STUDIES ON PHYSICO-CHEMICAL PROPERTIES AND RADIATION EFFECTS ON NATURAL RUBBER LATEX

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ABSTRACT

The natural rubber field latices of different clones and ages of the rubber plants were collected form rubber estates of Bangladesh. The characteristics like total solid content (TSC), dry rubber content (DRC), alkalinity, KOH number, volatile fatty acid number (VFA), pH, Viscosity, density, sludge content, coagulum content and nitrogen content of the latices have been determined. The total ash of the latices have been analyzed for water insoluble ash content and for metals like iron, manganese and copper. These characteristics have been compared among the latices of different clones and ages of the rubber plants from different rubber zones. In general TSC of the latex samples varies from 19% to 45% and DRC varies from 16% to 42%. TSC and DRC increase with the age of rubber trees. Nitrogen content of the total solid decreases with the age of the rubber plants. Density of latex decreases but viscosity increase with the increase of DRC.

The composition and properties of the TJIR clonal field latex from Rawzan rubber estate of Chittagong zone and PBIG clonal field latex from Satgaon rubber estate of Sylhet Zone have been studied at three months interval during 1991. It has been found that TSC and DRC are lower in the first and the last quarters of the year than those in the second and third quarters of the same year. The nitrogen in total solid of the latex samples from Rawzan rubber estate is lower than that in the samples of the Satgaon rubber estate.

The composition and properties of the rubber latices collected from the different rubber estate of Chittagong and Sylhet zones have been determined. The highest TSC and DRC have been found in the latex samples of the Rawzan rubber estate of Chittagong zone. The compositions of the total solid of the latex samples

of different rubber estates have been determined. The ash content varies from 1.30 to 1.52% and nitrogen varies from 0.52 to 1.12%. The metals in the solid vary from 0.98 to 6.41 ppm (Cu), 0.91 to 2.34 ppm (Mn) and 13.62 to 31.42 ppm (Iron).

Methods of concentration of the latices have been developed. The usual DRC can be raised to 60% by concentrating field latices. The centrifuge concentrated latex meets the requirements of the International standard.

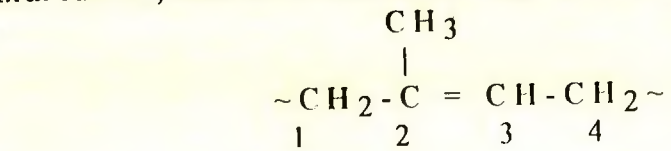
Radiation effects on the field latex and the concentrated latex have been studied. The latex samples from the Vatera and Satgaon rubber estates have been used for the study of radiation effects on the latex. The radiation effects on the field latex have been studied in the presence and in the absence of sensitizers. Of CCl_4, n-BA, n-BA + CCl_4 combination, n-BA + H_2O_2 combination, n-BA appears to be more promising as a sensitizer. Physical properties like tensile strength, elongation at break, modulus at 300% and 600% elongation, permanent set etc. of the films from the irradiated latex have been determined. The results compare favourably with the literature values and with the requirements of the international standard for gloves and similar commodities.

CHAPTER-1

1. INTRODUCTION

1.1 General

Natural rubber (NR),which is a polymer of isoprene, has all the isoprene units linked at carbon atoms 1 and 4 in a head to tail arrangement. All or nearly all the repeating units of isoprene in natural rubber possess the *cis* configuration and this regularity of micro-structure plays an important role in the characteristic properties of natural rubber, such as its extremely high tensile strength, tear resistance etc.



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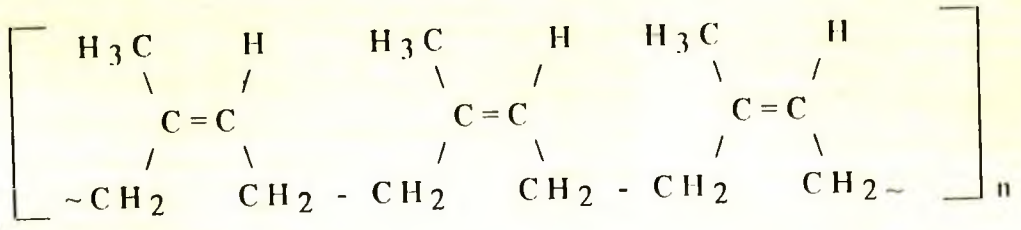

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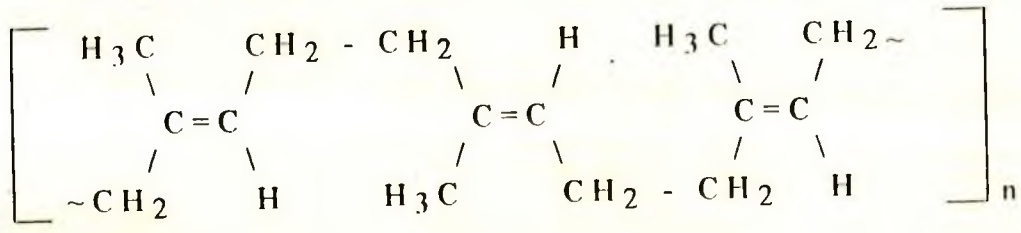


(c)

Fig. 1: Structure of (a) Isoprene unit (b) Natural rubber (c) Balata/Guttapercha.

Although natural rubber and balata/guttapercha have the same empirical formula $(C_5H_8)_n$ Fig.1 shows the structural difference between them. Natural rubber and balata/guttapercha are stereoisomers. Natural rubber is soft and flexible, whereas the balata or guttapercha is tough and horny.

Natural rubber latex (NRL), *cis* 1,4-polyisoprene rubber particle in aqueous medium (colloidal dispersion), is stabilized by a small amount of protein and fatty acids. Some plants yield natural rubber latex as a white milky substance when their surfaces are either cut or wounded. The original sources of these plants comprise many wild species of Hevea, Manihot glaziiovii, Castilloa elastica, Ficus elastica, Landolphia and other lesser known plants. Depending upon the sources the field latices differ in purity, molecular weight of the rubber hydrocarbon and other chemical and physical characteristics. Most of the rubber used today are collected from Hevea brasiliensis plant which was cultivated in the Amazon region of South America.

According to Otis D. Cole[1], Hevea rubber does not thrive well outside the belt of 15° latitude on both sides of the equator. According to G. Martin[2], if there is warm and damp climate, equitable distribution of rainfall and temperature, rubber tree will grow almost any where and survive a tremendous amount of ill-treatment.

Guttapercha is obtained from certain trees belonging to the family Sapotaceae, Dichopsis gutta and Palaquium gutta, which are natives of Malaya, Borneo and Sumatra[3]. The wild guttapercha was originally obtained by felling the tree and stripping the bark. Chemically, guttapercha is the trans isomer of polyisoprene, it is tough horny substance at room temperature but becomes soft and sticky upon warming to 100°C. Guttapercha are generally used in golf ball covers, sheeting, tubing and submarine cables. Balata which has the same chemical composition and commercial applications as guttapercha, is from south America.

The natural rubber latex is obtained from the tree by a systematic "tapping"

procedure which consists of cutting at an angle through the bark of the tree to the cambium. A small cup is hung at the end of the cut, the white latex flows from the wound and collected into the cup. The total solids content of the fresh latex, of the tree of average age is between 32-38%. The solid content of the latices from the younger trees is sometimes as low as 20% and from the older trees and trees that have not been tapped for a long period of times it is as high as 45%. Approximately 90% of the total solids of the latex is rubber hydrocarbon[4]. The non-rubber constituents found in the field latex are composed of protein, lipids, quebrachitol and inorganic salts. All of the last two components are entirely present in the aqueous phase or in the serum. The lipids are mainly found on the surface or in the interior of the rubber particle, and the proteins are distributed between the serum and the rubber-serum interface[5]. There are also present enzymes, sugars, tannins, alkaloids and some constituents as present in the bark of the tree. The particle size and molecular weight of the rubber from Malaysia have been studied and it is reported[6-9] that the particle diameter of this rubber is between 0.1 to 0.3 micron and the molecular weight is between 10^3-10^6.

The latex that flows from the trees is almost neutral, but the enzymatic and bacterial action soon change its pH to the acidic side. Under acidic condition the protein and lipid layers of the rubber particles get disintegrated and the rubber latex tends to coagulate and at a later stage putrification sets in giving bad odour. In order to keep the latex in a stable state and to prevent putrification preservatives and bactericides are added to the latex as soon as possible after it is collected from the tree. The common preservative for rubber latex is ammonia, but formaldehyde, sodium hydroxide, soap and certain bactericidal chemicals such as salt of pentachlorophenol are also used.

Among the preservatives mentioned above, ammonia is preferred to the other because in addition to its bactericidal properties it acts as an alkali, increases the pH of the system, thus making the latex more stable. For certain purposes the requirements of ammonia is decreased by simply adding formaldehyde which yield hexamethylenetetramine that acts as an accelerator during conventional vulcanization. Beside the bactericidal properties and alkalinity the ammonia reacts with the naturally occurring fatty acids in the latex forming soaps which is sorbed on the rubber particles and stabilize the latex and its fluidity is maintained. The disadvantages of the ammonia as preservative are its relative high cost and loss due to volatilization. Ammonia resistant bacteria may develop strain in the latex thus decreasing its storage life. The high ammonia preservative is also undesirable for practical difficulties involved in processing the resulting skim latex. Further high ammonia adds to bad odour and pollution.

Considering the advantage and disadvantage of ammonia, combination of preservatives, having low ammonia, are widely used for natural rubber latex. A typical combination of low ammonia (LA) preservative system[10] for natural rubber latex are as follows:

i) LA-SPP : 0.2% ammonia + 0.2% sodium pentachlorophenate on the weight of the whole latex.

ii) LA-ZL : 0.2% ammonia + 0.1% Zinc dithiocarbamate + 0.05% lauric acid on the weight of the whole latex.

iii) LA-BA : 0.2% ammonia + 0.24% Boric acid + 0.05% lauric acid on the weight of whole latex.

iv) LA-TZ : 0.2% ammonia + 0.13% TMTD + 0.013% ZnO + 0.05% lauric acid on the whole weight of the latex.

The latices to which preservatives have been added immediately after collection form the plants are known as field latices. The natural field latices are not uniform in composition and contain approximately 60-70% water. In order to get more uniform and higher solid containing natural rubber latex the field latex is to be concentrated. Generally four methods are used for the concentration of field latex. The methods for the concentration of latex are: electrodecantation, evaporation, creaming and centrifugation. Among the four methods the last one is predominating. Most of the natural rubber latex concentrates, now commercially available, are centrifuged latex. The requirements[11] for the natural rubber concentrate are specified in ISO 2004.

At present the natural rubber latex concentrates containing about 500,000 tones dry rubber are produced annually throughout the world. This quantity is expected to increases steadily. The natural rubber concentrate representing a single type of polymer have a surprisingly wide range of use. Its main uses are the production of dipped goods, such as house hold gloves, surgeons gloves, balloons, condoms, bladders, catheters etc. Other products of natural rubber latex are adhesives, binder, thread, carpet baking, moulded foam etc. At present the future of natural rubber concentrate seems to be assured by the strong upward trend in demand for rubber gloves. Most important use of the natural rubber latex concentrate is in the production of medical/surgical gloves. This products is the largest single items in tonnage term made from natural latex[12].

To ensure, a good future, latex concentrate producers need to improve the consistency of their products in certain respects, particularly in the reproducibility of processing behavior. The ability to do this depends on effective research in deter-

mining the relation between concentration and latex properties and processing performance. For the purpose of production of quality goods from natural rubber latex the properties like tensile strength, modulus, elongation at break, permanent set etc. have to be improved. These are done by means of cross-linking the rubber molecules, which is known as vulcanization. Usually natural rubber latex is vulcanized with vulcanizing agent such as sulphur and accelerator e.g. zinc diethyldithiocarbamate and activators such as zinc oxide and the like.

Other factors affecting the future prospects for natural rubber latex include the cytotoxicity , its effects upon the environment and nitrosoamine. The medical/examination gloves come in contact with the patient and medical personals and for these reasons the safety becomes important. Medical personnel must have confidence that the gloves they use should provide effective protection against the transmission of virus and bacteria. Catheters/tubing are often placed inside the body, in contact with body tissues, for relatively long periods and so for the sake of patient's health it is important that no adverse tissue reaction occurs. Unfortunately it has been reported that urethritis and/or urethral structures caused by urinary catheters related to cytotoxicities of the material used[13]. As a result of clinical complaints in Australia, the cytotoxicity titration assay included as a safety test for urinary catheters in Australian Standard[14].

Another field of the use of natural rubber latex is balloon. The market of the balloons have been growing fast for many years. Due to the presence of nitrosoamine in the latex some restrictions are being imposed upon the manufacture of balloon, babies-teats and baby-soothers in Germany[15]. The reasons for this proposed restriction is that the toys balloons, like teats and soothers come in contact

with the children's mouth. Environmental consideration may also become an important factor affecting the growth of balloon usage. Although thin latex films are biodegradable, the conventional formulation of rubber balloons do not favour biodegradation.

It is to be noted that the natural rubber latex (NRL) does not contain nitrosoamine. The presence of nitrosoamine in the rubber products is the resultant effect of the substances used in the latex formulation. In order to meet the existing nitrosoamine regulation it should be noted that

(i) the rubber should be free from extractable nitrosoamine or nitro-stable amine
(ii) the vulcanization system should be based on accelerators containing zero or low level of nitrosoamine
(iii) latex products should be leached with water to remove unwanted hydrophilic and water soluble materials.

Considering the above factors such as cytotoxicity, presence of nitrosoamine and the effects of natural rubber latex products on the environment, radiation cross-linking of natural rubber latex (radiation vulcanization) is getting popular. This process of vulcanization offers the possibility of solving some of these problems.

Radiation vulcanization/cross linking in natural rubber latex has been in use for about four decades. D.W. Pounder[16] first published a paper, which was subsequently patented, on irradiation of natural rubber latex in 1956. Although the radiation vulcanization of natural rubber latex is still in the development stage, it has

been shown that irradiated natural rubber latex (RVNRL) can be used satisfactorily in the production of coagulant dipped goods.

Malaysia, Indonesia, Thailand, China, Liberia and Srilanka are the main natural rubber producing countries of the world. Other rubber producers are Vietnam, Kampuchea, Brazil and Nigeria. To meet the demand of natural rubber, experimental rubber cultivation project are there in our country. At present about 52,000 acres of land are under rubber cultivation and about 2,300 tones of dry rubber are produced annually in Bangladesh. Here only R.S.S (Rubber Smoked Shees) are produced. Though no detail statistical data are available but it may be assumed that about 2,500 tones of natural rubber latex concentrate are used per annum in our rubber industries. The annual field latex production in Bangladesh is 7,600 tones (on the basis of 30% dry rubber content). If the entire field latex of the rubber estates of this country are used to produce the natural rubber latex concentrate then this will be more economic and the country will ultimately meet the demand of the natural rubber latex concentrate.

Ahammad Ullah *et al*[17], who appear to be the first in this country, were engaged in the rubber research. However it is yet to get momentum to produce desirable effect on the economy, research and development of the latex product of our country. We have started the present study of the field latex of Bangladesh. We have analyzed, studied radiation vulcanization of field latex, latex concentrate and tested the products.

1.2 Present status of the studies on rubber latex

A brief account on the collection, preservation and concentration of field latex, its preparation for radiation vulcanization and its properties before and after vulcanization is presented here.

1.2.1 *Collection, preservation and concentration of field latex.* Collection of Hevea latex in unwashed ceramic/clay cups results in an increase in volatile fatty acid number with time. Replacement of aluminum cups with clay tapping cups results in a lower yield of rubber and an increased in coagulum yield. To retain the quality of latex collected in ceramic/clay tapping cups when the latex can not be processed immediately preservative must be added as soon as possible[18]. Latices in polybags can be kept fluid up to four weeks by using TMTD-ZnO mixture type biocide. Concentrate produced from such latices can also be stored normally without showing any adverse technical properties of the rubber made from them[19].

Hevea latices are preserved and kept fluid by adjusting the latex pH up to 8 by repeated addition of ammonia or urea or both. Thus, field latex adjusted to pH 9 with ammonia and maintained at this pH by the addition of ammonia for 5 days found to remain fluid even after 21 days without further addition of ammonia[20]. The latex can also be stabilized by altering bacterial metabolic activity. Sometimes the volatile fatty acids develop quite rapidly in field latices preserved with ammonia and zinc dialkyldithiocarbamate even though they are virtually sterile. Using a culture medium containing latex serum and ammonia much higher bacterial counts were obtained. Ammonia-loving bacteria, very efficient producers of volatile fatty

acids, may account for the coagulation of apparently good latex concentrate after a few weeks storage[21].

The production of volatile fatty acids by bacteria and yeasts in Hevea brasiliensis field latex was reduced by heating up to 24 hours at 45-60°C with 0.3 wt% ammonia[22]. The volatile fatty acid formation, during the storage of ammonia preserved field latex caused by bacteria and enzymic contamination, was inhibited by the addition of 0.05-0.10% zinc oxide or 0.01-0.03% zincdiethyl-dithyocarbamate. Thus, volatile fatty acid number of ammonia-preserved latex, containing 0.05% zinc oxide, increased from 0.03 to 0.04 during 19 days of storage, whereas the same latex without zinc oxide it increased to 0.59 in the same period[23]. A stabilizing system, consisting of sodium-diethyldithiocarbamate (I), zinc oxide and lauric acid (II),is sometimes added to latex of 25-45% solid content to prevent degradation by bacteria or enzymes, and coagulation before, during, after concentration of latex to 55-70% solids. 0.10 - 0.50% ammonia and sufficient phosphate can precipitate all the magnesium ions present in the latex. When the stabilizing system, comprising (I) 0.005%, zinc oxide 0.010% and (II) up to 0.100%, is added to a 35% solid containing latex in the presence of 0.36% ammonia, the latex be stored for 1-5 days and then concentrated to 62% solids by centrifugation. The latex stability and also storage time increased with (II)content[24].

It has been reported that $MeNH_2$ (optimum concentration 0.3-0.7%) is more effective in preventing bacterial activity in latex concentrate than the conventional ammonia (concentration 0.7%). However, magnesium removal by $MeNH_2$ from the latex is not as effective as with ammonia. The mechanical stability, which was low with the $MeNH_2$ preserved latex, was increased by the addition of ammonium

laureate. The $MeNH_2$-preserved latices are used to produce dipped goods and latex foams without difficulty. The products are also comparable, in appearance, to those of ammonia preserved latex. Surface skim formation was negligible in the case of $MeNH_2$-preserved latices.[25]

The centrifugation is the best known method for concentration of rubber latex. It is rapid and can be adjusted to increase the dry rubber content up to 60%. Other methods include evaporation, creaming and electrodecantation. Evaporation is suitable for latex with a high rubber content. Creaming is simple but takes a long time to produce a large amount of concentrate . Electrodecantation is more complicated and relatively less used. Centrifugation is the most used method for latex concentration[26].

1.2.2. *Properties of field latex and its concentrate.* Chemical and physical properties of dried rubber and total solids from 10 clones have been studied at the Rubber Research Centre of Thailand. The clones were from high-yielding rubber plants and the results are comparable with the standard rubber.[27] The field latices from different clones have been characterized. The total solid content increases and the protein content decreases with increasing the age of the rubber trees. The average rubber particle sizes are found between 190 and 234 nm. The number average molecular weight($\bar{M}_n$) of rubber particles varies from 160,000 to 700,000, while the weight average molecular weight ($\bar{M}_w$) varies from[28] 500,000 to 1,000,000. Composition analysis of the field latex of Bangladesh reveals that its rubber and non-rubber constituents vary considerably during different seasons of the year. During the dry season (February to June) its total solid and rubber content increase, the maximum values being 37.90% and 32.60% respectively. During the

rainy season these values gradually decrease to 32.24% and 30.15% respectively. The average value of the total solid, dry rubber, rubber hydrocarbon, acetone extract, protein, ash, lipid and sugar etc. and water content during a year are (%): 35.74, 32.90, 31.13, 2.07, 1.77, 0.44, 0.33 and 64.24 respectively.[17]

The mechanical stability time (MST), KOH number, nitrogen content and volatile fatty acid number of the high-ammonia preserved Hevea latex concentrate stored in aerobic and anaerobic condition are affected by temperature and storage time. MST is affected by storage even for a month[29]. The KOH number increases with the increasing storage time and temperature indicating degradation during storage. The higher fatty acids and amino acids in latex are also affected leading to increase in carbon dioxide number, volatile fatty acid number and alcohol extract fraction. The condition of storage, aerobic or anaerobic, also affects the acid values of the extract corresponding to the observed values of MST, KOH number and CO_2 number. Storage of latex not only affects its chemical properties, it also affects the technological properties of rubber films from the stored latex significantly. The mechanical stability of the NR latex can be influenced by a number of factors, such as additives and storage condition. The effects of the most of the factors can be explain in terms of classical colloidal stability theory. The mechanical stability test remains valuable as a measure of the stability of latex particles towards mechanical influence[30].

Lipids, which form one of the major membrane components surrounding the rubber particles in NR latex, play an important role on the mechanical stability of the latex which is stored in the presence of ammonia. It has been found that major lipid components, glycolipid and phospholipid, in fresh rubber latices of six Hevea

brasiliensis clones do not vary considerably in the presence of ammonia. Consequently the volatile fatty acids generated in each clone expected to be equal. The MST of six clonal latices differ significantly, 1000 to 300 seconds. The formation of volatile fatty acid is not a major factor that contributes to the increase of MST of high-ammonia latex concentrate. This is contrary to what has been reported previously[31].

Soap producing natural higher fatty acids (HFA) in the NR latex is determined by cold extraction, which unlike hot extraction does not cause hydrolysis of lipids. The concentration of natural HFA in the NR latex increases with time, reaching a constant value in 3-6 weeks. The adsorption of the natural HFA on the surface of the NR particle increases the surface charge density which in turn increases the mechanical stability of the latex. When the natural HFA is stabilized by adsorption, further increase in MST is caused by aerial oxygen[32].

1.2.3. *Effects of radiation on NR latex*. NR latex containing 60% solids has been vulcanized by gamma-radiation upto to 300 kGy. Although rubber latex starts curing at relatively low dose of 10-50 kGy, but crosslink density at this radiation dose was very low[33]. The degree of vulcanization of latex at a given dose has been found to be higher than that of dry rubber. Exposer of NR latex, containing 3% carbon tetrachloride as sensitizer, to electron beam or gamma-radiation cause pre-vulcanization. Subsequent coagulation and drying at 70°C give a rubber with tensile strength equal to 250 kg/cm^2, elongation at break 1000%, modulus of 10 kg/cm^2 at 300% elongation and 5% residual compression[34]. Results of the use of reduced amount of carbon tetrachloride sensitizer are also available. The effect of monofunctional acrylic monomers, such as, butyl acrylate, ethyl acrylate, methyl

acrylate and methyl methacrylate in radiation vulcanization of natural rubber latex has also been studied. Butyl acrylate in small quantity 2 phr (per hundred of rubber), seems to be the best monofunctional acrylic monomer sensitizer[35]. A combination of Bu-acrylate with carbon tetrachloride in 1:1 ratio(2 phr) proved to be a promising sensitizer mixture. Using this mixture, the optimum dose of irradiation is about 20 kGy, while the film tensile strength is about seven times of its green strength.

Among several monomers, 2-ethylhexyl acrylate exhibited high vulcanizing efficiency. The maximum tensile strength 30 MPa can be obtained in this case at 30 kGy[36]. Vulcanization can be accelerated when NRL is irradiated in the presence of polyfunctional monomers. In this respect hydrophobic monomers are more effective than the hydrophilic monomers, presumably due to the high solubility of the former in rubber particles. Of the 26 poly functional monomers studied, neopentyl glycol dimethyl methacrylate exhibited the highest efficiency in accelerating the vulcanization. Advantages of using neopentyl glycol dimethyl methacrylate included high colloidal stability of the irradiated latex and the high resistance to dried rubber film[37]. The NRL has been vulcanized at low cost by irradiation with ionizing radiation in the presence of 2-ethylhexylacrylate and carbon tetrachloride. In this process NR latexes were stirred with 5 phr 2-ethylhexyl acrylate and 2 phr carbon tetrachloride, followed by 5 kGy gamma-radiation at room temperature. It was then cast on a glass plate and dried to get 0.45 mm thick film. The tensile strength of the film was 28.5 MPa and 990% elongation at break. However, when only carbon tetrachloride was used the film could be produced by irradiating the latex at 30 kGy gamma-radiation. The tensile strength and the elongation at break (%) of the film were 24.7 Mpa and 890% respectively[38].

When a hydroperoxide is used as a co-sensitizer for n-butyl acrylate (n-BA) in the presence of potassium hydroxide the NRL can be vulcanized at much reduced gamma dose. The latex, in which hydroperoxide had been used before n-BA was added, was found to be more stable than that with n-BA alone[39] Among the four hydroperoxides studied t-butyl hydroperoxide exhibited high vulcanization efficiency at low concentration and at a low dose of 8 kGy.

The effect of the addition of hydrogen peroxide before radiation vulcanization has also been studied. It has been found that the addition of small amount (2.5 phr of 30% of H_2O_2) not only decreases the optimum radiation dose but also increases the maximum tensile strength of the vulcanized film. However, the use of excessive amount of hydrogen peroxide causes reduction in the tensile strength and the crosslink density of the film[40].

n-Butyl acrylate (n-BA), as a sensitizer for radiation vulcanization of NRL, has several advantages. One of these is the easiness of removal of residue after drying. The efficiency of n-BA, as a sensitizer, without the addition of carbon tetrachloride as co-sensitizer, is so high that the optimum vulcanization dose is only 15 kGy with 5 phr n-BA. However, n-BA tends to destabilize NRL[41].

The sensitized radiation vulcanization of NRL has been carried out with a 3MeV, 25 mA dynamitron accelerator in the presence of n-butyl acrylate, 2-ethylhexyl acrylate and 1,6-hexanediol diacrylate over a dose rate of 0.3 to 60 kGy/sec. It has been found that the sensitized vulcanization of NRL with electron beams increases with the increase in the dose rate[42].

The radiation vulcanization of natural rubber latex (RVNRL) with electron beam from dynamitron accelerator at 1.5 MW and 20-25 mA and at a dose of 60 kGy with 5 phr trimethylolpropane trimethyl acrylate has been studied. Several kinds of rubber products such as surgical gloves, urinal condoms and cork soles were produced from the radiation vulcanized latex. Good running properties of the products have been reported. However it was found necessary to increase the tensile strength, to reduce the stickiness and the permanent set of these products[43].

A kinetic study has also been made on the sensitized radiation vulcanization of natural rubber latex with high dose rate electron beams. The rate of vlcanization (R_{vul}) depends on the sensitizer concentration (M) and the dose rate (I). Following equation was obtained

$$R_{vul} = K\, M^{0.5}\, I^{0.75}$$

An advantage of the high dose vulcanization has been reflected in the aging properties of RVNRL products. It is to be noted that the rubber film prepared from the electron beam vulcanized NRL has been found to be superior to those prepared from gamma-ray vulcanized NRL[44].

Correlation between protein content and the radiation dose, needed for the maximum tensile strength of the rubber film, has been found out. It appears that the radiation dose for the optimum tensile strength of the film varies inversely with the protein content of the latex. The optimum protein content, for which the tensile strength of the film is the highest, is between 1.0 to 2.0% on the basis of the total solid content[45] (TSC).

The non-rubber contents of the latex do not affect the cross link density of the film from RVNRL. However, latexes with comparatively lower non-rubber contents yielded films of better physical properties[46].

The effects of heating and leaching on the mechanical properties of RVNRL film have been investigated. It is reported[47] that heating and leaching improved the tensile strength of film considerably. The tensile strength has been found to increase as high as 25% upon heating alone at 70°C and as high as 75% upon leaching and heating at the same temperature. The increase in the tensile strength has been attributed to the reduction of the moisture content, better particle cohesion and improved entanglement of the molecular chain. Leaching and heating of the RVNRL film have been found to be important to obtain better and reproducible results when its mechanical properties were investigated[47]. The mechanical stability of RVNRL, its potassium hydroxide number and volatile fatty acid number remain within the limits of the British Standard Specification[48] for at least twelve weeks. The dried films, dipped goods and condoms prepared from RVNRL have low modulus, fairly high tensile strength, high ultimate elongation and low permanent set. Transparent and soft gloves are obtained from RVNRL by coagulant dipping process[49]. The mechanical properties of the gloves meet the Japanese industrial Standard Specification for protective gloves[50] .

1.3 Definition of terms

1.3.1 *Natural rubber latex.* It is a colloidal dispersion of rubber particles in aqueous phase. On visual inspection it looks milky white. It has no putrefactive or bad odour even after neutralization with boric acid. The blue or grey colour of the

latex indicates contamination with iron. Field latex is the term used for natural rubber latex to which ammonia solution has been added as preservative (preserved latex).

1.3.2 *Dry rubber content of latex*. It is the acid coagulable portion of latex after washing and drying.

1.3.3 *Non-rubber solids*. It is the portion of the latex which is not coagulated with acid. Its quantity is determined by the difference between the total solid and the dry rubber content of the latex.

1.3.4 *KOH Number*. The number of grams of KOH required to neutralize the acids present in 100 g of the total solids in the latex.

1.3.5 *Concentrated natural rubber latex*. It is the natural rubber latex with total solids content above 60%.

1.3.6 *Serum*. It is the dispersion medium of a latex.

1.3.7 *Centrifuged rubber latex*. It is the latex obtained in the concentrated form when the serum is removed by centrifugation.

1.3.8 *Creamed rubber latex*. It is the latex, the rubber concentration of which has been inreased by creaming and removal of serum.

1.3.9 *Preserved rubber latex*. It is the latex that has been treated to inhibit putrefaction and accompanying coagulation.

1.3.10 *Vulcanization*. This is a process by which rubber, through change in its chemical structure (for example cross-linking), is converted to a form upon which the elastic properties are conferred or they are re-established or improved or extended over a greater range of temperature.

1.3.11 *Prevulcanized rubber latex*. It is the latex in which the rubber particles have been partially vulcanized. Films and useful articles can be made from it by simple drying.

1.3.12 *Test piece*. A piece of material of appropriate shape and size, which is prepared for ready use in a test.

1.3.13 *Gauge length*. It is the standard length of a test piece, which is taken for the measurement of the elastic properties.

1.3.14 *Tensile strength*. It is the maximum tensile stress applied to a test piece immediately before its rupture.

1.3.15 *Tear strength*. It is the maximum force, acting substantially parallel to the major axis of a specified test piece, required to tear it.

1.3.16 *Permanent set*. It is the residual deformation remaining after complete release of the force producing the deformation.

1.3.17 *Elongation at break*. It is the percent elongation of a test piece at rupture.

1.3.18 *Green strength.* It is the tensile strength of the film produced from the field latex. The tensile strength measured without leaching or other treatment of the film.

1.4. Object of the present studies

Bangladesh is a good consumer of natural rubber. About 2,300 tons of dry natural rubber, equivalent to about 7,600 tons of natural field latex, is produced in Bangladesh annually. Rubber goods are produced here by conventional vulcanization of natural rubber. But for the manufacture of latex products prevulcanized latices are imported from Malaysia. Conventional vulcanization of rubber latex is a complicated process. This involves the use of sulphur, zinc oxide etc. as vulcanizing agent and stabilizers. Nitrosoamine is generated unavoidably by conventional vulcanization process. Natural rubber industries in Australia and Europe, specially in Germany, are facing nitrosoamine restriction. There are two aspects of nitrosoamine restrictions. These are (i) its concentration in the environment and (ii) its concentration in rubber products. It has been observed that radiation vulcanization of natural rubber latex can get rid of nitrosoamine in the products. The main uses of the natural rubber latex are for the production of surgical gloves, house hold gloves, bladders, catheters, balloons, condoms etc. These products often come in the close contact of the consumers body. Consequently it is important to produce these products of low cytotoxicity, which is kept to the minimum by radiation vulcanization of latex. Moreover, rubber goods

of better transparency and softness are obtained from rubber made by radiation vulcanization of latex.

Except some preliminary work by Ahammad Ullah *et al*[17] hardly any research has been done on the rubber latices of Bangladesh. The latices from different zones of rubber plantation of the country yet to be characterized. It is also necessary to find out the appropriate method and optimum conditions to concentrate the field latices before the radiation effects can be studied on them.

In this thesis results of study on the physical properties of latices, from different rubber plantations of Bangladesh, such as tensile strength, elongation at break, permanent set of the vulcanized latex, etc. have been presented. These will help evaluating the quality of the vulcanized latex. A method has also been developed for the radiation vulcanization of the natural rubber latex using lower radiation dose.

CHAPTER-2
EXPERIMENTAL
(*part-1*)

2.0 COMPOSITION AND PROPERTIES OF NATURAL RUBBER LATEX

2.1 Chemicals

Following chemicals were used without further treatment

Ammonia solution (BDH), acetic cid (BDH), alcohol 95% (Keru and Company, Bangladesh), nitric acid (BDH), sulphuric acid (BDH), hydrochloric acid (BDH), phosphoric acid (BDH), formaldehyde solution (BDH), sodium hydroxide (BDH), potassium hydroxide (BDH), barium hydroxide (BDH), ammonium sulphate (BDH), copper sulphate (BDH), citric acid (BDH), potassium hydrogen sulphate (BDH), ferrous ammonium sulphate (BDH), quinhydrone (BDH), 1,10-phenanthroline (BDH), potassium periodate (BDH), potassium permanganate (BDH), acetone (BDH), chloroform (BDH), boric acid (BDH), trichloroetane (BDH), sodium diethyldithiocarbamate (BDH), zinc sulphate hepta hydrate (BDH). anhydrous sodium sulphate (BDH), chromic oxide (BDH), anhydrous potassium sulphate (BDH).

2.2 Apparatus

2.2.1 *Temperature controlled vented air oven.* It was used to dry the latex for the determination of TSC and for drying latex films.

2.2.2 *Steam bath.* This was used for the digestion of acid coagulated latex for the determination of DRC.

2.2.3 *Magnetic stirrer.* This was used for mixing various substances with latex.

2.2.4 *Centrifuge.* It was operated at 2300 rpm with 50 mL pear-shaped centrifuge tube held in a centrifuge accessory. It was used to determine the sludge content of the latex.

2.2.5 *Stainless steel sieve (180 micron).* It was used to separate the coagulum from the latex. It was also used to remove the coagulated and suspended impurities from the latex during the preparation of cast latex film.

2.2.6 *pH meter (Digital, PW 9409, Phillips, England).* It was used for the measurement of pH of the latex. It was also used for the determination of KOH number of the latex.

2.2.7 *Recording Viscometer (Visconic ELD. R, Tokimec, Inc. Japan).* It was used to determine the viscosity of the latex.

2.2.8 *UV-160A UV-Visible spectrophotometer (Shimadzu, Japan).* It was used for the determination of copper, manganese and iron in the latex as ions.

2.2.9 *Latex concentrator.* Laboratory scale latex concentrator (Fuji Electrical Co. Ltd., Japan With SP-100 Starter Saito Separator Limited) was used for the production of concentrated latex. By controlling the feeding rate of the latex in the concentrator and using appropriate ring diameter the total solid content of the latex was raised up to 60%.

2.2.10 *Mechanical stability determination apparatus.* Mechanical stability determination apparatus (BS 1975, England) consists of a vertical shaft high-speed

stirrer capable of maintaining a speed of 14000 ± 200 rpm. The diameter of the stirrer shaft is approximately 0.25 mm and at its lower end the agitator disk is attached. The shaft is of sufficient length to reach conveniently the bottom of the latex container. The latex container is a flat bottomed cylinder of height not less than 90 mm, with 58 mm internal diameter and of approximately 2.5 mm wall thickness. The container had smooth internal surface.

2.2.11 *Kjeldahl apparatus*. Digestion flask of capacity 800 ml and Kjeldahl distillation unit, with a condenser, have been used for the determination of nitrogen.

2.2.12 *Soxhlet extraction apparatus*. It has been used for the determination of acetone and acetone : chloroform (1:2) extracts.

2.2.13 *Ground glass joint steam distillation apparatus. It has been* used for the determination of volatile fatty acids in latex and for direct determination of isoprene polymer or rubber hydrocarbon in the TSC of latex.

2.2.14 *IR Spectrometer*. Shimadzu IR-470, Japan, was used for recording IR Spectra of different latex films.

2.3 Preparation of Solutions

2.3.1 *Standard Sodium carbonate solution*. Sodium carbonate was heated at 250-260°C to constant weight. Requisite amount was taken in a volumetric flask and dissolved it in water to make solution of required strength. This solution was used to standardize sulphuric acid in the presence of methyl orange indicator.

2.3.2 *Sulphuric acid solutions.* Requisite volumes of the concentrated acid was carefully added to water to make solutions of different strengths.

2.3.3 *Oxalic acid solution.* Oxalic acid crystals, previously dried in a desiccator, were accurately weighed and dissolved with water in a volumetric flask to make solution of desired strength. This solution was used for the standardization of sodium and potassium hydroxide solutions in the presence of phenolthalein indicator.

2.3.4 *Carbonate free potassium hydroxide solution.* 10 mL portions of about 40% solution of KOH in distilled water were titrated with 10% barium chloride solution to determine the volume of the solution required to precipitate the carbonate present in the 40% KOH stock solution. After the addition of the requisite volume of barium chloride solution in the stock solution the precipitate was allowed to settle. The supernatant solution, which was found free from carbonate, was standardized prior to use. 0.50 M carbonate free solution was used to determine the KOH number of the latex.

2.3.5 *Barium hydroxide solution.* $Ba(OH)_2$, 8 H_2O was dissolved in freshly boiled and cooled distilled water to make a saturated solution. When required the supernatant solution was filtered and sufficient quantity of it was taken and standardized, using bromothymol blue indicator, to get 0.005 M solution. The standard solution was stored in a polyethylene bottle and used for the determination of volatile fatty acids in the latex.

2.3.6 *Acid Solutions*. 2% (v/v) acetic acid, 1:3 nitric acid, 1:3 hydrochloric acid, 1:5 sulphuric acid and 1:19 sulphuric acid solutions were prepared by diluting 98% acetic acid, 36% nitric and hydrochloric acid and 98% sulphuric acid respectively in water.

2.3.7 *Ammonia- Ethanol Solution*. Ammonia-ethanol solution was prepared by mixing 10 mL of 25% ammonia solution, 840 mL of 95% ethanol and 1000 mL water. This mixture was used for the determination of sludge content in the latex.

2.3.8 *5% (w/v) soap solution*. 5% aqueous solution of potassium oleate of pH 10 was prepared by dissolving 50 g potassium oleate in 1000 mL water. The solution was used to determine the coagulum content of the latex.

2.3.9 *5% acid free Formaldehyde solution*. Definite volume of USP grade formaldehyde solution (36%) was neutralized with 0.1 M KOH solution using phenolphthalein as an indicator. The same volume of the solution was taken and equivalent amount of KOH solution was added to it and finally diluted with distilled water to make 5% solution. This formaldehyde solution was used to adjust the ammonia content in the water phase of the latex during the KOH number determination.

2.3.10 *Ammonium sulphate solution*. 35% (w/v) solution was prepared by dissolving $(NH_4)_2SO_4$ in distilled water. This solution was used for the separation of serum from the latex during the determination of volatile fatty acids in the latex.

2.3.11 *Sodium alginate solution.* 2% (w/v) solution was prepared by dissolving sodium alginate in water with stirring for half an hour. This solution was used for latex concentration by creaming process.

2.3.12 *Catalyst solution.* 110 g K_2SO_4, 14.7 g $CuSO_4.5H_2O$, 3.7 g selenium powder and 600 mL sulphuric acid (Sp. Gr. 1.84) were taken in a 1 litre beaker and dissolved with heating. The catalyst solution was used for the digestion of dry latex for the determination of nitrogen.

2.3.13 *Chromic acid digestion mixture.* 200 g CrO_3 was dissolved in 500 mL water and 150 mL conc. sulphuric acid was carefully added to it. This solution was used to determine rubber hydrocarbon in the dry latex by direct oxidation method.

2.3.14 *Zinc diethyldithiocarbamate reagent.* 1g sodium diethyldithocarbamate was dissolve in water and 2g zinc sulphate hepta hydrate was added to it. The resulting zinc diethyldithiocarbate was extracted with 100 mL 1,1,1-trichloroethane. The trichloroethane layer was separated and diluted to 1 litre with trichloroethane and used for the spectrophotometric determination of copper.

2.3.15 *1,10-phenanthroline solution.* 0.5g 1,10-phenanthroline was dissolved in hot water and after cooling diluted to 500 mL. This solution is used for the determination of iron in the dry latex.

2.3.16 *Quinhydrone solution.* Saturated quinhydrone solution was prepared in the usual way.

2.3.17 *Buffer solution.* Buffer solution was fressly prepared by addition of 2.50 mL of concentrated sulphuric acid to a solution of 20.50g of sodium acetate, the final volume of the solution being 250 mL.

2.4 Collection, preparation and preservation of latex samples

Forty different field latex samples from 100 rubber trees of various clones and ages were collected from the eleven rubber estates of Chittagong and Sylhet rubber zones under the Bangladesh Forest Industries Development Corporation (BFIDC). The rubber estates of Chittagong zone were Rawzan, Dabua, Kanchannagar, Haludia, Datmara, Tarako and Ramu and the rubber estates of Sylhet rubber zone were Satgaon, Rupaichara, Sahajee Bazar and Vatara. The latices were preserved with 20-25 mL/L of 25% ammonia solution immediately after collection from the trees. In addition following latex samples were also collected

(1) Eight samples, four from the Rawzan rubber estate of Chittagong and four from the Satgaon rubber estate of Sylhet, at three months interval over one year

(2) Eleven samples, each from the bulk collection of the eleven rubber estates under BFIDC

All these samples were preserved in ammonia solution.

The remaining field latices from the above eleven rubber samples were mixed together to get one mixed portion of field latex sample. This mixed field latex

sample was divided into three portions. One portion was used as mixed field latex, another portion was used for the production of centrifuge concentrated latex and the third portion was used for the production of cream concentrated latex. The rubber and non-rubber contents that were left in the serum of the centrifugation and the creaming processes were coagulated or dried and preserved.

2.4.1 *Concentration of the field latex.* Due to the non-uniformity in quality and low solid content, field latices are not suitable for the production commercial items. In order to get uniformity in quality and to make them suitable for the manufacture of commercial products, latices need to be concentrated to get approximately 60% rubber content. In this study latices were concentrated by two different methods namely

(i) concentration by centrifugation and
(ii) concentration by creaming.

2.4.1.1 *Concentration of field latex by centrifugation.* The field latex was taken in a feed tank (a separating funnel) and desired quantity of latex was charged into the latex concentrator at a constant rate of 2 L/ hour. The diameter of the ring of the concentrator was 31.5 mm. These parameters were determined by trial and error. The solid concentration achieved was 60 ± 1%. The solid content of the serum was 10-12%.

2.4.1.2 *Concentration by creaming.* This method was used for the production of cream concentrated latex. A creaming agent was added in the latex to

accelerate the tendency of the latex to cream. For the convenience of handling and mixing 2% aqueous solution of sodium alginate was used as a creaming agent.

The creaming agent was mixed with 1 L latex in a separating funnel and the mixture was left at room temperature (≈ 30°C). The concentration of the solid increased with time, but the creaming was allowed to continue up to 24 hours. Table 1 shows the TSC, DRC and Density in the creamed concentrated latex at different sodium alginate concentrations. To get 60 ± 1% solid 8 phr 2% sodium alginate solution was used.

Table 1. TSC, DSC and Density of cream concentrated latex at different Sodium alginate concentration.

	Sodium alginate concentration, phr						
	4	5	6	7	8	9	10
TSC(%)	54.62	55.88	58.21	60.91	62.21	59.76	58.21
DRC(%)	52.31	53.60	55.89	59.10	60.35	57.71	56.18
Density at 30°C, g/mL	0.953	0.952	0.950	0.944	0.944	0.945	0.948

2.5 Determination of various components in latices

2.5.1 *Colour and odour of the latex*[51]. The colour of the latex was determined by visual inspection and odour of the latex was taken after neutralization of ammonia by boric acid.

2.5.2 *Total Solid Content (TSC)*[51,52]. The total solid contents of the field latex and its concentrate were determined by evaporating a known amount of

samples in a tared and weighed evaporating dish. The weighed samples were kept at 70 ± 2°C at least for 16 hours in a vented air oven until constant weight.

$$\% \text{ TSC} = 100(m_2 - m_0)/(m_1 - m_0)$$

m_2, m_1 and m_0 are the weights of the evaporating dish with the solid, the sample before evaporation and the empty evaporating dish respectively.

2.5.3 *Dry rubber content (DRC)*[51,53]. Well mixed latex/latex concentrate sample was accurately weighed (m, ≈10 g) and taken in a porcelain evaporating dish. The sample was diluted with water to make its TSC 25%. 80 mL of 2% (v/v) acetic acid was added slowly (time taken ≈ 5 min) with constant stirring. The contents of the dish were digested on a steam bath for 15 minutes. 5 mL of ethanol was added to remove the milkiness. The coagulated rubber was collected and washed with water until the washings were free from acid (tested with litmus paper). The rubber coagulum was then pressed to expel water and a uniform sheet (thickness below 2 mm) was obtained. The sheet was placed on watch glass and dried at 70 ± 2°C in the vented air oven until the weight was constant (w).

$$\% \text{ DRC} = 100w/m$$

2.5.4 *Rubber Hydrocarbon(1,4 poly isoprene)*[54,55]. Accurately weighed amount (m , about 2.0 g) of dried latex sample was wrapped with filter paper and a loose packet was made. The packet was then placed in the extraction cup of a Soxhlet apparatus and a previously weighed (x g) receiver was placed in position. The sample was extracted for 16 hours with a mixture of acetone and chloroform

(1:2). At the end of extraction the receiver was removed, the solvent was evaporated on a water bath and finally dried in an oven at 70 ± 2°C until constant weight(y g).

The percentage of extract = 100(y-x)/m.

The residue in the packet (unextracted material) was taken out and dried carefully in an oven at 70 ± 2°C. 50 mL chromic acid digestion mixture **(2.3.13)** was taken in the digestion flask of a steam distillation set and accurately weighed amount (w , ≈ 0.3g) of the residue was taken into the digestion flask, which was connected with the steam generator and a receiver. Water was taken in the receiver to keep the end of the condenser dipped in it. Steam was passed to the digestion flask and distillation was continued until about 500 mL of distillate was collected. The solution in the receiver was cooled to room temperature and titrated with standard (0.10 M) sodium hydroxide solution using phenolphthalein solution indicator.

A blank determination was made by using the same amount of all the reagents.

% rubber hydrocarbon in the TSC of the latex sample

= [9.08 x (A-B) x(100-C)]/(w x 100)

A = volume (mL) of NaOH solution required for titration,

B = volume (mL) of NaOH solution required for blank titration

C = Percentage of extraction

The factor 9.08 is incorporated to normalize the calculation in terms pure natural rubber.

2.5.5 *Non-rubber solids*. The percentage of non-rubber solids (NRS) was determined by subtracting % DRC from % TSC.

2.5.6 *Total NH_3 alkalinity*[51,56]. A portion (w, ≈ 5 g) of the well mixed latex/latex concentrate was accurately weighed in a weighing bottle and transferred to a beaker containing 200 mL water. The mixture was titrated with 0.10 M HCl solution. pH of the supernatant was measured after each addition of HCl. The addition of the acid was stopped when the pH of the solution was 6.0.

Total alkalinity (on the basis of NH_3 in the aqueous phase),%

$= (1.70 \times M \times V)/ w \times (1\text{-}TSC/100)$

where, M = molarity of the standard HCl solution and V = volume (mL) of the standard HCl solution

2.5.7 *pH of the latex*. pH of the latex samples were measured at 25°C by a standard pH meter. The pH meter was calibrated at pH 9.0 and 12.0.

2.5.8 *Sludge content*[51,57]. About 50 mL well mixed latex was taken in a weighing bottle. The weighing bottle, along with its content, was weighed. The sample was poured into a centrifuge tube and the weighing bottle was weighed again. The difference between the two weights was the mass (x g) of the latex sample taken into the centrifuge tube. Approximately the same mass of another latex sample was taken in a second centrifuge tube. The tubes were stoppered and centrifuged for 20 minutes at 2300 rpm. The creamy layer was scooped off and the supernatant latex was withdrawn carefully without disturbing the sludge that settled

at the bottom of the tubes. The centrifuge tubes were then filled with ammonia-alcohol solution and recentrifuged for 25 minutes. The supernatant liquids were pipetted out from the top of the sludge. This procedure was repeated until the supernatant liquid was clear after centrifugation. The sludge was then transferred quantitatively to a tared beaker (y g) with ammonia-alcohol mixture. The beaker was heated on a hot plate to remove most of the liquid and then finally dried at 70 ± 2°C in an oven until constant weight (z g) .

The sludge content (%) = 100(z - y)/x

2.5.9 *Coagulum content* of latex[51,58]. Well mixed latex sample (w, ≈ 200 g) was diluted with 200 mL soap solution and the mixture was filtered through the 180 mm mesh cleaned, dried and tared (x g) stainless steel wire screen. The coagulum retained by the screen was washed with 5% soap solution and finally with distilled water until the washing was neutral to litmus. The screen, with its content, was dried at 70 ± 2°C in an oven to constant mass (y g).

Coagulum content (%) = 100(y - x)/w

2.5.10 *Density of latex*[51,59]. Well-mixed latex free from air bubble, water and a pre-weighed density bottle were placed in a thermostated bath at 30.0 ± 0.2°C and allowed to come to the temperature of the bath. The bottle was filled with the latex, taken out of the bath and stoppered. The body of the bottle was wiped dry and then it was weighed. All these operations was completed within three minutes. The density bottle emptied and washed free from the latex. It was thermostated, filled with water, which was in the bath, and the bottle was weighed as before.

The density of the latex is given by $D = (M_t \times D_W)/M_W$

D = density of the latex at 30.0°C (g/mL).
M_t = mass of the latex in the density bottle,
D_W = Density of the water at 30.0°C.
M_W = Mass of the water in the density bottle at 30.0°C.

2.5.11 *Viscosity*[51]. About 1.0 to 1.5 mL latex was taken in the temperature controlled (30.0 ± 0.2°C) viscometer cup. The speed of the viscometer disk was adjusted according to the TSC of the latex. The viscosity (in mPa.s) was obtained from the recorder.

2.5.12 *Determination of Volatile Fatty Acid Number (VFA)*[51,59,60]. Accurately weighed (m, ≈ 50 g) well mixed latex was taken into a 250 mL beaker. 50.0 mL ammonium sulphate solution was added to it with stirring. The beaker with, its contents, was heated (at 70°C) on a water bath for 5 minutes to coagulate the latex. The coagulum was separated from the serum by filtering through a dry filter paper (Whatman No. 40). 25.0 mL (V) filtrate was pipetted into a conical flask, acidified it by 5.0 mL (v) dilute sulphuric acid (1:5) and mixed by swirling the flask. Steam distillation set was connected to the steam generator and steam was passed through it for 15 minutes, prior to pipetting 10.0 mL (V') acidified serum into the distillation flask. A measuring cylinder was placed under the outlet of the condenser and the flow of steam was regulated to collect the distillate at a rate of 3 to 5 mL per minute. The distillation was stopped when 100 mL distillate was collected. The distillate was transferred to a 200 mL conical flask and aerated by passing carbon dioxide free air, at the rate of 250 to 300 mL/minute, for 5 minutes.

It was then titrated with standard $Ba(OH)_2$ solution using bromothymol blue indicator.

The VFA number = $(A \times M \times 1122)(W \times \%TSC)$

A = mL of $Ba(OH)_2$ solution required for titration

M = molarity of the $Ba(OH)_2$ solution

W = mass of the latex in 10.0 mL (V') acidified serum

= $(m \times V)/[(50 + S) \times (V + v)/V']$

$50.0 + S$ = mL of $(NH_4)_2SO_4$ solution + mL of serum in m g of latex.

S = (100 - DRC)/(1.02 × 2), where 1.02 is the specific gravity of the serum.

2.5.13 *KOH Number*[51,59,61]. Accurately weighed (m, containing about 50g Solids) latex was taken in a 400 mL beaker. The ammonia content of the aqueous phase was adjusted to about 0.5% by addition of formaldehyde (1 mL 5% formaldehyde solution≡0.0189 g ammonia).

The latex was diluted to 30% solids by the addition of distilled water it was titrated pH-metrically with 0.50 M KOH solution. pH of the supernatant was recorded with each addition of KOH. The end point of the titration was determined from plot of second differential of pH vs. mL of added KOH solution.

KOH number = $(561 \times M \times v)/(m \times TSC)$

M = molarity of KOH solution

v = volume of standard KOH solution.

A typical calculation of v from data in Table 2 and Fig.2. is as follows

Table. 2 The change of pH of solution with the addition of 0.5 M KOH solution

mL KOH solution	pH	1st differential	2nd differential
5.0	9.87		
		0.10	
6.0	9.97		0.01
		0.11	
7.0	10.08		0.01
		0.12	
8.0	10.20		0.02
		0.14	
9.0	10.34		0.04
		0.18	
10.0	10.52		0.06
		0.24	
11.0	10.76		-0.05
		0.19	
12.0	10.95		-0.03
		0.16	
13.0	11.11		

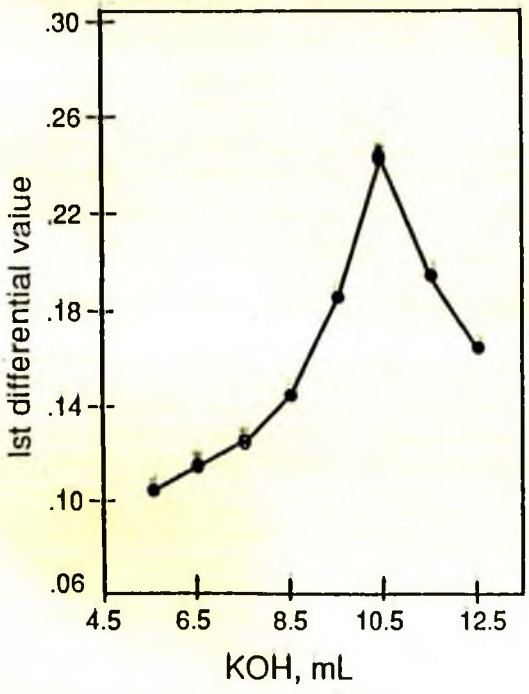


Fig. 2.a 1st. Differential vs KOH solution (mL)

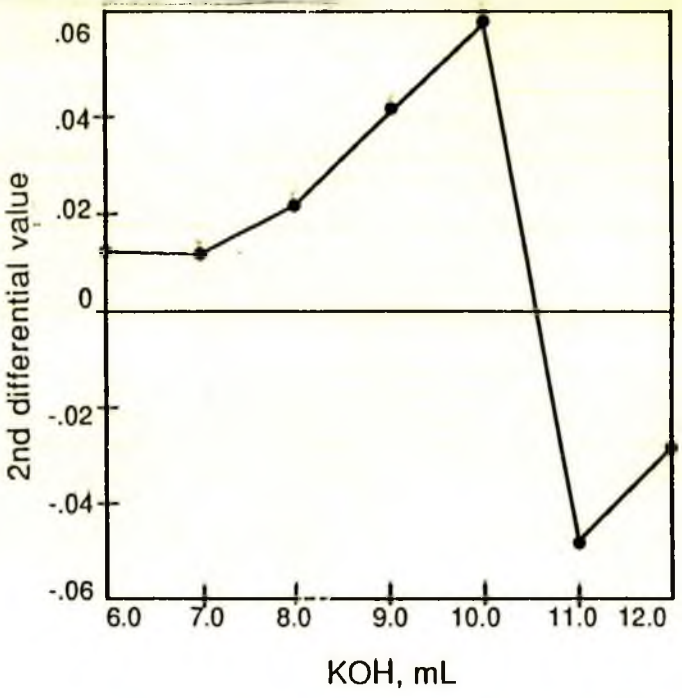


Fig. 2. b 2nd Differential vs KOH solution (mL)

The first differential reaches a maximum in the increment10.0 to 11.0 mL (Fig. 2.a) and the second differential changes from +0.06 to -0.05 (Fig. 2.b). Therefore the point of inflection lies at 10.0 + [0.06/(0.06 + 0.05)] = 10.545 mL which is the value of v.

2.5.14 *Nitrogen content*[62,63]. Sufficient quantity of well mixed latex (with TSC ≈2.0 g) was dried to constant weight following the method **2.5.2**. The dry and moisture free film was accurately weighed (m,g) and transferred to Kjeldahl digestion flask,65 mL of the catalyst solution was added to it. The content of the digestion flask was mixed by swirling and refluxed until the solution became clear. The digestion flask and its contents was allowed to cool to room temperature. 200 mL of water was added to it and the Kjeldahl digestion flask was connected with receiver through a distillation set. 75 mL of distilled water, 50.0 mL of 0.05 M H_2SO_4 and 2 drops of mixed indicator solution were taken in the receiver. Sufficient amount of sodium hydroxide solution added slowly to the distillation flask to make the solution alkaline. The contents of the flask were mixed carefully by swirling. The distillation was carried out until approximately 200 mL of the distillate was collected. The contents of the receiver was titrated with standard sodium hydroxide solution. A blank determination was carried out with the same quantities of the reagents.

Nitrogen (%) of the dried latex (i.e. TSC)

$$= 0.14\ M(V_2-V_1)/m.$$

V_2 and V_1 are volumes (mL) of sodium hydroxide required for the titration of the blank and the sample respectively. M is the molarity of NaOH solution.

2.5.15 *Ash content*[64,65]. A portion of accurately weighed (m, ≈3g.) moisture free dried latex film was taken in a previously ignited and weighed (x) porcelain crucible. The crucible with its content was heated carefully with a burner avoiding ignition. Heating was continued until the volatile products were completely removed and a charred residue was left. The crucible was then transferred to the muffle furnace and heated at 550 ± 10°C until the carbon was completely removed and the weight (y) was constant.

$$\text{Ash content (\%)} = 100(y - x)/ m$$

2.5.16 *Water insoluble ash*[66]. The ash from **2.5.15** was digested with distilled water for half an hour in a water bath and then filtered through a Whatman filter pater No. 40. The insoluble residue was dried and transferred, along with the filter paper, to a weighed (x) crucible. The crucible and its contents were then heated at 550 ± 10°C in the muffle furnace until constant weight (z).

$$\text{Water insoluble ash (\%)} = 100(z - x)/ m$$

2.5.17 *Alkalinity of the water soluble ash*[66]. The filtrate from **2.5.16** was collected in a conical flask, and titrated with standard 0.10 M HCl using methyl orange as indicator.

$$\text{Alkalinity of the ash as } K_2O \text{ (\%)} = (0.047 \times V \times M \times 100) / m$$

V (mL) is the volume of HCl solution required in the titration and M is its molarity. m is the mass of the dried latex taken for ash determination.

2.6 Standards for Analysis of metal ions

2.6.1 *Cu(II) (diethyldithiocarbamate method)*[59,67]. Standard Cu(II) solution was prepared by dissolving 0.393 g A.R. copper sulphate($CuSO_4,5H_2O$) in water, which was made acidic with 3 mL of concentrated sulphuric acid, and the volume was made 1000 mL in a measuring flask. The solution was further diluted by taking 10.0 mL and making the volume 100 mL with water in a measuring flask. 1.0 mL of this dilute solution contained 0.01 mg of Cu(II).

Calibration curve. 0, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 mL dilute Cu(II) solution, 5 mL 10% citric acid solution and 10 mL dil. sulphuric acid solution were taken in 7 separating funnels. Ammonia solution was added to each, drop by drop, until the solutions were just alkaline to litmus paper. 2 mL more ammonia solution, followed by 25.0 mL zinc diethyldithiocarbamate reagent in trichloroethane, was added to each funnel. The contents of the funnels were shaken for 2 minutes and the trichloroethane solutions were taken into the glass stoppered bottles, each of which contained about 0.1 g sodium sulphate.

The spectrum of Cu(II)(diethyldithiocarbamate) standard solution, prepared from 3.0 mL Cu(II) soltution, was taken using trichloroethane solution containing 0 mL Cu(II) solution as reference. The spectrum, with λ_{max} = 435 nm, was obtained. The absorbance values of solutions were measured at 435 nm using the same reference (Table 3). The plot of absorbance vs. concentration is a straight line passing through the origin (Fig. 3) ($\epsilon = 1.26 \times 10^4$ M^{-1} cm^{-1} at 30°C).

Table 3. Data for obtaining calibration curve of Cu(II) (diethyldithiocarbamate)

Sample : standrad Cu(II) solution

Solvent : Trichloroethane

λ_{max} of Cu(II)(diethyldithiocarbamate) = 435nm

Run No.	[Cu(II)] x 10 ^{5}M	Absorbance
1	0.63	0.08
2	1.26	0.162
3	1.89	0.24
4	2.52	0.315
5	3.15	0.402
6	3.78	0.48

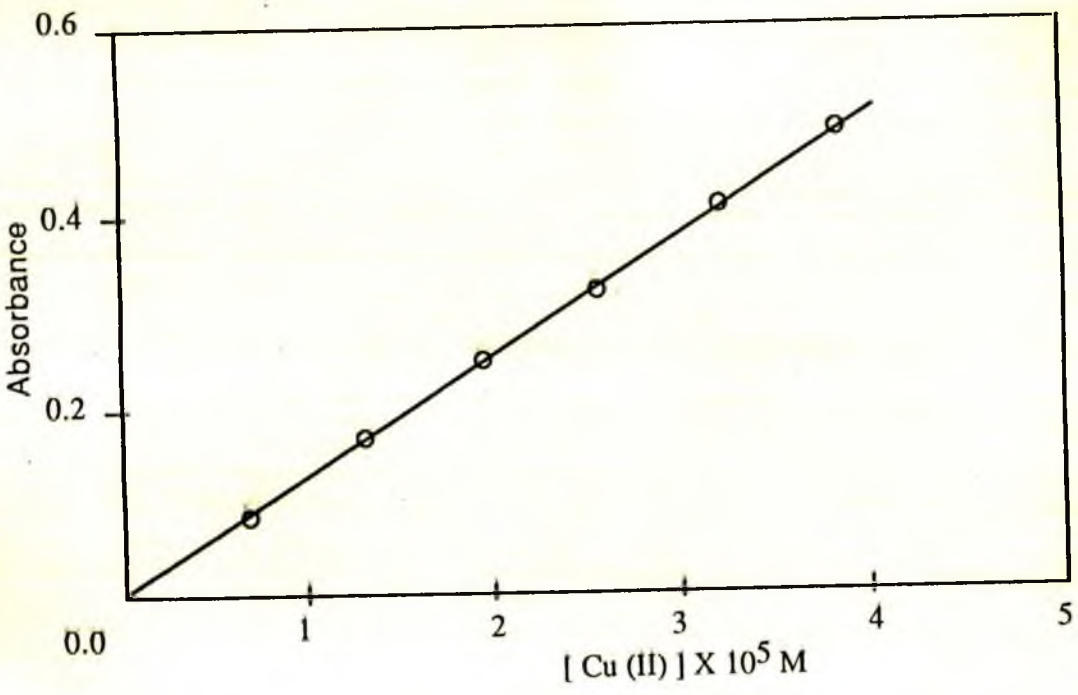


Fig. 3 Absorbance of Cu (II) diethyl-dithio Carbamate complex at various concentation.

2.6.2 *Mn(II) (periodate method)*[59,68,69]. Standard solution of Mn(II) was prepared by dissolving 0.77 g A.R. manganese(II) sulphate($MnSO_4$, H_2O) in water acidified with 2 mL concentrated H_2SO4 making the volume to 500 mL in a measuring flask. 10.0 mL of this solution was further diluted with water to 500 mL in a measuring flask. 1.0 mL of this solution contained 0.01 mg Mn(II).

Calibration curve. To prepare Mn(II) solutions of different concentrations 0, 1.0, 2.0,3.0, 4.0, 5.0 and 6.0 mL of standard Mn(II) solutions were taken in 50 mL beakers. 10 mL 10% H_2SO_4 solution, 3 mL conc. H_3PO_4 and 0.5 g KIO_4 were added to each beaker and heated for 15 minutes. The solutions were cooled, transferred to 25 mL measuring flask and the volume was made up with water. The spectrum of the solution containing 5.0 mL Mn(II) was taken using the solution with 0 mL Mn(II) as reference. The absorbance values of the solutions were measured at 525 nm (more intense λ_{max}). The absorbane data are given in Table 4. The absorbance values were plotted against Mn(II) concentration (Fig. 4).

($\epsilon = 2.89 \times 10^3$ M^{-1} cm^{-1} at 30°C).

Table 4. Data for obtaining calibration curve of permanganic acid

Sample : Standrad Mn(II) solution

Referenc : Manganese free acidic Periodate solution

λ_{max} of Permanganic acid = 525 nm

Run No.	[Mn(II)] x 10^5 M	Absorbance
1	0.72	0.021
2	1.44	0.042
3	2.16	0.063
4	2.88	0.082
5	3.60	0.103
6	4.32	0.123

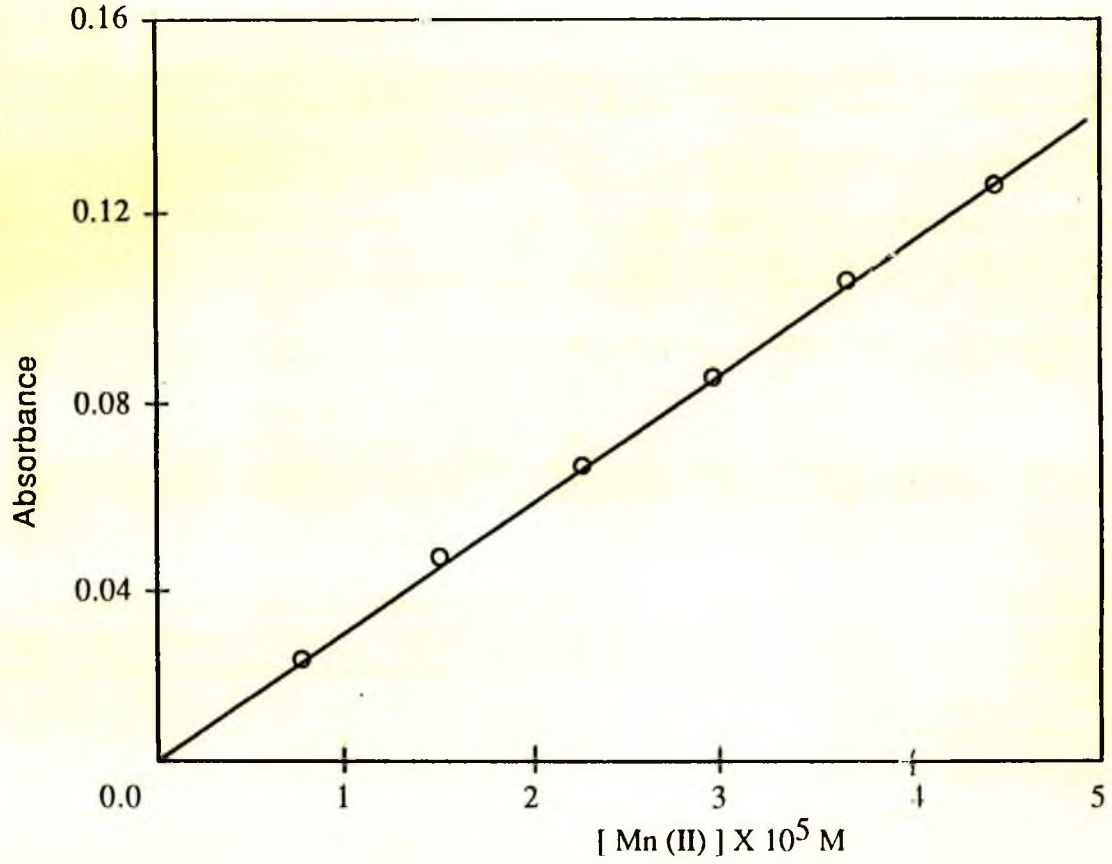


Fig. 4 **Absorbance of Mn (II) solution at various concentation.**

2.6.3 *Fe(II) (1,10-Phenanthroline method)*[59,70,71]. 0.980g Mohr's salt ($Fe(SO_4)_2.(NH_4)_2SO_4.6H_2O$) was dissolved with 0.05 M sulphuric acid in 100 mL measuring flask. This solution was further diluted with 0.05 M sulphuric acid to get a solution containing 0.0112 mg Fe(II) per mL.

A series of solutions containing 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 mL standard Fe(II) solution along with 2.0 mL 0.1% 1,10-phenanthroline, 5.0 mL sulphuric acid-sodium acetate buffer solutions were taken in 25 mL measuring flasks and the volumes were made up by 0.05 M sulphuric acid solution. The solutions were left in the dark for one hour. A reference solution was made by taking all the solutions except Fe(II) in a 25 mL measuring flask and making up the volume by 0.05 M sulphurtic acid solution. The spectrum of solution containing 5.0 mL was taken. The absorbance values of solutions were meassured at 510 nm (λ_{max}) using the same reference. The absorbance data are given in Table 4. The plot of absorbance vs. concentration was a straight line passing through origin (Fig. 5) ($\epsilon = 1.13 \times 10^4$ M^{-1} cm^{-1} at 30°C).

Table 5 Data for obtaining calibration curve of Fe(II) phenanthroline complex.

Sample : Standrad Fe(II) solution
Reference : Iron free solution containing phenanthroline, buffer and 0.05 mL sulphuric acid.
λ_{max} of Fe (II)-phenanthroline complex: 510 nm.

Run	[Fe(II)] x 10^5 M	Absorbance
1	2.40	0.270
2	3.20	0.362
3	4.00	0.440
4	4.80	0.538
5	5.60	0.633
6	6.40	0:735

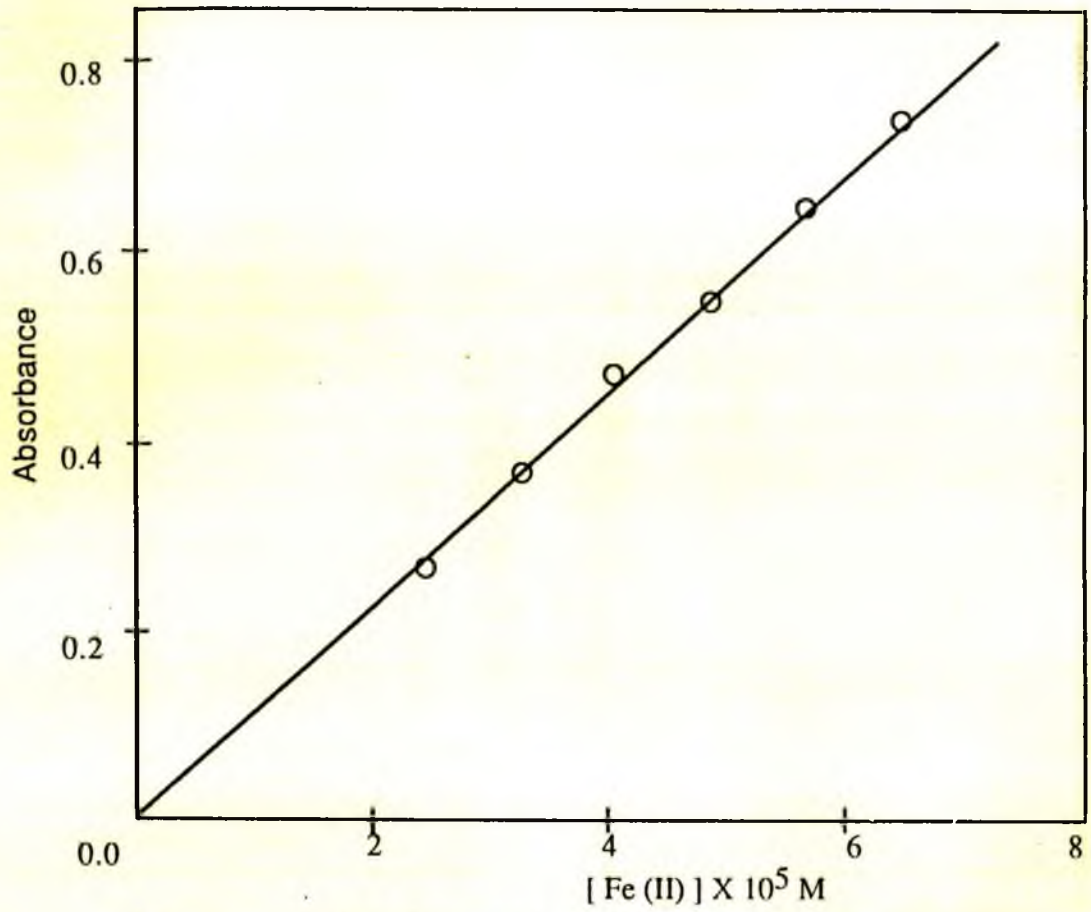


Fig. 5 **Absorbance of Fe (II) Phenanthroline complex at various concentation.**

2.7 Determination of metals from metal ions in latex samples

Latex samples, each with about 20 to 25 g total solid, were dried to get uniform sheets. The dried sheets were cut into small pieces and re-dried at 70 ±2°C to constant weight. These pieces were used for the determination of copper, manganese and iron in latex. The reported values are the meen of three determination.

2.7.1 *Copper from Cu(II).* About 5-10 g dry latex sheet was accurately weighed and taken in a clean and dry porcelain crucible and ignited to ash following the method **2.5.15**.

After cooling the contents of the crucible 1 mL water and 10 mL acid mixture [Hydrochloric and Nitric acid(2:1)] were added to it and digested on a water bath for half an hour. The solution was filtered and washed, 10 mLof 10 % citric acid solution was added to it. Ammonia solution was added drop by drop until the solution was just alkaline to litmus paper. The solution was then transferred to a seperatory funnel, 2 mL ammonia solution followed by 25.0 mL of zinc diethyldithiocarbamate reagent in trichloroethane was added to it. The content of the funnel was shaken for 2 minutes and the trichloroethane layer was drawn into a stoppered bottle, which contained about 0.1g of anhydrous sodium sulphate. The absorbance of the Cu(II) diethyldithiocarbamate solution so prepared was measured at 435 nm using a treated blank solution as reference. The amount of copper in the sample was determined and expressed in mg per kg of the dried latex.

2.7.2 *Manganese from Mn(II).* About 10 g dried latex sample was accurately weighed, wrapped with ash less filter paper and taken in a clean and dry porcelain crucible. 5 g $KHSO_4$ was placed on the top of the wrapped specimen and converted to ash following the method **2.5.15**.

The residue was cooled, 20 mL sulphuric acid (1:19) was added to it and the content was digested on a steam bath for 30 minutes. The solution was filtered and washed. 3.0 mL H_3PO_4 and 0.3 g KIO_4 was added to the filtrate and evaporated carefully to a volume lass than 20 mL. After cooling the solution was transfered to a 25 mL measuring flask and diluted up to the mark with distilled water. The absorbance of the solution was measured at 525 nm using the treated blank solution as a reference. The amount of manganese in the sample was determined and the result expressed in mg Mn per kg of dried latex.

2.7.3 *Iron from Fe(II).* Accurately weighed amount (about 10 g) of dried latex sample was ignited to ash in a porcelain crucible according to the method 2.5.14 .

After cooling 10 mL HCl (1:1) was added to the crucible and the mixture was digested on a steam bath for 45 minutes. The solution was filtered and washed. The filtrate and the washings were collected into a 50 mL measuring flask and diluted up to the mark with distilled water. 10 mL of this solution was transferred to a 25 mL flask. 2 mL quinhydrone solution (saturated),2 mL 0.1% 1,10-phenanthroline solution, 5 mL sulphuric acid-sodium acetate buffer solution were added to it and the volume was made up with 0.05 M sulphuric acid solution. The solution was left in the dark for one hour. The absorbance of the solution was measured at 510 nm, using the treated blank solution as reference. The amount of iron in the sample was determined and the result was expressed in mg Fe per kg of dried latex.

CHAPTER-3
RESULTS AND DISCUSSION
(part-1)

3.1 Composition and Properties of field latex

Experimentally determined characteristic properties of the field latices from three different clones of varying age of the rubber trees are shown in Table 6,7,8 and 9. The latex samples from the Chittagong rubber zone (Tables 6,7 and 8) were collected in the month of December 1991. The latex samples from the Sylhet rubber zone (Table 9) were collected in April 1992.

TSC of the TJIR clonal latex collected from the Chittagong rubber zone varies from 28.7% to 45.0% and DRC varies from 25.6% to 41.9%. These variations for PBIG clonal latex are 26.7% to 35.2% and 23.2% to 31.9% and that for RRIM 600 clonal latex are 19.1% to 28.4% and 15.6% to 25.4% respectively. TSC and DRC appear to increase with the age of the rubber trees. The maximum TSC is 45.0%, which is from the TJIR clonal rubber latex. Here the rubber plants are 30 years of age. The minimum TSC is 19.1%. This is from the 6 years old RRIM 600 clonal rubber plants. TSC of the latices from the plants of the same age (26/27 years) but of different clones, TJIR and PBIG, appear to be the same (35.1% and 35.2% respectively). However the PBIG and RRIM clone of 7 years old plants have considerably different TSC (26.8% and 19.7% respectively). TSC and DRC of the same clone and age of the rubber plants also differ from Chittagong zone to Sylhet zone. However, the variations in DRC of the latices of different clones in Sylhet zone are not that significant.

Generally NRS varies from about 2.5% to 4.0%. The nitrogen content of the latex of the Chittagong zone are almost the same for all the samples. Nitrogen content of the latex samples from Sylhet zone is slightly different. Nitrogen is the

indication of protein content in the rubber, as such,it is gererally independent of age and clone. However, when nitrogen was determined in the total solid (TSC) it was found to decrease with the increase of age of the rubber plants. The relationship between TSC, DRC and nitrogen in TSC is shown in Fig. 6, which is representative of all the clones.

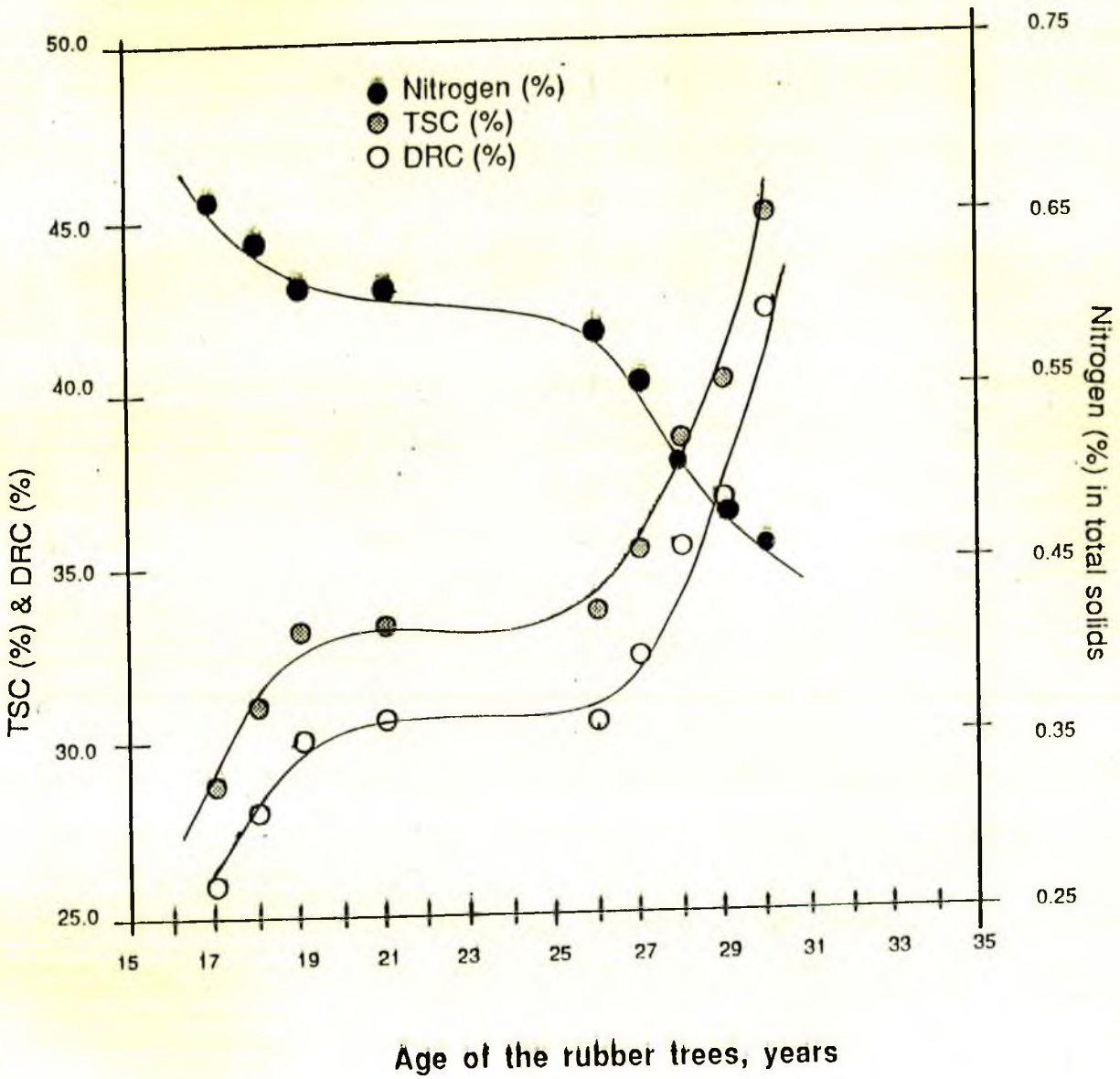


Fig. 6 TSC, DRC and Nitrogen in total solids of latices of rubber trees.(TJIR clone, Table 6)

Table 6. Composition and properties of the latex of the TJIR clone from the trees of different ages.

The samples were collected from the rubber estates of Chittagong rubber zone during the last week of December, 1991.

Composition & properties	Age of the rubber trees, years								
	17	18	19	21	26	27	28	29	30
TSC, %	28.72	30.78	32.82	32.90	33.18	35.05	38.24	39.89	44.99
DRC, %	25.57	27.55	29.70	30.26	30.10	31.98	35.28	35.91	41.91
NRS, %	3.15	3.23	3.12	2.64	3.08	3.07	2.96	3.98	3.08
NH_3(liquid phase) ,%	1.31	1.39	1.28	1.44	1.32	1.45	1.44	1.44	1.48
pH	10.07	10.11	10.04	10.11	10.04	10.09	10.11	10.22	10.29
Sludge, %	0.011	0.007	0.062	0.021	0.014	0.008	0.009	0.005	0.011
Coagulum, %	0.002	0.002	0.011	0.009	0.008	0.006	0.009	0.006	0.006
Density, g/mL	0.981	0.979	0.978	0.976	0.974	0.972	0.962	0.959	0.958
Viscosity, mPa. S	3.93	4.71	5.18	5.25	5.33	6.06	7.23	9.14	13.12
VFA number	0.027	0.031	0.029	0.031	0.026	0.021	0.021	0.026	0.024
KOH number	1.38	1.33	1.32	1.38	1.31	1.29	1.32	1.42	1.31
Nitrogen, %	0.19	0.19	0.19	0.21	0.19	0.19	0.19	0.18	0.19
Nitrogen(in TSC), %	0.67	0.63	0.58	0.89	0.57	0.54	0.50	0.47	0.45

The density and the viscosity of the samples are found to depend on the TSC/DRC of the latices. Viscosity was found to increase with the increase in TSC but density was found to decrease with TSC. The densities of the latex samples vary from 0.958 to 0.989 g/mL and the viscosities of the samples vary from 13.12 mPa.S to 2.86 mPa.S.

Table 7. Composition and properties of the latex of the PBIG clone from the trees of different ages

The samples were collected from the rubber estate of Chittagong rubber zone during the last week of December, 1991.

Composition & properties	Age of the rubber trees, years				
	7	9*	10	25	26
TSC, %	26.66	26.79	28.53	33.85	35.20
DRC, %	23.18	22.77	25.69	30.54	31.88
NRS, %	3.48	4.02	2.84	3.31	3.32
NH_3 (liquid phase), %	1.25	1.34	1.33	1.22	1.28
pH	9.96	9.99	10.03	10.01	10.11
Sludge, %	0.009	0.024	0.007	0.009	0.006
Coagulum, %	0.006	0.007	0.002	0.009	0.004
Density, g/mL	0.983	0.983	0.982	0.975	0.973
Viscosity, mPa. S	3.80	3.84	3.96	4.80	4.80
VFA number	0.042	0.042	0.041	0.022	0.028
KOH number	1.31	1.38	1.51	1.36	1.31
Nitrogen, %	0.22	0.21	0.19	0.19	0.19
Nitrogen in TSC, %	0.77	0.76	0.75	0.59	0.54

* Average results of three samples from defferent rubber estates.

Table 8. Composition and properties of the latex of the RRIM 600 clone from the trees of different ages

The samples were collected from the rubber estates of Chittagong rubber zone during the last week of December, 1991.

Composition & properties	Age of the rubber trees, years			
	6*	7**	8***	9
TSC, %	19.12	19.70	23.60	28.40
DRC, %	15.62	16.61	19.70	25.41
NRS, %	3.50	3.09	3.90	2.99
NH_3 (liquid phase), %	1.21	1.22	1.32	1.34
pH	9.87	9.86	10.03	10.05
Sludge, %	0.015	0.008	0.032	0.007
Coagulum, %	0.004	0.003	0.006	0.002
Density, g/mL	0.989	0.989	0.985	0.981
Viscosity, mPa. S	2.88	2.86	3.04	3.81
VFA number	0.043	0.039	0.042	0.051
KOH number	1.53	1.50	1.51	1.49
Nitrogen, %	0.20	0.20	0.20	0.20
Nitrogen in TSC, %	1.04	1.02	0.86	0.72

*, **, *** Average results of three, two and four samples respectively from defferent rubber estates.

Table 9. Comparison of composition and properties of latices of different clones of Sylhet rubber zones

Samples were collected during the last week of April, 1992.

Composition & Properties	Clone/age of the rubber trees, years						
	TJIR		PBIG			RRIM 600	
	16	24	6	7	10	9	10
TSC, %	41.18	44.31	35.85	36.99	37.34	38.44	39.30
DRC, %	36.20	41.60	33.00	34.34	34.66	32.22	35.42
NRS, %	3.98	2.71	2.85	2.65	2.68	3.22	3.88
NH_3 (liquid phase), %	1.32	1.47	1.25	1.24	1.22	1.29	1.32
pH	10.18	10.28	10.06	10.07	10.04	10.11	10.15
Sludge, %	0.029	0.010	0.011	0.022	0.033	0.021	0.023
Coagulum, %	0.004	0.003	0.003	0.005	0.004	0.003	0.004
Density, g/mL	0.957	0.956	0.975	0.966	0.965	0.964	0.962
Viscosity,mPa. S	9.90	12.00	6.12	7.17	7.50	8.02	9.20
VFA number	0.036	0.032	0.042	0.040	0.042	0.036	0.041
KOH number	1.49	1.41	1.41	1.43	1.56	1.51	1.45
Nitrogen , %	0.22	0.22	0.26	0.26	0.25	0.25	0.25
Nitrogen in TSC, %	0.55	0.49	0.71	0.71	0.69	0.65	0.64

The volatile fatty acid (VFA) number and KOH number of the samples are found to vary from 0.021 to 0.051 and 1.29 to 1.56 respectively. In fact KOH number accounts for all types of acids[72], present in the latex. This includes both the steam volatile, such as, formic, acetic and propionic and the non-volatile, such as stearic, oleic and amino acids (free or from polypeptides and proteins).

The difference between KOH and VFA number is a measure of the presence of the non-volatile fatty acids, which increase the stability of the latex by virtue of their surface activities.

3.2. Composition and Properties of latices at different times of a year

The properties of TJIR clonal latex collected from Rawzan rubber estate of Chittagong rubber zone at three monthly interval during 1991 are shown in Table 10

Table 10. Composition and properties of the field latex collected at three months interval from Rawzan rubber estate, Chittagong

Composition & Properties	Date of collection of the latex samples				
	4.1.1991	6.4.1991	12.7.1991	14.10.1991	Average
TSC, %	37.42	39.98	39.66	38.24	38.82
DRC, %	34.21	37.10	36.75	35.12	35.79
NRS, %	3.21	2.88	2.91	3.12	3.03
NH_3 (liquid phase), %	1.31	1.26	1.21	1.24	1.25
pH	10.32	10.29	10.32	10.28	10.30
Sludge, %	0.019	0.031	0.053	0.049	0.038
Coagulum, %	0.006	0.009	0.021	0.022	0.014
Density, g/mL	0.965	0.958	0.959	0.962	0.961
Viscosity, mPa. S	7.12	9.16	8.96	8.05	8.32
VFA number	0.031	0.038	0.042	0.034	0.036
KOH number	0.89	1.01	1.06	0.96	0.98
Nitrogen, %	0.20	0.22	0.22	0.21	0.21
Nitrogen in TSC, %	0.53	0.55	0.55	0.55	0.55
Ash of TSC, %	1.15	1.07	1.13	1.28	1.16

Table 11. Composition and properties of the PBIG clonal field latex sample collected at three months interval from the satgaon rubber estate (Sylhet)

Composition & properties	Date of collection of the latex samples				
	20.2.1991	24.5.1991	26.8.1991	22.11.1991	Average
TSC, %	34.81	38.05	36.76	33.92	35.88
DRC, %	31.85	35.24	33.47	30.71	32.82
NRS, %	2.96	2.81	3.29	3.21	3.06
NH_3 (liquid phase), %	1.24	1.11	1.21	1.07	1.16
pH	10.21	10.04	10.09	10.03	10.09
Sludge, %	0.016	0.029	0.038	0.031	0.028
Coagulum, %	0.004	0.016	0.013	0.012	0.011
Density, g/mL	0.973	0.962	0.970	0.975	0.970
Viscosity, mPa. S	5.98	7.08	6.86	5.45	6.34
VFA number	0.042	0.037	0.039	0.033	0.038
KOH number	1.55	1.45	1.51	1.42	1.48
Nitrogen, %	0.24	0.25	0.25	0.24	0.24
Nitrogen in TSC, %	0.69	0.66	0.68	0.70	0.68
Ash of TSC, %	1.26	0.97	1.03	1.24	1.12

and that for the PBIG conal latex of Satgaon rubber estate of Sylhet rubber zone are shown in Table 11. The TSC and DRC are lower in the first and the last quarter of the year than that of the second and the third quarters. The average TSC and DRC of the latex sample from Rawzan rubber estate are found to be 38.8% and 35.8% respectively. These results are in general higher than those reported by Ahmmad Ullah and co-workers[17] for the latex samples of the same rubber estate. The higher

results found in the present investigation, are apparently due to the age (about 4 years more) of the rubber plants that were chosen. The average TSC and DRC for the PBIG clonal latex collected from the Satgaon rubber estate are 35.9% and 32.8% respectively. In the case of Rawzan rubber estate nitrogen in the latex samples and that in the TSC remains virtually constant throughout the year. The higher nitrogen content in the samples from Satgaon rubber estate may be due to the local affects. The variation of TSC, DRC and NRS at different periods of a year are shown in Fig. 7.

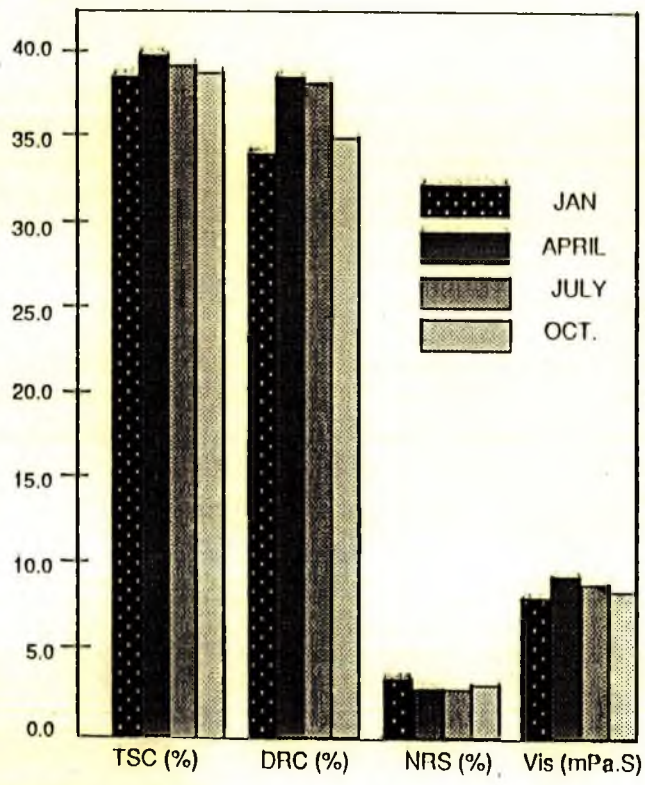


Figure 7 (a) TSC, DRC, NRS, Viscoscity (mPa.S) of latices, from Rawzan rubber estate (Chittagong), at three month interval.

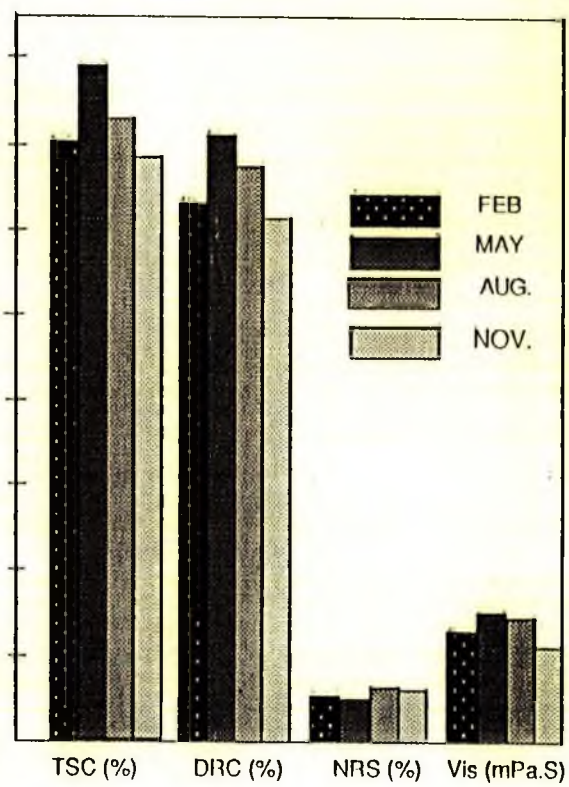


Figure 7 (b) TSC, DRC, NRS, Viscoscity (mPa.S) of latices from satgaon rubber estate (Sylhet), at three month interval.

3.3 Composition and Properties of latices from different rubber estates

The results of the latex sample collected from seven rubber estate of Chittagong rubber zone are shown in Table 12 and the results of the latex samples collected from the four rubber estate of Sylhet rubber zone are shown in Table 13. The TSC and DRC of the latex samples collected from the Rawzan rubber estate are found to be the highest. TSC and DRC are the lowest for the latex samples collected from Tarako rubber estate. The Rawzan rubber estate of the Chittagong rubber zone has the oldest rubber plants and Tarako rubber estate has the youngest rubber plants. This may explain the observed differences in TSC and DRC. Results of some latex samples are shown in Fig. 8.

Table 12. Composition and Properties of latex samples from the bulk production of the seven rubber estates of Chittagong rubber zone

Composition & Properties	Name of the rubber estate						
	Rawzan	Dabua	Haludia	Ramo	Dat-mara	Kanch-anagar	Tarako
TSC, %	41.95	31.76	30.60	29.99	28.98	22.56	20.98
DRC, %	39.29	28.70	27.45	26.66	25.78	19.53	18.24
NRS, %	2.66	3.06	3.15	3.21	3.20	3.03	2.74
NH_3 (liquid phase), %	1.32	1.24	1.27	1.29	1.27	1.21	1.23
pH	10.26	10.17	10.19	10.23	10.20	10.15	10.17
Sludge, %	0.012	0.004	0.014	0.023	0.037	0.041	0.021
Coagulum, %	0.006	0.007	0.006	0.008	0.007	0.009	0.004
Density, g/mL	0.956	0.976	0.978	0.982	0.982	0.988	0.990
Viscosity, mPa. S	10.30	4.02	3.84	3.73	3.62	3.42	3.22
VFA number	0.026	0.041	0.039	0.026	0.026	0.042	0.045
KOH number	1.34	1.41	1.41	1.32	1.32	1.56	1.53
Nitrogen, %	0.22	0.22	0.23	0.22	0.22	0.23	0.23

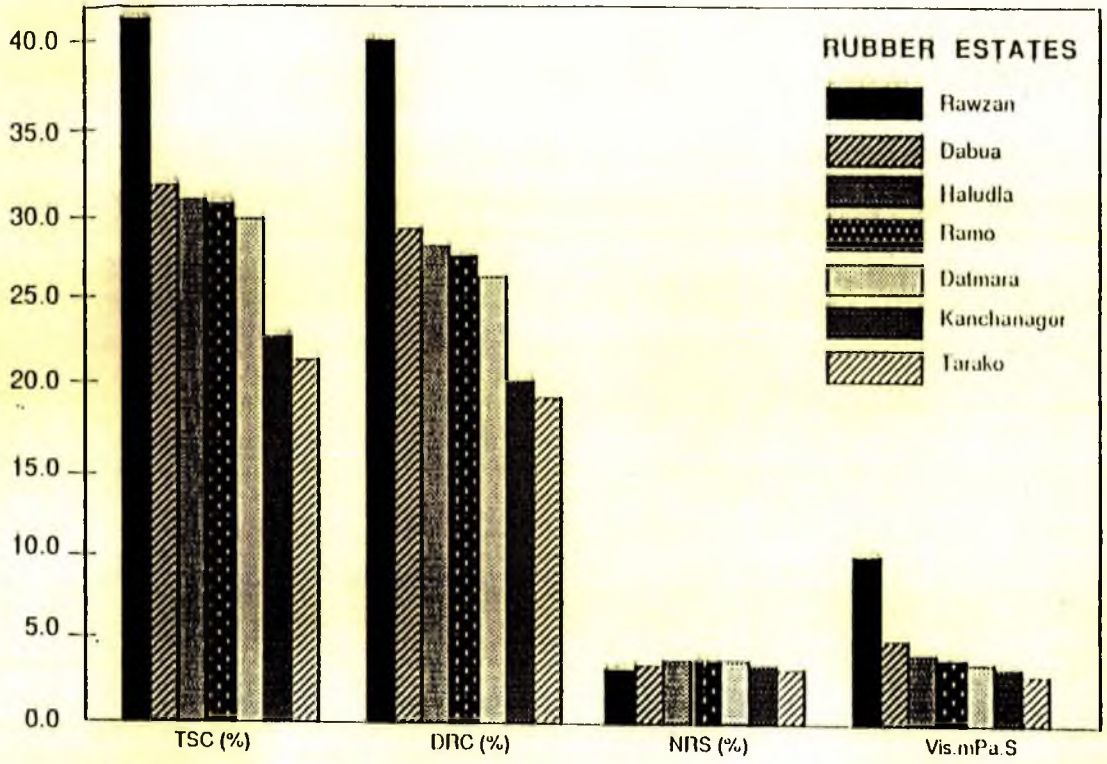


Fig. 8 (a) **TSC, DRC, NRS and Viscoscity (mPa.S) of latex samples from seven rubber estates of Chittagong zone**

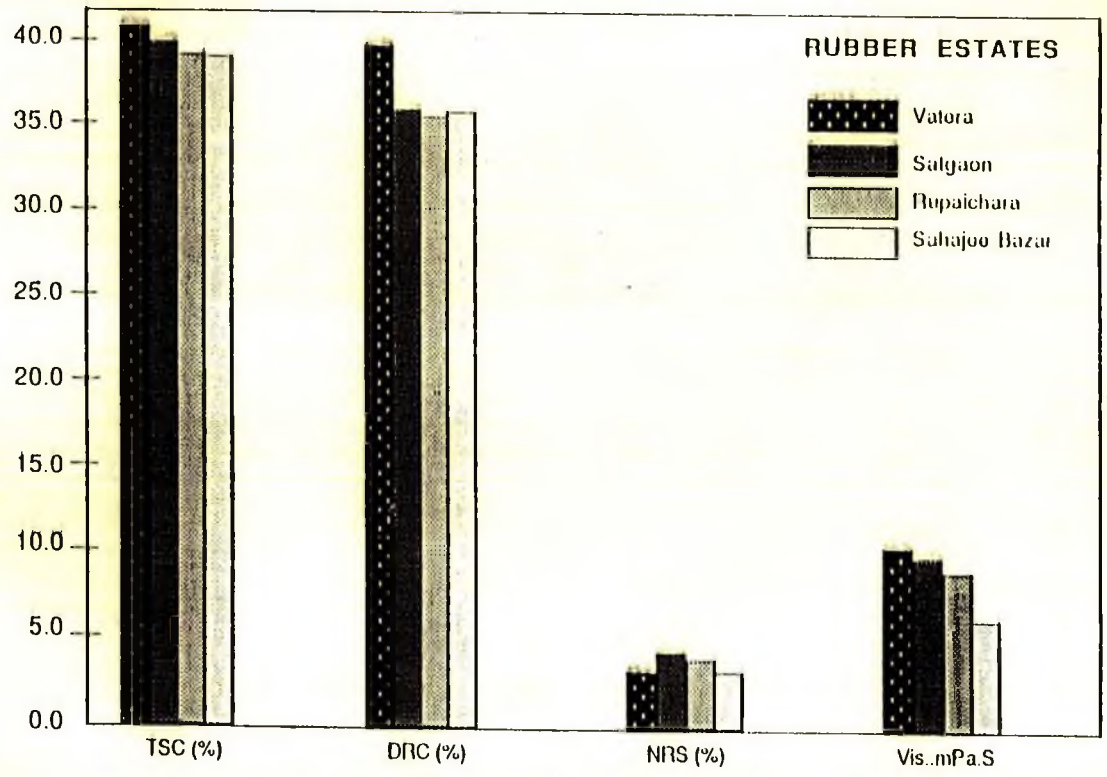


Fig. 8 (b) **TSC, DRC, NRS and Viscoscity (mPa.S) of latex samples from four rubber estates of Sylhet zone.**

Table 13. Composition and Properties of the latex samples from the bulk production of the four rubber estate of Sylhet rubber zone.

Composition & Properties	Name of the rubber estate			
	Vatera	Satgaon	Rupaichara	Sahajee Bazar
TSC, %	40.75	39.34	38.55	38.25
DRC, %	38.18	35.67	35.09	35.69
NRS, %	2.57	3.67	3.46	2.56
NH_3 (liquid phase), %	1.35	1.33	1.34	1.28
pH	10.27	10.28	10.25	10.22
Sludge, %	0.018	0.022	0.074	0.024
Coagulum, %	0.003	0.003	0.005	0.002
Density, g/mL	0.958	0.960	0.959	0.968
Viscosity, mPa. S	10.08	9.42	8.12	6.43
VFA number	0.036	0.039	0.041	0.014
KOH number	1.42	1.51	1.42	1.46
Nitrogen, %	0.23	0.23	0.23	0.23

3.4 Composition and properties of the concentrated latex

The commercial natural rubber latex should meet the requirements of the international standard. The specifications for the centrifuge and cream concentrated natural rubber latex, according to ISO : 2004-1991, are presented in Table 14. The characteristic properties of the eleven natural rubber latex concentrates prepared in the laboratory by the laboratory scale concentrator are shown in Table 15. Our results suggest that the concentrated natural rubber latex prepared in the

Table 14. Specifications for centrifuged and creamed concentrated natural rubber latex as per ISO 2004-1991

Characteristic properties	Centrifuged latex		Creamed latex	
	Type HA	Type LA	Type HA	Type LA
Dry Rubber content, %, Min	60.0	60.0	64.0	64.0
Non-Rubber Solids, % Max	2.0	2.0	2.0	2.0
Alkalinity as NH_3,% on latex weight	0.6 (Min)	0.29 (Max)	0.65 (Min)	0.35 (Max)
Mechanical Stability, Sec, Min	650	650	650	650
Coagulum content, % Max	0.05	0.05	0.05	0.05
Copper,mg/kg of total solid,Max	8.0	8.0	8.0	8.0
Manganese, mg/kg of total solid,Max	8.0	8.0	8.0	8.0
Sludge content, %, Max .	0.10	0.10	0.10	0.10
Volatile fatty acid number, Max	0.20	0.20	0.20	0.20
Potassium Hydroxide number, Max	1.0	1.0	1.0	1.0
Colour (visual inspection)	No blue or grey colour			
Odour (after neutralization of ammonia with boric acid)	No bad odour.			

laboratory by centrifugation meet the requirements of this international standard of the high ammonia (HA) rubber latex. On the other hand the properties of the cream concentrated latex samples prepared in the laboratory (Table 16) do not meet the requirements of the ISO standard. To get the desired TSC and DRC in the cream concentrated latex further study, in respect of temperature, time and concentration of the creaming agent etc., is needed.

Table 15. Composition and properties of the centrifuge concentrated latex samples

The concentrated latices were produced by concentrating the field latices of different rubber estates of Bangladesh.

Properties	Samples *										
	1	2	3	4	5	6	7	8	9	10	11
TRC (%)	61.58	61.98	61.76	61.89	61.79	62.23	62.08	61.98	62.45	61.89	62.14
DRC (%)	60.29	60.66	60.65	60.60	60.42	60.82	60.86	60.67	60.99	60.54	60.83
NRS(%)	1.29	1.32	1.11	1.29	1.37	1.41	1.32	1.31	1.46	1.35	1.31
NH_3 (%) on latex Weight	0.81	0.78	0.83	0.82	0.80	0.83	0.80	0.85	0.81	0.80	0.80
MST (Sec.)	680	720	690	730	725	725	675	730	720	765	740
Coagulum (%)	0.002	0.002	0.001	0.002	0.002	0.001	0.001	0.001	0.002	0.002	0.001
VFA number	0.012	0.015	0.016	0.015	0.015	0.016	0.018	0.013	0.014	0.012	0.014
KOH number	0.58	0.61	0.63	0.64	0.64	0.65	0.60	0.62	0.56	0.54	0.57
Copper ppm	1.22	1.19	1.25	1.20	1.25	1.18	1.19	1.35	1.08	1.21	1.23
Managanese	1.06	0.88	1.62	1.31	1.46	1.23	1.21	1.75	1.67	1.12	1.06
Sludge (%)	0.004	0.003	0.005	0.004	0.006	0.003	0.003	0.006	0.005	0.003	0.004
Density, g/mL	0.946	0.945	0.946	0.945	0.945	0.944	0.944	0.944	0.943	0.944	0.943
Viscosity mPa.S	83.2	84.7	89.4	87.2	83.2	84.7	92.6	83.3	89.5	84.3	85.1

*(1) Samples 1, 2, 3, 4, 5, 6 and 7 are latex from Rawzan, Haludia, Dabua, Kanchannagar, Datmara, Tarako and Ramo rubber estates respectively of Chittagong zone.

(2) Samples 8,9,10 and 11 are from of Satgaon, Vatera, Shahajee bazar and Rupaichara ubber estates reapectively of Sylhet zone.

Table 16 Composition and properties of the samples of cream concentrated latex.

These concentrated latices were produced by creaming the field latices

Composition & Properties	Samples*			
	1	2	3	4
TSC, %	62.35	62.32	62.23	62.14
DRC, %	60.60	60.45	60.43	60.39
NRS, %	1.75	1.87	1.80	1.75
NH_3, (%) on the latex weight	0.89	0.86	0.86	0.87
MST (Sec.), after 15 days	1980	2120	2075	1980
Coagulum content, %	0.002	0.003	0.003	0.002
VFA number	0.018	0.019	0.017	0.018
KOH number	0.69	0.72	0.69	0.76
Copper, mg/kg Solids	1.42	1.21	1.34	1.36
Manganese, mg/kg Solids	1.97	1.99	1.31	1.23
Sludge content, %	0.007	0.008	0.007	0.008
Density, mPa.S	0.945	0.944	0.944	0.943

* 1, 2, 3 and 4 are from Satgaon, Vatera, Sahajee bazar and Rupaichhari rubber estates respectively of Sylhet zone

3.4.1 Mechanical stability time (MST)of the concentrated latex

The mechanical stability times of the centrifuge concentrated latex are shown in Table 17. The MST of the cream concentrated latex is very high (≈ 2000 sec.)

when measured within 24 hours of its preparation (Table 16), with storage the MST of the cream concentrated latex hardly change. On the other hand MST of the centrifuge concentrated latex is quite low (60 to 70 sec.) when measured within24 hours of its preparation. However, MST of the centrifuge concentrated latices started increasing after 15 days of its preparation. The variation of MST of a typical centifuge concentrated latex with time is shown in Fig. 9.

Table 17. The effect of storage on the mechanical stability times of the centrifug concentrated latex

Samples were collected from different rubber estates of Bangladesh

Smaple No.	Mechanical stability time, seconds						
Storage (days) →	0	15	30	45	60	75	90
1	60	370	590	700	760	795	810
2	55	390	605	720	820	855	865
3	65	400	595	690	760	890	805
4	70	405	610	730	840	875	895
5	65	410	605	725	835	865	880
6	60	405	600	725	840	860	875
7	55	395	590	675	830	870	890
8	50	395	605	730	880	905	920
9	55	390	595	770	845	880	890
10	70	405	605	765	890	920	930
11	65	405	600	740	880	905	920

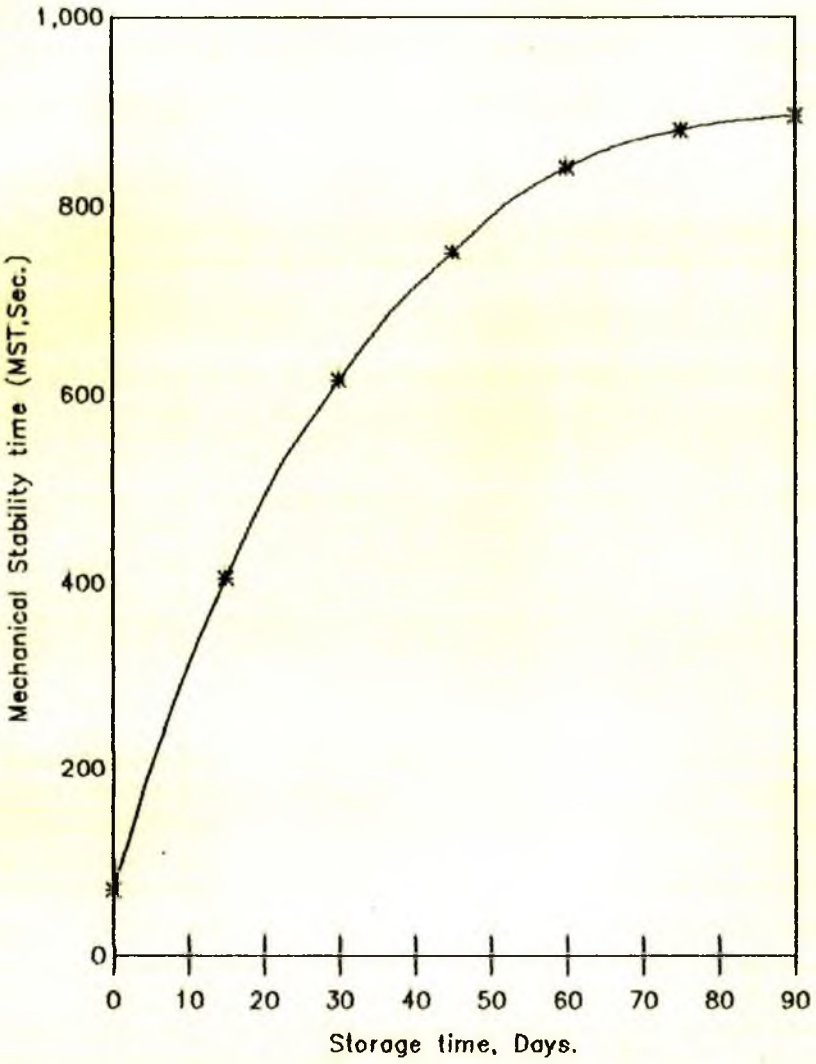


Fig. 9 Typical plot of storge time of centrifuge Latex vs mechanical stability time, sample–4

3.5. Comparison of some properties of the field and the concentrated latices and the serum from the concentrated latices

Comparison of some results of latices and the corresponding serums (Table 18) show that NRS and nitrogen are lower in the concentrated, by creaming or centrifugation, latices. This suggests that a portion of the non-rubber and the nitrogenous substances are removed, during concentration, into the serum. Nitrogen content of the concentrated latex by centrifugation appears to be slightly lower than

than that in the latex concentrated by creaming. The centrifugal force, during centrifugation, seems to transfer a portion of the proteinaceous material to the serum phase. Overall ash and acetone extract of the field latices are higher in comparison to the concentrated latices.

Table 18. Composition and density of the field latex, the concentrated latex and the serum

Composition & Properties	Field latex	Concentatrated latex		Latex serum from	
		Centrifuge	Cream	Centrifuge	Cream
TSC, %	38.95	62.06	61.98	11.32	11.44
DRC, %	35.38	60.75	60.23	7.21	7.99
NRS, %	3.57	1.31	1.75	4.11	3.45
Density	0.959	0.944	0.944	1.013	1.011
Analysis of TSC					
Ash, %	1.23	0.42	0.52	3.21	3.76
Nitrogen, %	4.06	1.93	2.46	8.51	7.51
Acetone extract, %	6.83	1.70	1.91	11.37	9.25
Rubber Hydrocarbon, %	85.33	95.34	94.73	47.52	45.45

3.7 Composition and nature of the total solids (TSC)

The composition of TSC of the latex samples collected from Chittagong and Sylhet rubber zones are presented Tables 19 and 20 respectively. Copper and manganese in the latex samples, are within the limit of the ISO specification for latex concentrates. There is no mention of iron in this specification. Copper and

manganse in the latex samples of Chittagong zone vary from 3.23 to 5.58 and 0.96 to 1.84 ppm respectively, and in the samples of Sylhet rubber zone vary from 2.85 to 4.52 and 1.34 to 4.71 ppm respectively. The variation of iron in the samples is from 17.9 to 42.5 ppm and from 12.5 to 19.1 ppm in the Chittagong and the Sylhet rubber zones respectively. The latex samples of Chittagong rubber zone appear to contain more copper and iron, but the latex samples of Sylhet rubber zone contain more manganese.

Ash, nitrogen, copper, manganese and iron in the solids from eleven latex samples of eleven different rubber estates are shown in Table 21. The ash varies from 1.30 to 1.52%, and nitrogen varies from 0.52 to 1.12% respectively. The metals in the solids vary from 0.98 to 6.41 ppm (Cu), 0.91 to 2.34 ppm (Mn) and 13.62 to 31.42 ppm (Fe). Compositions of TSC from the latices concentrated by creaming and centrifugation are shown in Table 22. The rubber hydrocarbon is about 95% in the latex concentrates and about 85% in the field latex. Table 23 shows that during the process of making the films from the dry rubber, whether from centrifuge concentration or from cream concentration, the usual composition of the rubber is not altered. However the process of concentration, has its influence on the composition of the films.

Table 19. Composition and nature of the total solid of field latices of different clones and ages of rubber trees of Chittagong rubber zone

Clone and age of the trees (Years)	Total ash(%)	Water insoluble ash(%)	Alkalinity of solution, K_2O(%)	Copper ppm	Manganese ppm	Iron ppm
TJIR/1961(30)	1.38	0.38	0.61	3.57	1.04	17.91
TJIR/1962(29)	1.28	0.40	0.62	3.23	1.21	32.33
TJIR/1963(28)	1.52	0.52	0.76	3.94	1.04	36.99
TJIR/1964(27)	1.40	0.40	0.78	4.56	1.02	42.51
TJIR/1965(26)	1.31	0.41	0.80	3.95	1.21	32.77
TJIR/1970(21)	1.26	0.48	0.66	3.68	1.14	21.21
TJIR/1972(19)	1.38	0.34	0.70	3.38	1.21	21.51
TJIR/1973(18)	1.33	0.42	0.60	3.70	1.55	35.41
TJIR/1974(17)	1.45	0.56	0.65	4.94	1.46	31.21
PBIG/1964(27)	1.39	0.34	0.76	3.44	1.23	28.11
PBIG/1965(26)	1.36	0.35	0.71	3.42	0.96	27.77
PBIG/1980(11)	1.51	0.52	0.71	4.99	1.77	27.41
PBIG/1981(10)	1.31	0.42	0.53	3.96	1.75	21.51
PBIG/1984(7)	1.38	0.48	0.58	4.48	1.76	23.54
PBIG/1982(9)	1.49	0.49	0.56	4.20	1.84	26.42
PBIG/1983(8)	1.51	0.55	0.81	5.17	1.52	25.56
PBIG/1984(7)	1.50	0.52	0.70	5.21	1.38	21.98
PBIG/1985(6)	1.53	0.49	0.76	5.58	1.23	18.51

Table 20. Composition and nature of the total solid of the field latices of different clones and ages of trees of Sylhet rubber zone

Clone & age of the trees (years)	Total ash (%)	Water insoluble ash (%)	Alkalinity of solution, K_2O (%)	Copper ppm	Manganese ppm	Iron ppm
TJIR/1967(24)	1.17	0.43	0.49	3.16	2.50	16.41
TJIR/1975(16)	1.94	0.56	0.90	4.24	2.94	16.42
PBIG/1981(10)	1.58	0.43	0.59	4.52	4.71	18.24
PBIG/1983(8)	1.09	0.46	0.46	3.43	2.66	12.48
PBIG/1984(7)	1.48	0.58	0.62	2.85	1.34	18.51
RRIM/1982(9)	1.02	0.34	0.45	3.35	1.73	15.34
RRIM/1983(8)	1.01	0.36	0.39	3.27	3.21	19.11

Table 21. Comparison of the compositions of TSC from latices of different rubber estates of Bangladesh

Rubber estate (Zone)	Composition of Solids				
	Ash (%)	Nitrogen (%)	Copper, ppm	Manganese pm	Iron pmm
Rawzan (Chittagong)	1.37	0.52	3.43	1.12	27.77
Dabua (Chittagong)	1.32	0.71	4.16	0.91	31.42
Haludia(Chittagong)	1.11	0.74	0.98	1.94	27.54
Ramo(Chittagong)	1.42	0.72	4.34	0.92	29.43
Dadmara(Chittagong)	1.46	1.00	4.79	1.86	23.58
Kanchannagar(Chittagong)	1.52	1.07	5.26	1.45	19.75
Tarako(Chittagong)	1.43	1.12	5.64	1.96	25.21
Vatera(Sylhet)	1.21	0.56	2.98	2.34	14.24
Satgaon(Sylhet)	1.24	0.60	6.41	2.28	18.10
Rupaichara (Sylhet)	1.21	6.60	2.68	1.30	17.18
Sahajee Bazar (Sylhet)	1.30	0.63	3.69	1.39	13.62

Table 22. Dependence of composition of the total solids (TSC) on the process of concetration of the field latex .

Sample No.	Composition of TSC				
	Ash (%)	Nitrogen(%)	Copper ppm	Manganese ppm	Iron ppm
1	0.39	0.28	1.22	1.06	1.56
2	0.36	0.31	1.19	0.98	1.21
3	0.38	0.30	1.25	1.62	1.54
4	0.41	0.31	1.20	1.31	1.38
5	0.38	0.32	1.25	1.46	1.45
6	0.37	0.32	1.18	1.23	1.32
7	0.38	0.32	1.19	1.21	1.33
8	0.45	0.30	1.35	1.75	1.41
9	0.38	0.25	1.08	1.67	1.23
10	1.41	0.27	1.21	1.12	1.12
11	0.39	0.32	1.23	1.06	1.16
12*	0.52	0.38	1.42	1.92	2.04
13*	0.55	0.36	1.21	1.99	1.97
14*	0.53	0.36	1.34	1.31	1.84
15*	0.51	0.38	1.36	1.23	1.89

* creamed latex

Table 23. Comparison of compositions of field latex and dry rubber films from centrifuge concentrated and cream concentrated latices.

Composition & properties of the latex films	Samples*					
	1	2	3	4	5	6
Ash, %	1.24	1.21	0.45	0.39	0.52	0.51
Nitrogen, %	0.63	0.66	0.30	0.32	0.23	0.22
Copper, ppm	0.41	2.68	1.25	1.23	1.42	1.36
Manganese, ppm	2.28	1.30	1.75	1.06	1.92	1.23
Iron, ppm	18.10	17.18	1.41	1.16	2.04	1.89
Acetone extract, %	6.66	6.97	1.64	1.75	1.89	1.93
Rubber Hidrocarbon, %	85.44	85.21	95.26	95.41	94.78	94.66

*(1) Samples 1 and 2 are the field latex from Satgaon and Rupaichara rubber estate, Sylhet zone.

(2) Samples 3 and 4 are the centrifuge concentrated latex and samples 5 and 6 are the cream concentrated latex of sample 1 and 2 respectively.

3.8. Infrared (IR) spectra of films from the field latex

The IR spectra of films made from the field latices of three different clones of various age of the rubber trees have been taken. The spectra of all the latex films are almost identical. The important major bands are

(i) C-H streaching vibration from $-CH_3$ at 2960 cm^{-1} and from ->CH at 2850 cm^{-1}.

(ii) C-H deformation at 1447 cm^{-1} and 1375 cm^{-1}.

(iii) The C=C streaching vibration at 1660 cm^{-1}, and

(iv) C-H out of plane deformation for cis R'C=CHR" at 837 cm^{-1}.

CHAPTER-4
EXPERIMENTAL
(*part-2*)

4.0 GAMMA RADIATION EFFECTS ON NATURAL RUBBER LATEX

4.1 Latex samples for irradiation

Field latices of the Vatera and Satgaon estates of Sylhet rubber zone were collected for the study of radiation effects. The Vatera rubber estate samples were used to study the effects of radiation dose on the latex in the presence and in the absence of the sensitizer . The samples collected from the Satgaon rubber estate was divided into three parts. One part was used as field latex and the other two parts were concentrated separately by creaming and by centrifugation. All of were subjected to radiation.

4.2. Chemicals

Following chemicals were used without further treatment.
Ammonia solution (BDH), sodium hydroxide (BDH), benzene (BDH), carbo tetrachloride (BDH), hydrogen peroxide (BDH), n-butyl acrylate BDH),

4.3 Apparatus

4.3.1 *Stainless steel sieve (180 micron).* It was used to separate the coagulum from the latex. It was also used to remove the coagulated and suspended impurities from the latex during the preparation of cast latex film.

4.3.2 *Radiation source.* 4.0 x 10^4 Ci Co-60 gamma radiation source was used for irradiation of natural rubber latex. The latex sample were irradiated at the dose rate of 13-14 kGy/hr (1.3 - 1.4 Mrad/hr) at room temperature (28^{o}C).

4.3.3 *Latex casting glass plate.* Approximately 30 x 10 cm raised rimmed glass plates were used for the preparation of the cast latex films of 0.3-0.5 mm thickness.

4.3.4 *Instron universal testing instrument.* Instron universal testing instrument (Model 1011 Instron) was used for the determination of tensile strength, modulus and elongation at break. The instrument is a power driven machine equipped to produce a uniform rate of grip separation of 500 -50 mm/min. The testing machine has a computerized recording device for measuring the applied force, modulus at different elongations and maximum elongation at break. For the determination of tensile strength dumbbell shaped specimen test pieces were used.

4.4 Experimental methods

4.4.1 *Preparation of latex samples for irradiation.* Known amount of latex sample (field latex from Vatera rubber estate) was strained through 180 micron stainless steel sieve into five different 1 liter beakers. The TSC of each sample was determined. 0.2 phr KOH, as stabilizer, was added to each beaker containing the latex sample and stirred magnetically. The beakers were marked in the following way

Beaker 1. No sensitizer was added

Beaker 2. CCl_4 (A) was added

Beaker 3. n-Butyl Acrylate, n-BA, (B) was added

Beaker 4. A mixture of CCl_4 and n-BA, in the ratio 1:1, (C) was added

Beaker 5. A mixture of n-BA and H_2O_2, in the ratio 1:1, (D) was added

5.0 phr of each sensitizer, A to D, was added to beakers 2 - 5, which were stirred for about one hour. The samples so prepared were left overnight at room temperature before irradiation.

Before irradiation TSC of the concentrated (by creaming or centrifugation) latex samples were adjusted to 50% by adding 1% ammonia solution. The samples were then strained through 180 micron stainless steel sieve into two beakers. 0.2 phr KOH, as stabilizer, and 5.0 phr n-BA, as sensitizer, were added to each beaker and the previously described procedure was followed. For comparison a sample of field latex was also irradiated under identical condition.

4.4.2 *Irradiation of natural rubber latex.* First of all radiation doses between 10 - 50 kGy (1.0 - 5.0 Mrad) were chosen. For 3 sets of measurements, each set consisting of 5 samples (one without sensitizer and others with sensitizer A to D) of field latex, 15 screw capped bottles were taken. 100 mL of the prepared field latex were taken in each bottle. Each set of samples were bound together by rubber bands and irradiated in the source compartment in such a way that the total doses of radiation received by the 1st, 2nd and the 3rd set were 10 kGy, 30 kGy and 50 kGy respectively.

Another six sets of experiments were planned. Each set had three samples. One of these was the field latex and the other two were the samples from the same origin but concentrated by two different processes. All of these samples were already prepared for irradiation. Accordingly, 100 mL portions of prepared samples were taken in 18 screw capped glass bottles. One set was set aside without irradiation and it was designated to have received 0 kGy. The bottles in each of the remaining five sets were bound together and irradiated. The total doses of radiation received by the sets are 10 kGy, 20 kGy, 30 kGy, 40 kGy and 50 kGy respectively.

4.4.3. *pH of the irradiated samples.* The pH of the irradiated samples and un-irradiated samples are measured by Standard pH meter.

4.4.4. *Preparation of films from the irradiated latex.* 40-50 mL latex samples, irradiated at different radiation doses, and un-irradiated samples, prepared for irradiation were poured on 30.5 X 10 cm raised rim levelled glass plates. Air bubbles were carefully excluded. The glass plates were left in air to dry at room temperature until transparent films (0.3-0.5 mm thick) were obtained. The films were immersed in water overnight to leach out the water soluble materials. Then they were washed with distilled water, air dried followed by drying in a vented air oven at 70°C for one hour . The latex films so prepared were sprinkled with calcium carbonate powder to reduce the stickiness and stored in a desiccator.

4.4.5 *Measurement of tensile strength, modulus and elongation at break.* The Tensile strength and percent elongation at break of the cast films were measured by the Instron Tensile Instrument using the standard methods[7] . Dumbbell shaped test pieces of 1.0 cm gauge length were used.

4.4.4 *Determination of Gel content.* Accurately weighed portions of(≈ 5g each) dry and moisture free irradiated latex were refluxed in benzene for 48 hours, cooled and filtered through a tared and weighed sintered glass crucible (No. 2). The solvent was completely removed by drying the crucible with its contents in a vacuum oven at 40°C. The weight of the undissolved fraction in each sample was determined from the initial and the final weights of the crucible. The gel content of each irradiated latex sample was found out from the ratio of the weight of the undissolved mass in a sample to that of its initial weight (expressed as percentage).

4.4.5 *The swelling volume ratio and the crosslink density.* Films of approximately 0.5 mm thickness were cut into 1.0 cm X 1.0 cm pieces and soaked in benzene for 24 hours. The excess solvent was removed by wiping with filter paper and the pieces were weighed. These weights were taken as the weights of the solvent free swollen samples. The samples were then dried in a vacuum oven at 40°C to constant weights. The swelling volume ratio (Q) of each sample was calculated by using the following equation[74],

$$Q=V_2/V_1 = 1+(d_r/d_s)\,(W_2/W_1) - d_r/d_s$$

V_1, V_2 W_1 and W_2 are the volumes and weights of the sample before and after soaking in benzene respectively. and d_r and d_s are the densities of rubber (0.93 g/mL) and benzene (0.896 g/mL) respectively.

The degree of crosslink of a polymer can be measured by measuring the swelling volume ratio which based on the Flory and Rehner equation[74-75] as follows:

$$V_o = K \times Q^{-5/3}$$

Where, V_o = crosslink (C.L) density, C.L/mL

$K = 4.71 \times 10^{20}$ for benzene/NR system,

The minimum crosslink density of the natural rubber film needed to form three dimensional network through the rubber matrix is predicted to be about $3.01 \times 10^{24} \times \bar{M}_n^{-1}$ crosslink/mL. The molecular weight of the natural rubber varies from 17×10^4 to 70×10^4. Accordingly, the minimum of 17.7×10^{18} crosslink unit/mL is needed to from a three dimensional network.

4.4.6 *Determination of permanent set.* For the determination of permanent set dumbbell shaped test pieces were used. The gauge lengths (20 mm in each case) were indicated on samples by a marker and they were extended to 300% elongation and held under the tension for 24 hours. The tension was then released and the samples were allowed to stabilize. After one hour the distance between the two marks on each sample was measured. The permanent set was calculated using the expression

$$PS = 100(L_1 - L_0)/ L_0$$

where, L_0 is the gauge length and L_1 is the distance between the marks after release of the tension.

CHAPTER-5
RESULTS AND DISCUSSION
(part-2)

5.1. Effects of radiation dose and sensitizer on latices

The composition of the field latex samples which were used for the study of the radiation effects are given in. Table 24. These samples were used for the study of the effects of radiation in the absence and in the presence of sensitizer.

Table. 24. Composition and properties of the latex samples used for irradiation

Composition & Properties	Field latex		Concentrated latex	
	Vatera	Satgaon	Centrifuge	Cream
TSC, %	39.45	37.55	61.46	62.07
DRC, %	37.12	34.61	60.22	60.44
NRC, %	2.33	2.94	1.24	1.63
NH_3 (liquid phase), %	1.98	2.14	2.55	2.29
KOH number	0.76	0.96	0.58	0.66
VFA number	0.07	0.039	0.018	0.021
Coagulum content, %	0.005	0.007	0.002	0.003
Sludge content, %	0.021	0.19	0.002	0.001
Green strength (MPa)	1.6	1.7	2.1	2.4

Table 25. shows that there is slight decrease of pH after irradiation at 10 kGy. Subsequent increase in doses of radiation and the presence of sensitizer do not have much effect on the pH. However a slight decrease of pH with the increase of radiation dose is noticed . The pH of the field latex seems to decrease more with the increase of radiation dose (Table 26). The pH change is the least in case of creamed latex.

Table 25. pH of the irradiated latex in the presence and in the absence of the sensitizers

Source : 4.0 x 10^4 Ci Co-60,
Temperature :28°C (ambient temp.)
Sample : Field latex from Vatera rubber estate
Stabilizer : 0.2 phr KOH.

Sensitizers.	pH before irradiation	pH after irradiator at different dose (kGy)		
		10	30	50
Nil	10.65	10.52	10.41	10.34
CCl_4	10.55	10.50	10.40	10.36
n-BA	10.62	10.51	10.43	10.38
CCl_4 + n- BA	10.58	10.47	10.40	10.34
CCl_4 + H_2O2	10.56	10.45	10.39	10.35

Table 26. pH of the different irradiated latice

Source : 4.0 x 10^4 Ci Co-60,
Temperature: 28°C (ambient temp.)
Sample : Field latex from Shahjee Bazar rubber estate
Sensitizer : n-BA,
Stabilizer : 0.2 phr KOH

Latex type	Radiation dose (kGy)					
	0	10	20	30	40	50
Field	10.54	10.48	10.44	10.40	10.37	10.33
Centrifuge	10.50	10.45	10.43	10.41	10.39	10.37
Cream	10.47	10.44	10.42	10.40	10.38	10.36

Radiolysis of the latices may produce various species, including hydrogen ions. The small decrease in pH may suggest the presence of some hydrogen ions which are left free. However the relative change of the pH in different latices can not be explained on the basis of over all composition of the latices.

Table 27. Swelling volume ratio (Q) and cross link density (C.L/mL) at various radiation dose and sensitizer

Source : 4.0×10^4 Ci Co-60,
Temperature : 28°C (ambient temp.)
Sample : Field latex from Shahajee Bazar rubber estate
Stabilizer : 0.2 phr KOH

Senssitizer	Radiation dose (kGy)	Swelling volume ratio	Crosslink Density x 10^{-18}
Nil	10	24.2	2.3
	30	15.0	5.2
	50	11.0	8.7
CCl_4	10	11.4	8.2
	30	6.2	22.5
	50	5.8	25.2
n-BA	10	11.2	8.4
	30	6.1	23.3
	50	5.7	25.9
n-BA + CCl_4	10	10.2	9.8
	30	5.9	24.4
	50	5.3	29.2
n-BA + H_2O_2	10	15.3	5.0
	30	8.2	14.1
	50	7.6	16.0

The swelling ratio and crosslink density of rubber films at various radiation doses are shown in Table 27. and figures 10 and 11. The increase in crosslink density and decrease in the swelling volume ratio of the film indicate the increase in vulcanization. Increase of radiation doses increase the crosslink density and decrease the swelling volume ratio in all the cases.

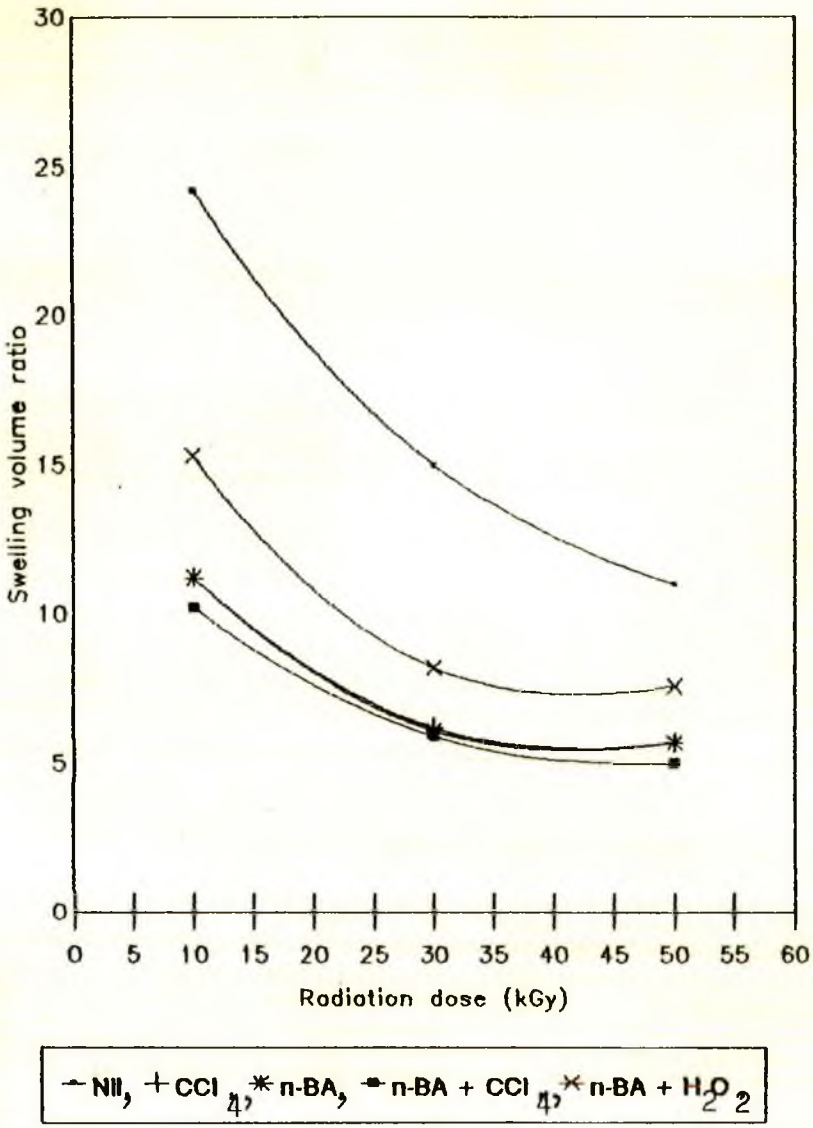


Fig. 10 Swelling volume ratio vs radiation dose

The maximum crosslink density is obtained with the n-BA + CCl_4 combination. The addition of sensitizers, except n-BA + H_2O_2 combination, increases the vulcanization spectacularly. For example at 30 kGy radiation the crosslink density changed from 5.0 x 10^{18} to about 23 x 10^{18} in the presence of n-BA and n-BA+CCl_4 combination (Table 27).

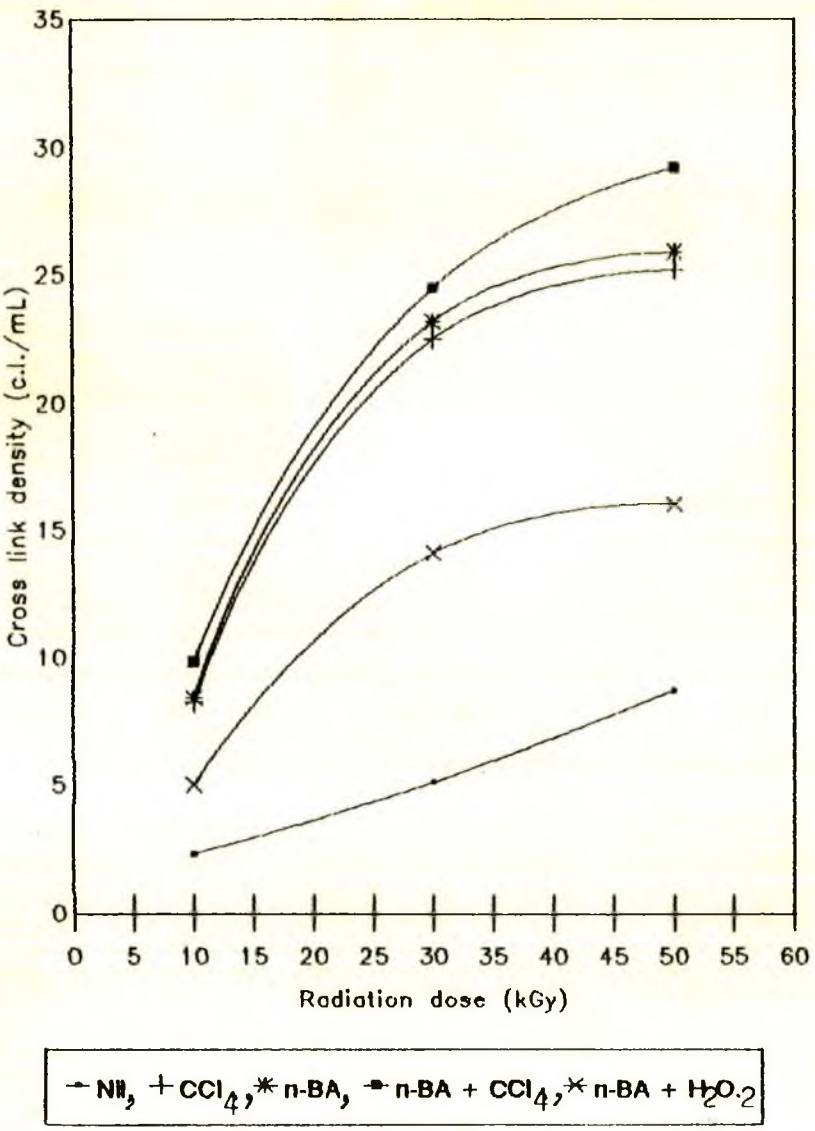


Fig. 11 Cross-link density vs radiation dose

Table 28 Swelling volume ratio (Q) and cross-link density (C.L./mL) for different type of latex at various radiation doses

Source : 4.0×10^4 Ci Co-60,
Temperature : 28°C (ambient temp.)
Sample : Field latex from Shahjee Bazar rubber estate
Sensitizer : n-BA,
Stabilizer : 0.2 phr KOH.

Latex type	Radiation dose (kGy)	Swelling volume ratio	Crosslink Density $\times 10^{-18}$
Field	10	12.4	7.1
	20	9.0	12.1
	30	7.4	16.8
	40	6.5	20.8
	50	5.7	25.9
Centrifuge	10	8.5	13.3
	20	5.9	24.4
	30	5.1	31.2
	40	5.0	32.2
	50	4.9	33.3
Cream	10	9.2	11.7
	20	7.5	16.4
	30	6.5	20.8
	40	5.8	25.2
	50	5.2	30.2

The vulcanization of the latex is considerably affected by its concentration (Fig.12, Fig.13 and Table 28). In the presence of n-BA sensitizer the swelling

volume ratio of the film made from the irradiated latices, decreases sharply and cross link density increases sharply with the increase of the radiation dose from 10-25 kGy (Fig. 12 and Fig.13). The results suggest that a radiation of dose 30 kGy cause desirable vulcanization of centrifuge concentrated latex in the presence of n-BA sensitizer.

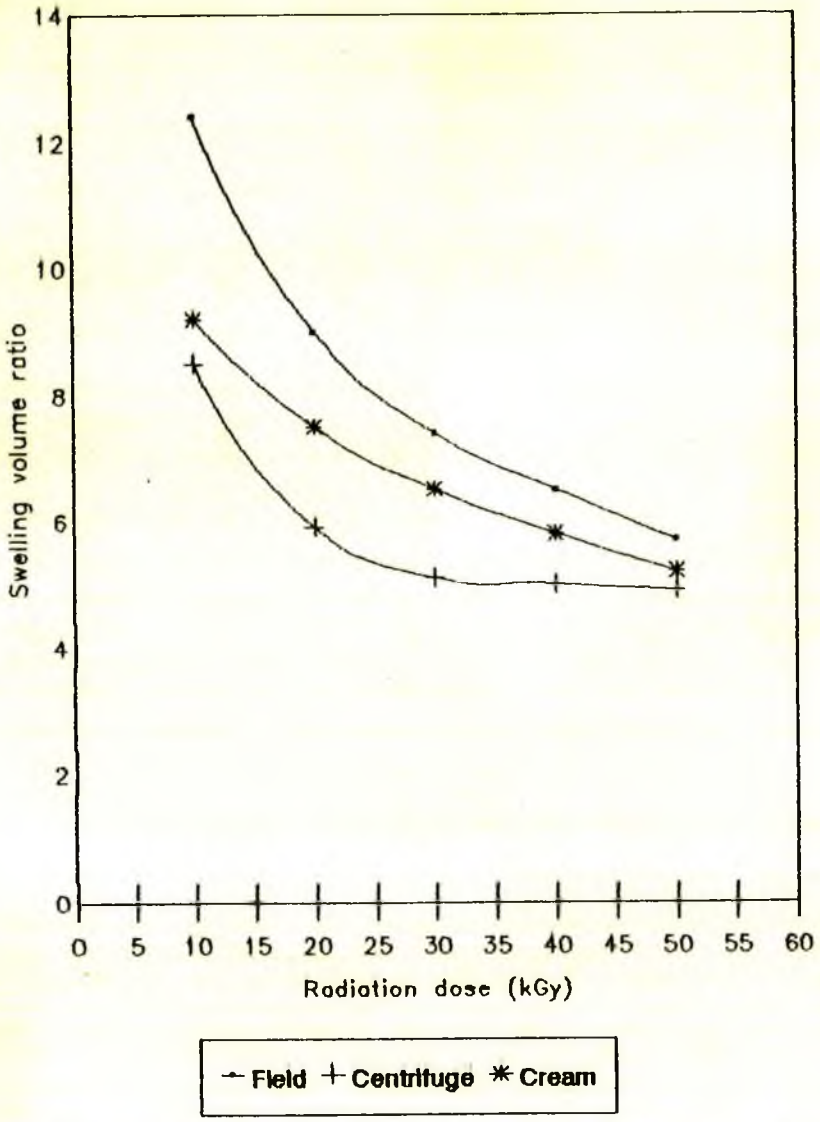


Fig. 12 Swelling volume ratio vs radiation dose

The minimum crosslink density 17.7 X 10^{18}C.L./mLrequired for the latex to get three dimensional network is achieved in the present study by the centrifuged latex at 20 kGy. It is to be noted that to much of crosslinks hinders the stretching and consequently reduces the tensile strength.

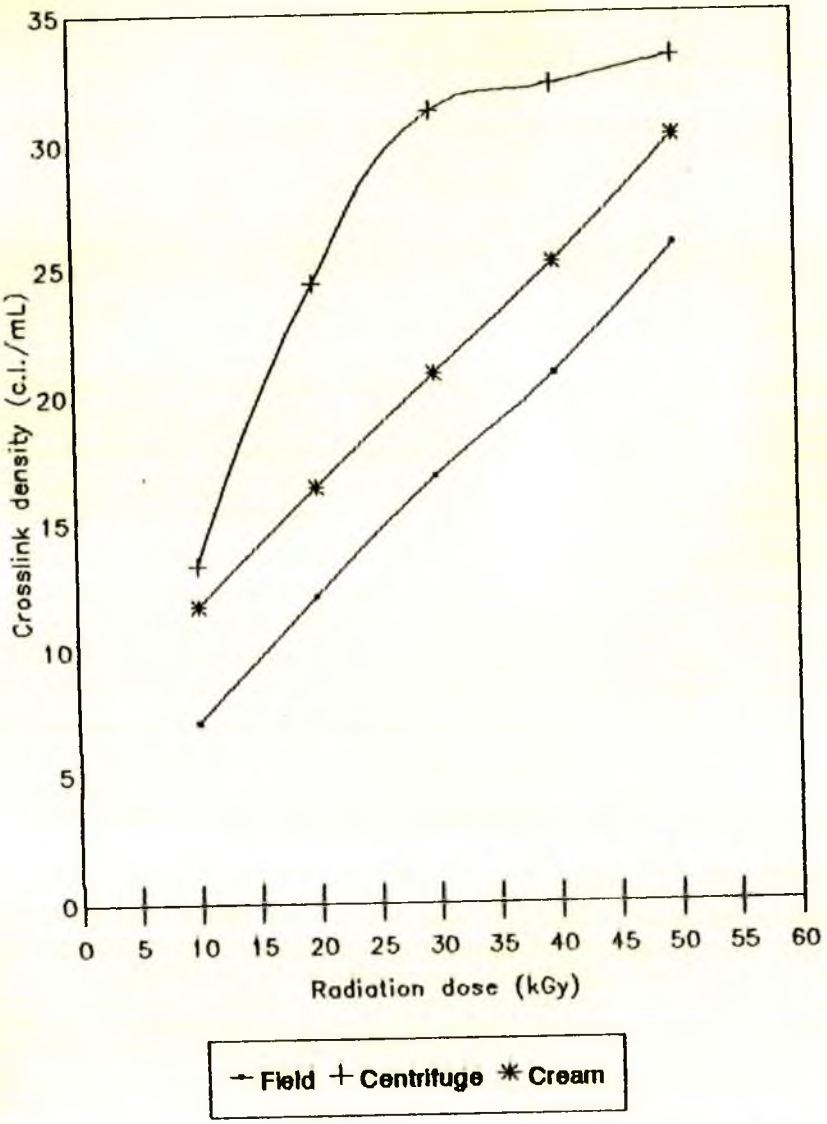


Fig. 13 Crosslink density vs radiation dose

Table 29. The effect of radiation dose and sensitizer on Modulus, Tensile strength (TS) and Elongation at break(EB)

Source : 4.0×10^4 Ci Co-60,
Temperature : 28°C (ambient temp.)
Sample : Field latex from Vatera rubber estate
Stabilizer : 0.2 phr KOH

Sensitizer	Radiation dose (kGy)	Modulus at 300 % elongation (MPa)	Modulus at 600 % elongation (MPa)	Tensile Strength (MPa)	Elongation at break (%)
Nil	10	0.5	0.9	1.2	1080
	30	0.5	0.9	7.3	1065
	50	0.5	1.0	7.5	1060
CCl_4	10	0.6	1.1	7.7	1000
	30	0.8	3.8	14.5	910
	50	1.1	5.5	12.4	800
n-BA	10	0.6	1.2	8.1	1010
	30	0.9	3.9	14.6	920
	50	1.2	5.7	13.0	820
CCl_4 + n-BA	10	0.7	1.2	8.3	1000
	30	1.0	4.0	14.9	890
	50	1.3	5.8	12.9	800
n-BA + H_2O_2	10	0.6	0.9	8.0	1010
	30	0.6	0.9	9.2	960
	50	0.6	1.0	11.0	890

Table 29 (Figures14 and 15) shows that modulus at 300% and 600% elongation increases with the radiation dose in almost all cases, but this increase in the modulus is much promenent in the presence of n-BA and n-BA + CCl_4. n-BA + H_2O_2 combination is not effective in this respect. Elongation at break shows expected trend of decrease as modulus increases.

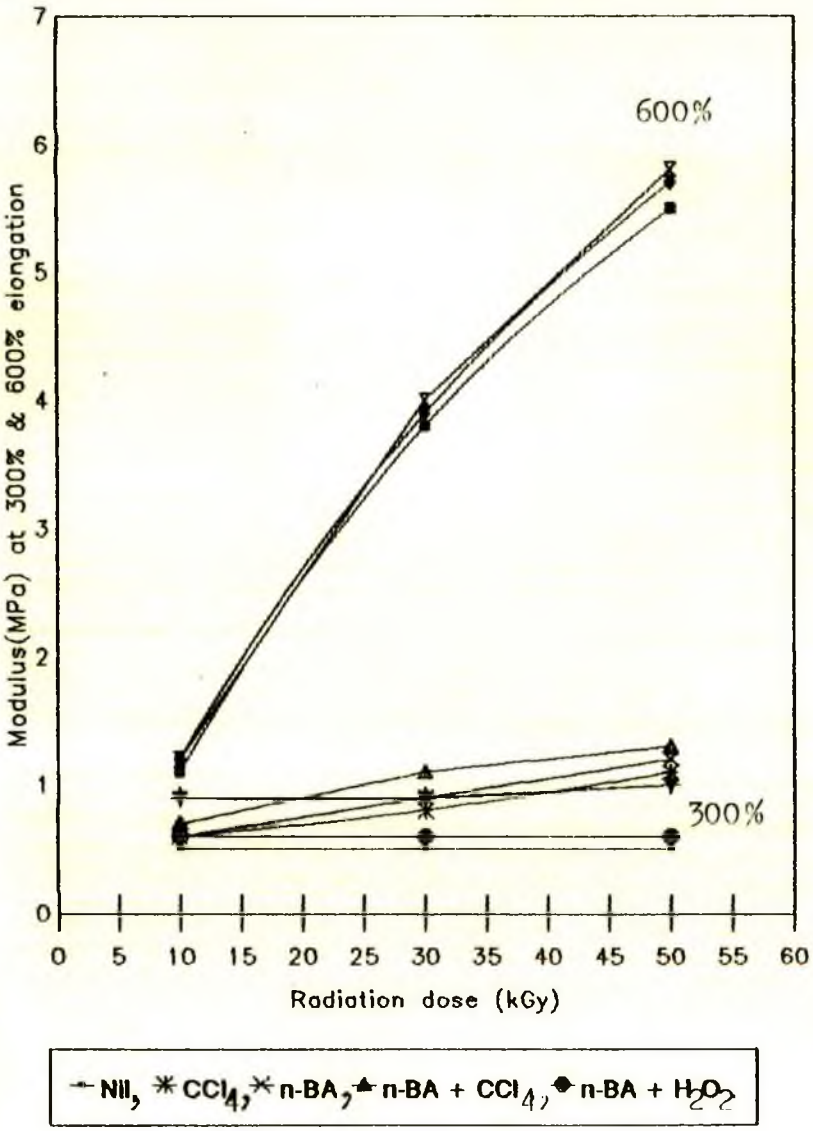


Fig. 14 Modulus vs radiation dose

The tensile strength is maximum at 30 kGy radiation in the presence of sensitizers (except n-BA + H_2O_2 combination). It is to be noticed that elongation at break decreases with the increase of radiation dose for all the sensitizers.

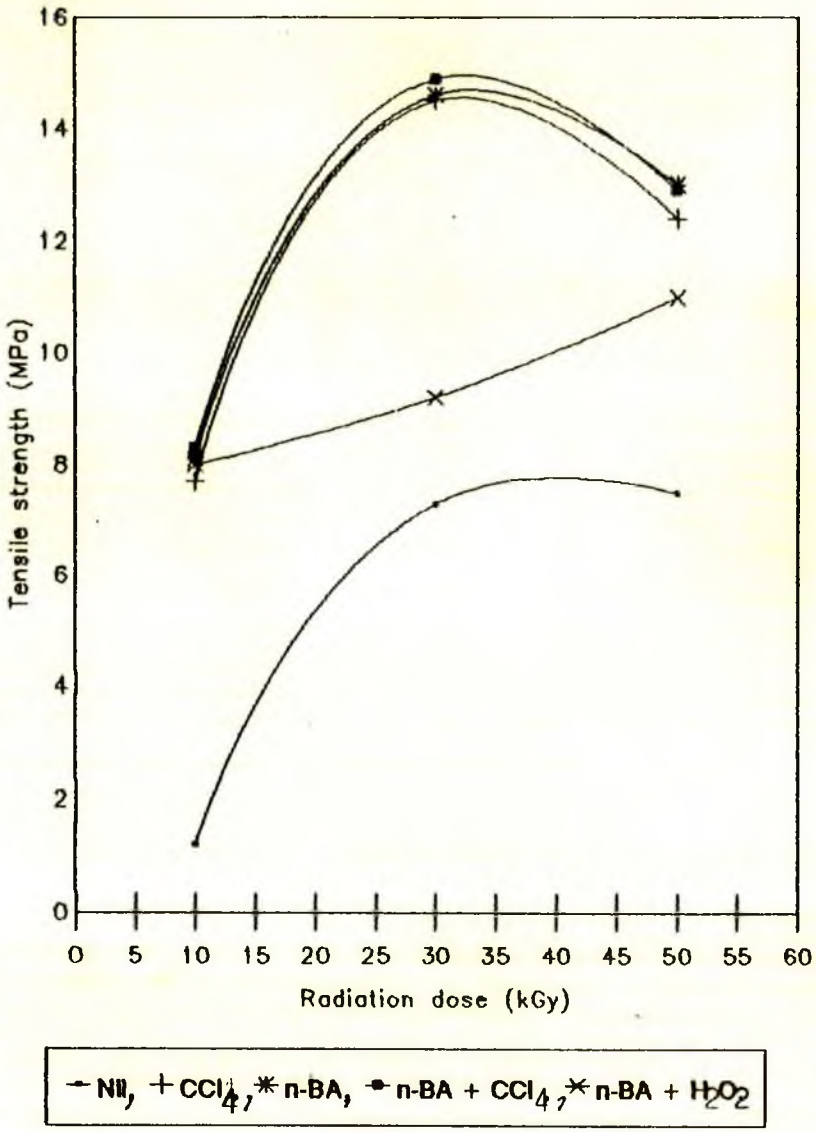


Fig. 15 Tensile strength vs radiation dose

Table 30. Tensile strength (TS), Modulus and Elongation at break (EB) at various radiation dose for different types of latex

Source : 4.0×10^4 Ci Co-60
Temperature : 28°C (ambient temp.)
Sample : Field latex from Shahajee Bazar rubber estate
Sensitizer : n-BA,
Stabilizer : 0.2 phr KOH.

Latex type	Radiation dose (kGy)	Modulus at 300% (MPa)	Modulus at 600% (MPa)	Tensile Strength (MPa)	Elongation at break (%)
Field	10	0.7	1.9	11.1	1010
	20	0.8	2.6	17.6	990
	30	0.9	3.0	18.2	970
	40	0.9	3.2	16.0	940
	50	0.9	3.4	12.1	920
Centrifuge	10	0.95	2.0	16.2	1090
	20	1.0	2.9	21.6	1070
	30	1.1	3.5	25.9	1060
	40	1.1	3.9	22.2	990
	50	1.1	4.1	20.1	990
Cream	10	0.7	2.0	13.7	1070
	20	0.8	2.6	20.2	1070
	30	0.9	3.0	20.7	1000
	40	1.0	3.4	18.2	970
	50	1.0	5.1	15.5	920

The effect of radiation dose on the tensile strength, moduli at 300% and 600% elongation and elongation at break are given in Table 30. The relation between radiation dose, modulus and tensile strength(TS) of the irradiated latex film are shown in Fig-16, and 17. The film from the irradiated field latex has the lowest tensile strength and the centrifuge concentrated irradiated latex has the

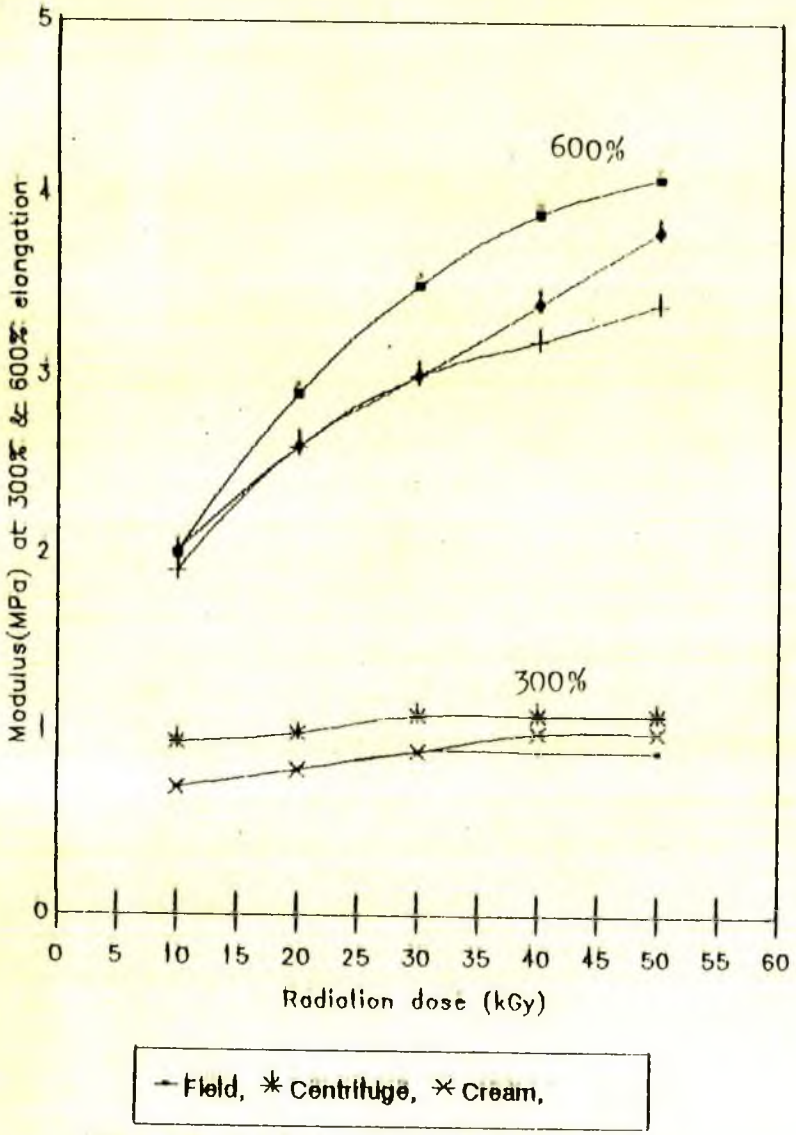


Fig. 16 Modulus vs radiation dose

highest tensile strength. The tensile strength of all the samples increases with readiation dose and reaches maximum at 30 kGy. Further increase of radiation dose decreases the tensile strength of the film. This is because high dose of radiation may cause chain scission in the rubber molecules. It is likely that at high radiation dose chain scission process tends to predominate the crosslink density.

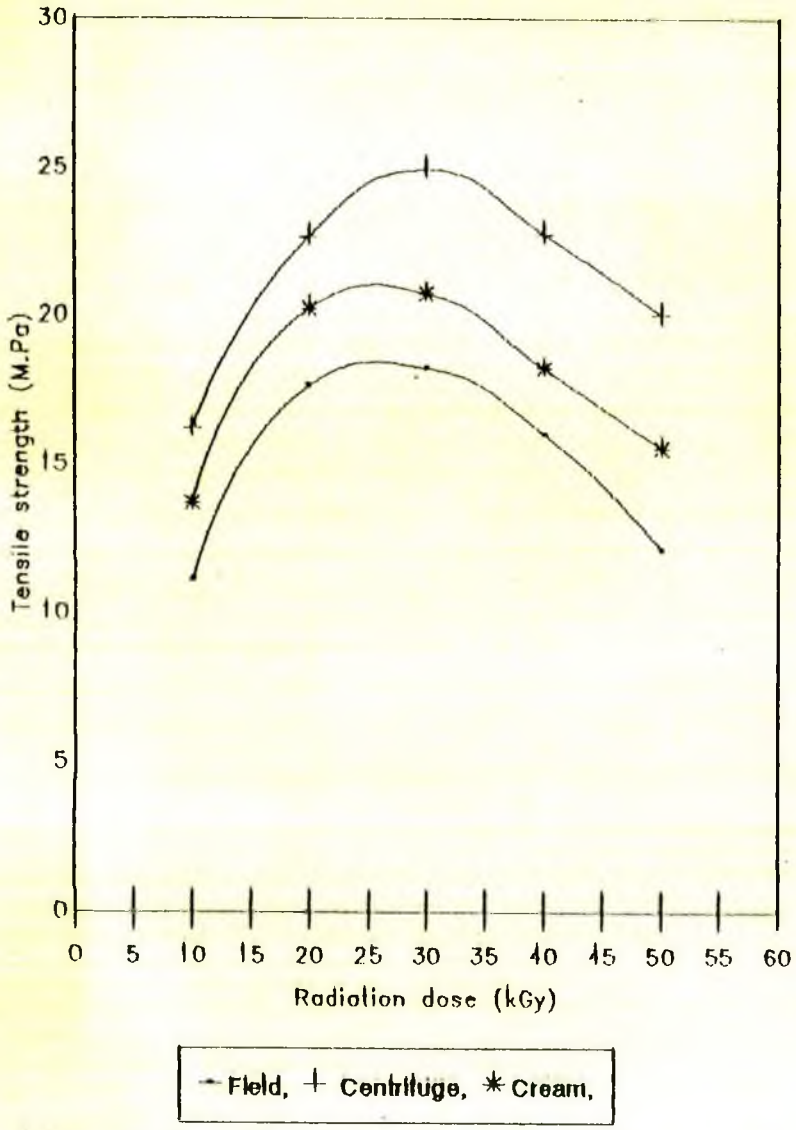


Fig. 17 Tensile strength vs radiation dose

Table 31. Gel content (%) of the film from irradiated field latex

Source : 4.0×10^4 Ci Co-60
Temperature : 28°C (ambient temp.)
Sample : Field latex from Vatera rubber estate
Stabilizer : 0.2 phr KOH.

Sensitizer	Gel content (%), at kGy			
	0	10	30	50
Nil	5.9	32.1	75.6	80.2
CCl_4		85.9	94.1	95.8
n-BA		86.2	95.3	96.1
n-BA + CCl_4		87.6	95.5	96.8
n-BA + H_2O_2		74.2	80.6	89.2

Table 32 Gel content (%) of the film from latices irradiated at different radiation doses

Source : 4.0×10^4 Ci Co-60
Temperature : 28°C (ambient temp.)
Sample : Field latex from Shahajee Bazar rubber estate
Sensitizer : n-BA,
Stabilizer : 0.2 phr KOH.

Latex type	Gel content (%), at kGy.					
	0	10	20	30	40	50
Field	10.40	80.4	89.4	90.9	91.0	91.0
Centrifuge	9.1	82.3	93.5	94.6	94.5	94.6
Cream	9.6	81.2	91.4	92.3	92.3	92.3

The gel content of the film of the latex is only 5.9 % before irradiation (Table 31.). This increases with the increase of radiation dose in all cases. The use of sensitizers (except n-BA + H_2O_2 combination) further increasethe gel content (Fig. 18).

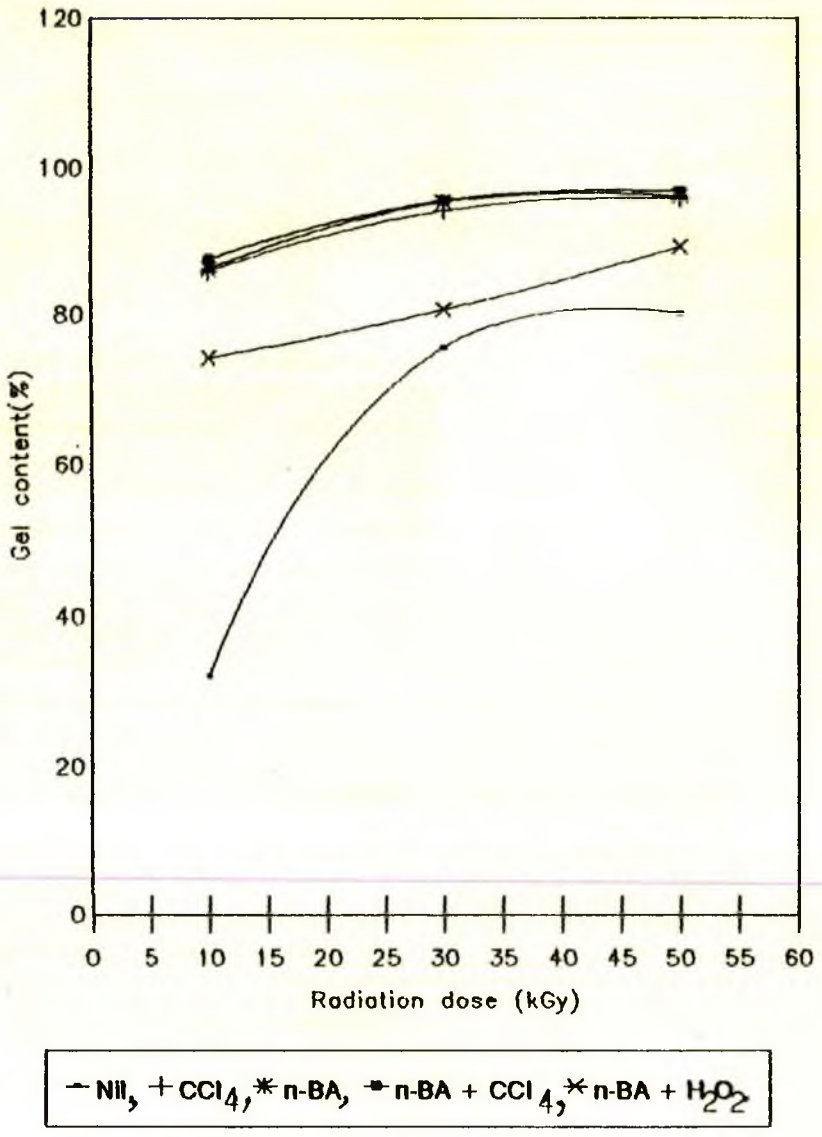


Fig. 18 Gel content vs radiation dose

The relationship between the gel content and irradiation dose is shown in Table 32. The gel content of the film increases rapidly with increase in the radiation doses for all types of latices and reaches maximum value at about 30 kGy. (Fig. 19). The initial gel content of the film from the field latex is the highest and lowest for the centrifuged latex. This is due to the presence of lower quantity of non-rubber material in the centrifuged latices. Subsequent increase in the gel content is due to the increase in the cross link density of latices by irradiation.

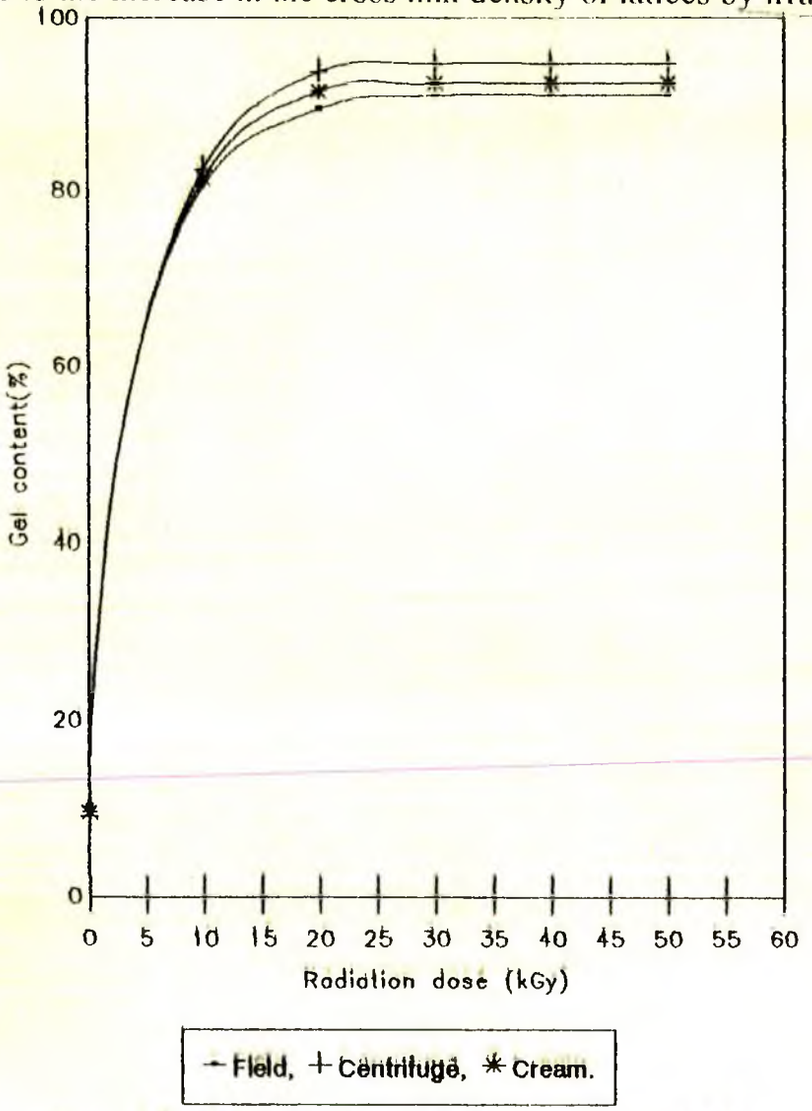


Fig. 19 Gel content vs radiation dose

The permanent set of the film decreases with the radiation dose at which the latex is irradiated. The permanent set decreases sufficiently at about 20 kGy radiation. The permanet set is a measure of the residual elongation after release of tension applied to the rubber films. Thus, it is related to the elastic properties of the film. Films from the unirradiated latex recover only about 50 % of its elasticity.

Table 33 Effect of radiation dose on permanenet set for varioue type of latex film

Source : 4.0×10^4 Ci Co-60, gamma.
Temperature : 28°C (anbient temp.)
Sample : Field latex from Shahajee Bazar rubber estate
Sensitizer : n-BA,
Stabilizer : 0.2 phr KOH.

Latex type	Permanent set (%), at kGy					
	0	10	20	30	40	50
Field	52.5	25.5	18.0	13.5	9.0	5.0
Centrifuge	45.5	18.0	7.5	4.5	3.0	0.5
Cream	48.0	18.0	12.0	7.5	4.5	3.0

However irradiation of the latices enhances this recovery. Under similar condition of irradiation film from concentrated latices are more elastic. Higher radiation dose (> 40 kGy) makes films almost 100% elastic (Fig. 20).

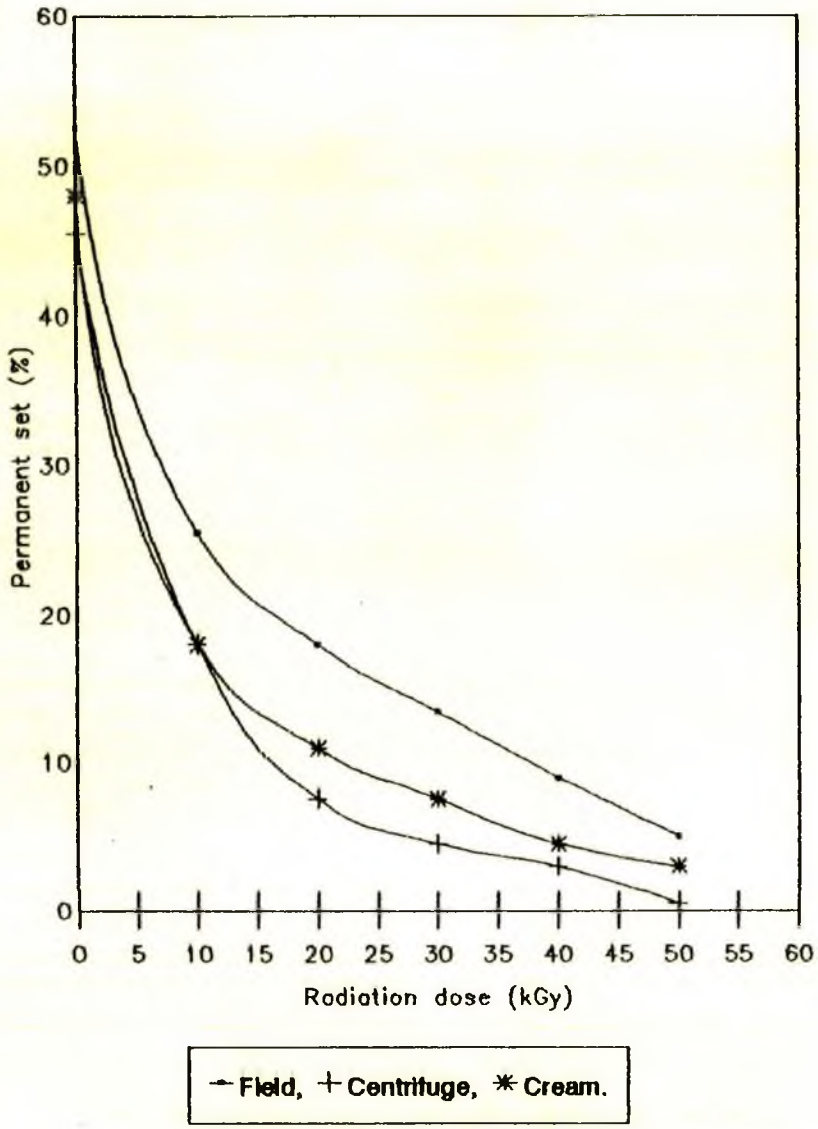


Fig. 20 Permanent set vs radiation dose

The maximum elasticity is found in the film from centrifuged latex, which contains least non-rubber solids and the minimum elasticity is found in field latex which contains higher amount of non-rubber solids. This means that the non-rubber solids prevent the rubber untis from coming closer.

5.2 Mechanism of radiation vulcanization

The irradiation of rubber molecules (poly isoprene) with gamma radiation or electron beam makes them ionized and excited. The excited molecules form free radicals through energy transfer. This leads to crosslinking reaction between the molecules[76]. The unusually long exposure time, to get desirable crosslinking, is shortened by using sensitizers. The sensitizers are organic molecules that give relatively higher number of free radicals at a given radiation dose. The energy transfer between these radicals and the chains of rubber molecules leads to their activation and increase the corsslinking efficiency. The formation of crosslinks in the rubber molecules is called vulcanization. The degree of crosslinking is usually measured by the crosslink density and volume swelling ratio. This crosslinking is affected not only by the sensitizers but also by the non-rubber substances present in the latex. The nature of the non-rubber substances will decide whether they will be affected by radiation. Accordingly the crosslinking process will also be influenced.

A general scheme of reaction leading to radiation vulcanization may be as follows :

$$RH + S^{\bullet} \xrightarrow{\gamma} R^{\bullet} + SH$$

$$R^{\bullet} + R^{\bullet} \xrightarrow{\gamma} R - R$$

Where RH is the rubber molecule $S^{\bullet}$ is the radical produced from the sensitizer by radiation and $R^{\bullet}$ is the radical formed from the rubber molecule and R-R is the crosslinked rubber (NR). The ions produced from the sensitizer by gamma radiation

can also attack rubber in the latex and produce R·. The G value of conversion of the sensitizer molecule to radicals (S·) is much higher than the G value of the conversion of rubber molecules to radicals (R·). Thus the extent of crosslink reaction in presence of sensitizer is also quite high.

n-BA and CCl_4 have been tried as sensitizer[45]. Both of this substances have high G value of conversion to radicals[77- 79].

$$CCl_4 \xrightarrow{\gamma} {}^{\cdot}Cl + {}^{\cdot}CCl_3$$

$$H_2C = CH - COOB \xrightarrow{\gamma} HC^{\cdot} = CH - COOB + H^{\cdot}$$

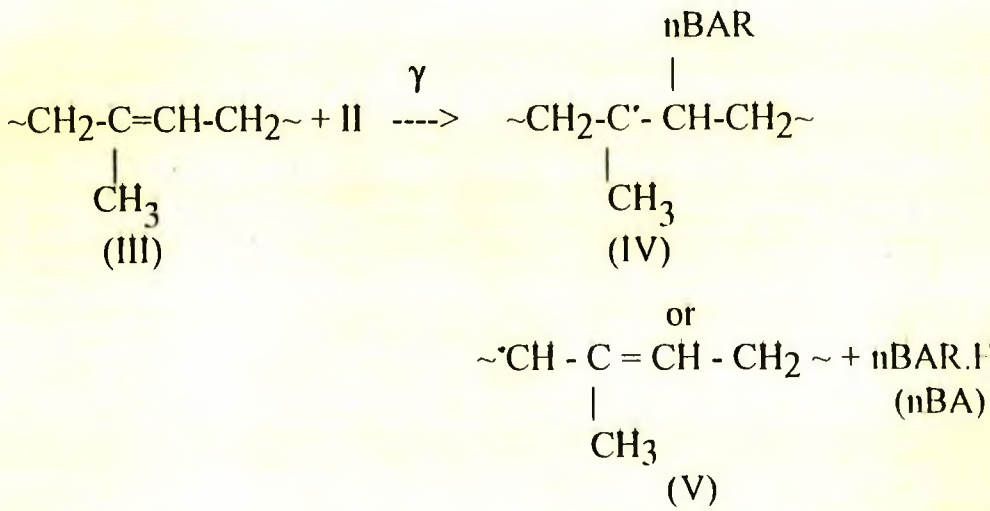
Here B stands butyl radicals — n-BA radical (n-BAR)

In the scheme of the mechanism of radiation vulcanization of liquid isoprene rubber (LIR) with 2-ethyl hexyl acrylate(2-EHA) as sensitizer, it has been suggested[80-81] that the product from 2-EHA is grafted on the backbone of LIR. The unreacted double bond in the pendant 2-EHA molecule serves as the site for further reaction which ultimately leads to cross linking. On the basis of this scheme the mechanism of radiation vulcanization of NR latex in the presence of n-BA can be as follows

$$\underset{\text{(B, butyl radical)}}{H_2C= CH\text{-}COOB} \xrightarrow{\gamma} {}^{\cdot}CH=CH\text{-}COOB + H^{\cdot}$$

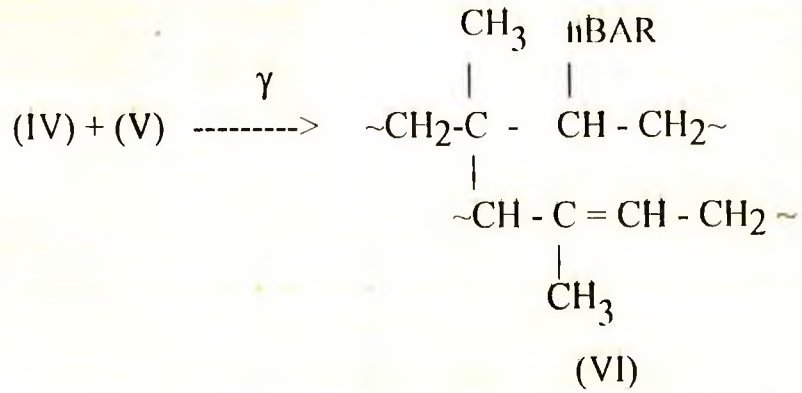
(I) — (II) n-BA radical (nBAR)

The nBAR (II) is more mobile[82] than the rubber chain or radical and attacks a double bond in the adjacent chain

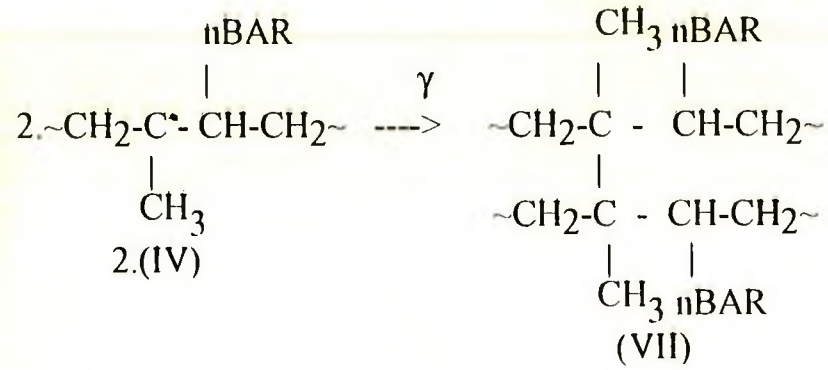


The radicals may either recombine or attack a double band to produce crosslink.

a.



b.



c. $\sim CH_2\text{-}C(CH_3)=CH\text{-}CH_2\sim + IV \xrightarrow{\gamma} \sim CH_2\text{-}C(CH_3)\text{-}CH(nBAR)\text{-}CH_2\sim$

$\sim CH_2\text{-}C(CH_3)\text{-}{}^{\bullet}CH\text{-}CH_2\sim$ $(R^{\bullet})$

d. $\sim CH_2\text{-}C^{\bullet}(CH_3)\text{-}CH(nBAR)\text{-}CH_2\sim + (R^{\bullet}) \xrightarrow{\gamma} \sim CH_2\text{-}C(CH_3)(R')\text{-}CH(nBAR)\text{-}CH_2\sim$

The probability of the individual reaction is not well known and some of them might be impossible for energetic or stearic reasons.

The natural rubber also contributes to the formation of radicals

$\sim CH_2\text{-}C(CH_3)=CH\text{-}CH_2\sim \xrightarrow{\gamma} \sim {}^{\bullet}CH\text{-}C(CH_3)=CH\text{-}CH_2\sim + H^{\bullet}$

$(R^{\bullet})$

The rubber radicals may also participate in the vulcanizing process.

It is to be noted that concentration of radicals produced by radiation depends on the dose of radiation, G values of conversion for each kind of compounds and weight fraction of the compounds. The G value of conversion of natural rubber appears

to be quite low. This is reflected in the low crosslink density in the absence of sensitizer (Table 27).

The above scheme is highly speculative and we do not have any evidence to support it. CCl_4 sensitizer may also form crosslinks according to the above scheme. Moreover nBA is less toxic than CCl_4, but have the same efficiency of cross link formation as that of CCl_4 . However n-BA tends to destabilize NR latex[41]. This destabilizing effect is sufficiently hindered by the addition of 0.2 phr KOH as stabilizer. Consequently the latex can stand upto 5 phr n-BA.

5.3 Comparison of some physical properties of the films from irradiated latex

Table 34. Comparison of some physical properties of the film from irradiated latex with the literature values and the requirement of the international specifications.

Physical properties	present work, at 30 kGy	Literature values [10, 49, 83, 84]			Standard[85-88]	
		films, 30 kGy	Products from NVRNL	Products form S vulcanized	BS	JIS
Tensile strength (MPa)	25.9	23.0	22.6	30.6	24.0(min)	24.5 (min)
Elongation at break, %	1060	990	970	840	560(min)	700 (min)
Permanent set, %	4.5	-	-	-	-	10 (max)
Modulus at 300% elongation	1.1	-	1.01	1.64	-	-
Modulus at 600% elongation	3.5	-	2.42	5.68	-	-

Our study has enabled us to obtain some valuable results of commercial importance. The field latex from the trees of about 10 years age, when concentrated by centrifugation and irradiated with 30 kGy (3.0 Mrad) gives rubber which can be used to produce gloves and similar commodities. The tensile strength, the elongation at break, permanant set and modulus of the films that has been produced favourably compare (Table 34) with those of similar products marketed as consumer goods. Moreover, these properties of the irradiate latex meet the available international [British (BS) and Jupanese (JIS)] standards.

References

1. O. D. Cole in *Introduction to rubber technology*, Auther : M. Morton, Reinhold, New York, 1959, P.61.
2. G. Martin in *The Applied Science of Rubber* editor W. J. Naunton, Edward Arnold, London 1961, P.158.
3. J .N . Dean in "Gutta-percha and Balata", *The Chemistry and Technology of Rubber*, Davis and Blake, Reinhold, New York, 1937, P.123.
4. C. F. Flint, *The Chemistry and Technology of Rubber latex*, Van Nostrand, New York, 1938, P. 62.
5. B. L. Archer and B. C. Sekar *J. Biochem*, 1955, **61**503.
6. S. Subramaniam, *RRIM Technology Bulletin*, 1980, **4**,1.
7. G. M. Briston and B westall, *Polymer*, 1967, **4**, 609.
8. A. Subramaniam, *Chemical Technology*, 1972, **45**, 246.
9. R. L. Wagner and P. J. Flory., *J. Am. Chem. Soc.* 1952, **74**, 195,
10. M. Utama, "Irradiated latex and its application" Presented at the National Training Course on RVNRL INST, SAVAR, DHAKA, 1989
11. ISO. 2004: 1991 *International Standard for Natural Rubber Latex* Concentrate Centrifuged or Creamed, ammonia-preserved type-specification.
12. T. D. Pendle, "The natural rubber industry and its future prospects", *Procedings of the International Symposium on RVNRL*,1990 27-45.Japan Atomic Energy Research Institution (JAERI).
13. D. T. Graham, G. E. Mark and A. R. Pomery, *J. Biomed. Mater. Research*, 1984, **18**, 1125.

14. AS 2696: 1984. " Australian Standared for single use urethral catheters (sterile) for general medical use", Standard Association of Australia.

15. Gorton A.D.T. and Mc Sweeney G.P. *NR Technol* 1987, 18(1), 1-12. **Chem. Abstr**. 1967, **107**, 60369q.

16. D. W. Pounder, "Curing of rubber latex and the production of article therefrom" *BS. Patent* 853: 923, 1956.

17. Ahammad Ullah, A. K. M. A. Manaf, M. A. Hashem, M. N. H. Bhuyia and M. N. Islam, *Bangladesh J. Sci. Ind. Res.*, 1989, **24**,1.

18. T. S. Utami and S. Oerip *Menara Perkebunan* 1980, 48 (2), 51. **Chem. Abstr.** 1981, **95**, 151926u.

19. M. M. Said, W. N. P. Chin and M. A. Latif, *J. Nat. Rubber Res.* 1991, 6 (2), 115. **Chem. Abstr**. 1992, **116,** 130897x.

20. C. J. Kuruvilla and N. J. Arthur, Brit 1, 293. **Chem. Abstr**.1973, **78**, 59535s.

21. K. C. Shun, W. G. Wren, *J. Rubber Res. Inst. Malayasia*. 1977, 25 (2), 69. **Chem. Abstr**. 1978, **88**, 137639b.

22. C. J. Kuruvilla, Brit 1, 431, 176 **Chem. Abstr.**1976, **85**, 178757v.

23. K. C. Sekar, *Rubber news (India)* 1976, 15 (6), 28-32. **Chem. Abstr.** 1976, **85,** 109739d.

24. M. T Cough John. B. Pedido, PI. 7403, 890. **Chem. Abstra.**1976, **85**, 161584p.

25. N. M. M Varghese, R. L. Kothandaraman and E. V. Thomas *Rubber Board Bulletin (India)*, 1976, 13 (3), 58. **Chem. Abstr,** 1978, **88**, 122392s.

26. T. Lapananon, *Thai. J. Agric. Sci.* 1984, 17 (3), 221. **Chem. Abstr.** 1984, **101**, 231726m.

27. A. Chandumpai, *Warason Songkhla Nakkharin* 1984, 6 (2), 121-7 (Thai). **Chem. Abstr.** 1985, **102**, 186409t

28. M. Utama, F. Sundardi, M. Sumartim, S. Iskandar, D. Iramani. K. Makuuchi and Y. Yoshii. "Characterisition of Natural Rubber from Indonesia" *Proceedings of the Internaional Symposium on RVNRL.1990,* 169-171 (JAERI).

29. H. C. Chin, M. M. Singh and S. E. L. Oke, *Plast. Rubber Matter Appl* 1979, 4 (4), 164.

30. T. D. Pendle and A. D. T. Garton, *Rubber Chem. Technol.* 1978, 51 (5), 986. **Chem. Abstr**. 1979, **90**, 73093a.

31. H. J. Hasma. *Nat Rubber Res.* 1991, 6 (2), 105. **Chem. Abstr**. 1992, **116**, 153546w

32. S. Fong, Ng. Chiew Sum. *Rubber Technol.* 1984, 57 (2), 243. **Chem. Abstr**.1984, **101**, 74076e

33. A. B. Majid, *National Symp. Isot. Appl. Ind. Proc.* 1977, 245. India Dep. Atomic Energy. **Chem. Abstr.** 1979, **91** 108849b.

34. L. Jean, *Rev. Gen. Caout Plast* 1973, 50 (11), 8979 (Fr). **Chem. Abstr.** 1974, **80**, 109540d.

35. S. Yanti, S. F. Suncardi and A. H. Kuncono , *Radiat. Physc. Chem.* 1990, 36 (6), 815. **Chem. Abstr**.1991, **114**, 8094b.

36. K. Makuuchi, K. Tsushina, N. G. Kyokaishi 1988, 61 (7). **Chem. Abstr.** 1989, **110**, 25202v.

37. K. Makuuchi, H. Miyuki, *J. Appl. Polym. Sci.* 1984, 29 (3), 965. **Chem. Abstr**. 1984, **100**, 40590a.

38. K. Makuuchi, R. Debendra, I. Ishigaki and F. Yoshii, *Jpn. Koku Tokkyo Koho* JP, 01, 193, 325 89, 193, 235. **Chem. Abstr.** 1990, **112**, 22190v.

39. P. Aroonvisoot and K. Makuuchi, "Selection of Hydroperoxides as co-sensitizer for n-Butyl Acrylate" *proceedings of the International Symposium on RVNRL*, 1990, 305-309 (JAERI).

40. Y. S. Sabarinah and F. Sundardi. "Effects of Hydrogen Peroxides on the RVNRL Snsitizer with CCl4 and n-BA" *Proceedings of the International Symposium on RVNRL*, 1990, 319-321(JAERI).

41. C. Zhonghai and K. Makuuchi ,"n-Butyl acrylate as radiation Vulcanization of Natural Rubber Latex" *Proceedings of the International Symposium on RVNRL*, 1990, 326-329(JAERI).

42. C. Zhonghai and K. Makuuchi. " Radiation Vulcanization of Natural Rubber latex with 3MeV Electron Beams, part-1" *Proceedingg of the International Symposium on RVNRL, 1990.* 358-362(JAERI).

43. Bez. Willford (Kaut-chuk-Gesellschaft, Frankfurt, West Germany) **Chem. Abstr**. 1991, **114**, 166068a.

44. S. Samantha Sooriyarachchi; K. Makuuchi, F. Yoshii and I. Ishigaki. " Radiation volcanization of Natural Rubber latex with 3MeV Electron Beams, part-2" *Proceedings of the International Symposium on RVNRL*, 1990, 368-372(JAERI).

45. N. Mohid, K. Makuuchi, F. Yoshii and I. Ishigaki. "Effects of non-rubber components of sensitized Radiation Vulcanization of Natural Rubber Latex" *Proceedings of the International Symposium on the RVNRL*, 1990.157-163(JAERI).

46. E. V. Thomas, "Effects of non-rubber solids and stabilizing Agents on Radiation Vulcanization of Natural Rubber Latex" Proceedings of the International Symposium on RVNRL, 1990, 178-183(JAERI).

47. Shukri Bin HJ, A. B Wahab, K. Makuuchi, R. Devendra, C. P. Pansa "Effect of Heating and Leaching on Mechanical Properties of Radiation Vulcanization of Natural Rubber Latex" *Proceeding of the International Symposium on RVNRL*, 1990, 216 (JAERI).

48. B. S. 4355: 1968, Specification for various Natural rubber latex concentrate.

49. Kyogo Tsushma, K Makuuchi, F Yoshii, I Ishigaka, " Commercial application of RVNRL" *Proceedings of the International Symposium on RVNRL*, 1989, P-127-130 (JAERI).

50. JIS -Z- 4810 the *Japanese Industrial Standard Specification* for Protective rubber gloves for radioactive commination.

51. Annual Book of *ASTM* (American Society for testing and material), 1985, Section 9, **Vol. 9.01, D-1076-80**, Specification for Rubber Concentrated, Ammonia Preserved, Creamed and Centrifuged Natural Rubber latex.

52. ISO 124, 1992. *International Standard, Rubber latex*- Determination of Total Solids Content.

53. ISO 126, 1989. *International Standard, Rubber latex*- Determination of Dry Rubber Content.

54. BS 903, Part B 12: 1960, *British Standard Methods*, Determination of Rubber (Polymer) Content.

55. BS 903. Part 4, 1950 Section 4.2 *British Standard Methods*, Determination of rubber hydrocarbon by direct oxidation method.

56. ISO 125, 1985. *International Standard, Rubber latex*- Determination of Alkalinity (as NH_3) on latex concentrate.

57. ISO 2005-1974 *International Standard, Natural Rubber latex*- Determination of Sludge content.

58. ISO 706, *International Standard Natural Rubber latex*- Determination of Coagulum content.

59. SLS 325: 1974, *Sri Lanka Stadard Methods of testng rubber latices.*

60. ISO 506, 1992. *International Standard, Natural Rubber latex*, Determination of volatile fatly acid number (VFA).

61. ISO 127, 1984. *International Standard Natural Rubber Latex*-Determination of KOH number.

62. Annual Book of *ASTM*, Sec. 9, **Vol. 9.01, D-3533-82**, standard method of testing, Rubber-Nitrogen content.

63. ISO 1656: 1988, *International Standard, Rubber, raw rubber & rubber latex natural*- Determination of Nitrogen content.

64. ISO 247, 1990. *International Standard for rubber*-Determination of ash. .

65. Annual Book of *ASTM* Sec. 9, **Vol. 9.01, D-1278-84**, Method for rubber from natural sources- Chemical analysis.

66. AOAC *(Association of official Analytical chemists)*, Ditermination of Ash, Acid insoluble (Water-soluble, Alkalinity of etc.), 1975, **31.016.**

67. ISO 8053,1987 *International Standard Rubber and latex* Determination of Copper content- Photromatric method.

68. ISO 7780. 1987 *International Standard Rubber and Rubber latices* Determination of manganese, Sodium periodate photometic method.

69. A.I. Vogel, *"A Textbook of Quantitative Inorganic Analysis"*, 4th ed., ELBS, Longman Group Ltd., 1978, P 746.

70. ISO 1657- 1986, *International Standard, Rubber & Rubber Latex*, Determination of Iron Content, 1,10,Phenanthroline photomatric method.

71. A.I. Vogel, *"A Textbook of Quantitative Inorganic Analysis"*, 4th ed., ELBS, Longman Group Ltd., 1978, P 741.

72. D.C Blackley, *High polymer latices*, **Vol. 11,** Macloaren and sons London 1956, P-64.

73. Annual Book of ASTM, D 412-83, Standard Test methods for Rubber properties in Tension.

74. Y. Minoura and M. Asao, *J. Appl. poly. Sci,* 1961, **5**, 401

75. D.K. Sumbogo, F. Sundardi and M. Utama "Effect of antioxidant and the aging property of rubber film Prepared from Radiation Vulcanized Natural rubber Latex", *Proceedings of the international Sysposium of RVNRL*, 1990, 234-237 (JAERI).

76. Lu Li Kang, "Study on radiation vulcanization of Rubber and discussion of its industrial applications". (Report of Shenyang Industrial Rubber products Research Institute, China, 1990).

77. Y. Minoura and M. Asao, *J. Appl. poly. Sci,* 1961, **5**, 233.

78. K. Makuuchi and T. Serizwa, *Radiat. Phys. Chem.*, 1984, **24**, 2

79. K. Peter and R.W. Hein, *J. Am. Chem. Soc.*, 1959, **81**, 1187.

80. W.A. Salman and L.D. Loan, *J. Appl. Polym Sci,* 1972, **16**, 671.

81. I. A. Abu-Isa, *J. Radiat*, Curing **19**, 1981

82. Chyagrit Siri - Upathum, K. Makuuchi and I. Ishigaki "Radiation vulcanization Mechamism of liquid Isoprene with 2-Ethylhexyl Acrylate", *Proceedings of the International Symposium on RVNRL*, 1990, 336-342 (IAERI).

83. F. Sundardi, M. Utama, S. Iskandar and Herwinarni, "Development of Condoms and gloves from Radiation Vulcanized Natural Rubber", *Proceedings of the International Symposium on RVNRL*, 1990, 132-140. (JAERI)

84. N. Q. Hien, D. Binh, V. T. Thien, L. Hai, N. T. Man and V. T. Thanh," Development of surgical glove from Radiation Vulcanized Natural Rubber latex. *Proceedings of the International Symposium on RVNRL*, 1990, 260-264. (JAERI).

85. JIS T 9111-1985, *Japanese Industrial Standard* " Rubber Condoms"

86. BS 3704: 1989 *British Standard Specification*, for "Natural Rubber latex Condoms".

87. JIS T 9107-1992, *Japanese Industrial Standard* " Surgical rubber gloves".

88. BS 4005 : 1984, *British Standard Specification*, Single use, Sterilized Surgiecal Rubber gloves.