STUDIES ON RADIATION VULCANISATION OF NATURAL RUBBER LATEX USING n–BUTYL ACRYLATE AS SENSITISER AND ITS RHEOLOGICAL BEHAVIOUR

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IN
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BY

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Certified that the thesis entitled **"Studies on Radiation Vulcanisation of Natural Rubber Latex using n-Butyl Acrylate as Sensitiser and its Rheological Behaviour"** being submitted by Smt.G RAJAMMAL in partial fulfilment for the award of the degree of Master of Technology in Polymer Technology of Cochin University of Science & Technology, Cochin-22 is a record of bonafide work done by her under my guidance and supervision.

Dr.E.V.Thomas
Director,
(Processing & Product Development)

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Radiation Vulcanisation of Natural Rubber Latex(RVNRL) using gamma rays promises to provide a material with exceptional good qualities for the manufacture of latex products for use in the medical and surgical field.[1] Latex vulcanised by this technique contains no sulphur , zinc oxide or products of accelerator breakdown.Hence it is free from nitrosoamine and has low cytotoxicity compared to sulphur vulcanised latex. A review of the developments in the radiation vulcanisation of natural rubber latex is given in this chapter.

1. Natural rubber latex

Natural rubber latex is mainly obtained from the bark of <u>Hevea Brasiliensis</u> by the process of tapping.The freshly tapped latex is a whitish fluid of density between 0.975 and 0.980 g ml^{-1} , pH from 6.5 to 7.0[2] and surface free energy from 40 to 45 ergs cm^{-2} . The rubber content of latex varies between 25 and 40 percent by weight and this variation is owing to factors such as type of tree, tapping intensity, soil conditions and the season. In addition to the rubber hydrocarbon,a number of non rubber constituents such as proteins, carbohydrates,lipids, inorganic salts etc. are also present in latex.The rubber hydrocarbon in latex is predominantly cis-1,4-polyisoprene and it occurs as molecular aggregates in the form of discrete particles which are usually spherical with diameter ranging from about 0.02-3.0 microns.[3]

1.2 Preservation and Concentration of latex

Natural rubber latex in vessels of rubber tree is sterile, but as it comes out,it gets contaminated by bacteria and yeasts.[4] The micro organisms metabolise the non rubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which lead to coagulation of latex.[5] Therefore,preservatives are added to latex immediately after collection. Among the preservatives, ammonia is still widely used and it inhibits bacterial growth,acts as an alkaline buffer, raise the pH and neutralise free acid formed in latex.[6] But ammonia has the disadvantage that it is pungent smelling, and prolonged exposure to the gas can cause discomfort to workers.Also high concentration of ammonia leads to processing problems. Therefore, attempts have been made to develop low ammonia preservation systems.[7,8,9] A commonly used low ammonia system is LA-TZ which contains 0.2% ammonia, 0.013% TMTD,0.013% zinc oxide and 0.05% lauric acid.[10,11]

Preserved field latex is unsuitable for most latex applications as its rubber content is low.For most product manufacture, a latex of minimum 60% rubber content is required.[12]The important methods for concentration of preserved field latex are evaporation, creaming, centrifuging and electrodecantation. Only centrifuging and creaming are commercially used for the production of latex concentrate.[12]NR latex concentrate is a highly specified material.The latex properties of significance are dry rubber content(drc), non rubber solids(NRS), mechanical stability time,volatile fatty acid number(VFA),potassium hydroxide(KOH)number and alkalinity.The significance of these properties has been discussed by Blackley[13] and Cockbain.[14] Latex concentrate is a non newtonian fluid and its viscosity decreases with increasing shear rate.[15]

1.3.Vulcanisation.

Vulcanisation is the process by which the mainly viscous rubber is converted into elastic rubber through the crosslinking of the macromolecules at their reactive sites.It is an intermolecular reaction which increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force.According to the theory of rubber elasticity, the retractive force resulting from a deformaton is proportional to the number of network supporting polymer chains per unit volume of elastomer.[16] Vulcanisation usually produces network junctures by the insertion of chemical crosslinks between polymer chains.The crosslinks may be formed through chains of sulphur atoms,single sulphur atom or carbon-carbon bonds.The vulcanisate properties are affected by the crosslink density,type of crosslinks,nature of polymer type and amount of filler etc.[16] Vulcanisation was first discovered by Charles Goodyear(1839)and by Thomas Hancock(1843) by heating rubber with sulphur.[17] The introduction of organic accelerators then enabled to reduce the vulcanisation time and sulphur dose required for optimum physical properties,improve the ageing resistance of rubber goods and prevent blooming of sulphur.[18]

1.4.Prevulcanised latex

The term " prevulcanised latex" refers to a chemically modified latex which on drying gives a vulcanised film.[19] This type of latex is prepared from field latex or concentrates either in the rubber plantation factory or in the consumers factory. It is especially useful for the small to medium sized dipping factory, since compounding of the latex is either unnecessary or is limited to the incorporation of the desired pigments. The manufacture of medical dipped items, feeding teats and toy balloons are usually based on prevulcanisd latex. The crosslinking of rubber in latex can be effected by reaction with sulphur[20], sulphur donors[21], peroxides[22,23] or irradiation[24]. Commercially, prevulcanised latex is prepared by reacting latex with ingredients such as sulphur and accelerators (dithiocarbamate type, usually, zinc diethyl dithiocarbamate) and heating in a water jacketed vessel at 60-70 °C[25].

1.5. Radiation Vulcanisation of Natural Rubber Latex (RVNRL)

Considerable interest has been shown in recent years in the production of prevulcanised latex by gamma-irradiation. The resulting radiation vulcanised (RV) NR latex can be used for the manufacture of latex products by the conventional dipping process. The procedure of RVNRL consists of three steps.(1) Mixing NR latex with sensitiser.(2) Irradiating with gamma rays(3) Adding antioxidants.The properties of RVNR latex depend on the quality of NR latex, amount of sensitiser and kind of antioxidant.The advantages of RVNR latex products are absence of carcinogenic nitrosoamines, low cytotoxicity and high transparency[24].

The first paper on radiation vulcanisation of natural rubber latex is a patent by Pounder D.W.in 1956[25]. He has claimed the possibility of prevulcanising natural rubber latex by irradiation with X-rays, gamma-rays and high energy electrons. However, the vulcanisation dose (Dv dose) at which the maximum tensile strength of dried film of irradiated latex is found is more than 30MRad which is too high to be used for industrial application. In 1961 Asao et al[26] reported that halogenated hydrocarbons such as carbon tetra chloride, chloroform etc. act as sensitisers which reduce the radiation dose required for vulcanisation. It was found that Dv is around 5M Rad with 5 phr of CCl_4[26]. .Since then research on RVNRL were carried out in France, U.S.S.R, China, Poland, India and Indonesia. Among them France was very eager to commercialise the process. However, the RVNRL technique had not been used in industries. The high cost of irradiation for vulcanisation and low quality of products from the RVNR latex were believed to be the main reasons for the lack of interest from the industry.[27] In 1982, the International Atomic Energy Agency and United Nations Development Programme implemented a regional project of RVNRL as a part of co-operative programme for Asia and the Pacific regions. As a result of this research project, the situation has changed drastically. A promising new technology of RVNRL will become available to rubber industry with the development of suitable sensitiser for bringing about the vulcanisation at a radiation dose of 1.0-1.5M Rad.The progress made by the programme is summarised below.

1.5.1. Sensitisers

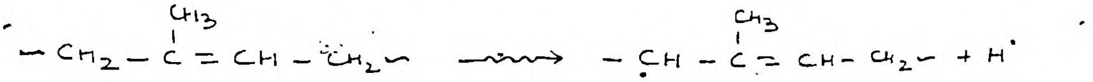
One of the aims of the programme was to find out a sensitiser system which could reduce the vulcanisation dose below 3 MRad. French, Polish and Indonesian research groups have used carbon tetra chloride as sensitiser for their attempts to commercialise RVNRL.It was found that CCl_4 in combination with other sensitisers such as 2-ethyl hexyl acrylate enhances the sensitising effect further.[28] However, the use of CCl_4 will be banned in near future because it destroys the stratospheric ozone layer. It is toxic to human beings and environment.[29]

The Japanese research group has evaluated the use of polyfunctional monomers (PFM) to accelerate radiation induced crosslinking of polymers.[29] Polyfunctional monomers such as 1,6-hexane diacrylate (HDDA) and trimethylol propane triacrylate are found to be very effective sensitisers for RVNRL. However, PFM cannot be acceptable for RVNRL because trace amount of remaining PFM in rubber products will cause skin irritation. Mono functional acrylates such as 2-ethyl hexyl acrylate (2EHA) and n-butyl acrylate(n-BA) also accelerate RVNRL through less sensitising efficiencies than PFMs.[30] With 2EHA, it is difficult to remove the remaining 2EHA from the latex products due to low vapour pressure of the monomer. The residual monomer causes skin irritation and gives bad smell.[31] n-BA has got higher vapour pressure and sensitising efficiency than 2EHA. However, it has a tendency to destabilise the latex. It has been reported that the addition of KOH can stabilise NR latex sufficient to withstand against the addition of nBA. Further attempts to reduce the Dv was by use of hydroperoxides such as cumene hydroperoxide, tert-butyl hydroperoxide as co-sensitisers.[32] Majali et al have evaluated the use of urea as a co-sensitiser.[33]

1.5.2. Radiation chemistry aspects of latex irradiation

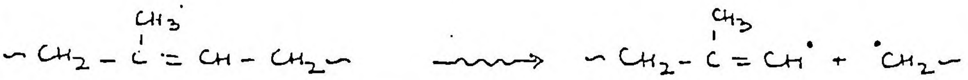
The radiation chemistry of natural rubber latex is not clearly understood because latex represents a complex system varying with the growing conditions of Hevea and its origin. From the radiation chemistry point of view, it can be seen to be composed of two phases:[51] the rubber phase and the serum phase.Radiation can interact with the latex in two ways.(1) Direct effect on the rubber particles.

IN RUBBER PHASE



$$\sim CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim \;\rightsquigarrow\; - \underset{\bullet}{C}H - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim + H^{\bullet}$$

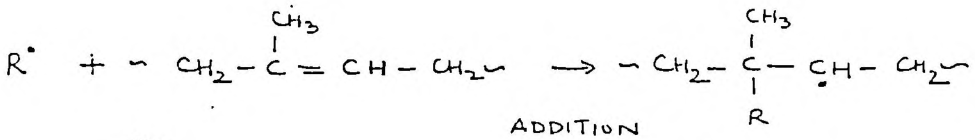
RADICAL FORMATION BY
H- ABSTRACTION



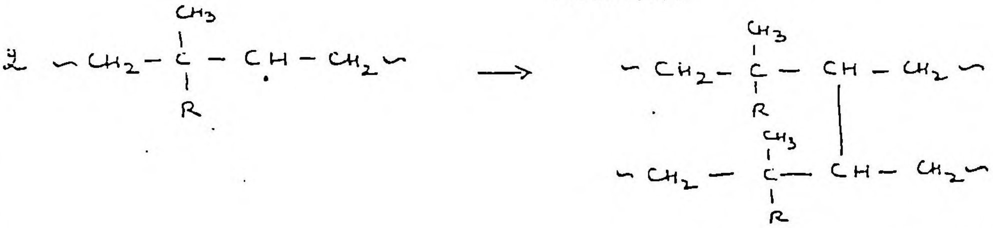
$$\sim CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim \;\rightsquigarrow\; \sim CH_2 - \overset{CH_3}{\overset{|}{C}} = CH^{\bullet} + {}^{\bullet}CH_2 \sim$$

RADICAL FORMATION
BY CHAIN SCISSION

LET US DENOTE RADICAL FORMED AS $R^{\bullet}$

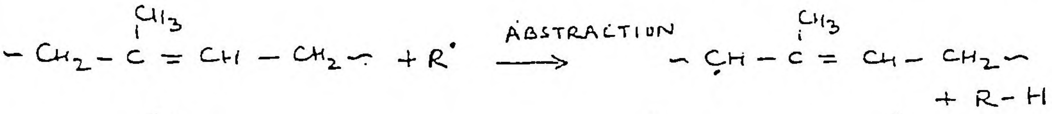


$$R^{\bullet} + \sim CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim \xrightarrow[\text{ADDITION}]{} \sim CH_2 - \underset{R}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - \underset{\bullet}{C}H - CH_2 \sim$$

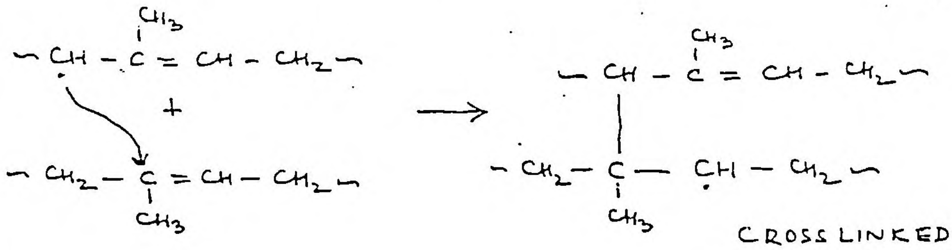


$$2 \sim CH_2 - \underset{R}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - \underset{\bullet}{C}H - CH_2 \sim \;\longrightarrow\; \begin{array}{l} \sim CH_2 - \underset{R}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - CH - CH_2 \sim \\ \qquad\qquad\qquad\quad | \\ \sim CH_2 - \underset{R}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - CH - CH_2 \sim \end{array}$$

CROSSLINKED STRUCTURE



$$- CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim + R^{\bullet} \xrightarrow{\text{ABSTRACTION}} \sim \underset{\bullet}{C}H - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim + R-H$$



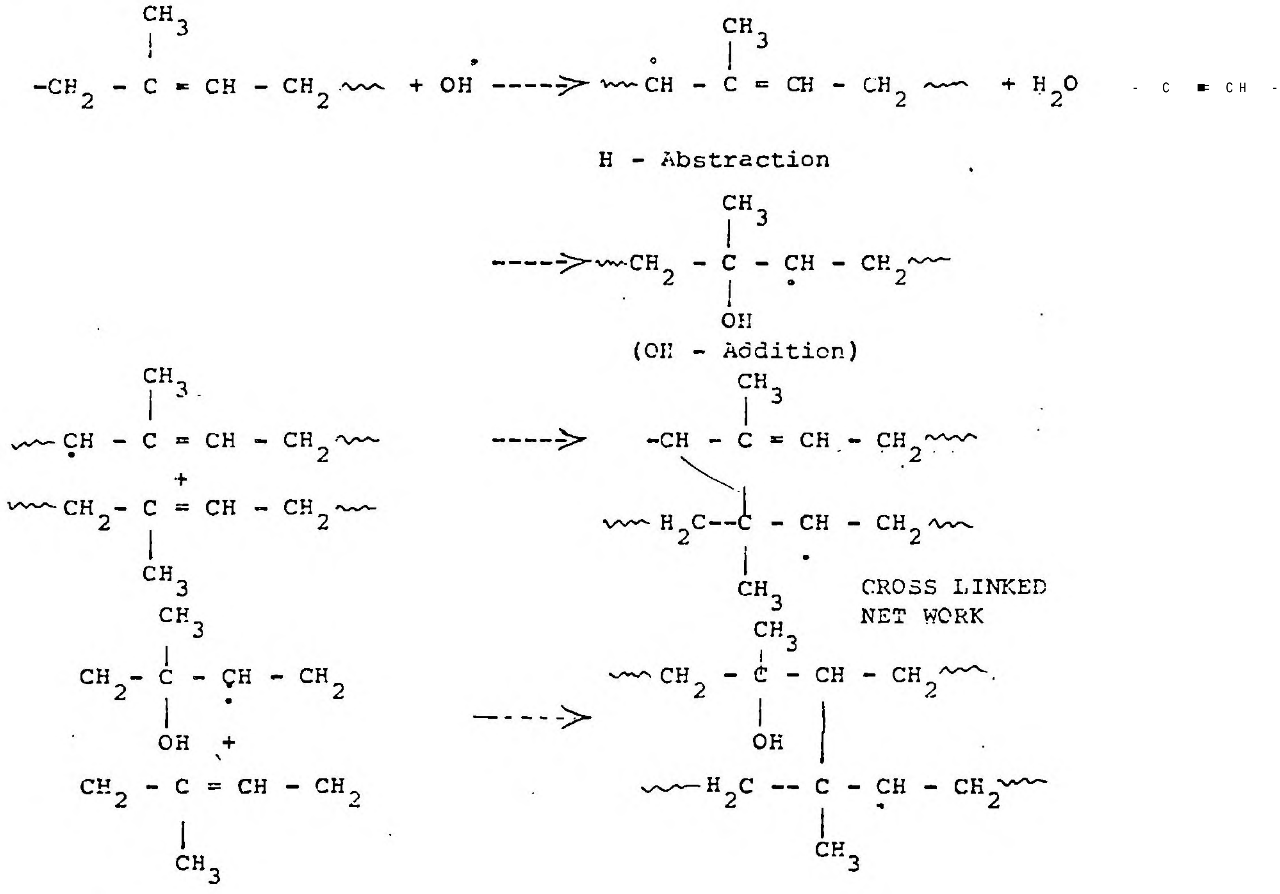
$$\begin{array}{l} \sim \underset{\bullet}{C}H - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim \\ \qquad\qquad + \\ \sim CH_2 - \underset{CH_3}{\underset{|}{C}} = CH - CH_2 \sim \end{array} \;\longrightarrow\; \begin{array}{l} \sim CH - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim \\ \quad\;\; | \\ \sim CH_2 - \underset{CH_3}{\underset{|}{C}} - \underset{\bullet}{C}H - CH_2 \sim \end{array}$$

CROSSLINKED
NETWORK

(2)Indirect effect through the free radicals generated in the rubber phase

$$H_2O \dashrightarrow \dot{H} + \dot{OH}$$

In the presence of air/oxygen, $\dot{H}$ radicals react with oxygen to form radicals which are much less reactive than the primary radicals themselves. Thus, $\dot{OH}$ radicals are the major species that are involved in the radiation induced process. $\dot{OH}$ radicals can generally react with unsaturated organic compounds either by addition to double bond or by H-abstraction reaction. The $\dot{OH}$ reactions with rubber can be represented by the following scheme.



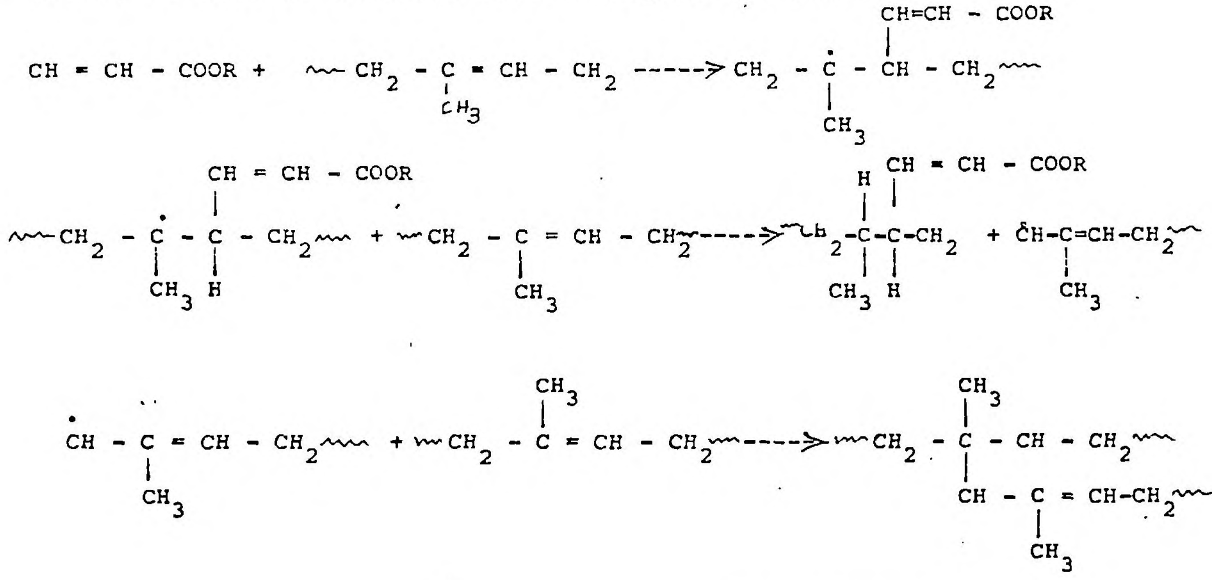
1.5.3. Role of sensitisers

Since the radiation chemical yield (G) of $O\dot{H}$ radicals in water radiolysis is only 2.8 molecules/100 eV of energy absorbed, the dose required to bring about vulcanisation is very high. The role of sensitisers is to reduce the dose required for vulcanisation. They diffuse into the rubber phase, produce free radicals with high G values and have high probability of chain transfer reaction.The sensitising action of organic halogen compounds is due to the occurrence of chain reactions which lead to the formation of radicals with high G values. The mechanism of crosslinking through polyfunctional acrylate is a two step reaction - a graft polymerisation of PFM on to the backbone of the polymer occurs first and then formation of pendent chains containing double bonds.[34]

The mechanism of sensitising action by mono functional acrylate can be represented in the following manner .

$$CH_2 = CH - COOR \xrightarrow{r} H\dot{C} = CH - COOR + \dot{H}$$

As acrylate radical is more mobile than the rubber chain, it attacks a double bond in adjacent chains.



$$CH = CH - COOR + \sim CH_2 - \underset{CH_3}{C} = CH - CH_2 \dashrightarrow CH_2 - \underset{CH_3}{\dot{C}} - \overset{CH=CH-COOR}{CH} - CH_2\sim$$

$$\sim CH_2 - \underset{CH_3}{\dot{C}} - \underset{H}{\overset{CH=CH-COOR}{C}} - CH_2\sim + \sim CH_2 - \underset{CH_3}{C} = CH - CH_2\sim \dashrightarrow \sim CH_2 - \underset{CH_3}{\overset{H}{C}} - \underset{H}{\overset{CH=CH-COOR}{C}} - CH_2 + \dot{C}H - \underset{CH_3}{C} = CH - CH_2\sim$$

$$\dot{C}H - \underset{CH_3}{C} = CH - CH_2\sim + \sim CH_2 - \overset{CH_3}{C} = CH - CH_2\sim \dashrightarrow \sim CH_2 - \underset{CH - \underset{CH_3}{C} = CH - CH_2\sim}{\overset{CH_3}{C}} - CH - CH_2\sim$$

CROSS LINKED STRUCTURE

The sensitising mechanism of monofunctional acrylate has been investigated by use of liquid polyisoprene and 2EHA as the model system.[34] The intermediate products before gelation were isolated by a preparative GPC and their structure was analysed by NMR. The formation of a three dimensional network is through the grafting of 2EHA on to the backbone of the NR while the unreacted pendent double bonds in 2EHA molecules serving as the active site for the network formation.

1.5.4. Selection of NR latex for RVNRL

The suitable NR latex for radiation vulcanisation is the one for which vulcanisation dose is low and tensile strength is high. Conclusions arrived at, after evaluation of a number of latices are (1) Tensile strength of HA latex is higher than those of LA-TZ.(2) Reduction in the protein content reduces tensile strength.(3) Vulcanisation dose decreases with increasing green strength of rubber(4) Green strength increases with increasing microgel content which increases with increasing nitrogen content. The green strength increases during storage. Therefore the matured latex having higher green strength or high microgel content is preferable for RVNRL.

Two types of non rubber components are present in field latex, accelerator and inhibitor, in terms of RV.[27] Generally, the inhibiting component supposed to be phenols can be removed by centrifugation of the field latex. Thus the centrifugation is preferable method for concentration of field latex. The accelerating component is supposed to be proteins. Mg content must be rigidly controlled less than 10 ppm in centrifuged latex as Mg gives rise to low MST in NR latex, resulting in low tensile strength. Diammonium hydrogen phosphate treatment of field latex is effective to remove Mg from field latex.

1.5.5. Properties of RVNR latex.

The quality of products from RVNR latex depend largely on the origin of the latex. However, process factors such as leaching, drying and treatment with antioxidants affect the qualities of the products.[35,36] The tensile strength increases quite sharply upon leaching of the film. This is due to better fusion of the rubber particles by removing of the water soluble non rubber components adsorbed on the surfaces of the rubber particles. The increase in tensile strength upon heating is due to better fusion of the rubber particles and better chain entanglements of rubber molecules.The high temperature resistance of radiation vulcanisate (C-C crosslinks) is superior to that of sulphur vulcanisate (C-S-C crosslinks) in principle, because the bond energy of C-C is higher than that of C-S bond. However, there is a decrease in the resistance to thermal oxidative degradation. The reasons are attributed to(1) Irradiation of NR latex produce $OH^{\bullet}$ and $H^{\bullet}$ radicals. The non rubber constituents including antioxidants may be oxidised by $OH^{\bullet}$ radical.(2) The absence of dithio carbamates that function as strong antioxidants. The effective way of improving the thermal oxidation degradation of radiation vulcanisate is by use of powerful non staining antioxidants.

1.5.6. Advantages of RVNRL.

The advantages of RVNR latex are summarsised below:-

(1) Absence of N-nitrosoamine

The RVNR latex contains no detectable nitrosoamine because RV does not use dithiocarbamates. Nitrosoamines regarded as strong carcinogen are formed from dithiocarbamates used as accelerators in sulphur vulcanisation.[27]

(2) Low cytotoxicity

The RVNR latex shows very low cytotoxicity because of the absence of dithiocarbamates.[37]

(3) Absence of sulphur and zinc oxide

(4) Transparency

(5) Softness (low modulus)

The C-C direct bonds are formed by RV. This crosslink structure results in lower modulus compared with C-S-C and C-S-S-C bonds.

1.5.7. Development of Products from RVNR latex

Rubber products for medical and health field are the most promising products because the absence of nitrosoamine and low cytotoxicity are strongly required in these products. Test production of various rubber products such as condoms, surgical gloves are now being carried out.[38] Test production of condoms started from 1987 using an existing condom factory in Indonesia. Few private companies in Indonesia intend to build a factory for producing surgical glove using RVNR latex. In Japan, in March 1989, rubber gloves for workers in nuclear power plants have been commercialised.[39] The balloon for optical laser endoscope and drainages have been developed using the RVNR latex in Japan.[40]

1.5.8. Cost Estimation.

Reliable cost estimation is essential to transfer RVNRL technology to industry.Different types of irradiators have been designed.Typical irradiators are(1) Small irradiator, dry source storage, laboratory scale,150 ton/y at 10 kCi Co-60(2) Middle scale irradiator,dry source storage,500 ton/y at 100 kCi Co-60(3) Commercial irradiator,pool type Panoramic Irradiator,1,000 ton/y at 500 kCi Co-60. Cost analysis of investment and operation costs of all the three irradiators in different country conditions have been carried out.The irradiation cost is found to be acceptable in most participating countries.

1.6. Vulcanisate properties

(a) Modulus

The force necessary to deform the material is often known as modulus, ie, tensile stress at a given elongation. It is proportional to the number of crosslinks formed and hence to the degree of vulcanisation or crosslinking.

(b) Tensile strength and elongation at break.

Tensile strength unlike modulus does not rise continuously with the number of crosslinks. Therefore, tensile strength is less suitable than modulus in showing whether or not the optimum degree of vulcanisation has reached.[41] Tensile strength varies appreciably with vulcanisation system. This variation may be due to difference in the crystallinity extension relationship. Elongation at break decreases with increasing degree of crosslinking.

(c) Swelling

Crosslinked rubber does not dissolve, but merely swells and the swelling decreases with increasing crosslinks.

According to the Flory-Rehner equation, the increase in volume becomes less and less, as the degree of crosslinking rises. A rapid method for determining the degree of crosslinking has also been reported.[42]

.7. Rheology

For many of the latex goods manufacturing processes, the flow behaviour of latex compound is critical.[43] A latex compound with low viscosity and some thixotropic nature is good for dipping operations. The count of latex thread is largely influenced by the viscosity of the latex compound. But very few studies have been conducted in latex rheology.

Natural rubber latex is a pseudoplastic fluid and when sheared, the rubber particles are progressively aligned and offers less resistance to flow.[44] So the apparent viscosity of latex decreases on increasing shear rate and continues until the flow curve becomes linear. The viscosity of latex also depends on its total solids content and temperature.[45] Due to the non newtonian behaviour, a single viscosity measurement of latex at a particular temperature is not enough to understand its flow behaviour.Collins et al[46] studied the factors affecting the rheological behaviour of latex. The important factors include shear rate, particle size, particle size distribution and electrolytes. The flow properties of a latex are strongly influenced by the incorporation of surface active agents. The effect of various surface active agents on the rheological properties of centrifuged and creamed latex compound has been reported.[47] The effect of sodium polyacrylate as a thickener in NR latex has been studied by Schroeder and Brown.[48]

Scope of the Present Work

Radiation vulcanised natural rubber latex is a modified form of latex in which the dispersed rubber particles are crosslinked[1]. The process consists of mixing NR latex with sensitiser, irradiating with gamma rays and adding antioxidants. Latex vulcanised by this technique contains no sulphur, zinc oxide or accelerator. It is free from the decomposition products of the accelerators, particularly the carcinogenic nitrosoamine. It gives transparent films and has low cytotoxicity compared to sulphur prevulcanised latex. These properties mean that it has much potential in medical/hygienic uses. An international research programme known as the Regional Co-operative Agreement (RCA) has been implemented in 1982 by the International Atomic Energy Agency and United Natiions Development Programme. The main objectives of the programme are to develop new products from RVNR latex and reduce the cost of irradiation. Extensive investigationsare being carried out in the member countries like Japan, Indonesia, Sri Lanka, India, Thailand, etc. for the application of RVNR latex in gloves, catheters, balloons, etc.

For use of rubber products in the medical and surgical field, they must not cause skin irritation when in contact with the body for any length of time. That is, it should have the lowest possible dermatological effect and cytotoxicity. Radiation vulcanised latex, eventhough free from nitrosoamines, are found to cause skin irritaion due to the presence of residues of sensitisers such as CCl_4, 2EHA, etc in the final product. The use of sensitisers is inevitable as it reduces the radiation dose. In this context, the development of sensitisers which produces no cytotoxicity in the final rubber product is of vital significance.

The sensitiser system at present used in India is a combination of 1 phr of CCl_4 and 1 phr of n-BA. Since CCl_4 is toxic to human beings, a study is planned to produce RVNR latex using n-BA as sensitiser. n-BA is less toxic and since its vapour pressure is high, the amount of residual monomer in the product will be negligible. The study involves the standardisation of the radiation dose required for optimum vulcanisation by measuring the vulcanisate properties.

For the manufacture of latex products, the flow behaviour of latex compound is critical. Natural rubber latex is a pseudoplastic fluid and its viscosity decreases with increasing shear rate and temperature. Natural rubber latex is subjected to different shear rate during the process of gamma irradiation and manufacture of latex products by dipping, extrusion, etc. The rheological behaviour of RVNR latex is also studied in this work as a knowledge of this will lead to better process control in the production and use of RVNR latex.

CHAPTER 2

EXPERIMENTAL

2. EXPERIMENTAL

2.1. Materials used

2.1.1. Centrifuged latex

High ammonia (HA) type 60% centrifuged latex conforming to the specifications of the Bureau of Indian Standards BIS 5430- 1981 obtained from M/s PLPC, Chethackal is used in this study. The properties of the latex are as follows.

Parameters.	Value
(1) Dry Rubber Content % by mass	60.00
(2) Non Rubber Solids % by mass	1.50
(3) Coagulum content% by mass	0.03
(4) Sludge content, % by mass	0.007
(5) Alkalinity as ammonia, % by mass	0.68
(6) KOH Number	0.65
(7) Mechanical stability time (MST) seconds	945.00
(8) Volatile fatty acid number	0.04
(9) Copper content, ppm on total solids	3.00
10) Manganese content, ppm on total solids	0.50

2.1.2. Other Chemicals

(a) n-Butyl acrylate . It is obtained from M/s Indian Petrochemicals Ltd., Baroda.

(b) Potassium hydroxide, oleic acid, benzene and ammonia are of analytical grade, supplied by M/s E.Merck (India) Ltd., Bombay.

(c) Ammonium laurate - It is an anionic soap, soluble in water and is used as a stabilising agent in latex. This is prepared from chemically pure lauric acid and ammonia solution.

(d) Cumene hydroperoxide - supplied by M/s Crystal Corporation, Bombay is used as co-sensitiser.

(e) Wingstay L - Butylated reaction product of p-cresol and dicyclopentadiene manufactured by M/s Goodyear.

2.2. Treatment of Latex

Centrifuged latex was stabilised with 0.2 phr potassium hydroxide and 0.05% ammonium laurate. The sensitiser, n-Butyl acrylate (5 phr) was added in drops whilst stirring the latex using a magnetic stirrer. The latex was then diluted to 50% total solids content using 1% ammonia solution. The mixture was then kept one overnight at room temperature and subjected to gamma radiation for different doses.

In trials, using cumene hydroperoxide as co-sensitiser, 0.25 phr cumene hydroperoxide was added to the treated latex, one hour before irradiation, and stirred slowly using a magnetic stirror. The mixture was then irradiated for different radiation doses. The details of RVNR latex samples with different sensitisers and radiation dose are given in Table 2.I.

2.3. Irradiation

Irradiation was done using CO-60 rays using a gamma chamber Model 900 supplied by M/s Bhaba Atomic Research Centre, Bombay. It offers an irradiation volume of approximately 900 cc. The unit essentially consists of the following components:-

(a) source cage (b) biological shield for the source (c) central drawer incorporating the sample chamber (d) drive system (e) control panel (f) external cabinet. The main features of the chamber are shown in fig 2.1. The source cage holds the radiation source pencils vertically and symmetrically distributed along its periphery. The central drawer passes through the source cage. The cage can hold a maximum of 24 pencils containing CO-60 in the form of pellets and is designed to provide maximum uniformity of dose rate inside the sample chamber. The biological shield is a lead-filled steel container and surrounds the source cage. It consists of two parts : main outer shield and inner removal plug. The radiation source is housed in the main outer shield. The central drawer is one long cylinder consisting of 2 stainless steel clad lead sheets with the sample chamber fitted in between them. The sample chamber is 10 cm in diameter, 14 cm in height and made of stainless steel. The central drawer is raised or lowered by a wire rope passing over a system of pulleys and wound on a drum by a geared motor. This enables the sample chamber to be moved up or down as is required. For irradiation, the drawer is lowered until the sample chamber reaches the centre of the source cage. Control panel allows the smooth functioning of the equipment. A schematic diagram of the equipment is shown in Fig 1. The radiation is emitted at a rate of 0.0526 MRad / hour.

After the irradiation the RVNR latex was stabilised with 1 phr of antioxidant (wingstay L) and used for further testing.

2.4. Determination of Vulcanisate properties of RVNR latex Films.

2.4.1. Preperation of Latex Films

Latex films were cast on glass cells using the irradiated latex as described by Flint and Naunton.[49] The size of the glass cells was 6"X 6" and about 30-35 ml of the latex compound was poured and distributed so that a film of thickness 1-1.25 mm was obtained on drying. The films were then leached in deionised water for 24 hours at room temperature and dried at room temperature. Heat treatment of the films were carried out at 70 C for 4 hours. These were then conditioned for at least 24 hours before testing for tensile properties and swell index.

2.4.2. Modulus, Tensile strength, Elongation at Break and Tear Strength

In the present work, these tests were carried out using an Instron Universal Testing Machine (UTM) Model 4301 as per ASTM-d-3188. The machine consists of a load frame and an electronic control unit. Load measuring device is a load cell fixed at the top of the load frame. Below the load cell ia a moving platform driven by a continuously variable speed motor. Grips suitable for dumb bell specimens are fixed on to the load cell and the moving platform. During testing, the specimen is subjected to stretching at constant speed. Force and elongation are continuously monitored by the electronic circuit. As soon as the test specimen breaks, test results are displayed in the electronic circuit and printed as a table.

All the tests were carried out at ambient temperature (30 C). Dumbshell specimens were cut from the cast films for measuring tensile properties. The thickness was measured by bench thickness gauge. The moving crosshead is adjusted by operating the switch. The velocity of the moving crosshead is adjusted to 500 mm/min.

The specimen is elongated and the values corresponding to ultimate tensile strength, elongation, modulus 300 and modulus 500 are measured. Results are given in Table 3.1.

The tear strength was determined by cutting angular test pieces from the cast films as per ASTM D-624-73.

2.4.3. Swell Index Determination of volume fraction of rubber

Samples of approximately 1 cm dia, 0.25 cm thick and 0.3 gram were punched from the central portion of the vulcanised film and allowed to swell in toluene at room temperature. Swollen samples were taken after 48 hour period, blotted with filter paper and weighed quickly in a stoppered weighing bottle. Samples were dried in an oven for 24 hours at 70 $^{\circ}$C and then in vacuum and finally weighed after allowing them to cool in a desiccator. Duplicate readings were taken for each sample. The volume fraction of rubber "Vr" was calculated by the method reported by Ellis and Welding, which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

$$Vr = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0 \rho_s^{-1}}$$

where T is the weight of test specimen, D, its deswollen weight, F, the weight fraction of insoluble components and A_0 is the weight of the adsorbed solvent, corrected for the sweling increment, ρ_r and ρ_s are the densities of rubber and solvent respectively.

ρ_r (NR) = 0.92

ρ_s (toluene) = 0.86

The value of Vr can be taken as a measure of crosslink density. The results of swell Index are given in 3.2.

2.5. Rheological Behaviour of NR Latex

Rheological measurements

The selection of the most suitable measuring system depends on the properties of the substance to be measured. Factors determining the choice of measuring system includes:-

- nature of the substance

- temperature of substance during measurement
- pressure or vacuum
- approximate viscosity range
- volume of substance available
- purpose of measurement
- chemical and physical properties of substance, eg. corrosive, abrasive, etc.

Two different geometries are mainly used in rheoloical measurements:

- concentric cylinder system
- cone/plate system

The advantages of concentric cylinder systems are (i) higher accuracy, (ii) larger temperature range, (iii) easier handling, and (iv) self-centering measuring bobs for most substances. It consists of a rotor and a stator, with the test substance lying between them. The torque required to drive the rotor is proportional to the shear stress, whereas the shear rate is proportional to the rotational speed. The ratio of the shear stress to shear rate is the viscosity, which is often not a constant value and may depend on shearing time. The unit of measurement of viscosity is the Pascal second (Pa.S.). Viscosity is closely related to temperature.

Haake-Viscotester VT 550

For measurement of the rheological behaviour of the latices under study, Haake-VT 550 was used. (fig 2.2.) (This rheometer has been designed to meet the most sophisticated requirements of continuous shear rheometry with 3 rotational speed steps in geometric progression from 0.5 to 800 min (rpm). The rotational speed accracy is maintained over the entire range by a closed loop control system.

For use in the present studies, the rotor "Sensor system NV" is selected (Fig2.3.) The equipment operates over a temperature system from -40°C to 100°C, shear rate from 0 to 1000 sec-1 and torque from 0.01 to 3 Nm. 9 ml ofthe latex sample to be tested was taken in the measuring gap of the sensor system NV and the latex was sheared from 0 to 200 sec -1 at different temperatures (30 °C, 40°C and 50°C). The built in computer calculates the apparent viscosity , (in mPas), shear rate (in s-1) and shear stress (Pa). Accurate shear stress - shear rate and viscosity-shear rate plots are obtained as the latex is sheared continuously. The temperature sensor measures the temperature in °C. The results are given to a computer printer via the RS 232 interface.

$\tau = K(\dot{\gamma})^n$ (where there is no yield stress

$\tau - \tau_0 = K(\dot{\gamma})^n$ (where τ_0 =yield stress)

τ = shear stress in Pascals

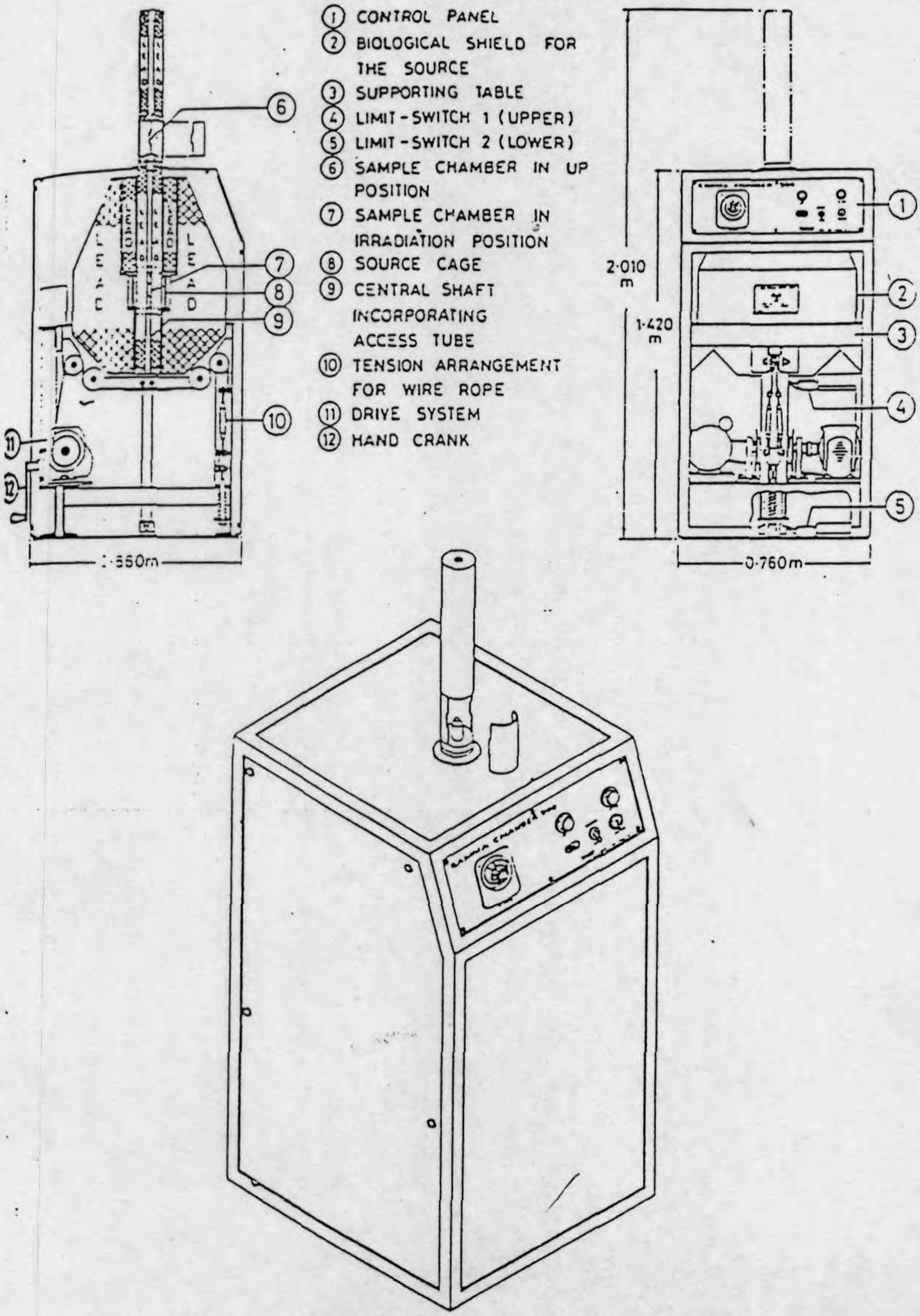
$\dot{\gamma}$ = shear rate (sec-1)

n = pseudo plasticity index

K = viscosity index.

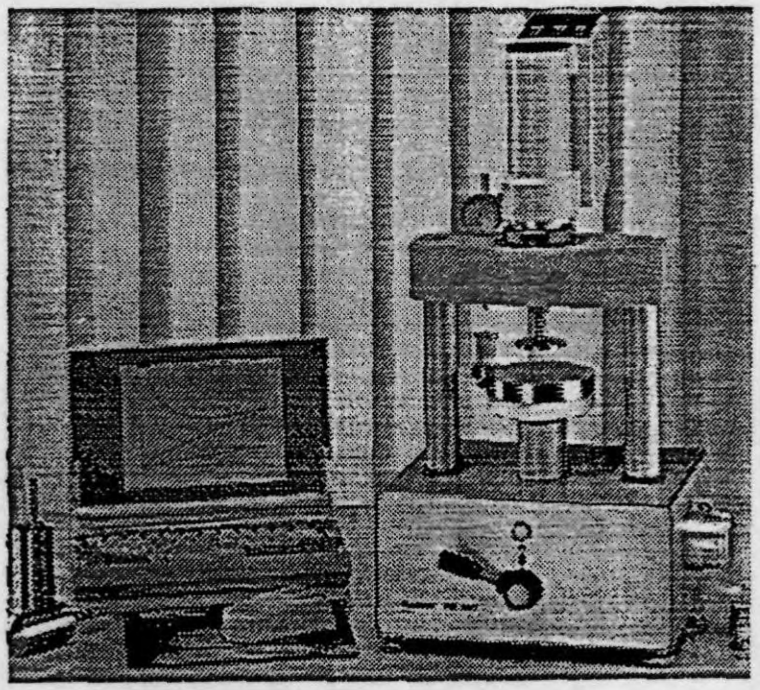
The rheological behaviour of six samples A-O, A-1, A-2, A-3, A-4, A-5 (Table 2.1.) were studied at different temperatures, 30°C, 40°C and 50°C. The effect of shear rate on shear stress given in Fig 3.3. The effect of shear rate and shear viscosity are given in Fig 3.4.

The pseudo plasticity, n, and viscosity index K at different temperatures are given in Table 3.3.



① CONTROL PANEL
② BIOLOGICAL SHIELD FOR THE SOURCE
③ SUPPORTING TABLE
④ LIMIT-SWITCH 1 (UPPER)
⑤ LIMIT-SWITCH 2 (LOWER)
⑥ SAMPLE CHAMBER IN UP POSITION
⑦ SAMPLE CHAMBER IN IRRADIATION POSITION
⑧ SOURCE CAGE
⑨ CENTRAL SHAFT INCORPORATING ACCESS TUBE
⑩ TENSION ARRANGEMENT FOR WIRE ROPE
⑪ DRIVE SYSTEM
⑫ HAND CRANK

Fig. 2·1 Schematic diagram of gamma chamber.



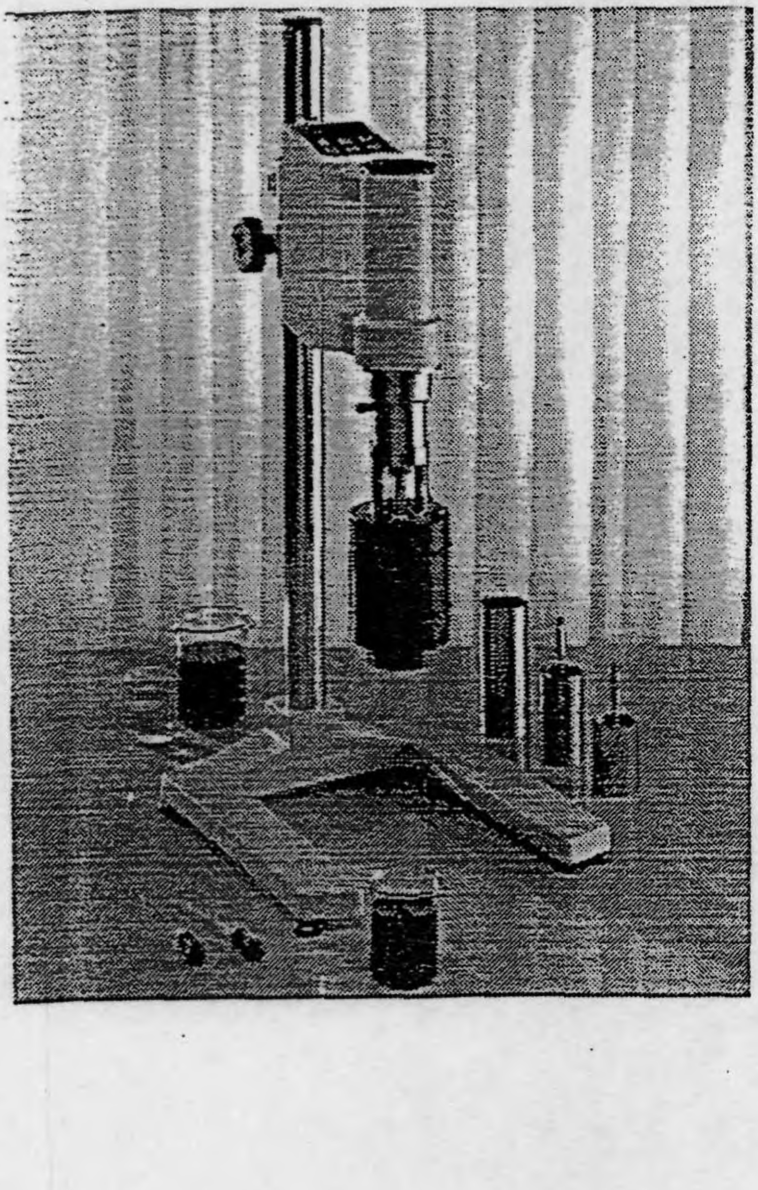


Fig 2.2

Viscotester VT 550

FIG 2·3

Sensor Systems

Sensor System	**NV**
System No.:	*8*
Inner Cylinder (Rotor) Radius R_2; R_3 (mm) Height L (mm)	 17.85; 20.1 60
Outer Cylinder (Cup) Radius R_1; R_4 (mm)	 17.5; 20.5
Radii Ratio R_a/R_i Gap Width (mm) Sample Volume V (cm^3) Temperature (°C)	1.02 0.35 9.0 –30/100
System Factors f (Pa/Ncm) M (min/s)	 36.3 5.41

Table 2.1 - **DETAILS OF RVNR LATEX SAMPLES WITH DIFFERENT SENSITISERS AND RADIATION DOSE**

Sample	nBA (phr)	CHP (phr)	Radiation dose (MRad)
A-0	nil	nil	nil
A-1	5	nil	0.5
A-2	5	nil	1.0
A-3	5	nil	1.5
A-4	5	nil	2.5
A-5	5	nil	4.0
B-1	5	0.25	0.5
B-2	5	0.25	1.0
B-3	5	0.25	1.5

CHAPTER 3

RESULTS AND DISCUSSIONS

3. RESULTS AND DISCUSSION

3.1. Effect of Radiation dose and sensitisers on the tensile properties of RVNR latex films.

Effect of radiation dose on the tensile properties of films prepared from RVNR latices containing different sensitiser systems are given in Fig 3.1. and Table 3.1. The sensitiser systems used are (1) 5 phr n-Butyl Acrylate. (nBA) (2) 5phr nBA and 0.25 phr Cumene Hydro Peroxide (CHP). From Fig 3.1, it is seen that for a sensitiser system(1) tensile strength reaches a maximum at 1.5.MRad and thereafter decreases. With system (2), the maximum tensile strength is reached at 1MRad followed by a decrease in tensile strength. This shows that the radiation dose can be substantially reduced by the addition of 0.25 phr CHP as co-sensitiser along with 5 phr n-BA.

From Table 3.1, it is seen that modulus 300% and modulus 500% increase as radiation dose increases for both the sensitiser systems. The modulus values obtained at 1.5 MRad with sensitiser system(1) and at 1 MRad with sensitiser system(2) are comparable. This shows that the rate of modulus development is higher with sensitiser system (2) Or in other words, the incorporation of 0.25 phr of CHP as co-sensitiser along with 5 phr nBA helps to reduce the radiation dose required for vulcanisation. Elongation at break decreases as radiation dose increases with the two senstitser systems.

The crosslonk formation on irradiation has also been investigated by swelling the latex films in toluene and the results are given in Table 3.2. It can be seen that the volume fraction of the rubber (Vr) in the swollen network increases as the radiation dose increases in both the systems. A Vr value of 0.15 is obtained at 1.5 MRad with nBA alone as sensitiser, but this Vr value is reached at about 1MRad with nBA and CHP as sensitiser system. This also shows that the addition of CHP as cosensitiser increases crosslink density as shown by modulus values in Table 3.1.

The tear strength of the vulcanisates at different radiation doses are given in fig 3.2. Here also, with system (1), tear strength increases with radiation dose, reaches a maximum at 1.5 MRad and then decreases. For system(2), with CHP as cosensitiser, the maximum tear strength is obtained at 1 MRad followed by a reduction in tear strength.

These results indicate that the rubber particles in latex have become crosslinked as reported by earlier workers. As a result, the tensile strength, modulus, tear strength and Vr of the latex films increase and elongation at break decreases.

When NR is stretched, crystallisation occurs due to the orientation of the polymer chain (strain crystallisation).[50] This crystallisation further enhances the intermolecular attractive forces and results in still higher tensile strength. The tear strength is also influenced by the strain induced crystallisation. The decrease in tensile strength and tear strength after reaching the optimum values may be attributed to the restricting effect of more random crosslinks on the strain induced crystallisation of NR.

It has been reported that gamma radiation produces crosslinking through C-C linkages and the reaction proceeds through a free radical mechanism.[51] The polymer free radicals are less mobile and hence the formation of radicals which combine together are less. The addition of n-butyl acrylate as sensitiser increases the rate of crosslinking reaction. n-Butyl acrylate diffuses in to the rubber phase, produces acrylate free radicals by gamma radiation and get grafted on to the rubber molecule. The unreacted pendent double bonds in acrylate molecules serve as the active site for the network formation.

NR latex contains naturally occurring radical scavengers which inhibit radiation vulcanisation and oxidising agents can decompose the radical scavengers. The effect of cumene hydroperoxide may be that this being an oxidising agent, liberate oxygen and radical scavengers are removed resulting in high crosslinks.

3.2. Rheological Behaviour of RVNR Latices.

To study the rheological behaviour of RVNR latices, HAAKE- Viscotester VT-550 is used. The flow behaviour of latex samples A-0, A-1, A-2, A-3, A-4 and A-5 (Refer Table 2.1.) is being investigated in the shear rate range 0-200 s-1. The effect of increasing shear rate on shear stress is given in Fig 3.3. It is seen that there is no yield stress for RVNR latex samples. As shear rate increases, shear stress increases for all samples.

The effect of increasing shear rate on viscosity is given in Fig 3.4. It is also seen that the viscosity of RVNR latex decreases as the radiation dose is increased, and the effect is more predominant at lower shear rate than at higher shear rate. The high viscosity of sample A-1 may be due to the presence of higher amount of residual n-BA in the latex. As the radiation dose increases, the amount of n-BA in the latex may become reduced as n-BA undergo polymerisation and becomes grafted on to the polymer.

The monomer n-BA is an orgainc solvent which is having higher miscibility with the polymer than with the acqueous phase. Therefore, presence of n-BA in latex may cause a gradual thickening. Usually, thickening is accompanied by an increasee in particle size. The mechanism of thickening by n-BA may be due to the gradual imbibition of the monomer by the polymer with consequent swelling of the rubber particles. The rubber parcticles are occluded in the network caused by the organic monomer. As a result their brownian motion is partially arrested. This will lead to the recombination or coalescense of rubber particles leading to an increase in viscosity or eventually coagulation with an inversion of phase.

Pseudoplasticity index

The effect of radiation dose on the flow behaviour indices (n) and viscosity indices (K) of the RVNR samples are given in Table 3.3. The extent of non-newtonian behaviour of the system can be judged from the n value. Pseudoplastic materials are characterised by n below 1. Therefore, a high value of n shows low pseudoplastic nature of the material. From Table 3.3, it is clear that RVNR latices are more pseudoplastic than NR latex. The pseudoplasticity increases in the order A-0 < A-5 < A-4 < A-3 < A-2 < A-1.

The increased pseudoplasticity of the latex sample A-1 may be due to the presence of residual n-BA in the sample. The viscosity is high as motion of the latex particles is hindered by swollen network. But on subjecting the latex to high shear rate, there is a rapid decrease in viscosity of the system. This may be due to the displacement of the n-BA molecules from the rubber particles at high shear rate. The solvent network becomes loose and the tendency of the rubber particles to slide past each other will be enhanced. The pseudoplastic behaviour decreases as nBA is consumed for crosslink formation at higher radiation doses.

Effect of Temperature

Effect of varying the temperatue on viscosity of RVNR latices at different shear rates viz 33, 65 and 130 sec $^{-1}$ are given in Fig 3.5, 3.6 and 3.7 respectively. It is seen that viscosity decreases as temperatue is increased. This may be due to the fact that as temperature increases, the particles become more energetic, have more free volume to move and become less organised. The effect of temperature is more predominant in the temperature range 30 - 40 ^{o}C than in the temperature range 40 - 50 ^{c}C. The variation of pseudoplasticity and viscosity index with temperature is given in Table 3.3. It is seen that pseudoplasticity index decreases and viscosity index decreases with increase in temperature.

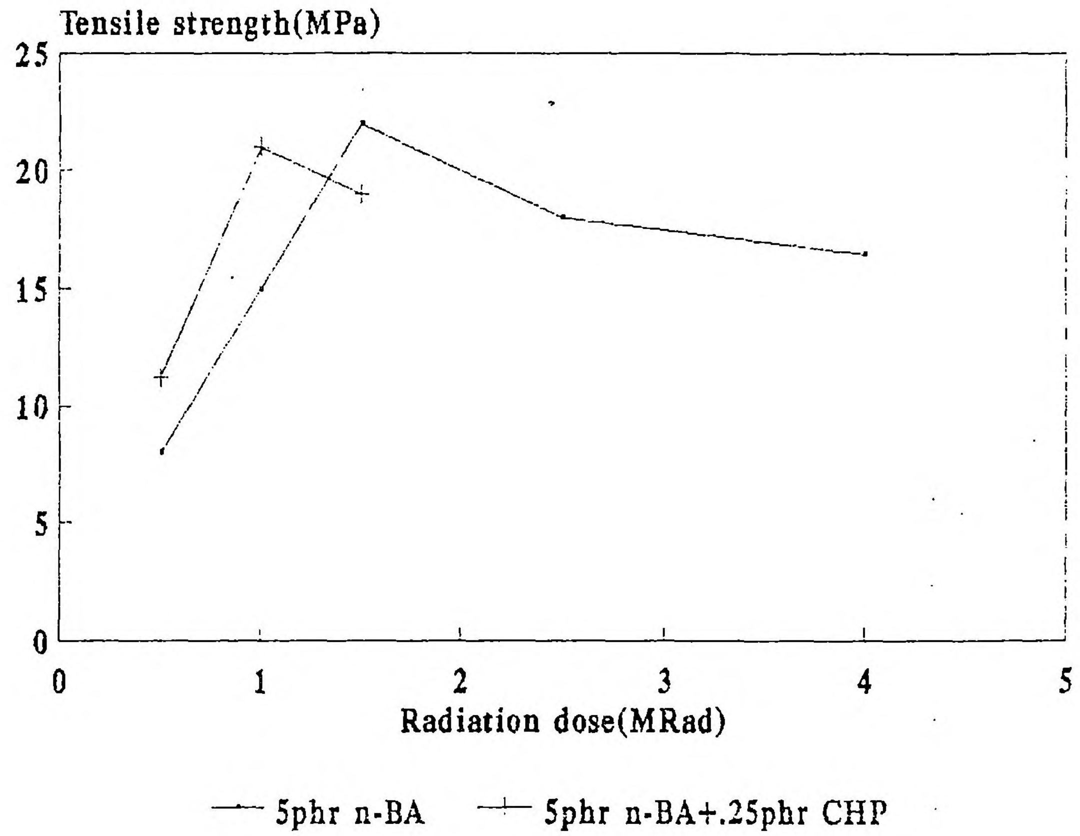


Figure 3.1 - EFFECT OF RADIATION DOSE ON TENSILE STRENGTH OF RVNR LATEX FILMS

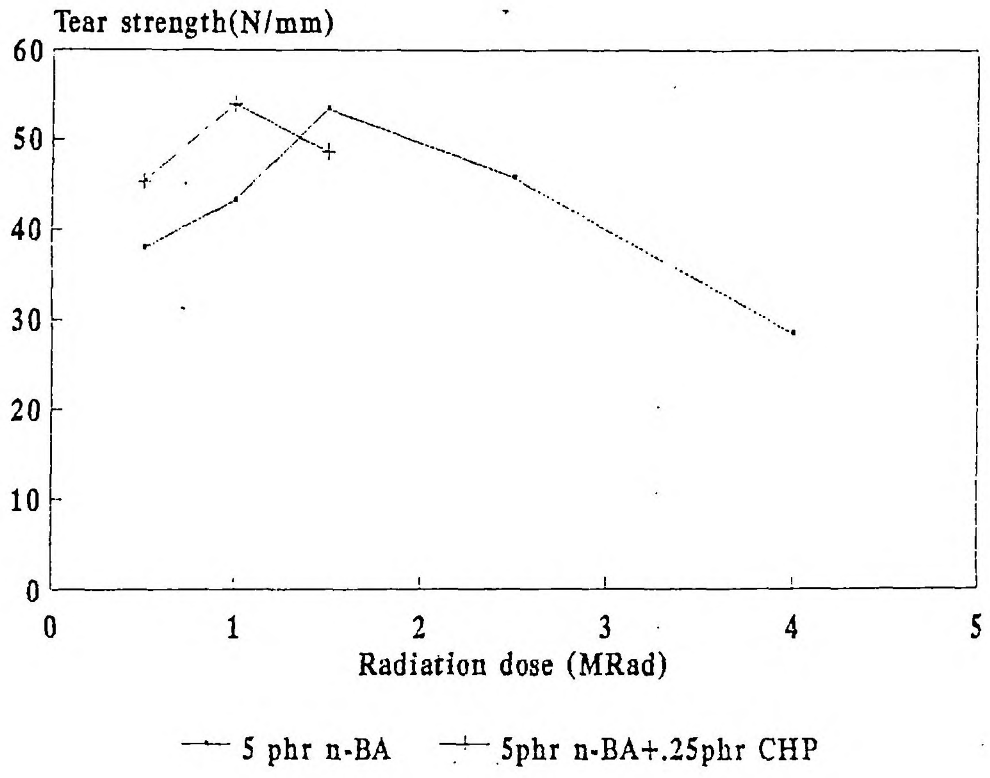


Figure 3.2 - EFFECT OF RADIATION DOSE ON TEAR STRENGTH OF RVNR LATEX FILMS

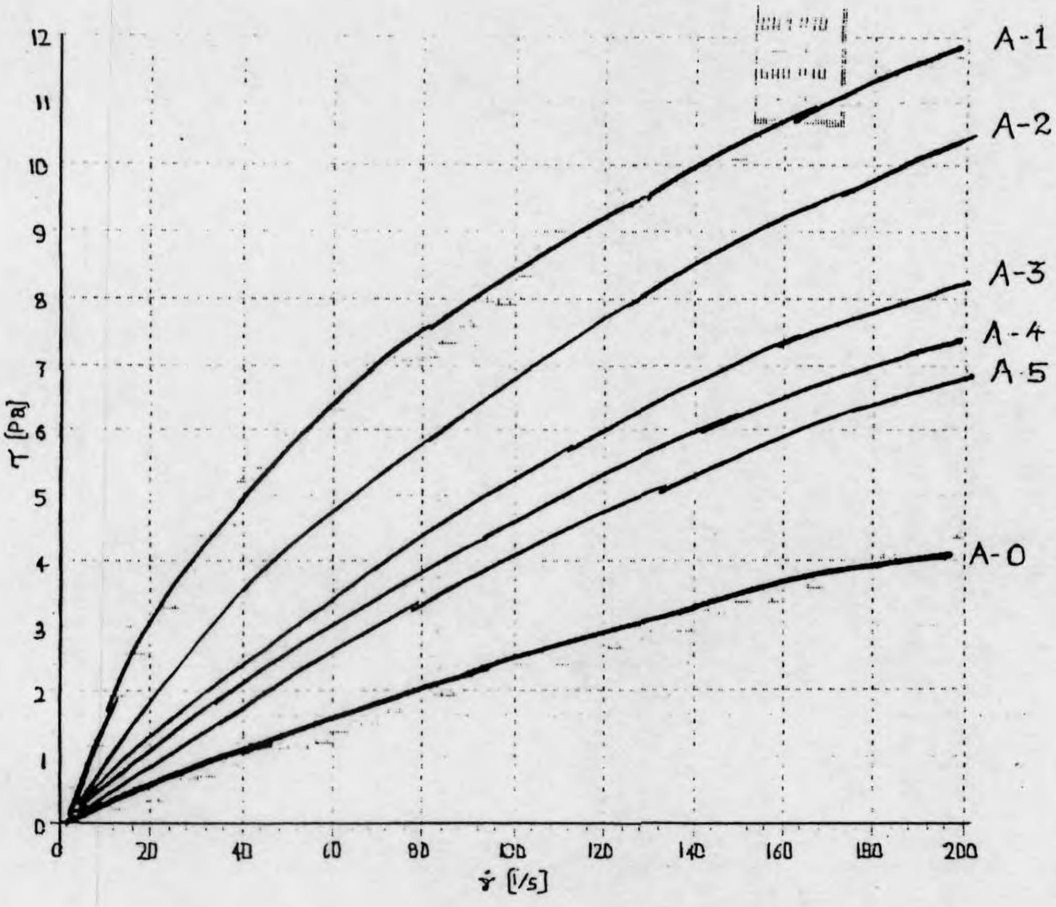


Figure 3.3 - EFFECT OF SHEAR RATE ON SHEAR STRESS OF RVNR LATICES

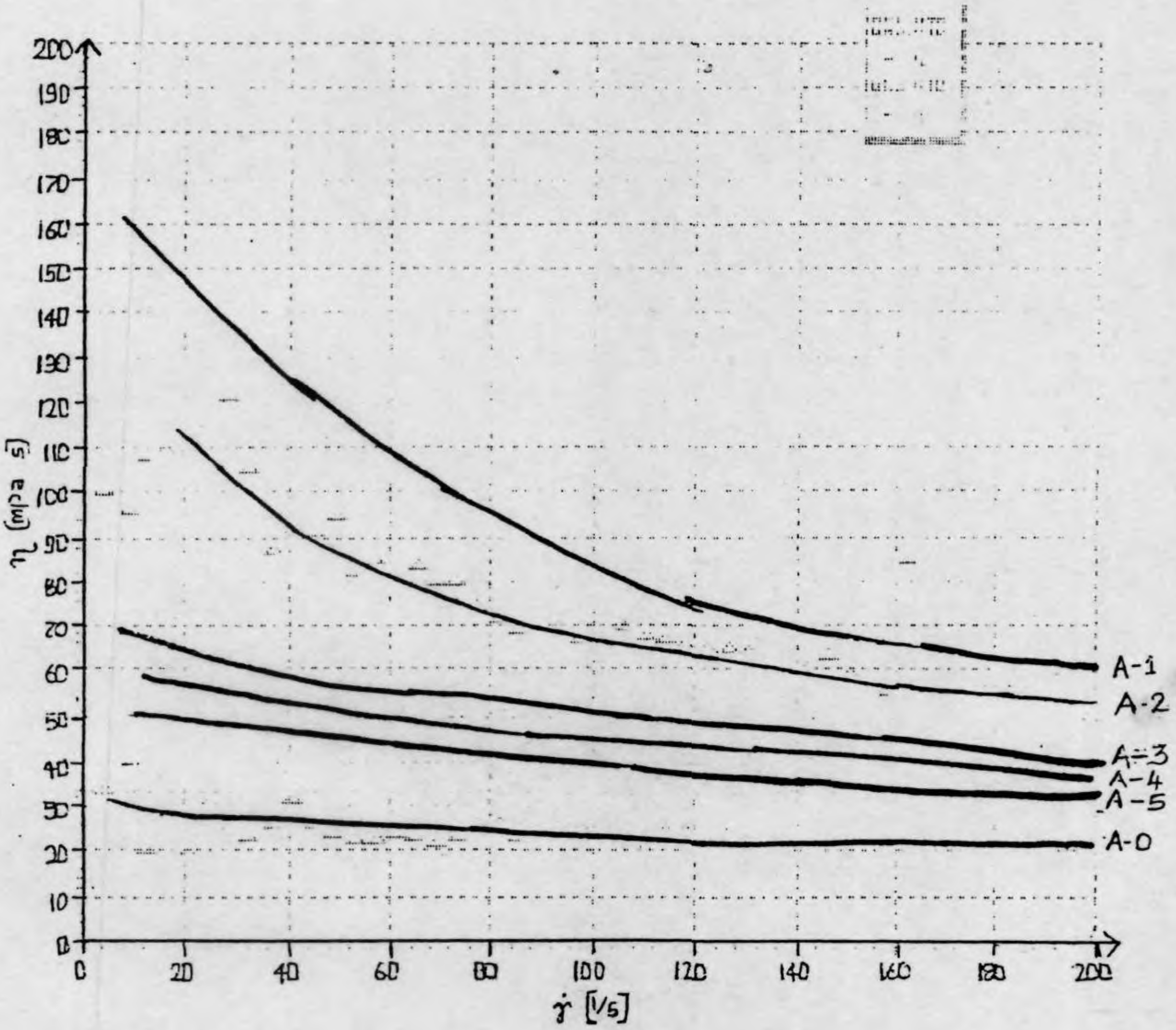


Figure 3.4 - EFFECT OF SHEAR RATE ON VISCOSITY OF RVNR LATICES

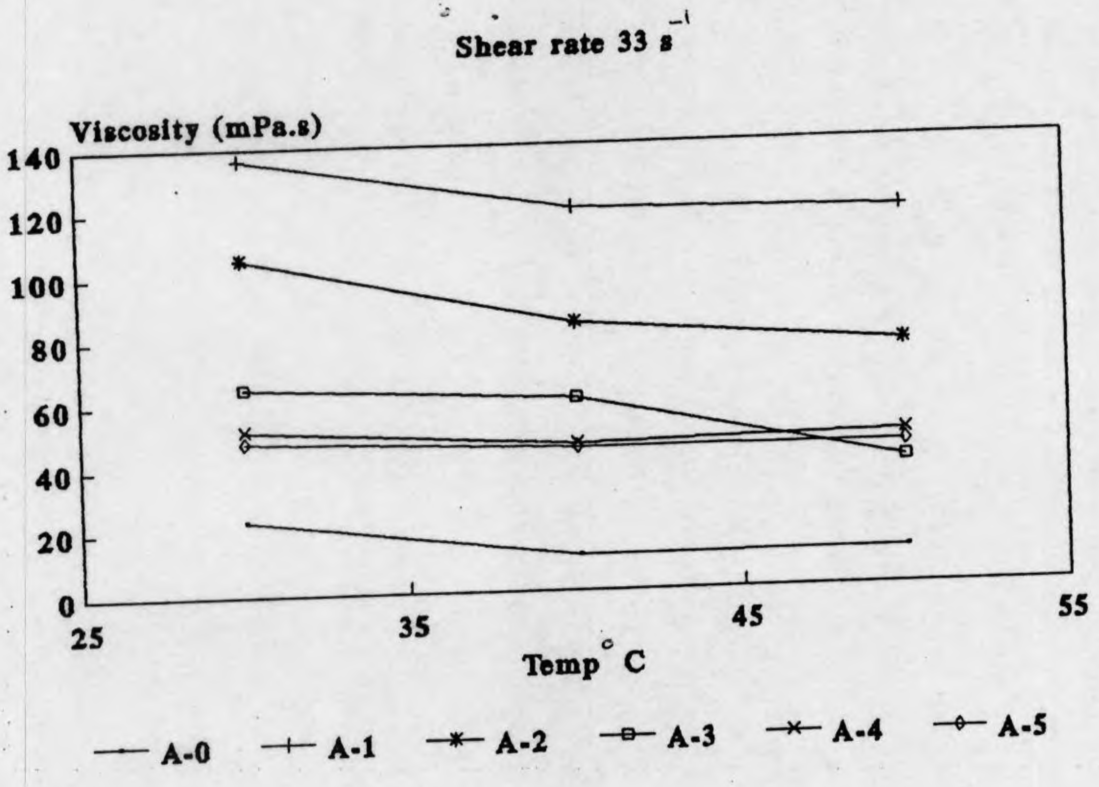


Figure 3.5 - EFFECT OF TEMPERATURE ON VISCOSITY OF RVNR LATICES

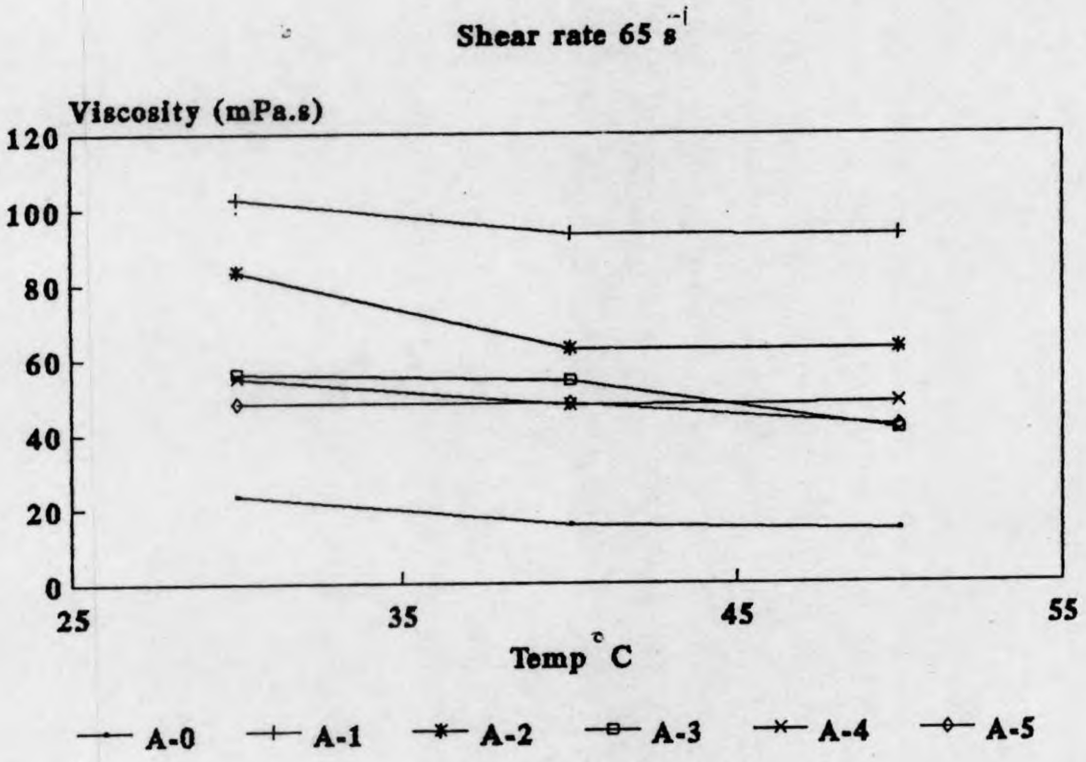


Figure 3.6 - EFFECT OF TEMPERATURE ON VISCOSITY OF RVNR LATICES

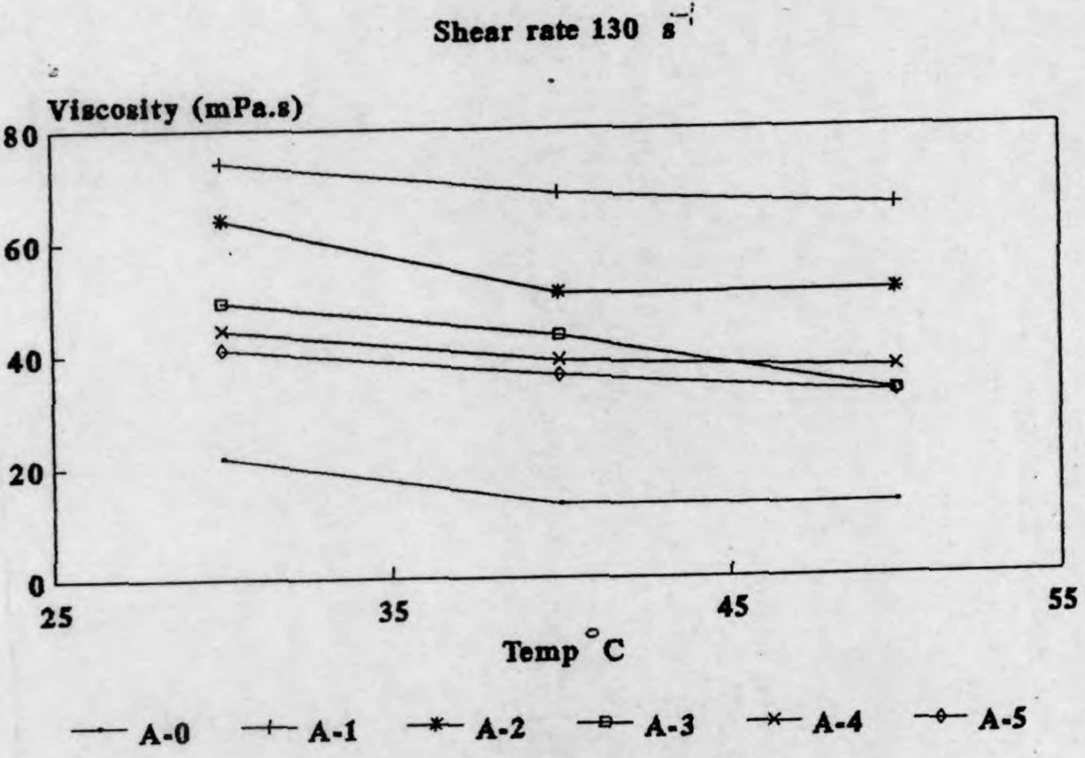


Figure 3.7 - EFFECT OF TEMPERATURE ON VISCOSITY OF RVNR LATICES

Table 3.1 - EFFECT OF RADIATION DOSE ON TENSILE PROPERTIES OF RVNR LATEX FILMS

(1) Using 5 phr nBA as sensitiser

RVNRL	Rad: dose MRad	Mod 300 (MPa)	Mod 500 (MPa)	Tensile strength (MPa)	Elongation at break %
A-1	0.5	0.82	1.14	8.00	1100
A-2	1.0	0.89	1.21	14.98	1050
A-3	1.5	0.95	1.41	22.00	1075
A-4	2.5	1.16	1.68	18.00	924
A-5	4.0	1.19	1.72	16.50	926

(2) Using 5 phr nBA and 0.25 phr CHP as sensitisers

B-1	0.5	0.85	1.21	11.20	975
B-2	1.0	0.95	1.40	21.00	1000
B-3	1.5	1.02	1.40	19.00	950

Table 3.2 - *EFFECT OF RADIATION DOSE ON* Vr
OF RVNR LATEX FILMS

RVNRL	Radiation Dose (MRad)	Vr
A-1	0.5	0.122
A-2	1.0	0.133
A-3	1.5	0.149
A-4	2.5	0.171
A-5	4.0	0.196
B-1	0.5	0.1419
B-2	1.0	0.160
B-3	1.5	0.160

Table 3.3

EFFECT OF RADIATION DOSE ON PSEUDOPLASTIC BEHAVIOUR OF RVNR LATICES

Sample	Pseudoplasticity index (n)			Viscosity index (k)		
	30°C	40°C	50°C	30°C	40°C	50°C
A-0	0.894	0.852	0.841	0.042	0.027	0.040
A-1	0.631	0.563	0.561	0.613	0.578	0.530
A-2	0.656	0.648	0.642	0.330	0.280	0.28
A-3	0.712	0.728	0.716	0.172	0.164	0.088
A-4	0.784	0.761	0.781	0.125	0.128	0.103
A-5	0.834	0.781	0.79	0.087	0.105	0.088

CHAPTER 4

SUMMARY AND CONCLUSIONS

4.SUMMARY AND CONCLUSIONS

In the present work, effect of radiation dose on the radiation vulcanisation of natural rubber latex using different sensitisers have been studied and an optimum dose has been standardised. The rheological behaviour of the RVNR latices has also been investigated.

From the results obtained, the following conclusions are drawn.

(1) When 5 phr of n-butyl acrylate (nBA) is used as sensitiser, the optimum radiation dose for vulcanisation is 1.5 MRad. By the addition of 0.25 phr cumene hydroperoxide as co-sensitiser, the radiation dose can be reduced to 1 MRad.

(2) RVNR latices are pseudoplastic in nature. At low radiation dose, viscosity and pseudoplasticity are much higher than NR latex. But as the radiation dose increases, viscosity and pseudoplasticity decreases.

nBA has high sensitising action, vapour pressure and volatility. Hence the amount of residual nBA in the final product will be negligible. This will lead to less cytotoxicity and dermatological effect, when the latex is used for surgical and medical products.

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