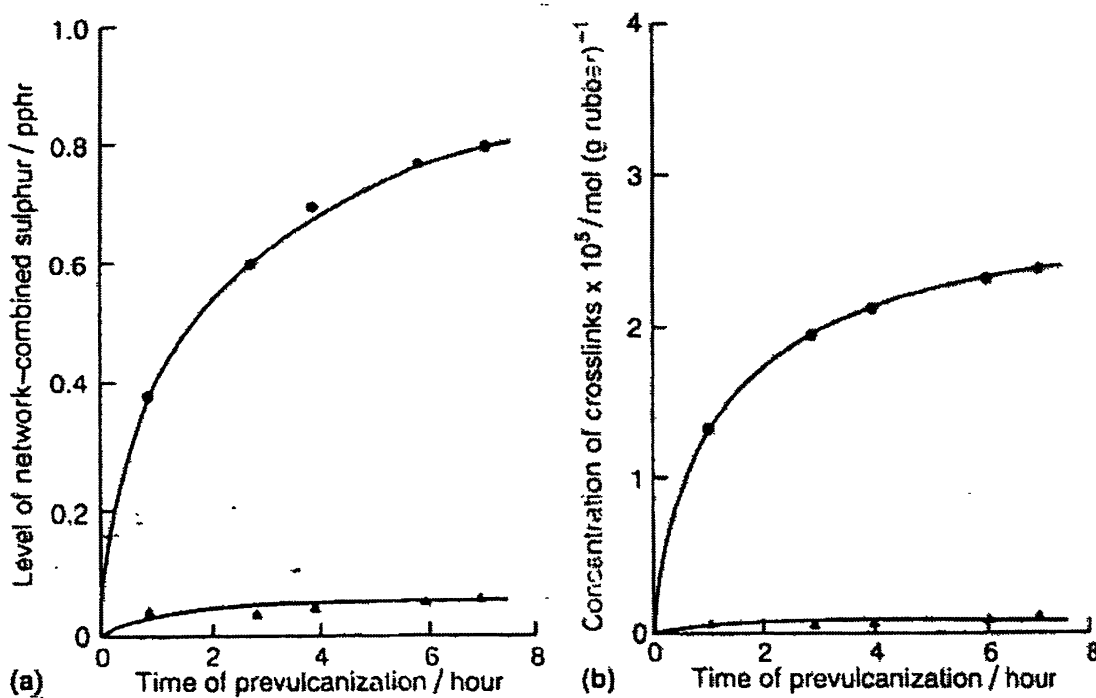


Figure 2.7 Vulcanization of natural rubber latex and dry natural rubber at 50° C : (a) variation of network-combined sulphur with time of pre-vulcanization or vulcanization; (b) variation of concentration of chemical cross-links in vulcanizates with time of pre-vulcanization of vulcanization. Formulation (parts by mass dry): natural rubber 100, sulphur 1, zinc di-*n*-butyldithiocarbamate 1.3. Significance of points: ● rubber as latex , ▲ dry rubber

Figure 2.7(a) shows the variation with time of pre-vulcanization or vulcanization at 50° C of network-combined sulphur for the rubber in pre-vulcanizing natural rubber latex and the rubber in a vulcanizing solid natural rubber of the same composition. The latter was obtained by evaporating to dryness at low temperature the compounded latex which was used for the pre-vulcanization experiment. Figure 2.7 (b) gives results for the concentration of chemical cross-links in these vulcanizates. These results confirm the indication from experience of the sulphur vulcanization of solid natural rubber that, notwithstanding the use of extremely fast vulcanization accelerators for the sulphur-pre-vulcanization reaction, pre-vulcanization readily proceeds at far lower temperatures than would be expected (Blackley 1966).

CHAPTER 3

METHODOLOGY

3.1 Characterization of latex sample

3.1.1 Determination of dry rubber content (DRC)

Procedure

The determination of dry rubber content of the centrifuged latex sample was carried out by using recommended quick DRC method. Three Petri dishes were numbered. Then about 1g of latex was taken to each dish. After that about 2-5 ml quick method solution (C₂H₅OH: CH₃COOH, 95: 5) was slowly added into each dish. Using a glass stopper flat film was made (the film should have a thickness less than 2 mm). The film was rinsed by using distilled water until no acetic. It was kept in microwave oven at medium low power level for 20 minutes. The dry weight was taken and kept in the oven again weighed until three was no weight loss.

Calculation

Initial weight - m_0

Dry weight - m_1

$$\% \text{ Dry rubber content (DRC)} = \frac{m_1}{m_0} \times 100$$

3.1.2 Determination of total solid content (TSC)

Procedure

Determination of total solid content of the centrifuged latex sample was carried out according to the procedure given in ISO 124:1997(E). A dish was weighed in to the nearest 0.1mg. About 2.0 ± 0.5 g of latex was pour into the dish and weighed to the nearest 0.1mg. The contents in the dish were swirled to ensure that latex covered the bottom of the dish. If desired, 1cm³ of distilled water may be added and mixed with the latex by swirling. The dish

was placed in the oven horizontally and heated it at $70 \pm 2^{\circ} \text{C}$ until sample has lost its whiteness (about 2 hours). Then the dish was cooled in a desiccator. The dried sample was replaced and weighed. The dish was returned into the oven for 15 minutes. Dish was cooled in a desiccator and weighed. The drying procedure was repeated for intervals of 15 minutes until loss in mass between two successive weighings is less than 0.5mg.

Calculation

The mass in grams of the test portion – m_0

The mass in grams of the dried sheet – m_1

$$\% \text{ Total solid content (TSC)} = \frac{m_1}{m_0} \times 100$$

3.1.3 Determination of mechanical stability time (MST)

Procedure

Determination of mechanical stability time of the centrifuged latex sample was carried out according to the procedure given in ISO 35:1995(E). About 100 g of latex sample was weighed into a beaker and diluted into $55 \pm 0.2\%$ total solid content by using 0.6% (m/m) ammonia solution. Without delay the sample was warmed (by using water bath) up to 36°C to 37°C with gentle stirring. Immediately this sample was filtered and weighed 80 ± 0.5 g of the filtered latex into the container (check that the temperature was $35 \pm 1^{\circ}\text{C}$). The container was placed in position and stirred the sample with the rotational frequency $14000 \pm 200 \text{ min}^{-1}$ until the end point was passed (The arrival of the end-point was preceded by a marked decrease in the depth of the vortex around the stirring shaft). The end point was determined by sampling the latex intervals of 15 second and spreading the sample gently on the palm of the hand. The end point was taken as the first appearance of floccules (The mechanical stability time was expressed in time required initiating visible flocculation).

Dilution of latex

If TSC is more than 55%,

$[(1.8182 \times \text{TSC}) - 100]$ ml of NH_3 solution should be added to the latex.

0.6 % NH_3 solution was used for dilution.

3.1.4 Determination of volatile fatty acid number (VFA)

Procedure

Determination of volatile fatty acid number of the centrifuged latex sample was carried out according to the procedure given in ISO-506:1992(E). Initially the total solid contents and dry rubber content have to be determined. Into beaker 50 g of latex was weighed and it was accurate to nearest 1 g. Accurately 50.00 ml of $(\text{NH}_4)_2\text{SO}_4$ solution [30 % (m/m) solution] was added into the above beaker with constant stirring. The beaker was immersed in the water bath at about 70 °C with continuing the stirring of the latex until total coagulation was obtained. The beaker was covered by a watch glass and left it in the water bath for 15 minutes. The serum was decanted through dry filter paper. The coagulum was pressed and all the serum was collected and filtered by the same filter paper. Into a 50 ml conical flask 25.00 ml of filtered serum was obtained. It was acidified by 5.00ml of H_2SO_4 solution [50 % (m/m) solution] Mixed well by swirling the flask. Before the introduction of this solution into the distillation apparatus, steam was passed through the apparatus for 15 minutes. During the passing of steam 10.00 ml of acidified serum was introduced into the inner tube. Continuous distillation was carried out until 100 ml of distillate had been collected into a 250 ml titration flask. After that it was passed through a stream of air free from carbon dioxide at a rate of $200\text{cm}^3/\text{min}$ to $300\text{cm}^3/\text{min}$ for approximately 3min. Then it was titrated with 0.01mol dm^{-3} $\text{Ba}(\text{OH})_2$ solution using phenolphthalein as an indicator.

Calculation

The volatile fatty acid number (VFA) was calculated by using following formula.

$$\text{VFA} = \frac{[134.64cV]}{[m\text{TSC}]} \times \frac{[50 + m(100 - \text{DRC})]}{100\rho}$$

Where,

c – Concentration of the barium hydroxide solution, expressed in moles per cubic decimeter

V – volume, in milliliters of $Ba(OH)_2$ solution required to neutralize the distillate

m – Mass in grams, of the test portion

ρ – Density of the serum in mega grams per cubic meter

DRC – Dry rubber content of the latex sample

3.1.5 Determination of viscosity

Viscosity was determined by using Brook field viscometer.

3.1.6 Determination of Alkalinity

Procedure

10 cm³ of stabilizer solution was added into a 200 cm³ of water contained beaker. Then 10g of latex concentrate was weighed into a nearest 10mg from a weighing bottle and it was added and stirred well. The mixture was immediately titrated with 0.05 moldm⁻³ Sulphuric acid solution. Bromomethyl Blue was used as an indicator and the colour change was blue to yellow.

Calculation

$$\text{Alkalinity (as NH}_3\text{)} = \frac{F_1 c V}{m}$$

Where

F_1 - A factor 3.4

c - Concentration of sulphuric expressed in moles per cubic decimeter

V - Volume of sulphuric used, in cubic centimeters

m – Mass of the test portion in grams

3.2 Preparation of pre-Vulcanized natural rubber latex

3.2.1 Preparation of chemicals for the pre-vulcanization of latex

3.2.1.1 Preparation of dispersions

For preparing dispersions for latex a coarse slurry is made of the powder with water which contains small amounts of dispersing agent and stabilizer, and then to grind the slurry in a ball mill to produce a dispersion of small particle size.

Sulphur dispersion (50%)

Sulphur was used as a curing agent for the preparation of pre-vulcanized natural rubber latex. 50% Sulphur dispersion was prepared by ball milling the following chemicals for 72 hours.

Table 3.1 Formulation for 50% Sulphur dispersion

Material	Parts per hundred
Sulphur	50
Dispersing agent	2
Water	48

Zinc Oxide dispersion (50%)

Zinc Oxide is used as an activator for the preparation of pre-vulcanized latex. 50% Zinc Oxide dispersion was prepared by ball milling the following chemicals for 24 hours.

Table 3.2 Formulation for 50% Zinc Oxide dispersion

Material	Parts per hundred
ZnO	50
Dispersing agent	1
Water	49

ZDEC dispersion (50%)

ZDEC (Zinc Diethyldithiocarbamate) act as an accelerator in the preparation of pre-vulcanized latex. 50% ZDEC dispersion was prepared by ball milling the following chemicals for 24 hours.

Table 3.3 Formulation for 50% ZDEC dispersion

Material	Parts per hundred
ZDEC	50
Dispersing agent	1
Water	49

Antioxidant dispersion (50%)

Commercially available ralox is used as an antioxidant for the preparation of pre-vulcanized natural rubber latex. Ball milling was carried out for 24 hours using following chemicals for the preparation of pre-vulcanized natural rubber latex.

Table 3.4 Formulation for the 50% antioxidant

Material	Parts per hundred
Antioxidant	50
Dispersing agent	1
Water	49

3.2.1.2 Preparation of solvents

KOH Solution (20%)

KOH was used as a stabilizer in the preparation of pre-vulcanized latex. 20 g of KOH was weighed and was dissolved in 80 g of water for the preparation of 20% KOH solution.

Wettam (10%)

Wettam was used as a stabilizer in the preparation of pre-vulcanized natural rubber latex. 10 g of wettam was weighed and was dissolved in hot water.

3.2.2 Pre-Vulcanizing of natural rubber latex

Concentrated NR latex was used for the preparation of pre-Vulcanized natural rubber latex. Commercially available centrifuged natural rubber latex was bought by S & C Latex (Private) Limited, Kalawellava Road, Bellapitiya, Horana, Sri Lanka.

Centrifuged natural rubber latex sample was compounded according to the following formula.

Table 3.5 Formulation of the series of NR latex compound

Ingredient	Amount (g)
60% NR latex	167.0
10% Wettam	0.5
20% KOH	0.5
50% Sulphur	1.0
50% ZnO	0.4
50% ZDEC	1.0
50% Ralox	1.0

Centrifuged natural rubber latex sample was partially deammoniated by stirring. Then pre-vulcanization was achieved by adding all compounding ingredients (Table 3.5) to the centrifuged latex sample by constant stirring and heating the mixture at 70°C for 45 minutes.

In the meanwhile the required state of pre-vulcanization was judged by using chloroform-coagulation test as the coagulum has the form of non-tacky agglomerates. Then the pre-vulcanized sample was allowed to cool while stirring.

3.3 Test for measuring the extent of cure

3.3.1 Chloroform-coagulation test

Chloroform-coagulation test is a very simple rough test for measuring the extent of cure. In this test a small volume (typically 10 cm³) of the latex is mixed with an equal volume of chloroform, and the mixture was stirred until coagulation occurs as a consequence of the latex particles having absorbed much of the chloroform. The physical character of the coagulum is

then examined. The required state of vulcanization was identified as the coagulum having the form of non-tacky agglomerates.

3.3.2 Modified Swollen Diameter test

Swollen diameter test is used for this purpose more quantitatively than the chloroform coagulation test. But it requires more time to perform. A thin film of pre-vulcanized latex was spread upon a glass plate and allowed to dry. The surface of the dried film was dusted with talc. The film was removed from the glass plate, and both sides dusted with talc. After removal from the glass plate, the film was dried further for half an hour at 100°C. Circular discs are cut from the film. Excess talc was wiped off, and the discs were swollen by immersion in a toluene containing petri dish. The diameter of the disc was measured after immersion for 25-27 minutes in the toluene. The measurements were taken by placing the Petri dish over a graph paper. The diameter was measured in two directions, and the average value calculated.

The % swelling was calculated using the following equation.

$$\% \text{ swelling} = \frac{(\text{Average swollen diameter} - \text{Unswollen diameter})}{\text{Unswollen diameter}} \times 100$$

Table 3.6 % Swelling values corresponding to different states of cure

State of Cure	% Swelling
Un-vulcanized	160
Slightly vulcanized	100-160
Moderately vulcanized	80-100
Fully vulcanized	75

3.4 Re-centrifuging of pre-vulcanized latex using techniques

3.4.1 Preservation of field latex for re-centrifuging

3.4.1.1 Preparation of Chemical solutions

Ammonia solution (10%)

The stock solution was prepared by diluting 1 litre of 25% strong ammonia with 1.5 litres of water.

Ammonium laurate solution (10%)

To make 10% solution, 4.6kg of lauric acid was dissolved on 4.0kg of hot water and 5kg of 10% ammonia solution was added before mixing the contents well. Then 4.5kg of cool water was added to the mixture to make it a 10% solution.

DAHP solution (10%)

10g of DAHP (Diammoniumhydrogenphosphate) solution was dissolved in a 90g of water.

TMTD/ZnO dispersion (25%)

Dispersion was prepared by ball milling a mixture of the following ingredients for approximately 48 hours in a suitable ball mill until a stable dispersion was obtained.

Table 3.7 Formulation for 25% TMTD/ZnO dispersion

Material	Parts per hundred
TMTD	12.5
ZnO	12.5
Dispersol LR	1.0
Bentanoit clay	0.5
water	73.5

3.4.2 Procedure for Preservation of field latex

For the manufacture of LATZ (Low Ammonia-TMTD/ZnO) latex, 0.2% of ammonia was added to the field latex from above prepared 10% ammonia solution. Then 10% of DAHP solution was added at a rate of 68cm³ for 4500cm³ of latex. After that 0.05% of lauric acid was added to the latex from 10% ammonium laurate solution. Finally TMTD/ZnO was added at the rate of 1 litre for 1000 litres of latex. So that the level of TMTD/ZnO would be 0.025% on latex.

3.4.3 Recentrifuging of prevulcanized latex

After the compounding, the compounded latex was separated into two portions as Sample P and Sample Q, Sample P to be treated as control and Sample Q to be divided into 3 portions. These three portions were treated in three different techniques and those samples were named as A, B, C respectively.

Three portions are,

Technique 1- Replacing 40% of the pre-vulcanized latex with field and re-centrifuging was carried out

Technique 2- Replacing 30% of the pre-vulcanized latex with field latex and re-centrifuging was carried out

Technique 3- Replacing 20% of the pre-vulcanized latex with water and re-centrifuging was carried out

3.5 Determination of latex quality parameters for four samples

Above four samples were stored in room temperature and latex quality parameters such as MST, TSC, viscosity, alkalinity was tested. Following the criteria described in 3.1. Quality parameters of four samples were tested weekly.

3.6 Test for cast films

3.6.1 Determination of the tensile properties

Cast films of each sample were prepared (see: 3.3.2) and vulcanized them for half an hour at 100°C. Then dumb-bell shape tensile test pieces were cut including control P. Thickness of test pieces were measured by a micrometer gauge. The foot of which exerts pressure of 20 kPa on the rubber. Width was assumed to be equal to the width between the cutting edges of the narrow central part of the dye. Four test pieces were tested from one sample. Test piece was placed centrally in the grip of the tensometer and the following measurements were taken while the test piece was stretched.

- 1) The force on the test-piece

- 2) The elongation of the test-piece as shown by the distance between the gauge marks on the test-piece

The experiment was carried out for each sample weekly.

Calculation

Tensile strength = $\frac{\text{Force at break (F)}}{\text{Initial cross section area (A)}}$

Initial cross section area (A)

3.6.2 Determination of extent of cross-linking

Extent of cross-linking was measured using Swollen Diameter test for four samples. Following the criteria described in 3.3.2.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Quality parameters of the Concentrated NR latex used for the study

Concentrated natural rubber latex used for the tests showed total solid content to be 61.6% and dry rubber content was 60.2%. The mechanical stability time was shown to be 800 Sec and volatile fatty acid number was 0.025. The viscosity was shown to be 81.5cPs and alkalinity was 0.22%. The summary is given in table 4.1.

Table 4.1 properties of concentrated NR latex

Material	Properties
Natural rubber latex (LA-TZ)	TSC-61.6% DRC-60.2% MST-800 Sec. VFA-0.025 Viscosity-81.5 cPs Alkalinity-0.22%

4.2 Modified Swollen Diameter Test results for Pre-vulcanized natural rubber latex

The % Swelling was shown to be 110. The result indicates that the pre-vulcanized NR latex sample was slightly vulcanized (Table 3.6).

4.3 Quality parameters of pre-vulcanized natural rubber latex

Quality parameters of pre-vulcanized natural rubber latex were tested. The total solid content was shown to be 59.2% and dry rubber content was 59.0%. The mechanical stability time was shown to be 495 Sec. The summary is given in table 4.2.

Table 4.2 Quality parameters of pre-vulcanized NR latex

Quality Parameter	Value
DRC	59.0%
TSC	59.2%
MST	495 Sec

4.4 Quality parameters of re-centrifuged pre-vulcanized samples

Designation of samples:

Sample A - 40% of field latex + 60% of pre-vulcanized latex re-centrifuged

Sample B - 30% of field latex + 70% of pre-vulcanized latex re-centrifuged

Sample C - 20% of Water + 80% of pre-vulcanized latex re-centrifuged

Control - Centrifuged latex without any re-centrifuging

Quality parameters of re-centrifuged pre-vulcanized samples were tested. The total solid content of sample A, sample B, sample C and control sample were shown to be 62.4%, 62.9%, 60.4%, 59.2%. The dry rubber content of sample A, sample B, sample C and control sample were 61.0%, 61.5%, 59.0%, 59.0%. The summary is given in table 4.3.

Table 4.3 Quality parameters of re-centrifuged pre-vulcanized samples

Sample	TSC (%)	DRC (%)
A	62.4	61.0
B	62.9	61.5
C	60.4	59.0
Control	59.2	59.0

4.5 Quality parameters of re-centrifuged samples with storage period

4.5.1 Variation of mechanical stability time

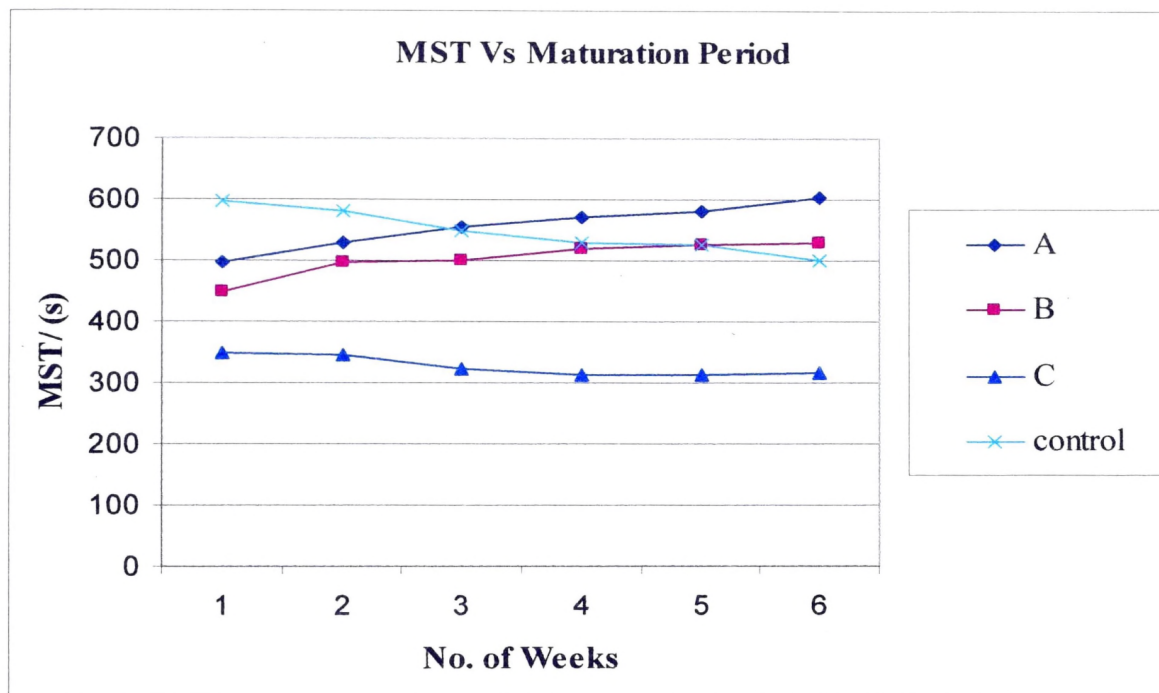


Figure 4.1 Variation of mechanical stability time of re-centrifuged pre-vulcanized Samples with maturation period

The variation of the mechanical stability time of the four systems with storage period is shown in Figure 4.1. MST as a function of maturation period was studied for six weeks. The results indicated that the sample which contains 40% of field latex and 60% of pre-vulcanized latex showed slight increase in MST through out the six weeks from 498 Sec up to a level of 604 Sec. The sample which contains 30% of field latex and 70% of pre-vulcanized latex showed slight increase in MST from 450 Sec to 500 Sec within first two weeks and gradually increases up to 528 Sec within the period of six weeks. The sample which contains 20% of water and 80% of pre-vulcanized latex showed slight drop in MST through out the six weeks from 350 to 317. Similarly, the control sample showed a significant drop in MST within the first four weeks from 598 Sec to 530 Sec, and a gradually decreases from 530 Sec to 500 Sec within 4th to 6th weeks.

Gradual increase of MST with time in samples A and B may be due to the addition of preserved field latex prior to re-centrifuging. The increase of MST can be explained as follows. Vulcanizing ingredients remaining even after re-centrifuging of the mixture of pre-vulcanized and fresh preserved lattices may have reacted with fresh field latex resulting reduction of residual amount of vulcanization ingredients in the system which may be a strong possibility that the MST to increase on storage.

As such higher MST of sample A than sample B can be anticipated since quantity of preserved filed latex is higher than that of sample B.

According to the results it is observed that in the first and second weeks pre-vulcanized control sample has higher MST value compared to other three samples. Due to mechanical force impart on samples during re-centrifuging a drop in MST could be expected. However, subsequent increase in MST could be expected in those samples due to the formation of long chain fatty acids as lipids present in the latex break down slowly.

The MST value of control sample is gradually decreases with maturation. This is due to the over vulcanization of the control sample with time which is the result of the presence of residual vulcanization ingredients. In addition presence of zinc oxide may also reduce the stability of latex because of zinc oxide thickening in the presence of Ammonia.

Higher level of stability is needed for the manufacturing conditions, since the latex is subjected to considerable mechanical agitations or shear forces.

The mechanical stability time of the sample A is higher than that of samples B & C and it is gradually increases with maturation. Hence, sample A is suitable for production of rubber articles. Other two samples B and C possess lower MST values than A.

4.5.2 Variation of the Viscosity

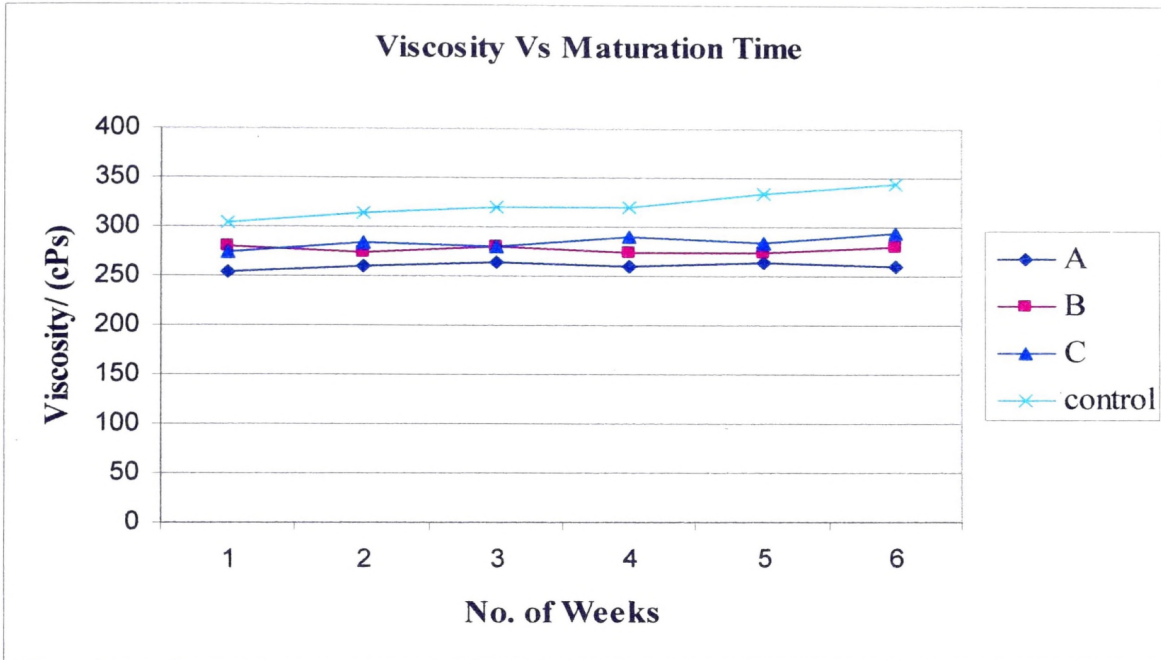


Figure 4.2 Variation of viscosity of the samples with maturation

Figure 4.2 shows the Variation of viscosity of the samples as a function of maturation period was studied for six weeks. The results indicated that control sample showed gradual increase in viscosity through out the first four weeks from 305 to 320 and significant increases within 4th to 6th week from 320 to 345. The viscosities of other three samples remain at a constant level through out the six weeks and it varies between 250 cPs and 350 cPs.

Control sample has higher viscosity than those of other three samples during maturation period and it is increases with time. Reason for that is ZnO thickening and over vulcanization of control sample. Therefore, ordinary centrifuged lattices may become unusable for product manufacture if they are kept over a long period of time.

Viscosity of sample A, B and C do not possess much more variation with maturation period. However, sample A has the lowest viscosity than those of B and C with maturation and the viscosity remain above 250 and lower than 350. As such, the viscosity of sample A is much superior in comparison to other three samples on storage.

4.5.3 Alkalinity

Alkalinity of four samples was checked. It was maintained around 0.2%. If it decreases beyond 0.2%, pre-vulcanized samples may coagulate. On the other hand, when the ammonia content is high; ZnO thickening may also take place resulting higher viscosity and such lattices may not be suitable for the product manufacture. The quality parameters such as MST, viscosity are highly dependant on the concentration of ammonia. As such, ammonia content should always be maintained around 0.2% in centrifuged latex.

4.6 Variation of tensile properties of four samples

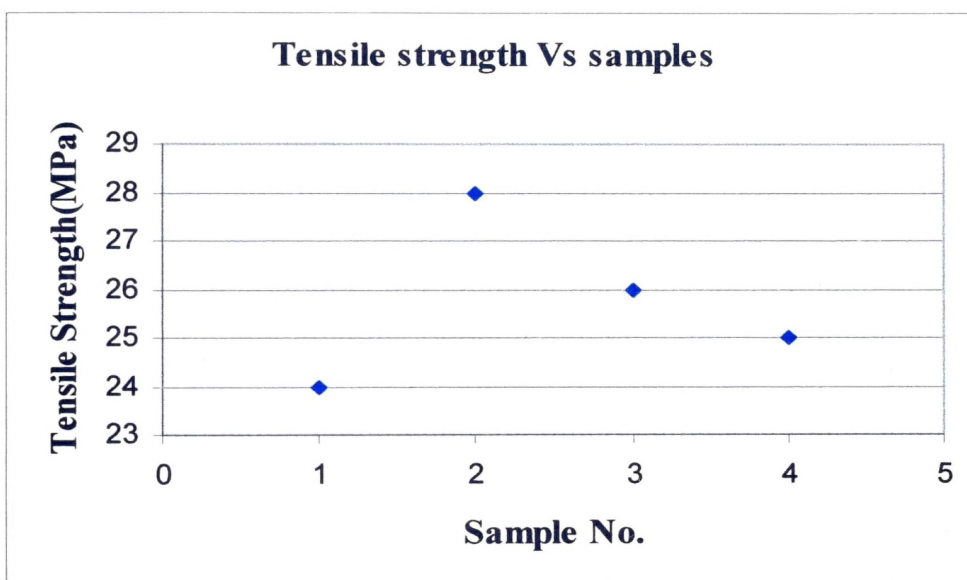


Figure 4.3 Variation of tensile strength with the varying of sample

The figure 4.3 illustrates the variation of tensile properties of four samples. Tensile strength of four samples was studied for six weeks. The tensile strength of control sample was shown to be 24 MPa and tensile strength of sample which contains 40% of field latex and 60% of pre-vulcanized latex was 28 MPa. Tensile strength of sample which contains 30% of field latex and 70% of pre-vulcanized latex was shown to be 26 MPa and sample which contains 20% of water and 80% of pre-vulcanized latex was shown to be 25 MPa.

The sample which contains 40% of field latex and 60% of pre-vulcanized latex shows higher tensile properties in comparison with the other three samples. The increase in tensile strength may

be due to the increase in cross-linking. Blackley and Merrill reported that the tensile strength of the film from pre-vulcanized natural rubber latex compounds depends on the ability of particles to coalesce and integrate, when the film dries, as well as on the concentration of the crosslink in the rubber.

4.7 Variation of extent of cross-linking of samples

The extent of cross-linking of four samples was measured. The results indicate that % swelling of control sample was 111. The % swelling of sample A which contain 40% of field latex, sample B which contains 30% of field latex and Sample C which contain 20% of water was shown to be 115, 104, 106 respectively. The summary is given in table 4.4.

Table 4.4 Extent of cross-linking of the pre-vulcanised latex systems

Sample	% Swelling
Control	111
A	115
B	104
C	106

The extent of cross-linking (or state of cure) of the control sample and the three samples, A, B and C are given in Table 4.3. The results indicate that the % swelling values of the four systems vary between 100-160 which indicates these four samples were slightly vulcanized.

Sample A (prepared according to Technique 1 - replacing 40% of the pre-vulcanized latex with field latex and re-centrifuging) has higher tensile properties and higher storage stability than those of samples B and C. This is a clear indication of less over vulcanization of sample A compared to the other samples.

CHAPTER 5

CONCLUSION

The three techniques used to re-centrifuge the pre-vulcanized latex were selected basically to minimize the residual chemicals that remain after pre-vulcanization and thereby to restrict further vulcanization.

The extent of cross-linking (or state of cure) of the control sample and the three samples results revealed that all four samples were slightly vulcanized as can be seen in table 4.3.

The variation of the mechanical stability time of the four systems with storage period was as can be seen in figure 4.1. The control sample has a lower value than other three samples. The higher level of stability is needed for the manufacturing condition, since the latex is subjected to considerable mechanical agitations or shear forces. So sample prepared according to technique 1 (replacing 40% of the pre-vulcanized latex with field latex and re-centrifuging) shown better storage stability when compared to sample prepared according to technique 2 (replacing 60% of the pre-vulcanized latex with field latex and re-centrifuging) and technique 3 (replacing 20% of the pre-vulcanized latex with water and re-centrifuging).

Viscosity of three samples did not possess much variation on storage. However, viscosity of the control sample was seen to increase with time and it shows higher value than the three samples. The lowest viscosity indicates the highest quality of the latex for the use in the product manufacture. Therefore, pre-vulcanized latex prepared according to technique one is the best.

Tensile strength of control sample was shown to be the lowest value in comparison with the other three samples. Tensile strength of the sample prepared according to technique 1 yielded the highest strength which indicates the latex quality as per this technique produces the best product over the others tested.

It is apparent from the results of this study that the residual vulcanizing ingredients of the pre-vulcanized latex can be minimized by using the three techniques 1, 2 and 3. Among these three techniques pre-vulcanized lattices prepared according to technique 1 yielded the highest storage stability, higher quality and it produces cast films of good mechanical properties in comparison with the other techniques.

Hence, it can be concluded that pre-vulcanized lattices prepared as per the technique 1 is the most suitable way of preparing pre-vulcanized lattices for higher storage stability and long term use for the product manufacture.

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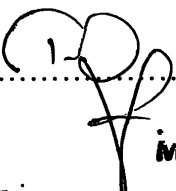
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