STUDIES ON VULCANIZATION, RHEOLOGY AND REINFORCEMENT OF NATURAL RUBBER LATEX WITH SPECIAL REFERENCE TO ACCELERATOR COMBINATIONS, SURFACE ACTIVE AGENTS AND GAMMA IRRADIATION

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Sri. N.R. Peethambaran under my supervision and guidance. No part of the work reported in this thesis has been presented for any other degree from any other institution. Two research papers have been published and three papers accepted for publication in international journals from the present work.

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DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the supervision of Dr. A.P. Kuriakose, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-682022 at the Rubber Research Institute of India, Kottayam. No part of this thesis has been presented for any other degree from any other institution.

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CHAPTER - I

INTRODUCTION

Natural rubber latex has been known to the civilized world for the last few centuries. But the technology of rubber latex did not develop much until the early nineteenth century. Prior to that, the processing of rubber latex was a primitive handicraft and the products were only a subject of great curiosity. The two major defects with the products made at that time were stiffness in cold weather and tackiness in hot weather. The latter was overcome by the discovery of vulcanization. In 1839, Charles Goodyear and in 1843, Thomas Hancock independently discovered the process of vulcanization which brought about drastic changes in the properties of rubber products. The strength and elasticity of the product was increased greatly and it did not soften in hot weather. Even after this, the latex industry was not developed as the latex coagulated within a few hours of leaving the tree.

This problem was solved with the discovery of ammonia as a preservative for natural rubber latex by Johnson and Norris in 1853[1]. Commercial use of latex did not take place until concentrated latex was marketed in 1920[2]. A number of patents relating to latex products were taken during this period[3]. The two most notable products to emerge from this new industry were extruded thread and foam rubber. These products were markedly different from anything obtainable from dry rubber. By 1940, a substantial proportion of rubber thread used in clothing industry was made from natural rubber latex. Also, foam rubber seating found outlets in vehicles, public buildings and hospitals[4,5].

The past twentyfive years have witnessed considerable changes in the types of products made from natural rubber latex concentrates. Now natural rubber latex is predominantly employed in those applications where its supreme film forming ability and high wet gel strength are required. Dipped goods, latex thread, foam and adhesives are therefore likely to remain as its major outlets in the foreseable future. But the observed changes in latex consumption have not been accompanied by corresponding changes in production technique[6]. Most manufacturing units are using the same processes with only minor changes from what they were using twenty or twentyfive years ago. Improved formulations, test methods and process control are adopted reluctantly or not at all. The compounding and production process are often based on dubious ideas about the nature of raw materials and physical processes involved.

I. AN OUTLINE OF PROCESSING OF NATURAL RUBBER LATEX

I.1. NATURAL RUBBER LATEX

Natural rubber latex is mainly obtained from the bark of Hevea brasiliensis 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 and surface free energy from 40 to 45 ergs cm^{-2}[7]. The rubber content of latex varies between 25 and 40 per cent 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 large number of nonrubber constituents 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 to 3 microns[8].

I.1.1. Composition of latex

NR latex is a hydrosol in which the dispersed rubber particles are protected by a complex film containing proteins and phospholipids[8]. Excluding rubber and water, the substances present are proteins, lipids, quebrachitol and inorganic salts. The total protein content[9] is about 1-2 per cent of which 20 per cent is adsorbed on the surface of the rubber particles and the rest is dissolved or dispersed in the serum. The lipids consist of fats, waxes, sterol esters and phospholipids and its total content is about 0.9 per cent. The total concentration of inorganic materials is about 0.5 per cent, the main constituents being salts of potassium, magnesium, copper, iron, sodium, calcium and phosphorus.

I.2. PRESERVATION AND CONCENTRATION OF LATEX

As the latex comes out of the tree, it gets contaminated with microorganisms like bacteria and yeast[10]. The microorganisms metabolise the nonrubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which lead to coagulation of latex[11]. Therefore preservatives are added to latex immediately after collection[12, 13, 14]. Among the preservatives, ammonia is still used widely and it inhibits bacterial growth, acts as an alkaline buffer and raise the pH and neutralise free acid formed in latex. But ammonia has the disadvantage that it is pungent smelling and prolonged exposure to the gas can cause discomfort to workers. Some of the western countries have introduced legislation regarding the maximum permissible limit of ammonia in a factory atmosphere. Also high concentrations of ammonia leads to processing problems. Therefore attempts have been made to develop low-ammonia preservation systems[15, 16, 17]. A commonly used low-ammonia system is LA-TZ which consists of 0.2 per cent ammonia, 0.013 per cent TMTD, 0.013 per cent zinc oxide and 0.05 per cent lauric acid[18, 19].

Preserved field latex is unsuitable for most latex applications as its rubber content is low. For most product manufacture, a latex of 60 per cent minimum rubber content is essential[20]. The important methods for the concentration of preserved field latex are (i) evaporation, (ii) creaming, (iii) centrifuging, and (iv) electro-decantation. The first method involves removal of water only and hence the particle size distribution remains unaffected. On the other hand the other three methods involve partial removal of nonrubber constituents and the particle size distribution of the concentrate differs from that of the initial latex as a proportion of the smaller particles are eliminated in the serum. Only centrifuging and creaming are commercially used for the production of latex concentrate[20].

I.3. PROPERTIES OF LATEX CONCENTRATE AND EFFECT OF AMMONIATION

NR latex concentrate is a highly specified material. The latex properties of significance are[21]; dry rubber content (d.r.c.), nonrubber solids content (NRS), mechanical stability time (MST), volatile fatty acid number (VFA), potassium hydroxide number (KOH) and alkalinity. The significance of these properties has been discussed by Blackley[21] and Cockbain[22]. Latex concentrate is a non-Newtonian fluid and its viscosity decreases with increasing shear rate[23]. Natural rubber latex has a measurable electrical conductivity due to the salts dissolved in the aqueous phase and in most centrifuged latices it range from 3.0 to 5.0 mS at 25°C[24].

The nonrubber materials in the serum of the latex concentrate comprises a variety of chemical species. In consequence to the addition of ammonia for preserving it, the proteins and lipid materials are believed to be hydrolysed slowly releasing fatty acids which form soaps which are adsorbed on to the particle surface[24]. The adsorption of these soaps is thought to account for the spontaneous rise in mechanical stability when ammoniated latex concentrate is stored[25,26]. Eventhough a great deal is known about the composition of latex concentrate and its serum content, the relation between composition and properties is still vaguely understood. The real cause for batch to batch variation in processing behaviour is still largely unexplored. Recently it was pointed out that the amount or the nature of serum anions are not sufficient to explain the observed processability variations and it seems that the answer may lie in variability at the particle serum interface[6].

I.4. LATEX COMPOUND AND ITS PROCESSING

The convertion of NR latex into a product is accomplished in many ways and a stable colloidal system is maintained until it is converted into a solid product[27]. The different ingredients used in a latex compound are (i) surface active agents, (ii) vulcanizing agents, (iii) accelerators, (iv) activators, (v) antioxidants, (vi) fillers, and (vii) special additives. The water soluble materials are added as solutions, insoluble solids as dispersions and immiscible liquids as emulsions[27]. The particle size of the ingredients should be reduced to that of the rubber particles in latex for getting uniform distribution in the latex compound[28,29,30,31,32]. Further, the colloidal stability of the dispersions and emulsions should be comparable to that of the latex for maintaining the colloidal stability of the final mix.

I.4.1. Surface active agents

Surface active agents are substances which can bring about marked modifications in the surface properties of aqueous media, eventhough they are present in small amounts (of the order of 1 per cent or less). This has great importance in latex technology and in this respect latex technology differs significantly from that of dry polymer or polymer solutions[28]. Stabilising agents, dispersing agents, emulsifiers, wetting agents, viscosity modifiers and protective colloids come under this group. They are classified as anionic, cationic, amphoteric and non-ionic types[28]. The dispersing agents prevent the dispersed particles from reaggregating and alkyl sulfonates are generally used for this. Emulsifying agents are soaps, usually oleates formed *in situ*. Wetting agents are used to reduce the interfacial tension between two surfaces. Proteins, alginates, polyvinyl alcohols and cellulose derivatives are used as protective agents and viscosity modifiers in the processing of latex compound[28,33,34].

I.4.2. Vulcanizing agents

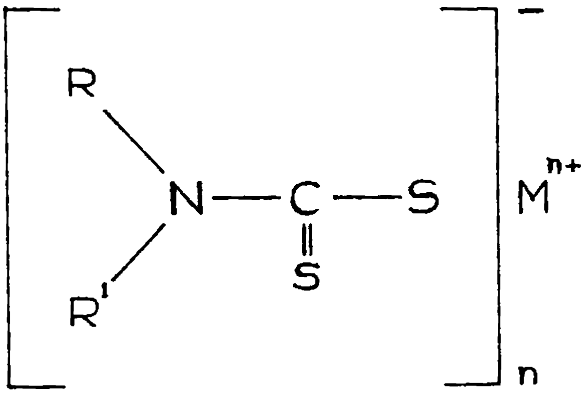
Sulfur is the most important vulcanizing agent for NR latex. Thiuram polysulfides along with thiourea is used as vulcanizing agent for heat resistant products[35]. Dunn reported[36] that butyl xanthogen disulphide in conjunction with a zinc dithiocarbamate may be used to vulcanize latex film in the absence of sulfur. It has also been reported that organic peroxides and hydroperoxides may be used to vulcanize latex films[28].

I.4.3. Accelerators

The important classes used in latex compounding are the metallic dialkyl dithiocarbamates[28]. The thiozoles and to a lesser extent thiurams are of importance as secondary accelerators in conjunction with dithiocarbamates[28].

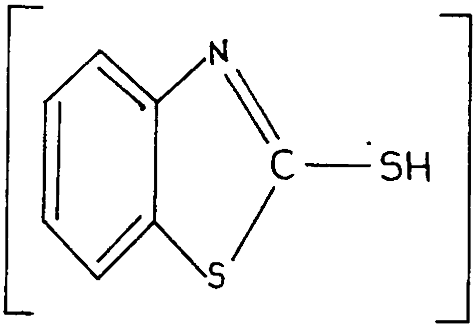
(a) Dithiocarbamates

The salts of the dialkyl dithiocarbamic acid have the generic structure as shown below:



Although a considerable range of accelerators are available under this, zinc diethyldithiocarbamate is the most widely used (ZDC). This is very active in latex mixes even in the absence of zinc oxide and activates thiozole accelerators[37].

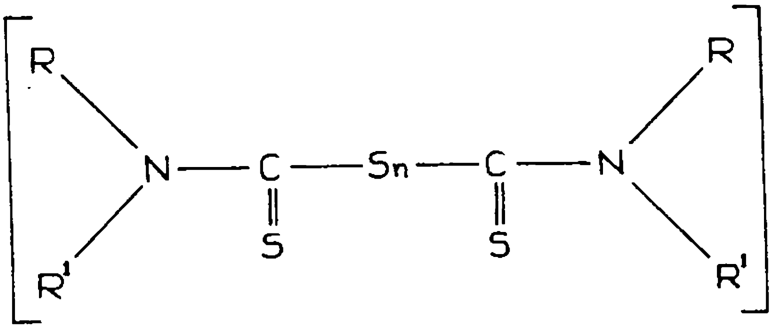
(b) Thiozoles



MBT

Thiozoles are insufficiently active to be used on their own for latex work, but they function as secondary accelerators for the dithiocarbamate, giving vulcanizate of high modulus[39]. The most common thiozole in latex compounding is the zinc salt of 2-mercaptobenzthiozole (ZMBT). It is activated by thiurams and dithiocarbamates[37].

(c) Thiuram sulphides



As a class, thiurams are insufficiently active to accelerate satisfactorily vulcanization of latex. In combination with other accelerators, the most commonly used thiuram in latex compounding is tetramethylthiuram disulphide (TMTD)[28].

I.4.4. Activators

Zinc oxide is used as an activator to the vulcanization process and its effect include increase in the tensile strength and modulus of the vulcanizate.

I.4.5. Antioxidants

Due to discolouration, amino derivatives which are powerful antioxidants in dry rubber are not used in latex compounds. Phenolic derivatives, which are not much effective, but which have the advantage of being non-discolouring find use in latex systems. Styrenated phenol is a widely used antioxidant in the latex industry.

I.4.6. Fillers

Fillers are added to natural rubber latex in order to modify its properties and to reduce cost[38]. It is seen that no effect analogous to the reinforcement of dry rubber by fillers are observed when the same fillers are added to latex compounds[28]. The important nonblack fillers used in latex compounding are precipitated silica, precipitated calciumcarbonate and chinaclay. The use of chinaclay in latex compounding has been studied by Van Rossem.[39]

I.4.7. Special additives

Depending on the nature of process or on end use, ingredients like gelling agents, foaming agents, flame proofing agents, tackifiers, colours, etc. are added[27].

I.5. LATEX PRODUCT MANUFACTURE

The important processes for latex product manufacture are (i) dipping, (ii) foaming, (iii) extrusion, and (iv) spreading and casting. Dipping process consists in the immersion of a former into a suitably compounded latex, followed by slow withdrawal in such a way as to leave a uniform deposit of latex on the former. The process is completed by drying, leaching and vulcanizing the deposit[40]. In the extrusion process, a suitably compounded latex is continuously extruded through a glass capillary into an acid bath, followed by drying, and vulcanization[42]. Latex foam is made by foaming compounded latex followed by gelling, vulcanization and drying[40,41].

I.5.1. Degradation of latex products

Degradation of latex products cannot be prevented, but it can be retarded[45]. Exposure of latex products to any of the following environmental conditions causes degradation.

- * Heat
- * Humidity
- * Ultraviolet light
- * Gamma radiation
- * Ozone
- * Oxygen
- * Chemicals, detergents, etc.
- * Stress

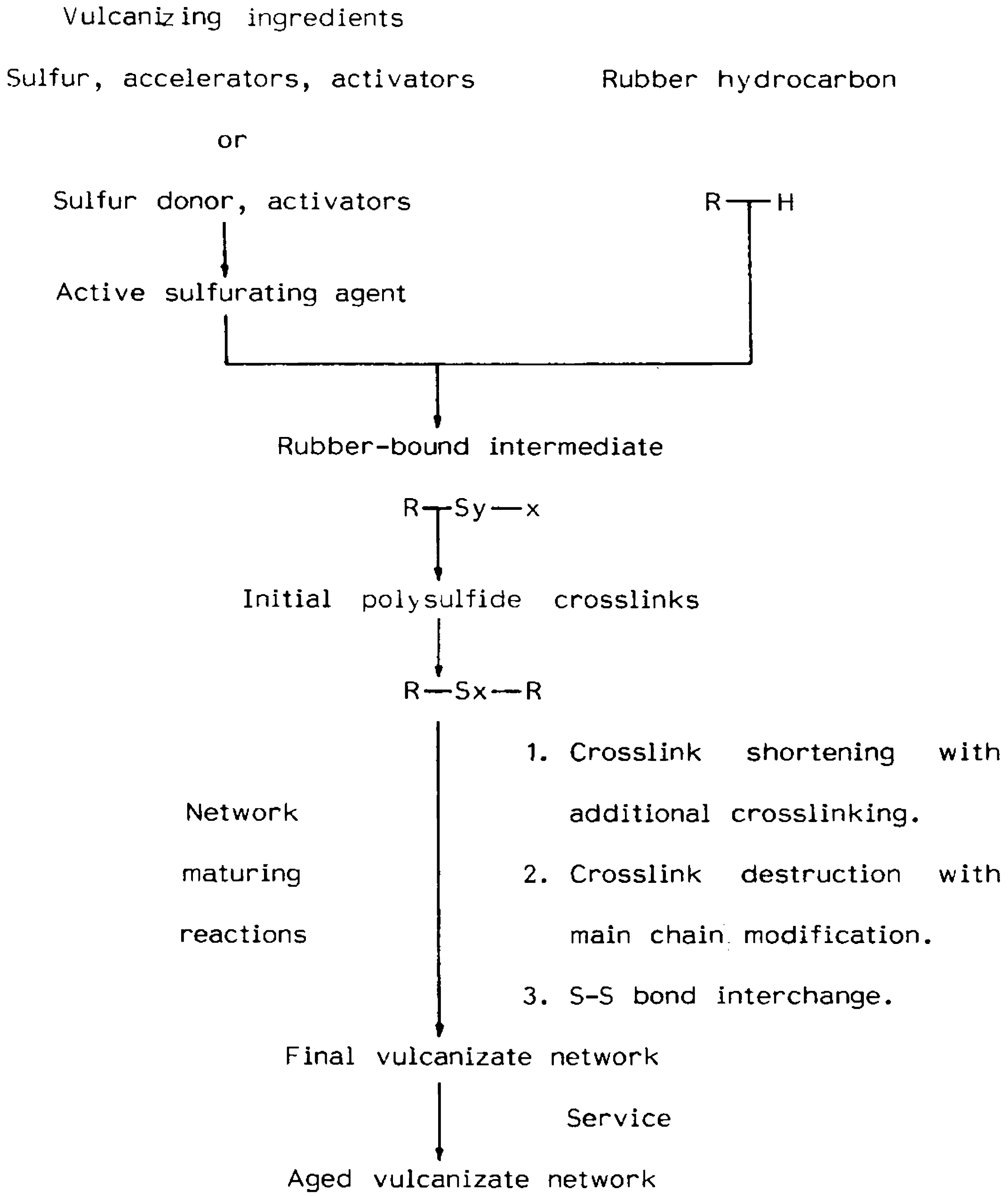
The article is often simultaneously subjected to several types of exposure which in turn, accelerate the rate of degradation. Degradation of latex vulcanizates by detergents and ozone has been well investigated[43,45]. Poor process control and improper compounding will accelerate the degradation process[45]. Latex products like elastic thread are more susceptible to degradation due to its large surface area and the limitations of nonstaining antioxidants[43]. Hence improvement in the quality of latex products depends on factors like improvement in processing, vulcanization, protection and reinforcement.

II. VULCANIZATION

Vulcanization 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 deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer[46]. Vulcanization usually produces network junctures by the insertion of chemical crosslinks between polymer chains. The crosslinks may be formed through chains of sulfur atoms, single sulfur atom or carbon-carbon bonds. The vulcanizate properties are not functions of crosslink density only; they are affected by the type of crosslink, nature of polymer, type and amount of fillers, etc.[46,47]. The most generally favoured and widely used vulcanization procedure even today is merely elaborations of the original method of heating rubber with sulfur discovered by Charles Goodyear (1839) and by Thomas Hancock in 1843[48]. The introduction of organic accelerators in the vulcanization of rubber which began more than 75 years ago led to revolutionary changes in the manufacturing of rubber products[48]. The accelerators enabled vulcanization time to be reduced. The proportion of sulfur required for optimum physical properties could be reduced, thus improving the resistance of rubber goods to ageing and preventing blooming of sulfur[48].

II.1. ACCELERATED SULFUR VULCANIZATION

The overall course of accelerated sulfur vulcanization can be represented as follows[49].



The structural modifications of the main chain which can occur during the accelerated vulcanization process has already been studied in detail[49]. The function of accelerator combination is to increase the crosslinking efficiency and to minimise wastefully combined sulfur by decreasing (i) cyclic monosulfide formation, (ii) vicinal crosslinks, (iii) the length of sulfur chain 'Sx' in crosslinks[50]. Although the primary requirement of vulcanization is covalent crosslinking of the rubber chains, other modifications can occur concurrently at sites distant from the crosslinks. The accelerators have a great effect on physical, mechanical and service properties of the finished article.

II.2. VULCANIZATE 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 vulcanization 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 vulcanization has reached[51]. Tensile strength varies appreciably with vulcanization system. This variation may be due to differences 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[52] 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[53].

II.3. EFFECT OF CROSSLINK STRUCTURE ON PROPERTIES

The properties mentioned above depend mainly on degree of crosslinking but they also depend to some extent on the way in which the vulcanizate is crosslinked. This is owing to the fact that the free mobility of the chain segments depend on the structure of the crosslinks (C-C, C-S-C, C-Sx-C). A number of studies have been conducted in this line. At a given degree of crosslinking the tensile strength is the highest in the vulcanizate with polysulfide bonds. The poorest tensile strength values are found in association with pure C-C crosslinks. Towards heat ageing, the vulcanizates with C-C or C-S-C crosslinks have the best performance compared to those with sulfide crosslinks. The vulcanization system and vulcanizing conditions determine the structure of crosslinks and the extent to which the polymer chains are modified chemically during vulcanization.

II.4. ACCELERATORS IN LATEX COMPOUNDING

The use of organic accelerators in latex compound is basically different from their use in dry rubber compounds[59,60]. Natural latex contains a lot of nonrubber materials which function as accelerators and activators. In addition to this, the vulcanization temperature for a latex compound is substantially lower than that for a dry rubber compound. In the manufacture of high quality products two or more accelerators are being used[61]. A combination of ZDC and ZMBT is used for getting improved modulus[28], and a combination of TMTD, thiourea and ZDC is used as vulcanization system in heat resistant products[43]. But no systematic study involving the different accelerator combinations under conventional and efficient (low sulfur) vulcanization has been reported. According to Blokh[62], the protection of a vulcanizate against ageing depends mainly on the nature of accelerators employed and only less on antioxidants.

II.5. PREVULCANIZATION

Prevulcanization is defined as a system of vulcanization in which the rubber particles are chemically crosslinked at the latex stage so that on drying a vulcanized latex product is obtained without further heating. It is made by heating the raw latex with accelerators and sulfur at about 70°C until the required degree of crosslinking is obtained[63,64]. The rate of prevulcanization varies with different vulcanization systems and the extent of vulcanization has got profound effect on the final vulcanizate properties. Studies conducted in this line are based on general vulcanization systems only[65]. Prevulcanization is more complicated than the vulcanization of latex films because account has to be taken of the diffusion of reactants in the rubber particles. The use of prevulcanized latex in latex dipping is also reported[63].

III. RHEOLOGY OF LATEX

Latex rheology is very important in practical technology but very few studies have been conducted in this line. Owing to the non-Newtonian behaviour, a single viscosity measurement of latex at a particular temperature is not enough to understand its flow behaviour. Maron and co-workers have investigated the rheology of styrene-butadiene rubber latex[66]. Effect of total solids content and temperature on viscosity of NR latex has been investigated[67,68]. In all these studies the effect of shear rate upon apparent viscosity was neglected.

In latex compounding either centrifuged or creamed latices are used. At the raw latex stage itself, the viscosity of creamed latex is high compared to that of centrifuged latex[69]. The creamed latex contains smaller rubber particles also that are not usually present in centrifuged latex. But only very little study has been reported on the rheology of these latices.

The relation between the shear stress and shear rate for latices may be given[70] as per equation given in Chapter II.

In the case of styrene-butadiene copolymer latex containing rosin acid soaps, the flow is reported[66] as Newtonian at concentrations upto about 25 per cent total solids content, but at higher concentrations it is markedly non-Newtonian. The nature of the departure from non-Newtonian behaviour at higher solids content is such that the curve of fluidity against shear stress is concave upwards. At higher shear rates Newtonian behaviour is approached.

III.1. EFFECT OF SURFACE ACTIVE AGENTS

At a given solids content, larger particle latices are more fluid than are corresponding latices with smaller particles[71]. In addition to particle size, the effect of surface active agents also is important. During compounding, different types of surface active materials are used. Some of them may be stabilizers and the others may be added specifically to increase the viscosity. Such substances are hydrocolloids soluble in water to give viscous solutions which display the properties of a typical hydrophilic colloid system[71,72]. The whole relationship between shear rate and applied stress for the system may be radically modified by the inclusion of these materials. In particular, important characteristics such as thixotropy and structural viscosity may be imparted by their inclusion. These substances also function as stabilizers and in this respect they are often referred as protective colloids. The effect of one or more protective colloids may not be a simple additive function, but interactions are possible. In fact all of them are surface active in themselves. A general study on the effect of protective colloids on polymer latices has already been conducted[72]. There is very little correlation between the viscosity of aqueous solutions of a hydrocolloid and its efficiency as a thickner for various latices. The mechanism of thickening does not involve merely an increase in the viscosity of the continuous phase. One complicating effect is reversible clustering or floculating of latex particles of the type which is associated with the acceleration of creaming. Also weak bonds may develop between particles and between molecules which break down under stress and which reform when the stress is removed. Such bonds give rise to thixotropic effect and to the phenominon known as structural viscosity.

III.2. EFFECT OF TEMPERATURE

Temperature has got a tremendous effect on the viscosity of latex. Latex becomes less viscous as the temperature is increased. This is due primarily to the reduction of viscosity of the dispersion medium. The studies conducted in this line is only general[68,71] and there is no specific report on the effect of temperature on creamed and centrifuged latices.

Among the various physicochemical properties, viscosity is the most important one which influences the processing characteristics. Control of viscosity is more important than that of concentration. As the viscosity varies with shear rate and temperature, the knowledge of viscosity of a latex compound at a particular shear rate is not enough in products manufacture[73].

IV. REINFORCEMENT

Inorganic fillers and pigments are commonly added into latex in order to cheapen and stiffen the product or to colour it. The fillers may also affect the flow behaviour of latex. It may be mentioned that no effect, analogous to the reinforcement of dry rubber by certain inorganic fillers, are observed when the same fillers are incorporated in latex compounds. Some studies have been conducted in this line and the poor rubber-filler interaction in latex vulcanizates is attributed to many factors such as insufficient distribution of fillers, non-simultaneous deposition of filler and rubber particles and the presence of protective layer of stabilizers around the rubber and filler particles in latex which prevent direct contact between them. A study was earlier conducted in styrene butadiene rubber latex using carbon black as filler[57]. It was reported that casein, which is a surface active agent could improve rubber-filler interaction in SBR latex. It was suggested that casein replaced the already existing protective layer around the rubber particles in latex and the filler particles and in this process, caused better rubber-filler interaction. The increase in viscosity of the latex compound owing to the addition of casein also caused simultaneous deposition of rubber and filler particles. It has also been reported through microscopic investigations that aggregation of rubber and carbon black are formed while adding casein to a mixture of SBR latex and carbon black[74].

In general, the total effect of fillers is to weaken the rubber film rather than improving it and the modulus and set are increased. As an approximation 25 per cent of a filler such as clay or whiting will reduce the tensile strength of natural rubber latex compounds to 50 to 70 per cent of normal. In synthetic latices small amounts of fillers may increase tear strength. It is also pointed out that small additions of bentonite clay enhance the tensile strength of the vulcanized deposit. It has also been reported that ageing resistance of natural rubber sulfur vulcanizates may be improved by the incorporation of small amounts (3 per cent) of fine particle silicas. Further, the addition of such silicas was found to improve the already outstanding ageing resistance of thiuram polysulphide 'sulfurless' vulcanizates which contain zinc mercaptobenzimidazole as an antioxidant. The mechanism of these effects however has not been investigated[75].

V. EFFECT OF GAMMA IRRADIATION

When a polymer is exposed to ionising radiation the following reactions are possible. A general representation is as follows in which RH represents the polymer molecule[76,77].

$$\mathrm{RH} \rightsquigarrow \mathrm{R}^{\cdot} + \mathrm{H}^{\cdot} \qquad \mathrm{V(i)}$$

$$\mathrm{H}^{\cdot} + \mathrm{RH} \longrightarrow \mathrm{R}^{\cdot} + \mathrm{H}_2 \qquad \mathrm{V\ (ii)}$$

$$2\mathrm{R}^{\cdot} \longrightarrow \mathrm{R} - \mathrm{R} \qquad \mathrm{V(iii)}$$

As a result of these reactions crosslinks, rearrangement and degradation occurs. It was suggested by Miller that crosslinking will occur when the building blocks of a polymer contains at least an α-hydrogen[77]. Charlesby and others have developed theoretical expressions[78,79] for the changes in molecular weight of polymers on irradiation. When chain scission and crosslinking occur simultaneously during irradiation of a polymer it may be assumed that these two processes are independent of each other. Crosslinking can be effected by means of primary transient species or by free radicals. When no crosslinking occurs with the free radicals, it is assumed that these radicals are stabilized.

V.1. VULCANIZATION OF NR LATEX BY GAMMA IRRADIATION

Gamma irradiation has also been used for the vulcanization of latex[80,81]. An irradiation dose of 30-40 KGy is enough to vulcanize natural rubber latex, with sensitisers such as carbon tetrachloride and chloroform. As the network structure of rubber is dependent to a certain extent on vulcanization temperature, there can be differences in the distribution of chemical crosslinks in radiation vulcanization which is taking place at a lower temperature compared to conventional vulcanization. Its remarkable advantages are (i) due to the absence of accelerators, sulfur and zinc oxide in the vulcanizate it is free from nitrosamines[82], and (ii) it is good for the production of medical rubber goods[84].

V.2. DEGRADATION OF POLYMERS

A significant finding is that radiation induced deterioration can be markedly reduced by additives known as 'anti-rads' whose efficiency does not correlate with their behaviour as antioxidants or antiozonants[84]. The effect of different ingredients of a latex compound on the rate of vulcanization has also been studied. Carbon black and silica were found to enhance crosslinking[85]. Thiuram disulphide (TMTD), diphenyl guanidine and mercaptobenzothiozole inhibit radiation crosslinking[86]. In polymer systems one problem is to separate and estimate the effect of crosslinking and molecular degradation which commonly proceed concurrently. The most general method of estimating chain scission during network formation or degradation is sol gel analysis[87].

V.3. RUBBER-FILLER INTERACTIONS

When rubber particles are exposed to high energy radiation, free radicals are formed. The contribution of free radicals in the reinforcement of dry rubber by fillers has been well established[88]. During mastication with or without chemical reagents macroradicals are formed in rubber which might combine with filler effecting reinforcement. The free radicals are able to interact with reactive sites on the surface of the filler particles and so unite filler and rubber matrix into a bonded structure. This will clearly not occur if the mastication step is absent. It is perhaps significant that if latex products which contain reinforcing fillers are subjected to mastication after drying down and before curing, then the vulcanizates subsequently obtained from the products are found to display the properties normally associated with the presence of reinforcing filler. It has been reported that some reinforcement of latex films by carbon black can be achieved if the compounded latex is subjected to irradiation by CO^{60} rays[89]. Vulcanization ingredients may be included in the latex, but the effect of vulcanization owing to irradiation were found to be marginal. The development of reinforcement is attributed to free radicals which are produced either in rubber or in carbon black or in both by the ionising radiation.

VI. SCOPE OF THE PRESENT WORK

A thorough understanding of the effect of accelerator combinations on network structure and physical properties will help in evolving latex formulations for improved quality and for cost reduction. An understanding of the rheological behaviour of different types of concentrated latices and of the effect of various surface active materials on them will lead to better process control in the manufacture of latex products. Improved rubber-filler interaction in latex compound is essential for the production of latex goods with better strength properties.

The review outlined earlier in this chapter indicates that an indepth study on the above aspects of latex technology is lacking. Eventhough a few accelerator combinations are being used at present in product manufacture, reports are not available on such aspects as effect on nature of crosslinks, physical properties, heat ageing, degradation, effect of ionising radiations, etc. An ideal example is the latex thread, in which manufacturers are bound to use accelerator combinations to improve physical properties without knowing their effects on heat ageing.

Similarly, in the preparation of prevulcanized latices, the rate of prevulcanization is dependent on the types of accelerators used. Excpet for a few reports based on general vulcanization systems, the rate of vulcanization has not been studied with special reference to more specific accelerator combinations.

Another aspect of latex technology where very little study is reported is its rheology. Creamed and centrifuged latices are used in the manufacture of various products. Also, surface active materials like casein, polyvinyl alcohol, sodium alginate and sodium carboxymethylcellulose, are also used either as a protective agent or as a viscosity modifier[72]. Except for a few reports on its effect on viscosity, no systematic study is reported on the effect of shear rate and temperature on the viscosity of centrifuged and creamed latices with or without these additives.

Poor rubber-filler interaction is a problem in latex compounding. Eventhough some work is reported on synthetic latices and carbon black vis-a-vis latex-filler interactions, not much study is reported on rubber-filler interactions on natural rubber latex with nonblack fillers.

The use of latex products in radiation therapy is also increasing (eg., cathetors). A survey of literature indicates that not much work is reported on the effect of radiation on ageing of latex products. Hence a study on the effect of gamma irradiation on the degradation of latex films was also included.

In the present work, some of the above aspects of latex technology have been investigated which we hope will enable the manufacturers exercise better process control and bring about products with better physical properties. The thesis is divided into the following chapters.

Chapter I deals with a general introduction and survey of literature in the field of vulcanization, rheology, reinforcement and degradation of latex vulcanizates. The experimental techniques are given in chapter II. The third chapter describes the effect of different accelerator combinations under conventional and efficient vulcanization systems on cure rate index, network structure and physical properties of natural rubber latex vulcanizates. The effect of accelerator combinations on the rate of prevulcanization and its effects are also included in this chapter. The fourth chapter describes the effect of surface active agents on rubber-filler interaction and on rheology of NR latex. The effect of gamma irradiation on rubber filler interactions and degradation of natural rubber latex vulcanizates are described in chapter V. The sixth chapter gives overall conclusions from the studies. The importance of the relevant results in the manufacture of latex products is also given wherever required.

The list of publications from this work is given at the end.

REFERENCES

1. W. Johnson, British Patent (1853) 467.

2. D.F. Twiss, History of the rubber industry, P. Schidrowitz and T.R. Dawson, Ed., Cambridge (1952) 91.

3. W.H. Stevens, Trans. Instn. Rubb. Ind., 23 (1947) 118.

4. R.G. James, Trans. Instn. Rubb. Ind., 24 (1949) 220.

5. E.A. Murphy, Trans. Instn. Rubb.Ind., 31 (1955) 90.

6. K.F. Gazeley, A.D.T. Gorton and T.D. Pendle, Natural Rubber Science & Technology, A.D. Roberts, Ed., MRPRA, Oxford University Press (1988) 62-98.

7. D.C. Blackley, High Polymer Latices, Vol. I., Maclaren & Sons Ltd., London (1966) 214-240.

8. B.L. Archer, D. Barnard, E.G. Cockbain, P.I. Dickens and A.I. McMuller, The Chemistry and Physics of Rubber-like Substances, L. Bateman, Ed., Maclaren & Sons Ltd., London (1963) 41-94.

9. B.L. Archer, E.G. Cockbain, Biochem. J., 75 (1960) 236.

10. D.C. Blackley, High Polymer Latices, Vol. I., Maclaren & Sons Ltd., London (1966) 180-214.

11. J.S. Lowe, Trans. Instn. Rubb. Ind., 36 (1960) 225.

12. S.N. Angove, Trans. Instn. Rubb. Ind., 40 (1964) 251-261.

13. S.N. Angove, Trans. Instn. Rubb. Ind., 41 (1965) 136.

14. A.D.T. Gorton and N.M. Pillai, Plrs. Bull., Rubb. Res. Inst. Malaya, 105 (1969) 282.

15. E. Rhodes, J. Rubb. Res. Inst. Malaya 8(3) 324-30.

16. C.K. John, M. Nadarajh, P.S. Rama Rao, C.M. Lam and C.S. Ng, Proc. Int. Rubb. Conf. 4 (1975) 339-357.

17. P.S. Rama Rao, C.K. John, C.S. Ng, M.G. Smith and C.F. Robert, RRIM Planters Conference (1976) 324-333.

18. C.K. John, N.P. Wong, A.C. Chin and Abdul Latiff, Proc. Int. Rubb. Conf. 2 (1985) 451-467.

19. A.D.T. Gorton and T.D. Pendle, Proc. Int. Rubb. Conf., Kuala Lumpur, Vol. II (1985) 468.

20. D.C. Blackley, High Polymer Latices, Vol. I., Maclaren & Sons Ltd., London (1968) 192-212.

21. D.C. Blackley, High Polymer Latices, Vol. II, Applied Science Publishers Ltd., London (1966) 439-485.

22. E.G. Cockbain and M.W. Philpott, The Chemistry and Physics of Rubber-like Substances, L. Bateman, Ed., Maclaren & Sons Ltd., London (1963) Chapt. I.

23. J.R. Van Wazer, J.W. Lyons, K.Y. Kim and R.E. Colwell, Viscosity and flow measurement, Inter Sciences, New York (1966). 6.

24. K.F. Gazeley, A.D.T. Gorton and T.D. Pendle, Natural Rubber Science & Technology, A.D. Roberts, Ed., MRPRA, Oxford University Press, London (1988) 71.

25. S.F. Chen and C.S. Ng, Rubb. Chem. Technol. 57(2) (1984) 243.

26. H.C. Chin, M.M. Singh and S.E. Like, Proc. Int. Polymer Latex Conf., PRI London (1978).

27. K.F. Gazeley, A.D.T. Gorton and T.D. Pendle, Natural Rubber Science & Technology, A.D. Roberts, Ed., MRPRA, Oxford University Press, London (1988) 100-140.

28. D.C. Blackley, High Polymer Latices, Vol. I, Maclaren & Sons Ltd., London (1966) 70-154.

29. A.D.T. Gorton and T.D. Pendle, NR Technol. 12 (1981) 21.

30. A.D.T. Gorton and T.D. Pendle, NR Technol. 12 (1981) 1.

31. British Standards-3900, Determination of fineness of grind, (1983).

32. A.D.T. Gorton and T.D. Pendle, Proc. Eml. Polym. Conf., PRI London (1982) June.

33. G.L. Brown and B.S. Garret, J. Appl. Polym. Sci. 1 (1959) 283.

34. W.D. Schroader and G.O. Brown, Rubb. Age, 69 (1951) 433.

35. M.W. Philpott, Proc. Rubb. Techn. Conf., IRI London (1962) 470.

36. J.R. Dunn, Trans. Instn. Rubb. Ind., 34 (1958) 249.

37. G.A. Blokh, Organic accelerators in the vulcanization of rubber, IPST, Jerusalem (1968) 16-68.

38. R.J. Noble, Latex in Industry, Rubber Age, New York (1953) 261-263.

39. Van Rossem, J.A. Plaizier, Proc. Rubber Tech. Conf., London (1938) 197.

40. D.C.Blackley, High Polymer Latices, Vol. II, Applied Science Publishers, London (1966) 525-637.

41. E.W. Madge, Latex Foam Rubber, Maclaren & Sons Ltd., London (1962) 4-15.

42. R.G. James, Trans. Instn. Rubb. Ind., 12 (1936) 104.

43. A.D.T. Gorton, NR Technol. 8(1) (1977) 79.

44. A.D.T. Gorton and P.H. Hannam, Eur. Rubb. J. 156(8) (1974) 36.

45. Robert F. Mausser, Rubb. India, AIRIA, 37(1) (1985) 9-15.

46. A.Y. Coran, Science and Technology of Rubber. Frederick R. Erich, Ed., Rubber Division of ACS (1978) 291-335.

47. B.A. Dogadkin, Z.N. Tara Sova and Golberg, Proc. 4th Rubb. Technol. Conf., London IRI (1962) 65.

48. L. Bateman, C.G. Moor, M. Porter and B. Saville, The Chemistry and Physics of Rubber-like Substances. L. Bateman, Ed., Maclaren & Sons Ltd., London (1963) 451-561.

49. A.V. Chapman and M. Porter, Natural Rubber Science & Technol., A.D. Roberts, Ed., MRPRA, London (1988) 511-601.

50. L. Bateman, R.W. Glazebrook and C.G. Moor, J. Appl. Polym. Sci. 1 (1959) 257.

51. W. Hofman, Vulcanization and vulcanizing agents, Maclaren & Sons Ltd., London (1967) 98-195.

52. W. Hofman, Vulcanization and vulcanizing agents, Maclaren & Sons Ltd., London (1967) 12-16.

53. A.D.T. Gorton, NR Technol. 7 (1976) 97.

54. C.G. Moore and W.F. Watson, J. Polym. Sci., 19 (1956) 237.

55. B. Saville, A.A. Watson, Rubb. Chem. Technol. 40 (1967) 100.

56. D.S. Campbell, J. Appl. Polym. Sci., 13 (1969) 1201.

57. A.D.T. Gorton, Plast. & Rubb. Inst. Int. Polym. Latex Conf., London (1978) Oct.

58. A.D.T. Gorton, NR Technol. 10 (1979) 9.

59. G.A. Blokh, Organic accelerators in the vulcanization of rubber, IPST, Jerusalem (1968) 16-68.

60. M.W. Philpott, Proc. 4th Rubb. Techn. Conf., IRI (1962) 470-484.

61. L. Bateman, C.G. Moore, M. Porter and B. Saville, Chemistry and Physics of Rubber-like Substance, L. Bateman, Ed., Maclaren & Sons Ltd., London (1963) 508.

62. G.A. Blokh, Organic accelerators in the vulcanization of rubber, IPST, Jerusalem (1968) 294-319.

63. D.C. Blackley, High Polymer Latices, Vol. II, Applied Science Publishers Ltd., London (1966) 383.

64. M.E. Myers, A.M. Wims and W.R. Ten, Rubb. Chem. Tech., 46 (1973) 464-9.

65. A.D.T. Gorton, NR Technol., 10(1) (1979) 9.

66. S.H. Maron and R.J. Belner, J. Coll. Sci., 10 (1955) 523.

67. Edgar Rhodes and H. Fairfield Smith, J. RRIM, 9 (1939) 171.

68. H. Fairfield Smith, J. RRIM, 11 (1941) 44.

69. K.O. Calvert, Polymer Latices and their applications, Applied Science Publishers Ltd., London (1983) 15-30.

70. J.A. Brydson, Flow properties of polymer melts. The Plastics and Rubber Institute, London. (1981) 1-17.

71. D.C. Blackley, High Polymer Latices, Vol. II, Maclaren & Sons Ltd., London (1966) 113-131.

72. G.L. Brown and B.S. Garret, J. Appl. Polym. Sci., 1 (1959) 283.

73. K.O. Clavert, Polymer Latices and their applications, Applied Science Publishers Ltd., London (1982) 187.

74. B.A. Dogadkin, L.G. Senatorskaya, V.I. Gusev and P.I. Zakharchenko, Rubb. Chem. Tech., 31 (1958) 635-661.

75. A. Anderson, Kautu. Gummi. 11 (1958) WT 244.

76. D.T. Turner, The Chemistry and Physics of Rubber-like Substances, L. Bateman, Ed., Maclaren & Sons Ltd., London (1963) 563-589.

77. A.A. Miller, E.J. Lawton and J.S. Balwit, J. Polym. Sci., 14 (1958) 503.

78. A. Charlesby, J. Polym. Sci., 11 (1953) 513.

79. A. Charlesby, Proc. Roy. Soc. London A222 (1954) 60.

80. K. Sumarno and E. Sundardi, J. Appl. Polym. Sci., 21 (1977) 3077.

81. D.J. Lyall, Proc. Int. Conf. Radiation Processing for Plastics and Rubbers, Vol. II (1984) 16-1.

82. A.D.T. Gorton, G.P. Mc Sweeney and B.K. Teed, NR Technol. 1 (1987) 18.

83. K. Makuchi, F. Yozhii and I. Ishigaki, Int. Rubb. Tech. Conf., Penang (1988) Abstract No. 3.

84. J.W. Born, WADC Tech. Reports (1954-55) 55-58.

85. J. Blackford and R.G. RObertson, J. Polym. Sci., 2 (1965) 1325.

86. G. Kraus and R.L. Collins, Rubber World, 139 (1958) 219.

87. G.M. Bristow, J. Appl. Polym. Sci., 7 (1963) 1023.

88. W.F. Waston, Ind. Engg. Chem., 47 (1958) 1981.

89. A. Lamm and G. Lamm, Rubb. Chem. Tech., 35 (1962) 848.

CHAPTER - II

EXPERIMENTAL TECHNIQUES

I. MATERIALS USED

The materials used and the experimental procedures adopted in the present investigations are described in this chapter.

I.1. CENTRIFUGED LATEX

High ammonia type 60 per cent centrifuged latex conforming to the specifications of the Bureau of Indian Standards: BIS 5430-1981, obtained from M/s Padinjarekara Agencies, Kottayam was used in this study. The properties of the latex estimated by us is 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	0.75
6.	KOH number	0.65
7.	Mechanical stability time, seconds	1075
8.	Volatile fatty acid number	0.04
9.	Copper content, ppm on total solids	3
10.	Manganese content, ppm on total solids	0.5

I.2. CREAMED LATEX

The creamed latex used in the study was prepared from preserved field latex (1 per cent ammonia content), collected from the fields of the Rubber Research Institute of India. The creaming was done as per the method given in Blackley[1] using tamarind seed powder as creaming agent. The latex was treated with 0.04 per cent potassium oleate (10 per cent solution) and 0.3 per cent tamarind seed powder (3 per cent solution) and was mixed well and left aside for creaming. After 5 days, the cream was collected, homogenised and tested. The various quality parameters of the latex used are given under:

Parameters	Value
1. Dry rubber content, % by mass	60.20
2. Non-rubber solids, % by mass	1.72
3. Coagulum content, % by mass	0.04
4. Sludge content, % by mass	0.02
5. Alkalinity as ammonia, % by mass	0.75
6. KOH number	0.50
7. Mechanical stability time, seconds	877.00
8. Volatile fatty acid number	0.03
9. Copper content, ppm on total solids	3.83
10. Manganese content, ppm on total solids	0.97

Since the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber latex are affected by clonal variation, season, age of the tree etc.[2,3], centrifuged and creamed latices from the same lot has been used in each experiment.

I.3. RUBBER CHEMICALS

I.3.1. Accelerators

The accelerators used in this study were obtained from M/s Indian Explosives Limited (IEL), Calcutta. A short description of the important accelerators used are given below:

(a) Zinc diethyldithiocarbamate (ZDC)

This ultra accelerator is a cream-white powder of density 1.47-1.5 g/cm^3; m.p. 173-180°C; soluble in carbon disulfide, benzene and chloroform and is non-toxic. It ensures rapid low temperature vulcanization in the presence of a small amount of sulfur and is active in latex mixes even in the absence of zinc oxide.

(b) Zinc salt of 2-mercaptobenzthiazole (ZMBT)

A light yellow powder, density 1.63-1.65 g/cm^3, non-toxic, soluble in benzene, ethanol and chloroform. It is a slow accelerator and it cannot be used alone in latex work.

(c) Tetramethyl thiuramdisulfide (TMTD)

A white powder, density 1.29-1.33 g/cm^3. Soluble in chloroform, benzene and hot alcohol and is an ultra accelerator.

(d) Diphenylguanidine (DPG)

White powder, density 1.13-1.19 g/cm^3, m.p. 144-146, soluble in chloroform. It is activated by thiozoles and thiurams. Compounds containing DPG are not very resistant to heat ageing.

I.3.2. Other chemicals

(a) Antioxidant SP:

This is styrenated phenol and was obtained from M/s Indian Explosives Limited, Calcutta.

(b) Thiourea, oleic acid, zinc oxide (ρ = 5.5), stearic acid (ρ = 0.92) and elemental sulfur (ρ = 1.9) were of commercial grade. Anatase form of titanium dioxide (Tio_2) was obtained from M/s Travancore Titanium Products, Trivandrum.

I.3.3. Special chemicals

Propane-2-thiol and piperidene were of analytical grade and were obtained from Fluke A.G., West Germany.

I.3.4. Solvents

Benzene, n-heptane, petroleum ether and carbontetrachloride were of analytical grade.

I.4. SURFACE ACTIVE AGENTS

I.4.1. Dispersol F

It is sodium salt of a sulphonic acid manufactured by M/s Indian Explosives Limited, Calcutta. It was used as a dispersing agent in the preparation of dispersions of solid ingredients.

I.4.2. Potassium laurate

It is an anionic soap, soluble in water and is used as a stabilising agent in latex. This was prepared from chemically pure lauric acid and potassium hydroxide.

I.4.3. Casein

It is a phosphoprotein, which is obtained from caseinogen, the raw protein of milk. Acid casein has a molecular weight of the order of 40,000 and is a very pale buff-coloured powder which contains about 10 per cent moisture. It is very sparingly soluble in water, but is readily soluble in acids and alkalis. The isoelectric point of casein is in the region of pH 4.6. In order to prevent it from bacterial attack, preservatives such as sodium pentachlorophenate are added. The solution is mildly surface active. Casein used in the present work was obtained from M/s Loba-Chemie, Bombay.

I.4.4. Polyvinyl alcohol (PVA)

Polyvinyl alcohol is obtained from polyvinyl acetate by acidic or alkaline hydrolysis. This tends to become insoluble in water after prolonged storage and heating. This surface active material was obtained from M/s Loba-Chemie, Bombay.

I.4.5. Sodium alginate

Alginic acid which is a high molecular weight linear poly-1-4-β-D anhydromanuronic acid occurs mainly as the insoluble calcium salt in various common marine algae, from which it can be extracted as the soluble sodium salt by digestion with aqueous sodium carbonate. Sodium alginate, used in this study, was obtained from M/s Cellulose Products of India Limited, Ahmedabad.

I.4.6. Sodium carboxymethylcellulose (NaCMC)

It is the most widely known soluble cellulose derivative. The introduction of small alkyl substituents 'open up' the cellulose structure allowing penetration and dissolution by strongly polar solvents. This weakly surface active material was obtained from M/s Loba Chemie, Bombay.

I.5. FILLERS

Precipitated silica, china clay and precipitated calcium carbonate used in this study were of commercial grade.

II. COMPOUNDING OF LATEX

II.1. PREPARATION OF DISPERSIONS

The solid ingredients were added into latex as dispersions. The materials are made to disperse in water by grinding action and the dispersing agent prevent the dispersed particles from reaggregating. The quantity of dispersing agent to be used for preparing dispersions depends on the nature of materials to be dispersed. For very fine particle size ingredients like zinc oxide the quantity of dispersing agent required is about 1 per cent by weight whereas for materials like sulfur 2 to 2.5 per cent is required. There are different types of grinding equipments - ball mill, ultrasonic mill and attrition mill. In the present study a ball mill was used for making the dispersions of the ingredients.

A ball mill consists of a cylindrical container in which the slurry is placed together with a charge of balls. When the mill is working the balls are carried round with the container a short way and then cascade. It is this process of cascading which causes the particles of slurry to be comminuted. The efficiency of ball mill depends on speed of rotation of the jar, size and material of the ball, viscosity of the slurry, period of ball milling, etc.

The formulations of the dispersions used in this study are given below:

(1) Sulfur dispersion (50%)

Sulfur : 100
Dispersol F : 3
De-ionised water : 97

Ball milled for 72 hours

(2) ZDC dispersion (50%)

ZDC : 100
Dispersol F : 2
De-ionised water : 98

Ball milled for 48 hours

(3) ZMBT dispersion (50%)

ZMBT : 100

Dispersol F : 2

KOH : Trace

De-ionised water : 98

Ball milled for 24 hours

(4) TMTD dispersion (50%)

TMTD : 100

Dispersol F : 2

10% Ammonium caseinate : 5

De-ionised water : 93

Ball milled for 48 hours

(5) Titanium dioxide dispersion (33%)

Tio_2 : 100

Dispersol F : 2

De-ionised water : 198

Ball milled for 48 hours

(6) Precipitated silica (25%)

Precipitated silica : 100
Dispersol F : 2
De-ionised water : 298

Ball milled for 24 hours

(7) Precipitated calcium carbonate (50%)

Precipitated calcium carbonate : 100
Dispersol F : 2
De-ionised water : 98

Ball milled for 24 hours

(8) China clay (50%)

China clay : 100
Dispersol F : 2
De-ionised water : 98

Ball milled for 24 hours

II.2. PREPARATION OF EMULSIONS

The liquid antioxidant SP is immiscible with water and is added into latex compounds as an emulsion. The following recipe was used for preparing emulsions:

Antioxidant SP (50%)

Antioxidant SP	:	100	A
Oleic acid	:	3	
Liquor ammonia	:	3	B
De-ionised water	:	94	

Part A was warmed and added to B in small quantities under high speed stirring.

II.3. DE-AMMONIATION OF LATEX

As HA type concentrated latex was used, it was de-ammoniated to 0.3 per cent by stirring in a laboratory type de-ammoniation tank for 3 hours. The high ammonia content in latex will create problems in its conversion to solid products or in the stability of the latex compound in the presence of zinc oxide. The concentration of ammonia in latex was estimated as per BIS: 3708-Part I 1966.

II.4. COMPOUNDING

The mixing of the ingredients was done as per the order given in the compound formulations given in the respective chapters.

The stabilisers were first added as solutions, followed by the other ingredients. Mixing was done in a glass vessel and stirring for homogenisation was done using a laboratory stirrer at 10-20 rpm. It was occasionally stirred during storage in order to prevent settling of the ingredients.

II.5. MATURATION

The latex compound was matured at ambient temperature for 24 hours. This was done with the following objectives.

1. To equilibrate the added surface active agents and those naturally present between the aqueous and interfacial phases.
2. To remove the air bubbles introduced in the compound while compounding.
3. To dissolve the vulcanizing agents in the aqueous phase and make them migrate into the rubber particles which can offer better technological properties.
4. To obtain a certain degree of pre-vulcanization to the latex.
5. To allow time for the reaction of ammoniated latex with zinc oxide for getting uniform physico-chemical properties.

II.6. PRE-VULCANIZATION

The latex compound was put in a jacketed vessel with a stirrer and heated by passing hot water through the jacket. The temperature was adjusted at 70°C and the latex kept at this temperature with stirring till the required degree of crosslinking was obtained. The latex compound was then immediately cooled to room temperature and kept for further processing.

III. PREPARATION OF TEST SAMPLES

III.1. LATEX FILM

Latex films were cast on glass cells using the latex compound as described by Flint and Naunton[4]. Cellophane adhesive tapes were stuck to the edges of the glass plates to form the cells. 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 upon drying. The glass cells with the latex compound were placed on levelled table and dried overnight at ambient temperature.

III.2. PREPARATION OF LATEX THREAD

Latex thread is prepared by extruding the latex compound through a glass capillary tube into an acid bath (25 per cent acetic acid). As the latex filament passed through the bath, acid diffused into the centre of the thread and total gelation occured. The thread was then washed, dried and vulcanized. The diameter of the latex thread was controlled by adjusting the following factors:

1. Hydrostatic pressure on the latex compound in the capillaries.
2. The internal diameter of the capillaries.
3. The rubber content and viscosity of the latex compound.
4. The rate at which the transfer rollers remove the thread from the acid bath.

A schematic diagram of the latex thread plant used in this experiment is given in Figure II-1. The plant consists of header tank, constant pressure head device, coagulant bath, washing bath, drying chamber and the talc dusting system. Constancy of the extrusion pressure is ensured by feeding the nozzles through a manifold which is supplied from the constant pressure head. The level of this constant head may be altered within limits if desired.

The compounded latex after maturation|pre-vulcanization was stored in the header tank. From the header tank the latex passed to a manifold extruding head which distributed the compound to the capillaries through flexible tubes. Glass nozzles of 0.8 mm diameter were used and immersed in a bath of 25 per cent acetic acid. The length of the acid bath was 10 feet. The coagulated thread was transferred to the washing bath of 6 feet length containing water at 70°C. After washing the thread entered the air drying oven of 12 feet length set at 100°C, where it was dried. Talc powder was then applied over the thread to remove tackiness and the thread was wound on wooden frames. The drying was completed at ambient temperature.

IV. VULCANIZATION OF TEST SAMPLES

IV.1. LATEX FILMS

The dried latex film was used for determining the cure rate index and for the preparation of vulcanized dumbell samples.

IV.1.1. Cure rate index

The dried latex films were plied up to give a total thickness of approximately 2.5 mm and test specimens were cut from the plied sheet. The cure characteristics were determined using a Monsanto Rheometer (R-100) at 120°C according to ASTM D-2084(83). The cure rate index was determined from the rheographs of the respective mixes.

$$\text{Cure rate index} = \frac{100}{t_{90} - t_2} \qquad \text{II.1}$$

where t_{90} and t_2 are the times corresponding to the optimum cure and two units above minimum torque respectively.

IV.2 DETERMINATION OF OPTIMUM VULCANIZATION TIME IN AIR OVEN

The vulcanization of latex films was carried out in a laboratory air oven at 120°C/100°C. The time for developing maximum crosslink density was determined by vulcanizing the film at different durations (15 min, 30 min, 60 min, 90 min, etc) and determining the crosslink density of the sample in each case. For the crosslink density, the volume fraction of rubber (V_r) in the swollen vulcanizate in benzene was determined. The method of determination is described elsewhere [VII(1)]. The time for optimum crosslink density was then determined by plotting 'V_r' values against vulcanization time (t) as given in (Fig. II.2).

IV.3 VULCANIZATION OF LATEX THREAD

The thread was vulcanized in an air oven as per the time and temperature standardised as above.

V. DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES

V.1 VISCOSITY OF LATEX COMPOUND

Many methods are used for this. Brookfield (LVT model) is a technical viscometer and is used for determining the viscosity of latex compounds. It consists of a rotating member which is usually a cylinder driven by a synchronous motor through a beryllium-copper torque spring. The viscous drag on the cylinder causes an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disc is rotating. The torque and therefore the viscosity is indicated by means of the pointer and scale. A range of speed of the discs and cylinders are available so that a wide range of viscosity may be covered. The shear rate is not definable in a viscometer of this type in which a single element rotates in a mass of fluids of rather indefinite extent. Brookfield viscometer readings are affected by turbulance and to a certain extent by the angle of immersion of the spindle. Natural rubber latex is a non-Newtonian fluid and its viscosity decreases with increasing shear rate. In the present study the viscosity of the latices was measured at ambient temperature at 6 and 60 rpm.

V.2 EFFECT OF SHEAR RATE AND TEMPERATURE ON VISCOSITY

V.2.1 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 geometrics are mainly used in rheological 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.

Rheomat-30

For measurement of the rheological behaviour of the latices under study, Rheomat-30 was used. This rheometer has been designed to meet the most sophisticated requirements of continuous shear rheometry with 3 rotational speed steps in geometric progression from 0.047 to 350 min^{-1} (rpm). The rotational speed accuracy is maintained over the entire range by a closed loop control system. One revolution at the slowest speed takes about 20 minutes. For control of the Rheomat-30, a special programming unit for use with an x-y recorder, enabling different shearing programmes to be imposed on the substance has been developed.

For use in the present studies, the 'B' cup was selected. The equipment operates over a temperature range from ambient to 300°C, shear rate from 0.0088 sec^{-1} to 662 sec^{-1} and viscosities ranging from 0.3 cps to 1.3×10^8 poise. An accurate stress-strain plot was obtained as the latex was sheared continuously at different temperatures (25°C, 35°C and 45°C). The calculation of the viscosity was done as follows:

$$\sigma = \kappa\gamma^n \qquad \text{(where no yield stress)} \qquad \text{II.2}$$

$$\sigma - \sigma_o = \kappa\gamma^n \qquad \text{(when } \sigma_o = \text{yield stress)} \qquad \text{II.3}$$

σ = shear stress in pascals

σ_o = yield stress in pascals

γ = shear rate (sec^{-1})

n = pseudoplasticity index

By plotting log σ Vs log γ the values of ' κ ' and ' n ' are obtained as slope and intercept. Then the apparent viscosity 'η' was calculated using the equation:

$$\eta = \kappa\gamma^{n-1} \qquad \text{II.4}$$

VI. GAMMA IRRADIATION

Irradiation was done by Co^{60} rays using a gamma chamber Model 900 supplied by M/s Bhabha Atomic Research Centre, Bombay. It offers an irradiation volume of approximately 100 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. II.3. The source cage holds the radiation source pencils vertically and symmetrically distributed along its periphery. The cage can hold a maximum of 24 pencils containing Co^{60} in the form of pellets or aluminium clad slugs. The biological shield is a lead-filled steel container and surrounds the source cage. It consist 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 two cylindrical stainless steel clad lead shields 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 enable 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. II.3. The radiation is emitted at a rate of 3 KGy/h.

VI.1. LATEX-FILLER INTERACTION

Latex compound was mixed with the filler dispersion and irradiated to different dosages. After irradiation the latex filler system was cast into film of 1-1.25 mm thickness. The films was then vulcanized to optimum cure as described earlier.

VI.2. DEGRADATION OF LATEX FILMS

The latex film prepared using different accelerator combinations and various fillers were cut into dumbells conforming to ASTM D-412 after proper vulcanization. The dumbell samples were irradiated to the required dosage. These were then used for chemical and physical testing.

VII. CHEMICAL TEST METHODS

VII.1. DETERMINATION OF VOLUME FRACTION OF RUBBER

Samples of approximately 1 cm diameter, 0.25 cm thickness and 0.3 g weight were punched from the central portion of the vulcanized latex film and allowed to swell in thiophane-free benzene containing 0.5 per cent phenyl-β-naphthylamine at 35°C in a thermostatically controlled water bath. Swollen samples taken after 1, 3, 5, 9, 16, 25, 36 and 49 hours interval were blotted with filter paper and weighed quickly in a stoppered weighing bottle. For NR vulcanizates, the 36 hour period was found to be sufficient for attaining equilibrium. Samples were dried in an oven for 24 hours at 70°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 'V_r' was calculated by the method reported by Ellis and Welding[5], which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

$$V_r = \frac{(D-FT)\,\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_o\,\rho_s^{-1}} \qquad \text{II.5}$$

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

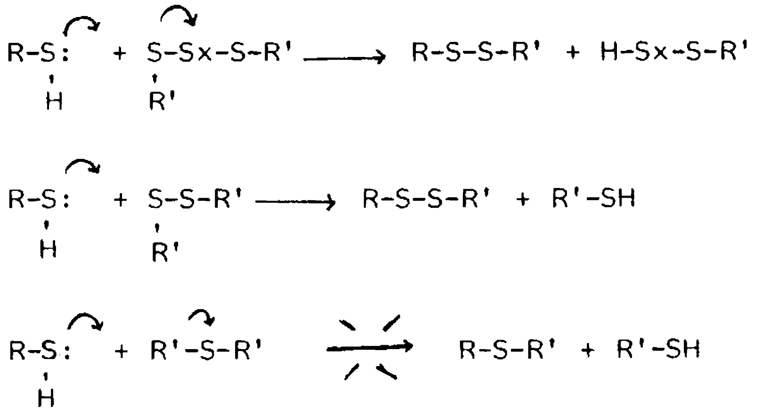
ρ_r(NR) = 0.92

ρ_s(benzene) = 0.875

From the collected data, the value of A_o was calculated. The value of 'V_r' can be taken as a measure of crosslink density.

VII.2. DETERMINATION OF CONCENTRATION OF DIFFERENT TYPES OF CROSSLINKS

The concentration of polysulfidic crosslinks (-Sx-) was estimated from the determination of chemical crosslink densities of the vulcanizate before and after treatment with thiolamine. Treatment of the vulcanizate with propane-2-thiol (0.4 M) and piperidine (0.4 M) in n-heptane at room temperature for 2 hours cleavs the polysulphidic crosslinks in the network. The experimental method used is as described in detail by Campbell[6,7]. Action of propane 2-thiol is based on nucleophilic displacement reactions by alkane thiols on sulfur atoms of polysulphides to cleave the sulfur bonds as shown below. They depend on the relative rates of the two displacement reactions and high resistance of the carbon-sulfur linkage in monosulphides to such nucleophillic displacement.



$$R\text{-}\underset{\overset{|}{H}}{S}: + \underset{\overset{|}{R'}}{S}\text{-Sx-}S\text{-}R' \longrightarrow R\text{-}S\text{-}S\text{-}R' + H\text{-Sx-}S\text{-}R'$$

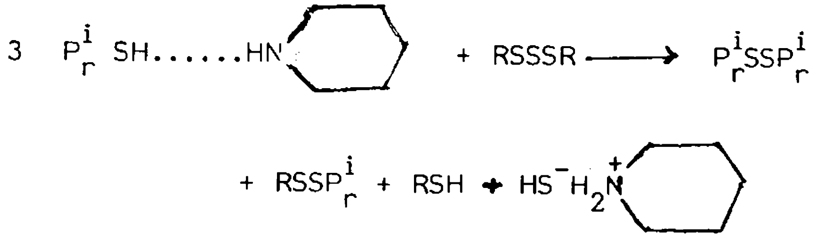
$$R\text{-}\underset{\overset{|}{H}}{S}: + \underset{\overset{|}{R'}}{S}\text{-}S\text{-}R' \longrightarrow R\text{-}S\text{-}S\text{-}R' + R'\text{-}SH$$

$$R\text{-}\underset{\overset{|}{H}}{S}: + R'\text{-}S\text{-}R' \not\longrightarrow R\text{-}S\text{-}R' + R'\text{-}SH$$

VII.3. TREATMENT WITH PROPANE-2-THIOL

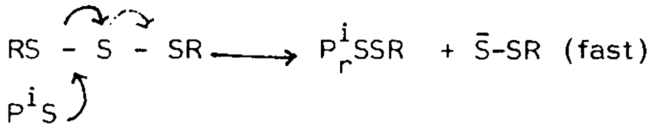
The samples (1 mm thick and 0.3 g weight) were placed in a cylindrical tube 30 cm long and 3 cm in diameter, clamped horizontally and purged with nitrogen. The specimens were well covered with 100 ml of the thiol-amine reagent (prepared by dissolving in n-heptane and making upto one litre with further pure heptane[8]). The gas tap was closed to maintain the nitrogen blanket in the tube. The solution was agitated occasionally during the two hour period.

After renewing the stream of nitrogen through the apparatus the reagent was run off and replaced by 100 ml of petroleum ether (b.p. 40°C-60°C) and the apparatus was agitated occasionally during one hour. This cold extraction was repeated with fresh petroleum ether every hour until four such extractions were made under nitrogen. The specimens were then removed and dried overnight in vacuum to constant weight. Then the chemical crosslink density was measured by equilibrium swelling method as described earlier (VI.1). When the sample thickness was more than 1 mm, the specimens were swollen in n-heptane overnight at room temperature under nitrogen and sufficient propane-2-thiol and piperidine were added to give concentrations of 0.4 M for each reagent in the final solution. The cleavage reaction in the presence of propane-2-thiol, piperidine and n-heptane is exemplified for trisulfide in the following equation:

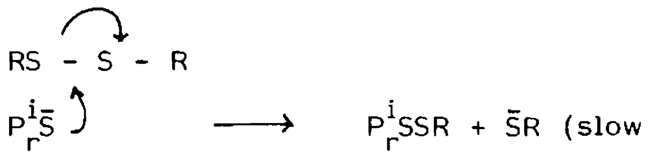


where P^i_r = Isopropyl.

The thiol-amine combination gives an associate, possibly piperidinium propane-2-thiolate in ion pair, in which the sulfur atom has enhanced nucleophilic properties[9] which is capable of cleaving organic trisulphides and higher polysulphides within 30 minutes at 20°C, while reacting with corresponding disulphides at about one thousandth of this rate. The favoured polysulphide cleavage is due to delocalization of the displaced 6-electron pair of RSS^- as shown in equation II.7.



3 p electron delocalization within a pπ – dπ bond. II.6



$$\mathrm{RS - S - R}$$

$$P^{i}_{r}\bar{S} \longrightarrow P^{i}_{r}SSR + \bar{S}R \text{ (slow}$$

(no 3 p electron delocalization) II.7

$Pr^{i}S^{-}$ is used to represent the nucleophilic thiol-amine associate.

The difference in the V_r values of the sample before and after thiol-amine chemical probe gives the polysulfidic crosslink content in the vulcanizate.

VII.4. DETERMINATION OF SOL CONTENT

The extent of chain scission in a vulcanizate was estimated by determining its solc ontent. The estimation was done by the method described by Bristow[10] in which the samples were extracted with cold acetone in the dark for 8 to 10 days, the acetone being replenished four times during this period. The samples were then dried to constant weight in vacuuo at room temperature. Weighed samples of the extracted vulcanizates (about 2 g) were further extracted with cold benzene in the dark for 8 to 10 days, the benzene being replenished four times during this period. After benzene extraction, the samples were dried to constant weight in vacuuo. The sol content is the weight loss during benzene extraction.

VII.5. DETERMINATION OF RUBBER-FILLER INTERACTION

Cast latex films containing the fillers were prepared and vulcanized to optimum crosslink density. Then the 'V_r' values of the filled (V_{rf}) and the gum (V_{ro}) vulcanizates were determined. The extent of rubber-filler interaction was then studied using the equation given by Cunneen and Russel[11].

$$\frac{V_{ro}}{V_{rf}} = ae^{-z} + b \qquad \text{II.8}$$

where v_{ro} and V_{rf} are the volume fractions of rubber in the gum and filled vulcanizates respectively, swollen in benzene, z is the weight fraction of the filler in the vulcanizate and 'a' and 'b' are constants. By plotting V_{ro}/V_{rf} against e^{-z}, values of 'a' (slope) and 'b' (intercept) were determined. The higher the value of 'a' (slope), the higher the swelling restriction and better the rubber-filler interaction.

VII.5.1. Ammonia-modified swelling

The samples of the vulcanized latex films containing different filler contents were swollen for 48 hours in flat dishes containing benzene in ammonia atmosphere[12]. For this the samples were put in a desiccator the bottom of which contained liquor ammonia. After swelling in ammonia atmosphere the samples were thoroughly washed with benzene and dried in a vacuum desiccator at room temperature (30°C) and tested for V_r by swelling in benzene. The difference in chemical crosslink density as obtained by swelling in benzene of the original vulcanizate and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond. In this, the ammonia permeates the benzene solvent and preferentially cleaves the rubber-filler attachment.

VIII. PHYSICAL TEST METHODS

VIII.1. LATEX FILMS

At least three specimens per sample were tested for each property and the mean values reported.

Modulus, Tensile Strength and Elongation at Break

In the present work these tests were carried out using a Zwick Universal Testing Machine (UTM) Model 1474. 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 is a moving platform driven by a continuously variable speed motor. The speed of movement of the platform can be varied to any value between 0 and 100. 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 unit. As soon as the test specimen breaks test results are displayed in the electronic unit.

All the tests were carried out at ambient temperature (30°C). Specimens were cut out from the cast films (Fig. 3). 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 be 500 mm/min.

The specimen is elongated and the values corresponding to ultimate tensile strength, elongation and modulus are obtained.

VIII.2. LATEX THREAD

Modulus, Tensile Strength and Elongation at Break

Five test pieces were tested for each sample and testing was done as per ISO 2321-1975(E) using a Zwick Universal Testing Machine[13].

VIII.3. RESISTANCE TO DRY HEAT

This method covers the extent of deterioration of rubber thread by measuring the reduction in physical properties when it is maintained at a constant elongation under conditions more severe than those encountered in service. The initial physical properties of the thread were determined in accordance with ASTM D-2433. Test samples from the same latex thread maintained at 100 per cent elongation were subjected to ageing in an air circulating hot air oven as given below. The residual physical properties were then measured and the percentage change reported.

	Class of test	Temperature°C	Time
1.	Normal	70°C	14 days
2.	Heat resistant	150°C	2 hours

The performance of the thread as percentage retention of the selected physical property is expressed as follows:

$$\text{SRM} = \frac{P_a}{P_o} \times 100 \qquad \text{II.9}$$

where SRM = Property retained by the test specimen after dry heat treatment.

P_o = Initial value of the selected property.

P_a = Value of the property after ageing period.

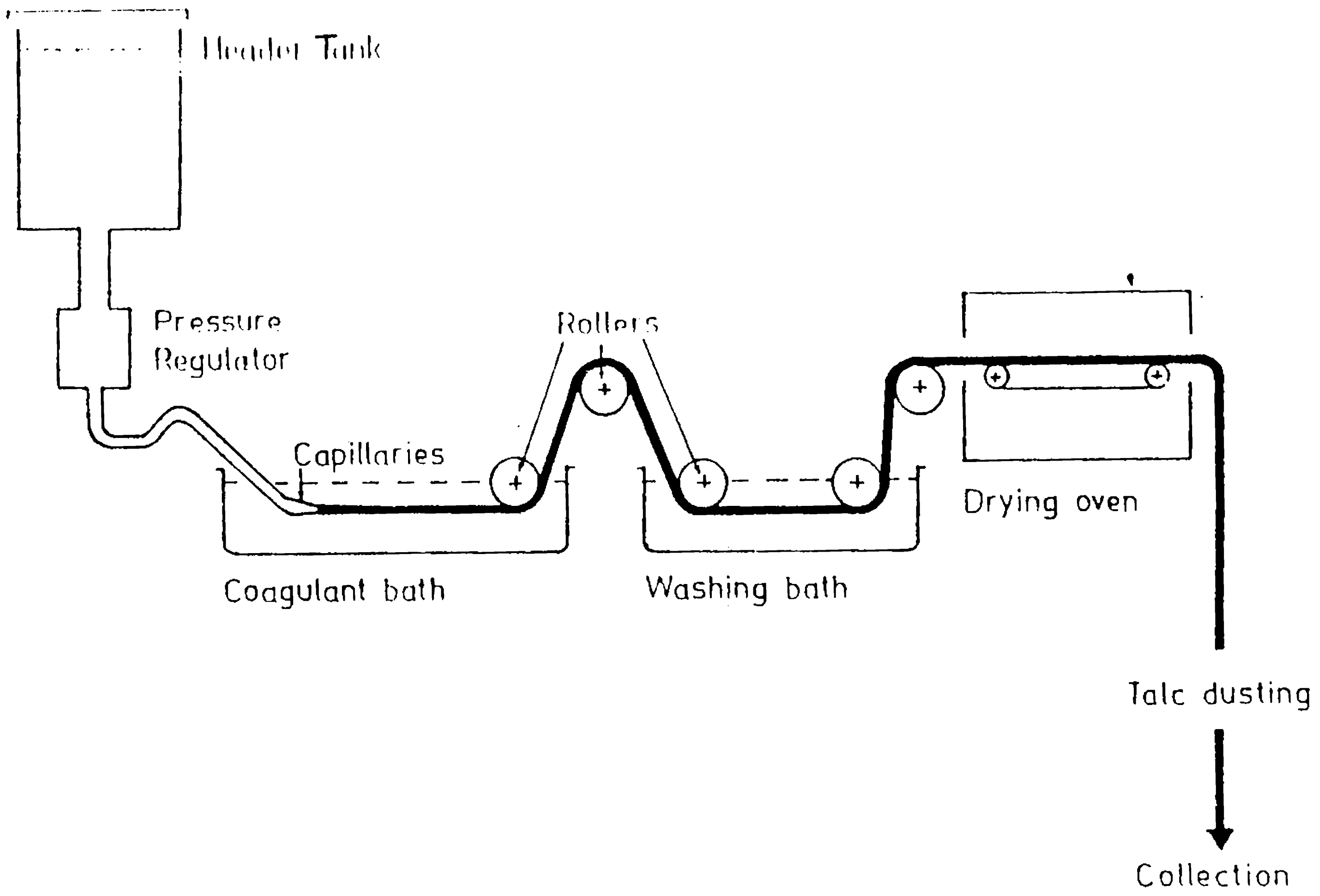


Fig. II.1. Schematic diagram of the elastic thread plant.

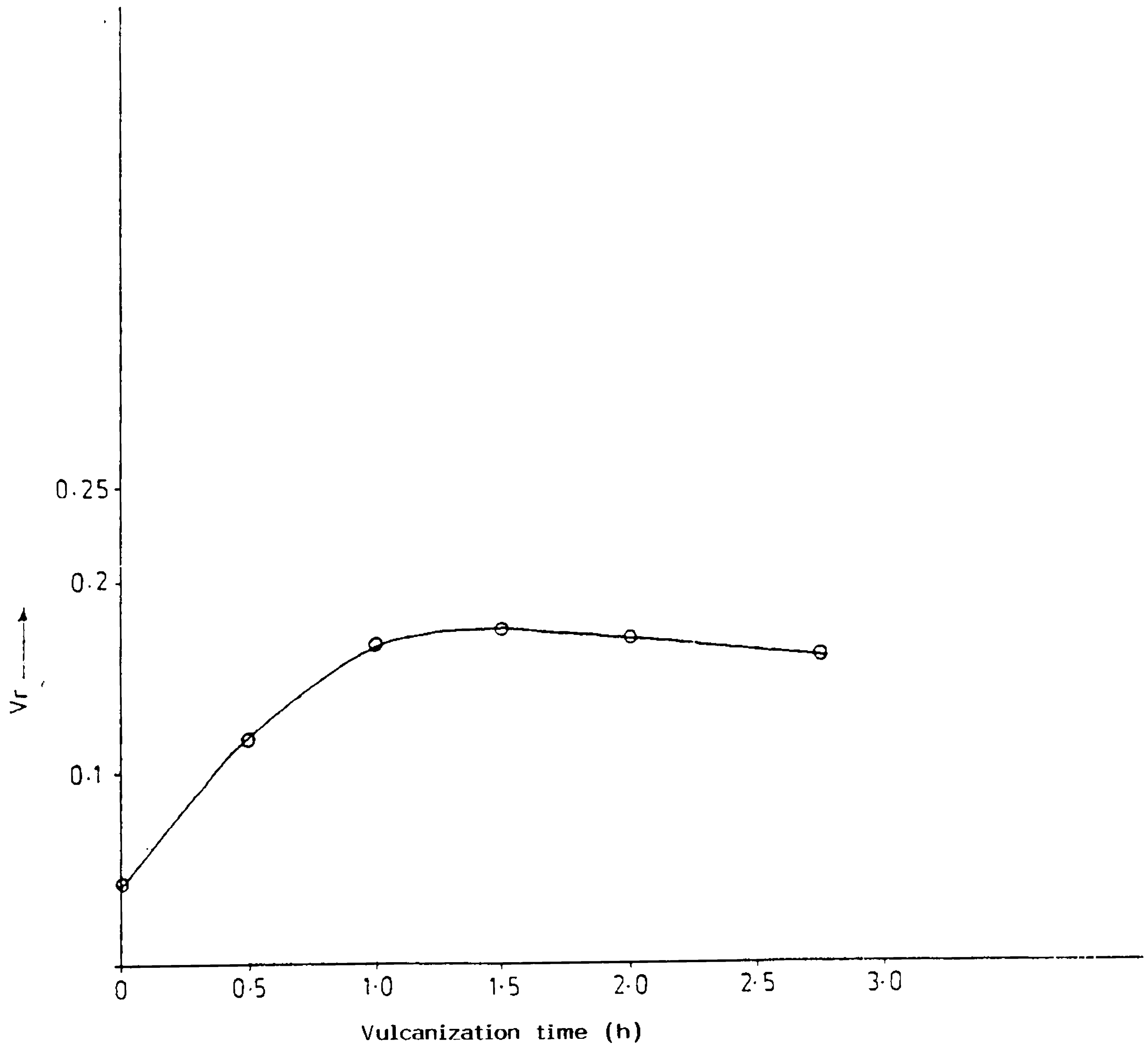


Fig. II.2. Plot of V_r against vulcanization time.

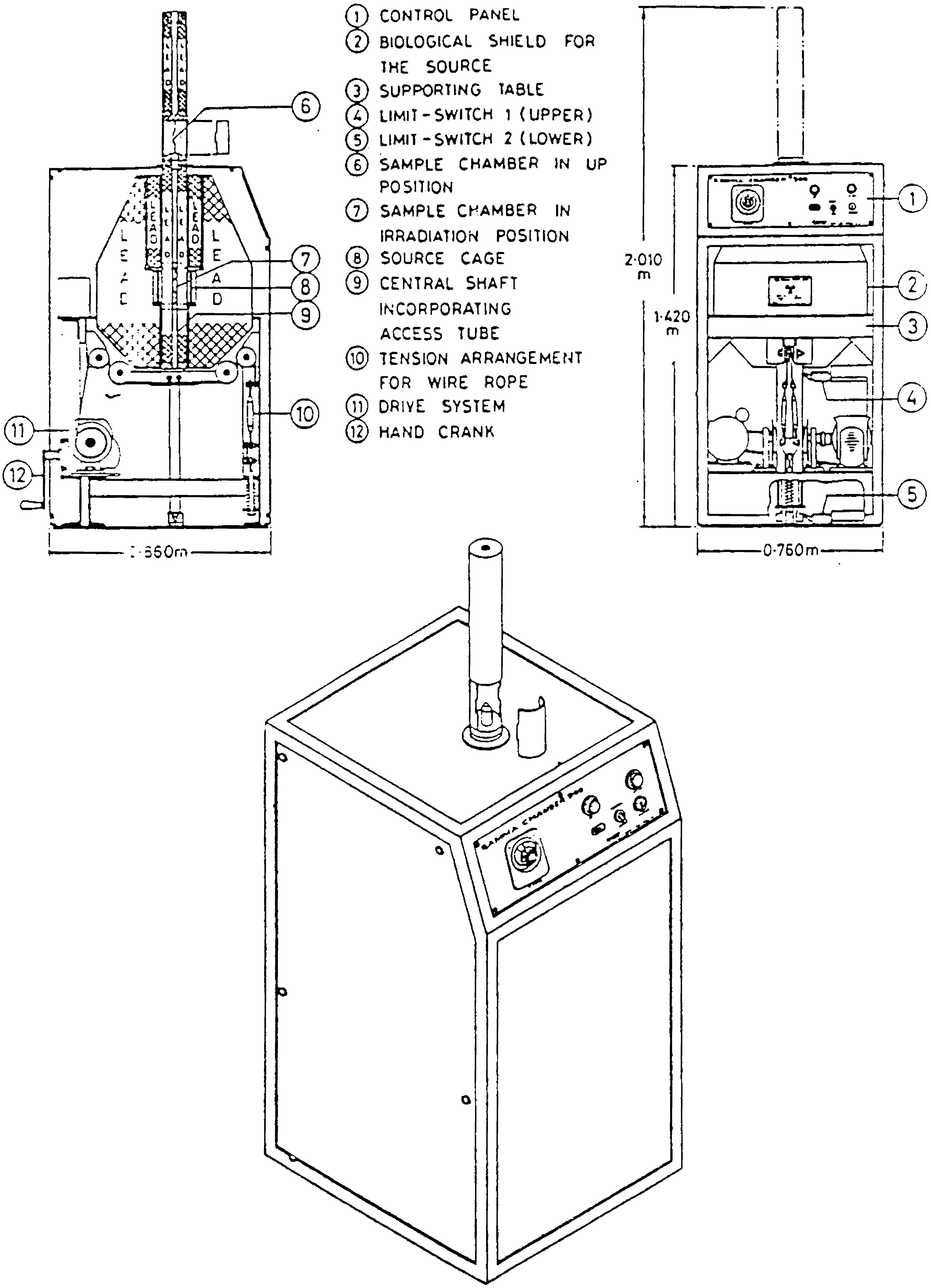


Fig. II.3. Schematic diagram of gamma chamber.

REFERENCES

1. D.C. Blackley, High Polymer Latices, Vol. I, Maclaren & Sons Ltd., London (1966). 194.

2. B.C. Archer, D. Barnard, E.G. Cockbain, P.B. Dickenson and A.I. Mc Muller. The Chemistry and Physics of Rubber-like Substance, L. Bateman, Ed., Maclaren & Sons Ltd., London (1963) Chap. 3.

3. A. Subramanyam, Rubb. Chem. Technol. 45 (1972) 364.

4. C.F. Flint, W.J.S. Naunton, Trans. Instn. Rubb. Ind. 12 (1937) 367.

5. B. Ellis and G.N. Welding, Techniques of Polymer Science, Society of Chemical Industry, London, 17 (1964) 46-52.

6. D.S. Campbell, J. Appl. Polym. Sci. 13 (1969) 1201.

7. D.S. Campbell and B. Saville, Proc. Int. Rubb. Conf., Brigton (1967) 1.

8. B. Saville and A.A. Watson, Rubb. Chem. Technol. 40 (1967) 100-145.

9. M.B. Evans and B. Saville, Proc. Chem. Soc. (1962) 18.

10. G.M. Bristow, J. Appl. Polym. Sci. 7 (1963) 1023.

11. J.I. Cunneen and R.M. Russel, Rubb. Chem. Technol. 43 (1970) 1215-1224.

12. K.E. Polmanteer and C.W. Lentz, Rubb. Chem. Technol. 48 (1975) 795-809.

13. ISO 2321-1975(E), Rubber Thread-Methods of Test.

CHAPTER - III

STUDIES ON VULCANIZATION CHARACTERISTICS BASED ON ACCELERATOR COMBINATIONS

PART - I EFFECT OF ACCELERATOR COMBINATIONS ON CURE RATE INDEX, NETWORK FORMATION AND PHYSICAL PROPERTIES OF A TYPICAL LATEX PRODUCT, VIZ., LATEX THREAD.

PART - II (A) EFFECT OF ACCELERATOR COMBINATIONS ON PRE-VULCANIZATION.

(B) EFFECT OF PRE-VULCANIZATION ON PHYSICAL PROPERTIES OF LATEX THREAD.

PART - I EFFECT OF ACCELERATOR COMBINATIONS ON CURE RATE INDEX, NETWORK FORMATION AND PHYSICAL PROPERTIES OF A LATEX PRODUCT, VIZ., LATEX THREAD.

Small amounts of substances known as vulcanization accelerators are added to rubber during compounding and these have a great effect on cure characteristics and on the physical, mechanical and service properties of rubber products. The most important accelerators are organic compounds and they act in many ways; not only is the vulcanization process accelerated, but many properties of the finished rubber product are altered. This is because, the presence of accelerators affect the spatial structure of the rubber molecules; which in turn determines the physical, mechanical, chemical and service properties of the product[1]. In modern rubber compounding advantage is frequently taken of the combined action of two or more accelerators. Vulcanizates obtained by using binary accelerator systems are found to have superior physical and chemical properties[2,3]. But all the accelerator combinations do not give satisfactory results. The combinations are more effective when[4] (a) the accelerators activate one another, (b) a compound which is readily dissociated into free radicals is formed by redox reactions, (c) one or more of the accelerators bring about a more rapid activation of sulfur and a more rapid reaction with the polymer[4,5]. The accelerators accelerate the vulcanization by forming active sulfur fragments and free radicals; including polymeric free radicals as well as reactive intermediate compounds which are unstable and readily decomposable. As a result of the reaction between these free radicals and sulfur fragments with molecules of rubber or with polymeric free radicals, tridimentional crosslinking occurs at various sites of the chain. The vulcanizate will contain more than one type of crosslinks: covalent C-C, C-S-C, C-S-S-C, C-Sx-C etc. The nature of the bond, its energy and proportion of bonds of a given type determine to a large extent the physical and mechanical properties of the vulcanizate. The heat resistance of the vulcanizate is also the result of the result of the different spatial structures which are in turn determined by the accelerators used and the vulcanization system as a whole[5]. This is true for both dry rubber and latex vulcanizates.

The use of accelerators in latex compounds is some what different from their use in dry rubber. As there is no danger of scorching, ultra accelerators are used in latex compounding and the accelerators should be dispersed uniformly in the latex mixture without causing it to coagulate or to thicken. In order to achieve uniform dispersion in the latex, the accelerators must be readily dispersible in water. As the vulcanization temperature for a latex compound is substantially lower than that for a dry rubber compound, the choice of accelerators and their proportion is different from that of a dry rubber compound and has to be made carefully. It has been shown that accelerators in which sulfur is combined as S-S, C-S-C or S-N are virtually inactive at temperatures below 100°C because of the high thermal stability of their S-bond. It has also been proved that sulfur containing nucleophiles enable such accelerators to become active even at lower vulcanization temperature. The cleavage of the S-S bond by the nucleophile may be represented as

$$R\text{-}S\text{-}S\text{-}R'+Y^{-} \longrightarrow RSY+R'S^{-}$$

The use of cure systems involving accelerators such as TMTD, ZDC, ZMBT etc in latex has to be viewed in this context. The use of thiourea in these systems has the function of a nucleophile as mentioned above which enables the vulcanization to be carried out at or around 100°C. Thiourea also helps in preparing heat resistant vulcanizates.

A typical latex product of which the technological properties can be significantly altered by the use of accelerator combinations is latex thread. The natural rubber latex compound used for making the thread is normally free of reinforcing fillers and its properties mainly depend upon the vulcanization system and the protective agents used. The important properties of the thread, set out in standard specifications include its diameter, tensile strength, modulus, elongation at break and ageing resistance[7]. The thread is more vulnerable to ageing than other natural rubber products due to its lower bulk volume and larger surface area. In addition to normal ageing tests for ordinary type threads conducted at 70°C, heat resistant threads have to withstand high temperature ageing @150°C. The modulus of the thread is also very important for its textile applications[8]. These properties are to a great extent controlled by the vulcanization system used for manufacture of the thread. The vulcanization system may be conventional type using elemental sulfur or a special system involving sulfur donor such as tetramethyl thiuram disulphide[9]. Even though some studies have been reported in these lines[10,11], not much systematic work has been conducted on the effect of vulcanization systems on the chemical characteristics and physical properties of latex products. In the present work the effect of secondary accelerators on the above properties of a latex product viz., latex thread has been investigated. Special emphasis has been given to its ageing resistance under conventional and sulfur donor vulcanization systems.

Formulations of the latex compounds are given in Tables III-1 and III-2. There are six different compound formulations under each table. Latex compounds in the conventional vulcanization systems (Table III-1) were prepared with varying dosages of the accelerators ZDC, ZMBT and TMTD and the latex compounds in the sulfur-donor systems (Table III-2) were prepared with varying amounts of ZDC and ZMBT while the TMTD dosage is kept constant. The centrifuged latex was first de-ammoniated to 0.4 per cent ammonia content and was stabilized by adding potassium hydroxide and potassium laurate solutions. The vulcanizing agents, accelerators, zinc oxide and titanium dioxide were added as dispersions and antioxidant SP as an emulsion in water. The latex compounds were then matured for 96 h and sieved through 100 mesh sieve.

For determining the cure behaviour of latex compounds, cast latex films (1-1.5 mm thickness) were prepared and the cure rate index was determined using the Rheometer (R-100) at 120°C. The results are given in Table III-3. As the latex products are generally vulcanized in hot air, the cure characteristics of the cast latex films were also determined by heating the films in air oven at 120°C for different durations and estimating the crosslink concentration formed at each instant. The concentration of chemical crosslinks was measured by estimating the V_r values as described in Chapter 2. The results are depicted in Figures III-1 and III-2.

The network structure of the vulcanizates from each latex compound was characterized on latex films which were vulcanized to its optimum crosslink density at 120°C, as obtained from the Figures III-1 and III-2. The total concentration of chemical crosslinks and the percentage polysulfidic content of the hot air vulcanized samples were then determined (Table III-4).

Another part of each latex compound was run on the pilot plant for thread manufacture using a glass nozzle of diameter 0.6 mm. The threads were then vulcanized to its optimum crosslink density. The initial physical properties and dry heat resistance of the thread were then evaluated (Tables III-5, III-6 and III-7).

The cure rate indices of the different compounds are given in Table III-3. In the case of conventional vulcanization systems (Compounds A to F) the cure rate index was much higher for the ZDC + TMTD combination than ZDC alone and ZDC + ZMBT combinations. This may be attributed to the positive synergestic effect of these two ultra accelerators. In the case of sulfur donor vulcanization systems also (I to N) the ZDC + TMTD combinations were found to give the highest cure rate index.

The cure behaviour of latex films prepared using the different latex compounds in the air oven at 120°C is shown in Figures III-1 and III-2. Among the conventional vulcanization systems (Figure III-1) the compound E showed a higher rate of crosslink formation and its reversion rate is also high. But in the case of compound B and C, the rate of crosslink formation was slow and the same trend was retained in the degradation of crosslinks. Even though the crosslink formation was slow in the case of compound F, on prolonged heating the degradation was more. This may be attributed to the higher proportion of ZMBT which can absorb more oxygen which may enhance the degradation process. In the case of sulfur donor vulcanization systems (Fig. III-2) the compound I shows a very low rate of crosslink formation. The compound J which contains ZDC only and compound L which contains a high proportion of ZDC showed higher rate of crosslink formation than the compound containing higher proportion of ZMBT compared to ZDC (compound M and N). The compounds M and N were also found to be more prone to degradation as seen from Figure III-2.

The chemical characteristics of the vulcanized latex films are given in Table III-4. The total crosslink concentration (V_r) is found to be higher in the case of ZDC + TMTD combinations both in the conventional and sulfur-donor vulcanization systems (compound E and J). The polysulfidic content of the crosslinks varied with the vulcanization systems and it is the lowest in the sulfur-donor vulcanization systems. In the conventional vulcanization systems, the polysulfidic content is higher in the ZDC + TMTD combination and in sulfur-donor systems the highest percentage of polysulfidic content is recorded in the TMTD + ZMBT combinations.

The physical properties of the threads prepared using conventional vulcanization systems are given in Table III-5. The threads prepared using compounds A, B and C gave good ageing resistance. But as the proportion of ZMBT increased, greater reduction in ageing resistance (compound D) was observed. Similarly when ZDC and TMTD were used, the ageing resistance of the thread was found to be reduced. But its original physical properties were improved considerably. Both high tensile strength and ageing resistance are required for products like latex thread. In the case of threads using ternary accelerator systems such as ZDC, ZMBT and TMTD, original physical properties were good. But ageing resistance was low compared to ZDC as a single accelerator. The better ageing resistance of the thread when ZDC alone is used (compound A) may be attributed to the fact that ZDC, apart from accelerating the vulcanization reaction functions as an antioxidant also[12].

The cure rate index of the compounds from A to C was lower than that of compounds D to F. These compounds which showed a lower rate of cure had better retention of properties after ageing. This may be due to the fact that slow curing compounds undergo reversion at a slow rate as is evident from the cure behaviour of the latex compounds in the air oven as given in Figure III-1. Another important factor which controls the ageing resistance of rubber compound is the amount of total crosslinks and the percentage of polysulfidic crosslinks in it. From Table III-~~7~~5, it is seen that compound E which gave the lowest ageing resistance has got the highest amoung of polysulfidic crosslinks. This indicated that both cure rate index and polysulfidic linkage formation influence the ageing resistance of latex products. Results indicated that ZDC-ZMBT combination is better than ZDC-TMTD systems in retaining the physical properties on ageing at 70°C in the case of conventional vulcanization systems examined in this study.

The physical properties of the thread made from latex compound containing sulfur-donor vulcanization systems (heat resistant threads) are set out in Tables III-6 and III-7. Test results showed that the physical properties of the threads using the basic vulcanization system alone are poor. It was also seen that the maximum original physical properties were attained by incorporating ZDC and ZMBT along with the basic system (compound L, M and N). The tensile strength of the thread was found to be increasing with the addition of ZDC and ZMBT. In this case also as the proportion of ZMBT increased the ageing resistance of the thread is lowered (compound M and N). The same trend was observed in the high temperature ageing also (Table III-7). In the case of compound K which contained only ZMBT, low original tensile strength was observed. The cure rate index of this compound was also low and its retension in tensile strength in the lower temperature ageing (70°C) was high. But in the high temperature ageing its retension of tensile strength was found to be low (Table III-7). The amount of total crosslinks and the percentage of polysulfidic crosslinks in compounds I to N are given in Table III-4. It can be seen that the compound I is having only very low V_r value even though it contained the lowest percentage of polysulfidic crosslinks. It may also be pointed out that as the ZMBT content increased in compounds L to N, the polysulfidic linkage formation is also slightly increased. Its low ageing resistance may be attributed to this fact and also the tendency of ZMBT to absorb oxygen[5]. From the above discussions, it can be concluded that TMTD-ZDC system is better than TMTD-ZMBT system in retaining the tensile properties in high temperature ageing.

Table III-1. Formulations for latex thread compounds (conventional vulcanization systems)

Formulations	A	B	C	D	E	F
60% Centrifuged latex	167	167	167	167	167	167
10% Potassium hydroxide solution	4	4	4	4	4	4
20% Potassium laurate solution	2	2	2	2	2	2
50% Sulfur dispersion	3.5	3.5	3.5	3.5	3.5	3.5
50% Zinc diethyldithio carbanate dispersion (ZDC)	4	3	2	1	3	2
50% Zinc mercapto benzothiazole dispersion (ZMBT)	-	1	2	3	-	1
50% Tetramethyl thiuram disulfide dispersion (TMTD)	-	-	-	-	1	1
50% Titanium dioxide dispersion	10	10	10	10	10	10
50% Antioxidant SP emulsion	2	2	2	2	2	2
50% Zinc oxide dispersion	2	2	2	2	2	2

Table III-2. Formulations for latex thread compounds (sulfur-donor vulcanization systems)

Formulations	I	J	K	L	M	N
60% Centrifuged latex	167	167	167	167	167	167
10% Potassium hydroxide solution	4	4	4	4	4	4
20% Potassium laurate solution	2	2	2	2	2	2
50% Sulfur dispersion	0.5	0.5	0.5	0.5	0.5	0.5
50% Tetramethyl thiuram disulfide dispersion (TMTD)	6	6	6	6	6	6
20% Thiourea solution	5	5	5	5	5	5
50% Zinc diethyl dithiocarbanate dispersion (ZDC)	-	4	-	3	2	1
50% Zinc mercaptobenzothiazole dispersion (ZMBT)	-	-	4	1	2	3
50% Antioxidant SP emulsion	2	2	2	2	2	2
50% Titanium dioxide dispersion	10	10	10	10	10	10
50% Zinc oxide dispersion	2	2	2	2	2	2

Table III-3. Cure rate index of the latex films at 120°C.

Formulations	Cure Rate Index
A	23.8
B	23.5
C	23.0
D	26.0
E	30.0
F	27.0
I	22.2
J	40.0
K	28.0
L	40.0
M	40.0
N	37.0

Table III-4. Chemical characteristics of the vulcanized latex films.

Formulations	V_r	Polysulfidic crosslinks (%)
A	0.2203	18.0
B	0.2186	12.5
C	0.2178	12.8
D	0.2194	15.7
E	0.2260	22.0
F	0.2154	19.8
I	0.1290	4.0
J	0.2470	4.5
K	0.21420	6.5
L	0.23070	4.9
M	0.22936	7.2
N	0.22752	8.5

Table III-5. Physical properties of latex threads (conventional vulcanization systems)

Formulations	Modulus 300% (MPa)			Tensile Strength (MPa)			Elongation at Break (%)		
	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)
A	2.70	3.82	140	17.10	16.21	94.8	660	575	84.9
B	2.52	2.85	113	16.50	15.20	92.0	615	515	83.7
C	2.81	3.80	135	17.00	15.60	91.0	610	520	85.0
D	3.00	3.60	120	19.00	11.79	62.0	700	500	71.4
E	2.98	3.41	114	21.20	9.30	43.9	750	500	66.6
F	3.25	3.61	111	23.00	14.00	60.8	710	518	72.9

* Aged at 70°C for 14 days.

Table III-6. Physical properties of latex threads (sulfur-donor vulcanization systems)

Formulations	Modulus 300% (MPa)			Tensile Strength (MPa)			Elongation at Break (%)		
	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)
I	1.80	1.65	91.7	8.50	7.50	93.0	615	615	100.0
J	2.20	4.00	181.8	16.00	16.00	100	715	650	90.0
K	1.80	2.52	140.0	14.10	14.00	99.0	640	560	87.5
L	2.50	3.45	138.0	18.20	17.10	94.1	700	600	85.7
M	2.50	3.60	144.0	18.50	16.10	87.4	700	600	85.7
N	3.00	3.80	126.0	19.00	15.00	79.0	710	580	81.6

* Aged at 70°C for 14 days.

Table III-7. Effect of high temperature ageing on physical properties of threads (sulfur-donor vulcanization system)

Formulations	Modulus 300% (MPa)			Tensile strength (MPa)			Elongation at Break (%)		
	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)
I	1.80	1.31	72.7	8.50	4.20	49.4	615	570	92
J	2.20	1.82	82.7	16.00	9.00	56.2	715	525	83
K	1.80	1.40	77.7	14.10	6.50	46.0	640	500	78
L	2.50	1.95	78.0	18.20	9.50	52.3	700	580	82
M	2.50	1.81	72.4	18.50	8.30	45.0	700	535	76
N	3.00	1.80	60.0	19.00	7.20	39.0	710	530	75

* Aged at 150°C for 2 h.

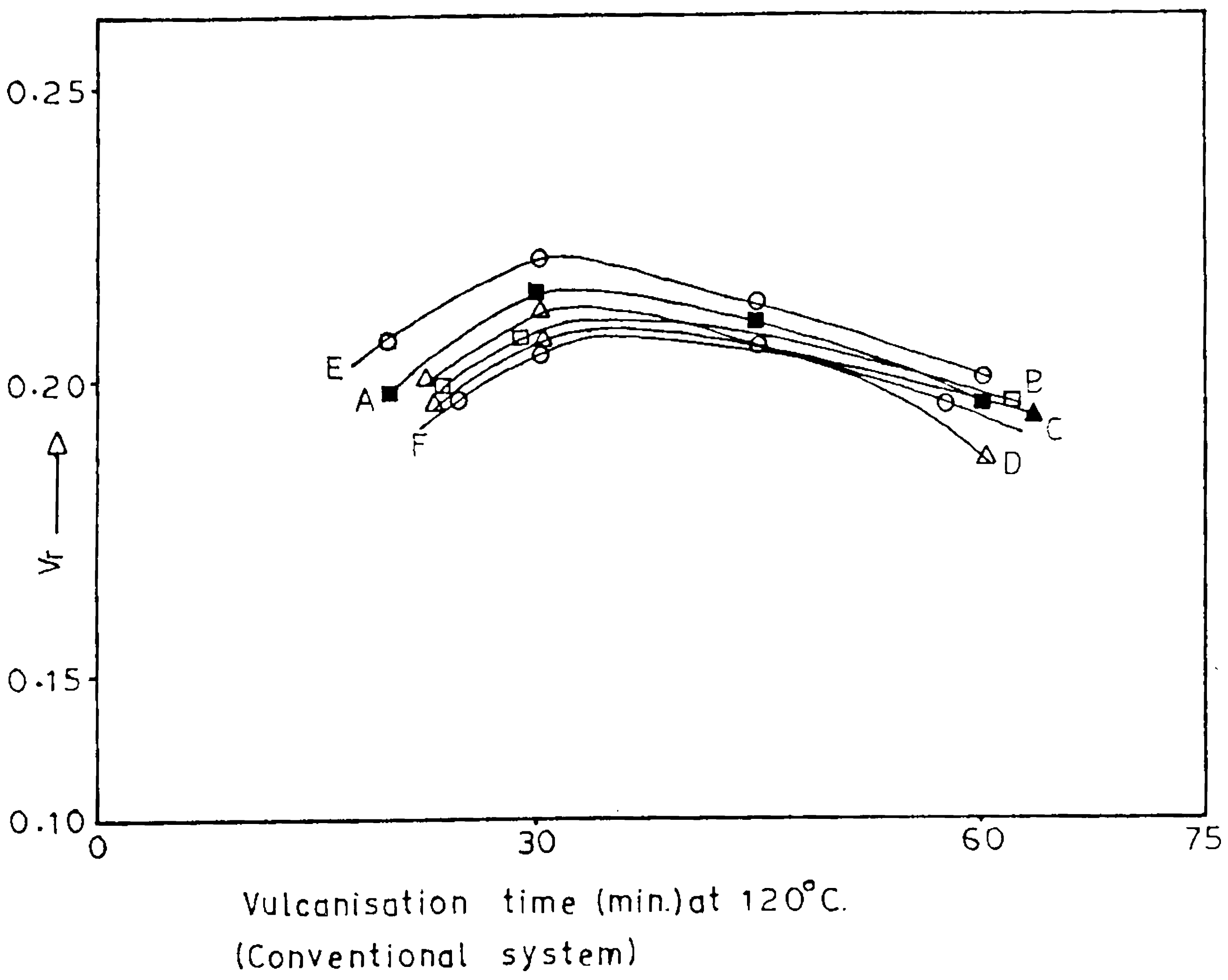


Fig. III-1. Plot of V_r values against cure time at 120°C, conventional system.

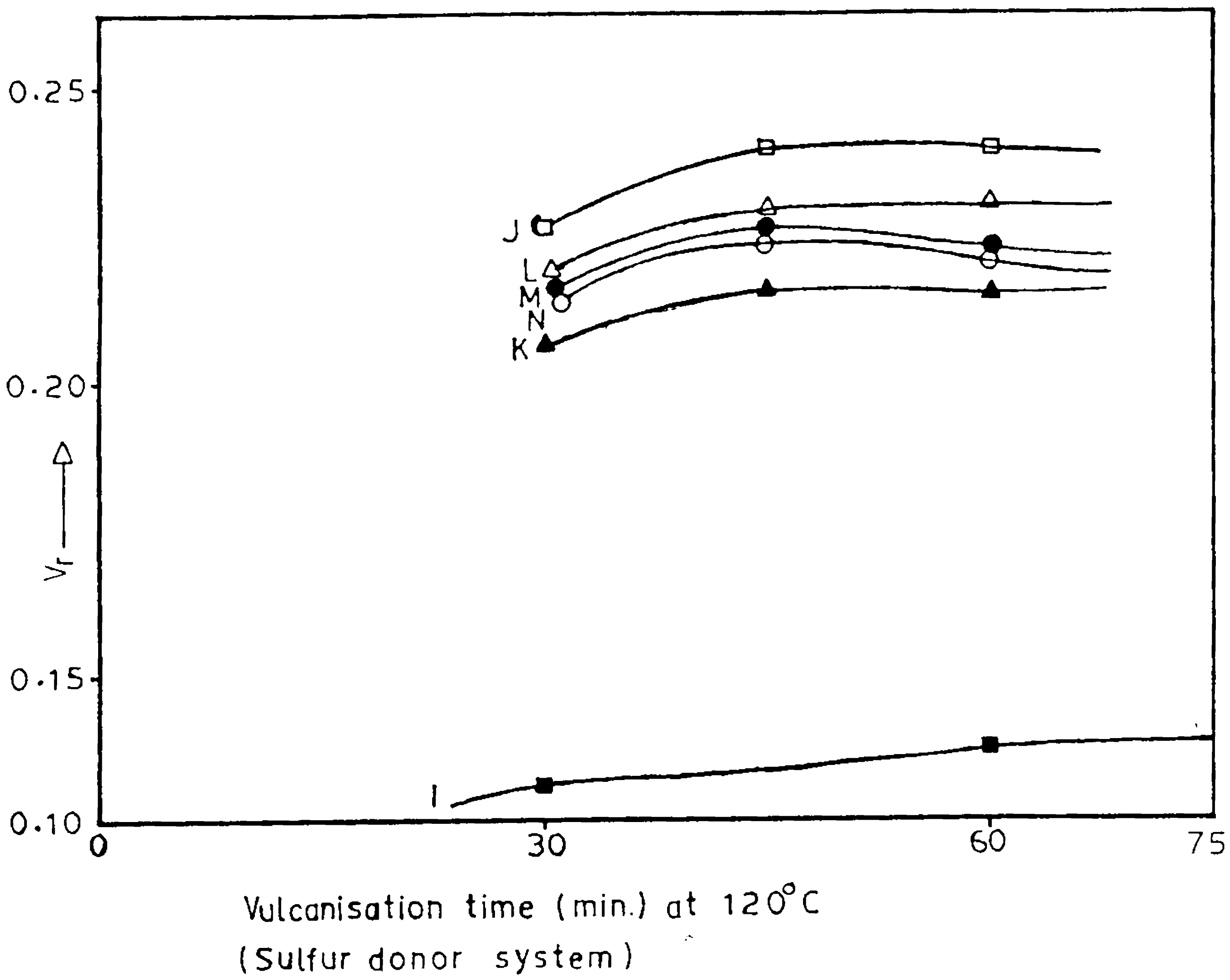


Fig. III-2. Plot of V_r values against cure time at 120°C, sulfur-donor system.

PART - II

(A) EFFECT OF ACCELERATOR COMBINATIONS ON PREVULCANIZATION.

(B) EFFECT OF PREVULCANIZATION ON PHYSICAL PROPERTIES OF LATEX THREAD.

A. EFFECT OF ACCELERATOR COMBINATIONS ON PREVULCANIZATION

Prevulcanization involves heating the raw latex with various compounding ingredients such as accelerator and sulfur at or around 70°C until the required degree of crosslinking is obtained[13, 14]. The prevulcanized latex is very similar in appearance to unvulcanized latex. The original fluidity is retained. The vulcanization reaction takes place in each of the individual latex particles without altering their state of dispersion. The particles have the same shape, size and size distribution as do those of the initial latex. The rate of prevulcanization varies with different vulcanization systems and the extent of prevulcanization has a profound effect on the final vulcanizate properties[15]. It has been reported that prevulcanized latex films are inferior in properties and are less resistant to heat and solvent. But studies conducted in this line are based on general vulcanization systems only[15,16]. The effect of accelerator combinations on the prevulcanization and its effect on flow properties of the latex and final vulcanizate structure was not studied in detail. This part of the investigations report the results of the studies on prevulcanization of a series of latex compounds containing conventional and efficient vulcanization systems with different accelerator combinations. The effect of different vulcanization systems on the extent of crosslinks formed has been investigated. Viscosity of latex compounds after different periods of prevulcanization and the network structure of these vulcanizates have also been studied.

Formulations of latex compounds used in this study are given in Tables III-8 and III-9. There are three compound formulations under each Table. The latex compounds were prepared as per these formulations and prevulcanized by heating under slow speed stirring in a glass beaker immersed in a constant temperature bath set at 70°C. Samples of prevulcanized latex compounds were taken at definite intervals for studying their processing behaviour, and extent of crosslink formation.

The crosslink concentration at each interval of heating was measured as V_r values after preparing latex films at room temperature on glass cells as described in Chapter 2. The results are given graphically in Figures III-3 and III-4.

As the latex compound is a non-Newtonian fluid, its viscosity changes with shear rate. So the flow behaviour of these latex compounds after definite intervals of prevulcanization was determined using a Brookfield Viscometer (Spindle No. 2). The viscosity of the latex compounds was measured at two different shear rates (6 and 60 rpm) and the results are given in Table III-10.

The optimum vulcanization time for the dried latex film was determined by vulcanizing them in an air oven at 100°C for different periods and then plotting V_r values against vulcanization time as given in Figures III-5 and III-6. The dried latex films obtained from the unvulcanized latex compounds and prevulcanized latex compounds were vulcanized/completed the vulcanization in the air at 100°C to its optimum crosslink density. The total concentration of chemical crosslinks and the percentage polysulfidic crosslinks of the vulcanized samples were also determined (Table III-11).

The extent of crosslink formation at different periods of prevulcanization at 70°C are given in Figures III-3 and III-4.

In the compounds containing conventional vulcanization systems, A, B and C, it may be noted that the reaction rate of the accelerator ZDC is activated by the incorporation of ZMBT and TMTD. The ZDC-TMTD system (C) has a higher reaction rate than the ZDC-ZMBT system (B) and in the former case, majority of crosslinks were formed within one and a half hour at 70°C. This may be attributed to the positive synergistic effect due to the combination of two ultra accelerators ZDC and TMTD in the vulcanization of natural rubber latex.

In the efficient vulcanization systems, D, E and F, the ZDC-TMTD system (D) is fast compared to ZMBT-TMTD system (E) in the formation of chemical crosslinks. The reaction rate of the ZDC-TMTD system decreased when a portion of ZDC was replaced with ZMBT in compound F.

As the extent of prevulcanization increased the viscosity of the latex compound increased and in all the compounds under study, the viscosity variation is almost the same (Table III-10). The determination of viscosity at different periods of prevulcanization under different shear rates showed that the flow behaviour of the latex compounds is little affected by prevulcanization.

The polysulfidic content in the vulcanizates from latex compounds prevulcanized to different periods are given in Table III-11. The V_r value which is a measure of total crosslinks, for the dried and vulcanized films are also given in Table III-11.

It can be seen that for samples A, B, C, D, E and F, where there was no prevulcanization and vulcanization was done at 100°C, contained only lower percentage of polysulfidic linkages. But in the case of samples from the same compound which were prevulcanized for different periods at 70°C and later postvulcanized at 100°C, showed a higher percentage of polysulfidic linkages. The percentage of polysulfidic linkages increased as the extent of prevulcanization increased even though the total crosslink concentration of the final vulcanizate is almost same irrespective of the extent of prevulcanization. It has been reported that in the vulcanization of dry rubber products, as the vulcanization temperature becomes lower, the chance of formation of polysulfidic type linkages is high[17]. The content of more polysulfidic linkages in the prevulcanized latex films may be attributed to the low prevulcanization temperature (70°C).

B. EFFECT OF PREVULCANIZATION ON PHYSICAL PROPERTIES OF LATEX THREAD

For obtaining good processing and technological properties for some latex products a certain extent of prevulcanization is necessary for the rubber particles in the latex compound. An ideal example for this is latex thread[18,19]. Even though different accelerator combinations are being used for the thread production very few specific report on the above aspects are available[20]. Completely prevulcanized latices are being used in the manufacture of certain dipped goods.

To study the effect of prevulcanization on technical properties, latex threads were prepared from prevulcanized latex compounds collected at different durations of heating. Compound B (Table III-8) having a conventional vulcanization system and compound F having the efficient vulcanization system were selected for the preparation of threads. Four threads were taken from each latex compound prevulcanized for four different timings (0, 0.5, 1.5 and 3 h). Latex thread obtained from each latex compound was vulcanized in an air oven at 100°C till optimum vulcanizate properties were obtained.

Testing of physical properties of the thread was carried out according to ISO 2321-1975(C). In the case of heat resistant threads produced using efficient vulcanization systems, ageing was conducted at 150°C for 2 h in an air oven and determined the tensile properties.

The properties of the thread produced from latex compounds 'B' and 'F' are given in Tables III-12 and III-13. The prevulcanized latex compounds are found to be better in extrusion and subsequent processing with respect to uniformity in count and is free from tackiness. Tensile strength and modulus of the thread are improved only upto a certain extent of prevulcanization of the latex compound (Table III-12) and above that level these properties decreased. In the case of compound B and F the ideal range of prevulcanization time lies between half an hour and one and a half hour. The low tensile properties for the threads from latex compounds having higher extent of prevulcanization (3 h duration) may be attributed to low inter-particle fusion. The tensile properties are not much improved after leaching and drying which can offer better inter-particle cohesion. One peculiarity with latex thread production is that a limited level of stretching at the wet gel stage occurs during the processing and this, in combination with low inter-particle cohesion of the wet gel may be one of the reasons for this low tensile properties.

The ageing resistance of the threads from prevulcanized latex compounds having 3 h. heating time is found to be inferior to that of threads obtained from unvulcanized latex compounds and that from latex compounds which were prevulcanized for shorter periods (Table III-13). This can be attributed to higher polysulfidic content in the threads which were obtained from prevulcanized latex compounds of 3 h. heating duration. The higher polysulfidic content is reported in Table III-11, Part A, of these Investigations.

Table III-8. Formulations of latex compounds (conventional vulcanization systems).

Formulations	A	B	C
60% Centrifuged latex	167	167	167
10% Potassium hydroxide solution	1	1	1
10% Potassium laurate solution	2	2	2
50% Sulfur dispersion	3.5	3.5	3.5
50% Zinc diethyl dithiocarbamate (ZDC) dispersion	4.0	3.0	3.0
50% Zinc mercapto benzothiazole (ZMBT) dispersion	-	1.0	-
50% Tetramethyl thiuram disulfide (TMTD) dispersion	-	-	1.0
50% Anatase titanium dioxide dispersion	10	10	10
50% Antioxidant SP emulsion	2	2	2
50% Zinc oxide dispersion	0.8	0.8	0.8

Table III-9. Formulations of latex compounds (efficient vulcanization systems)

Formulations	D	E	F
60% Centrifuged latex	167	167	167
10% Potassium hydroxide solution	1	1	1
10% Potassium laurate solution	2	2	2
50% Sulfur dispersion	0.5	0.5	0.5
50% Tetramethyl thiuram disulfide (TMTD) dispersion	6.0	6.0	6.0
20% Thiourea solution	5.0	5.0	5.0
50% Zinc diethyl dithiocarbamate (ZDC) dispersion	4.0	-	3.0
50% Zinc mercaptobenzothiazole (ZMBT) dispersion	-	4.0	1.0
50% Antioxidant SP emulsion	2.0	2.0	2.0
50% Anatase titanium dioxide dispersion	10	10	10
50% Zinc oxide dispersion	0.8	0.8	0.8

Table III-9. Formulations of latex compounds (efficient vulcanization systems)

Formulations	D	E	F
60% Centrifuged latex	167	167	167
10% Potassium hydroxide solution	1	1	1
10% Potassium laurate solution	2	2	2
50% Sulfur dispersion	0.5	0.5	0.5
50% Tetramethyl thiuram disulfide (TMTD) dispersion	6.0	6.0	6.0
20% Thiourea solution	5.0	5.0	5.0
50% Zinc diethyl dithiocarbamate (ZDC) dispersion	4.0	-	3.0
50% Zinc mercaptobenzothiazole (ZMBT) dispersion	-	4.0	1.0
50% Antioxidant SP emulsion	2.0	2.0	2.0
50% Anatase titanium dioxide dispersion	10	10	10
50% Zinc oxide dispersion	0.8	0.8	0.8

Table III-10. Flow behaviour of latex compounds.

Formulations	Duration of heating at 70°C (h)	Brookfield Viscosity (cps)	
		6 r.p.m.	60 r.p.m.
A	0	100	55
	0.5	125	60
	1.5	130	65
	3	150	72
B	0	100	55
	0.5	128	61
	1.5	135	67
	3	155	74
C	0	100	55
	0.5	120	60
	1.5	145	68
	3	200	75
D	0	100	55
	0.5	120	60
	1.5	135	65
	3	175	75
E	0	100	55
	0.5	130	65
	1.5	140	68
	3	160	78
F	0	100	55
	0.5	120	60
	1.5	140	68
	3	175	75

Table III-11. Effect of prevulcanization on network structure of the vulcanizates.

Formulations	Duration of heating at 70°C (h)	Vr values		Polysulfidic crosslinks in the vulcanizates (%)
		Dried films	Vulcanizates	
A	0	-	0.2203	20
	0.5	0.0881	0.2200	20
	1.5	0.1116	0.2198	24
	3	0.1649	0.2210	32
B	0	-	0.2186	16
	0.5	0.1130	0.2180	16
	1.5	0.1250	0.2184	18
	3	0.1662	0.2200	24
C	0	-	0.2260	18
	0.5	0.1597	0.2270	22
	1.5	0.1800	0.2288	28
	3	0.1957	0.2272	34
D	0	-	0.2270	10
	0.5	0.1500	0.2260	12
	1.5	0.1724	0.2250	12
	3	0.2004	0.2280	15
E	0	-	0.2140	8
	0.5	0.0760	0.2130	10
	1.5	0.1093	0.2145	12
	3	0.1308	0.2099	14
F	0	-	0.2207	10
	0.5	0.1388	0.2206	12
	1.5	0.1455	0.2227	12
	3	0.1750	0.2208	16

Table III-12. Physical properties of latex threads.

Formulations	Duration of prevulcanization (h)	Modulus 300% (MPa)			Tensile strength (MPa)			Elongation at break (%)		
		Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)
B	0	1.40	1.30	92.8	16.5	14.0	84.8	860	800	93.0
	0.5	2.10	1.90	90.4	17.2	14.5	84.0	868	790	91.0
	1.5	2.34	1.98	84.6	18.0	15.0	83.3	878	788	89.7
	3	1.85	1.34	72.4	12.9	6.8	52.9	836	641	76.6
F	0	1.80	2.00	111.0	15.0	14.5	96.6	650	600	92.3
	0.5	2.50	2.60	104.0	18.5	17.5	94.5	800	710	88.7
	1.5	2.40	2.35	97.8	18.0	16.5	91.6	780	685	87.8
	3	2.12	1.68	79.2	14.3	9.5	66.0	750	600	80.0

* Aged for 22 h at 100°C.

Table III-13. Effect of high temperature ageing on the properties of thread (efficient system)

Formulation:	Duration of prevulcanization (h)	Modulus 300% (MPa)			Tensile strength (MPa)			Elongation at break (%)		
		Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)	Unaged	Aged*	Retention (%)
F	0	1.80	1.45	80	15.0	7.8	52.0	600	500	83.0
	0.5	2.50	1.95	78	18.5	10.0	54.0	810	655	81.8
	1.5	2.40	1.80	75	17.5	8.5	48.5	780	600	76.9
	3	2.12	1.38	65	14.3	5.1	36.0	750	500	66.6

* Aged at 150°C for 2 h.

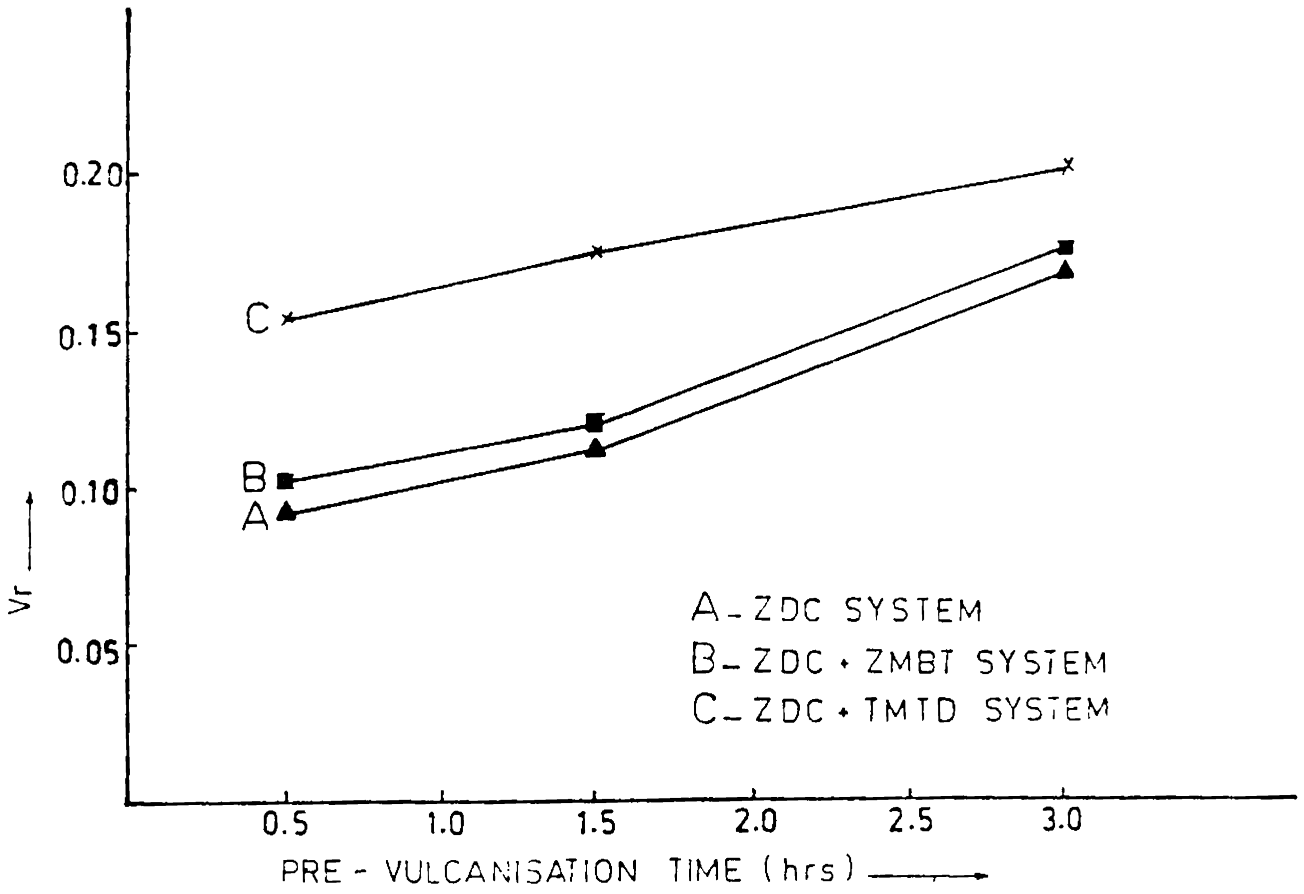


Fig. III-3. Plot of chemical crosslinks (V_r) vs. pre-vulcanization time, conventional system.

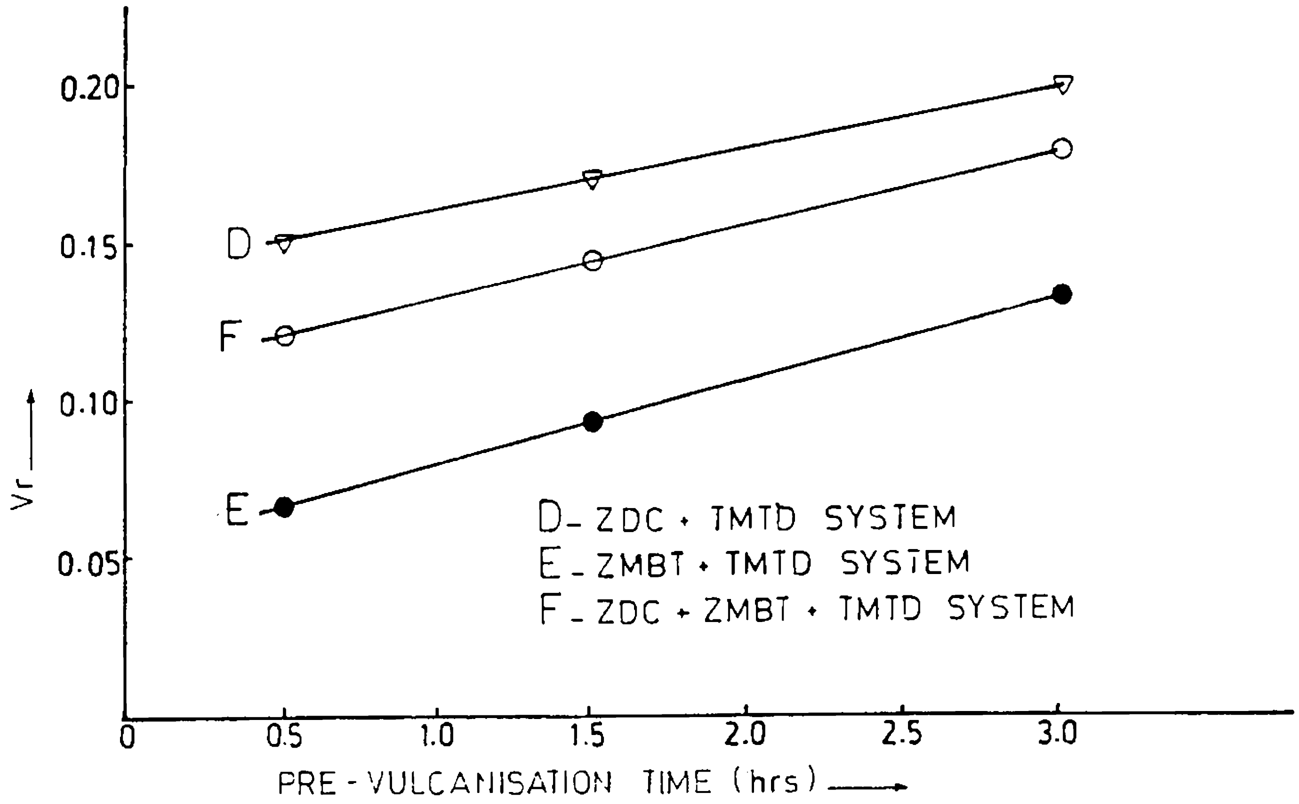


Fig. III-4. **Plot of chemical crosslinks (V_r) vs. pre-vulcanization time, efficient system.**

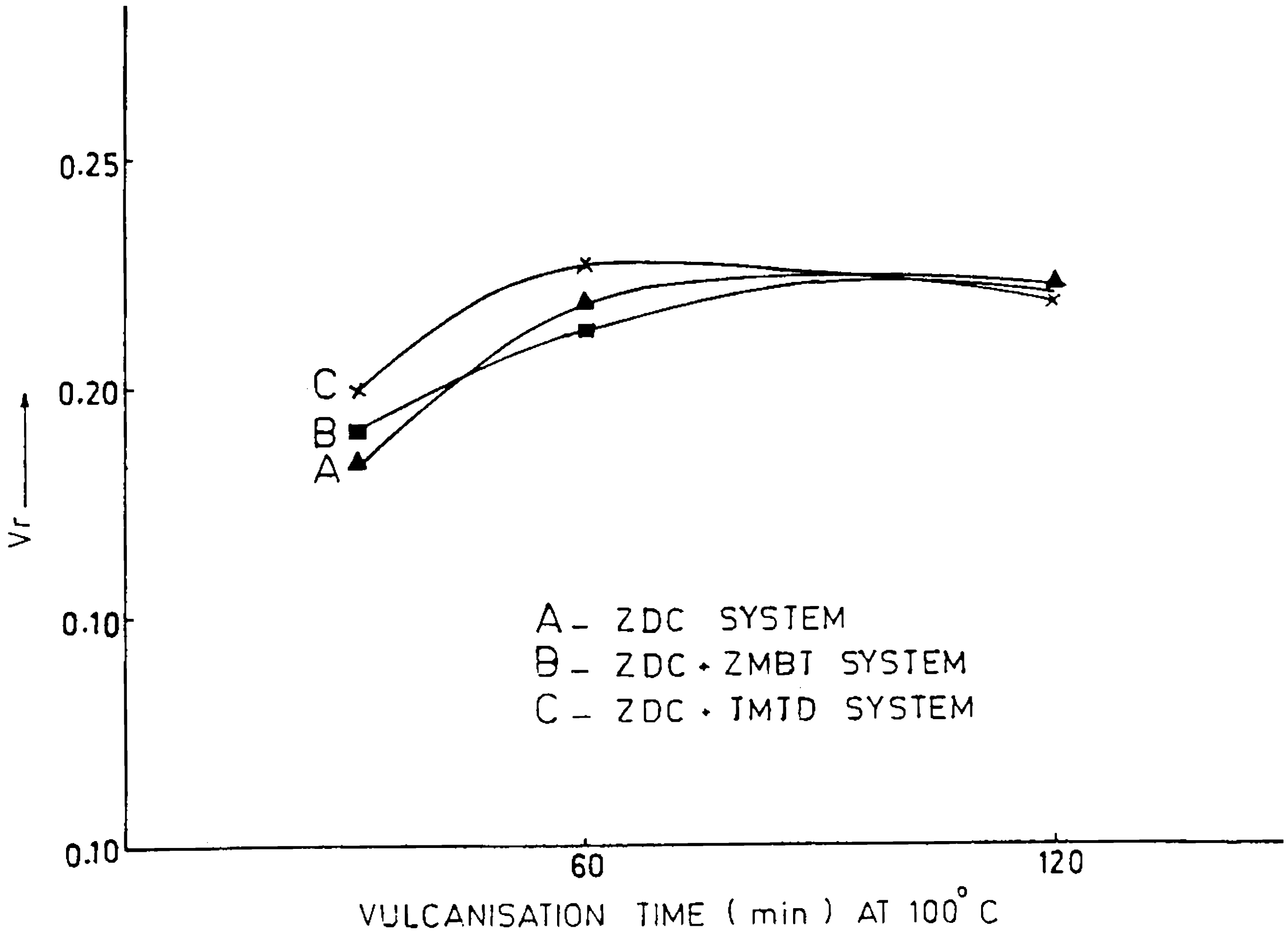


Fig. III-5. Plot of chemical crosslinks (V_r) vs. vulcanization time, conventional system.

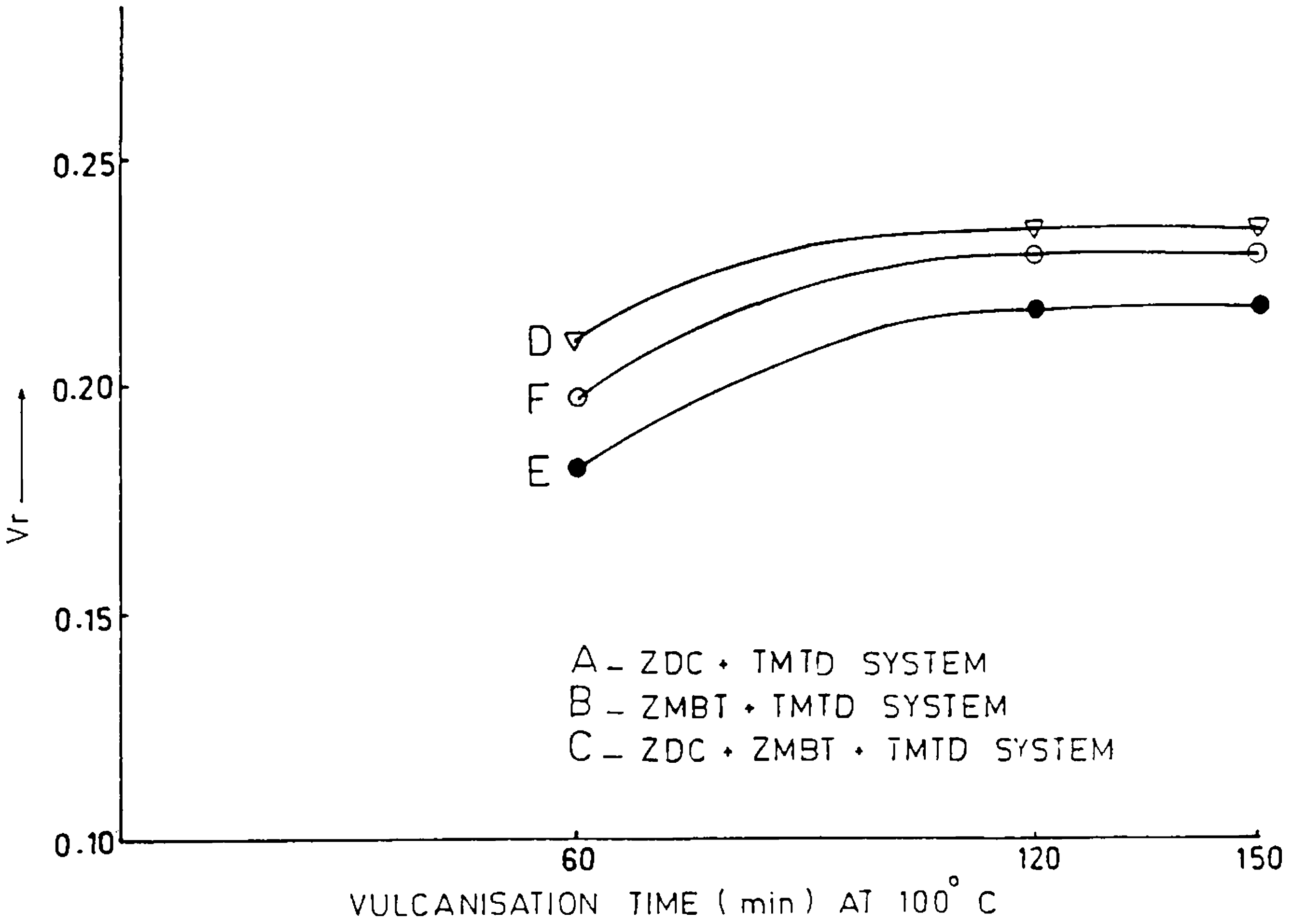


Fig. III-6. Plot of chemical crosslinks (V_r) vs. vulcanization time, efficient system.

REFERENCES

1. G.A. Blokh, Organic accelerators in the vulcanization of rubber, IPST, Jerusalem (1968) 261-266.
2. M.M. Das, D.K. Basu, A.K. Choudhiri, Koutch Gummi Kunststoffe, 36(7) (1983) 569-71.
3. B.A. Dogadkin, B.A. Shershnev, Rubb. Chem. Tech. **35**(1) (1962) 1-56.
4. L. Bateman, R.W. Glazebrook and C.C. Moore, J. Appl. Polym. Sci. (1959) 257.
5. G.A. Blokh, Organic accelerators in the vulcanization of rubber, IPST, Jerusalem (1968) 272-318.
6. M.W. Philpott, Proc. 4th Rubb. Technol. Conf. IRI, London (1962) 470-484.
7. ISO 2321-1975 (E), Rubber Threads - Methods of test.
8. J.L. Collins, A.D.T. Gorton, NR Technol. **15** (1984) 69-77.
9. D.C. Blackley, High Polymer Latices, Vol. I. Applied Science Publishers, London (1966) 73.
10. J.L. Collins, A.D.T. Gorton, NR Technol. 16(3) (1985) 52.
11. A.D.T. Gorton, NR Technol. 6(3) (1975) 52-64.
12. M. Morton, Rubber Technology, Van Nostrand and Reinhold Company, New York (1960) 296.
13. R.J. Noble, Latex in Industry, Rubber Age, New York (1953) 214-219.
14. D.C. Blackley, High Polymer Latices, Vol. I. Applied Science Publishers, London (1966) 383.

15. A.D.T. Gorton, NR Technol. 10(1) (1979) 9.

16. A.D.T. Gorton and T.D. Pendle, NR Technol. 7 (1976) 77.

17. C.T. Loo, Int. Rubber Conf. Kuala Lumpur, Preprints-Part 5 (1975) 1.

18. T.D. Pendle and A.D.T. Gorton, NR Technical Bulletin, MRPRA (1982) 1-10.

19. G.H.R. Weis, NR Technol. 10 (1979) 80.

20. J.L. Collins and A.D.T. Gorton, NR Technol. 16 (1985) 52.

CHAPTER - IV

EFFECT OF SURFACE ACTIVE AGENTS ON RUBBER-FILLER INTERACTION AND RHEOLOGY OF LATEX

PART - I EFFECT OF SURFACE ACTIVE AGENTS ON RUBBER-FILLER INTERACTION:

(a) in latex vulcanizates containing a reinforcing filler viz. silica.

(b) in latex vulcanizates containing precipitated calcium carbonate and china clay.

PART - II RHEOLOGICAL BEHAVIOUR OF NATURAL RUBBER LATEX IN THE PRESENCE OF SURFACE ACTIVE AGENTS AND FILLERS.

PART - I EFFECT OF SURFACE ACTIVE AGENTS ON RUBBER-FILLER INTERACTION:

(a) in latex vulcanizates containing a reinforcing filler viz. silica.

(b) in latex vulcanizates containing precipitated calcium carbonate and china clay.

Fillers are added into natural rubber latex in order to modify its processing and vulcanizate properties and to reduce cost. There are different types of fillers - reinforcing and non-reinforcing types. They are again classified into black and non-black types. In dry rubber compounding also fillers are added to reinforce the vulcanizates, to reduce its cost and improve processibility. Reinforcement of rubber is a complex phenomenon but may be defined as the enhancement of tensile strength, tear strength, hardness, modulus[1], etc. There are several limitations for the selection of a filler in latex compounding. The particle size must be sufficiently small so as to directly mix with the latex or it must be capable of being finely pulverised or ball milled to form a fine dispersion. Substances which have an acid reaction in water or which ionise to produce heavy metal ions are not suitable for use in latex compound. In latex compounding generally non-black fillers are used and the important among them are china clay, precipitated calcium carbonate, whiting, titatnium dioxide, precipitated silica, mica powder etc. Of these precipitated silica is a reinforcing filler. Titanium dioxide is considered the whitest of the commercial fillers and possesses a high degree of fastness to light and vulcanization. It has no effect on accelerators nor does it affect the ageing of rubber. Black type fillers are used only as a pigment in latex compounding. They have a strong tendency to thicken latex and can be used only in limited quantities[2].

In dry rubber compounding, fillers generally act as reinforcing agents but in latex they weaken the rubber film rather than improve its strength[2]. When added to latex compound fillers appear to act merely as diluent of the composition, surrounding and seperating the latex particles from each other[4]. In synthetic latices small amounts of fillers may increase tear strength. Some studies have already been conducted in this line and the poor rubber-filler interaction in latex vulcanizates is attributed to many factors such as insufficient distribution of fillers, non-simultaneous deposition of filler and rubber particles and the presence of protective layer of stabilizers around the rubber and filler particles in latex which prevents direct contact between them. A study was earlier conducted in styrene-butadiene rubber (SBR) latex using carbon black as filler[4]. It was reported that casein, which is a surface active agent could improve rubber-filler interaction in SBR latex. It was suggested that casein replaced the already existing protective layer around the rubber particles in latex and the filler particles and in the process, caused better rubber-filler interaction. The increase in viscosity of the latex compound by the addition of casein also caused simultaneous deposition of rubber and filler particles.

In the present work we have studied the effect of four surface active agents on vulcanization, network structure and technical properties of natural rubber latex vulcanizates which contained precipitated silica as filler. The surface active agents used are casein, polyvinyl alcohol, ammonium alginate and sodium carboxymethyl cellulose.

A base latex compound was prepared as per the formulation given in Table IV-1 and used in the experiments.

A part of the base latex compound was treated with the surface active agents at different dosages of 0, 0.5, 1.0, 1.5 and 2.0 parts per hundred rubber. Latex films of 1-1.25 mm thickness were prepared by spreading on glass cells, dried at 30°C and vulcanized at 120°C. To another portion of the base latex compound

30 phr of precipitated silica was added as a 25 per cent dispersion. The latex-filler system was then treated with the surface active agents at different dosages and vulcanised films were prepared as above. The tensile properties of the vulcanized films were determined and the results were plotted against the dosages of the surface active agents (Figures IV-1 and IV-2). From the Figures, the optimum dosages of the surface active agents required were calculated.

Another part of the base latex compound was mixed with 30 phr of precipitated silica as dispersion and the latex-filler system was treated with the optimum dosage of the surface active agents (1.0 phr) as obtained from the Figures IV-1 and IV-2. The Brookfield viscosity of the control and treated compounds were determined (Table IV-2). Latex films, 1-1.25 mm thickness were prepared and dried at 30°C. A portion of the dried sheets were plied up and determined its cure behaviour (Table IV-2). The remaining portions of the dried sheets were then vulcanized at 120°C in an air oven for its optimum crosslink density. The percentage polysulfidic content (Table IV-2) and the stress-strain beaviour (Figure IV-3) of the vulcanized films were then determined.

For determining the rubber-filler interaction, a portion of the base latex compound was mixed with 5, 10, 20 and 30 phr each of precipitated silica and was treated with the optimum dosage of surface active agents. Cast latex films of the treated and untreated compounds were prepared and vulcanized in air oven at 120°C, and used in the determination of rubber-filler interaction. For determining the rubber-filler interaction, V_r values of the filled (V_{rf}) and the gum (V_{ro}) samples were determined. The extent of rubber-filler interaction was then studied using the equation given by Cunneen and Russell as described in Chapter II. The results are depicted in Figure IV-4. Again, for assessing the rubber-filler attachment or the coupling bonds, the rubber-filler bonds were cleaved chemically by swelling the vulcanizate samples in ammonia atmosphere and determining the concentration of chemical crosslinks of the sample before and after ammonia treatment. The coupling bonds or the rubber-filler attachments was then determined as given in Chapter II. The results are given in Table IV-3 and Figure IV-5.

From Figures IV-1 and IV-2, it is evident that the surface active agents have no effect on the technical properties (modulus and tensile strength) of the latex vulcanizates at the gum stage. The effect of casein and polyvinyl alcohol is depicted only for the gum samples. Other two surface active agents have also got similar effect. But in the latex compound containing precipitated silica, certain surface active agents have marked effect on the modulus and tensile strength of the latex vulcanizates. It can be seen that the latex compounds containing polyvinyl alcohol offers the highest modulus. Modulus of a vulcanizate is solely governed by the total number of crosslinks including intermolecular chemical crosslinks and coupling bonds (rubber-filler attachment). In the present study the modulus enhancement is found to be more with polyvinyl alcohol than with casein. There was practically no improvement in modulus of the vulcanizates with ammonium alginate and sodium carboxymethyl cellulose. In the case of tensile strength, casein offers comparatively better tensile strength than polyvinyl alcohol. It may be mentioned that for a strain crystallising rubber like natural rubber, enhancement in tensile strength by reinforcing fillers is less predominant than that occurs in non-crystallising rubber. The optimum dosage of the surface active agents is found to be around 1.0 phr as seen in the Figures IV-1 and IV-2.

The effect of adding the optimum concentration of the surface active agents on viscosity and cure rate index of the compounds and the concentration of polysulfidic linkages of the latex vulcanizate are given in Table IV-2. It may be noted that the Brookfield viscosity is maximum when sodium carboxymethyl cellulose was incorporated and least with casein. It can also be seen that cure rate of the compound was not affected by the incorporation of the surface active agents.

It may also be noted from the Table IV-2 that the polysulfidic content in the treated and untreated latex vulcanizates remains almost the same. The stress-strain behaviour of the treated and untreated latex vulcanizates as given in Figure IV-3 shows that strain induced crystallization of natural rubber is practically unaffected by the presence of various surface active agents.

The plot of V_{ro}/V_{rf} against e^{-z} where 'z' is the weight fraction of filler in the vulcanizate is given in Figure IV-4. It may be seen that the latex compound containing polyvinyl alcohol and casein provides a higher slope than the mix containing no surface active agents. This gives an indication that better rubber-filler interaction is obtained by the incorporation of polyvinyl alcohol or casein. The same conclusion is also obtained from Figure IV-5 and Table IV-3 which shows the results of ammonia modified swelling. The reduction in the V_r values is found to be more in the latex vulcanizates containing polyvinyl alcohol or casein. This indicate a higher level of rubber-filler attachment due to the addition of polyvinyl alcohol or casein.

The enhancement in tensile properties on addition of polyvinyl alcohol or casein cannot be attributed to improved homogeneity of dispersion of the filler in the film as the same effect was not obtained with sodium alginate or sodium carboxymethyl cellulose.

In fact homogeneity of the filler could be better with the alginate and sodium carboxymethyl cellulose as they cause more pronounced thickening of the compound evidenced by the higher Brookfield viscosity. Hence the improvement in tensile properties is attributed to better rubber-filler attachment.

The rubber-filler attachment may be formed due to the interaction of polyvinyl alcohol or casein with the protective layer in the rubber and filler particles. During the interaction, partial desorption of protective layer on the rubber and filler particles may take place leading to direct contact between silica and rubber particles. It can also be pointed out that the polyvinyl alcohol is more surface active than casein and the surface activity of the sodium alginate and sodium carboxymethyl cellulose is very mild. Dogadkin et al[4] have proved through microscopic investigations that aggregates of rubber and carbon black are formed while adding casein to a mixture of SBR latex and carbon black. In the present study also a similar aggregation of rubber and silica is expected leading to the formation of coupling bonds and to improvement in tensile properties.

b) Effect of surface active agents on rubber-filler interaction in latex vulcanizates containing precipitated calcium carbonate and china clay.

Precipitated calcium carbonate or china clay is used in natural rubber latex in order to cheapen or to stiffen the vulcanizate[3]. They are only semi-reinforcing type fillers. China clay causes high modulus and permanent set in the vulcanized latex film. Precipitated calcium carbonate is also being used in latex for increasing the modulus of the film and also as an extender. The objective of the present investigation is to study the effects of precipitated calcium carbonate and china clay on the technical properties of latex vulcanizates in the presence of surface active agents such as casein and polyvinyl alcohol (PVA).

A base latex compound as per formulation given in Table IV-1 was prepared. Precipitated calcium carbonate and china clay (30 phr each) were mixed separatley as 50 per cent dispersions in the base latex compound. Each mix was then treated with casein/PVA at a dosage of 1.0 phr each. The dosage was fixed based on the preliminary experiments reported earlier. Latex films were prepared from these mixes in the thickness range of 1-1.25 mm. The control and treated samples were vulcanized at 120°C to their optimum crosslink density. Values of V_r is given in Table IV-5. The tensile properties of the aged and unaged samples were then determined and are given in Table IV-6 (a), (b) and (c). Rubber-filler interaction was determined by loading fillers at different levels and treating with the surface active agents. The results are given in Figures IV-6 (a) and (b).

V_r values of the different vulcanized samples are given in Table IV-4. The surface active agents have no effect on V_r values of the vulcanizate at the gum stage. But in the vulcanizates containing the fillers, V_r values are found to be increased with the addition of the surface active agents. The higher V_r values obtained in the case of precipitated calcium carbonate than in the case of china clay, may be attributed to the formation of more coupling bonds due to the interaction of the surface active agents on the rubber and filler particles. The tensile properties of the vulcanizates were also determined and are given in Tables IV-6 (a), (b) and (c). It can be seen that the modulus and tensile strength of the samples containing the fillers are improved by the addition of casein and PVA. This can be attributed to better rubber-filler interaction[5].

The effect of ageing the samples at 100°C is also given in Tables IV-6 (a), (b) and (c). It can be seen that the surface active agents have no effect on the aged properties of the samples. But it is observed that fillers have a minor role in controlling the ageing resistance. In air ageing, china clay imparted a better ageing resistance than precipitated calcium carbonate.

The plot V_{ro}/V_{rf} against e^{-z} is given in Figures IV-6 (a) and (b). It may be seen that the filled latex vulcanizates containing polyvinyl alcohol and casein provide slightly higher slopes than those containing no surface active materials. It may also be noted that in the case of precipitated calcium carbonate a better rubber-filler interaction was noted as is evident from its higher slope [Figure IV-6 (a)].

Table IV-1. Formulation of the base latex compound.

Ingredients	Parts by weight (wet)
60% Centrifuged latex	167.00
10% Potassium hydroxide solution	1.00
50% Sulfur dispersion	3.00
50% Zinc diethyldithiocarbamate dispersion	2.00
50% Antioxidant SP emulsion	2.00
50% Zinc oxide dispersion	1.00

Table IV-2. Effect of surface active agents on viscosity, cure rate index and network structure in the base latex compound containing 30 phr of silica.

Treatment	Brookfield viscosity (cps)	Cure rate index	Polysulfidic crosslinks (%)
Nil	128	28.6	50
Casein, 1 phr	200	28.5	49
Polyvinyl alcohol, 1 phr	210	28.5	48
Ammonium alginate, 1 phr	500	28.5	50
Sodium carboxymethyl cellulose, 1 phr	900	28.5	48

Table IV-3. V_r values before and after ammonia modified swelling.

Silica loading, phr	Treatment	V_r original	V_r after ammonia modified
0	Nil	0.1705	-
5	"	0.1640	0.1550
10	"	0.1655	0.1533
20	"	0.1715	0.1582
30	"	0.1757	0.1592
5	Polyvinyl alcohol, 1 phr	0.1720	0.1500
10	"	0.1755	0.1500
20	"	0.1991	0.1588
30	"	0.2153	0.1653
5	Casein, 1 phr	0.1722	0.1510
10	"	0.1767	0.1497
20	"	0.1915	0.1550
30	"	0.2050	0.1587

Table IV-4. V_r values of the samples.

Samples	Treatment	V_r
Gum (control)	Nil	0.1840
	1.0 phr casein	0.1835
	1.0 phr PVA	0.1842
Gum + 30 phr precipitated calcium carbonate	Nil	0.1810
	1.0 phr casein	0.1910
	1.0 phr PVA	0.1930
Gum + 30 phr china clay	Nil	0.1860
	1.0 phr casein	0.1890
	1.0 phr PVA	0.1900

Table IV-5 (a). Physical properties of gum latex vulcanizate.

Properties	Treatment		
	Nil	Casein	PVA
Modulus, 300% (MPa)			
(a) Unaged	1.40	1.41	1.42
(b) After ageing*	1.05	1.07	1.05
Retention (%)	75	76	74
Tensile strength (MPa)			
(a) Unaged	24.5	24.5	24.6
(b) After ageing*	8.28	8.34	8.21
Retention (%)	33.8	34.0	33.5
Elongation at break (%)			
(A) Unaged	1400	1405	1420
(b) After ageing*	980	983	994
Retention (%)	70	70	70

* Ageing in air at 100°C for 22 h.

Table IV-5 (b). Physical properties of latex vulcanizate (precipitated calcium carbonate).

Properties	Treatments		
	Nil	Casein	PVA
Modulus, 300% (MPa)			
(a) Unaged	2.50	3.10	3.25
(b) After ageing*	2.30	2.79	2.87
Retention (%)	92	90	89
Tensile strength (MPa)			
(a) Unaged	19.5	21.5	21.0
(b) After ageing*	8.40	8.77	8.28
Retention (%)	43.0	40.7	39.4
Elongation at break (%)			
(a) Unaged	1000	900	860
(b) After ageing*	900	800	774
Retention (%)	90	88	90

* Ageing in air at 100°C for 22 h.

Table IV-5 (c). Physical properties of latex vulcanizates (china clay).

Properties	Treatment		
	Nil	Casein	PVA
Modulus, 300% (MPa)			
(a) Unaged	2.30	2.60	2.65
(b) After ageing*	2.28	2.47	2.52
Retention (%)	95	95	95
Tensile strength (MPa)			
(a) Unaged	20.5	22.5	22.0
(b) After ageing*	11.50	12.00	11.75
Retention (%)	56.00	53.00	53.40
Elongation at break (%)			
(a) Unaged	1100	1120	1090
(b) After ageing*	1047	1057	1020
Retention (%)	95	94.3	93.5

* Ageing in air at 100°C for 22 h.

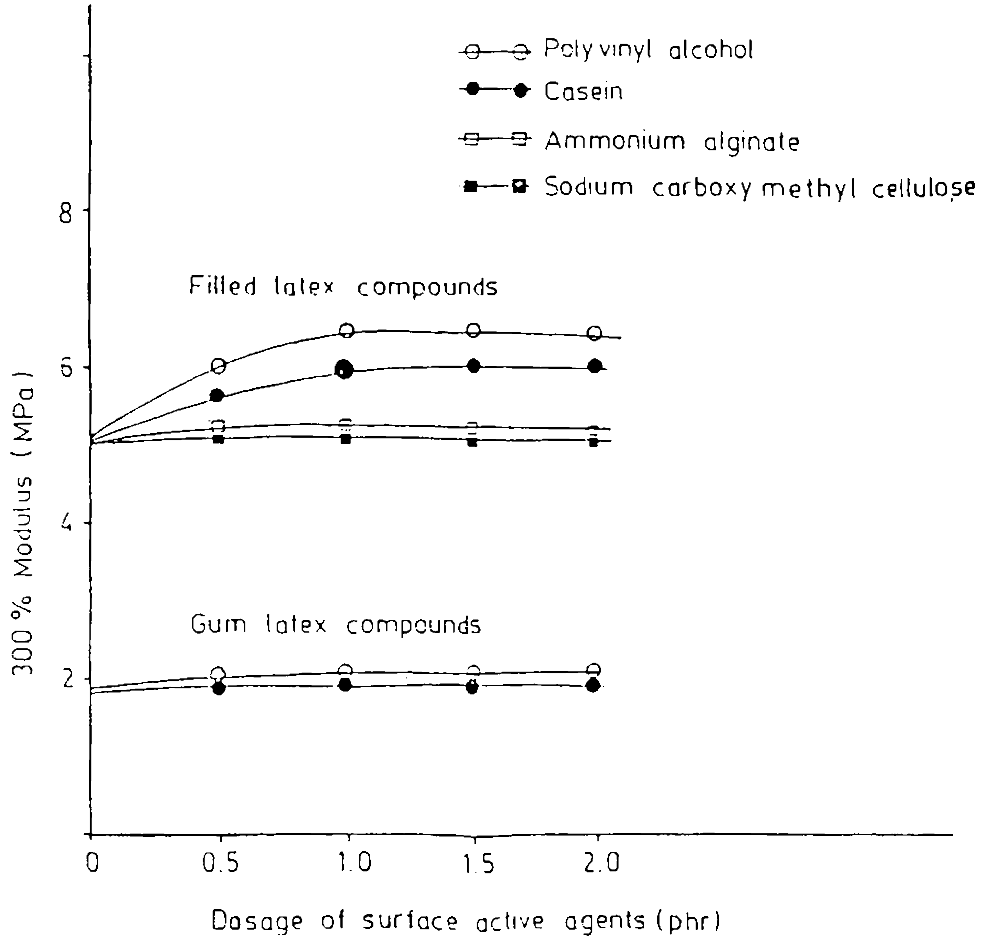


Fig. IV-1. Effect of surface active agents on modulus of latex vulcanizates.

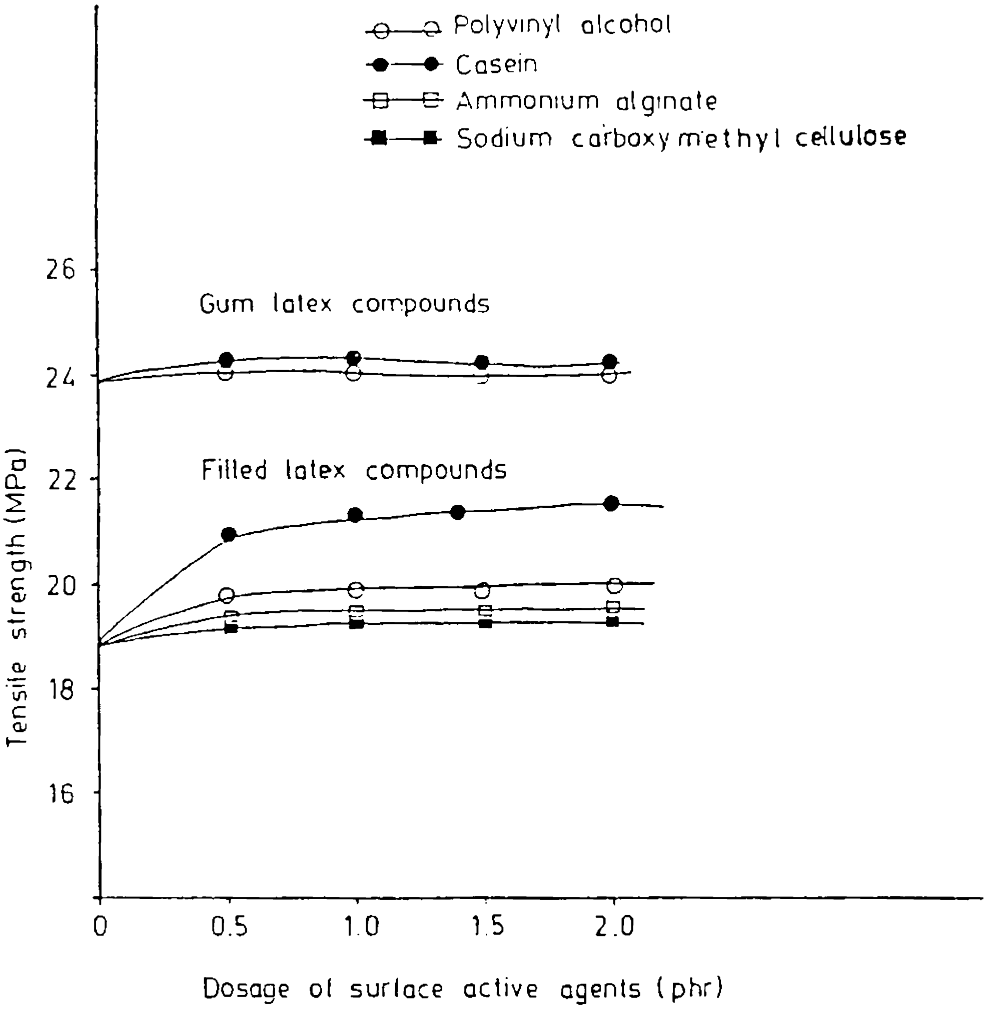


Fig. IV-2. **Effect of surface active agents on tensile strength of latex vulcanizates.**

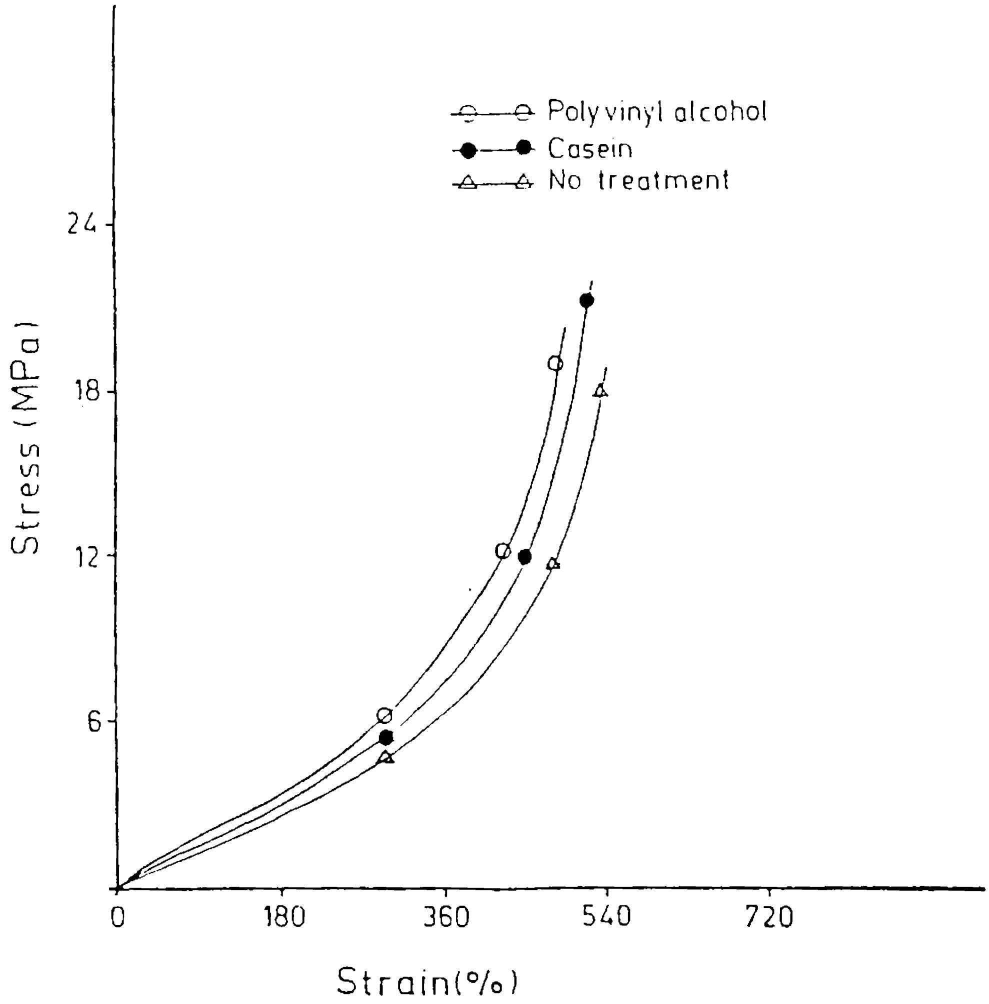


Fig. IV-3. **Effect of surface active agents on stress-strain behaviour.**

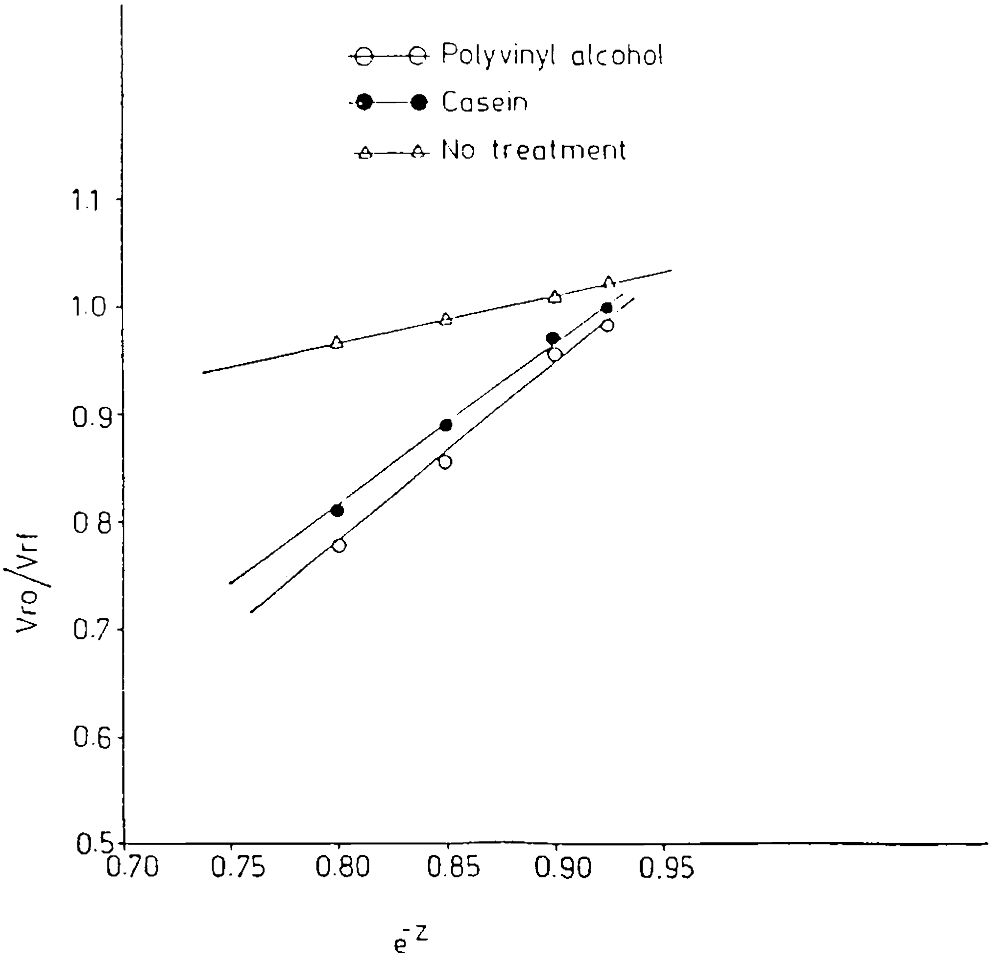


Fig. IV-4. Plot of $\frac{V_{ro}}{V_{rf}}$ against e^{-z}

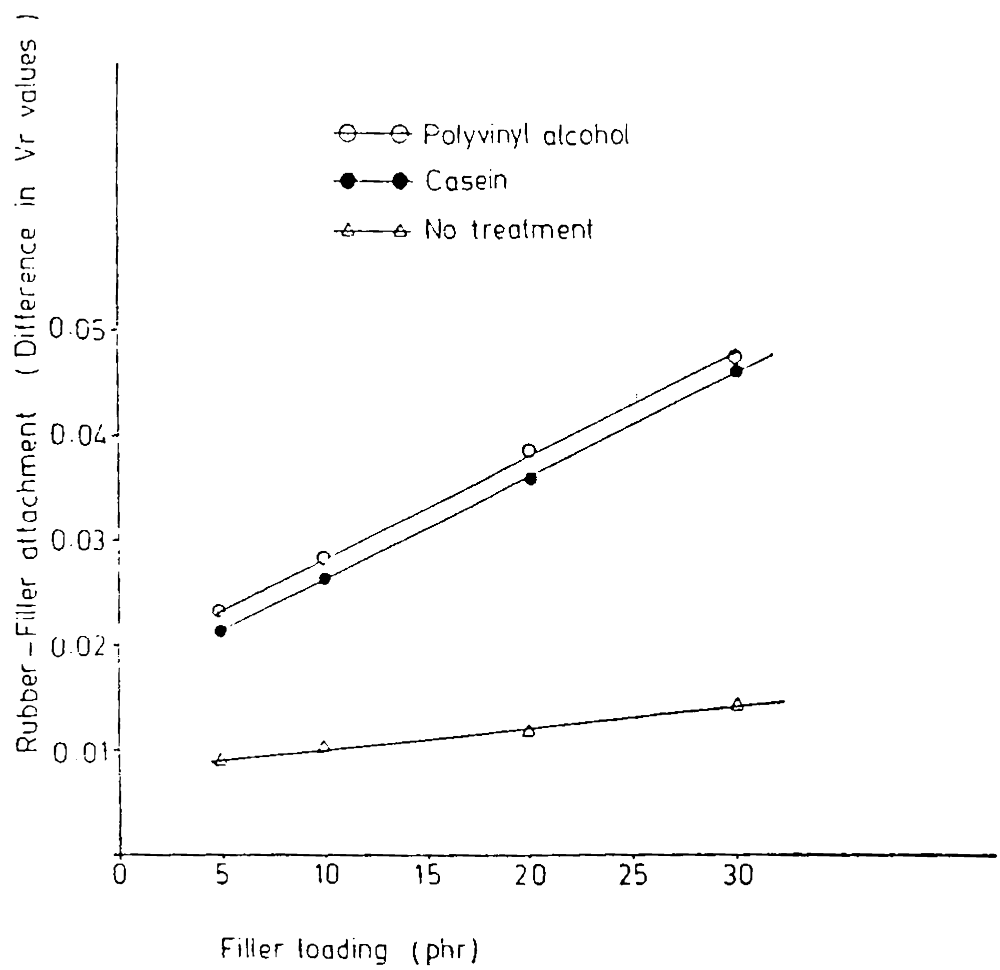


Fig. IV-5. **Effect of ammonia modified swelling of the silica filled latex vulcanizates in the presence of surface active agents.**

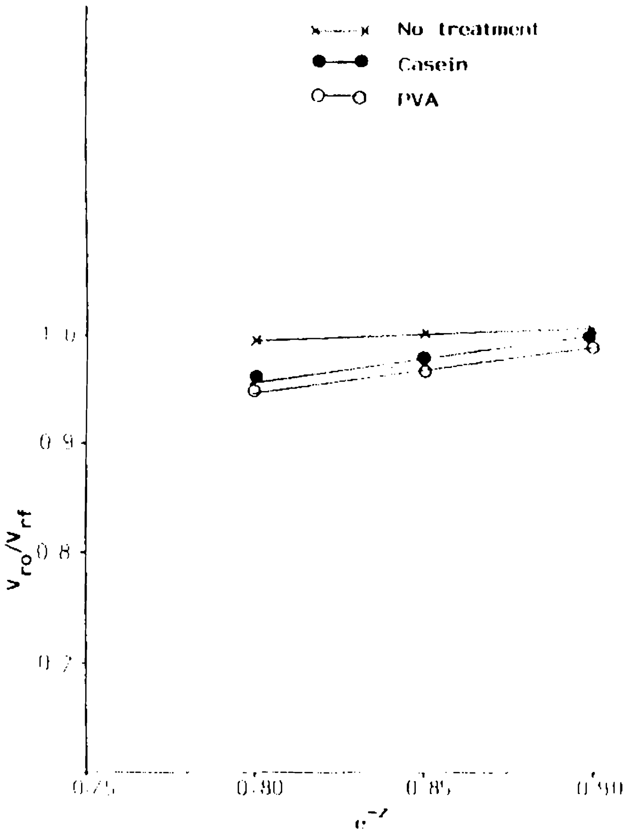


Fig. IV-6(a). Plot of V_{ro}/V_{rf} against e^{-z}

(precipitated calcium carbonate)

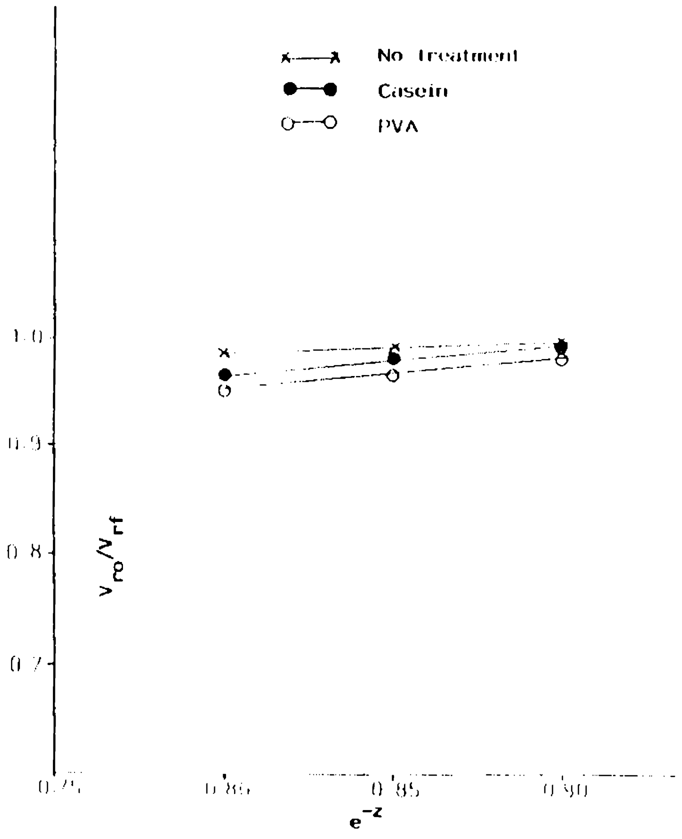


Fig. IV-6(b). Plot of V_{ro}/V_{rf} against e^{-z} (chinay clay)

PART - II RHEOLOGICAL BEHAVIOUR OF NATURAL RUBBER LATEX IN THE PRESENCE OF SURFACE ACTIVE AGENTS AND FILLERS.

Natural rubber latex is a pseudoplastic fluid and when sheared the rubber particles are progressively aligned and offers less resistance to flow[6]. So the apparent viscosity of the 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[7,8]. Due to the non-Newtonian behaviour, a single viscosity measurement of latex at a particular temperature is not enough to understand its flow behaviour. For many of the latex goods manufacturing processes,the flow behaviour of latex compound is critical[9,10]. A latex compound with low viscosity and some thixotropic nature is good for dipping operations[11]. The count of a latex thread is largely influenced by the viscosity of the latex compound[11,12].

The basic raw material for a latex compound may be either centrifuged or creamed latex. During compounding various surface active agents are added to modify the flow behaviour of latex to suit to the manufacturing process adopted. Some important surface active agents in use are casein, polyvinyl alcohol (PVA), sodium alginate and sodium carboxymethyl cellulose (NaCMC). Even though these chemicals have a profound influence on viscosity of the latex, no systematic study has been reported on the rheological behaviour of centrifuged or creamed latex and on the effect of these surface active agents on their flow properties under different shear rates and temperatures. In the present investigations, the effects of surface active agents on the viscosity of centrifuged and creamed natural rubber latex concentrates under different shear rates and temperatures have been studied.

60 per cent centrifuged and creamed latices were used as the basic material for this study. Typical latex compound as given in Table IV-6 was used to investigate the effect of surface active agents on the flow behaviour. The dosage of surface active agent was fixed at 0.5 phr based on preliminary experiments.

The flow behaviour of the raw latices and that of the latex compounds containing surface active agents was studied using Rheomat-30. As the study is to investigate the effect of shear rate as well as temperature, the concentric cylinder with 'B' cup is used for making the viscosity measurements. The study was made at three different temperatures, 25°C, 35°C and 45°C which are the normal range of temperatures for latex goods manufacture.

The effects of shear rate and temperature on viscosity of centrifuged and creamed latices are represented in Figures IV-7 and IV-8. From Figure IV-7, it is evident that the viscosity of creamed latex is higher than that of centrifuged latex both at low and high shear rates. In both cases, viscosity decreases with shear rate which indicated the pseudoplastic behaviour. The higher viscosity of creamed latex may be due to the adsorption of creaming agent on rubber particles which induces the formation of clusters of particles of different sizes. However, the difference between the viscosities of the centrifuged and creamed latex narrowed down as the shear rate is increased. As the shear rate is increased, the adsorbed layer of creaming agent gets displaced and causes the viscosity to be reduced sharply in the shear rate region of 10 to 50 sec^{-1}. It can be seen from Figure IV-8 that as the temperature is increased there is marked drop in the viscosity of creamed latex compared to that of centrifuged latex and this effect is more predominant in the temperature range of 25-35°C than in the range 35-45°C, both at low and high shear rates. This property of creamed latex may be due to the restricting effect of creaming agent on Brownian movement of latex particles and its effect on temperature[13]. With regard to pseudoplasticity, creamed latex is more pseudoplastic than centrifuged latex as indicated by the lower values of 'n' given in Table IV-7. Creamed latex exhibited yield stress also (Table IV-7). The pseudoplasticity decreases with rise in temperature and the viscosity index showed a sharp drop both for centrifuged and creamed latices.

The effect of shear rate and temperature on the viscosity of centrifuged latex compound in the presence of various surface active agents is shown in Figures IV-9 and IV-10 respectively. Among the surface active agents sodium carboxymethyl cellulose (NaCMC) offers the highest viscosity at low and higher shear rates. Polyvinyl alcohol (PVA) offers a higher viscosity than casein at low shear rates but as the shear rate increases (60-100 sec^{-1}) PVA offers a lower viscosity than casein (Fig. IV-9). This may be due to the easier displacement of the adsorbed layer of PVA from the surface of the rubber particles at higher shear rates than casein. Disturbances on the adsorbed layer causes the particles to slide past each other resulting in reduction of viscosity. Figure IV-10 depicts the effect of temperature on the viscosity of centrifuged natural latex compound containing the surface active agents. It may be noted that even though sodium alginate increased the viscosity of centrifuged latex, it has not affected the general behaviour of centrifuged latex towards temperature (Fig. IV-10). But all other surface active agents have got effect on the behaviour of centrifuged latex towards temperature. Among these, PVA imparts the highest sensitivity to temperature for the viscosity of the latex compound. But at low and high shear rates, the decrease in viscosity of the latex compound containing PVA is substantial with increase in temperature. This may be attributed to the high sensitivity of PVA solution to temperature[3]. But casein offers a peculiar behaviour towards temperature. In the lower temperature range (25-35°C) the reduction in viscosity of the centrifuged latex is of the same rate as that of the untreated one. But at higher temperature range (35-45°C) there is marked reduction in viscosity. This may be attributed to the alteration in the water binding of casein at higher temperature, which in turn affects the apparent viscosity of the casein solution[13]. It may also be noted that the pseudoplastic behaviour of centrifuged latex was little affected by the addition of casein (Table IV-8). The NaCMC offers the maximum pseudoplasticity and yield stress to the centrifuged latex compound. It can also be inferred from Table IV-8 that the pseudoplastic behaviour of latex compounds containing sodium alginate and NaCMC increased with increase in temperature.

The effect of shear rate and temperature on the viscosity of creamed latex compound in the presence of various surface active agents is shown in Figures IV-11 and IV-12. The effect of NaCMC on the viscosity of the creamed latex compound under different shear rate is similar to that of centrifuged latex compound. But the creamed latex compound becomes highly pseudoplastic on the addition of NaCMC as indicated by the low pseudoplasticity index 'n' in Table IV-9. The effect of PVA and casein on the viscosity of creamed latex is less marked even though these surface active agents enhance the pseudoplastic nature of the latex compound (Figure IV-11 and Table IV-9). This is attributed to the interaction of these chemicals with the creaming agents already adsorbed in the latex particles. It may also be noted that the addition of casein removes the yield stress present in the creamed latex compounds. The behaviour of surface active agents with respect to temperature in creamed latex compound is represented in Figure IV-12.

Effect of fillers on flow properties of latex compounds

Inorganic fillers and pigments are added to natural rubber latex compounds in order to cheapen and stiffen the product or to colour it. An ancillary effect is the effect of such fillers upon the flow properties of latex compounds[14]. Very little study has been reported on the effect of fillers on the flow properties of natural rubber latex compounds. In the present study the effect of precipitated silica and china clay on the flow properties of centrifuged latex compound was evaluated.

The compound was prepared using centrifuged latex as per the formulation given in Table IV-6. Precipitated silica (25 per cent dispersion) and china clay (50 per cent dispersion) were mixed with the centrifuged latex compound separately at a dosage of 15 phr each. The effect of shear rate on the viscosity of the latex compounds was determined using Rheomat-30. The results are depicted in Figure IV-13. The TS content of all the mixes were adjusted to 48 per cent before the measurement of viscosity.

The viscosity of the latex compounds is found to increase by the addition of silica and china clay as is seen from Figure IV-13. It can be seen that at low shear rates the filled latex compounds shows a much higher viscosity than the unfilled compound. The difference, however, disappears at higher shear rates. The restriction offered by the fillers to the Brownian movement of the latex particles seems to have been overcome at the higher shear rates.

Table IV-6. Formulation of the gum latex compound.

Ingredients	Parts by weight (p.b.w.)
60% Centrifuged/creamed natural rubber latex	167.00
10% Potassium hydroxide solution	0.50
50% Sulfur dispersion	3.00
50% ZDC dispersion	2.00
50% Zinc oxide dispersion	0.50
50% Antioxidant SP emulsion	1.00

Maturation : 24 h at 25°C.

Table IV-7. Effect of temperature on non-Newtonian behaviour of raw latices.

Sample	Pseudoplasticity Index (n)			Viscosity Index (k)			Yield Stress (Pascals)		
	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
Centrifuged latex (60%)	0.702	0.722	0.805	0.268	0.1819	0.1460	-	-	-
Creamed latex* (60%)	0.520	0.625	0.660	0.912	0.427	0.2820	1.22	0.81	0.81

* Prepared using tamarind seed powder as creaming agent.

Table IV-8. Effect of temperature on the non-Newtonian behaviour of centrifuged latex compound containing surface active agents.

Sample	Pseudoplasticity Index (n)			Viscosity Index (k)			Yield Stress (Pascals)		
	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
Centrifuged latex compound	0.658	0.704	0.760	0.239	0.199	0.1410	-	-	-
Centrifuged latex compound + 0.5 phr casein	0.640	0.660	0.720	0.436	0.363	0.186	-	-	-
Centrifuged latex compound – 0.5 phr PVA	0.460	0.500	0.540	0.9120	0.6607	0.5475	1.20	1.20	0.81
Centrifuged latex compound + 0.5 phr sodium alginate	0.470	0.468	0.456	1.072	1.023	1.00	1.20	1.20	1.20
Centrifuged latex compound + 0.5 phr NaCMC	0.460	0.420	0.422	1.430	1.413	1.318	1.60	1.20	1.20

Table IV-9. Effect of temperature on non-Newtonian behaviour of creamed latex compound containing surface active agents.

Sample	Pseudoplasticity Index (n)			Viscosity Index (k)			Yield Stress (Pascals)		
	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
Creamed latex compound	0.550	0.716	0.795	0.589	0.214	0.102	0.81	0.81	0.81
Creamed latex compound + 0.5 phr casein	0.500	0.520	0.580	0.794	0.631	0.372	-	-	-
Creamed latex compound + 0.5 phr PVA	0.530	0.540	0.630	0.631	0.389	0.257	1.22	0.81	0.81
Creamed latex compound + 0.5 phr NaCMC	0.375	0.404	0.415	1.905	1.413	1.259	2.40	1.62	1.22

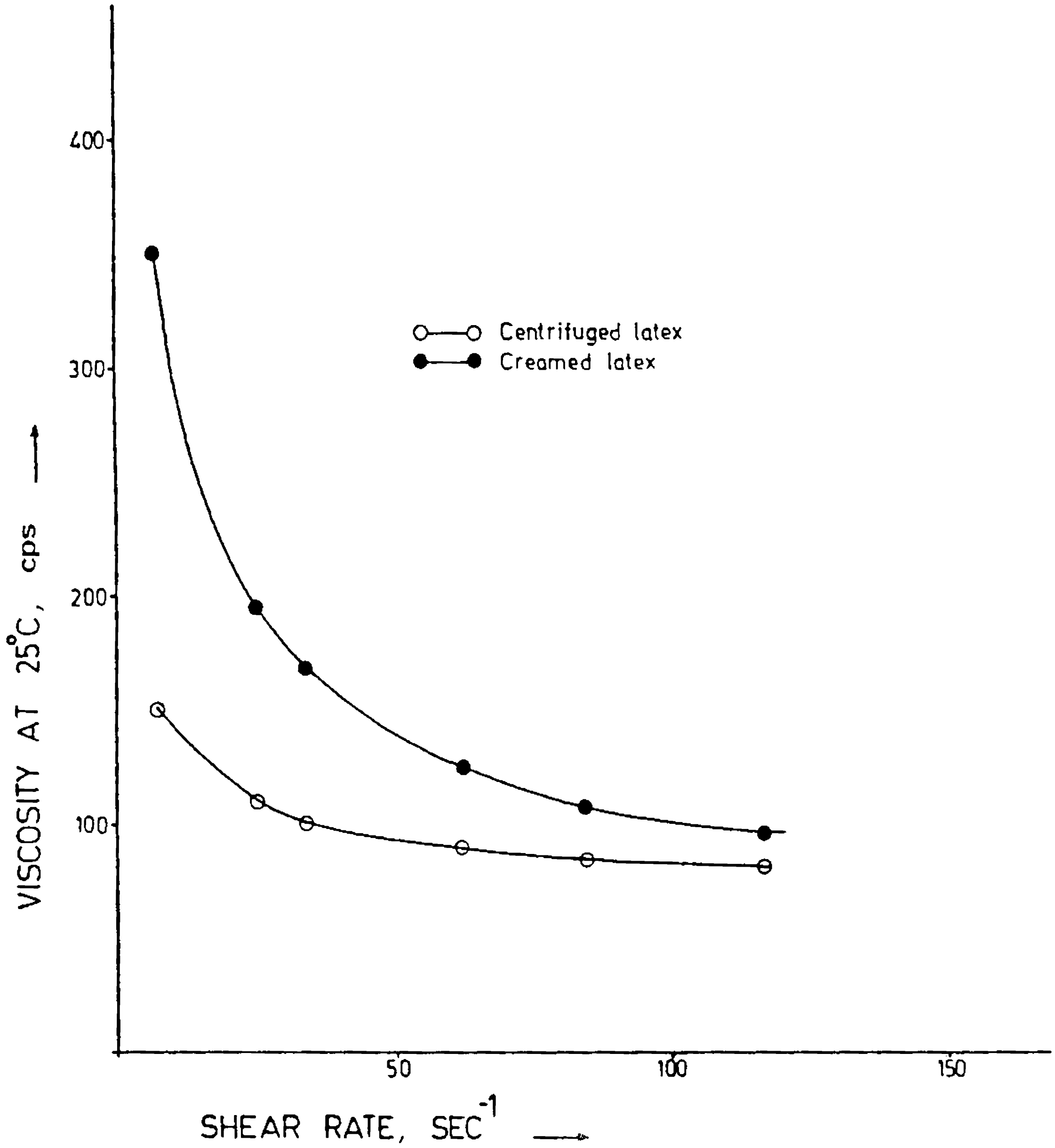


Fig. IV-7. Effect of shear rate on viscosity of concentrated NR latices.

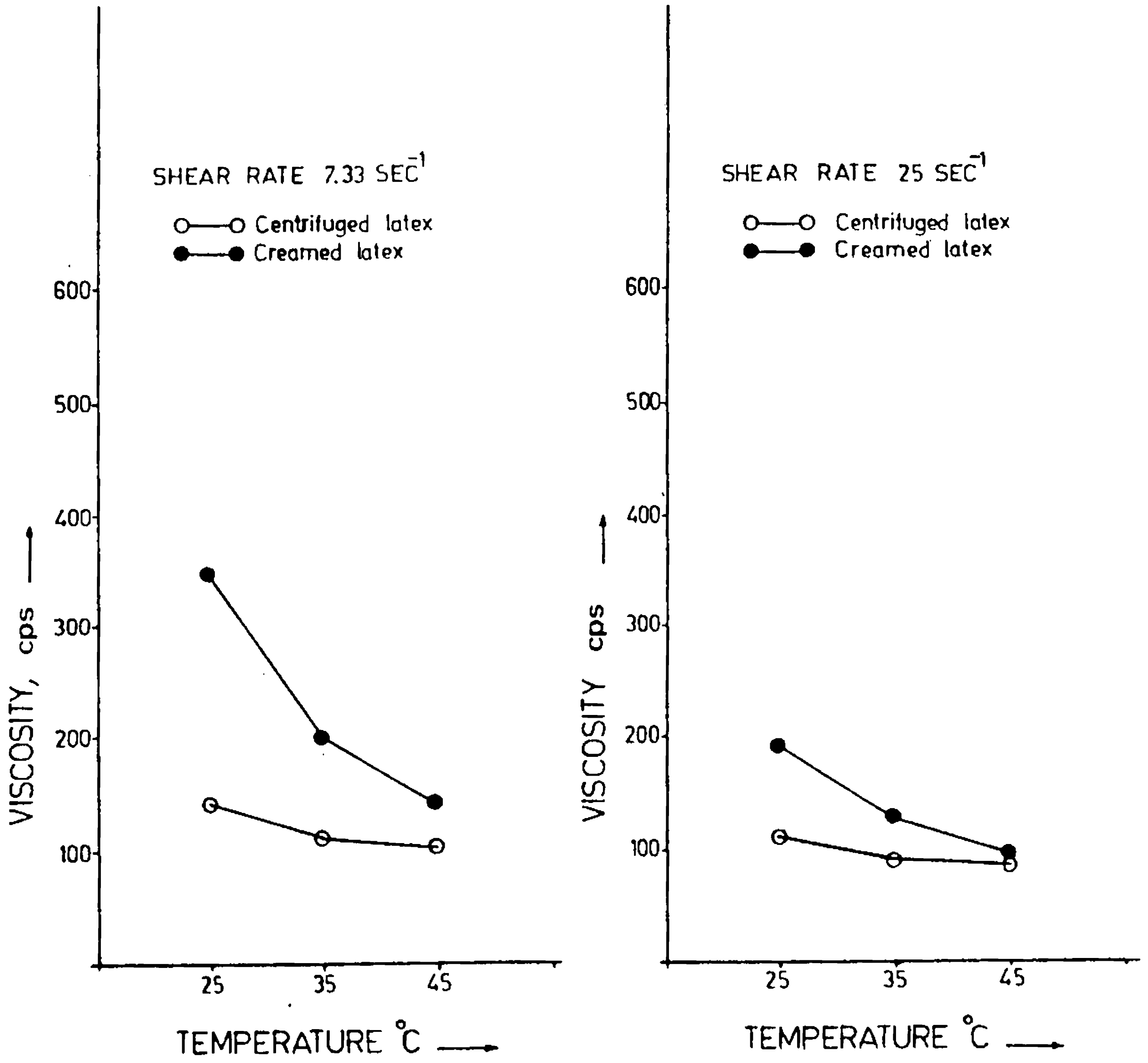


Fig. IV-8. Effect of temperature on viscosity of concentrated NR latices.

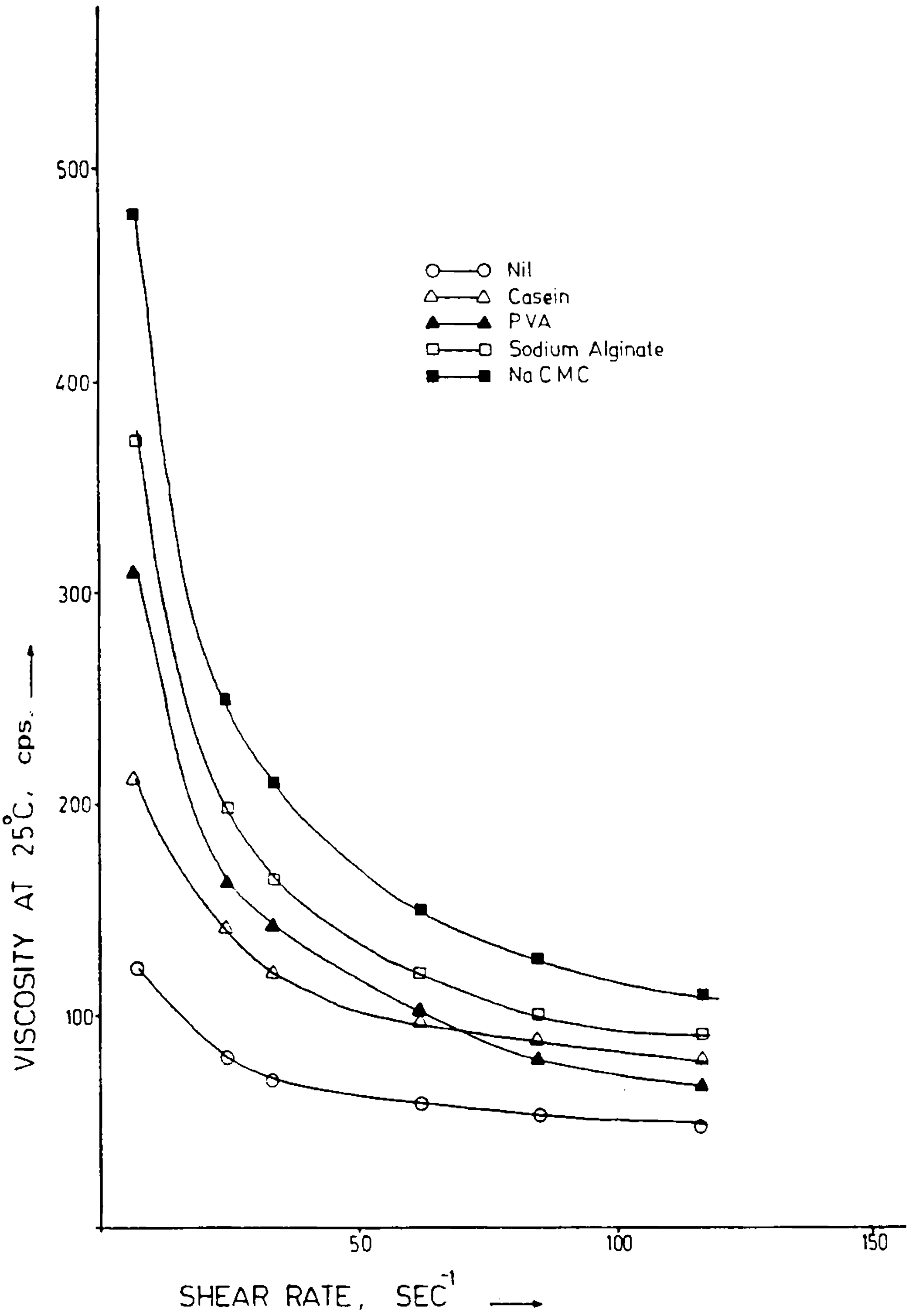


Fig. IV-9. Effect of shear rate on viscosity of centrifuged NR latex compound containing surface active agents.

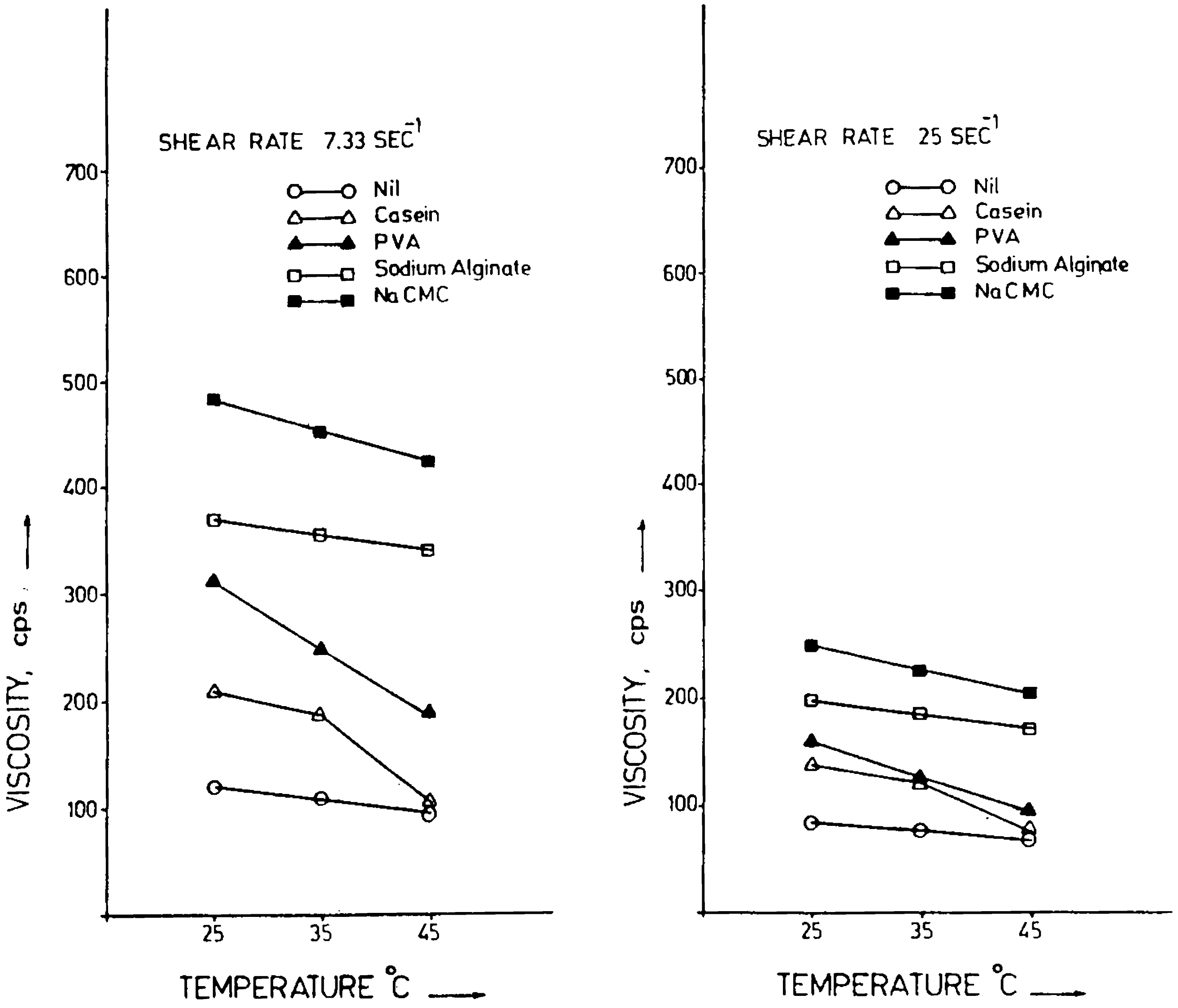


Fig. IV-10. **Effect of temperature on viscosity of centrifuged NR latex compound containing surface active agents.**

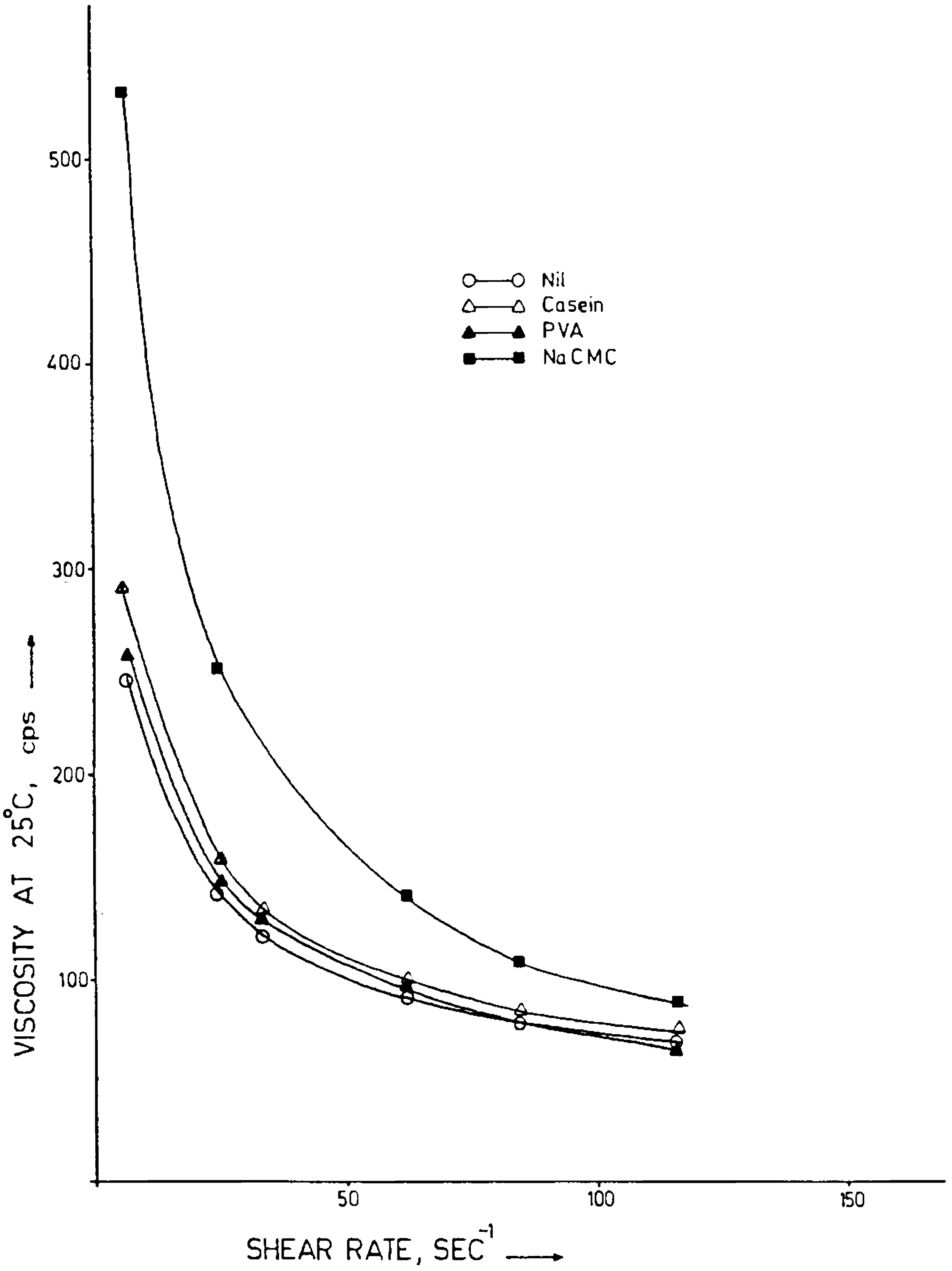


Fig. IV-11. Effect of shear rate on viscosity of creamed NR latex compound containing surface active agents.

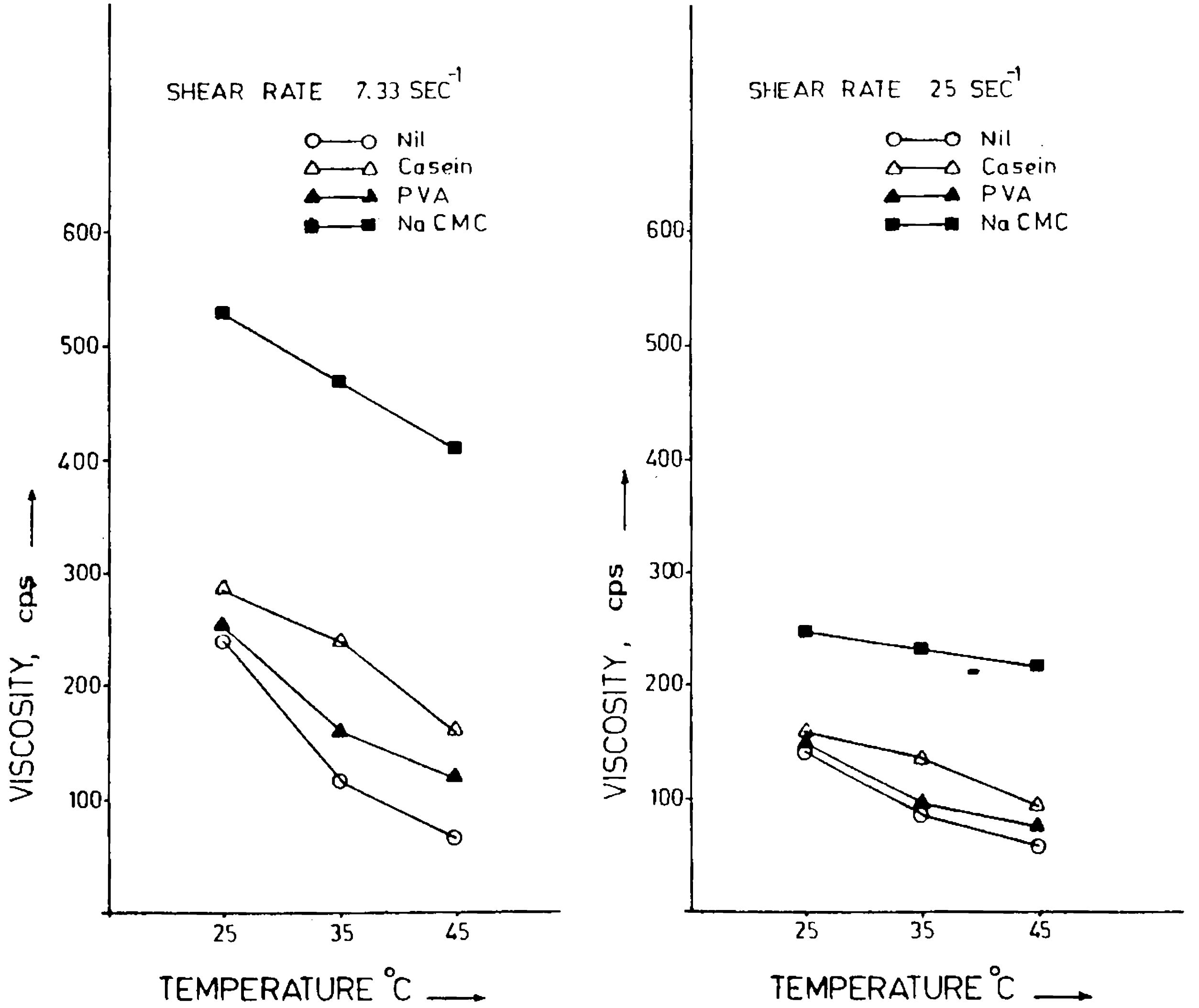


Fig. IV-12. Effect of temperature on viscosity of creamed NR latex compound containing surface active agents.

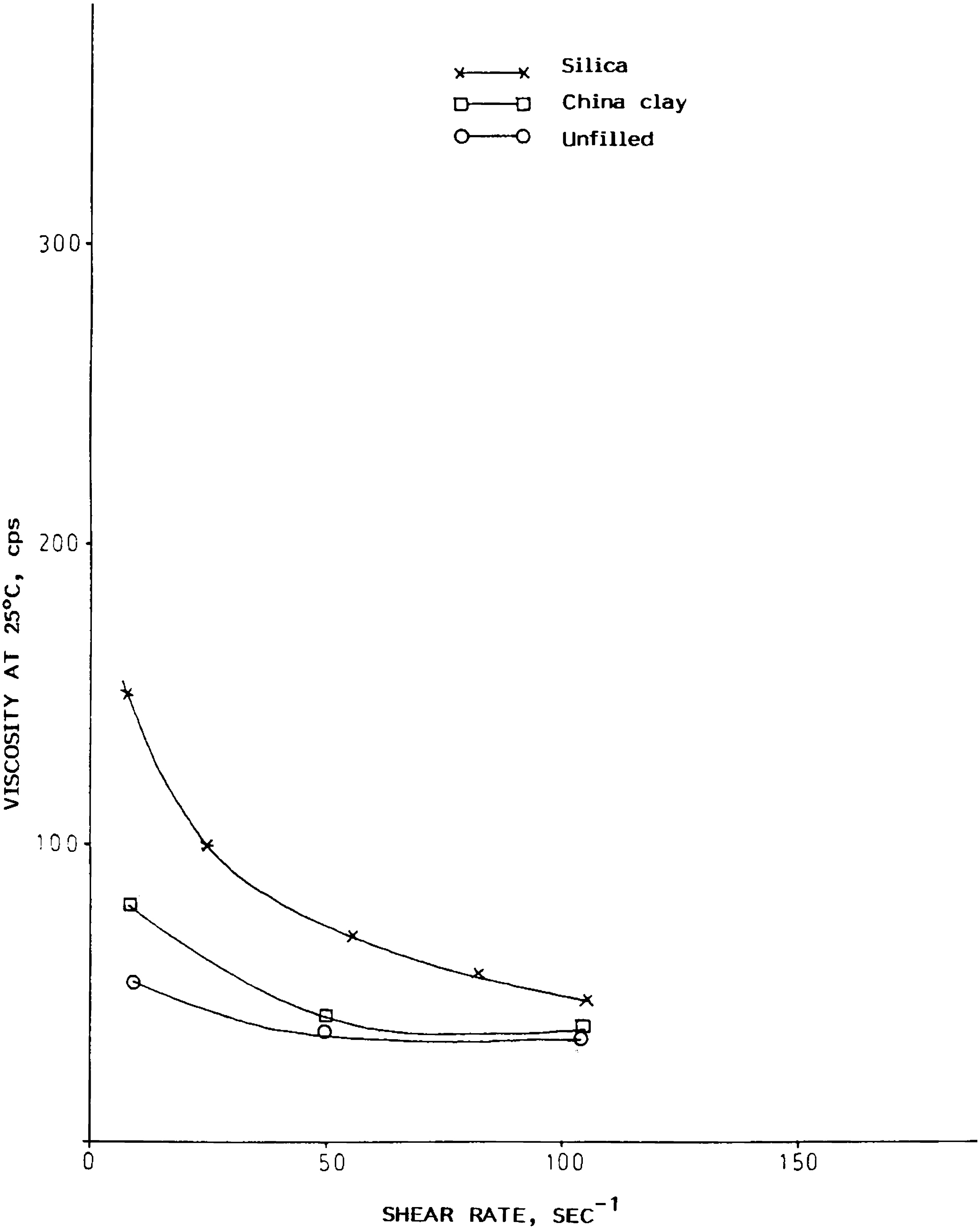


Fig. IV-13. Effect of fillers on the flow properties of centrifuged latex compound.

REFERENCES

1. Henry P. Stevens and W.H. Stevens, The Rubber Latex, British Rubber Publicity Association, London (1942) 36-42.
2. R.J. Noble, Latex in Industry, Rubber AGe, New York (1953) 261-263.
3. D.C. Blackley, High Polymer Latices, Vol. 1, Applied Science Publishers, London (1966) 97-200.
4. B.A. Dogadkin, L.G. Senatorskoya, V.I. Gusev, A.V. Suslyakov and P.I. Zakharchenko, Rubb. Chem. Technol. 31 (1958) 655-661.
5. N.R. Peethambaran and A.P. Kuriakose, Indian J. Nat. Rubb. Res. 1(2) (1988) 1-9.
6. W.L. Wilkinson, Non-Newtonian fluids, Pergmon Press, London (1960) 1-9.
7. Edgar Rhodes and H. Fairfield Smith, J. R.R.I.M. 9 (1939) 171.
8. H. Fairfield Smith, J. R.R.I.M. 11 (1941) 44.
9. E.W. Madge, Trans. Instn. Rubb. Ind. 10 (1933-34) 393.
10. A.D.T. Gorton and P.E. Swinyard, NR Technol. Vol. 10(4) (1973) 73.
11. K.O. Calvert, Polymer Latices, Applied Science Publishers, London (1982) 187.
12. D.C. Blackely, High Polymer Latices Vol. 2, Applied Science Publishers, London (1966) 817-820.
13. Clifford A. Hampel and Gessner G. Hawly, The Encyclopedia of Chemistry, Van Nostrand Reinhold Company, New York (173) 679-680.
14. D.C. Blackley, High Polymer Latices, Vol. 1. Maclaren and Sons Ltd., London (1966) 89-91.

CHAPTER - V

EFFECT OF GAMMA IRRADIATION ON RUBBER FILLER INTERACTION AND DEGRADATION

PART - I EFFECT OF GAMMA IRRADIATION ON RUBBER-FILLER INTERACTION IN PRECIPITATED SILICA AND CALCIUM CARBONATE FILLED NATURAL RUBBER LATEX VULCANIZATES.

PART - II EFFECT OF GAMMA IRRADIATION ON DEGRADATION OF LATEX VULCANIZATES CONTAINING DIFFERENT ACCELERATOR COMBINATIONS.

PART - I EFFECT OF GAMMA IRRADIATION ON RUBBER-FILLER INTERACTION IN PRECIPITATED SILICA AND CALCIUM CARBONATE FILLED NATURAL RUBBER LATEX VULCANIZATES.

Weakening of the latex vulcanizates by the addition of reinforcing fillers is attributed to poor rubber-filler interaction and different techniques have been suggested to improve this[1,2]. Ammonium caseinate has been used to get reinforcement in a mixture containing carbon black and styrene butadiene rubber latex[3]. An attempt to produce radicals in natural rubber latex by means of gamma rays and thus to achieve reinforcement by carbon black is also reported[4]. The contribution of free radicals in the reinforcement of solid rubber by fillers has been well established[5]. Macroradicals are formed in rubber during mastication, with or without chemical reagents and are believed to combine with the filler effecting reinforcement[6]. Similarly macroradicals are generated in latex through gamma irradiation and their effect on reinforcement is found to depend upon irradiation dose and the nature of filler. The formation of macroradicals in latex is influenced by sensitisers such as carbon tetrachloride or chloroform and is used in the vulcanization of latex through gamma irradiation[7].

A perusal of the literature indicates that irradiation studies on latex vulcanizates in presence of non-black fillers is lacking. This part reports our studies on the interaction of non-black fillers with rubber through gamma irradiation. Precipitated silica and calcium carbonate were used as the fillers and the following parameters have been included in this study: (a) effect of gamma irradiation dose and sensitiser on rubber-filler interaction, and (b) effect of gamma irradiation on network structure and physical properties.

Centrifuged natural rubber latex was used for this study. The vulcanizing agents and the fillers were prepared as dispersions and antioxidant, styrenated phenol (SP) as an emulsion. A gum latex compound as per the formulation given in Table V-1 was used in all the experiments.

Filled latex compounds as given in Table V-2 were prepared. A gamma chamber, Model 900, was used as the source for gamma irradiation and the dose rate was 3.0 KGy/h. Each latex compound was irradiated to different dosages of 1.5, 3.0, 6.0, 8.0 and 12 KGy and samples were collected. Latex films were prepared by casting on glass cells. The film thickness was controlled in the range of 1.0 to 1.25 mm and the films were vulcanized at 100°C for its optimum crosslink density as obtained from the plot of V_r against vulcanization time as described in Chapter 2 (Fig. II-2). The crosslink density of the vulcanized samples was determined byestimating the V_r values at their optimum vulcanization.

For measuring rubber-filler attachment (coupling bond) experimentally, rubber-filler bonds were cleaved chemically by swelling the vulcanizate samples for 48 h. in flat dishes containing benzene in ammonia atmosphere. After swelling in ammonia atmosphere the samples were washed with benzene and dried in a vaccum desicator at room temperature. The difference in total crosslink density as obtained by swelling studies in benzene of the original vulcanizate and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond. The results are given in Figures V-1(a) and V-1(b), V-2(a) and V-2(b).

Rubber filler interaction was also studied by plotting V_{ro}/V_{rf} against e^{-z} where z is the weight fraction of the filler in the vulcanizate. Precipitated silica and calcium carbonate at different dosages (0, 5, 10, 15 and 25 phr) were added to gum latex compound as 50 per cent dispersion and irradiated to 3 KGy for getting the optimum rubber filler interaction. Vulcanized latex films (1.0-

1.25 mm thickness) were prepared and the values of V_r for the gum samples (V_{ro}) and that of filled samples (V_{rf}) were determined as cited earlier. The extent of rubber-filler interaction was then studied using the equation given by Cunneen and Russel[8]. The results are given inFigures V-3(a) and V-3(b).

In order to assess the effect of irradiation on the technical properties of the filled samples, the tensile properties of the vulcanized films before and after ageing were determined as per ASTM D-412 using a Zwick Universal Testing machine (Model 1474). The chemical and physical properties of the latex films are given in Tables V-3(a) and V-3(b).

Rubber-filler interaction

The effect of gamma irradiation on rubber-filler interaction of latex-filler systems are given in Figures V-1(a) and V-1(b). As the radiation dose increases, the total crosslink density, which include chemical and coupling bonds (rubber-filler attachment) increases. The total crosslink density of the samples, after ammonia modified swelling, is also given in those figures. Ammonia modified swelling destroys the coupling bonds; and the total crosslink density, after this treatment, represents mainly intermolecular chemical crosslinks only. It can be seen that there is substantial difference in the total crosslink density before and after ammonia treatment which indicates that latex-filler interaction has been considerably improved on gamma irradiation under both precipitated silica and calcium carbonate systems. The formation of coupling bonds against irradiation dose is given in Figures V-2(a) and V-2(b), which show that iradiation dose around 3 KGy is enough to get optimum rubber-filler interaction. The effect of sensitiser in the formation of coupling bonds is practically negligible; the total crosslink density after prolonged irradiation (upto 12 KGy) also showed no increase compared with the sample without sensitiser (Figures V-1(a) and V-1(b). But this increase in crosslink density was retained after ammonia modified swelling also, which indicates that the crosslinks formed are intermolecular chemical bonds.

The rubber-filler interaction was also studied by plotting V_{ro}/V_{rf} versus e^{-z}, where 'z' is the weight fraction of the filler in the vulcanizate as given in Figures V-3(a) and V-3(b). It is found that the graph drawn in the case of irradiated samples give a higher slope than the control samples which indicates better rubber-filler interactions both in the case of precipitated silica and calcium carbonate. The extent of interaction is also found to be dependent on the nature of filler and between two fillers studied silica offers a higher interaction with the rubber particles.

Sato *et al.*[9] reported that the rubber-filler interaction includes both physical attractions and chemical bonds. It has been suggested that gamma irradiation increases the number of coupling bonds and hence the increase in adhesion between rubber and filler[10]. So the increase in the rubber-filler interaction reported in the present study may be attributed to some temporary bonds formed between rubber and filler particles.

From Tables V-3(a) and V-3(b), it is evident that the network structure of the samples was not much affected by gamma irradiation (3 KGy). The polysulphidic crosslink content in the control and irradiated samples is found to be not much different. The physical properties of the vulcanizates are also given in Tables V-3(a) and V-3(b) and it is indicated that the modulus showed marked difference between the control and irradiated samples. The improvement in modulus is solely governed by the total number of chemical and coupling bonds. The difference in the values of tensile strength between the control and irradiated sample is found to be less marked as is evident from Table V-3(a) and V-3(b). It may be pointed out that for a strain crystallising rubber like NR, the enhancement of tensile strength is not a criterion for rubber-filler interaction or reinforcement. The ageing resistance of the samples were assessed after heating the samples in air at 100°C for 22 h and determining the tensile properties. It was found that gamma irradiation at a dosage of 3 KGy did not affect the ageing resistance of the vulcanizates as evidenced from Tables V-3(a) and V-3(b).

Table V-1. Formulation of gum latex compound.

Ingredients	Parts by weight
60% Centrifuged latex	167.0
10% Potassium hydroxide solution	0.5
50% Sulfur dispersion	3.0
50% Zinc diethyldithio carbamate dispersion	2.0
50% Antioxidant SP emulsion	2.0
50% Zinc oxide dispersion	1.0

Table V-2. Formulations of filled latex compounds.

Ingredients	Parts by weight A	 B	 C	 D
Gum latex compound	175.5 (100 drc)	175.5 (100 drc)	175.5 (100 drc)	175.5 (100 drc)
25% Precipitated silica dispersion	100	100	-	-
50% Precipitated calcium carbonate dispersion	-	-	50	50
50% Carbon tetrachloride emulsion (sensitiser)	-	2	-	2

Table V-3(a). Chemical and physical properties of silica filled latex vulcanizates.

Properties	Silica load in phr							
	Control				Irradiated to 3 KGy			
	0	5	10	25	0	5	10	25
Chemical								
Total crosslinks (V_r)	0.1875	0.1802	0.1820	0.1838	0.1875	0.1913	0.1953	0.2106
Polysulphidic crosslinks in %	45	43	42	44	46	44	42	44
Physical								
Modulus 300%								
Before ageing MPa	1.40	1.55	1.80	3.20	1.41	1.75	2.25	4.20
After ageing in MPa	1.00	1.10	1.30	2.24	1.00	1.25	1.62	3.12
Retention %	71	71	72	70	71	71	72	74
Tensile strength								
Before ageing in MPa	23.0	21.0	20.0	18.50	22.0	22.0	21.0	19.0
After ageing in MPa	7.5	7.0	6.5	6.3	7.5	7.4	6.85	6.5
Retention %	33.0	34.0	33.0	34.0	34.0	33.6	32.6	34.0
Elongation at break								
Before ageing in %	1350	1250	1180	900	1350	1200	1100	800
After ageing in %	840	740	701	520	840	710	655	468
Retention %	62	59	59	57	62	59	60	58.5

Table V-3(b). Chemical and physical properties of calcium carbonate filled latex vulcanizates.

Properties	Calcium carbonate load in phr							
	Control				Irradiated to 3 KGy			
	0	5	10	25	0	5	10	25
Chemical								
Total crosslinks (V_r)	0.1874	0.1870	0.1868	0.1878	0.1874	0.1900	0.1940	0.2079
Polysulphidic crosslinks (%)	48	47	46	47	47	46	48	46
Physical								
Modulus, 300%								
Before ageing in MPa	1.40	1.50	1.70	2.50	1.38	1.60	2.00	3.20
After ageing in MPa	1.23	1.35	1.53	2.30	1.24	1.40	1.84	2.99
Retention %	88	90	90	92	90	88	92	93.7
Tensile strength								
Before ageing in MPa	23.0	22.0	21.0	20.0	22.5	22.5	21.5	20.5
After ageing in MPa	8.55	8.80	8.40	8.00	8.55	9.00	8.60	8.00
Retention %	37.0	40	40	40	38	40	40	39.5
Elongation at break								
Before ageing in %	1350	1250	1200	1000	1350	1250	1200	950
After ageing in %	1188	11125	1056	920	1188	1100	1068	860
Retention %	88	90	88	92	88	88	89	90.5

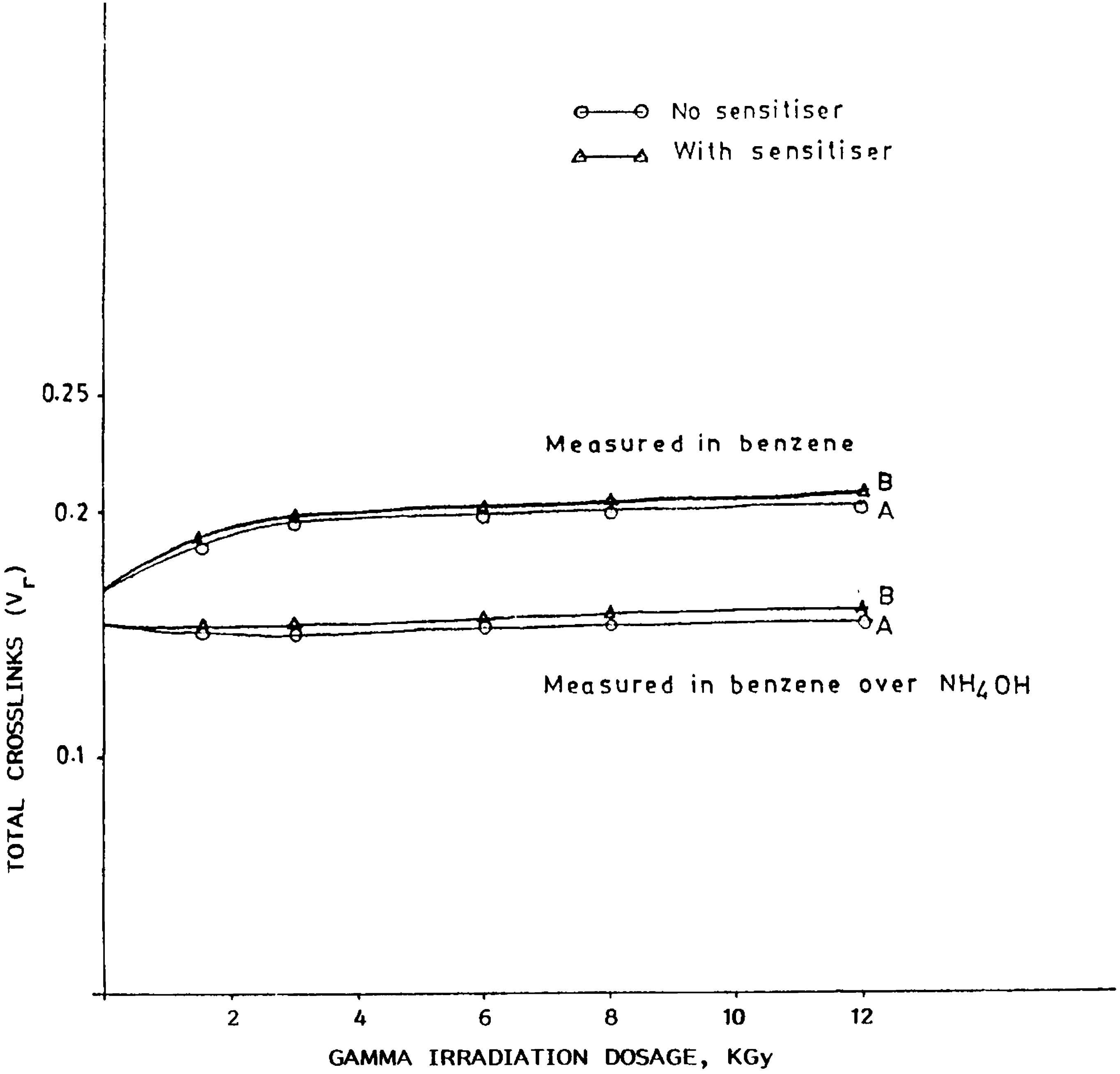


Fig. V-1(a). Effect of irradiation on rubber-filler interaction

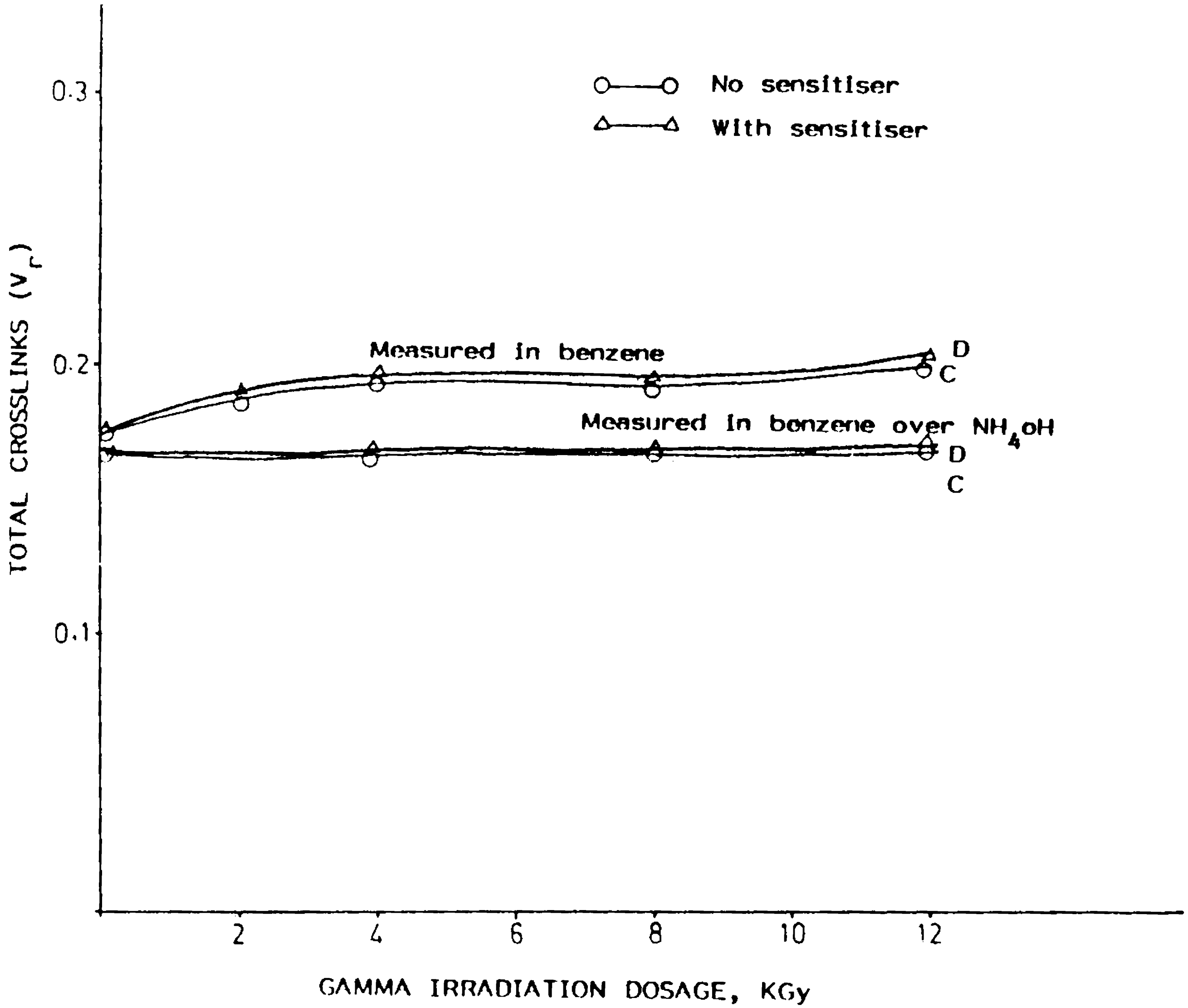


Fig. V-1(b). Effect of irradiation on rubber-filler interaction (precipitated calcium carbonate)

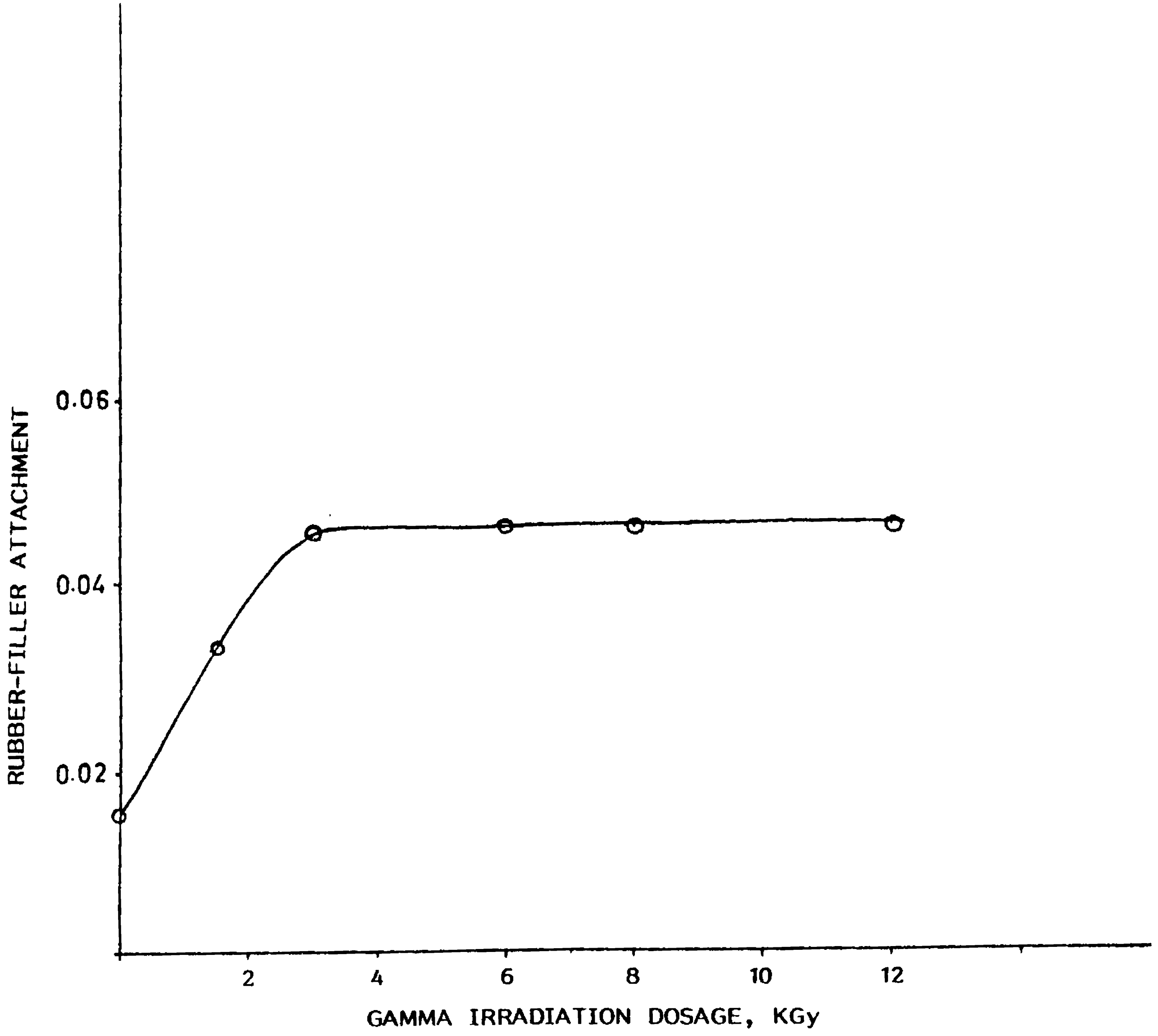


Fig. V-2(a). Effect of irradiation on rubber-filler attachment (precipitated silica)

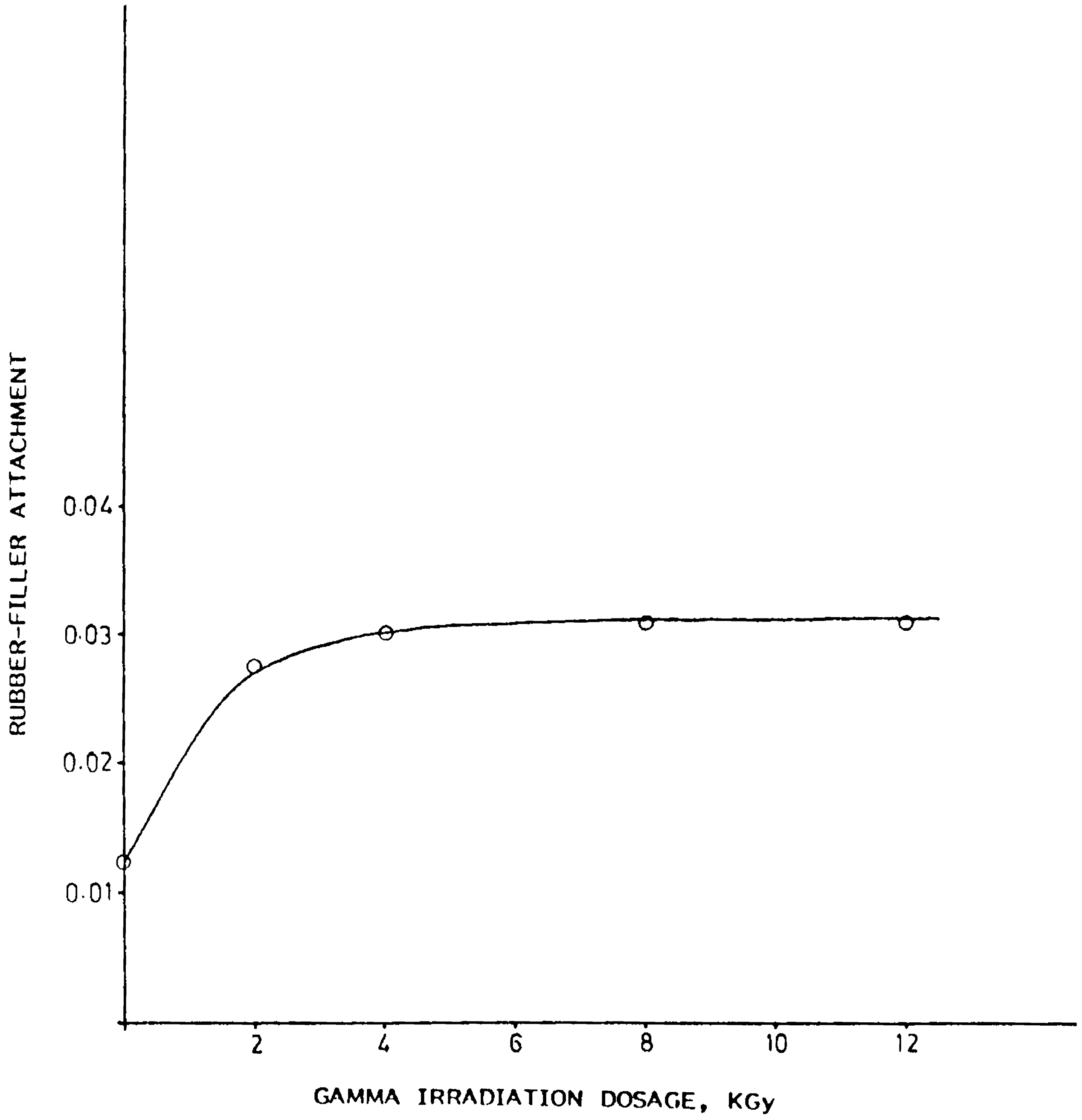


Fig. V-2(b). Effect of irradiation on rubber-filler attachment (precipitated calcium carbonate)

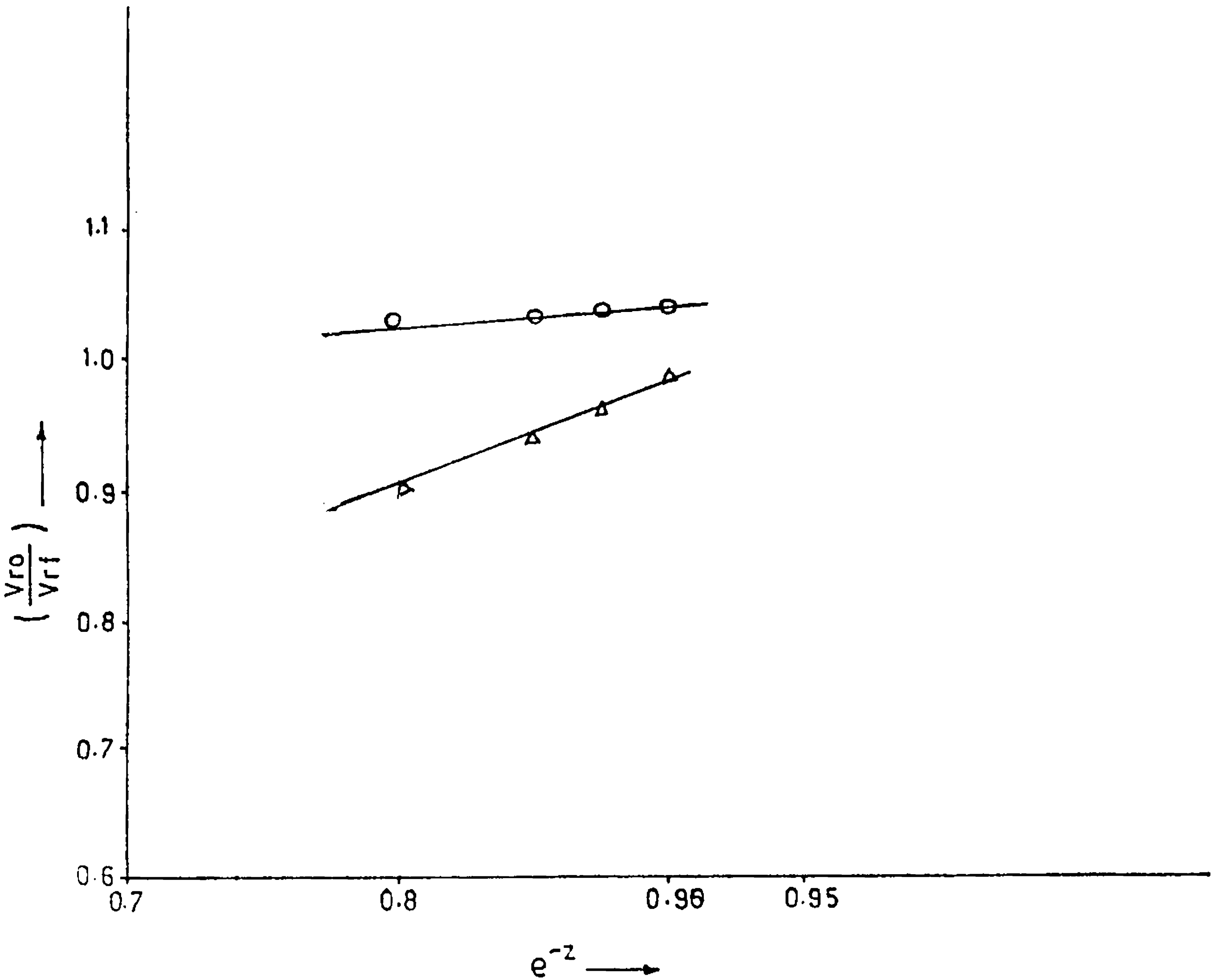


Fig. V-3(a). Plot of V_{ro}/V_{rf} Vs. e^{-z} (precipitated silica)

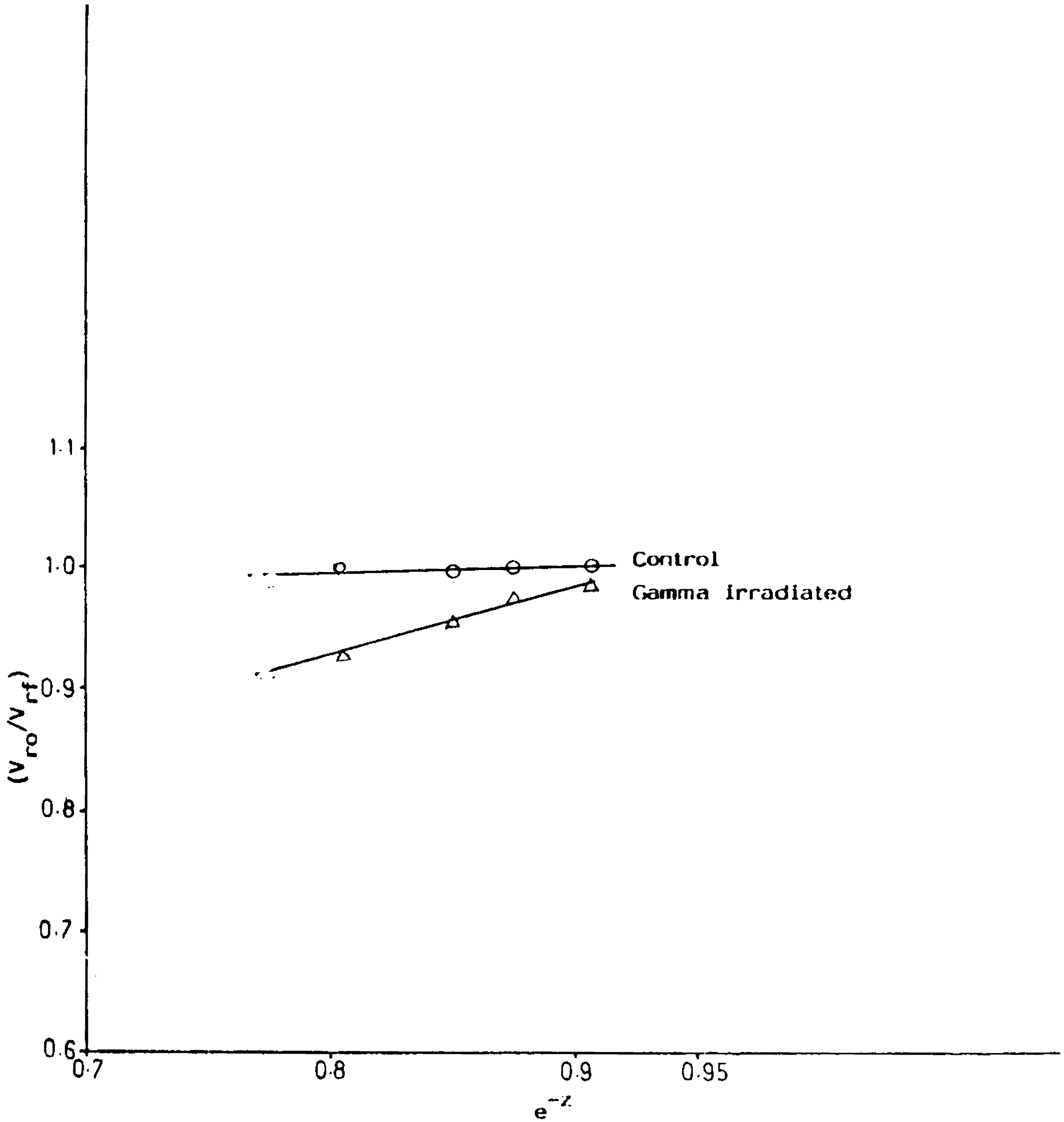


Fig. V-3(b). Plot of V_{ro}/V_{rf} Vs. e^{-z} (precipitated calcium carbonate)

PART - II EFFECT OF GAMMA IRRADIATION ON DEGRADATION OF LATEX VULCANIZATES CONTAINING DIFFERENT ACCELERATOR COMBINATIONS.

Applications of rubber components in radiation therapy, nuclear plants and medical equipments are increasing. Specially designed latex rubber catheters are also used in the treatment of tumours with radio active materials. Although much work has been done on the effect of gamma radiation on dry rubber vulcanizates[11-14], the effect of gamma radiation on degradation of latex vulcanizates has not been well studied. Not much work has been done on the effect of accelerator combinations on degradation resistance of latex vulcanizates by gamma irradiation. Thiuram disulfide, diphenyl guanidine and zinc mercaptobenzothiazole are reported to inhibit radiation crosslinking[15,16,17]. Hence these accelerators may also influence the degradation of latex vulcanizates. In polymer systems an outstanding problem is to estimate separately the effect of crosslinking and molecular degradation which proceeds concurrently. The most general method of estimating chain fracture during network formation or degradation is the analysis of sol content[18] as reported in Chapter II.

The present study is to examine the effect of different accelerator combinations under the conventional and efficient vulcanization systems on the degradation of latex vulcanizates by gamma irradiation. The extent of degradation was analysed by estimating the tensile properties, crosslink concentration (V_r) and the sol content.

Formulations of the different latex compounds are given in Tables V-4 and V-5. The latex compounds were matured for 24 h at 30°C and cast latex films of thickness 1.00 to 1.25 mm were prepared and vulcanized to the optimum level as reported earlier. The dumb bell shaped test pieces were cut from the samples and these were irradiated to different dosages of 40, 80 and 120 KGy in the Radiation Chamber having CO^{60} as radiation source. The tensile properties, crosslink concentration and sol content of the irradiated samples were then determined. The results are represented in Figures V-5 to V-8 and in Tables V-6 to V-8.

Figures V-4 and V-5 give the changes in modulus and tensile strength of the latex vulcanizates containing different accelerator combinations under conventional vulcanization systems after gamma irradiation. It can be seen that the sample with ZDC as a single accelerator (compound A) is poor in retaining the tensile properties on gamma irradiation compared to the other mixes. Among the other mixes, ZDC + DPG combination is found to be giving more retention of tensile properties than the ZDC + TMTD and ZDC + ZMBT combinations. This same conclusion can be drawn from Tables V-6 and V-7 which give the changes in the concentration of chemical crosslinks (V_r) and the sol content of their radiated samples. The reduction in concentration of chemical crosslinks was more in the sample prepared from compound A. The sol content is also found to be high in the latex sample which contained ZDC as a single accelerator.

The high amount of sol content indicated more cleavage in the molecular chain. It has been reported[17] that additives such as aromatic amines and disulphides are efficient scavengers of free radicals. Hence the above behaviour of the different accelerators under this study can be attributed to their efficiency in arresting the propagation of free radicals which contribute to the degradation process of the molecular chain.

The effect of gamma irradiation on the samples containing different accelerator combinations under efficient vulcanization systems are given in Figures V-6 and V-7 and in Tables V-6 and V-7. In this case also the mix containing DPG is found to give better resistance to radiation damage as indicated from the tensile properties of the samples in Figures V-6 and V-7. Comparatively, the mixes containing TMTD + DPG and TMTD + ZDC were found to show better radiation resistance than TMTD alone and the TMTD + ZMBT combinations. The concentration of chemical crosslinks and the sol content data of irradiated samples also confirm this.

Between the two vulcanization systems studied, it is evident that, the samples prepared from the conventional vulcanization systems are better in retaining the tensile properties (modulus and tensile strength) than the samples prepared using the low-sulfur system (efficient). The better retention in the tensile properties indicates better resistance to gamma irradiation. It has been reported[15] that the radiation resistance of sulfur vulcanizate appears to be associated with the relative amount and characteristics of crosslinks and with the amount of combined sulfur. So the above observation may be attributed to the formation of polysulphide radicals in the conventional system that can then recombine into the network. The low sol content value indicates only less main chain breakage in the samples prepared using the conventional system. In the low sulfur (efficient) system the chances for the main chain breakage was high as indicated by the high sol content values. In this case the lower amount of polysulfidic linkages may be the reason for the higher chances of main chain breakage.

The effect of non-black fillers on the radiation resistance of the latex vulcanizates was also investigated as a part of the study. Formulations of the filled latex compounds are given in Table V-8. The compounds were matured for 24 h at 30°C and cast latex films of thickness 1 to 1.25 mm were prepared and vulcanized to the optimum level. The dumb bell shaped test pieces were prepared and irradiated to different doses 40, 80 and 120 KGy. The tensile properties, crosslink concentration (V_r) and sol content of the samples were determined as described earlier. The results are represented in Figures V-8 and V-9 and Tables V-9 and V-10.

Figures V-8 and V-9 show that at low doses (40 KGy) the samples containing precipitated calcium carbonate and china clay offered better protection from radiation damage than the gum sample. The same observation can be verified from Tables V-9 and V-10 which give the 'V_r' and sol content values of the irradiated samples. At low dosages of irradiation, the V_r values of the filled samples were not affected and the sol content values are found to be low which indicates less main chain scission. The better protection from radiation of the filled samples may be due to the effect of rubber-filler interaction. However at higher dosages of irradiation significant degradation is found to occur.

Table V-4. Compound formulations (conventional system).

Sl. No.	Ingredients	Parts by weight A	B	C	D
1.	60% Centrifuged latex	167.0	167.0	167.00	167.0
2.	10% Potassium hydroxide solution	0.5	0.5	0.5	0.5
3.	10% Potassium laurate solution	1.0	1.0	1.0	1.0
4.	50% Sulfur dispersion	3.5	3.5	3.5	3.5
5.	50% Zinc diethyldithiocarbamate (ZDC) dispersion	4.0	3.0	3.0	3.0
6.	50% Zinc mercapto benzthiozol (ZMBT) dispersion	-	1.0	-	-
7.	50% Tetramethyl thiuram disulphide (TMTD) dispersion	-	-	1.0	-
8.	50% Diphenyl guanidine (DPG) dispersion	-	-	-	1.0
9.	50% Zinc oxide dispersion	0.5	0.5	0.5	0.5

Table V-5. Compound formulations (efficient system)

Sl. No.	Ingredients	Parts by weight E	F	G	H
1.	60% Centrifuged latex	167.0	167.0	167.0	167.0
2.	10% Potassium hydroxide solution	0.5	0.5	0.5	0.5
3.	10% Potassium laurate solution	1.0	1.0	1.0	1.0
4.	50% Sulfur dispersion	0.5	0.5	0.5	0.5
5.	50% Tetramethyl thiuram disulphide (TMTD) dispersion	6.0	6.0	6.0	6.0
6.	50% Zinc diethyl dithiocarbamate (ZDC) dispersion	-	3.0	-	-
7.	50% Zinc mercaptobenzthiozol (ZMBT) dispersion	-	-	3.0	-
8.	50% Diphenyl guanidine (DPG) dispersion	-	-	-	3.0
9.	20% Thiourea solution	5.0	5.0	5.0	5.0
10.	50% Zinc oxide dispersion	0.5	0.5	0.5	0.5

Table V-6. Changes in V_r values.

Compound	V_r values			
	Nil	40 KGy	80 KGy	120 KGy
A	0.205	0.195	0.189	0.180
B	0.212	0.204	0.200	0.196
C	0.225	0.220	0.215	0.210
D	0.228	0.220	0.216	0.214
E	0.180	0.173	0.170	0.166
F	0.230	0.212	0.202	0.200
G	0.220	0.200	0.190	0.185
H	0.237	0.217	0.207	0.204

Table V-7. Changes in sol content (%)

Compound	Sol content (%)		
	40 KGy	80 KGy	120 KGy
A	0.473	0.800	1.80
B	0.245	0.700	1.20
C	0.170	0.500	1.05
D	0.150	0.500	1.00
E	1.700	2.501	4.411
F	1.512	2.401	4.201
G	1.602	2.611	4.950
H	1.400	2.200	3.623

Table V-8. Compound formulations of filled latex compounds.

Sl. No.	Ingredients	Gum	Filled	
		I	J	K
1.	60% Centrifuged latex	167.0	167.0	167.0
2.	10% Potassium hydroxide solution	0.5	0.5	0.5
3.	10% Potassium laurate solution	1.0	1.0	1.0
4.	50% Sulfur dispersion	3.5	3.5	3.5
5.	50% ZDC dispersion	4.0	4.0	4.0
6.	50% Zinc oxide dispersion	0.5	0.5	0.5
7.	50% Precipitated calcium carbonate dispersion	-	50	-
8.	50% China clay dispersion	-	-	50

Table V-9. Changes in V_r values.

Compound	V_r values			
	Nil	40 KGy	80 KGy	120 KGy
I (gum)	0.206	0.200	0.195	0.190
J (precipitated calcium carbonate)	0.200	0.210	0.205	0.192
K (china clay)	0.202	0.209	0.200	0.194

Table V-10. Changes in sol content (%)

Compound	Sol content (%)		
	40 KGy	80 KGy	120 KGy
I	0.60	0.81	1.70
J	0.30	0.60	1.40
K	0.29	0.62	1.50

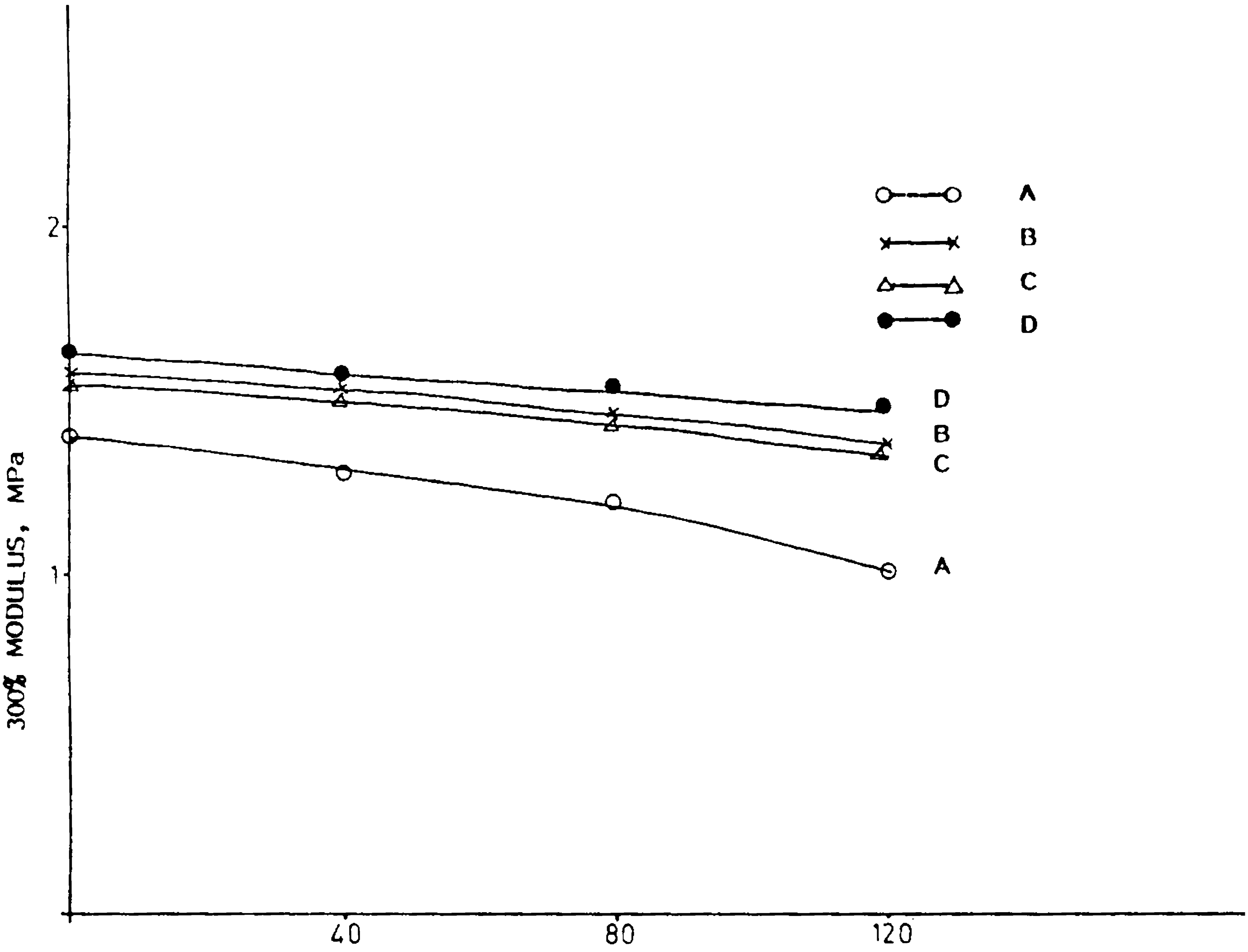


Fig. V-4. Effect of irradiation on modulus of latex vulcanizates (conventional systems)

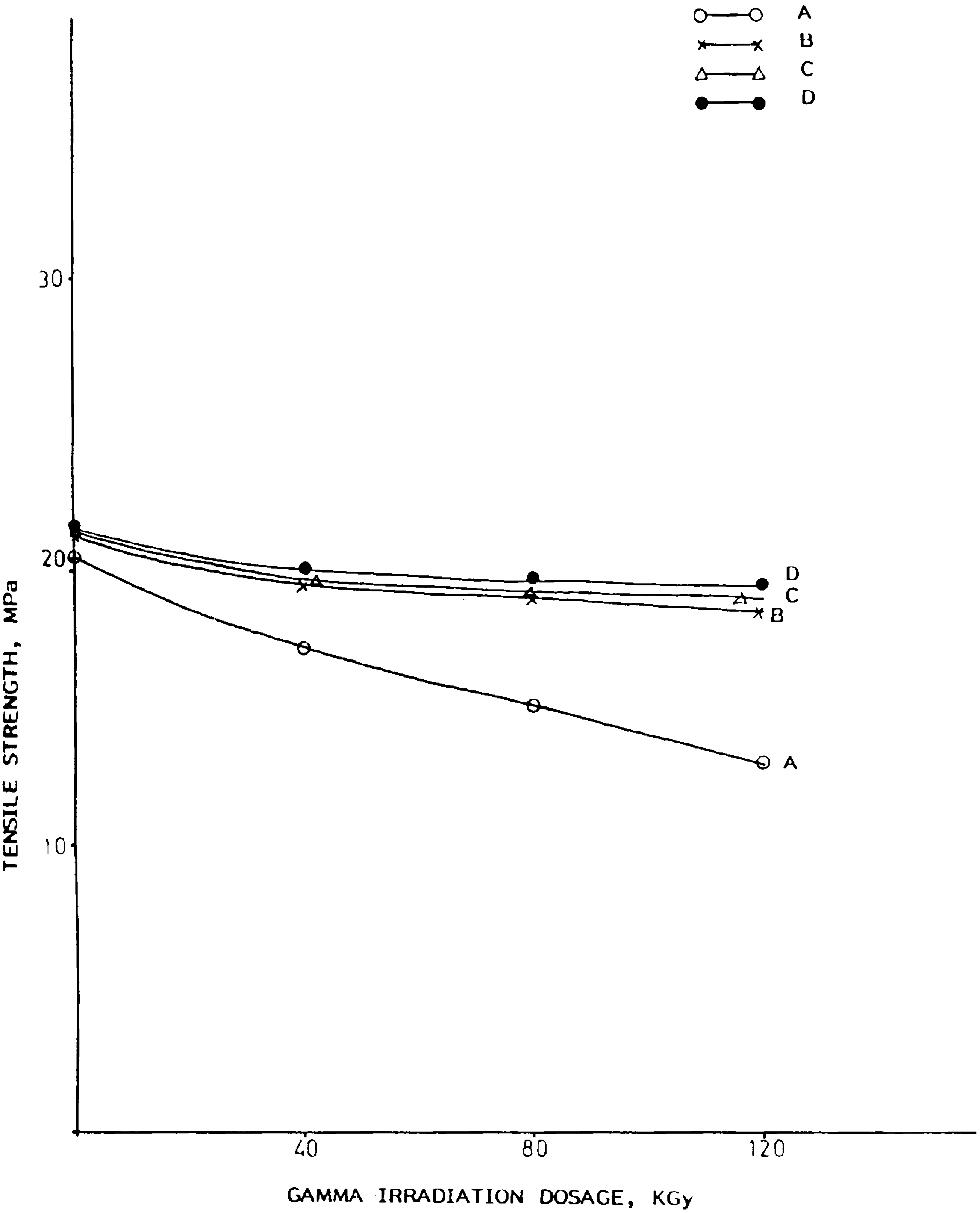


Fig. V-5. Effect of irradiation on tensile strength of latex vulcanizates (conventional systems)

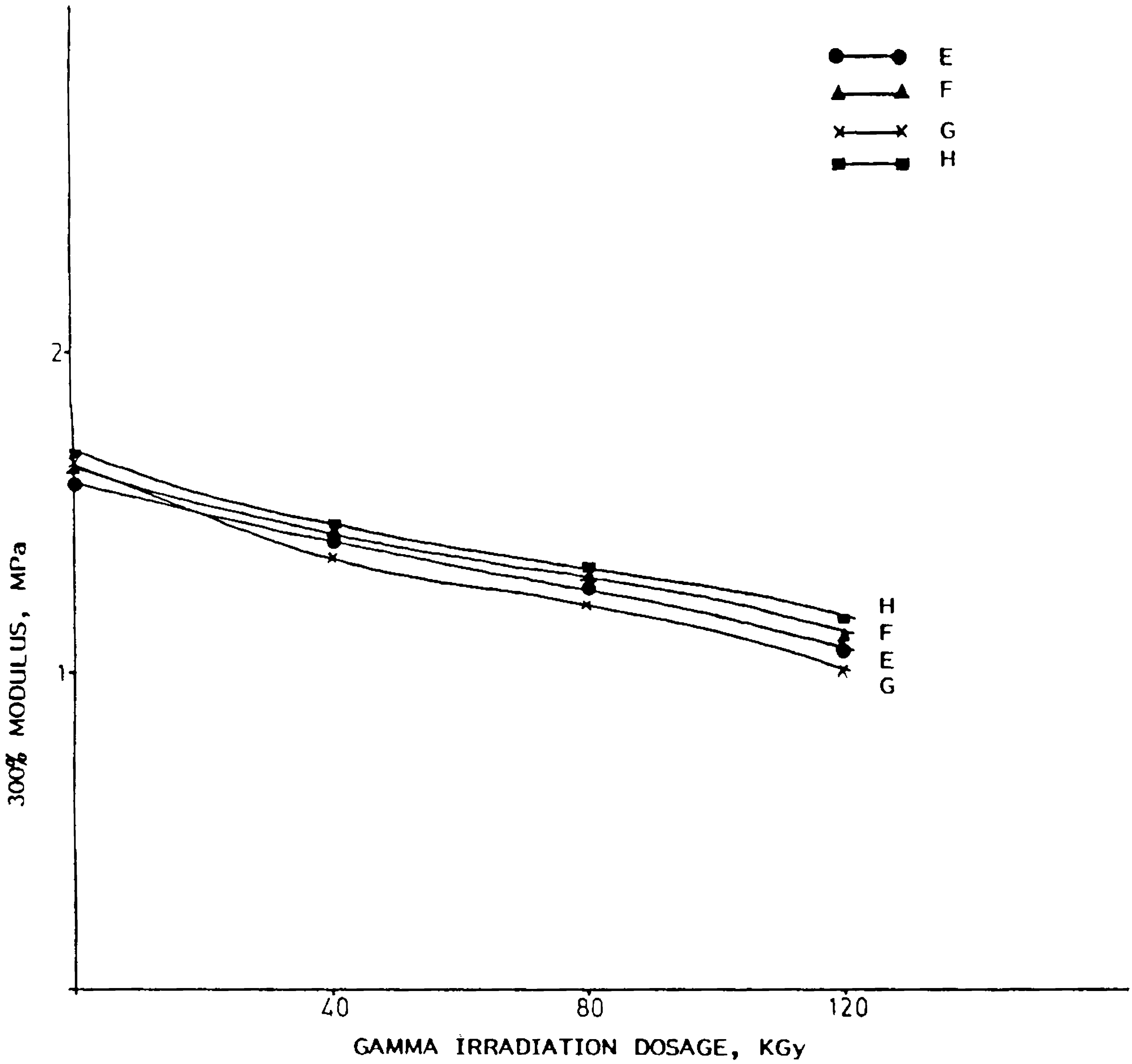


Fig. V-6. Effect of irradiation on modulus of latex vulcanizates (efficient system)

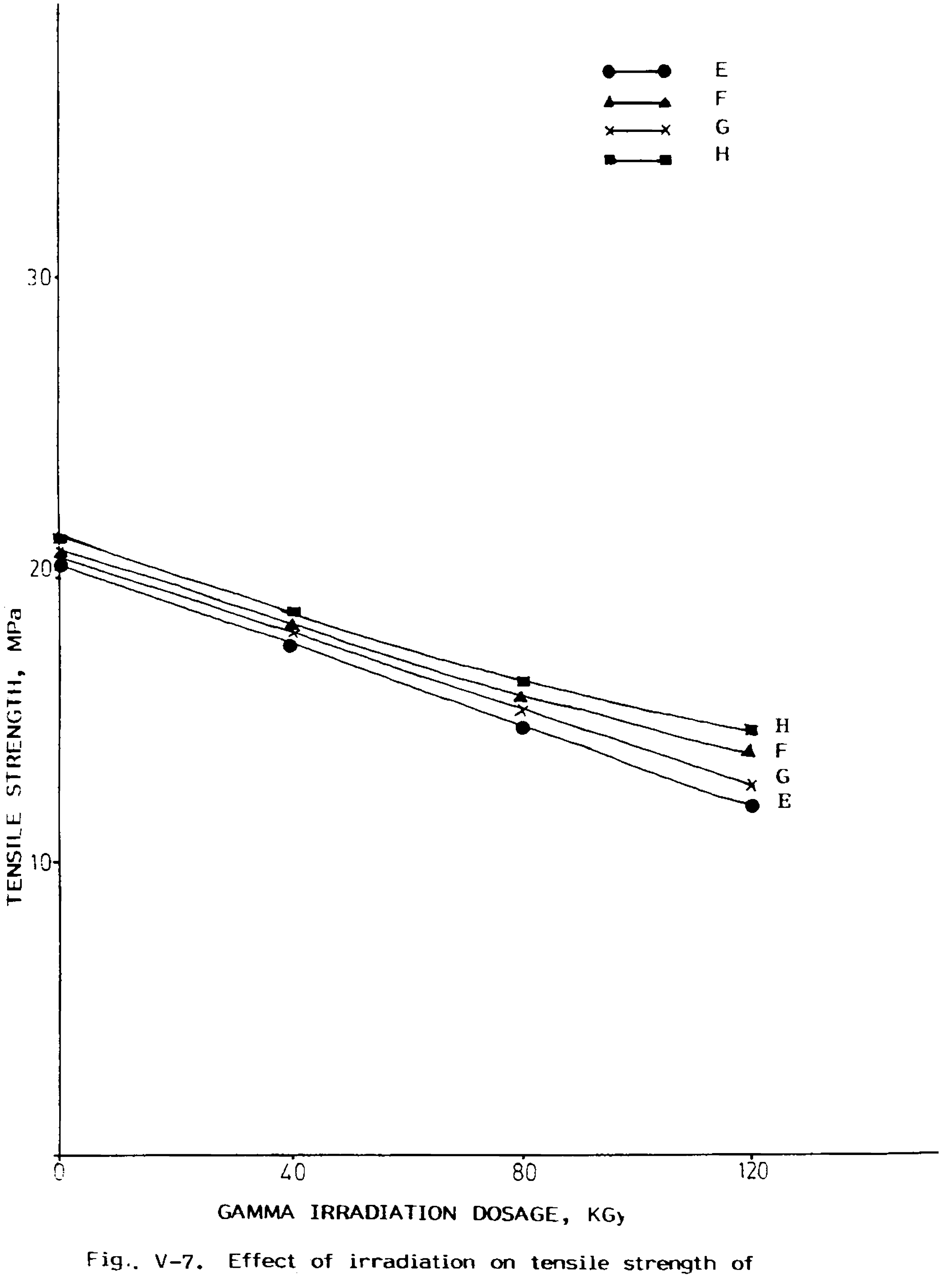


Fig.. V-7. Effect of irradiation on tensile strength of latex vulcanizates (efficient systems)

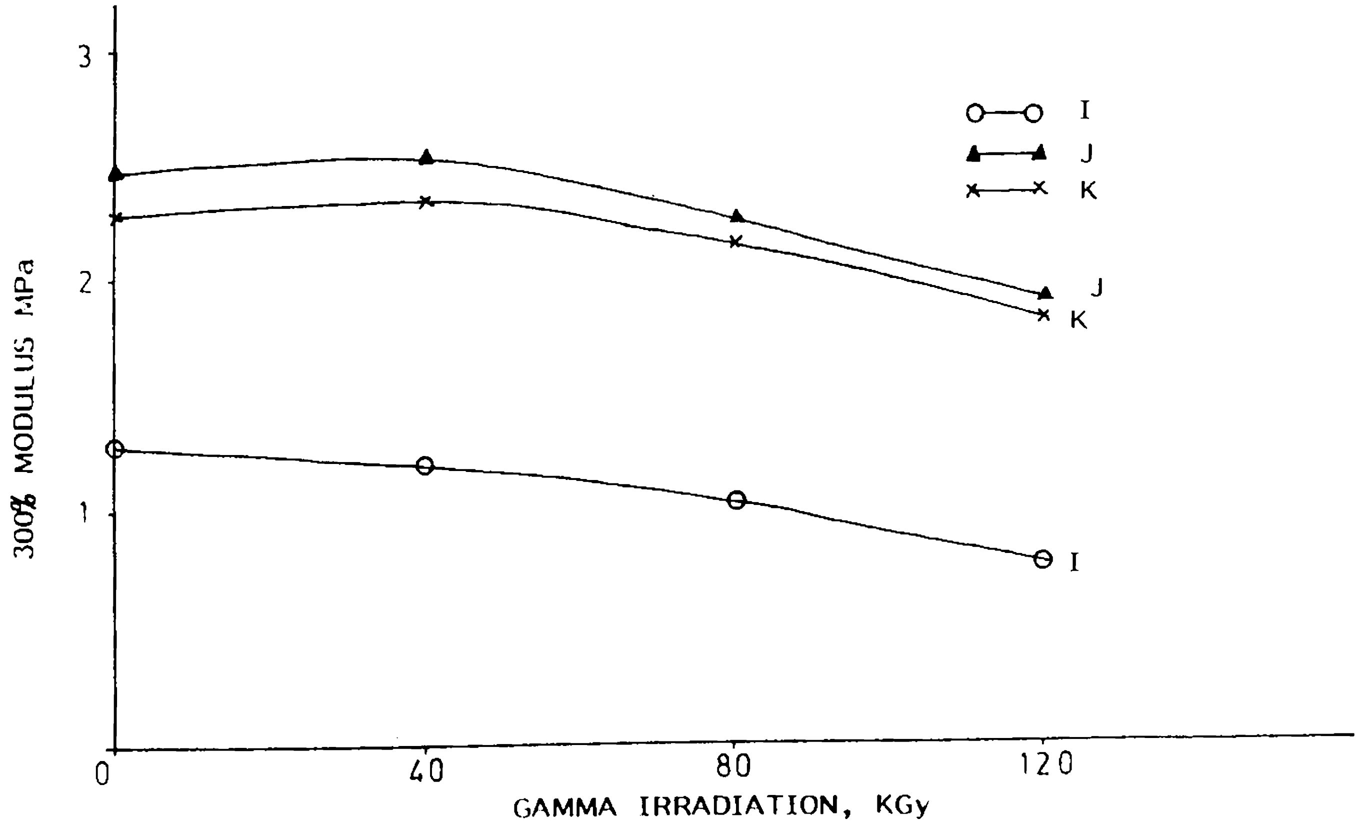


Fig. V-8. Effect of irradiation on modulus of filled latex vulcanizates

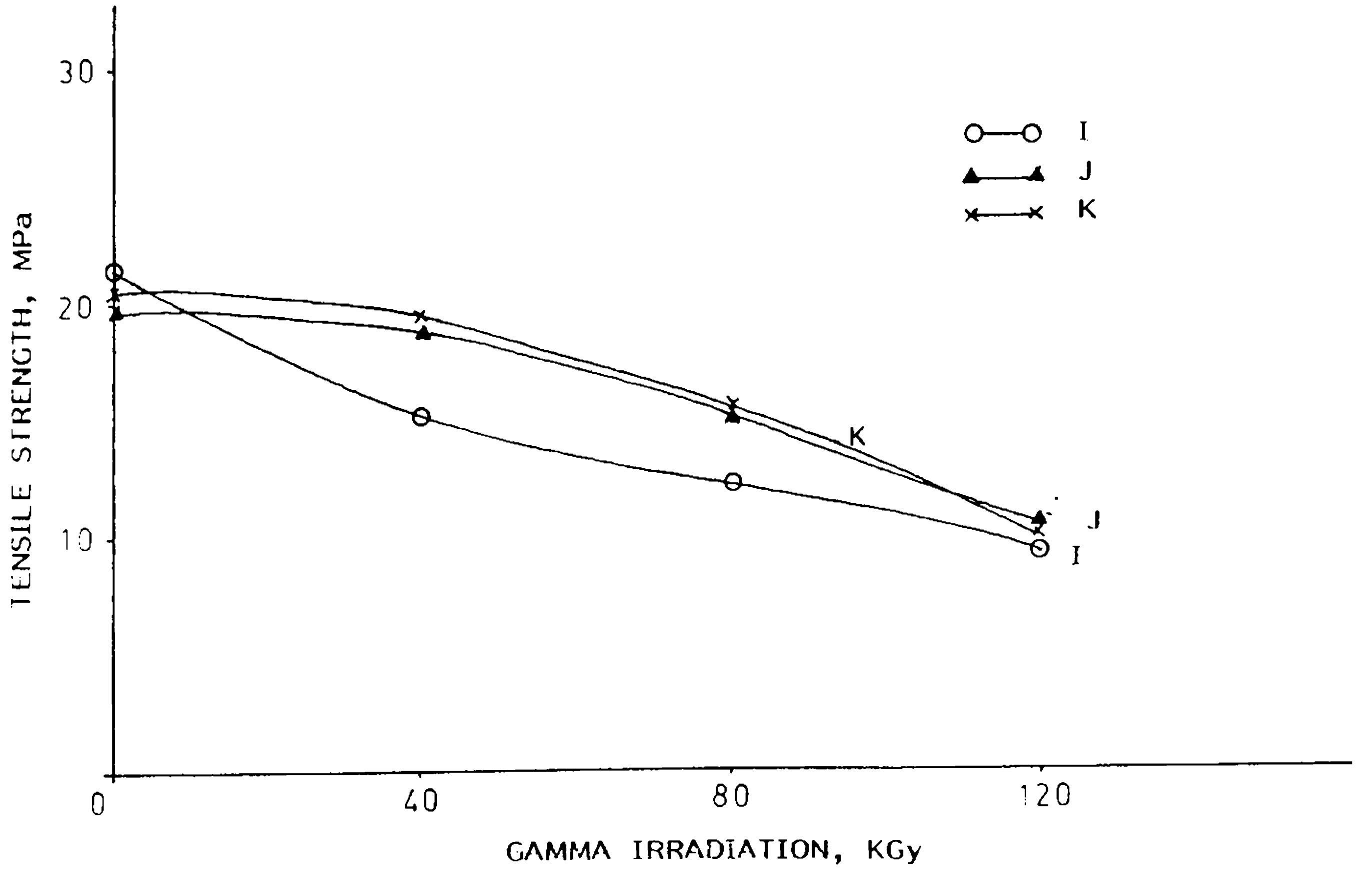


Fig. V-9. Effect of irradiation on tensile strength of filled latex vulcanizates

REFERENCES

1. R.J. Noble, Latex in Industry, Rubber Age, New York (1953) 216.

2. D.C. Blackley, High Polymer Latices, Applied Science Publishers, London (1960) 210.

3. B.A. Dogadkin, L.G. Senatorskoya, L.G. Guseve, A.V, Sublyakove and P.I. Zakharchenko, Rubber. Chem. Technol. 31 (1958) 655.

4. A. Lamm and G. Lamm. Rubber Chem. Technol. 35 (1962) 848.

5. G. Kraus and R.L. Collins, Rubber World, 139 (1958) 219.

6. W.F. Waston, Ind. Engg. Chem. 47-6 (1955) 1281.

7. K. Sumarno and F. Sundardi, J. Appl. Polymer Science, 21 (1977) 3077.

8. J.I. Cunneen and R.M. Russel, Rubb. Chem. Technol. 43 (1970) 1215-1224.

9. Y. Sato and J. Furakava, Rubber Chem. Technol. 36 (1963) 1081.

10. D.S. Pearson and G.A. Bohm, Rubber Chem. Technol. 45-1 (1972) 193.

11. H.R. Anderson, Rubb. Chem. Technol. 34 (1961) 228.

12. W.E. Shelberg and L.H. Gevantman, Rubb. Chem. Technol. 34 (1961) 250.

13. M. Ito, S. Odaka and I. Kuriyama, J. Meter. Sci. 16 (1981) 10.

14. R. Alex, N.M. Mathew and S.K. De, J. Radiat. Physics Chem. 33, 2 (1989) 91-95.

15. J. Blackford and R.G. RObertson, J. Polym. Sci. 2 (1965) 1325.

16. G. Kraus and R.L. Collins, Rubb. World. 139 (1958) 219.

17. D.T. Turner, J. Polym. Sci. 27 (1958) 503.

18. G.M. Bristow, J. Apply. Polym. Sci. 7 (1963) 1023.

CHAPTER - VI

SUMMARY AND CONCLUSIONS

In the present work, studies on vulcanization, rheology and reinforcement of natural rubber latex with special reference to accelerator combinations, surface active agents and gamma irradiation have been undertaken. In vulcanization, the choice of vulcanization system, the extent and mode of vulcanization and network structure of the vulcanizate are important factors contributing to the overall quality of the product. The vulcanization system may be conventional type using elemental sulfur or a system involving sulfur donors. The latter type is used mainly in the manufacture of heat resistant products. For improving the technical properties of the products such as modulus and tensile strength, different accelerator combinations are used. It is known that accelerators have a strong effect on the physical properties of rubber vulcanizates. But the effect of accelerator combinations on physical properties, network structure and ageing of latex vulcanizates have not been studied in a systematic way. Normally when fillers are added to latex they weaken the rubber film rather than strengthening it. But very little study has been reported on the reinforcement of natural rubber latex by non-black fillers which are commonly used in latex compounding. Therefore improving the strength of latex vulcanizates by the incorporation of fillers is an area which requires careful study. The latex compound is non-Newtonian in its flow behaviour and it varies with shear rate and temperature. Different surface active materials are used in latex compounding as stabilizers and viscosity modifiers which can affect the flow behaviour of the latex compounds. The rheological behaviour of latex compounds are very important in controlling the thickness of latex film in dipping, the count of latex thread in extrusion, etc. Gamma irradiation has got effect both in crosslinking and degradation of latex vulcanizates. As irradiation of polymer molecule produces free radicals, it has got effect in rubber-filler interaction also. The effect of gamma irradiation has a bearing on the added ingredients such as fillers, accelerators and sensitisers.

A perusal of the literature indicates that fundamental studies on the above aspects of latex technology are very limited. Therefore a systematic study on vulcanization, rheology and reinforcement of natural rubber latex with reference to the effect of accelerator combinations, surface active agents and gamma irradiation has been undertaken. The preparation and evaluation of some products like latex thread was also undertaken as a part of the study.

The thesis consists of six chapters. The first chapter gives a general introduction and a brief account of the earlier work in the field of vulcanization rheology and reinforcement of natural rubber latex.

The second chapter gives an account of the experimental procedures adopted in the present work.

The third chapter describes the effect of different accelerator combinations under conventional and efficient vulcanization systems on cure rate index, network structure and physical properties of natural rubber latex vulcanizates. The accelerator combinations are based on zinc diethyldithiocarbamate (ZDC), zinc mercaptobenzothiazole (ZMBT), tetramethyl thiuramdisulfide (TMTD) and thiourea. Twelve different combinations were investigated. The cure rate of the compounds and network structure of the vulcanizates were studied using latex film. The physical properties and ageing resistance of a typical latex product viz. latex thread which has a low bulk volume and large surface area was investigated using these compounds. It is observed that the cure rate index and the proportion of polysulfidic linkage is influenced by the accelerator combination in each system. In the conventional systems, ZDC-ZMBT combination gave better ageing resistance than ZDC-TMTD system. In the case of efficient vulcanization systems, ZDC-TMTD system was found to be better than ZMBT-TMTD system in retaining the tensile properties after ageing. The percentage of polysulfidic content and the cure rate index of the different systems are found to control the ageing resistance.

Effect of accelerator combinations on the rate of prevulcanization, network structure and flow properties has been reported in the second part of this chapter. The evaluation of processing and technical properties of latex thread prepared using prevulcanized latices is also included. Six different accelerator combinations were tried to evaluate their effect on rate of prevulcanization and on technical properties. The latex compounds were prevulcanized to different extent and the effect of prevulcanization on flow properties and network structure was studied. It is observed that under conventional systems, the reaction rate of the accelerator ZDC is activated by the incorporation of ZMBT and TMTD. The ZDC-TMTD system is having a higher reaction rate than ZDC-ZMBT system. In the former system, the majority of crosslinks are formed in about one and half hour at 70°C and in the latter it took 3 h. This may be attributed to the positive synergistic effect of the combination of two ultra accelerators ZDC and TMTD in the vulcanization. In the efficient systems, ZDC-TMTD combination is faster compared to ZMBT-TMTD system in the formation of chemical cross-links. As the extent of prevulcanization increased, the viscosity of the latex compound increased in all the systems under study; the viscosity variation was almost the same. Determination of the viscosity under different shear rates showed that the flow behaviour of the latex compound is little affected by prevulcanization. The percentage polysulfidic linkages was also found to be higher in the prevulcanized samples. In the case of latex thread preparation, the prevulcanised latex compounds are found to be better in extrusion and subsequent processing with respect to uniformity in count and is free from tackiness. Tensile strength and modulus of the threads are improved up to a certain extent of prevulcanization of the latex compound and above that level the properties decreased. The low tensile properties for the thread from latex compound having a higher extent of prevulcanization may be attributed to lower inter-particle fusion. One peculiarity with latex thread production is that a limited level of stretching at the wet gel stage occurs during processing and this in combination with low inter-particle cohesion of the wet gel may be one of the reasons for this low tensile strength.

The fourth chapter describes the effect of surface active agents on rubber-filler interactions and on rheology of the rubber latex. The surface active agents studied are casein, polyvinyl alcohol (PVA), sodium alginate and sodium carboxymethyl cellulose

(NaCMC). It was observed that rubber-filler interaction is improved by treatment with surface active agents such as casein and polyvinyl alcohol. But with sodium alginate and NaCMC, not much improvement has been noted. For the study of rubber-filler interaction, fillers used are precipitated silica, precipitated calcium carbonate and china clay. The rubber-filler attachment may be formed due to the interaction of polyvinyl alcohol or casein with the protective layer in the rubber and filler particles. During the interaction, partial desorption of protective layer on the rubber and filler particles may takes place leading to direct contact between the filler and rubber particles. It can also be pointed out that polyvinyl alcohol is more surface active than casein and the surface activity of the sodium alginate and NaCMC are very mild. Due to better rubber-filler interactions the tensile properties of the samples are improved.

The second part of this chapter deals with the rheological behaviour of natural rubber latex in the presence of surface active agents and fillers. Both centrifuged and creamed latices were used for the study. The viscosity of these latices were measured at different shear rates and temperature. The study was made at three different temperatures, ie. 25°C, 35°C and 45°C which are the normal range of temperatures for latex goods manufacture. It is found that creamed latex is more sensitive to shear rate and temperature than centrifuged latex. The pseudoplasticity and viscosity of the latices increased by the addition of surface active agents and the effect varies with the type of surface active agent used. Among the surface active agents, NaCMC offers the highest viscosity at low and high shear rates. Polyvinyl alcohol (PVA) offers a higher viscosity than casein at low shear rates but as the shear rate increases the PVA offers a lower viscosity than casein. This may be due to the easier displacement of the adsorbed layer of PVA from the surface of the rubber particles at higher shear rates. It is also noted that eventhough sodium alginate increased the viscosity of centrifuged latex, it has not affected the general behaviour of centrifuged latex towards heat. Among the surface active agents, PVA imparts the highest sensitivity to heat for the viscosity of the latex compound. But casein offers a peculiar behaviour towards heat. In the lower temperature range (25-35°C) the reduction in viscosity of the centrifuged latex is of the same rate as that of the untreated one. But at higher temperature range there is marked reduction in viscosity. This may be attributed to the alteration in water binding of casein at higher temperature, which in turn affects the apparent viscosity of the casein solution.

The viscosity of the latex compounds is found to increase by the addition of silica and china clay and it can be seen that at low shear rates the filled latex compounds show a much higher viscosity than the unfilled one. The difference, however, disappears at high shear rates.

The fifth chapter deals with the effect of gamma irradiation on rubber-filler interaction and on degradation of natural rubber latex vulcanizates. The rubber-filler interaction was studied using precipitated silica and precipitated calcium carbonate as fillers. Gamma irradiation of the filled latex compounds improved the rubber-filler interaction considerably and offered better technical properties. The optimum dosage of irradiation is also derived at and is found to be 3 KGy. Sensitisers have no effect in improving rubber-filler interaction. It was also found that the content of polysulfidic linkages and heat ageing resistance of the vulcanizates remained unaffected at the optimum level of irradiation. The increase in rubber-filler interaction on irradiation is attributed to the formation of coupling bonds between rubber and filler particles.

The second part of this chapter deals with the degradation of natural rubber latex vulcanizates by gamma irradiation. Even though in the previous part of this chapter a positive effect of gamma irradiation is reported; it can also degrade a latex film. But for degradation higher dosages (40 KGy-120 KGy) of radiation will be required. But it is observed that by changing the vulcanization system using various accelerator combinations the resistance of latex vulcanizates to degradation can be varied. The accelerator combinations selected for the present study are based on ZDC, ZMBT, TMTD, thiourea and DPG. In the conventional systems, ZDC + DPG and ZDC + TMTD gave better radiation resistance than

ZDC + ZMBT and ZDC system. In the efficient vulcanization systems, TMTD + DPG and TMTD + ZDC are found to be better in retaining the tensile properties than the TMTD + ZMBT system. It is also noted that in the degradation of latex vulcanizates by gamma irradiation, efficient vulcanization system has no added advantage. In fact from the sol content data, the conventional vulcanization systems are found to be better than the efficient vulcanization systems for getting better resistance from radiation. It is also found that non-black fillers such as precipitated calcium carbonate and china clay provide protection for latex vulcanizates from degradation by gamma irradiation up to about 40 KGy.

LIST OF PUBLICATIONS FROM THE PRESENT WORK

1. Effect of vulcanization systems on the chemical characteristics and physical properties of natural rubber latex thread.

   - Journal of Plastics and Rubber Processing and Applications, UK. **11**(3) 1989, 179-183.

2. Effect of pre-vulcanization of natural rubber latex on the chemical and physical properties of latex thread.

   - Journal of Applied Polymer Science, USA (in press).

3. Effect of surface active agents on rubber-filler interaction in silica filled natural rubber latex vulcanizates.

   - Indian Journal of Natural Rubber Research, 1(2), 1988, 1-9.

4. Rheological behaviour of natural rubber latex in the presence of surface active agents.

   - Journal of Applied Polymer Science, USA (in press).

5. Effect of gamma irradiation on rubber filler-interaction in silica filled natural rubber latex vulcanizates.

   - Koutschuk Gummi, Kunststoffe, West Germany (in press).