STUDIES ON PREVULCANIZATION OF RUBBER LATEX WITH SPECIAL REFERENCE TO INFLUENCE OF STORAGE AND AFTER TREATMENTS ON PROPERTIES OF FILMS

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COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
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DOCTOR OF PHILOSOPHY

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CERTIFICATE

Certified that the thesis entitled "Studies on prevulcanization of rubber latex with special reference to influence of storage and after treatments on properties of films", being submitted by Mrs. N.M. Claramma, M.Sc, for the degree of **Doctor of Philosophy** to the Cochin University of Science and Technology, is a record of bonafide research work carried out by her under my supervision and guidance.

Mrs. Claramma has worked on this research problem for about seven years. The results included in this thesis have not been submitted for the award of any other degree or diploma. It is also certified that Mrs. Claramma has fulfilled the necessary requirements for submission and has passed the qualifying examination.

N.M. Mathew.

DECLARATION

I hereby declare that the thesis entitled *"Studies on Prevulcanization of Rubber Latex with Special Reference to Influence of Storage and After Treatments on Properties of Films"* is the original work carried out by me under the supervision of Dr. N.M. Mathew, Joint Director, Rubber Research Institute of India, Kottayam- 686009, and no part of this thesis has been presented for any other degree from any other institution.

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LIST OF ABBREVIATIONS

Polymers

NR - Natural rubber
HA latex - High ammonia latex
LATZ latex - Low ammonia latex containing tetramethylthiuram disulphide and zinc oxide.
PVL - Prevulcanized latex

Additives

S - Sulphur
ZnO - Zinc Oxide
ZDC - Zinc diethlydithiocarbamate
TMTD - Tetramethylthiuram disulphide
SP - Styrenated phenol
NaCMC - Sodium carboxymethyl Cellulose
PVA - Polyvinyl alcohol

Other abbreviations

ASTM - American Society for Testing Materials
IS - Indian Standards
rpm - revolutions per minute
phr - parts per hundred rubber
MPa - MegaPascal
mPa s - milliPascal second
SEM - Scanning Electron Microscope
DRC - Dry Rubber Content
TSC - Total Solids Content
MST - Mechanical Stability Time
VFA - Volatile Fatty Acids

List of symbols

UV - Ultra Violet

Vr - Volume fraction of rubber network

ρ_r - Density of rubber

ρ_s - Density of solvent

η - Viscosity

$\dot{\gamma}$ - Shear rate

τ - Shear stress

K - Viscosity index

n - Flow index

σ_t - Stress at time t

σ_0 - Initial stress

CHAPTER 1

INTRODUCTION

Natural rubber latex is one of the most versatile of nature's vegetable products. It was only by about 1921 that the importance of rubber latex as a raw material was recognized in its own right. As methods were developed for preserving and transporting latex from tropical areas economically, a separate technology of latex developed. Several methods of concentrating latex encouraged these developments.

Natural rubber latex concentrates have been commercially available since about 1930 and subsequently have been thoroughly exploited for the manufacture of a great variety of products.[1] Natural rubber latex is now readily available anywhere in various forms and at different concentrations for the direct use not only in the manufacture of rubber goods, but in a variety of new uses.

The invention of the vulcanization process in 1839 opened up great possibilities for the rubber industry. It has a crucial role in economical production of quality goods from rubber. The development of organic accelerators that permit rapid curing of latex and the widespread dissemination of knowledge pertaining to colloidal chemistry, gave considerable impetus to the manufacturing technology of latex goods.

In the last thirty years consumption of natural rubber latex concentrates has increased steadily, and the types of products made from it have undergone radical changes. Now natural rubber latex is predominantly employed in those applications for which its supreme film forming ability and high gel strength make it the material of choice. Dipped goods, latex thread, foam and adhesive industries remain as its major consumers.

NATURAL RUBBER LATEX

Hevea brasiliensis tree is the most important commercial source of natural rubber latex. On controlled wounding of the bark of the tree (tapping) latex exudes spontaneously,[2] which is collected and processed. Natural rubber latex is a white opaque liquid 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}. Its viscosity is variable.

✓ Composition of latex

Rubber latex is a dispersion of very fine particles of rubber in serum. Rubber particles make up 30 to 40 per cent of the whole volume. The rubber hydrocarbon in latex is predominantly cis-1, 4 - polyisoprene with a molecular weight in the region of one million.[1] The molecules are heterogeneous with respect to molecular weight.[3] Rubber hydrocarbon occurs as molecular aggregates in the form of discrete particles of diameter ranging from about 0.015 to 3.00 microns[4] with the majority having 0.10 microns.[5] Rubber particles are usually spherical in shape but sometimes oval or pear shaped.[6] They are surrounded by a protective layer of proteins and phospholipids which imparts the lyophilic colloidal nature to latex and the stability of latex is mainly due to the negative electric charge present on the protective layer.[4]

Excluding rubber and water, the substances present in fresh latex are mainly carbohydrates, proteins, lipids and inorganic salts.[4] The total protein content is approximately 1 per cent by weight of which about 20 per cent is adsorbed on the surface of the rubber particles and the rest dissolved or dispersed in the serum. The lipids consist of fats, waxes, sterols, sterol esters and phospholipids[4] and their total content is about 0.9 per cent. Carbohydrates constitute about 1 per cent by weight of the whole latex. The total concentration of inorganic materials is about 0.5 per cent, the main ions being those of potassium, magnesium, copper, iron, sodium, calcium and phosphate.[4]

Preservation of latex

Latex in the latex vessels of rubber tree is sterile, but as it comes out, it gets contaminated by bacteria and yeast.[2] These organisms proliferate at the expense of the non-rubber constituents of latex, producing organic acids capable of coagulating latex.[7] Thus on keeping, latex gradually gets coagulated. At a later stage, putrefaction sets in, with the development of bad odours. Therefore, fresh latex cannot be kept for long periods without adding preservative.[8-10]

Ammonia is the first and even now the most popular preservative for NR latex. For long term preservation of field latex a minimum of 1 per cent ammonia and for concentrated latex about 0.7 per cent ammonia are required.

But ammonia has the disadvantage that to function as a bactericide, it is necessary to use ammonia at a high concentration causing strong odour, handling difficulties, pollution problems and processing problems like zinc oxide thickening. An additional deammoniation step during product manufacture may become necessary in certain cases. Therefore, attempts have been made to develop low ammonia preservation systems.[11,12] A commonly used low ammonia system is LATZ which consists of 0.2 per cent ammonia, 0.0125 per cent each of tetramethylthiuram disulphide (TMTD) and zinc oxide and 0.05 per cent lauric acid.[13,14]

Concentration of latex

Preserved field latex is unsuitable for most latex applications as its rubber content is low. For most product manufacturing processes, a high DRC latex is essential.[2]

The important methods of concentration of preserved field latex are evaporation, creaming, centrifuging and electrodecantation. 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 non-rubber constituents and the particle size distribution of the concentrate differs from that of the initial latex because a proportion of the smaller particles are eliminated in the serum. In India, only centrifuging and creaming are used for the production of latex concentrates.

Properties of concentrated latex

Requirements of composition and physico-chemical properties of centrifuged natural rubber latex are given in IS: 5430 - 1981. Requirements for creamed, ammonia preserved natural rubber latex are given in IS: 13101 - 1991.

Latex properties of significance to the user are dry rubber content (DRC), non-rubber solids (NRS) content, mechanical stability time (MST), volatile fatty acid (VFA) number, potassium hydroxide (KOH) number and alkalinity. The significance of these properties have been discussed by Blackley.[15] Latex concentrate is a non-Newtonian fluid and its viscosity decreases with increasing shear rate.[16] Natural rubber latex has a measurable electrical conductivity due to the salts dissolved in the aqueous phase.[1]

LATEX COMPOUNDING

Rubber particles in natural latex are polydisperse and of colloidal size. Because of the presence of alkali, the pH of latex is frequently in the range of 9 - 12. The conversion of NR latex into a product is accomplished in many ways. In all latex processes a stable colloidal system is maintained until it is desired to be destabilized and converted to a solid product.[17] Ingredients for a latex compound are selected so as to achieve the desired processing behaviour and product properties. The different ingredients used in a latex compound are (a) surface active agents, (b) vulcanizing agents, (c) accelerators, (d) activators, (e) antioxidants, (f) fillers and (g) special additives. The water soluble materials are added as solutions, insoluble solids as dispersions and insoluble liquids as emulsions.[17] The particle size of dispersions and the droplet size of emulsions should, as far as possible, be comparable with that of latex for getting uniform distribution in the latex compound.[18,19] Further, the colloidal stability of the dispersions and emulsions, their pH etc., should be comparable with those of latex for maintaining the colloidal stability of the final mix.

Surface active agents

Surface active agents are substances which bring about marked modifications in the surface properties of aqueous media, even though they are present only in very small amounts (of the order of 1% or less). These substances are of great importance in the technology of polymer latices and in this respect latex technology differs much from that of dry polymers and polymer solutions.[20] All chemicals that are used as stabilizers, dispersing agents, emulsifiers, wetting agents, foam promoters, foam stabilizers, viscosity modifiers and protective colloids come under this group. Chemically they can be classified as anionic, cationic, amphoteric and non-ionogenic types.[20] Anionic surface active agents have the characteristic that their surface activity is attributed to an anion, while in cationic surface active agents the activity is due to a cation. In both cases the active group contains a hydrocarbon part which is non-polar and an ionic part which is polar and carries an electric charge. The activity of amphoteric types depends on the pH of the solution, and the non-ionogenic types do not give rise to any ion formation. Usually anionic surface active agents are used. The dispersing agents prevent the dispersed particles from re-aggregating. Alkyl sulphonates are used for this. Emulsifying agents are used to make miscible two liquids which are normally immiscible. Soaps, usually oleates, formed *in situ*, function as emulsifying agents. Wetting agents are used to reduce the interfacial tension between two surfaces. Many of the stabilizers and dispersing agents are good wetting agents also. Proteins, alginates, cellulose derivatives and polyvinyl alcohol are used as viscosity modifiers and protective agents in the processing of latex compound.[20]

Vulcanizing agents

The normal vulcanizing agent for natural rubber latex is sulphur. Thiuram polysulphides such as tetramethylthiuram disulphide is used as curative in latex compounds which require specific properties such as heat resistance and non-staining of metal parts by sulphur. According to Philpott[21] certain sulphur containing compounds, notably thiourea, are able to activate vulcanization by thiuram polysulphides. It has been reported by Dunn[22] that butyl xanthogen disulphide in conjunction with a zinc dithiocarbamate, may be used to vulcanize natural rubber latex films in the absence of additional sulphur. Organic peroxides and hydroperoxides may also be used to vulcanize natural rubber latex films.[20]

Accelerators

The most important classes used in latex compounding are the metallic and amine dialkyldithiocarbamates.[20] The thiazoles and to a lesser extent the thiurams are of importance as secondary accelerators to be used in conjunction with dithiocarbamates. The metal xanthates also find limited application.

Dithiocarbamates:-

A considerable range of accelerators is available, but zinc diethyldithiocarbamate (ZDC) is the most widely used. ZDC is active in latex mixes even in the absence of zinc oxide and it activates thiazole accelerators.[23]

Thiazoles:-

Although thiazoles are insufficiently active to be used on their own, they function as secondary accelerators for the dithiocarbamates, giving vulcanizates of high modulus. The most suitable thiazole accelerator for latex work is the insoluble zinc mercaptobenzthiazolate (ZMBT). It is activated by thiurams and dithiocarbamates.[23]

As a class, the thiurams are insufficiently active to accelerate satisfactorily sulphur vulcanization of latex. They may be used as secondary accelerators in conjunction with the dithiocarbamates. The most commonly used thiuram in latex compounding is tetramethylthiuram disulphide (TMTD) which acts as ultra accelerator and vulcanizing agent.

Activators

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

Antioxidants

The common antioxidants used in latex work fall into two classes: (a) amine derivatives which are powerful antioxidants but which tend to cause discolouration of rubber during ageing; (b) phenolic derivatives which are generally less effective antioxidants but have the advantage of not causing discolouration. Phenolic type antioxidants, especially styrenated phenol, are widely used.

Fillers

Fillers are added to latex in order to modify its properties and to reduce cost[24]. No effect analogous to the reinforcement of dry rubber by fillers is observed when the same fillers are incorporated in latex compounds[20]. Precipitated silica, china clay, whiting and precipitated calcium carbonate are the important non-black fillers used in latex compounding.

Special additives

Depending on the nature of the process or on end use, ingredients such as gelling agents, foaming agents, flame proofing agents, tackifiers, colours, anti-tack agents are added.[17]

LATEX PRODUCTS

The important applications of NR latex are in the manufacture of (a) dipped goods, (b) latex foam, (c) elastic thread and (d) adhesives.

Dipped goods

A wide range of articles such as gloves, medical tubing, condoms, balloons, rubber band etc. are manufactured by dipping process. The 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.[25] The principal dipping methods are straight dipping, coacervant dipping and heat sensitized dipping. In straight dipping a deposit is formed by virtue of the viscosity of latex and of its tendency to wet out the former. This process is used for the manufacture of thin walled articles. In coacervant dipping, a coacervant is used to assist the build-up of a deposit, and is the most common dipping method. Heat sensitized dipping produces the thickest deposit. The principle is to employ a heated former and a heat sensitive latex compound.

Latex foam

The basic steps involved in the production of latex foam rubber [26,27] are (a) foaming of compounded latex, (b) gelling of the foamed latex and (c) vulcanization of the polymer. The important foam products are mattresses, pillows and cushions.

Elastic thread

The essence of elastic thread production process is the extrusion of a latex compound through spinnerets into a coagulant solution. The wet gelled filament is washed, dried and vulcanized.[28] This is used principally in clothing industry.

Adhesives

NR latex is renowned for its high cohesive strength and intrinsic tack and is widely used in paper and textile combining. The performance of the adhesive is controlled by various additives apart from the polymer. Compounds based on NR are used for self sealing envelopes and for general applications like combining paper, cardboard and leather.

VULCANIZATION

Vulcanization is an essential step in the manufacture of almost all rubber products. Vulcanization raises the modulus of the material, increases its strength or resistance to rupture and tearing.

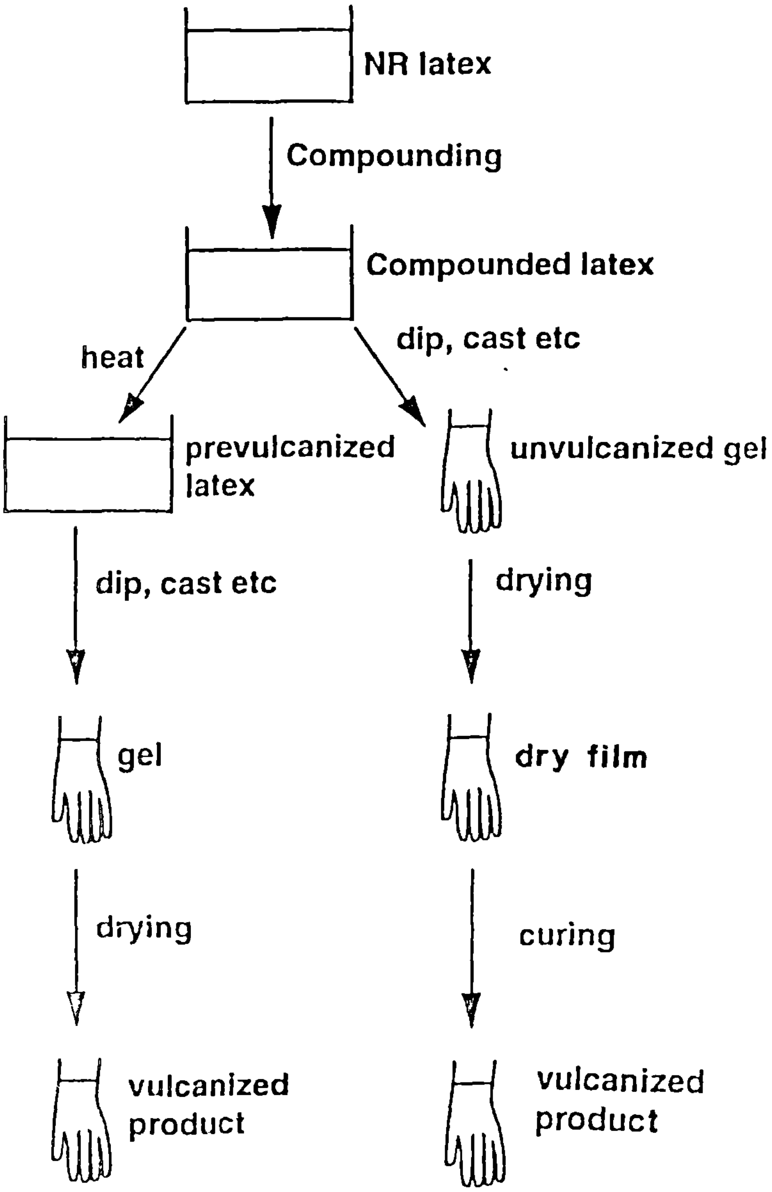
Vulcanization is the process by which the mainly viscous rubber is converted into elastic rubber through the crosslinking of the macromolecules at their reactive sites. The three dimensional structure so produced restricts the free mobility of all molecules. The crosslinks may be formed through chains of sulphur atoms, single sulphur atoms 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.[29,30]

Sulphur has been involved in rubber vulcanization since the process was first discovered by Goodyear about 150 years ago. Although rubber can be cured using sulphur alone the process is slow and the properties obtained are not ideal. Today sulphur is used in conjunction with one or more accelerators. Accelerated sulphur vulcanization remains the crosslinking process used for the overwhelming majority of rubber products both from dry rubber and from latex.

Vulcanization methods for latex products

For the sulphur vulcanization of products from latex two alternative methods exist (Scheme 1.1). The first involves mixing of chemicals required for vulcanization with the latex followed by forming into the required shape and drying. The dried rubber matrix containing the chemicals is then heated to effect vulcanization. This is termed postvulcanization, since crosslinking occurs essentially after the product has been formed.

Scheme 1.1
Manufacture of dipped latex product

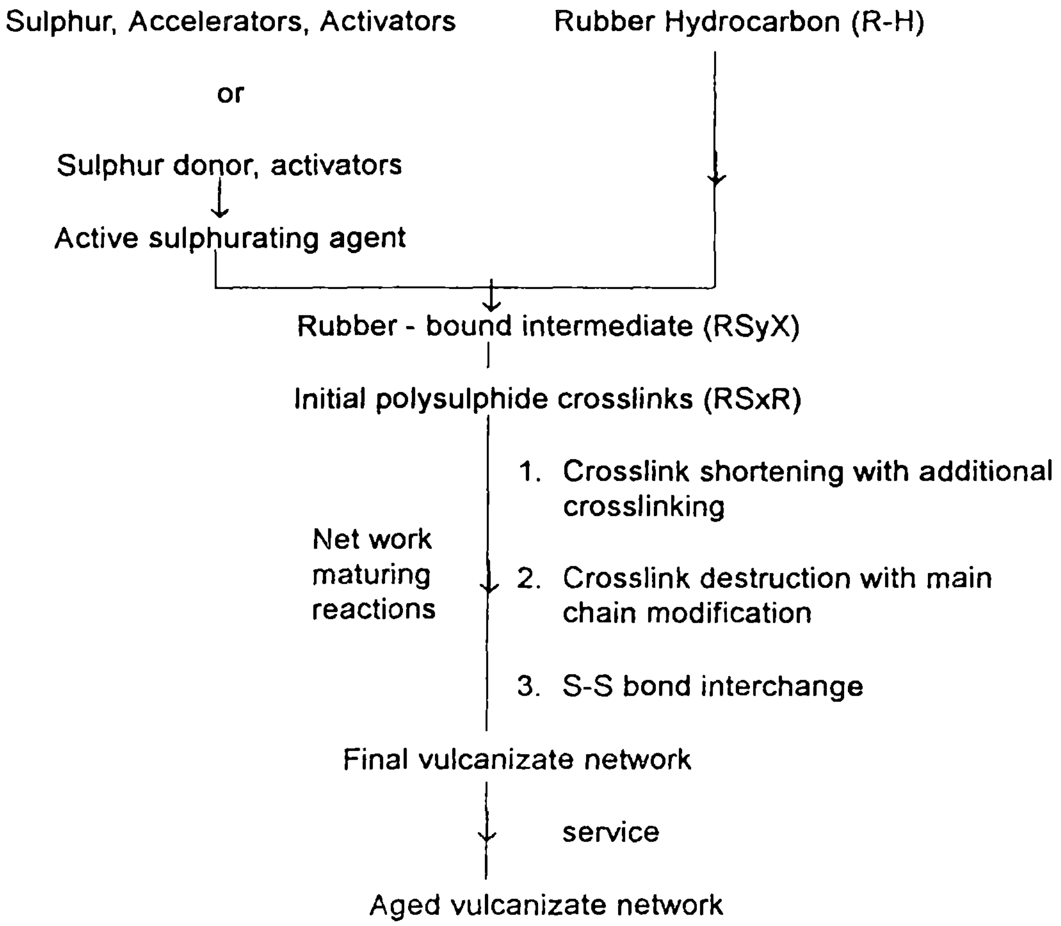


The other method involves heating the latex with the vulcanizing ingredients dispersed in it till the required level of vulcanization is obtained. This is called prevulcanization and the resulting prevulcanized latex can be formed into products in the normal way. Only drying is required to obtain the vulcanized rubber product.

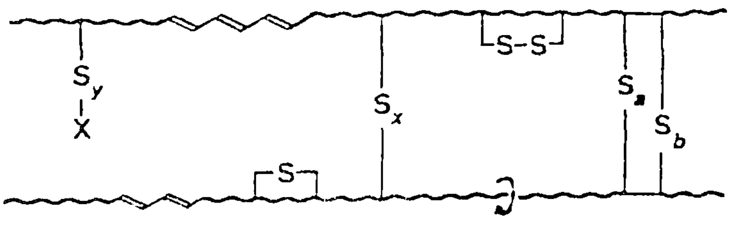
The vulcanization system used for prevulcanization are broadly similar to those used for postvulcanization and the mechanism is also thought to be the same. The obvious difference is that instead of occurring throughout a rubber product the whole process takes place within microscopic particles moving around in an aqueous medium. The process uses accelerators or combination of accelerators which are much more active than those used in dry rubber vulcanization.

The mechanism of accelerated sulphur vulcanization of natural rubber has been extensively studied over the years.[31,32] Although these studies were done primarily in dry rubber, the mechanism will be the same for both prevulcanization and postvulcanization of latex (Scheme 1.2). The generalized structure of a sulphur vulcanizate of natural rubber is shown in Scheme 1.3.

Scheme 1.2
Reaction sequence for sulphur vulcanization
(S = sulphur, X = accelerator residue, x,y = 1 - 6)



Scheme 1.3
Generalized structure of a sulphur vulcanizate of natural rubber
(S = sulphur, X = accelerator residue, x,y = 1 - 6)



The first step is the combination of accelerator with one or more activators which has the effect of solubilizing the accelerator in rubber. In latex compounds the most likely activators are carboxylates such as laurate which are added as stabilizers or naturally occurring amino compounds. The active accelerators react with sulphur to produce the active sulphurating agent. It is this agent which reacts with the rubber hydrocarbon to give a pendent group of a chain of sulphur atoms terminated with accelerator derivative. The pendent group can form a crosslink either by direct reaction with another polymer molecule or by disproportionation with another pendent group. In either case the initial crosslinks are polysulphidic. On continued heating these crosslinks undergo further reactions. The main reactions which occur are desulphuration or crosslink shortening, decomposition or crosslink destruction and sulphur - sulphur bond interchange or rearrangement. In postvulcanized latex systems decomposition is minimal because of the relatively low vulcanization temperatures. Desulphuration and rearrangement predominate leading to a stable network containing mono and disulphide crosslinks as well as polysulphidic ones. The relative proportions of the three types depends on the ratio of sulphur to accelerator and the curing time and temperature. But in most latex systems di and polysulphidic crosslinks predominate.[33]

Zinc oxide is widely used in latex vulcanization systems although it has been shown that zinc dialkyldithiocarbamate accelerated vulcanization can successfully occur without it.[17] Its role is thought to be to combine dithiocarbamic acid or tetraalkylthiuram disulphide which are by products of the crosslinking step, to regenerate accelerator. Zinc oxide thus prevents vulcanization coming to a premature halt due to depletion of accelerator and leads to a higher modulus than would otherwise be obtained.

PREVULCANIZATION

Prevulcanization of latex may be defined as a process in which crosslinking of the rubber takes place inside discrete particles dispersed in aqueous serum so that by deposition of the same followed by drying a coherent film of vulcanized rubber is obtained.

The vulcanization of latex was first investigated by Schidrowitz. [34] The crosslinking of rubber in latex can be effected by reaction with sulphur[35-40], sulphur donors[41], peroxides[42,43], hydroperoxides[44,45] or radiation.[46-50] However, only the dithiocarbamate accelerated sulphur systems have achieved commercial acceptance in the production of prevulcanized NR latex. The crosslinking efficiency of various dithiocarbamate accelerated sulphur systems have been evaluated.[38]

Sulphur prevulcanized latex is prepared by heating the raw latex with accelerators and sulphur at about 70°C until the required degree of crosslinking is obtained.[34] Earlier studies have been reported in this line. The rate of prevulcanization varies with different vulcanization systems and the extent of vulcanization has profound effect on the final vulcanizate properties. The crosslinking reaction takes place over a range of conditions such as temperature from 20 to 90°C for appropriate periods.[1] However at high temperatures latex tends to become destabilized and its coagulum content increases. Different grades of prevulcanized latex (Revultex) depending on the modulus of the vulcanizates, are available.[34]

Prevulcanized latex is very similar in appearance to raw latex and the original fluidity is retained. Vulcanization takes place in each of the individual latex particles without altering their state of dispersion appreciably. Thus the latex particles have the same shape, size and size distribution as that of the initial latex. Similar Brownian movement is also exhibited. Compared to dry rubber vulcanization, prevulcanization reaction of latex proceeds much more rapidly at the same temperature with the same vulcanizing ingredients. The speed of prevulcanization reaction seems to be associated primarily with the presence of water.[51] Humphreys and Wake[52] reported that no matter how much sulphur is included in the latex compound it is not possible to attain more than 1.8 per cent combined sulphur with the rubber hydrocarbon. Various formulations for the crosslinking of NR latex have been reported.[35,36] Porter [53] studied the properties of prevulcanized and postvulcanized films. He observed that there is not much difference in the rate of crosslinking in the two cases. This is contrary to the results of Loh reported earlier.[54]

The room temperature prevulcanization of NR latex using zinc dibutyldithiocarbamate accelerator is also reported.[37] It is generally assumed that it is advantageous to reduce the particle size of vulcanizing ingredients to that of rubber particles in latex. But little effect has been found on the role of particle size of sulphur and accelerator on the rates of prevulcanization and film properties.[19] Fine dispersions are essential to prevent sedimentation of the ingredients during processing and thus to guarantee homogeneity of dispersion during the manufacturing processes, but reaction can proceed from quite coarse dispersions if precautions are taken to prevent sedimentation. Prevulcanization employing different vulcanization recipes have been studied by Low.[35] According to him prevulcanization rates of different latex concentrates vary quite considerably. Recent investigations into the sulphur prevulcanization of NR latex have been summarized by Blackley.[39] The sulphur prevulcanization of natural rubber in latex form is contrasted with the sulphur vulcanization of natural rubber in the dry state at the same temperature using a similar formulation.[39] According to Gazeley[55] the rate of extraction of water soluble materials is faster from prevulcanized film than from postvulcanized film and increases with degree of vulcanization. Porter and Wong[56] investigated the factors affecting strength properties of prevulcanized and postvulcanized latex films and of bulk rubber vulcanizates. Maximum strength occurred at a lower overall crosslink density in prevulcanized films than in postvulcanized films. The effect of prevulcanization of natural rubber latex on the chemical and physical properties of latex thread has also been reported.[57] The marked beneficial effect of leaching on the properties of PVL films has been demonstrated.[36,58] Significant studies on the process have been carried out by Merrill.[59] He concluded that in a given system the rate of loss of free sulphur is first order with respect to its concentration and that the loss of free zinc diethyldithiocarbamate is zero order with respect to its concentration. The latter observation may well be explained by the low solubility of the accelerator in the serum of latex. More extensive work by Loh[54] indicated the appreciable solubility of sulphur in the serum facilitating its transfer to rubber phase. He also found that the superior crosslinking rates of NR latex is the result of the naturally occurring non-rubbers, such as proteins, lipids, soaps and amino acids. He also concluded that the crosslinks found in prevulcanized latex are predominantly of the polysulphidic type and this is in agreement with the observations of Chong and Porter[60] on the vulcanization of dried latex films. The proportion of mono and disulphidic crosslinks were found to be less than 20 per cent of the total chemical crosslink concentration. The high extent of polysulphidic crosslink formation on prevulcanization was reported by Peethambaran and George. [57] Micro changes in the rubber particles during sulphur prevulcanization of NR latex have been studied.[61] Vulcanization was found to be progressing during storage.[62] There are different schools of thought for the mechanism of prevulcanization. In some reports[63,64] the authors postulated that the reaction takes place as a result of direct contact between particles of reactants and rubber. Another set of commentators[54,65,66] postulated that the reactants must dissolve in the aqueous phase before diffusing into the rubber particles.

The chemistry of latex prevulcanization has recently been reported.[67] They explained the occurrence of prevulcanization on the basis that both the accelerator and sulphur dissolve in the aqueous serum of latex before migrating into the rubber phase and crosslink it. When the sulphur and accelerator reach the surface there are two possibilities, first the diffusion of these reactants into the rubber and then crosslinking. It is also possible that crosslinking can take place faster than diffusion. In this case the core portion will not be crosslinked. This is very important in the formation of films from vulcanized latex. If the particles are preferentially crosslinked near their surface, the reduced mobility of the rubber chains at the surface makes it more difficult for the particles to coalesce and a highly coherent film would not be expected. In the other case, if the latex particle is homogeneously crosslinked, the particle will coalesce well and form a film with optimal physical properties.

Hu et. al.[68] suggested that the rate of crosslinking is much greater than the rate of diffusion. There is no satisfactory explanation available for the reaction. Various tests for ascertaining the extent of cure in prevulcanized latex have been reported.[34]

Properties of films and deposits from prevulcanized latex

Mechanical properties of film

Films which have been prepared from prevulcanized latex closely resemble postvulcanized films. If relatively low drying temperatures are used tensile strength and elongation at break tend to be rather low. If the drying conditions are such that vulcanization continues after the particles of the film have integrated, then higher tensile strength and elongation at break are obtained. Tear strength of prevulcanized latex films tend to be inferior to those of postvulcanized deposits. This restricts the application of prevulcanized latex in products of fairly thick wall section.

Behaviour towards solvents

When immersed in solvents such as benzene or carbon tetrachloride, it is found that deposits from prevulcanized latex swell considerably to give gels which are mechanically rather weak. Comparing the behaviour of prevulcanized latex deposits with those of unvulcanized latex deposits and postvulcanized deposits, unvulcanized latex deposits exhibit unlimited swelling and imbibition of solvent until eventually dissolution takes place; whereas postvulcanized deposits behave like normal rubber vulcanizates and swell to a limited extent, depending upon the nature of the solvent and the crosslink density of the vulcanizate. Thus a prevulcanized film is readily ruptured if a drop of solvent is placed on it whilst it is held in an extended condition. This does not happen with postvulcanized films.

An interesting fact reported by Humphreys and Wake[52] is that the equilibrium swelling of prevulcanized latex deposits is very much less sensitive to combined sulphur content than is a normal sulphur vulcanizate. They have also found that the chloroform extract of acetone extracted prevulcanized latex deposits is negligible and inferred that the rubber within the individual latex particles is completely crosslinked. However, the distribution of crosslinks is non-uniform at low combined sulphur levels, being more dense near the surface of the particles and less so in the interior.

Structure of deposits from prevulcanized latex

This subject has been the centre of considerable discussion and controversy. Broadly speaking, three theories have been put forward to account for the strength of prevulcanized latex films:[34]

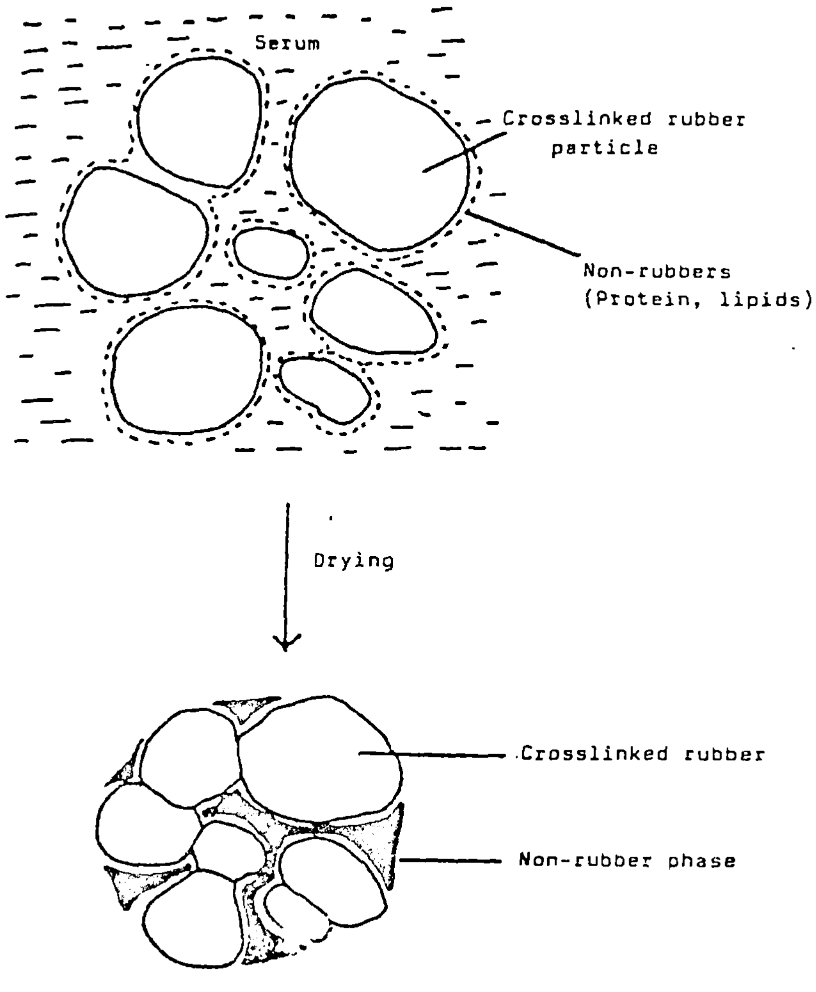
a. The strength is attributed to primary valence bonds formed between the molecules of adjacent particles;

b. The film is made up of discrete particles of vulcanized rubber cemented together by means of non-rubber constituents derived from the initial latex,and

c. The strength of films is due to secondary valence bonds formed between the molecules of adjacent particles.

Of these, the last gives the best account of properties of the deposits. Film formation of prevulcanized natural rubber latex as given by Teik and Poh[38] is shown in Figure 1.1.

Figure 1.1
Formation of prevulcanized natural rubber latex film



The secondary valence bond theory

According to this theory, the coherence of films from prevulcanized latex derives mainly from the totality of secondary valence bonds which come into being between the molecules of each pair of particles as the latex is dried down and the particles come closer to one another. Each particle contains a large number of individual rubber molecules.

If the particle is 1 μ in diameter and the primary molecular weight of the rubber hydrocarbon is taken as 3,00,000, then the particle contains about 10^6 primary rubber particles. These will be arranged in a tangled, haphazard fashion. As a result of the vulcanization reaction probably all the molecules of any one particle will be linked to one another, so that the particle itself may be regarded as one giant single network. Whilst the secondary valence bonds set up between any two molecules of adjacent particles will be very weak, the totality of such forces between two given particles will be appreciable, since they are scaled up by a factor of the order 10^6.

This theory accords well with the observed properties of prevulcanized latex films. The tensile stress strain behaviour is explained as follows. The initial extension will lead to a rearrangement of the molecules in the region of overlap between two particles since at this stage these molecules are able to move substantially independently of one another, the stress strain curve will approximate to that of unvulcanized rubber, it being generally agreed that the coherence of unvulcanized latex films is due almost entirely to secondary valence forces. As extension proceeds, however, there will come a stage where the molecules in the region of overlap, are not able to move independently of one another because they are attached to large number of other molecules by means of crosslinks. In order to continue the extension of the film, it is now necessary to overcome at one and the same time the secondary valence forces operating between increasingly large number of molecules. In this way the general shape of stress stain curve can be explained in a convincing manner. The initial flat region of low modulus is due to the molecules in the region of overlap moving independently of one another, so that the behaviour is similar to that of unvulcanized rubber. The increasing stiffness observed after some 500 per cent extension is considered to be due to the increasing lack of independence of these molecules. Thus the ultimate tensile strength of a prevulcanized film will be intermediate between that of an uncured film and that of a postcured film.

The behaviour towards solvents is also satisfactorily explained by the secondary valence bond theory. In the presence of a solvent the particles will swell and the secondary valence forces weaken as the average separation between molecules increases. If no primary valence bonds have been formed between the molecules of adjacent particles, then the swollen gel should eventually disintegrate to a dispersion of particles of swollen, vulcanized rubber corresponding to the individual particles of the original latex.

The secondary valence bond theory to account for the strength of prevulcanized latex films has been confirmed by Lebedev et al.[69] From their studies it is inferred that the polarity of the polymer is an important factor in determining the strength of a film from a vulcanized latex and that, the strength determining bonds are predominantly of the van der Waals type. Furthermore, the process of sulphur vulcanization enhances significantly the polarity of the polymer which is contained within a vulcanized latex. This enhancement of polarity is an important factor in determining the strength of films deposited from sulphur vulcanized natural rubber latex.

Other methods of prevulcanization

Various other curatives were investigated in connection with the vulcanization of natural rubber latex. Philpott[41] discovered that prevulcanized latex can be prepared from compounds containing a sulphur donor such as tetramethylthiuram disulphide accelerated with a nucleophile such as thiourea.

The crosslinking of latex by free radicals generated from peroxide [42,43] and hydroperoxide[44,45] systems have been known for some time. However, there has been little commercial development. The products made from it are normally transparent, lightly tinted and less toxic to human tissue.

Considerable interest has been shown in recent years in the possibility of crosslinking latex by the use of high energy ionizing radiations. Natural rubber latex when irradiated with gamma rays from a Co^{60} source, will become crosslinked[46,47] and form a prevulcanized latex. The degree of crosslinking relates to the dosage of radiation and the process may be enhanced by the use of sensitizers such as chloroform, carbon tetrachloride or monofunctional monomers.[48-50] The crosslinks in irradiated latex are probably carbon - carbon type similar to those in peroxide cures. The attraction of radiation prevulcanized latex is its potential for medical applications. However, it is more difficult and expensive to produce because of the need for a source of radiation.

Advantages

Prevulcanized latex is a convenient form of material for the latex goods manufacturing industry especially the dipped goods industry. The latex does not require compounding and vulcanization by the product manufacturer. It is especially suitable for products made by dipping because of the convenience of vulcanizing latex in bulk in relation to the trouble and expense of curing the equivalent amount of rubber in the form of thin deposits over innumerable formers. It also finds application in adhesives, textile combining, carpet backing and cast rubber products.[38] Better quality control can be achieved by the use of prevulcanized latex in product manufacture. Other advantages are shorter drying time and products of high clarity, particularly if prevulcanized latex is clarified before use.

Disadvantages

Prevulcanized latex does not find application in latex foam manufacture mainly on account of its poor wet gel strength. Films prepared from prevulcanized latex exhibit lower tensile strength, modulus and elongation at break as compared with postvulcanized films. Tear strength of prevulcanized latex films tend to be inferior to those of postvulcanized films, which restricts the application of prevulcanized latex to products of fairly thick wall section. When immersed in solvents such as benzene or carbon tetrachloride, deposits from prevulcanized latex swell considerably to give gels which are mechanically rather weak. Prevulcanized latex films exhibit also inferior resistance to oils and greases. Thus a prevulcanized film is readily ruptured if a drop of solvent is placed on it whilst it is held in an extended condition. Latex gloves which have been produced from prevulcanized latex are more readily damaged by oil and grease than are those which are produced by postvulcanization.

RHEOLOGY

The flow properties of latex are of vital importance in the manufacture of many latex products. Natural rubber latex is a non-Newtonian fluid which exhibits psuedoplastic flow pattern. At rest the rubber particles in latex are in random movement and when sheared the rubber particles are progressively aligned and offers less resistance to flow.[70] Hence, the apparent viscosity of latex decreases on increasing shear rate and continues until the flow curve becomes linear. The viscosity of latex also depends on its total solids content and temperature.[71,72]

Under processing conditions, latex is subjected to different forms of stress and undergoes flow and other deformations. Hence, study of rheology is significant and very much relevant for understanding and evaluating the scope and limitations of its uses and applications. Diverse types of flow behaviour are encountered during processing at different temperatures by various techniques such as dipping, extrusion, casting, brushing, spraying etc. Each process or technique involves, at different stages of operation, a critical relation between temperature, applied stress and inherent fluid property such as viscosity. A thorough evaluation and understanding of the rheological characteristics are necessary pre-requisites for satisfactory operation and control of such processes. During the manufacture of dipped rubber products by straight dipping the thickness of the film deposited on the former depends on the viscosity of the latex compound.[73]

The flow behaviour of latex can be modified by the incorporation of viscosity modifiers to suit the manufacturing process involved. Viscosity modifiers are hydrocolloids soluble in water to give viscous solutions which exhibit the properties of a typical lyophilic colloid. Hydrocolloids find their principal application in latex technology as modifiers of bulk flow behaviour. They are often referred to as thickeners. The effects of hydrocolloid thickeners upon polymer latices have been discussed by Brown and Garrett.[74] According to them the flow behaviour of a latex thickener system is not usually a simple additive function of the flow behaviour of its separate components. Gorelik et al. [75] studied the effect of thickening agents on the properties of foam rubber. They observed that thickening agents increase the degree of dispersion and stabilize the latices. Schroeder and Brown[76] studied the effect of sodium polyacrylate as a thickener in NR latex. The rheology of rubber solutions, suspensions, latex and latex compounds has been studied by Leaman.[77] According to Gorton[78] the source of rubber affects its molecular weight and distribution characteristics and thus influences the flow properties of rubber. Collins et al.[79] studied the factors affecting the rheological behaviour of latex. The important factors include shear rate, particle size, particle size distribution and electrolytes. The rheology of styrene butadiene latex has been investigated by Maron and Fok.[80] The effect of electrolyte content on synthetic latex flow behaviour has been reported.[81] Addition of electrolyte reduces the viscosity to a minimum value. Kulkarni et al.[82] developed a model for the viscosity of polymer latices. Rheological behaviour of natural and synthetic rubber latices in the presence of surface active agents has been investigated.[83] The rheological behaviour of blends of natural rubber and styrene butadiene rubber latices is also reported.[84] The effect of various surface active agents on the rheological properties of centrifuged and creamed latex concentrates has been reported.[85]

STORAGE OF LATEX AND FILMS

Field latex is processed into latex concentrate in plantations and it is consumed by manufacturing industries mostly in far away places. There are occasions of storing latex at the producer's end and also at the manufacturer's end. Since this material is in effect the preserved and concentrated contents of living plant cells, it is hardly surprising that many complex biochemical changes occur during storage. During pumping, transportation and storage, latex is subjected to mechanical agitation, aeration and even temperature variation. It is known that the chemical composition of latex changes significantly due to the action of bacteria, enzymes and preservatives. Changes will also be effected by many other factors including handling, seasonal effect, whether the latex is stored under aerobic or anaerobic conditions and contamination either from the material of which the container is made or from extraneous substances.

The chemical composition of ammonia preserved latex after storage differs from that of fresh latex.[2] The quantities of both proteins and resinous substances tend to fall and their places to be taken by amino acids, peptides, soaps, glycerol, organic bases and inorganic phosphates.

The overall concentration of ions present in the serum tends to increase, particularly the concentration of fatty acid, phosphate, low molecular weight carboxylic acid and amino acid anions. The corresponding cations are derived mainly from the ammonia which is present as a preservative. The concentration of ionic magnesium in the serum is greatly reduced.

The anions of volatile fatty acids (VFA) such as formic, acetic and propionic are formed by the action of micro-organisms upon certain serum carbohydrates. Ammonia retards the formation of these anions. Temperature has a profound effect upon the activity of enzymes which are responsible for VFA formation.[2] The activity rises sharply to a peak at about 35°C and then falls rapidly as they are deactivated by heat.

When ammonia is added to latex as a preservative, hydrolysis of the interfacial protein occurs slowly, the polypeptides and amino acids so formed passing into the aqueous phase. The phospholipids hydrolyze more rapidly so that by the time the ammoniated and concentrated latex has reached the industrial user, they have been largely hydrolyzed to fatty acid soaps, among other products, while much of the original interfacial proteins remain unhydrolyzed. These fatty acid soaps are adsorbed on to the rubber particle surface which is thought to account for the spontaneous rise in mechanical stability when ammoniated latex concentrate is stored.[86] The interfacial film at this stage consists essentially of a soap/protein mixture, the composition of which changes as the latex ages. All the soap formed by lipid hydrolysis do not remain at the interface, some passes into the aqueous phase and a dynamic equilibrium between the soap in the serum and that at the interface is set in. In the case of the proteins, on the other hand, adsorption at the interface is largely irreversible since soluble proteins on adsorption usually undergo changes in structure (denaturation) which markedly reduce their solubility.

The mechanical stability and chemical stability of stored ammonia preserved latex are products of several factors, the most important of which are VFA formation which tends to reduce stability and lipid hydrolysis which tends to enhance the stability, the final stability being largely determined by the balance between the two.[2] Latex which has been stored under nominally air free conditions which prevail in an almost fully filled container, suffers a progressive reduction in stability whereas the stability of latex which has been stored under aerobic conditions, in half - filled containers, increases markedly and passes through a maximum. On storage the mechanical stability and chemical stability of the latex change considerably and these, in turn, cause processing problems.

The presence of materials which exert an antioxidant effect in latex has been recognized for many years.[87] Choline compounds present in latex are vulcanization accelerators and show antioxidant properties in raw rubber.[4] Changes in the chemical composition of latex can also cause changes in the properties of films prepared from it. Studies of Chin et al.[88] showed that although storage of latex affected its primary properties the physical properties of postvulcanized rubber films prepared from the stored latex are not adversely affected for a storage period of up to eight months. Such studies on prevulcanized latex film are very rare.

It is not uncommon that prevulcanized latex may be required to be stored for long periods before it is used. Further vulcanization of latex on storage is likely to influence the processing of latex such as wet-gel extensibility and finished product properties. Any significant postvulcanization is not a desirable feature.

Room temperature prevulcanization of NR latex using a dithiocarbamate cure[37] system showed that tensile strength of the film decreased with storage of both unclarified and clarified prevulcanized latices. Prolonged storage of prevulcanized latex with a high level of zinc dibutyldithiocarbamate was detrimental to tensile strength of films.[38] According to Low[35], the unreacted vulcanizing ingredients continue to vulcanize latex during storage of PVL and most of the postvulcanization occurred within the first month of storage.

Rubber products usually have to be stored at ambient temperature before they reach the ultimate user. Besides, during service life certain products are kept at ambient conditions. Therefore, storage properties of films also have to be examined. It has been reported[58] that the tensile strength of untreated radiation vulcanized NR latex film increased on storage at room temperature. Storage of leached prevulcanized latex films exhibited good tensile properties after twelve weeks' storage.[38]

AFTER-TREATMENTS OF FILMS

After-treatments include treatments intended to modify the properties of a deposit once it has been formed.[25] Depending upon the product a variety of after-treatments may be given. Halogenation of gloves is frequently practised in order to attain a smooth surface of pleasing feel. Roughening of gloves in order to provide a convenient grip and flocking in order to give a pleasing, velvety feel are also practised. Jazzing is applied primarily to balloons to give a variegated colour effect.

The films from prevulcanized latex exhibit inferior properties compared to postvulcanized films. The properties are affected by leaching them in cold water and by heating.[1] A pronounced effect of leaching is reported giving rise to increased tensile strength and modulus values with minor alteration in elongation at break. Heating the film has similar effect on the tensile properties but the changes are less pronounced.[1,36,40,58] The process of leaching is performed on most products made by dipping and also on latex thread and moulded foam.[17] It is of particular interest in medical goods and in electrician's gloves[89] where the presence of hydrophilic materials would cause absorption of atmospheric moisture and consequent reduction in electrical resistance. The purpose of leaching in postvulcanized films is to remove water soluble materials and the efficiency of the process may have a significant effect on characteristics such as clarity, blooming, discolouration, surface tack etc. Leaching operations are of two types: (a) dry film leaching and (b) wet gel leaching. In dry film leaching the product is leached after drying and stripping from the former. In wet gel leaching the article is leached while still on the former as a wet gel. Wet gel leaching is more efficient than dry film leaching. Leaching of latex thread is always done on the wet gel.

The parallel processes of leaching and water absorption occur more rapidly in prevulcanized films than in postvulcanized films and the behaviour is more complicated. This is a result of structural differences due to reduced coalescence of rubber particles and the formation of a more effective capillary structure.[17]

REINFORCEMENT

Inorganic fillers are commonly added to latex in order to cheapen and stiffen the product. Fillers may also affect the flow behaviour of latex.[20] It may be mentioned that no effect, analogous to the reinforcement of dry rubber by certain fillers, is observed when the same fillers are incorporated in latex compounds. This is attributed to the absence of a mastication step in the case of latex products. 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.[90-92]

Reinforcement by filler is the enhancement of one or more properties of an elastomer by the incorporation of the same, thus making it more suitable for a given application.[93,94]

According to van Rossem and Plaizier[95] small additions of bentonite clay enhanced the tensile strength and modulus of the vulcanized deposit. For the production of filled latex compounds of high strength it is necessary to ensure; (a) a high degree of dispersion of fillers and other ingredients added to latex, (b) simultaneous precipitation of the particles from the latex mix and (c) conditions which result in direct contact between the rubber and filler particles without intermediate layers of protective substances which reduce the rubber filler interaction.[96]

SCOPE OF THE PRESENT WORK

It is a matter of great importance to reduce cost of production in all possible ways for competitive marketing of rubber products. In this respect prevulcanization of latex in bulk assumes importance. The need for ensuring consistency in quality is a must for international marketing of products. Although prevulcanized latex is a convenient form of material for the rubber industry very little published information especially with regard to scientific aspects, is available on the subject.

For many of the latex goods manufacturing processes, the flow properties of latex are critical. An understanding of the rheological properties of prevulcanized latex and the effect of various viscosity modifiers on it, may lead to better process control during the manufacture of latex products. Hardly any report is available in this line.

The colloidal nature of latex and the presence of compounding ingredients, make the vulcanization reactions in latex compound more complicated than those in dry rubber compound. These reactions are likely to be affected by the nature of the adsorbed layer of surface active agents on the rubber particle which is likely to change during storage. Very few studies have been conducted on the effect of storage of latex on quality of PVL films.

Systematic investigations on the methods of improving the properties of PVL films through after-treatments, have been very limited.

As far as latex goods industry is concerned the main function of fillers is to increase modulus and to reduce cost of production. Fillers also affect the flow properties of latex. Information on this aspect is also not available.

The changes in chemical composition of latex occurring during storage are reflected in certain properties of latex and may cause processing problems. Sufficient information on storage behaviour of LATZ latex in comparison with HA latex towards quality of films made either adopting postvulcanization or using prevulcanized latex, is not available.

For competitive marketing of products improvement in quality as well as appearance are of great importance. There is always a market preference for transparent rubber products, although transparency is not an important technological property. There has been no systematic investigation on the influence of prevulcanization and compounding ingredients on transparency of NR latex films and methods to be adopted to improve film transparency.

In the light of the above, the following investigations have been taken up.

1. Effect of temperature of prevulcanization on properties of NR latex films.
2. Rheological properties of prevulcanized latex.
3. Effect of storage of latex and after-treatments on the quality of films from prevulcanized latex.
4. Effect of fillers on properties of PVL films.
5. Influence of storage on properties of NR latex concentrates and vulcanizates.
6. Influence of prevulcanization and compounding on the transparency of NR latex films.

This thesis is divided into the following chapters:

Chapter	**1**	**Introduction**
Chapter	**2**	**Materials and Experimental Techniques**
Chapter	**3**	**Studies on temperature of prevulcanization and rheology of prevulcanized latex**
Part	A	Effect of temperature of prevulcanization on properties of NR latex films
Part	B	Rheological properties of prevulcanized latex
Chapter	**4**	**Effect of storage, after-treatments and fillers on quality of PVL films**
Part	A	Effect of storage of latex and after-treatments on the quality of films from prevulcanized latex
Part	B	Effect of fillers on properties of PVL films
Chapter	**5**	**Influence of storage on properties of NR latex concentrates and vulcanizates**
Chapter	**6**	**Influence of prevulcanization and compounding on the transparency of NR latex films**
Chapter	**7**	**Summary and Conclusions**

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CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

This chapter deals with the materials used and the experimental techniques adopted in the present investigations.

MATERIALS

Centrifuged latex

High ammonia (HA) type centrifuged latex concentrate conforming to the specifications of the Bureau of Indian Standards : IS 5430-1981, obtained from the Pilot Latex Processing Centre of Rubber Board was used for the investigations, except for the studies on storage behaviour. The properties of the latex were found to be as given in Table 2.1.

Table 2.1
Properties of centrifuged latex

Sl.No.	Parameters	Values
1.	Dry rubber content, per cent by mass	60.05
2.	Non-rubber solids, per cent by mass	1.40
3.	Coagulum content, per cent by mass	0.03
4.	Sludge content, per cent by mass	0.007
5.	Alkalinity as ammonia, per cent 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	3.00
10.	Manganese content, ppm on total solids	0.50

Field latex

Field latex used in the study was collected from the Experiment Station of the Rubber Research Institute of India. The latex was sieved through a 40 mesh sieve and was ammoniated. The properties of the latex were found to be as given in Table 2.2.

Table 2.2
Properties of field latex

Sl. No.	Parameters	Values
1.	Dry rubber content, per cent by mass	30.60
2.	Non-rubber solids, per cent by mass	3.10
3.	Alkalinity as ammonia, per cent by mass	1.20
4.	Volatile fatty acid number	0.03

Creamed latex

Creamed latex used in the study was prepared from preserved field latex (1.2 per cent ammonia content) collected from the Experiment Station of the Rubber Research Institute of India. Creaming was done as per the method given in Blackley[1], using tamarind seed powder and also using ammonium alginate as creaming agents. The latex was treated with 0.05 per cent potassium laurate (10 per cent solution) and 0.3 per cent tamarind seed powder/0.25 per cent ammonium alginate as 3 per cent solutions and was mixed well and kept undisturbed for creaming. After 6 days, the cream was collected, homogenized and tested. The properties of the creamed latex were found to be as given in Table 2.3.

Table 2.3
Properties of creamed latex

	Parameters	Values Creaming agent Ammonium alginate	 Tamarind seed powder
1.	Dry rubber content, per cent by mass	60.10	59.90
2.	Non-rubber solids, per cent by mass	1.70	1.72
3.	Coagulum content, per cent by mass	0.04	0.04
4.	Sludge content, per cent by mass	0.02	0.02
5.	Alkalinity as ammonia, per cent by mass	0.75	0.76
6.	KOH number	0.52	0.50
7.	Mechanical stability time, seconds	888.00	870.00
8.	Volatile fatty acid number	0.03	0.03
9.	Copper content, ppm on total solids	3.30	3.28
10.	Manganese content, ppm on total solids	0.80	0.81

The details of rubber chemicals and allied materials are given below.

RUBBER CHEMICALS.

Materials	Description
Sulphur	Sp. gr. 1.9, Standard Chemical Company Pvt. Ltd., Madras
Zinc diethyldithiocarbamate	SP. gr. 1.49; ICI (India) Ltd.
Tetramethylthiuram disulphide	Sp. gr. 1.30; Polyolefins Industries Ltd., Bombay
Zinc oxide	Sp. gr. 5.5; Meta zinc Ltd., Bombay
A/O SP	Styrenated phenol; ICI (India) Ltd.
Dispersol F	Sodium salt of a sulphonic acid, ICI (India) Ltd.
Casein	Phosphoprotein; Reagent grade
Polyvinyl alcohol	Mol. wt 14,000, Reagent grade
Sodium carboxymethyl cellulose	Loba - Chemie, Bombay
Tamarind seed powder	Commercial grade
Ammonium alginate	Cellulose products of India, Ahmedabad
Ammonia	Commercial grade
Ammonium laurate	Prepared in the laboratory from ammonia and lauric acid
Potassium laurate	Prepared in the laboratory from pot. hydroxide and lauric acid
Diammonium hydrogen orthophoshate	Commercial grade
Tilanium dioxide	Anatase type; Travancore Titanium Products, Trivandrum
Precipitated silica	Commercial grade

Materials	Description
China clay	Commercial grade
Whiting	Commercial grade
Magnesium carbonate	Commercial grade
Paraffinic oil	Commercial grade
Talc	Commercial grade
Silicone emulsion	Commercial grade
Formic acid	Reagent grade
Acetic acid	Reagent grade
Calcium nitrate	Reagent grade
Potassium hydroxide	Reagent grade
Toluene	Reagent grade
Lauric acid	Reagent grade

PRESERVATION AND CONCENTRATION OF LATEX BY CENTRIFUGING

Field latex (400 litres) was collected from the Central Experiment Station of the Rubber Research Institute of India at Chethackal, sieved through a 40 mesh sieve and was bulked in a tank. The latex was then ammoniated to 0.3 per cent using ammonia solution (10 per cent). From this a batch of 200 litres was transferred to one barrel and ammoniated to 1 per cent. To the rest of the latex, 0.025 per cent each of zinc oxide and tetramethylthiuram disulphide were added as 50 per cent dispersions and kept in another barrel. Diammonium hydrogen orthophosphate was added to both the latices as 10 per cent solution to precipitate magnesium. On the next day both the batches were centrifuged separately using an Alpha Laval Centrifuge (Model LRB 510) at the Pilot Latex Processing Centre of the Rubber Board. The concentrate from the first barrel was ammoniated to 0.7 per cent (HA latex) and that from the second barrel was ammoniated to 0.25 per cent (LATZ latex). To the LATZ latex 0.05 per cent ammonium laurate was also added. The two latices were stored in polythene containers under laboratory conditions. These samples were used for studying storage behaviour.

LATEX COMPOUNDING

Compounding ingredients were added to latex as aqueous solutions, dispersions or emulsions according as they are water soluble solids, water insoluble solids or water immiscible liquids.

Preparation of dispersions

The dispersions were prepared using a ball mill.[2] The materials were made to disperse in water by grinding in the presence of a dispersing agent. Dispersol F was used as the dispersing agent. The quantity of the dispersing agent to be used depends on the nature of materials to be dispersed. The formulations of dispersions used in the study were as follows.

Sulphur dispersion (50%)

Sulphur : 100
Dispersol F : 3
Deionized water : 97

Ball milled for 72 h

ZDC dispersion (50%)

ZDC : 100
Dispersol F : 2
Deionized water : 98

Ball milled for 24 h

ZnO dispersion (50%)

ZnO : 100
Dispersol F : 2
Deionized water : 98

Ball milled for 24 h

TMTD dispersion (50%)

TMTD : 100
Dispersol F : 2
Deionized water : 98

Ball milled for 24 h

Magnesium carbonate dispersion(50%)

Magnesium carbonate:	100
Dispersol F :	2
Deionized water :	98

Ball milled for 24 h

Titanium dioxide dispersion (33%)

Titanium dioxide :	100
Dispersol F :	2
Deionized water :	198

Ball milled for 24 h

Precipitated silica dispersion (25%)

Precipitated silica:	100
Dispersol F :	2
Deionized water :	298

Ball milled for 24 h

Whiting dispersion (50%)

Whiting :	100
Dispersol F :	2
Deionized water :	98

Ball milled for 24 h

China clay dispersion (50%)

China clay	:	100
Dispersol F	:	2
Deionized water	:	98

Ball milled for 24 h

Preparation of emulsions

Water immiscible liquids such as antioxidant SP, process oil etc., were added into latex compounds as emulsions. The formulations used for preparing emulsions were as follows.

Antioxidant SP emulsion (50%)

Antioxidant SP	:	100	A
Oleic acid	:	3	
Ammonia solution (25%)	:	3	B
Deionized water	:	94	

Part A was warmed to 60°C and added to B in small quantities under high speed stirring.

Paraffinic oil emulsion (50%)

Paraffinic oil	:	100	A
Oleic acid	:	3	
Ammonia solution	:	3	B
Deionized water	:	94	

Part A was warmed to 60°C and added to B in small quantities under high speed stirring.

Compounding

The mixing of ingredients with latex was done as per the order given in the formulations in the respective chapters. The stabilizers were first added as solutions, followed by the other ingredients.

PREVULCANIZATION

The latex compound in a glass beaker was immersed in a water bath set at the required temperature. The compound was subjected to continuous slow stirring and the beaker was kept covered to minimize loss of ammonia. After a predetermined time the compound was immediately cooled to room temperature. On the next day the latex was decanted and filtered through a 100 mesh sieve and stored for further processing.

PREPARATION OF LATEX FILM

Casting

Films were prepared by casting the latex compound / prevulcanized latex in shallow glass cells as described by Flint and Naunton.[3] Strips of glasses were fixed on edges of glass plates (20 cm x 20 cm) to form the cells of size 15 cm x 15 cm. About 25 ml of the latex compound/ prevulcanized latex was poured into the glass cell and distributed so that film of thickness approximately 0.75mm was obtained on drying except for the studies on the transparency of films. The glass cells with the test samples were placed on a levelled table and dried overnight at ambient temperature.

Dipping

Latex films were also prepared by coagulant dipping.[4]

AFTER-TREATMENTS OF PREVULCANIZED LATEX FILMS

The films were removed from the glass cells and subjected to different types of treatment as follows.

1. Leaching in water at different temperatures and drying at room temperature.
2. Heating in air at 100°C for 30 minutes.
3. Combined treatment : Leaching in water at room temperature for 24 h, drying at room temperature followed by heating in air at 100° C for 30 minutes.
4. Leaching in water at different pH at room temperature for 24 h and drying at room temperature.

Coagulant dipped films were given after-treatments 1 to 3. For studies on the transparency of films, Treatment 3 was extended up to 3 h.

POSTVULCANIZATION

The latex compound was prepared as described earlier and was matured for 24 h. Latex films were prepared by casting in glass cells as described earlier. The vulcanization of latex films was carried out in a laboratory air oven at 100° C. The time for developing maximum crosslink density was determined by vulcanizing the films for different periods from 15 minutes to 120 minutes and determining the crosslink density of the samples. For the crosslink density, the volume fraction of rubber (Vr) in the swollen vulcanizate in toluene was determined. The method of determination is described later. The time for achieving optimum crosslink density was then determined by plotting (Vr) values against time (t). The latex films for physical property measurements were vulcanized to optimum crosslink density.

Latex property measurements

Property	Method
Dry rubber content	IS : 3708 (part I) 1985
Total solids content	IS : 9316 (part IV) 1988
Alkalinity	IS : 3708 (part IV) 1985
Potassium hydroxide number	IS : 3708 (part V) 1985
Volatile fatty acid number	IS : 3708 (part VII) 1986
Mechanical stability time	IS : 3708 (part VI) 1985
Coagulum content	IS : 9316 (part III) 1987
Sludge content	IS : 3708 (part II) 1985
Copper content	IS : 9316 (part VII) 1987
Manganese content	IS : 9316 (part IX) 1987

Viscosity

For determining viscosity of latex a Brookfield viscometer (model RVT) was used. 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 is indicated by means of a pointer and scale. The scale reading is converted to viscosity values by the use of a conversion table.

Effect of temperature and shear rate on viscosity

A Haake Viscotester VT550 was used to study the effect of temperature and shear rate on viscosity. This has been designed to meet the most sophisticated requirements of continuous shear rheometry with 60 different rotational speed steps covering a wide range from 0.5 rpm to 800 rpm. The functional units consists of viscotester VT550 and power supply unit, temperature control vessel with sensor system, Pt100 temperature sensor and stand. The equipment operates over a temperature range from -30 to 150°C. Thirty different sensor systems are available. Sensor system NV was used for this study.

Latex is located in the measuring gap of the sensor system. Rotational speed, measuring time, number of measuring points and measuring temperature are preset. The rotor is rotated at the preset speed. The latex exerts a resistance to the rotational movement due to its viscosity which becomes apparent as a torque value applied on the measuring shaft of the VT550. The computer attached to the system calculates the relevant values for the following factors from the measured variables of speed, torque and sensor geometry.

Viscosity η in mPa s

Shear rate $\dot{\gamma}$ in s^{-1}

Shear stress τ in Pa

The temperature T is also measured in °C . In the present study measurements were taken at 25, 35 and 45°C at shear rate from 1 to 150 s^{-1}.

The rheological behaviour of the latex has been analysed using Power Law equation

$\tau = K \dot{\gamma}^n$

where τ = shear stress (Pa)

K = viscosity index

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

n = flow index

By plotting log τ vs. log $\dot{\gamma}$ the values 'K' and 'n' are obtained as slope and intercept by regression analysis.

The apparent viscosity, η is the ratio of shear stress to shear rate

i.e., $\eta = K\dot{\gamma}^{n-1}$

Zinc oxide viscosity

ZnO causes destabilization and thickening of latex. The chemical stability of latex is inversely proportional to the viscosity at a given time after the addition of ZnO. Total solids content (TSC) of the latex was determined and a sample of latex containing 100 gm TSC was taken in a beaker. To this 1 part of potassium oleate was added as 20 per cent solution. Sufficient water was added to adjust the total solids of the latex compound to 57 per cent. The beaker was placed in a thermostatic water bath to attain a temperature of 25°C. 0.5 parts of ammonium sulphate as 10 per cent solution and 5 parts of zinc oxide as 40 per cent dispersion were added to it. A stop watch was started and the contents stirred for one minute. The viscosity of the latex compound at 28°C was determined using a Brookfield viscometer with spindle No.2 at 50 rpm, at the end of 5 minutes.

CHEMICAL TESTS

Determination of volume fraction of rubber

Samples of approximately 0.3g were punched from the vulcanized latex film and allowed to swell in toluene for 48 h. The swollen samples were blotted with filter paper and weighed quickly in a stoppered weighing bottle.

Samples were dried in an air oven for 24 h 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 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.

$$Vr = \frac{(D-FT)/\rho r}{(D-FT)/\rho r + Ao/\rho s}$$

Where T is the weight of the test specimen, D, its deswollen weight, F, the weight fraction of insoluble components, Ao is the weight of absorbed solvent,corrected for the swelling increment, ρr and ρs are the densities of rubber and solvent respectively. From the collected data, the volume fraction of rubber (Vr) was calculated. Vr can be taken as a measure of crosslink density.

Determination of rubber- filler interaction

Ammonia - modified swelling

The samples of the prevulcanized latex films containing different fillers were swollen for 48 h in flat dishes containing toluene in an ammonia atmosphere.[6] For this the samples in toluene were placed in a desiccator, the bottom of which contained liquor ammonia. After swelling in ammonia atmosphere the samples were thoroughly washed with toluene and dried in a vacuum desiccator at room temperature and Vr was determined. The difference in Vr values of the vulcanizate swollen in toluene and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond. In this, it is presumed that ammonia permeates the toluene swollen rubber matrix and preferentially cleaves the rubber-filler attachment.

Water absorption and leaching behaviour

Water absorption and extracted soluble matter during leaching of vulcanizates were determined according to ASTM D 471-79.

PHYSICAL TEST METHODS

Tensile stress - strain behaviour

Tensile properties of vulcanizates were determined according to ASTM D 412-87 using dumbbell specimens (Type C) on a Zwick

Universal Testing Machine (model 1474) at a crosshead speed of 500 mm/min at 28 ± 2°C. The results reported are the mean values of five measurements.

Ageing

Dumbbell specimens were subjected to accelerated ageing in an oven at 70°C. The duration of ageing was varied for different studies. When the ageing period was over, samples were taken out and kept at ambient conditions for not less than 16 h and not more than 96 h in a strain free condition and then used for the measurements.

Stress relaxation behaviour

Stress relaxation measurements were carried out according to Mackenzie and Scanlan[7] in a Zwick Universal Testing Machine (model 1474) using dumbbell specimens. The samples were pulled to 600 per cent elongation at a crosshead speed of 2.5 mm/min. The decay of stress as a function of time was recorded for a period of 9000 seconds. Slope of the line obtained by plotting σ_t/σ_0 vs log time, is a measure of stress relaxation of the sample; σ_t being the stress at time t and σ_0 the initial stress.

MORPHOLOGICAL STUDIES

Optical microscope

Test samples containing 5 phr of filler were prepared by casting as described earlier. Photomicrographs were taken on a Leica Wild M8

Zoom Stereo Microscope and Wild mps 46/52 Photoautomat using NOVA FP_4 films.

Scanning electron microscopy

The surface of the cast latex film was sputter coated with gold and examined under a JEOL JSM 36C model scanning electron microscope.

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CHAPTE

STUDIES ON TEMPERATURE PREVULCANIZATION AND RHEOLOGY PREVULCANIZED LAT

PART A

EFFECT OF TEMPERATURE OF PREVULCANIZATION ON PROPERTIES OF NR LATEX FILMS

Prevulcanized latex (PVL) is a very convenient raw material for the latex goods manufacturing industry since it can be used directly for the manufacture of latex products, thus eliminating the need for compounding other than the addition of antioxidant or pigment. Drying of prevulcanized latex produces a crosslinked film without the need for further vulcanization. The crosslinking of rubber in latex can be effected by reaction with sulphur[1-3], sulphur donors[4] peroxides[5] or radiation.[6] However, only sulphur prevulcanization has attained wide commercial acceptance.

Several studies were reported on sulphur prevulcanized NR latex. Various formulations for the crosslinking of NR latex were reported.[1] The production of prevulcanized latex and the marked beneficial effect of leaching on the properties of films were demonstrated.[2] The rate of prevulcanization varies with different vulcanization systems and the extent of prevulcanization has a profound influence on the final vulcanizate properties. The crosslinking reaction in latex takes place over a range of conditions such as temperature.[7] As the temperature is lowered crosslinking takes place very slowly. However, at high temperatures latex tends to become destabilized and its coagulum content increases. By proper stabilization of latex, prevulcanization conducted at higher temperatures reduces the vulcanization time appreciably. This study reports the effect of temperature and duration of heating on sulphur prevulcanization of NR latex. The extent of crosslinking and tensile properties of the films prepared therefrom were evaluated. Water absorption and leaching characteristics of the films from latex prevulcanized at 60 and 70°C have been evaluated. Stress relaxation characteristics of selected films has also been monitored.

EXPERIMENTAL

The latex compound was prepared according to the formulation given in Table 3.1. Centrifuged latex conforming to the specifications of the Bureau of Indian Standards (BIS) was stabilized by adding potassium hydroxide and potassium laurate solutions. Sulphur, zinc diethyldithiocarbamate and zinc oxide were added as dispersions in water.

Prevulcanization and film preparation

Prevulcanization of the latex compound was carried out at different temperatures (60, 70, 80 and 90°C) as described in Chapter 2. After the latex compound has attained the required temperature (60°C was attained in 15 minutes and 90°C in 30 minutes of heating), samples of the latex compound were removed at appropriate time intervals. The samples were immediately cooled to room temperature. On the next day films were prepared as described in Chapter 2. The films after drying were leached in water for 24 h and dried at room temperature.

Testing of films

The volume fraction of rubber, tensile properties, water absorption, leaching and stress relaxation characteristics were determined as stated in Chapter 2.

RESULTS AND DISCUSSION

Volume fraction of rubber

Figure 3.1 shows the effect of prevulcanization conditions on volume fraction of rubber, which is a measure of the crosslink density of films. It can be seen that when the prevulcanization was conducted at 60°C, the volume fraction of rubber increased as the heating time increased from 0.5 to 6 h. But the rate of increase was very slow and the value of Vr obtained was much lower compared to that realized at the higher temperatures studied. When prevulcanization was conducted at 70°C a higher Vr value was obtained which was found to increase with the heating time and the rate of increase was also higher compared to that found at 60°C. Prevulcanization at 80° and 90°C further increased the Vr values. A maximum was, however, observed at a definite period for each temperature after which a drop in the value was observed. At 80°C maximum Vr was obtained at 2 h of heating. On extending the heating time beyond 2 h,Vr decreased appreciably. At 90°C maximum Vr was obtained at 1 h of heating. On further heating Vr dropped abruptly. The drop in Vr is due to overvulcanization. Crosslinks and pendent groups undergo a variety of further reactions which take place at the same time as crosslinking, during overcure and during the service life of the vulcanizate.[8] Crosslink shortening and crosslink decomposition are the two most important types of reaction occurring after crosslinking. Crosslink decomposition leads to an overall loss of crosslinks[9] which accounts for the observed drop in Vr value.

Tensile properties

Figure 3.2 shows the effect of prevulcanization conditions on modulus at 100% elongation. At 60°C as the heating time increased, modulus increased and the rate of increase slowed down after 4 h of heating. At 70° C as the heating time increased modulus increased, the rate of increase being faster compared to that at 60°C, attaining almost maximum modulus at 3 h of heating, beyond which the increase was only nominal. At 80°C when the heating time increased from 0.5 to 1 h a sharp increase in modulus was noticed. Afterwards the rate of increase slowed down attaining maximum at 2 h. On further heating modulus decreased steadily. This is in line with changes in Vr values as is shown in Figure 3.1. The fact that maximum Vr value and maximum modulus were attained at 2 h of heating indicated that during this period maximum crosslinking had taken place. Beyond this period due to overvulcanization and the consequent restricted coalescence of rubber particles,a decrease in Vr and modulus was observed.

At 90° C maximum modulus was obtained at 1 h of heating. On extending the heating time, modulus decreased and the rate of decrease was very fast beyond 1 h which slowed down after 3 h of heating, showing that maximum crosslinking had taken place during 1 h of heating as is evident from Vr values given in Figure 3.1. At 90°C beyond 1 h of heating the latex particles become overvulcanized as stated earlier which resulted in poor cohesion of the particles thereby exhibiting lower modulus.

Figure 3.3 shows the effect of prevulcanization conditions on tensile strength of films. Unlike Vr and modulus, high tensile strength was obtained when prevulcanization was conducted at 60°C. For each temperature better tensile strength was obtained at shorter period of heating. As the heating was continued tensile strength decreased. This is in line with the observation made by Gorton.[2] At 90°C a drastic decrease in tensile strength was obtained beyond 1 h of heating and the films exhibited very low tensile strength at 2 to 4 h of heating. This shows that tensile strength of prevulcanized film is governed not only by the introduction of crosslinks but also by the ability of particles to coalesce among themselves. When latex is prevulcanized the rubber particles are internally crosslinked. By increasing the temperature or the heating time the rubber particles become more and more crosslinked and hence become harder. Thus when the film is prepared from a highly crosslinked latex, coalescence of rubber particle becomes more difficult resulting in lower tensile strength.

Figure 3.4 shows the effect of prevulcanization conditions on elongation at break (EB) of the films. EB was high when prevulcanization was conducted at 60°C. At each temperature higher elongation was obtained at shorter time of heating. On prolonged heating EB decreased. Maximum reduction was obtained when prevulcanization was conducted at 90°C for a heating time of 2 to 4 h. When the rubber particles are lightly crosslinked coalescence of particles is better, causing higher elongation.

Water absorption and leaching behaviour

Figure 3.5 shows water absorption of the films from latex prevulcanized at 60°C for different periods. It can be seen that in the case of samples prevulcanized for 0.5 to 2 h, the percentage of water absorbed by the films slowly increased during 24 h. When the prevulcanization time was increased to 3 h, the films attained maximum water absorption in 8 h. On further extending the time of heating to 6 h, the maximum water absorption was attained during 4 h.

Figure. 3.6 shows water absorption of films from latex prevulcanized at 70°C for different periods. This figure also shows that at shorter prevulcanization time equilibrium water absorption was attained slowly. As the period of prevulcanization increased the films attained equilibrium water absorption faster. During 0.5 to 1 h of prevulcanization, the films did not attain equilibrium even after 24 h, but when the time of heating increased to 2 h, the films attained equilibrium in 3 h. On extending the prevulcanization time to 3 h the equilibrium was attained at a still faster rate.

The extent of capillary flow would be relatively small in lightly crosslinked particles where the constraints on particle coalescence are less. In such a network, water absorption rate is low. When the level of prevulcanization is increased the rubber particles become harder and the films prepared therefrom become discontinuous and porous. Thus equilibrium is attained more rapidly when the extent of prevulcanization is increased.

When the films are immersed in water, absorption and leaching occur simultaneously. The extract after leaching the films in water for 24 h is shown in Table 3.2. It can be seen that when the extent of prevulcanization was increased by increasing the temperature or the heating time, the extract from the films also increased. This can be attributed to the structural differences as explained earlier.

Stress relaxation characteristics

Figures 3.7, 3.8, 3.9 and 3.10 present the stress relaxation curves of films cast from prevulcanized latex prepared at different conditions. The relaxation patterns of the samples were studied at 600% elongation. Table 3.3 shows the slope of these lines. It is seen that when the extent of prevulcanization increased, the rate of stress relaxation also slightly increased. There are two important mechanisms which can lead to stress relaxation in a crosslinked elastomer:[10] (a) physical stress relaxation due to molecular rearrangements requiring little primary bond formation or breakage and (b) chemical stress relaxation due to chain scission, crosslink scission or crosslink formation. Under normal conditions, both physical and chemical stress relaxations occur simultaneously. However, at ambient temperature the rate of chemical stress relaxation in a rubber such as NR is very low and the relaxation behaviour is dominated by physical processes except for very long periods. From Table 3.3, it is seen that the slope of the lines increases with increase in the extent of prevulcanization. When the extent of prevulcanization is increased, there is only limited interdiffusion of the rubber particles which accounts for the slightly higher rate of stress relaxation.

CONCLUSIONS

Maximum crosslinking was obtained when prevulcanization was conducted either at 80°C for 2 h or at 90°C for 1 h. At lower temperatures the rate of reaction was slow. On extending the prevulcanization time, crosslink density was observed to pass through a maximum. Modulus of the films varied in line with Vr values. Tensile strength and elongation at break were better when prevulcanization was conducted at lower temperature and at each temperature, with a shorter heating time. The rate of extraction of water soluble materials increased with the extent of prevulcanization. The rate of stress relaxation slightly increased when the extent of prevulcanization increased. Based on overall balance of properties the optimum conditions for prevulcanization are 70 °C and 2 h.

Table 3.1
Formulation of latex compound.

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Potassium laurate solution, 20%	1.3
Sulphur dispersion, 50%	3.0
Zinc diethyldithiocarbamate dispersion, 50%	2.0
Zinc oxide dispersion, 50%	0.4

Table 3.2
Extract after leaching of films in water for 24 h at room temperature

Prevulcanization time at 60°C (h)	Extract (%)	Prevulcanization time at 70°C (h)	Extract (%)
0.5	1.08	0.5	1.57
1.0	1.10	1.0	2.04
2.0	1.15	2.0	2.58
3.0	1.93	3.0	2.75
4.0	2.04	4.0	2.86
6.0	2.14	- -	- -

Table 3.3 Effect of prevulcanization conditions on stress relaxation of films.

Prevulcanization		
Temperature (°C)	Time (h)	Slope of the lines
60	4.0	0.0535
60	6.0	0.0568
70	2.0	0.0566
70	4.0	0.0625
80	1.0	0.0578
80	2.0	0.0653
90	0.5	0.0609
90	1.0	0.0788

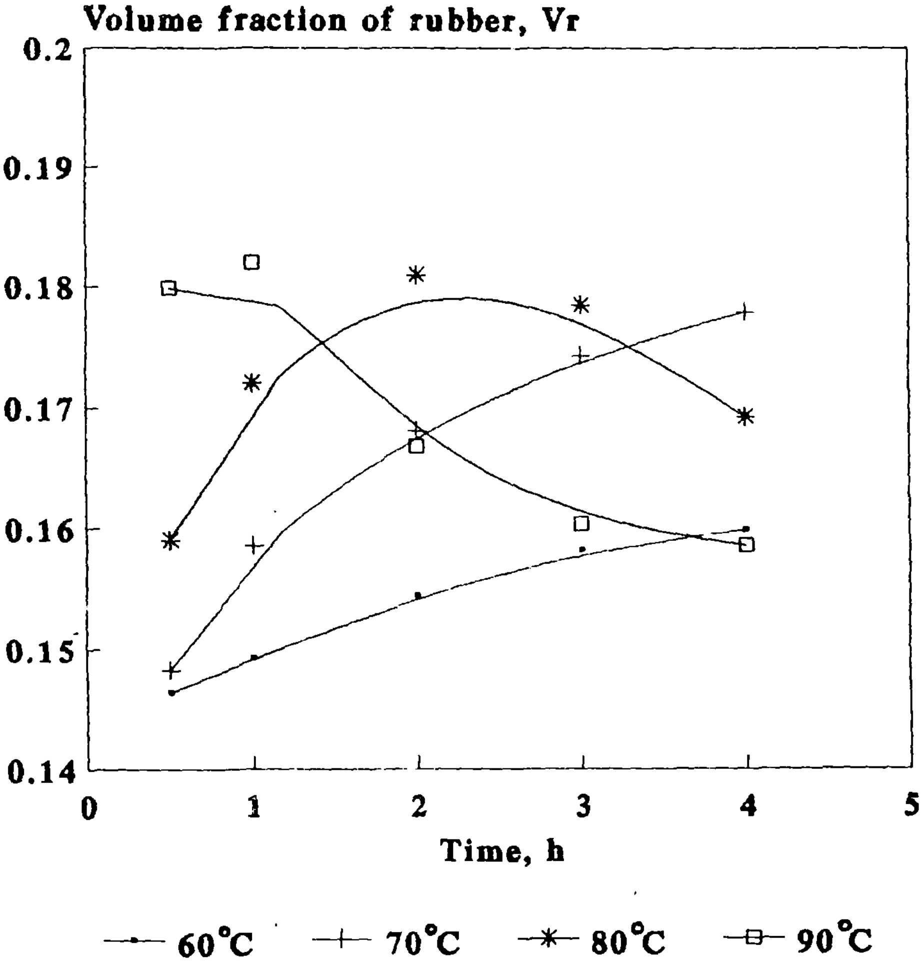

Fig.3.1. Effect of prevulcanization time and temperature on volume fraction of rubber

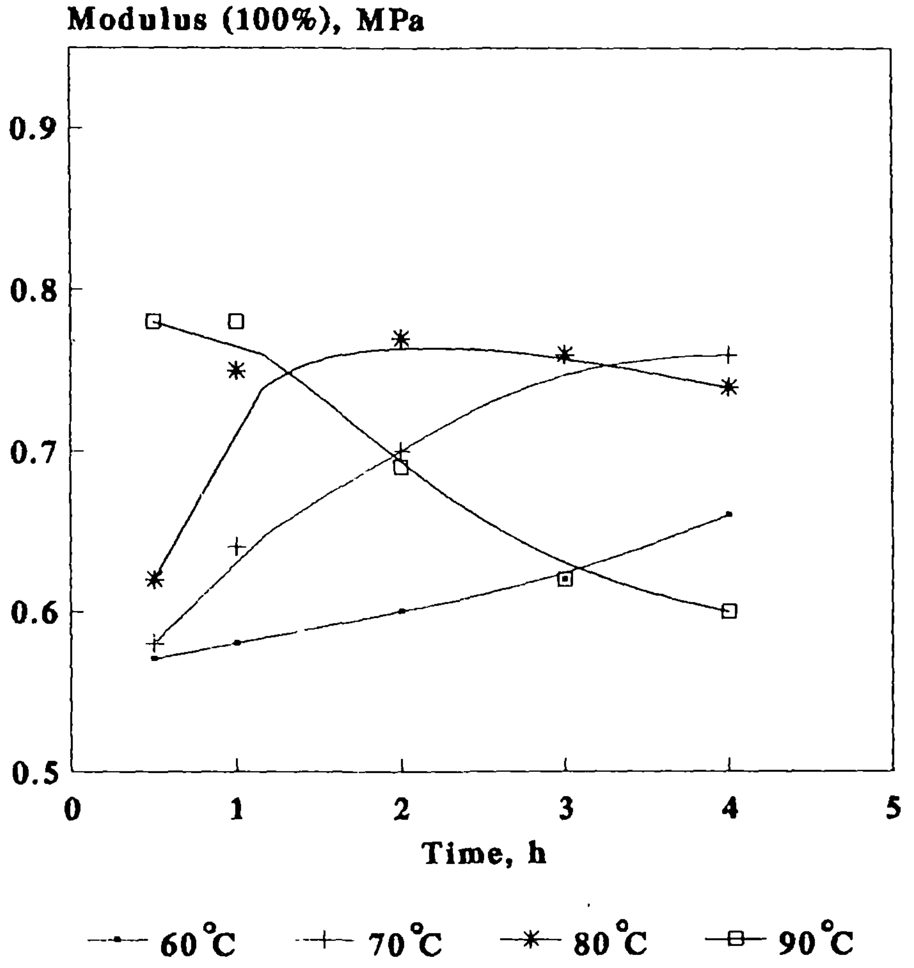

Fig.3.2. Effect of prevulcanization time and temperature on modulus at 100% elongation.

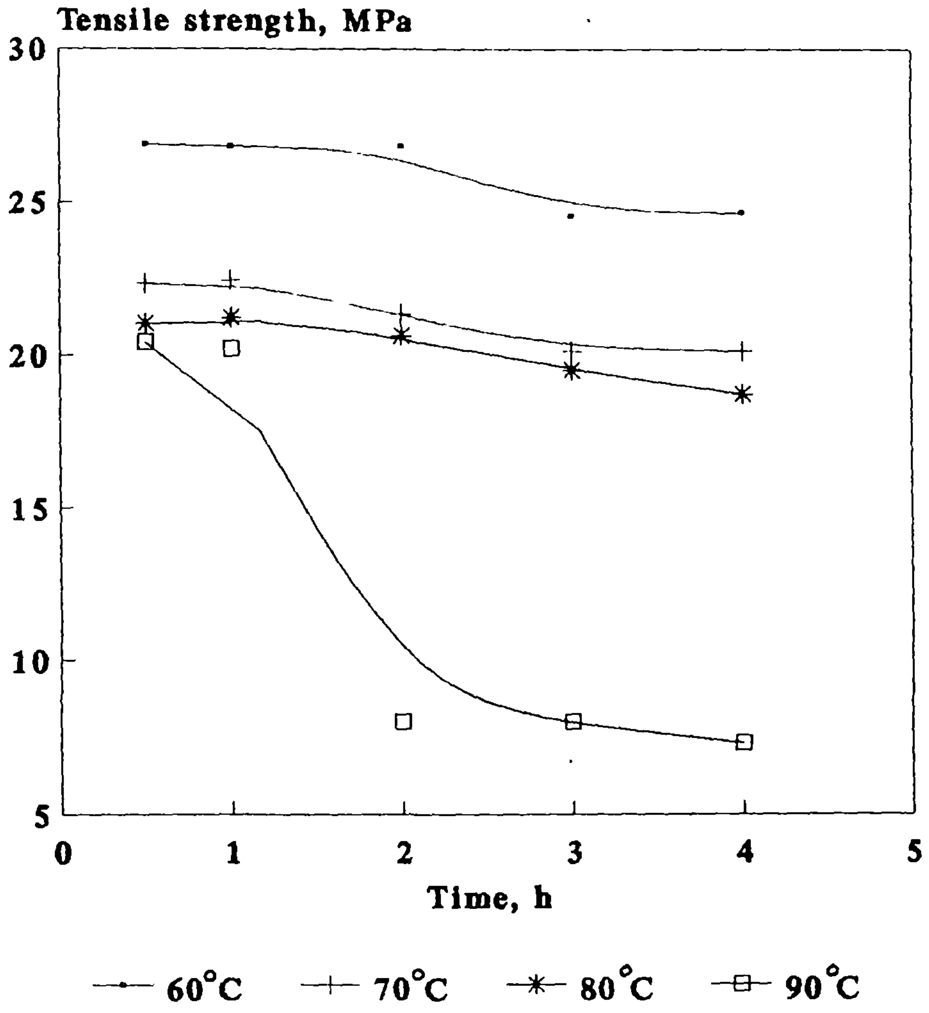

Fig.3.3. Effect of prevulcanization time and temperature on tensile strength

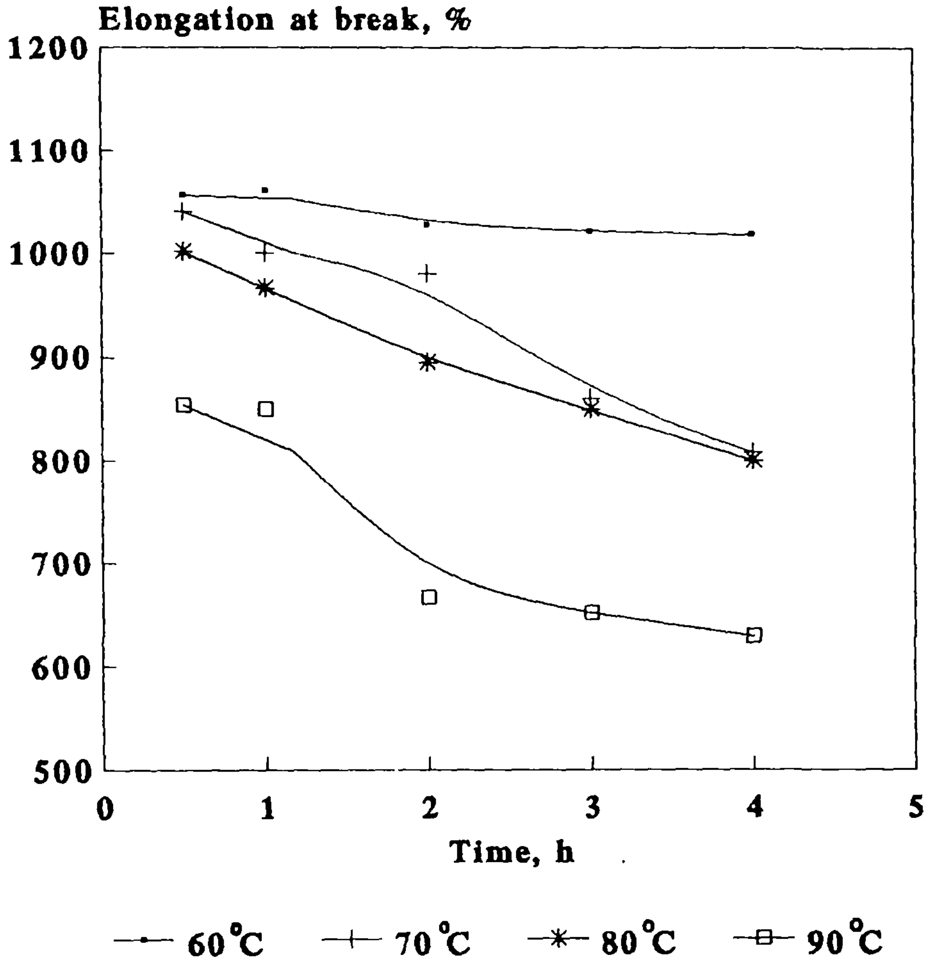

Fig.3.4. Effect of prevulcanization time and temperature on elongation at break

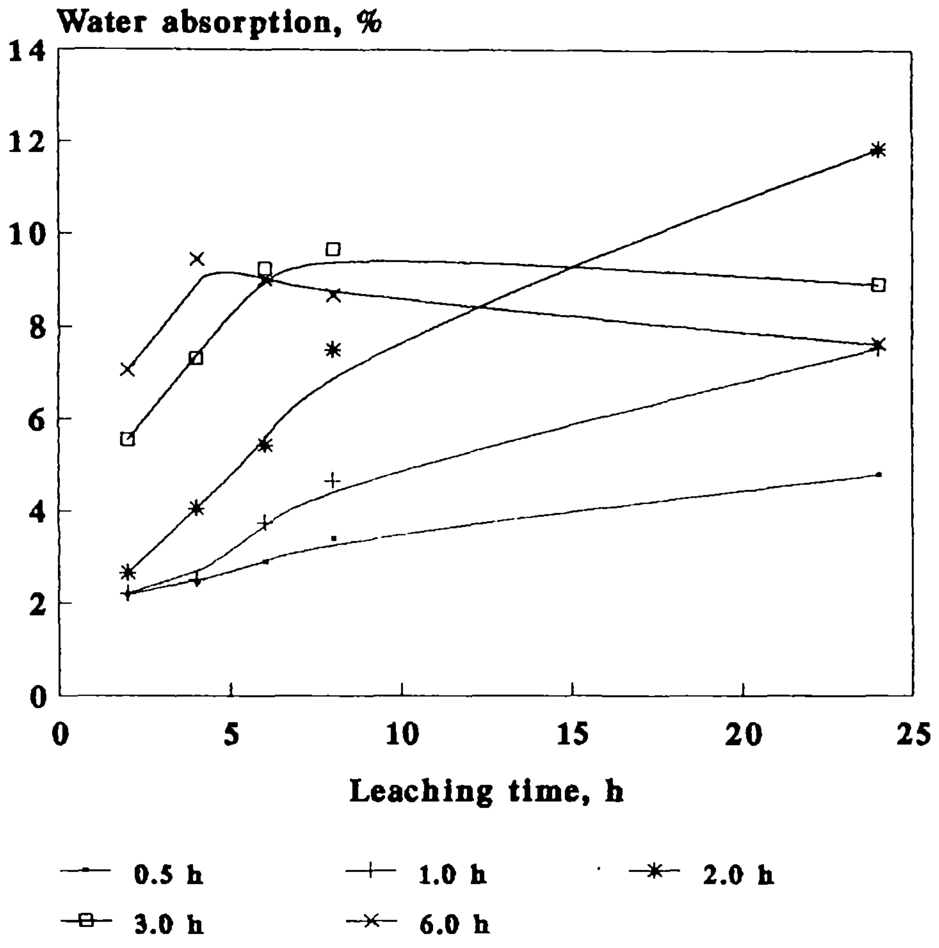

Fig.3.5. Effect of leaching time on water absorption of films from latex prevulcanized at 60°C for different periods.

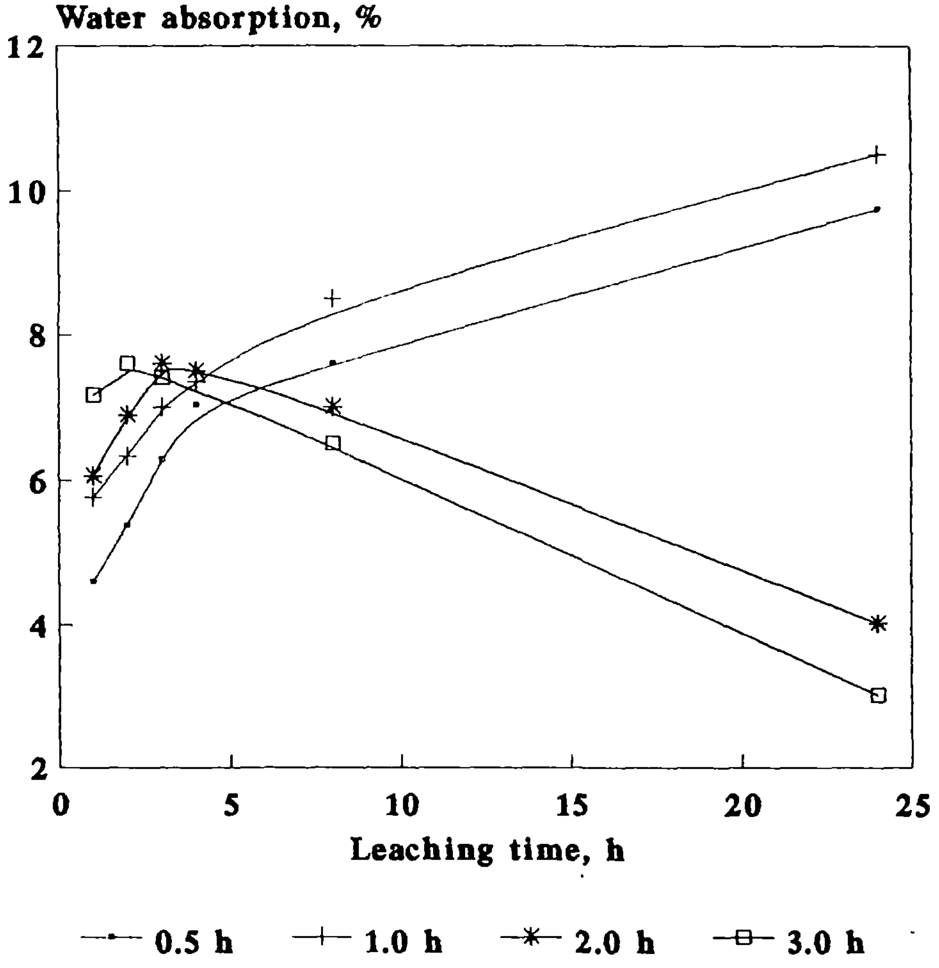

Fig.3.6. Effect of leaching time on water absorption of films from latex prevulcanized at 70°C for different periods.

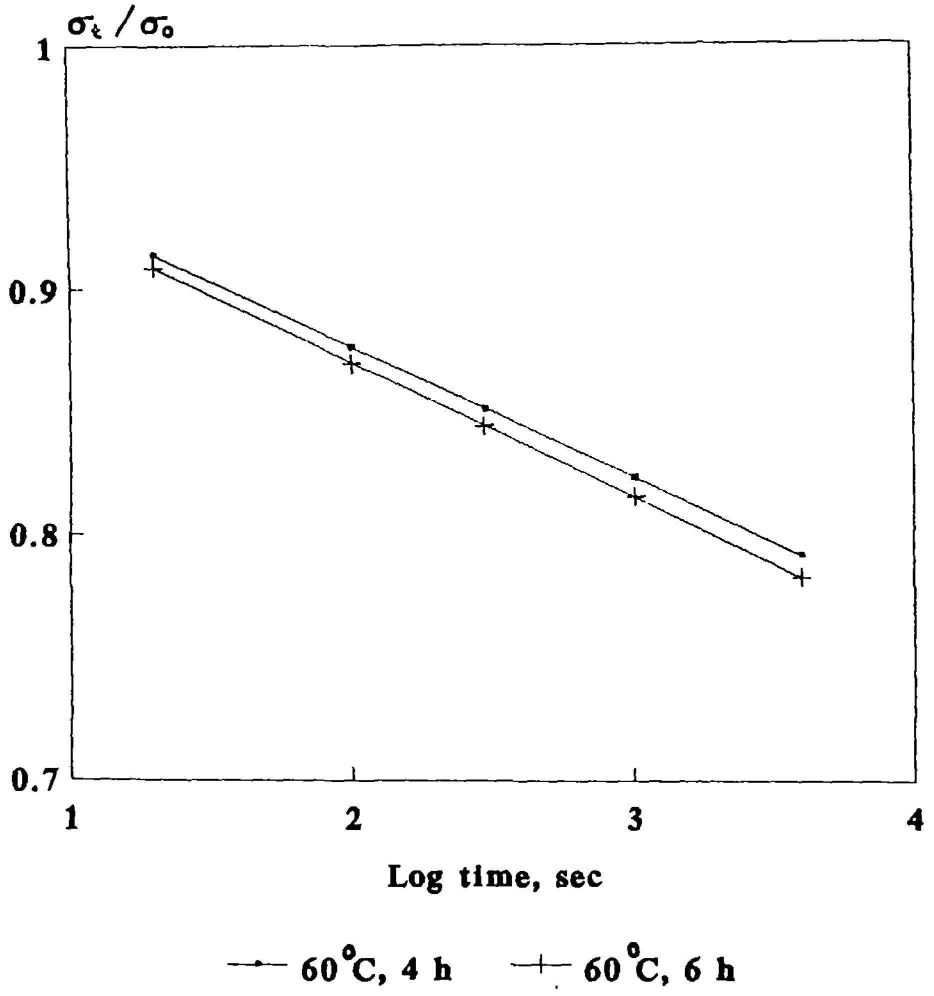

Fig.3.7. Semilog plots of stress decay as a function of time for films from latex prevulcanized at 60°C,4h and 6h

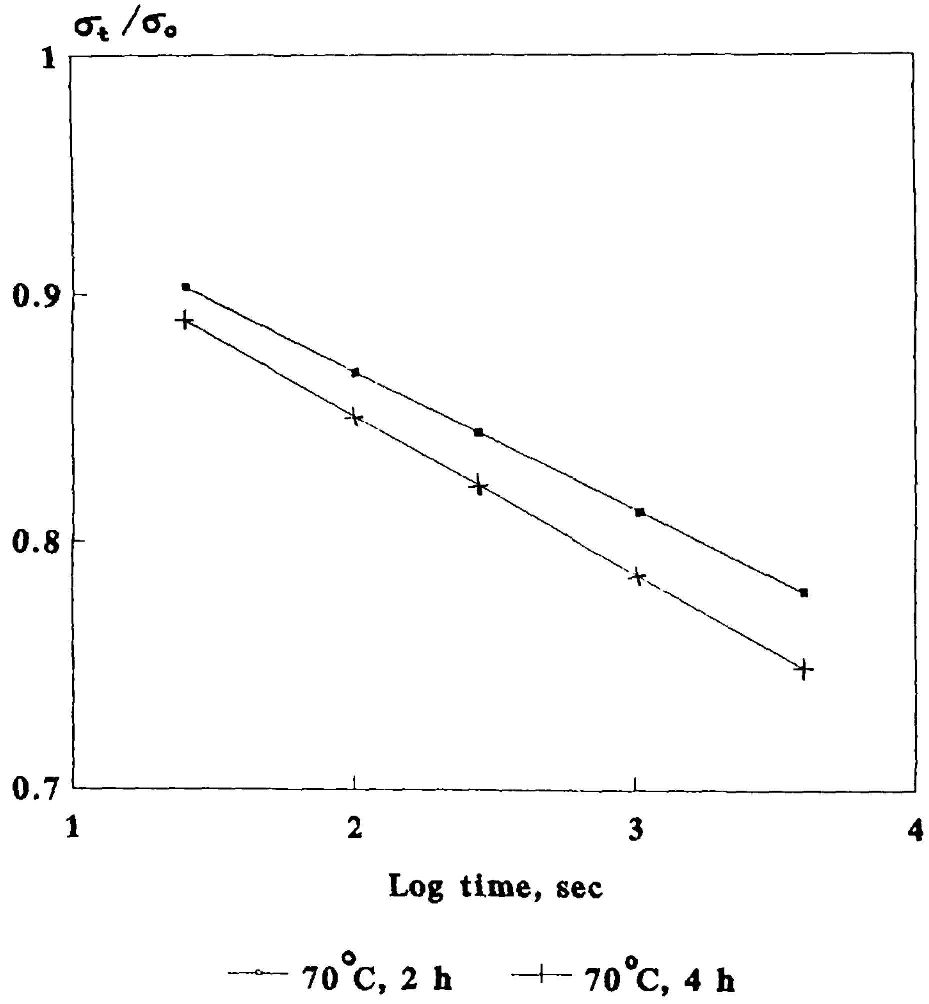

Fig.3.8. Semilog plots of stress decay as a function of time for films from latex prevulcanized at 70°C, 2h and 4h

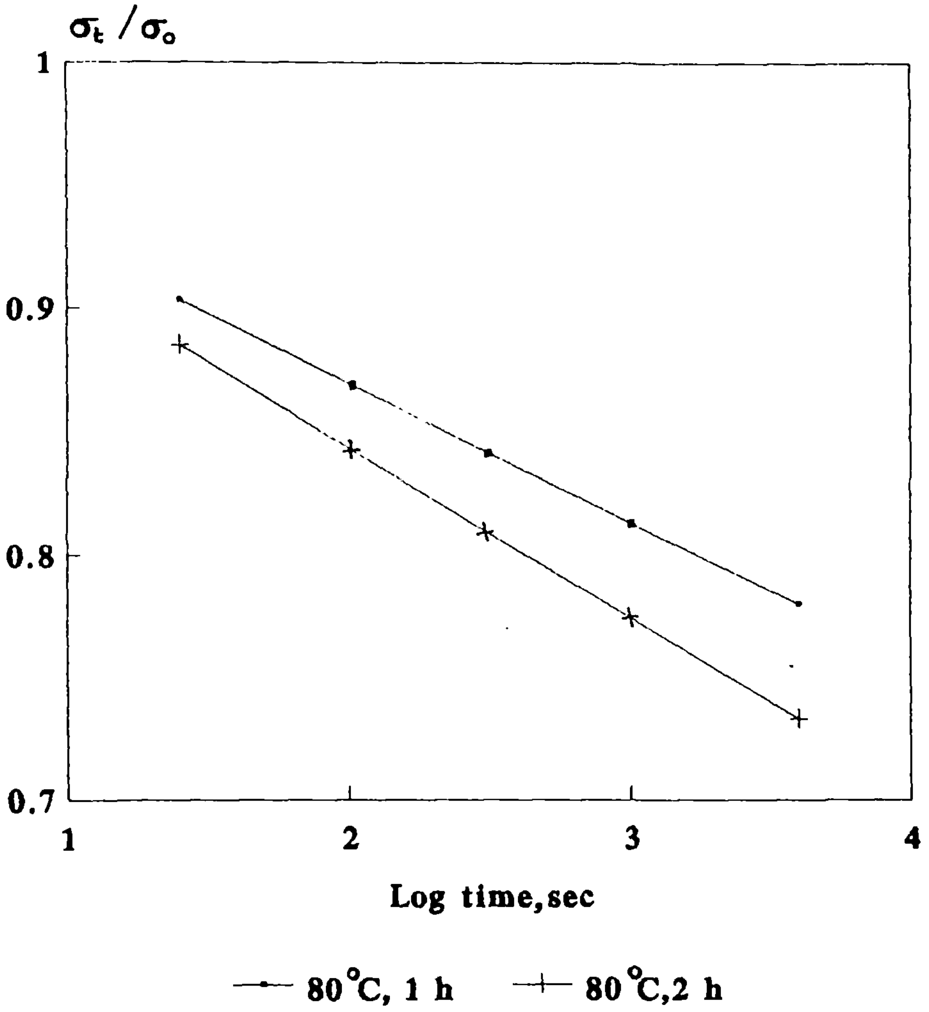

Fig.3.9. Semilog plots of stress decay as a function of time for films from latex prevulcanized at 80°C,1h and 2h

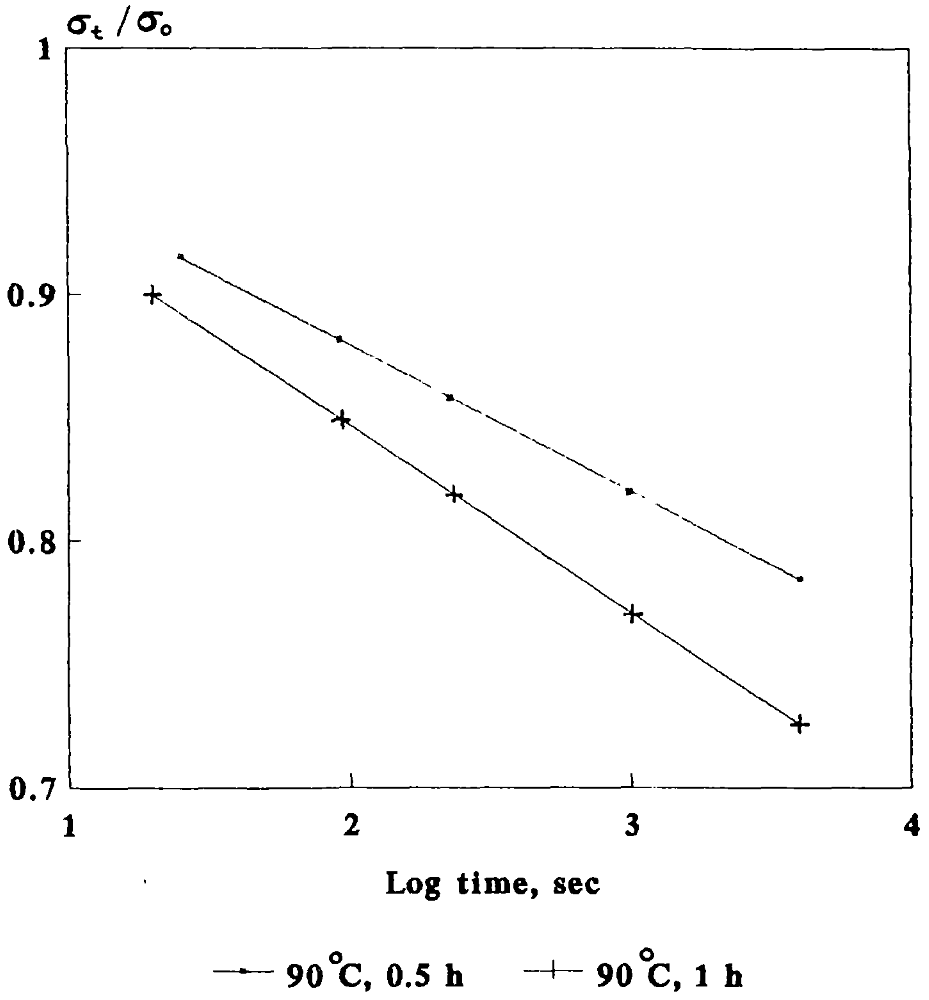

Fig.3.10. Semilog plots of stress decay as a function of time for films from latex prevulcanized at 90 °C,0.5h and 1h

PART B

RHEOLOGICAL PROPERTIES OF PREVULCANIZED LATEX

During processing, latex is subjected to different forms of stress which may cause flow. Various techniques such as dipping, extrusion, casting, brushing, spraying etc. are employed for manufacture of products from latex. Each technique involves a critical relation between temperature, stress and inherent fluid property such as viscosity of latex. A thorough evaluation and understanding of the rheological characteristics and of the factors that can be used to alter the flow behaviour of latex are of vital importance for satisfactory operation. Viscosity of latex depends considerably on its solid content and particle size distribution.[11] Effect of dry rubber content and temperature on viscosity of NR latex was investigated.[12] The flow behaviour of latex can be modified by the incorporation of viscosity modifiers to suit the manufacturing process involved. The effect of surface active agents on the rheological properties of centrifuged and creamed latex have been reported.[13]

The rheology of rubber solutions, suspensions, latex and latex compounds had been studied by Leaman.[14] According to Collins et al., [15] the important factors affecting rheological behaviour of latex are shear rate, particle size distribution and presence of electrolytes.

Studies[16] on the rheological behaviour of natural and synthetic rubber latices in presence of surface active agents showed that addition of the surface active agents increased the viscosity of NR and SBR latices while they decreased that in the case of ENR latex. The rheological behaviour of blends of natural rubber and styrene butadiene rubber latices has also been reported.[17]

This study reports the rheological behaviour of prevulcanized natural rubber latex with special reference to influence of viscosity modifiers and fillers on its flow properties under different shear rates and temperatures.

EXPERIMENTAL

Centrifuged natural rubber latex (high ammonia preserved) conforming to IS 5430-1981 was used for this study. The insoluble ingredients were prepared as dispersions by ball milling.

Prevulcanization

Latex compound was prepared as per the formulation given in Table 3.1. Prevulcanization was carried out at 70°C for 2 h. The latex was immediately cooled and stored at room temperature. On the next day it was decanted and filtered through a 100 mesh sieve. The total solids of the latex was adjusted to 58 per cent.

Viscosity modifiers

Viscosity modifiers such as casein, polyvinyl alcohol and sodium carboxymethyl cellulose were prepared as 5 per cent solutions in water. The dosage of viscosity modifiers used was 0.25 phr.

Fillers

Fillers such as china clay and whiting were prepared as 50 per cent dispersions in water, while precipitated silica was prepared as 25 per cent dispersion in water. The dosage of fillers used was 10 phr. The total solids content of the mixes were adjusted to 48 per cent before making rheological measurements.

Rheologcal measurements

The flow behaviour of PVL and that containing viscosity modifiers and fillers was studied using a Haake Viscotester VT550. Sensor system NV was used for the measurements. The study was conducted at three different temperatures 25, 35 and 45°C and at shear rate from 1 to 150 s^{-1}

RESULTS AND DISCUSSION

Effect of shear rate on viscosity

Figure 3.11 shows the effect of shear rate on viscosity of PVL at 25,35 and 45°C. On increasing the shear rate, viscosity of latex decreased which indicated its pseudoplastic behaviour. The effect is more pronounced at low shear rates, approaching near-Newtonian behaviour at high shear rates. NR latex is a non-Newtonian liquid which exhibits pseudoplastic flow pattern.[18] During prevulcanization crosslinking takes place in each of the individual rubber particles without altering their state of dispersion appreciably. Thus the particles have the same shape, size and size distribution after prevulcanization.[19] At rest the particles are extensively entangled and/or randomly oriented. Under shear the particles become oriented in the direction of flow and the points of entanglements are reduced, which causes the observed reduction in viscosity on increasing shear rate.[20] In NR latex a layer of tightly bound water molecules is present around the rubber particles.[21] At high shear rate orientation may be maximum exhibiting near-Newtonian behaviour.

Effect of viscosity modifiers

Figure 3.12 shows the effect of shear rate on viscosity of PVL in the presence of viscosity modifiers such as casein, polyvinyl alcohol (PVA) and sodium carboxymethyl cellulose (NaCMC). Viscosity modifiers are hydrocolloids and give viscous solutions in water which display the properties of a typical lyophilic colloid. They find their principal application in latex technology as modifiers of bulk flow behaviour and produce thickening effect when added to latex. Figure 3.12 shows that all the viscosity modifiers increased the viscosity of PVL both at low and high shear rates. Among these the most significant effect is obtained by the addition of NaCMC. PVA offers a higher viscosity than casein at low shear rates but as the shear rate increases (20 to 150 s^{-1}) PVA offers a marginally lower viscosity than casein. This may be due to the easier displacement of the adsorbed layer of PVA from the surface of rubber particles at higher shear rates. The increase of viscosity by the addition of viscosity modifiers is more pronounced at low shear rate and narrows down as shear rate increases. Generally viscosity modifiers are distributed along the interphase and the aqueous phase. A network will be formed between molecules of the viscosity modifiers adsorbed on the surface of the rubber particles and those present in the aqueous phase. This partially restricts the brownian movement of the rubber particles. This will lead to agglomeration of rubber particles which causes an increase in particle size and thereby increase in viscosity.

Compared to raw PVL, that containing viscosity modifiers exhibited more pseudoplasticity as is evident from the rapid decrease in viscosity with increase in shear rate (Fig. 3.12). When shear rate increases viscosity modifiers are easily displaced from the rubber particles and the network becomes loose and the tendency of the rubber particles to slide past each other will be enhanced.

The higher pseudoplastic nature of the system containing viscosity modifiers is also evident from the flow index (n) values shown in Table 3.4. The value of n for a real fluid gives a relative measure of how its behaviour deviates from that of an ideal (Newtonian) fluid characterized by an n value of unity. The flow index (n) can be considered as an inherent property of the fluid. A value of $n>1$ indicates dilatant behaviour while $n<1$ indicates pseudoplastic behaviour. A low value of n reveals more pseudoplastic nature. Table 3.4 shows that compared to raw PVL,those containing viscosity modifiers have lower values of n which indicate more pseudoplastic nature. Among the three viscosity modifiers, NaCMC imparts the maximum effect. The effectiveness of the viscosity modifiers in increasing pseudoplasticity of PVL decreases in the order, NaCMC > PVA > casein

Zero shear viscosity

The zero shear viscosity of PVL and that containing viscosity modifiers are given in Table 3.5. Among the viscosity modifiers, the highest zero shear viscosity was exhibited by the system containing NaCMC followed by PVA and casein. The system with the highest zero shear viscosity exhibited more pseudoplastic behaviour.

Effect of Temperature

Viscosity of rubber depends on different factors such as shear rate, temperature and chemical composition. As with increase in shear rate, increase of temperature also decreased the viscosity of PVL and that containing viscosity modifiers as is shown in Figure 3.13. It is also clear form Table 3.4 that the value of flow index increased as the temperature is increased from 25 to 45°C indicating that an increase of temperature decreased pseudoplasticity of PVL. Addition of viscosity modifiers also exhibited the same effect. Latex contains two distinct flow units a Newtonian solvent (water) and polymer particle (rubber). As temperature is increased free volume increases and as a result the flow units become less restricted, more highly energized and less organized thus resulting in decreased viscosity.[22]

Effect of fillers

Inorganic fillers are added to latex in order to cheapen and stiffen the product. An ancillary effect is the effect of such fillers upon the flow properties of latex.[23]

Effect of shear rate

Figure. 3.14 shows the effect of shear rate on viscosity of PVL in the presence of fillers such as precipitated silica, china clay and whiting. Precipitated silica and china clay increased the viscosity of PVL both at low and at high shear rates, while whiting slightly decreased it. As shear rate increased the viscosity of PVL containing all the fillers decreased, indicating pseudoplastic flow pattern. Table 3.6 shows the flow index values of PVL containing fillers. Addition of precipitated silica and china clay increased the pseudoplastic nature of PVL while that of whiting slightly decreased it.

The increase in viscosity caused by precipitated silica is due to its small particle size. Small particle size filler tends to remove surfactants from rubber particles to a greater degree than large particle size fillers.[24] The increase in viscosity caused by china clay is due to its slightly acidic nature which causes destablization of latex.

Effect of temperature

Figure 3.15 shows the effect of increasing temperature on viscosity of PVL containing fillers. As temperature increased viscosity of PVL and that containing fillers decreased. A rise in temperature increases the free volume and the flow units become less restricted, more highly energized and less organized, thus decreasing the viscosity.

Zero shear viscosity

Table 3.7 shows the zero shear viscosity of the mixes. It can be seen that the mix containing silica exhibited maximum zero shear viscosity followed by clay. Whiting exhibited lower zero shear viscosity than raw PVL.

CONCLUSIONS

Prevulcanized natural rubber latex exhibited pseudoplastic flow pattern. Addition of viscosity modifiers such as casein, PVA and NaCMC increased the viscosity and pseudoplasticity of PVL. Addition of fillers such as precipitated silica and china clay also increased the viscosity and pseudoplasticity of PVL while the addition of whiting slightly decreased them. Temperature sensitivity of PVL remained unaffected by the addition of viscosity modifiers and fillers.

Table 3.4

Flow index values of PVL containing viscosity modifiers at different temperatures.

Sample	Flow index (n)		
	25°C	35°C	45°C
PVL	0.7660	0.7744	0.7811
PVL + casein	0.6008	0.7360	0.7378
PVL + PVA	0.5618	0.6189	0.6734
PVL + NaCMC	0.4379	0.4546	0.4564

Table 3.5

Zero shear viscosity of PVL containing viscosity modifiers at 25°C

Sample	Zero shear viscosity (mPa s)
PVL	134.8
PVL + casein	179.2
PVL + PVA	228.1
PVL + NaCMC	616.0

Table 3.6
Flow index values of PVL containing fillers at different temperatures

Sample	Flow index (n)		
	25°C	35°C	45°C
PVL	0.7660	0.7744	0.7811
PVL + whiting	0.7700	0.7768	0.7797
PVL + clay	0.6623	0.6625	0.6633
PVL + silica	0.6147	0.6217	0.6349

Table 3.7
Zero shear viscosity of PVL containing fillers at 25°C

Sample	Zero shear viscosity (mPa s)
PVL	134.8
PVL + whiting	120.2
PVL + clay	160.4
PVL + silica	231.0

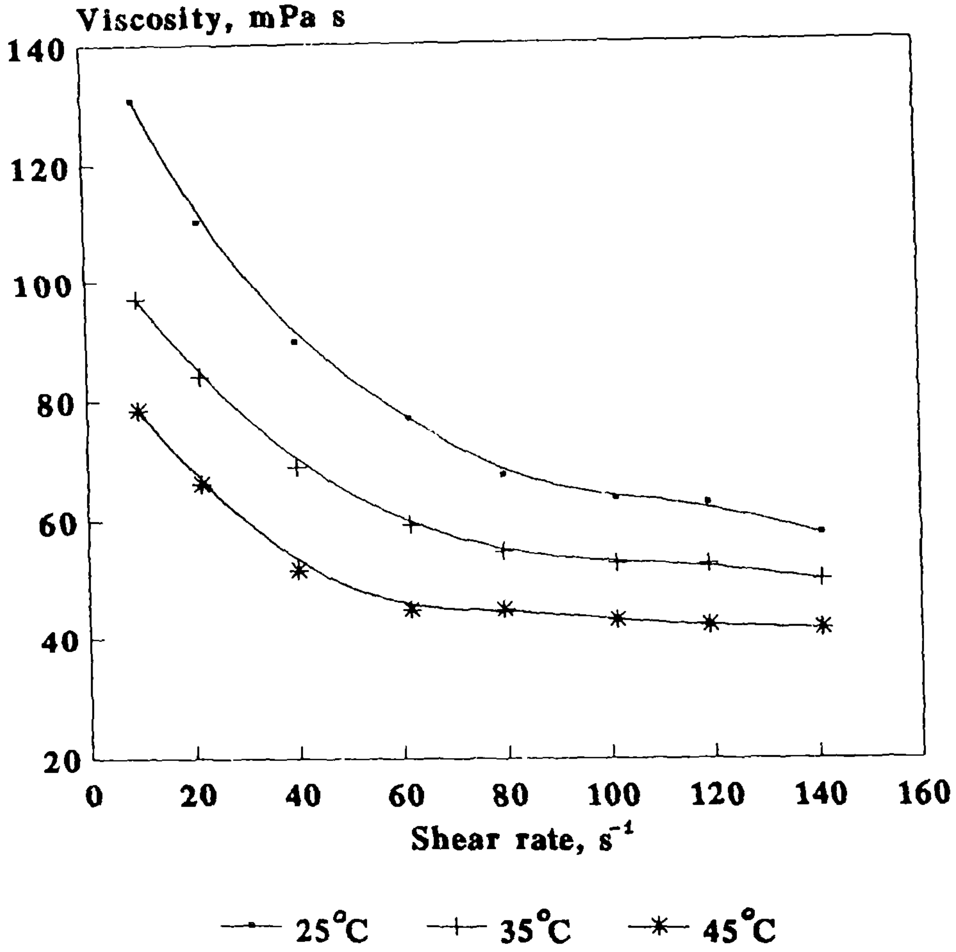

Fig.3.11. Effect of shear rate on viscosity of PVL at different temperatures

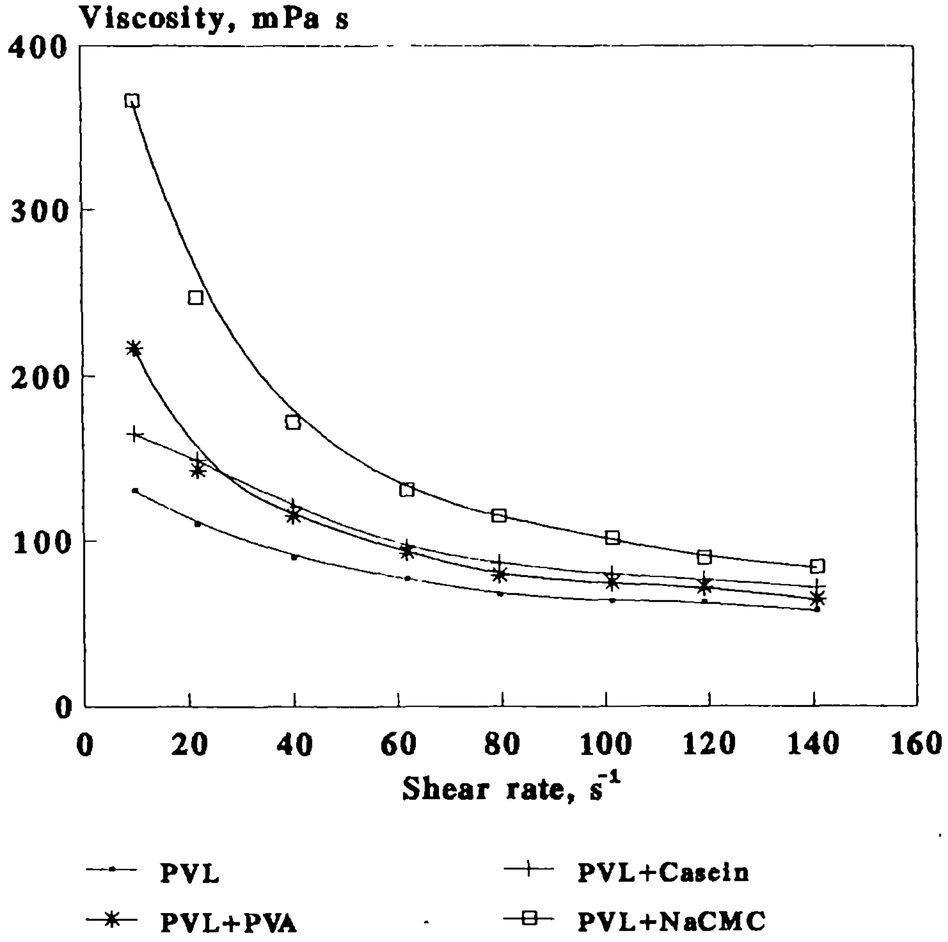

Fig.3.12. Effect of shear rate on viscosity of PVL containing viscosity modifiers at 25°C

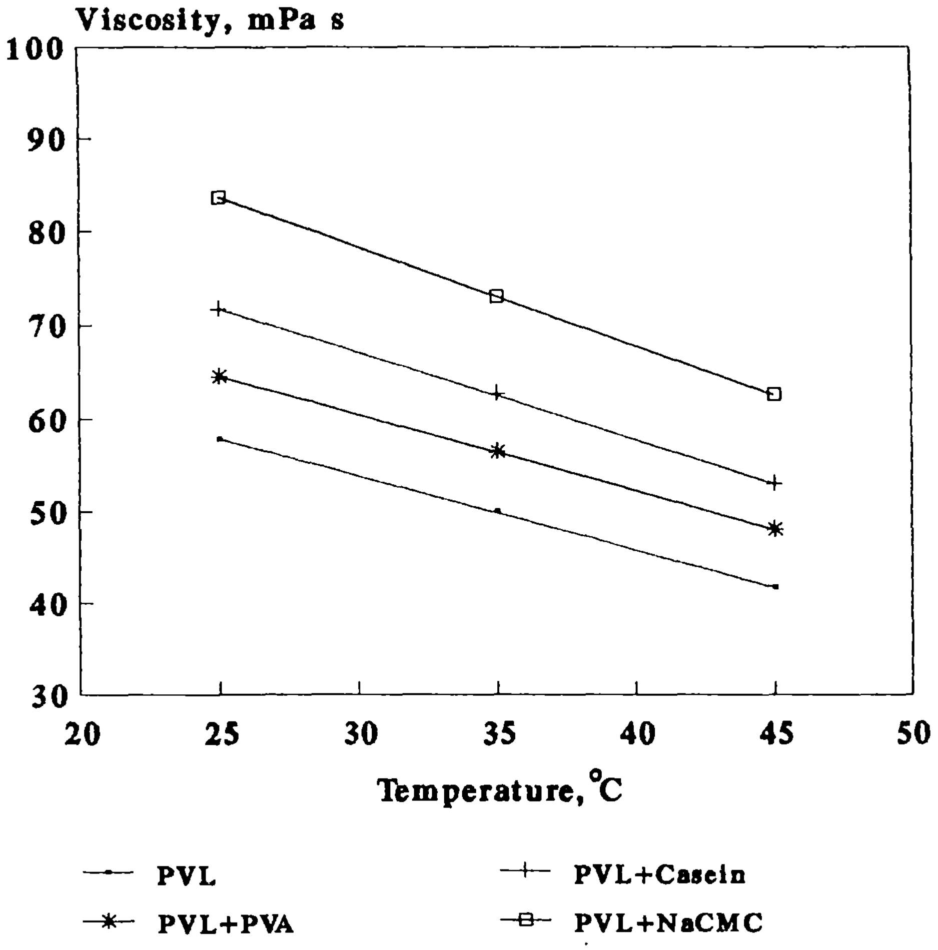

Fig.3.13. Effect of temperature on viscosity of PVL containing viscosity modifiers at shear rate of 140.7 s^{-1}

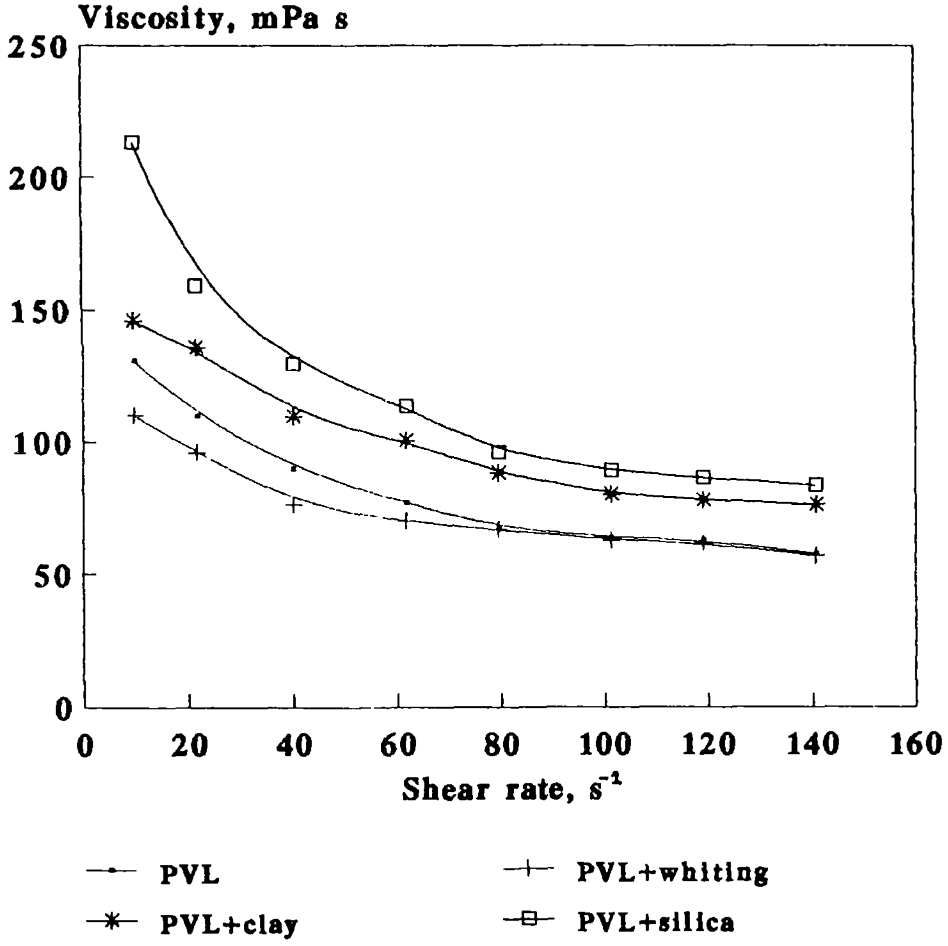

Fig.3.14. Effect of shear rate on viscosity of PVL containing fillers at 25°C

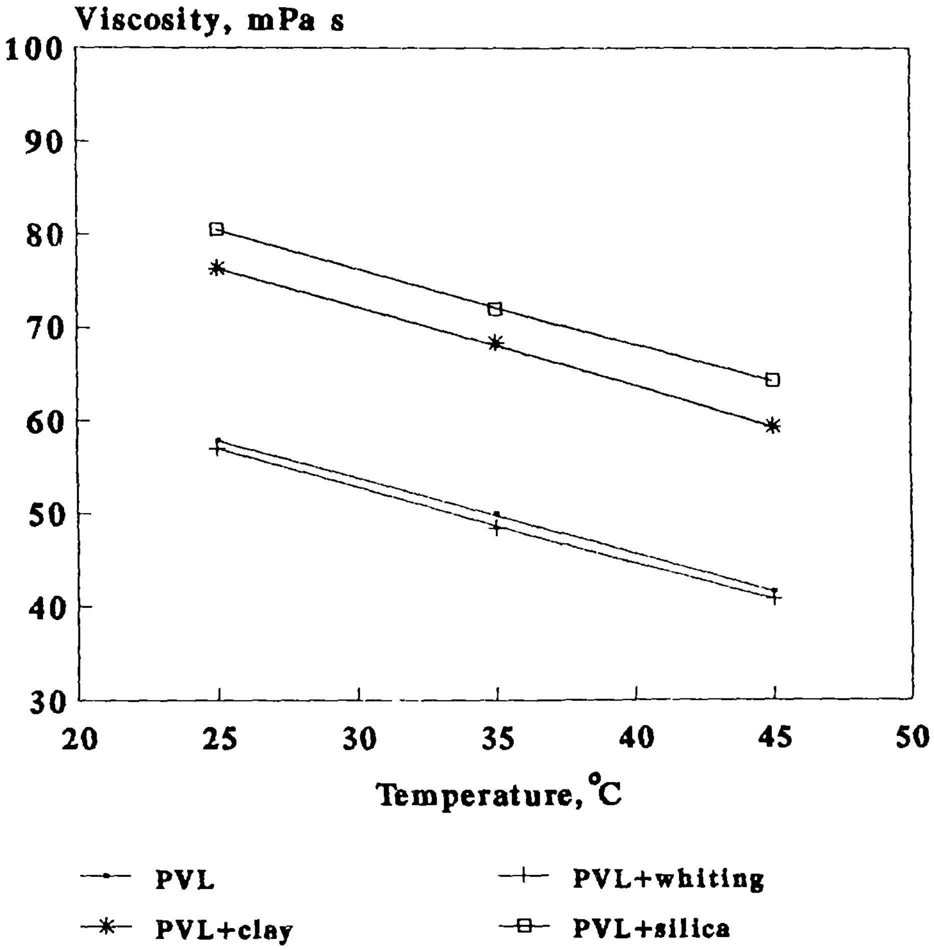

Fig 3.15. Effect of temperature on viscosity of PVL containing fillers at shear rate of 140.7 s^{-1}

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CHAPTER 4

EFFECT OF STORAGE, AFTER-TREATMENTS AND FILLERS ON QUALITY OF PVL FILMS

PART A

EFFECT OF STORAGE OF LATEX AND AFTER-TREATMENTS ON THE QUALITY OF FILMS FROM PREVULCANIZED LATEX

A number of products including medical items are commercially made from prevulcanized latex. The properties of prevulcanized latex film are affected by leaching in cold water and by heating.[1] The process of leaching is performed on most products made by dipping and also on latex thread and moulded foam. It is of particular interest in medical goods and in electricians' gloves, where the presence of hydrophilic materials would cause absorption of atmospheric moisture and reduction in electrical resistance.[2] Wet gel leaching is reported to be more efficient than dry film leaching.[3]

The present study reports the effect of storage of centrifuged NR latex on properties of prevulcanized latex film prepared therefrom. The effects of after-treatments, storage and ageing characteristics of the films are also reported. A comparison is also made between high ammonia and low ammonia preserved centrifuged latices. The effect of storage of prevulcanized latex was also studied.

EXPERIMENTAL

High ammonia and low ammonia preserved centrifuged latices conforming to the specifications of the Bureau of Indian Standards (BIS), IS: 5430-1981, were freshly prepared as described in Chapter 2 and stored for periods of up to 18 months. Sulphur, zinc oxide and zinc diethyldithiocarbamate were used as 50 per cent dispersions in water. The other ingredients were used as solutions in water.

Prevulcanization and film preparation

Latex samples were withdrawn periodically and compounds were prepared according to the formulation given in Table 4.1. Prevulcanization was conducted at 70°C for 2 h and films were prepared by casting in glass cells as described in Chapter 2.

After-treatments of films

The films after drying were removed from the glass cells and subjected to different treatments as follows.

1. Leaching in water at 30°C for 24 h and drying at room temperature.
2. Heating in air at 100°C for 30 min.
3. Treatment 1 followed by 2.

A few samples were kept without any treatments to study the effect of storage of film at ambient conditions on tensile properties.

In another trial prevulcanized latex was prepared from HA latex. A part of the latex was used for preparing films by casting and also by coagulant dipping as described in Chapter 2. Cast films were leached at different temperatures and also at different pH. Coagulant dipped films were given after-treatments 1 to 3 as stated earlier. Another part of the latex was stored for periods of up to 3 months. The properties of the latex and the films prepared from it were tested periodically.

Ageing studies

Tensile test pieces, punched out from the after-treated PVL films (Treatment 3), were aged in an air oven at 70°C for 14 days. Tensile properties of the aged samples were determined after conditioning the specimens for 16 h at room temperature.

RESULTS AND DISCUSSION

Properties of PVL films without after-treatment

Table 4.2 shows the effect of storage of HA latex up to 4 months on tensile properties of PVL films without after-treatment. It can be seen that the PVL film prepared from fresh latex is having low tensile properties. When the storage period of latex was two months, the films showed better tensile properties. On increasing the storage period to four months the tensile properties remained more or less constant. This shows that the strength of PVL film is affected by the storage period of latex and the optimum storage period is around 2 months. The results with LATZ latex (Table 4.3) also show the same trend.

During prevulcanization, each individual latex particle is vulcanized and immediately on formation of the film primary bonds may not form between the rubber particles. The structure of the rubber film obtained by drying vulcanized latex is therefore, discontinuous and the forces which unite the latex particles can only be the secondary forces or van der Waals forces.[4] The tensile strength of such a film is governed mainly by the magnitude of these secondary forces and thus depends, in a very large measure, on the extent to which the particles in the film can approach one another. The adsorption layer of proteins and phospholipids present on the surface of the rubber particles in latex[5] also plays an important role during the formation of film from vulcanized latex. When the latex is fresh, the adsorption layer is thick and compact and more firmly attached to rubber particles so that interparticle fusion is less favoured, thus exhibiting low tensile properties. When the latex is aged, structural changes occur on the adsorption layer on the rubber particles [6] and the predominantly protein- phospholipid layer is largely replaced with a fatty acid soap layer. Interparticle fusion is made easier, thus increasing the strength properties of film.

Effect of after-treatments of film

The effect of after-treatments of PVL films prepared from HA and LATZ latices are also shown in Tables 4.2 and 4.3 respectively. The treatments substantially improve the tensile properties of the films irrespective of the storage period of latex used for prevulcanization. Treatment 1 (leaching) was found to be better than 2 (heat treatment). In the case of a purely prevulcanized film there is only limited interdiffusion of the rubber molecules among individual internally crosslinked rubber particles as the mobility of the molecular chain ends becomes restricted. This results in a film in which the original particles are held together principally by chain entanglement. During leaching most of the soluble hydrophilic materials are washed away thus facilitating better cohesion of the rubber particles, allowing greater degree of entanglement between molecules anchored in different particles and enhanced tensile properties.

Table 4.4 shows the effect of after-treatments of PVL films on volume fraction of rubber (Vr). It is seen that by Treatment 2 (heating) more crosslinks are introduced. By Treatment 1 (leaching) the degree of crosslinking remained almost the same, but in Treatment 3 (leaching followed by heating) a slight increase in Vr was obtained which is lower than that obtained in Treatment 2. All these treatments improved the tensile properties of the films. Although maximum Vr values were realized by Treatment 2, Treatments 1 and 3 gave better properties to the films. This shows that in prevulcanized latex film, tensile properties are not governed solely by the degree of crosslinking, but the degree of cohesion of the particles also has same influence.

Effect of leaching at different conditions

Table 4.5 shows the effect of leaching at different temperatures. By increasing temperature of leach water the time required for leaching can be reduced and at 30°C optimum properties are obtained at 4 h of leaching. Beyond 4 h properties did not improve significantly. But for convenience, samples for the other experiments were leached for 24 h.

The effect of leaching at different pH on tensile properties before and after ageing is shown in Table 4.6. Before ageing the tensile properties are more or less unaffected by leaching of the films at different pH. But after ageing, the properties slightly decreased on increasing the pH of water. This may be due to the alkaline hydrolysis of protiens in the film.

Effect of after-treatment of coagulant dipped films

The effect of after-treatment of coagulant dipped films is shown in Table 4.7. The after-treatments improved the properties of the films and as in the case of cast films, leaching was better than heat treatment.

Effect of storage of PVL film at room temperature

Figure 4.1 shows the effect of storage of prevulcanized film prepared from HA latex stored for different periods on tensile strength. When the film was stored at room temperature its tensile strength increased and attained a maximum value, irrespective of the storage period of latex used for prevulcanization. However, the maximum tensile strength obtained by PVL film from fresh latex was low compared to that from stored latex. As the storage period of latex increased to two months the maximum value attained also increased. A further increase in the storage period to four months did not cause any appreciable change. This shows that properties of untreated film improves on keeping at room temperature. The improvement is not influenced by storage of original latex beyond 2 months.

Modulus and elongation at break (Figs. 4.2 and 4.3 respectively) show a similar trend, but in the case of elongation at break the PVL film prepared from latex stored for 60 days and beyond showed only marginal increase on storage.

Figures 4.4, 4.5 and 4.6 show the effect of storing PVL film obtained from LATZ latex stored for different periods on tensile strength, modulus and elongation at break respectively. The same trend as in the case of films prepared from HA latex was observed.

On storing the films at room temperature, further gradual coalescence occurs[7] which improves film properties. Coalescence is also influenced by the adsorption layer on rubber particles. When the latex is aged structural changes occur due to the presence of enzymes, bacteria and preservatives. During a two months storage period major changes occurring in latex are stabilized and further storage does not cause significant changes.

Effect of ageing

The tensile properties before and after ageing of after-treated (Treatment 3) PVL films prepared from HA and LATZ latices are shown in Tables 4.8 and 4.9 respectively. It is seen that before ageing, the tensile properties are more or less unaffected by storage of latex up to 6 months. But when the latices were stored for 1 year and above, properties decreased. On ageing the properties decreased as the storage period of latex increased. The decrease was faster when the storage period was 1 year and more.

Table 4.10 shows the effect of storage of latices on volume fraction of rubber (Vr) in the swollen vulcanizates. Vr can be taken as a measure of crosslink density. As the storage period increases Vr decreases. This also contributes to the reduction in tensile properties.

The presence of materials which exert an antioxidant effect in latex has been recognized for many years.[8] Choline compounds present in latex are vulcanization accelerators and also show antioxidant properties in rubber. The higher the concentration of undegraded phospholipids in latex the higher the rate of cure.[9] During long term storage the natural accelerators and antioxidants present in latex are getting converted into other products and/or are used up which causes a reduction in tensile properties and ageing resistance of the vulcanizates.

Effect of storage of prevulcanized latex

The properties of prevulcanized latex during storage of up to 3 months are shown in Table 4.11. Viscosity and MST of the latex did not change significantly during the three months period. The unreacted vulcanizing ingredients continue to vulcanize the rubber during storage as seen from the increase in modulus values. It appears that most of the postvulcanization occurred within the first month of storage.

CONCLUSIONS

Storage period of centrifuged latex affected the tensile properties and ageing resistance of prevulcanized latex films prepared from it. PVL film prepared from fresh latex showed low tensile properties, while that from stored latex exhibited better properties. After-treatments of the films substantially improved the tensile properties irrespective of the storage of latex. Out of the treatments studied, leaching in water imparted better properties to the films than heat treatment and at 30°C optimum properties were obtained at 4 h of leaching. PVL films from HA and LATZ latices exhibited the same trend. Storage of prevulcanized latex did not significantly affect the latex properties. The unreacted ingredients continue to crosslink the rubber during the first month of storage.

Table 4.1
Formulation of latex compound

Ingredients	Parts by weight (wet.)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Potassium laurate solution, 20%	1.3
Sulphur dispersion, 50%	2.0
Zinc diethyldithiocarbamate dispersion, 50%	1.0
Zinc oxide dispersion, 50%	0.4

Table 4.2
Properties of PVL film with and without after-treatments from HA latex stored for different periods

Storage period of latex (months)	After-treatments of of PVL film	Modulus, 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)
0		0.60	11.5	810
2	Nil	0.70	17.3	898
4		0.71	17.7	921
0	Heating at	0.76	26.4	939
2	100°C for	0.76	25.8	935
4	30 minutes	0.79	25.9	943
0	Leaching at	0.78	28.9	927
2	30°C	0.81	30.0	930
4	for 24 h	0.82	31.4	940
0	Leaching,	0.79	29.5	938
2	followed by	0.79	29.8	940
4	heating	0.80	30.6	932

Table 4.3
Properties of PVL film with and without after-treatments from LATZ latex stored for different periods

Storage period of latex (months)	After-treatments of of PVL film	Modulus, 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)
0		0.57	9.0	802
2	Nil	0.67	14.5	883
4		0.69	15.5	900
0	Heating at	0.75	25.9	940
2	100°C for	0.76	25.0	927
4	30 minutes	0.80	27.1	940
0	Leaching	0.76	28.0	933
2	at 30°C	0.80	29.2	930
4	for 24 h	0.81	30.9	936
0	Leaching,	0.77	29.4	945
2	followed by	0.78	29.7	934
4	heating	0.80	30.8	941

Table 4.4
Effect of after-treatments of PVL film on volume fraction of rubber.

	Volume fraction of rubber of PVL film from	
After -treatment	HA latex	LATZ latex
Without treatment	0.1628	0.1610
Heating (100°C, 30min)	0.1743	0.1740
Leaching in water (30°C, 24h)	0.1632	0.1615
Leaching followed by heating	0.1674	0.1670

Table 4.5
Effect of leaching in water at different temperatures on tensile properties

Conditions of leaching	Modulus, 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)
Without leaching	0.64	21.8	930
60°C, 1 h	0.72	26.9	936
50°C, 2 h	0.74	27.7	952
40°C, 4 h	0.75	27.2	940
30°C, 1 h	0.66	21.5	928
30°C, 2 h	0.68	23.0	932
30°C, 3 h	0.70	24.2	930
30°C, 4 h	0.75	28.5	948
30°C, 6 h	0.76	28.1	939
30°C, 8 h	0.76	27.8	945
30°C, 24 h	0.78	28.2	947

Table 4.6
Effect of leaching in water at different pH on tensile properties before and after ageing

pH of water	Modulus, 100% (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing
10.0	0.82	0.74	28.9	12.2	936	839
10.5	0.82	0.72	28.6	8.0	952	800
11.0	0.81	0.71	27.8	6.1	949	802

Table 4.7
Effect of after-treatments of coagulant dipped films on tensile properties

After-treatment	Modulus, 100%(MPa)	Tensile strength (MPa)	Elongation at break (%)
Nil	0.65	17.0	843
Heating (100°C, 30 min.)	0.74	24.5	898
Leaching in water (30°C, 24 h)	0.79	28.0	926
Leaching followed by heating	0.78	26.6	915

Table 4.8
Effect of ageing of the after-treated PVL film at 70°C for 14 days, prepared from HA latex stored for different periods.

Storage period of latex (months)	Modulus, 100% (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing
0	0.79	0.75	29.5	24.6	938	848
2	0.79	0.74	29.8	23.1	940	841
4	0.80	0.72	30.6	23.0	932	836
6	0.80	0.72	29.6	22.0	928	833
12	0.70	0.66	26.6	16.5	898	759
18	0.64	0.55	21.0	8.0	886	741

Table 4.9

Effect of ageing of the after-treated PVL film at 70°C for 14 days, prepared from LATZ latex stored for different periods.

Storage period of latex (months)	Modulus, 100% (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing
0	0.78	0.74	29.4	24.2	945	842
2	0.77	0.74	29.7	24.0	934	838
4	0.80	0.73	30.8	23.0	941	836
6	0.79	0.72	28.0	22.7	925	830
12	0. 68	0.66	25.1	17.9	890	768
18	0.61	0.52	20.0	8.0	880	747

Table 4.10

Effect of storage and subsequent prevulcanization of HA and LATZ latices on volume fraction of rubber

	Volume fraction of rubber of PVL film from	
Storage period (months)	HA latex	LATZ latex
0	0.1674	0.1670
12	0.1650	0.1648
18	0.1588	0.1570

Table 4.11
Properties of prevulcanized latex during storage

Properties	Storage period (months)		
	0	1	3
Total solids content (%)	58	58	58
pH at 28°C	9.9	9.9	9.9
MST (seconds)	510	525	532
Viscosity at 28°C (mPa s)	105	98	96
Tensile strength (MPa)	28.2	27.5	27.7
Modulus, 100% (MPa)	0.78	1.05	1.00
Elongation at break (%)	947	908	910

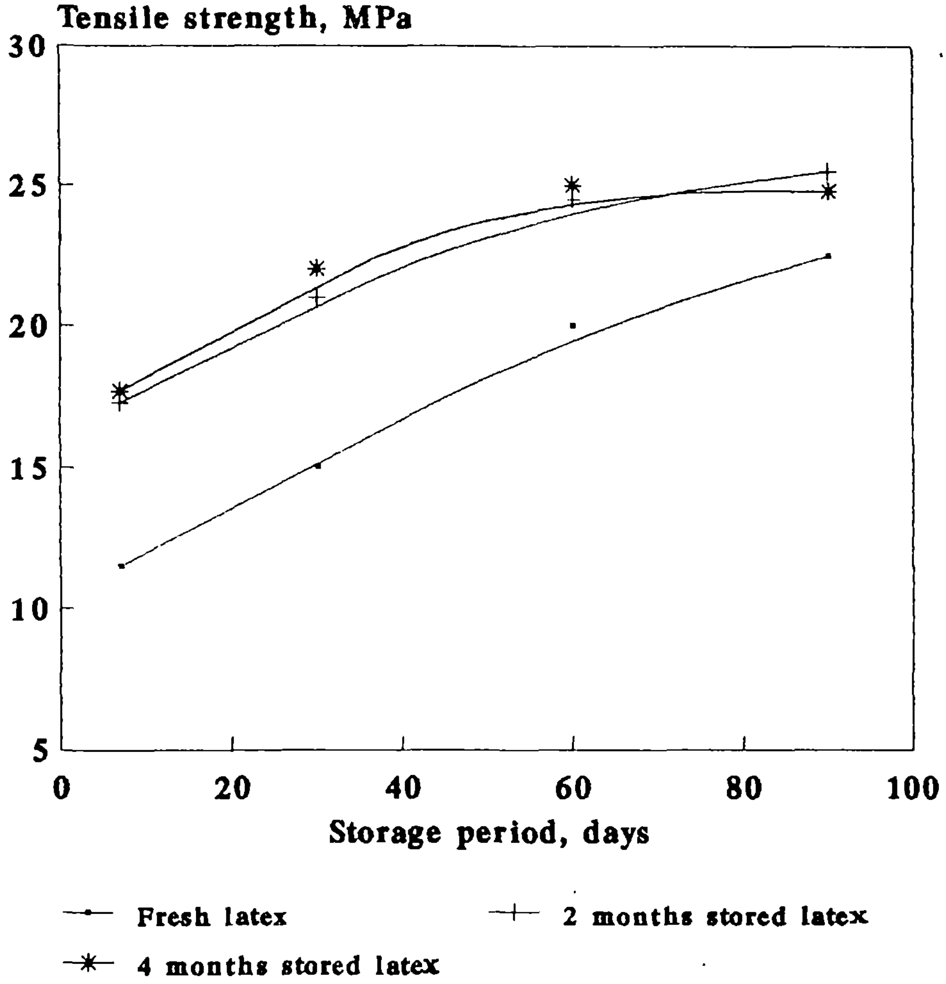

Fig4.1. Effect of storage of PVL film from HA latex on tensile strength

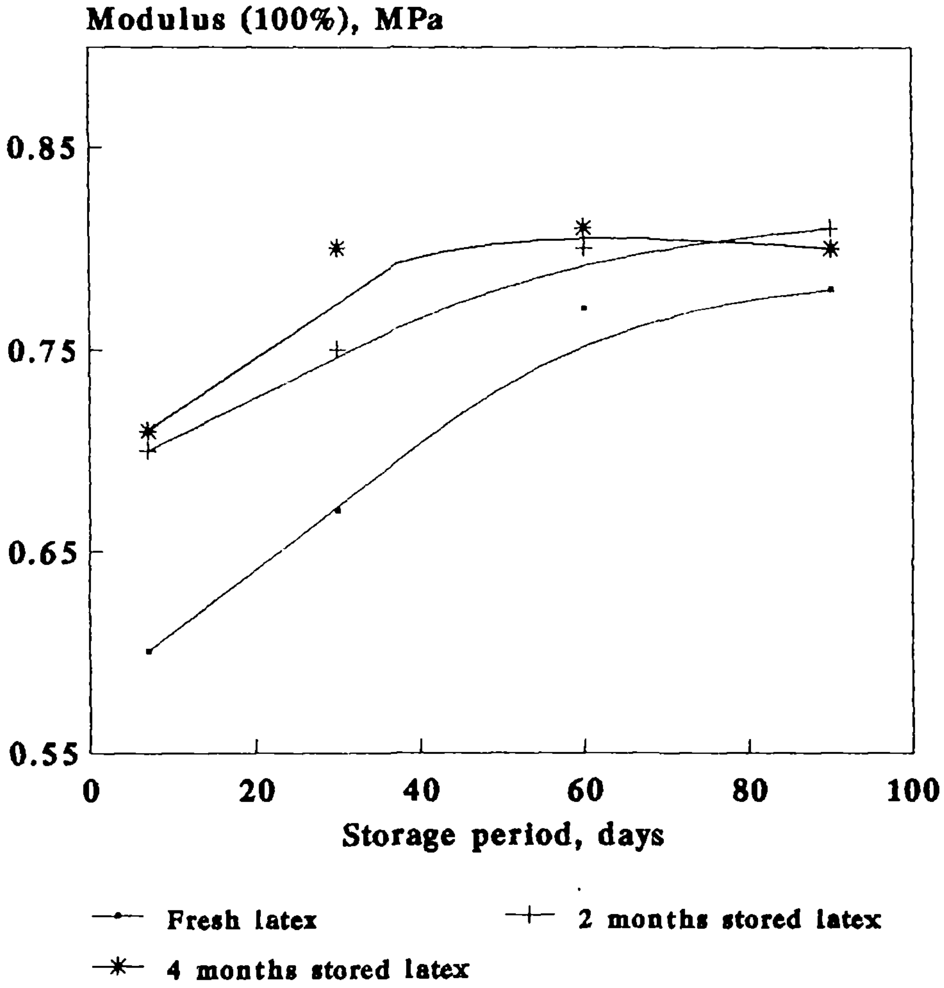

Fig.4.2. Effect of storage of PVL film from HA latex on modulus

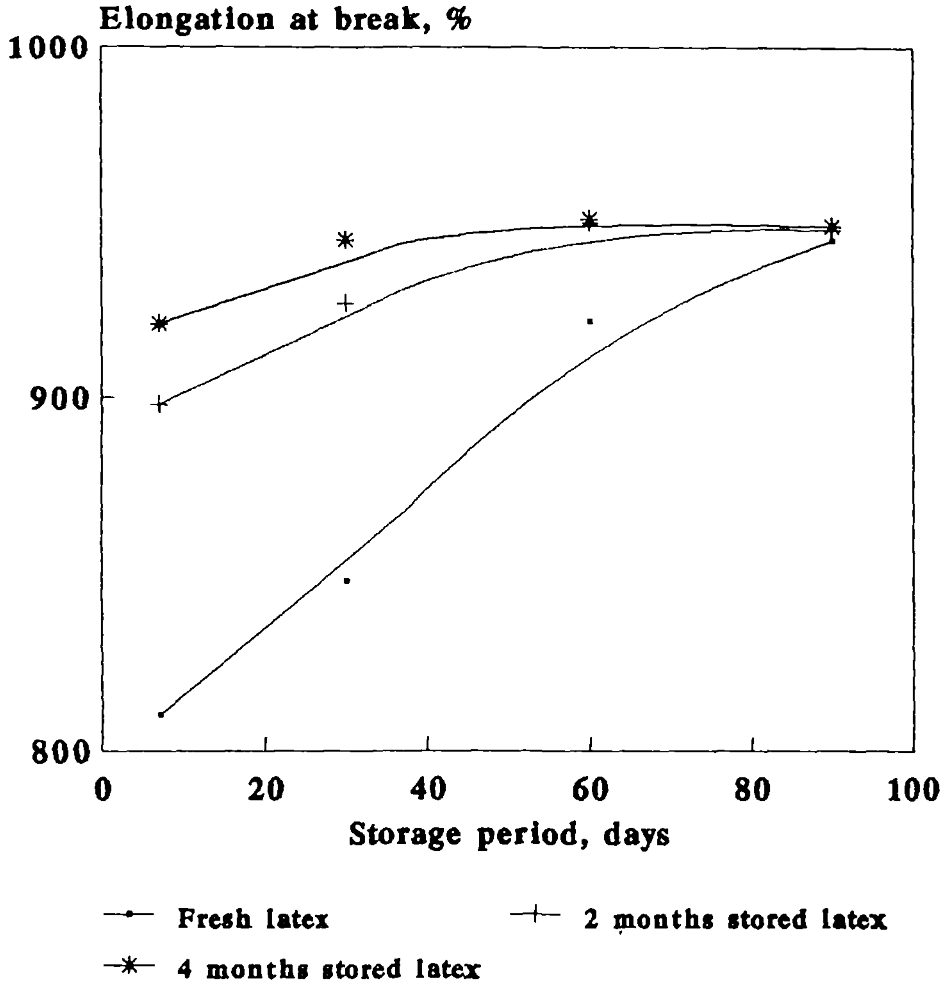

Fig.4.3. Effect of storage of PVL film from HA latex on elongation at break

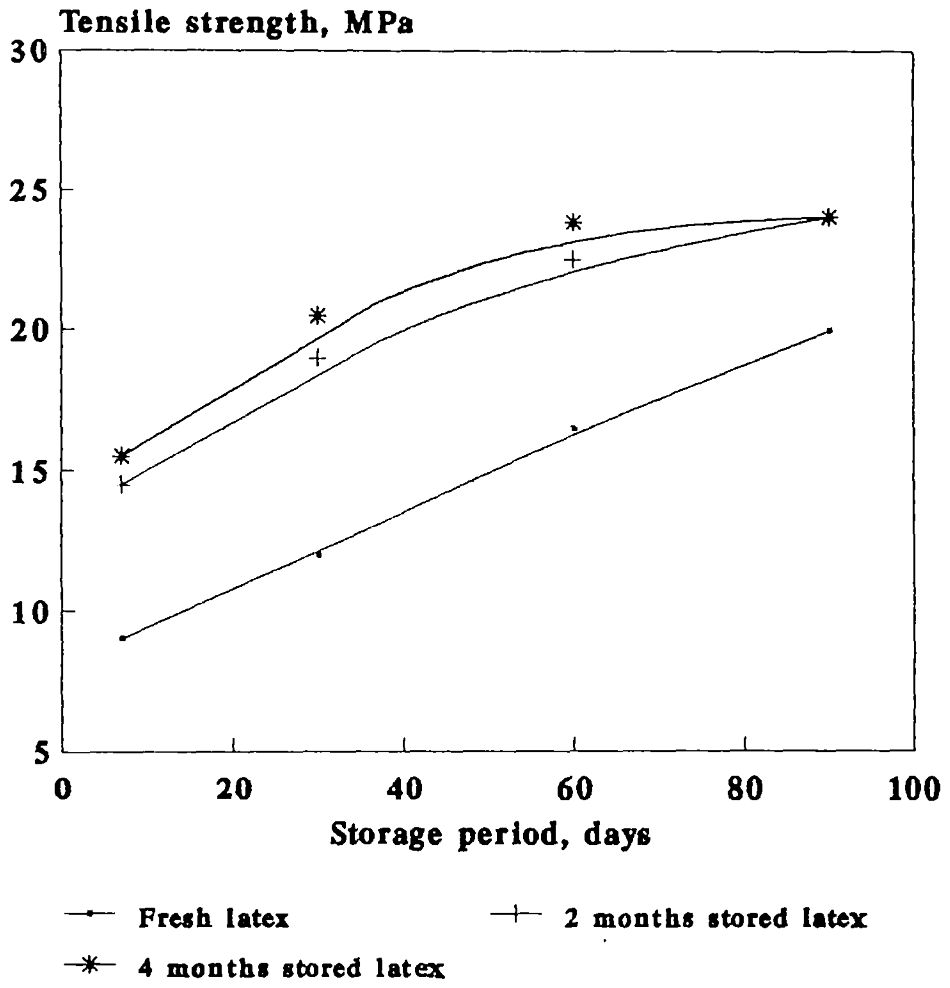

Fig.4.4. Effect of storage of PVL film from LATZ latex on tensile strength

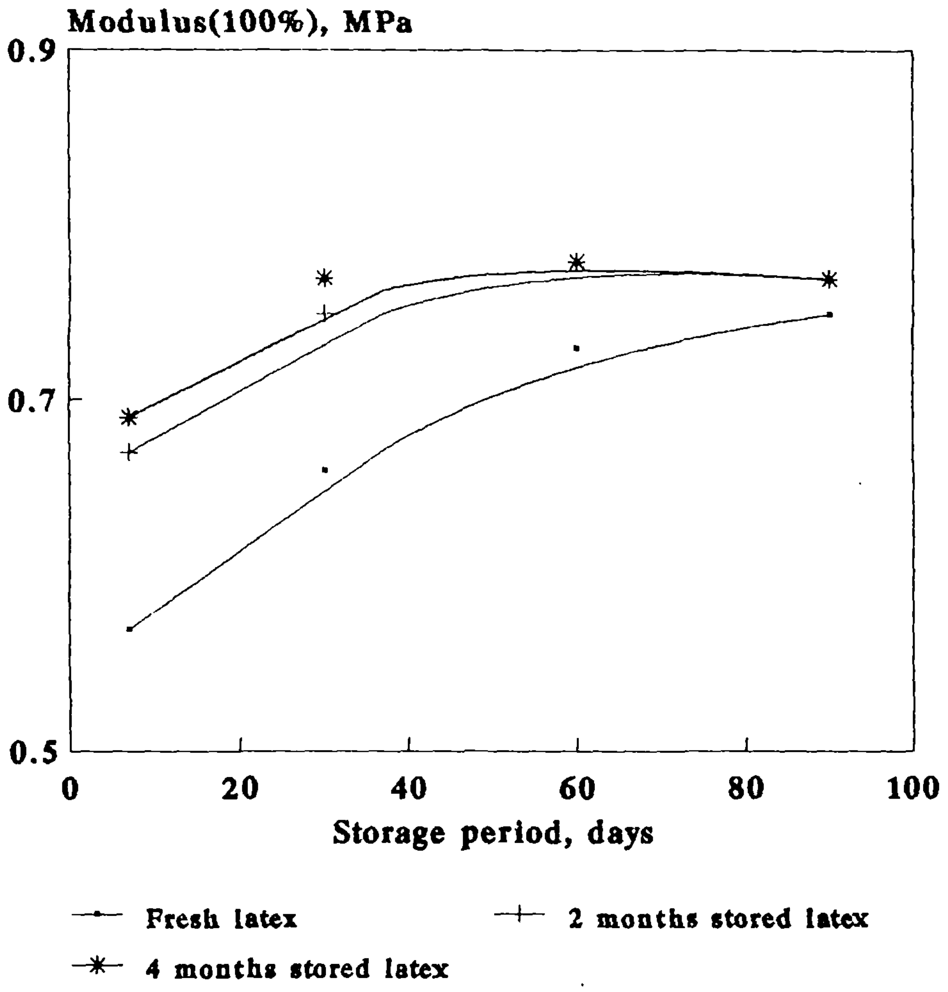

Fig.4.5. Effect of storage of PVL film from LATZ latex on modulus

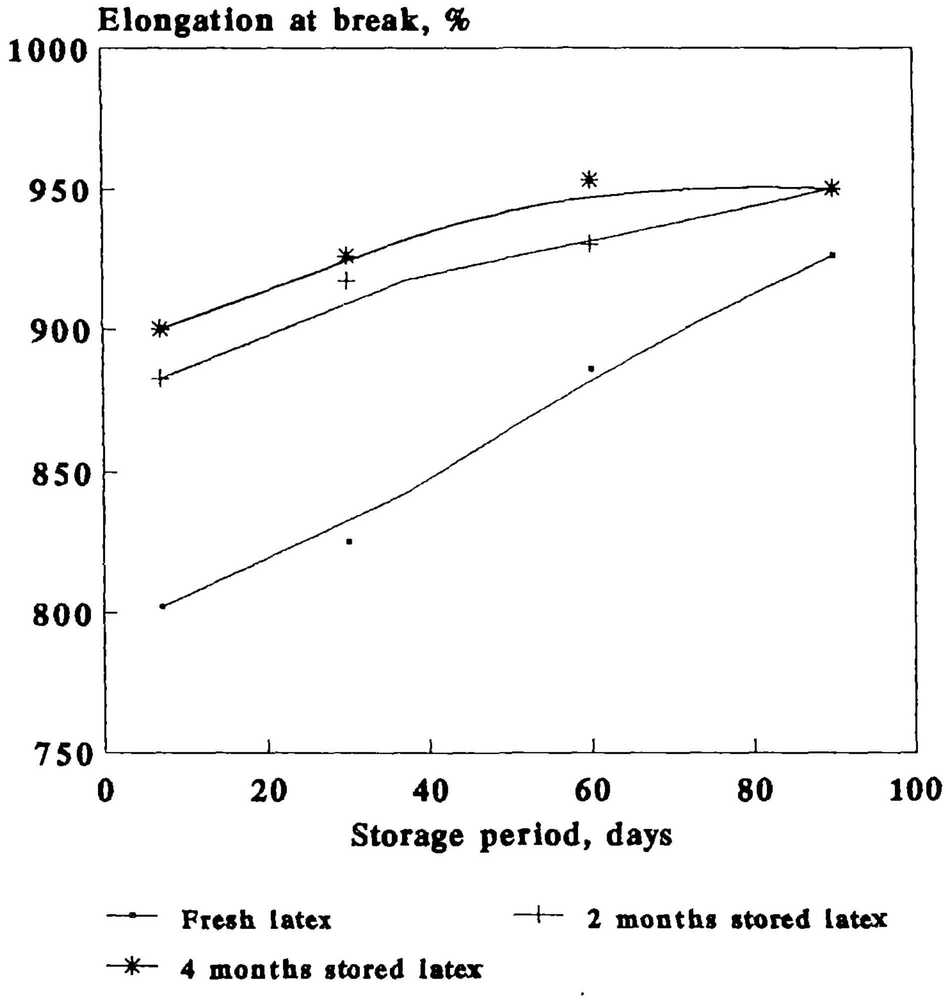

Fig.4.6. Effect of storage of PVL film from LATZ latex on elongaton at break

PART B

EFFECT OF FILLERS ON PROPERTIES OF PVL FILMS

The major advantages of adding fillers to rubber are improvement in processability, enhancement of certain properties of products and reduction in cost. Reinforcement of dry rubber is obtained by certain inorganic fillers, but no effect analogous to this are observed when the same fillers are incorporated in latex compounds.[10] The poor rubber filler interaction in latex vulcanizates is attributed to many factors such as absence of chemical interaction between filler and rubber, difficulty an achieving simultaneous deposition of filler and rubber particle, and the presence of a protective layer of stabilizers around the rubber and filler particles which prevent direct contact between the two.[11] Many methods have been suggested to improve this. Gamma irradiation of silica-filled NR latex has improved the rubber-silica interaction considerably.[12] Polyethylene glycol acts as a surface active agent in latex compounding, improving polymer filler interaction.[13] Silica-filled NR latex vulcanizates were found to show better tensile properties in the presence of polyvinyl alcohol or casein.[14]

Reports on the influence of fillers on properties of prevulcanized latex film are very limited. This part reports the effect of addition of fillers such as precipitated silica, china clay and whiting on properties of prevulcanized latex films. The effect of after-treatments on strength properties and ageing resistance of PVL films were also investigated.

EXPERIMENTAL

A base latex compound was prepared as per the formulation given in Table 4.12. Precipitated silica, china clay and whiting were added at 5, 10 and 20 phr. Precipitated silica was added as 25 per cent dispersion while china clay and whiting were added as 50 per cent dispersions. The total solids content of the latex compounds were adjusted to 48 per cent. The compounds were then prevulcanized at 70°C for 2 h and films were prepared as described in Chapter 2 After drying, a set of films were kept without any after-treatment. All other films were leached in water for 4 h and dried at room temperature.

RESULTS AND DISCUSSION

Crosslink density

The volume fraction of rubber slightly increased on increasing the filler content as is found in Table 4.13. This is mostly owing to the restricted swelling offered by the presence of fillers. The effect was comparatively more pronounced in the case of silica followed by clay and less in the case of whiting. The difference in Vr values as obtained from swelling measurements in toluene in the original vulcanizates and the same after ammonia treatment give a measure of rubber-filler interaction. This is comparatively higher for silica followed by clay and whiting. However, the level of interaction is observed to be much lower compared to that in the case of dry rubber mixes.

Tensile properties

Table 4.14 shows the effect of fillers on tensile properties of PVL films without any after-treatment. Addition of fillers decreased the tensile strength and elongation at break, but increased the modulus of the films marginally. As the filler content increased the effect became more pronounced. These observations are comparable to the earlier reports[13] on postvulcanized films. Table 4.14 also shows that films containing precipitated silica exhibited the highest increase in modulus followed by those containing china clay and whiting. The properties of postvulcanized films containing 10 phr of filler as shown in Table 4.15 also show that the effect of fillers in prevulcanized films are comparable to those in postvulcanized films.

The filled rubber can be considered as a two phase system of hard and soft segments. On application of stress, deformation takes place in the soft region and the filler particles do not deform. Thus the applied load is distributed among the polymer chains only. However, there could be stress concentration in the polymer filler interphase, resulting in low tensile strength and elongation at break and a consequent increase in modulus.

Effect of leaching

The effect of leaching of films on tensile properties is shown in Table 4.16. Leaching improved the properties of the films, but the trend on increasing the filler content on tensile properties remained the same as in the case of the unleached films.

During leaching most of the soluble hydrophilic materials are removed thus facilitating better cohesion of the rubber particles, allowing greater degree of entanglement between molecules anchored in different particles and enhanced tensile properties.

Ageing properties

The effect of ageing of the films on tensile properties is shown in Table 4.17. It is observed that ageing resistance of the films is increased by the addition of silica. It has been reported that ageing resistance of NR sulphur vulcanizates may be improved by incorporation of fine particle silicas.[15,16] Percentage retention in tensile strength and EB have been found to be decreasing with filler dosage. The minimum effect is shown by precipitated silica and the maximum by whiting. As clay and whiting are prepared directly from natural deposits, chances of contamination are more. Many of the contaminants including metal ions are known to be proxidants for rubber.

Tear strength

Figure 4.7 shows that addition of precipitated silica and china clay improved tear strength of the films. The effect was more pronounced in the case of precipitated silica. Tear strength was not significantly affected by the presence of whiting in the film. Improvement in tear strength can be attributed to the improvement in modulus and to the fact that the tear proceeded in a knotty manner.

Stress relaxation characteristics

Figures 4.8 and 4.9 show the stress relaxation pattern of PVL film without filler and films containing 10 phr each of precipitated silica, china clay and whiting . Table 4.18 shows the slope of these lines. The rate of stress relaxation was more for the film containing precipitated silica followed by that containing china clay and whiting.

The phenomenon of stress relaxation is the result of physical and chemical changes in the rubber, both of which can occur simultaneously. The physical changes are due to the viscoelastic nature of rubber and the chemical effects due to changes in the molecular structure by ageing, oxidation etc. Physical effects are more important at normal temperatures. A low level of rubber-filler interaction is observed (Table 4.13) in the case of vulcanizates containing silica. The linkages formed due to the interaction are getting reduced on stretching which causes a higher stress relaxation rate.

Morphology

The photomicrographs of films containing 5 phr of filler are given in Figures 4.10, 4.11and 4.12. These reveal the uniform distribution of silica in the rubber matrix

CONCLUSIONS

Presence of fillers such as precipitated silica, china clay and whiting decreased the tensile strength of PVL films. Leaching of the films improved them. Addition of precipitated silica improved the ageing resistance of the films. Improvement in tear strength is possible by the addition of precipitated silica and china clay. The rate of stress relaxation was slightly more for the films containing precipitated silica followed by china clay and whiting.

Table 4.12
Formulation of the base latex compound

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Potassium laurate solution, 20%	1.3
Sulphur dispersion, 50%	3.0
Zinc diethyldithiocarbamate dispersion, 50%	2.0
Zinc oxide dispersion, 50%	0.4

Table 4.13
Volume fraction of rubber with and without presence of ammonia

Type of filler	Concentration (phr)	Vr original	Vr in ammonia atmosphere	Difference in Vr
Nil	0	0.1689	-	-
Silica	5	0.1690	0.1548	0.0142
	10	0.1694	0.1547	0.0147
	20	0.1726	0.1451	0.0275
Clay	5	0.1691	0.1552	0.0139
	10	0.1692	0.1556	0.0140
	20	0.1710	0.1489	0.0221
Whiting	5	0.1656	0.1518	0.0138
	10	0.1659	0.1519	0.0140
	20	0.1664	0.1524	0.0140

Table 4.14
Effect of fillers on tensile properties

Type of filler	Concentration (phr)	Modulus, 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)
Nil	0	0.76	24.0	868
Silica	5	0.77	22.8	827
	10	0.89	21.3	810
	20	0.94	18.8	700
Clay	5	0.77	23.2	841
	10	0.79	22.6	825
	20	0.85	19.9	770
Whiting	5	0.76	23.0	835
	10	0.77	22.0	808
	20	0.80	19.0	735

Table 4.15
Effect of 10 phr of filler on tensile properties of postvulcanized films

Type of filler	Modulus at 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)
Nil	0.73	27.7	1025
Silica	1.00	21.8	880
Clay	0.84	27.5	987
Whiting	0.80	26.0	990

Table 4.16
Tensile properties of filled PVL films after leaching

Type of filler	Concentration (phr)	Modulus, 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)
Nil	0	0.78	28.0	875
Silica	5	0.81	25.9	835
	10	0.93	25.4	815
	20	1.28	20.5	705
Clay	5	0.80	27.5	847
	10	0.86	27.0	830
	20	1.04	25.6	785
Whiting	5	0.79	27.4	838
	10	0.83	26.1	811
	20	0.88	23.7	780

Table 4.17
Effect of ageing at 70° C for 14 days on tensile properties

Type of filler	Concentration (phr)	Retention in properties (%)		
		Modulus, 100%	Tensile strength	Elongation at break
Nil	0	98.6	50.5	80.2
Silica	5	118.2	89.1	98.2
	10	110.3	85.2	97.6
	20	92.1	78.3	97.0
Clay	5	115.4	50.2	98.0
	10	106.3	48.5	97.8
	20	90.1	45.3	96.0
Whiting	5	103.4	45.2	86.2
	10	100.2	44.4	83.7
	20	90.5	28.2	68.4

Table 4.18
Effect of fillers on stress relaxation

Type of filler	Slope of the lines
Nil	0.0545
Silica	0.0658
Clay	0.0575
Whiting	0.0554

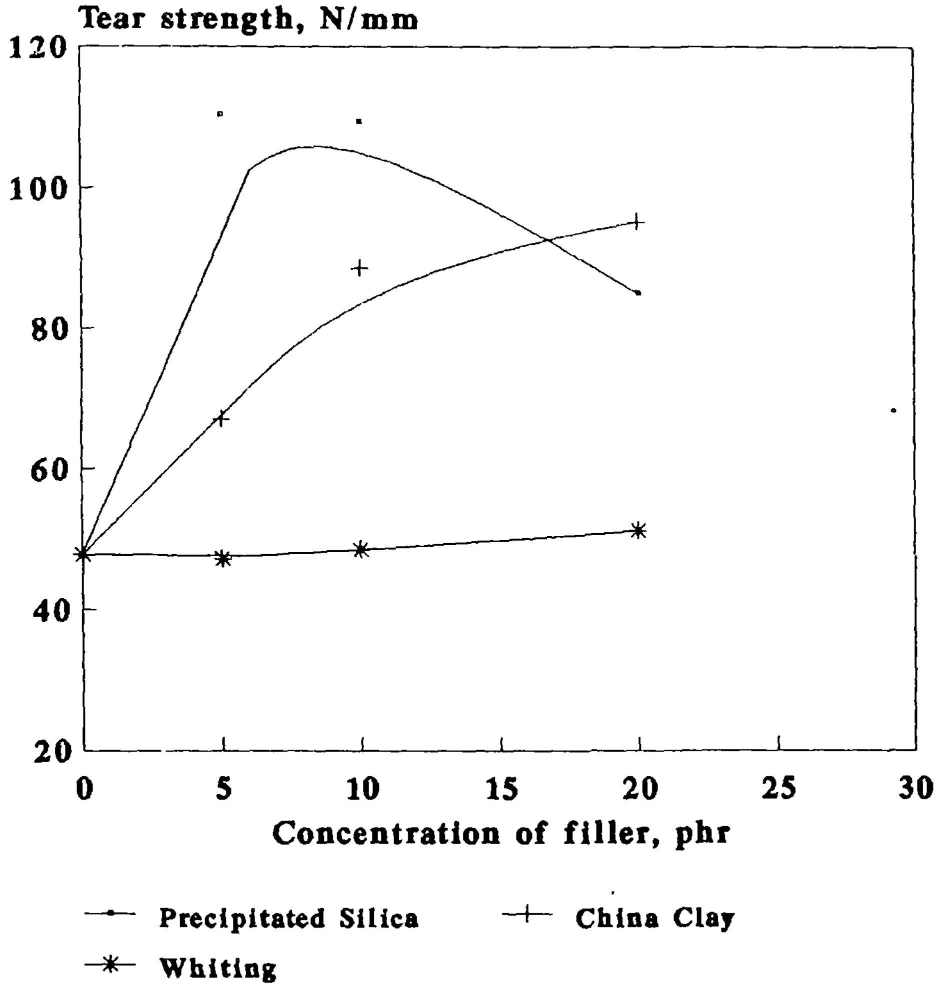

Fig.4.7. Effect of fillers on tear strength

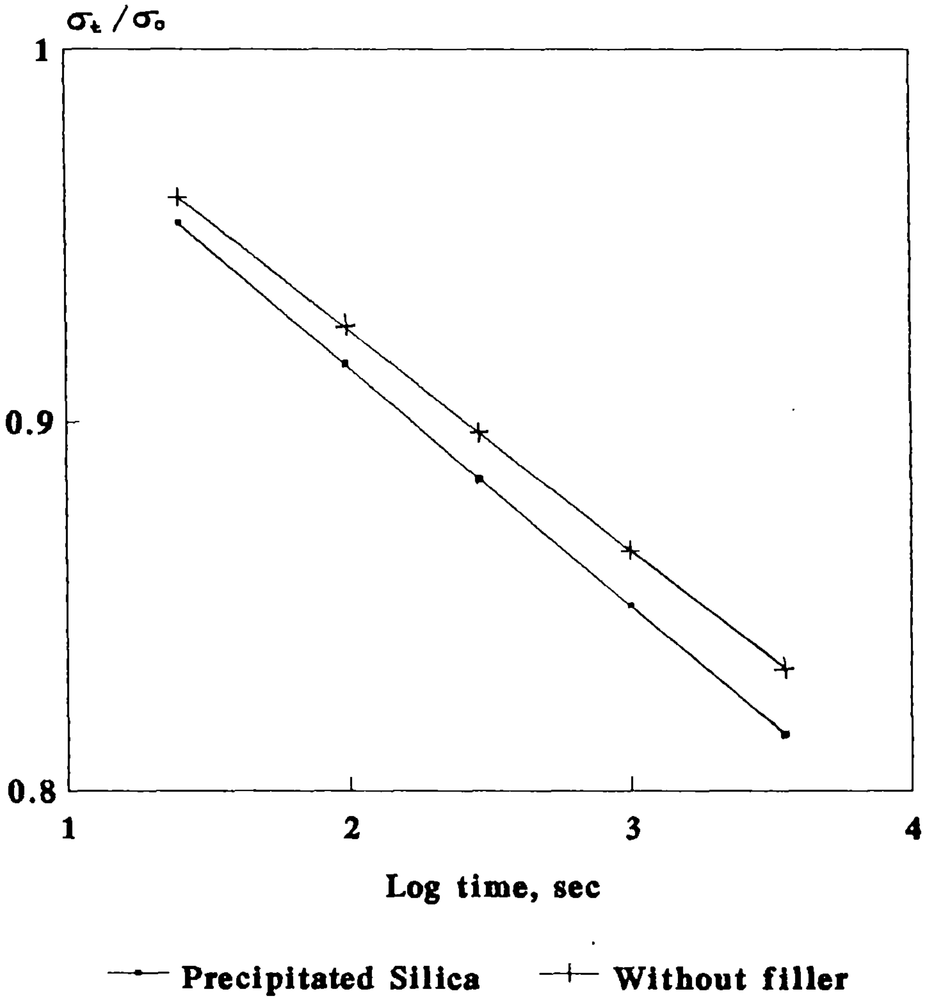

Fig.4.8. Semilog plots of stress decay as a function of time for PVL films with and without filler

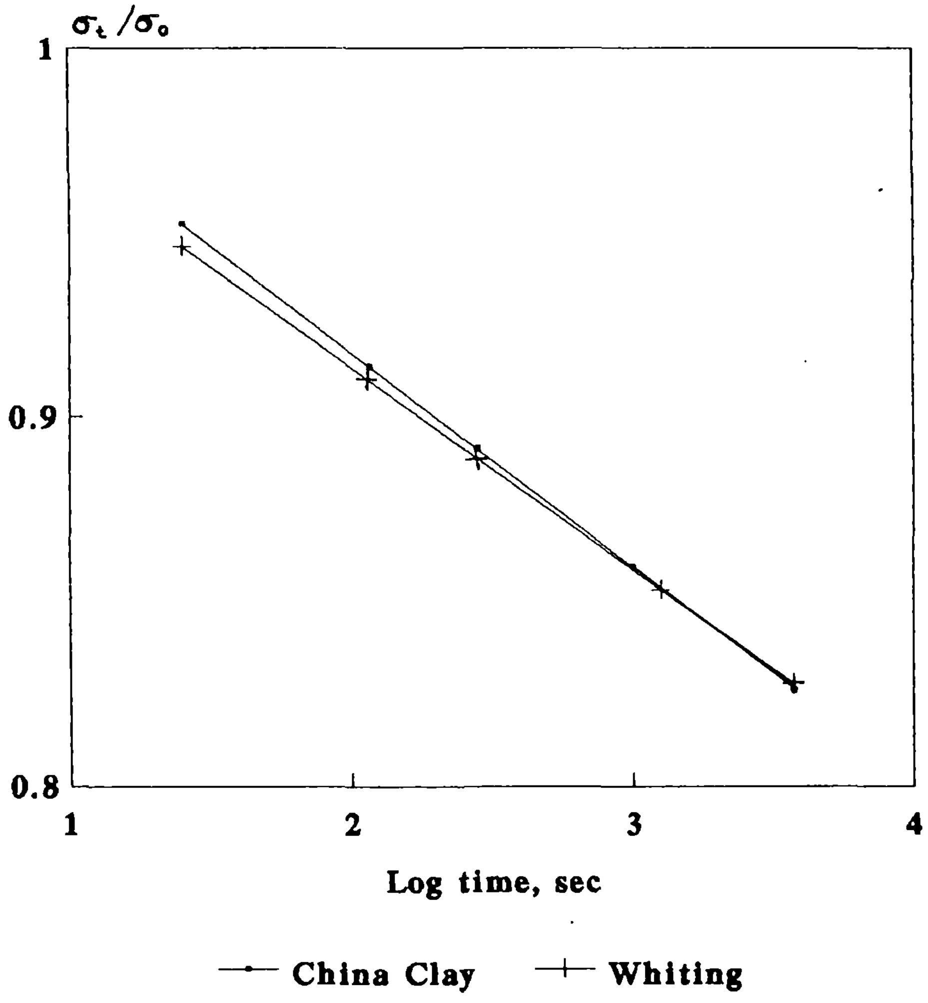

Fig.4.9. Semilog plots of stress decay as a function of time for PVL films with filler

Fig. 4.10. Optical micrograph of PVL film containing 5 phr of silica (x 120)

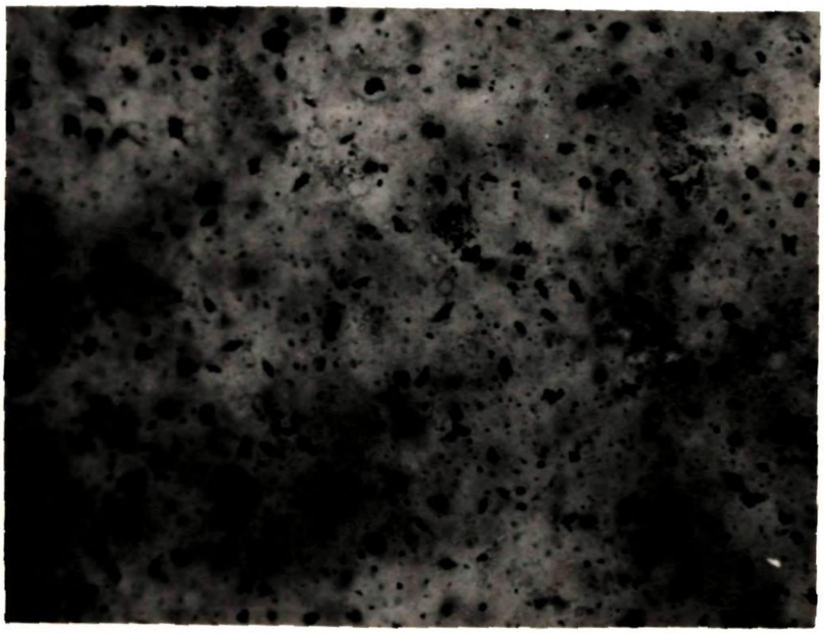

Fig. 4.11. Optical micrograph of PVL film containing 5 phr of clay (x 120)

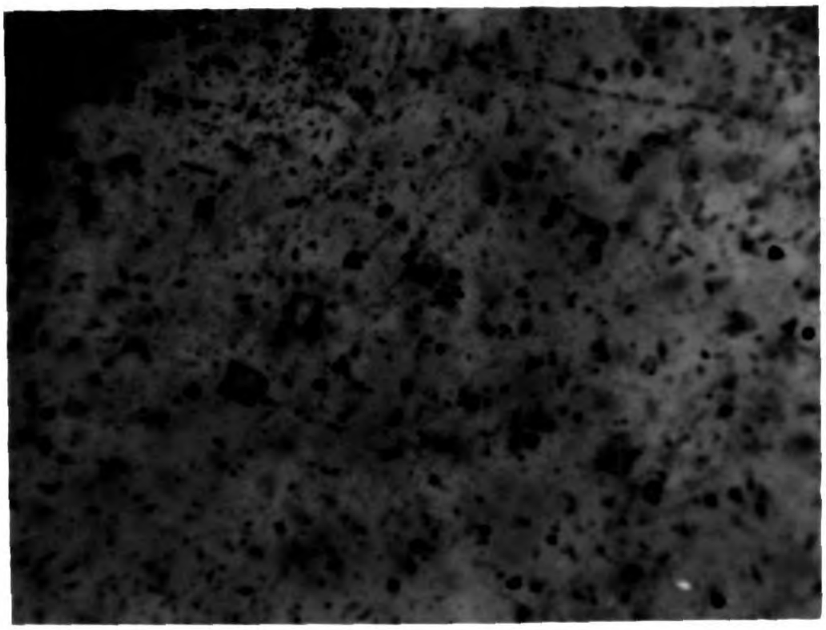

Fig. 4.12. Optical micrograph of PVL film containing 5 phr of whiting (x 120)

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CHAPTER 5

INFLUENCE OF STORAGE ON PROPERTIES OF NR LATEX CONCENTRATES AND VULCANIZATES

In India about 12 per cent of the natural rubber produced is processed into latex concentrate. Concentration is usually done in plantations and the latex is consumed in far away places usually after a storage period of a few weeks to a few months During pumping, transportation and storage latex is subjected to mechanical agitation, aeration and even temperature variation which are known to influence its properties. It is also known that the chemical composition of latex changes due to the action of bacteria, enzymes and preservatives. These changes in chemical composition are reflected in the properties of latex particularly, mechanical stability time (MST), volatile fatty acid (VFA), number and potassium hydroxide (KOH) number. Several investigations have been carried out on the changes in properties of latex concentrate on storage. Mcgavack and Bevilacqua[1] reported that ammonia preserved latex concentrate showed an increase in stability and a decrease in viscosity, when it was exposed to aerobic conditions.

According to Collier[2] increase of VFA of latex concentrate was more pronounced when it was stored in anaerobic conditions. Lowe [3] reported that pumping of latex concentrate accelerated the formation of VFA. Pillai,[4] however, reported that commercial pumping operation did not have any deleterious effect on the properties of latex. Reports from RRIM[5] indicated that MST, VFA and KOH number of latex concentrate increased on storage.

According to Chin et.al. [6] although storage of latex affects its primary properties, the physical properties of vulcanized rubber films prepared from the stored latex are not adversely affected for a storage period of up to eight months. This part of the investigation reports a comparative evaluation of high ammonia and low ammonia preserved natural rubber latex concentrates with respect to the effect of storage on primary properties of latex and physical properties and ageing characteristics of vulcanizates (postvulcanized) prepared therefrom.

A comparison is also made between prevulcanized and postvulcanized films prepared from HA latex with respect to water absorption and desorption pattern and leaching behaviour. Morphological studies of the films were also conducted.

EXPERIMENTAL

High ammonia and low ammonia preserved centrifuged latex concentrates were freshly prepared as described in Chapter 2 and stored for periods of up to 18 months. Latex samples were withdrawn periodically and tested.

Latex properties

The primary properties of latex such as total solids content, dry rubber content, mechanical stability time, potassium hydroxide number, volatile fatty acid number, viscosity, zinc oxide viscosity and alkalinity were determined as stated in Chapter 2.

Vulcanizate properties

Films were prepared periodically by postvulcanization. Latex compounds were prepared according to the formulation given in Table 5.1. After maturation films of thickness approximately 0.75 mm were cast in glass cells. After drying the films were vulcanized in an air oven at 100°C for 1 h. The films were aged at 70°C for 7, 14 an 21 days and then tested for tensile properties before and after ageing as per ASIM D 412-87.

Comparison of prevulcanization and postvulcanization

In another experiment a latex compound was prepared using HA latex according to the formulation given in Table 5.1. A portion of the latex compound was prevulcanized at 70°C for 2 h and films were prepared as described in Chapter 2. Another portion of the latex compound was matured, films were cast and vulcanized at 100°C for 1 h as stated earlier.

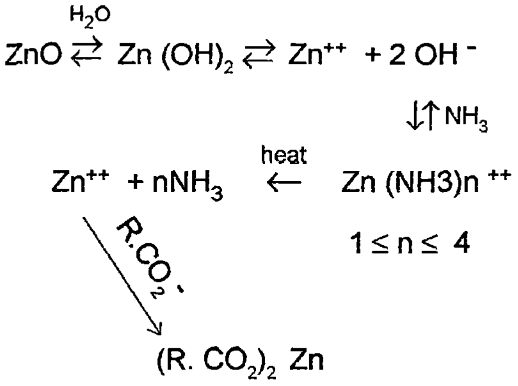
The films (prevulcanized and postvulcanized) were leached in water at room temperature for 24 h. Water absorption by the samples was measured at different intervals and the extract obtained from the samples after leaching for 24 h was also determined according to ASTM D 471-79. The leached samples were dried at room temperature. During drying the desorption pattern was studied by measuring the water content of the samples at definite intervals. The leached samples after drying were again leached in water at room temperature for 24 h. The reabsorption of water was also measured as before. The morphology of raw latex film, prevulcanized and postvulcanized films was examined using a scanning electron microscope (Model JEOL JSM 36C).

RESULTS AND DISCUSSION

Latex properties

Table 5.2 shows the effect of storage of HA and LATZ latices on TSC, DRC, and ammonia content. It can be seen that TSC and DRC of the two latices are more or less unaffected by storage up to 18 months. A slight decrease in ammonia content is observed during the above period. Table 5.3 shows the effect of storage of the latices on viscosity. A slightly higher viscosity is observed initially, which decreases on storage for one month and thereafter is maintained more or less constant. The decrease in viscosity is due to the changes in the adsorbed layer of stabilizers on rubber particles during storage.

Table 5.4 shows the effect of storage of the latices on zinc oxide viscosity. For HA and LATZ latices zinc oxide viscosity increases on storage. For LATZ latex the increase is very slow compared to that of HA latex. HA latex shows a very rapid rise in zinc oxide viscosity during storage and after a period of one year the latex gets coagulated during the test. The lower stability of HA latex to zinc oxide is due to the higher ammonia content and ammonium ions of latex which cause more zinc oxide to dissolve in the serum,[7] as is explained in the



insoluble zinc soap or proteinate precipitated on the surface of the particles, with consequent distabilization.

Table 5.5 shows the effect of storage on VFA and KOH numbers. VFA consists mostly of formic, acetic and propionic acids resulting from bacterial attack on the substrates present in latex.[8]

The magnitude of VFA number is therefore, a good index of the state of preservation of latex. For both types of latices, VFA number slightly increases on storage, LATZ latex has lower VFA number than HA latex during storage up to one year. The difference is more pronounced during the early period of storage. In other words when the storage period of latex was above three months the difference in the VFA of HA and LATZ latices narrowed down and on keeping the latex for 18 months, LATZ latex exhibited a higher VFA number than HA latex, though still within permissible limits.

The KOH number of HA and LATZ latices increased during storage (Table 5.5) which indicates an increase in concentration of acids which are present as ammonium salts.[9]

Table 5.6 shows the effect of storage on MST. Results show that for fresh latex, MST is very low and it rises during storage. For HA latex during the first 20 days, the rate of increase in MST was very rapid, followed by a slower increase. The maximum MST was observed in 75 days of storage and afterwards a slow decrease has been noted. The higher MST values for LATZ latex is due to the presence of added ammonium laurate during its preparation.

Mechanical stability has been closely related to the process of lipid hydrolysis which produces higher fatty acids resulting in increased stability of latex, to the process of protein hydrolysis which produces amino acids having a destabilizing effect on the latex and to the formation of the glucose/amino acid complex,[3] a primary substrate for volatile fatty acid formation. In fresh latex the protective layer of rubber particles consists mainly of proteins and phospholipids. When ammonia is added to latex, hydrolysis of proteins and phospholipids occur. During the first 75 days of storage hydrolysis of lipids is predominant. The liberated fatty acid anions are adsorbed at the particle interface and thus enhance the stability of latex due to higher surface charge and therefore, a higher energy of repulsion between particles. After 75 days of storage, hydrolysis of lipids slows down and that of proteins dominate. Thus the composition of protective layer again changes. This, along with the increase in ionic strength of the aqueous phase of latex, causes the observed reduction in MST when the latex is stored for long periods.

VULCANIZATE PROPERTIES

Physical properties

Figure 5.1 shows the effect of storage of HA and LATZ latices on tensile strength of their vulcanizates. It can be seen that tensile strength is unaffected by storage of latex up to three months, but thereafter it decreases slowly up to six months and then rather rapidly. Modulus and elongation at break (Figs. 5.2 and 5.3 respectively) also show the same trend.

Effect of storage on Vr

Table 5.7 shows the effect of storage on volume fraction of rubber (Vr) in the swollen vulcanizates. For the two latices Vr values decreased as the storage period increased. Vr can be taken as a measure of crosslink density. Tensile strength is strongly dependent upon crosslink density of the vulcanizate. [10] A decrease in tensile strength of the vulcanizate is thus associated with a decrease in the degree of crosslinking when the latex is stored for long periods.

Ageing characteristics

Table 5.8 shows the effect of ageing of vulcanizates obtained from HA and LATZ latices, stored for different periods, on tensile strength. It is seen that tensile strength decreases on ageing. But the rate of decrease is less for fresh latex. As the period of storage increases the rate of decrease in tensile strength becomes more pronounced. The same trend is also observed from the modulus and elongation values as given in Tables 5.9 and 5.10 respectively.

The presence of materials which exert an antioxidant effect in latex has been recognized for many years.[11] Choline compounds present in latex are vulcanization accelerators and show antioxidant properties in raw rubber.[12] During storage latex undergoes changes associated with bacterial and hydrolytic actions. Changes are also caused by factors such as handling, seasonal effect and storage conditions. Hence it is concluded that during long term storage the natural antioxidants present in latex get converted to other products and / or are used up, which causes a reduction in ageing resistance of the vulcanizates.

COMPARISON OF POSTVULCANIZED AND PREVULCANIZED FILMS

Water absorption

Figure 5.4 shows the absorption of water by prevulcanized and postvulcanized films. It is seen that for postvulcanized film the amount of water absorbed increases slowly and the film does not attain equilibrium even after 24 h of immersion. But in the case of prevulcanized film the rate of water absorption is rapid and the film attains equilibrium in 3 h of immersion. This is due to the difference in structure of the two films. When latex is prevulcanized the rubber particles become harder and the films prepared therefrom do not attain the level of coalescence which is possible in postvulcanized films and this lack of proper interparticle coalescence results in a capillary network leading to larger water uptake. Thus the relatively high initial water absorption suggests a residual capillary structure while the reduction in water absorption with time indicates that these capillaries are gradually getting reduced.[13]

Water extract

Table 5.11 shows the extract obtained after leaching the films for 24 h. When the films are immersed in water, absorption and leaching occur simultaneously. It can be seen that leaching proceeded more rapidly in the case of the prevulcanized film than that of postvulcanized film. This can also be attributed to the structural differences as explained earlier. This observation is in line with that of Gazeley.[14]

Desorption of films

Figure 5.5 shows desorption pattern of the films during drying at room temperature. It can be seen that the rate of desorption is also fast in the case of prevulcanized film than in the case of postvulcanized film. This is also due to the structural difference between the two.

Effect of reimmersion of leached films on water absorption

Figure 5.6 shows the effect of leaching of already leached films. Although a higher amount of water is absorbed by the prevulcanized film, the absorption pattern was almost the same as that of postvulcanized film. The two films did not attain equilibrium in 24 h of immersion.

During the first leaching of prevulcanized film, most of the soluble hydrophilic materials are washed away thus facilitating better cohesion of the rubber particles.

Morphology of films

Figures 5.7 and 5.8 show the SEM photographs of postvulcanized and prevulcanized films respectively. These confirm the porous structure of prevulcanized film.

CONCLUSIONS

DRC and TSC of high ammonia and low ammonia latices were more or less unaffected by storage of latex up to 18 months. Freshly prepared latex exhibited a slightly higher initial viscosity which decreased during one month's storage and remained rather constant on further storage. Zinc oxide viscosity increased during storage of latex. For LATZ latex the increase was very slow. However, HA latex showed a very rapid rise in ZOV as the latex ages. VFA number of HA and LATZ latices slightly increased on storage and LATZ latex exhibited a lower initial VFA number than HA latex. But on storage the difference narrowed down and after a period of 18 months, LATZ latex exhibited a higher VFA than that of HA latex, but within permissible limits. KOH number of the latices also increased on storage.

Physical properties of latex vulcanizates were more or less period, a decrease in tensile properties was observed. Ageing resistance of the vulcanizates was also found to be affected by the storage period of latex. When the storage period was beyond one year, the rate of decrease in ageing resistance was more for both latices.

Water absorption and leaching proceeded more rapidly in prevulcanized film than in postvulcanized film. For prevulcanized film rate of drying was faster compared to postvulcanized film. Prevulcanized latex film showed a porous structure.

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Table 5.1
Formulation of latex compound

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Sulphur dispersion, 50%	2.0
Zinc diethyldithiocarbamate dispersion, 50%	1.0
Zinc oxide dispersion, 50%	0.4

Table 5.2
Effect of storage of latex on TSC, DRC and ammonia content

Period of storage (months)	TSC (%)		DRC (%)		Ammonia content (%)	
	HA	LATZ	HA	LATZ	HA	LATZ
0	61.45	61.70	60.15	60.25	0.81	0.29
1	61.50	61.65	60.10	60.11	0.81	0.29
2	61.56	61.62	60.18	60.21	0.81	0.28
4	61.43	61.61	60.10	60.22	0.74	0.24
6	61.40	61.65	59.90	60.08	0.73	0.24
12	61.34	61.60	60.10	60.00	0.72	0.21
18	61.33	61.70	59.84	60.00	0.71	0.20

Table 5.3
Effect of storage of latex on viscosity

Period of storage (months)	Brookfield viscosity (Pa s) HA 5 rpm	HA 50 rpm	LATZ 5 rpm	LATZ 50 rpm
0	0.14	0.077	0.12	0.070
1	0.13	0.074	0.11	0.067
2	0.13	0.074	0.11	0.067
4	0.13	0.075	0.11	0.067
6	0.13	0.073	0.11	0.068
12	0.13	0.074	0.11	0.067
18	0.13	0.073	0.11	0.066

Table 5.4
Effect of storage of latex on zinc oxide viscosity

Period of storage(months)	Zinc oxide viscosity (Pa s); 50 rpm HA	LATZ
0	0.072	0.044
1	0.080	0.048
2	0.084	0.050
3	0.104	0.052
4	0.120	0.052
5	0.392	0.060
6	0.720	0.068
7	out of range	0.084
12	coagulated	0.104

Table 5.5
Effect of storage of latex on VFA and KOH numbers

Period of storage (days)	VFA number		KOH number	
	HA	LATZ	HA	LATZ
6	0.017	0.006	0.40	0.48
15	0.023	0.008	0.41	0.49
20	0.023	0.009	0.54	0.59
30	0.024	0.011	0.54	0.60
60	0.026	0.019	0.54	0.60
90	0.027	0.025	0.56	0.64
120	0.027	0.025	0.56	0.64
150	0.028	0.025	0.56	0.66
180	0.028	0.024	0.60	0.72
365	0.033	0.030	0.62	0.77
545	0.048	0.096	0.78	1.10

Table 5.6
Effect of storage of latex on MST

Period of storage (days)	MST (seconds)	
	HA	LATZ
6	125	>1200
10	293	>1200
15	607	>1200
20	816	>1200
25	885	>1200
50	980	>1200
60	1160	>1200
75	1395	>1200
90	1300	>1200
120	1211	>1200
160	1029	>1200
180	1028	>1200
365	872	>1200
545	387	1200

Table 5.7
Effect of storage of latex on volume fraction of rubber

Period of storage (months)	Volume fraction of rubber (Vr)	
	HA	LATZ
0	0.1676	0.1670
12	0.1562	0.1559
18	0.1442	0.1444

Table 5.8
Effect of storage of latex on tensile strength after ageing

Period of storage (months)		Tensile strength after ageing for different periods, days (MPa)			
		0	7	14	21
0	HA	31.9	28.0	27.3	21.7
	LATZ	30.7	27.1	24.7	18.0
6	HA	29.2	21.5	13.9	5.3
	LATZ	28.7	20.1	11.4	4.2
12	HA	20.3	14.9	5.5	-
	LATZ	18.5	15.6	5.0	-
18	HA	14.0	5.0	-	-
	LATZ	13.0	4.8	-	-

Table 5.9
Effect of storage of latex on modulus at 100% elongation after ageing

Period of storage (months)		Modulus, 100% after ageing for different periods, days (MPa)			
		0	7	14	21
0	HA	0.73	0.70	0.68	0.67
	LATZ	0.72	0.70	0.66	0.63
6	HA	0.70	0.68	0.65	0.53
	LATZ	0.69	0.67	0.63	0.49
12	HA	0.59	0.57	0.45	-
	LATZ	0.61	0.54	0.42	-
18	HA	0.54	0.48	-	-
	LATZ	0.54	0.43	-	-

Table 5.10
Effect of storage of latex on elongation at break after ageing

Period of storage (months)		Elongation at break after ageing for differnt periods, days (%)			
		0	7	14	21
0	HA	1252	1238	1220	1192
	LATZ	1225	1256	1234	1210
6	HA	1246	1158	1072	875
	LATZ	1213	1180	1065	844
12	HA	1117	1005	920	-
	LATZ	1096	956	901	-
18	HA	989	890	-	-
	LATZ	974	908	-	-

Table 5.11
Effect of method of vulcanization on extracted soluble matter in films

Method of vulcanization	Extract (%).
Prevulcanized	2.58
Postvulcanized	0.20

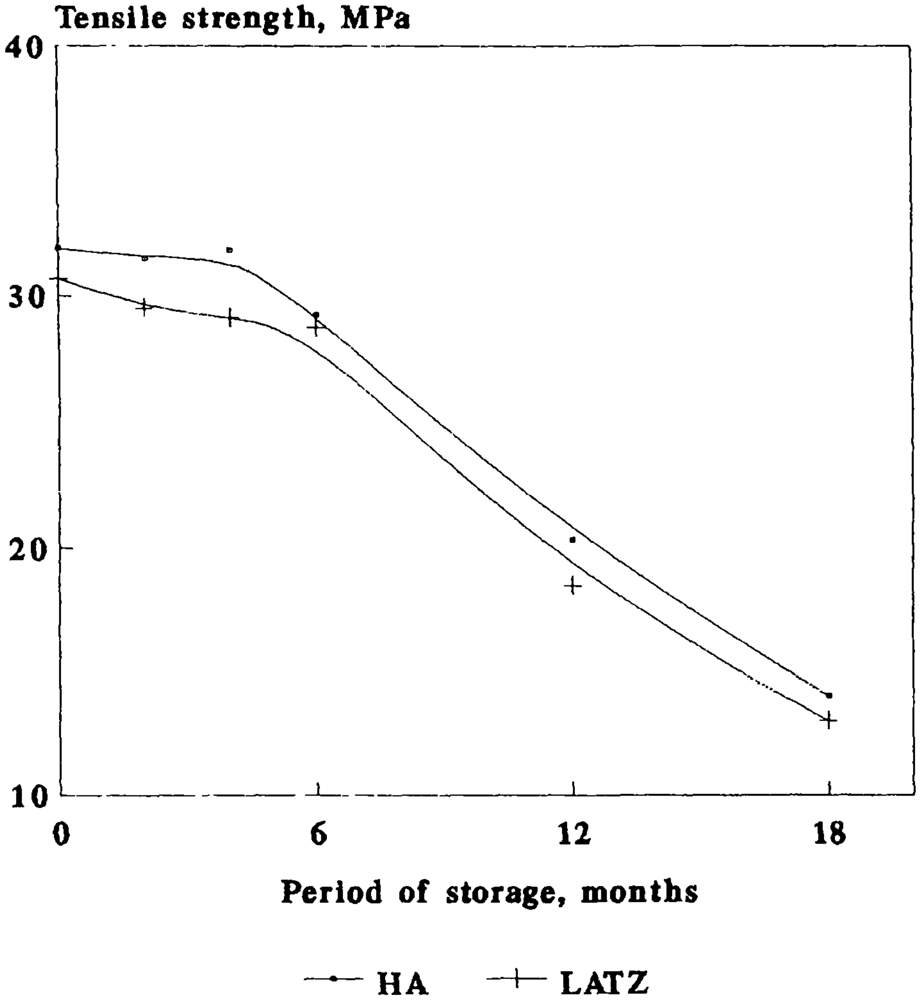

Fig.5.1. Effect of storage of latex on tensile strength

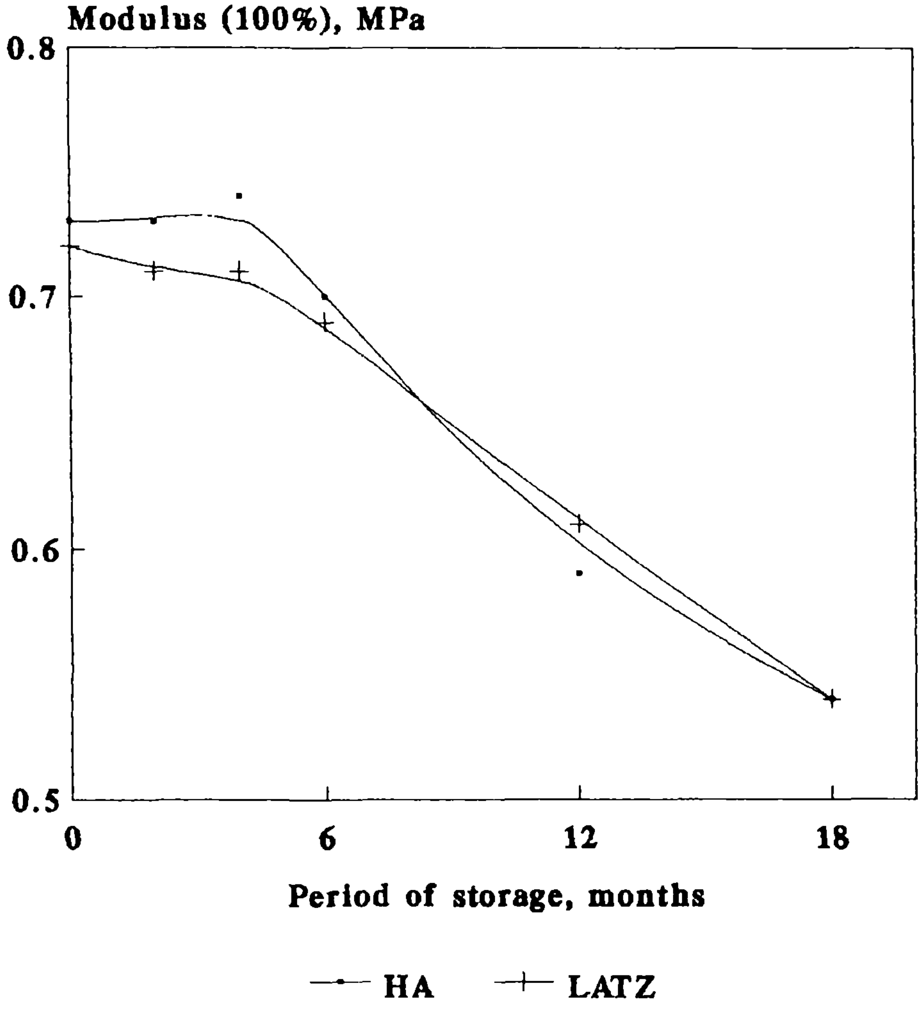

Fig.5.2. Effect of storage of latex on modulus

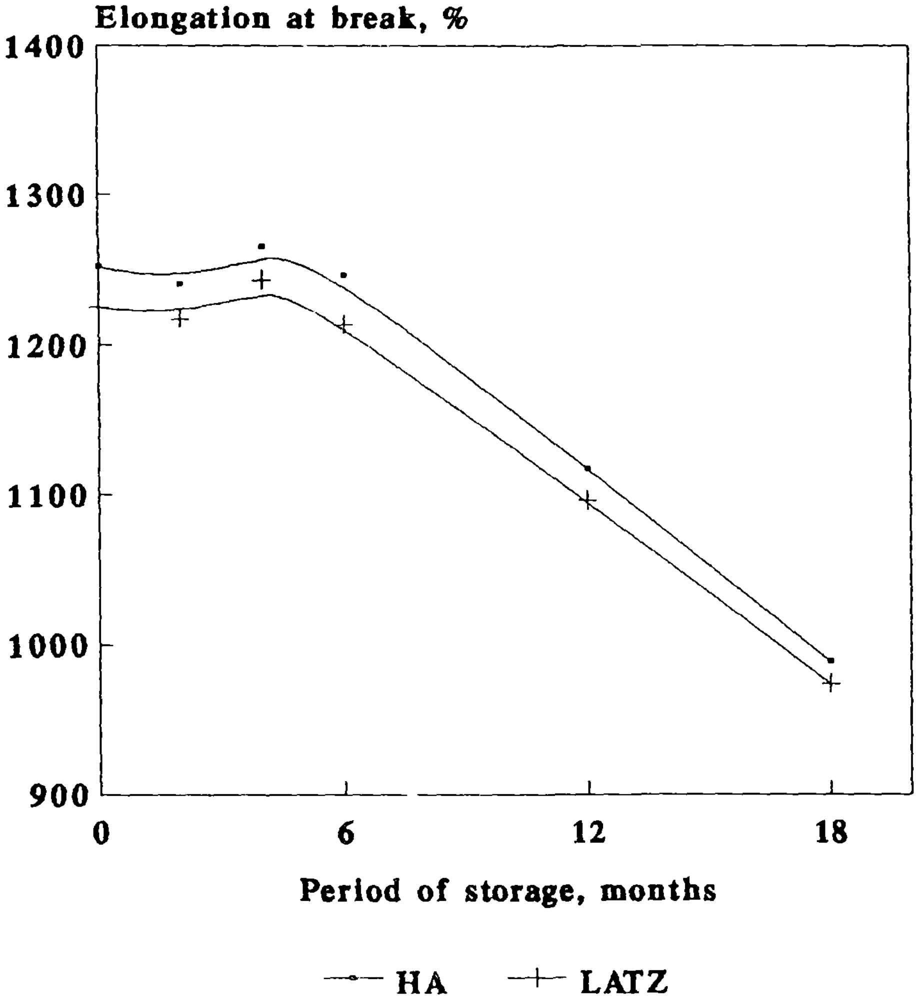

Fig.5.3. Effect of storage of latex on elongation at break

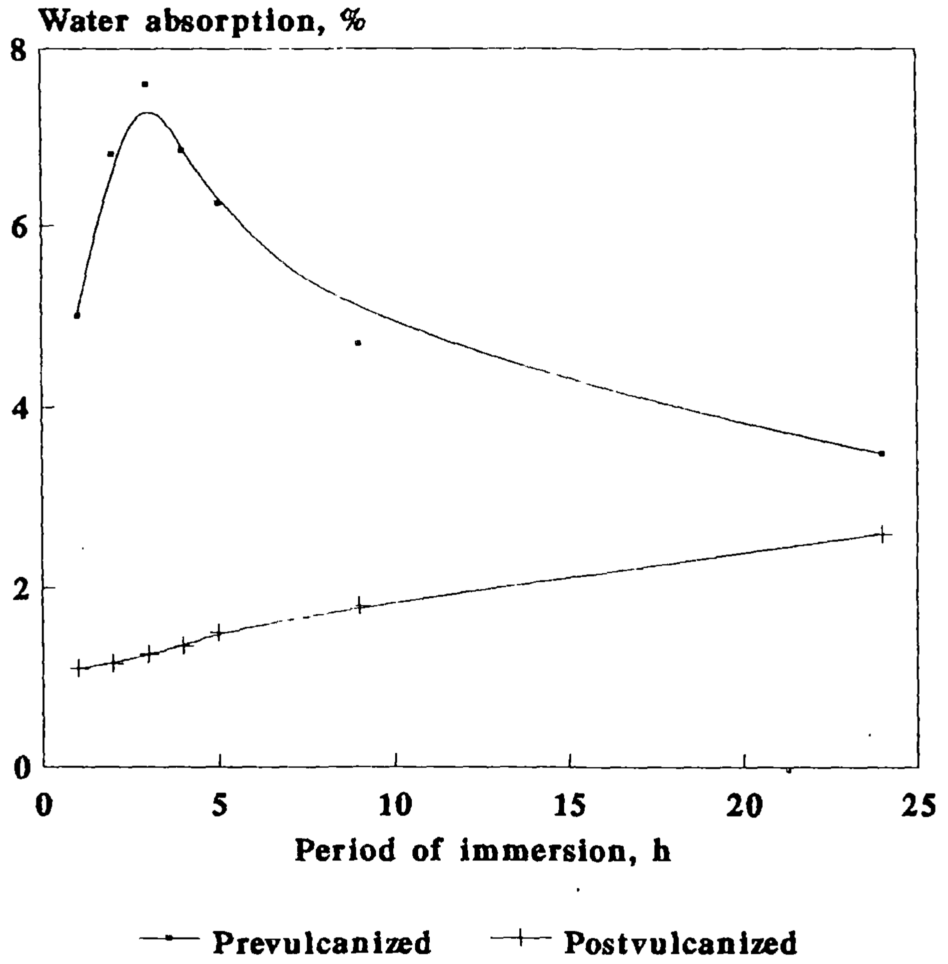

Fig.5.4. Effect of vulcanization method of latex on water absorption by films

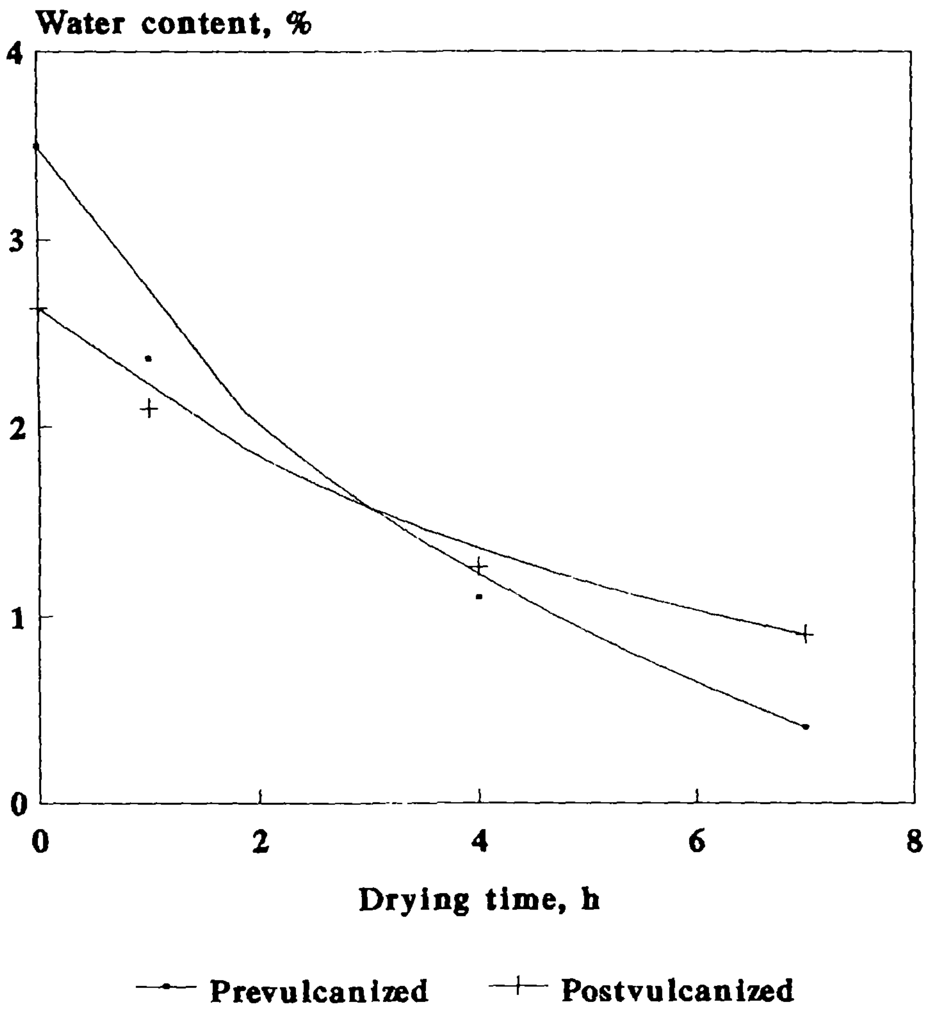

Fig.5.5. The desorption pattern of leached latex films

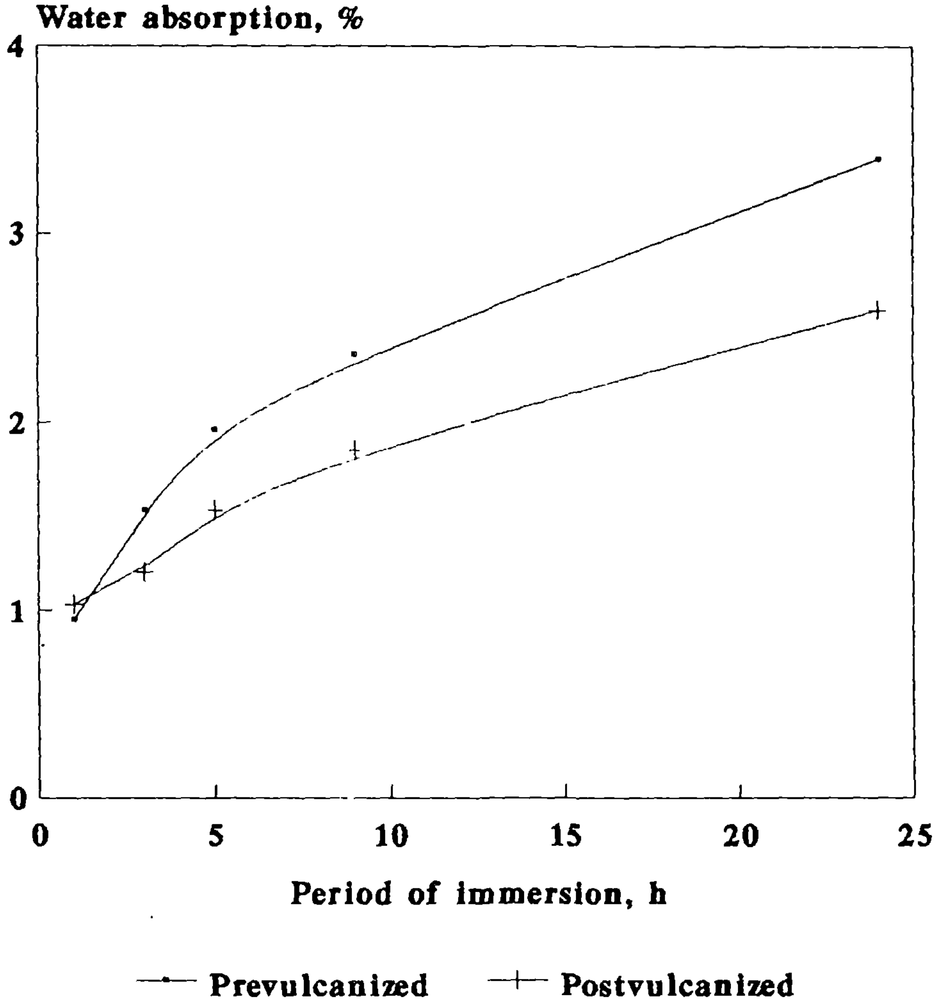

Fig.5.6. Water absorption by already leached films

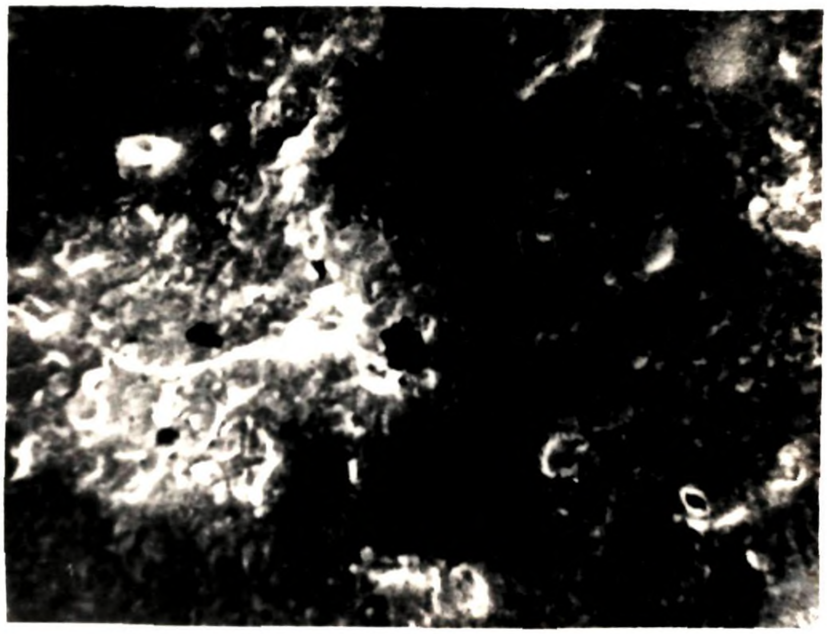

Fig. 5.7. Scanning electron micrograph of leached postvulcanized latex film (x 5000)

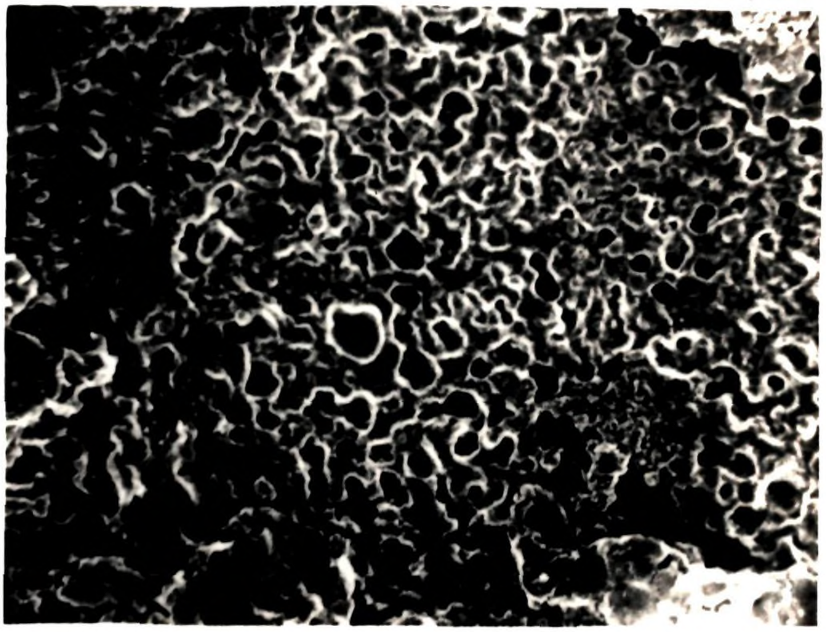

Fig.5.8. Scanning electron micrograph of leached prevulcanized latex film (x 5000)

CHAPTER 6

INFLUENCE OF PREVULCANZATION AND COMPOUNDING ON THE TRANSPARENCY OF NR LATEX FILMS

Latex mixes which yield transparent films on drying are often preferred for products such as teats, soothers, tubings, rubber bands, certain types of gloves etc., although transparency is not an important technological property for rubber products. Production of transparent rubber articles requires special attention in the choice of polymer and compounding ingredients. Sulphur, accelerators, activators etc., in latex compounding have a marked influence on the transparency of a product. Other compounding ingredients employed and production techniques adopted also may influence transparency of vulcanizates.

For preparing a good quality rubber product antioxidants are usually added in order to protect the product from deterioration by oxygen, ozone, heat, light etc. For special applications process oils are added to latex during compounding. For making dipped products from latex, methods like straight dipping, coagulant dipping and heat sensitized dipping are being practised. The thickness of the film obtained by the dipping process is affected by the viscosity of the compound especially in straight dipping. Viscosity modifiers are usually added to latex during compounding for increasing the viscosity of the compound.

Fillers for transparent rubber products shall have an index of refraction very close to that of rubber as otherwise the filler particles may cause opacity to the finished product. In the case of other ingredients also refractive index shall be as close to that of rubber in order to have a transparent vulcanizate.

Latex products are made either from centrifuged latex or from creamed latex. For preparing creamed latex, creaming agents such as tamarind seed powder or ammonium alginate are usually added.

For the vulcanization of latex products two alternative methods exist, prevulcanization and postvulcanization. One of the advantages of prevulcanized latex is that the sedimentable impurities and unreacted ingredients can be removed which may cause blooming and affect the transparency of the films.

In the production of dipped rubber products, coagulant dipping is usually practised. Acid coagulants and salt coagulants are made use of. After-treatment of the films also have some influence on transparency. Leaching of latex vulcanizates improves the film clarity. The surface of natural rubber latex vulcanizates usually exhibits a degree of self tack. Tackiness is reduced by application of detackifiers. Storage conditions of a product also influence its transparency.

Insoluble solid ingredients are added to latex as fine dispersions which are prepared by ball milling. This process reduces the ultimate particle size as well as disperses any agglomerates which may be present.[1]

According to Blokh[2], the protection of a vulcanizate against ageing depends mainly on the nature of accelerators employed and only less on antioxidants. Apart from accelerating the vulcanization reaction, ZDC functions as an antioxidant also.[3] Of the various dithiocarbamates and indeed of all the latex accelerators zinc diethyldithiocarbamate is the most widely used.

Studies on transparency of vulcanizates from dry rubber have been reported. [4-10] A few reports on transparency of latex vulcanizates are also available.

The effect of formulation on the transparency of prevulcanized latex film has been reported by Gorton.[11] Latex films prepared using the activator /accelerator complex FIC 3/5 were reported to have higher transparency than those obtained using zinc oxide[12].

In the present work various factors affecting transparency of films made from NR latex have been investigated with a view to designing formulations and developing manufacturing techniques which will render maximum transparency.

EXPERIMENTAL

Centrifuged latex (HA) conforming to the specifications of the Bureau of Indian Standards, IS:5430-1981, field latex from the RRII Experiment Station and creamed latex prepared in the laboratory, were used for this study. Insoluble solid compounding ingredients were added as 50 per cent dispersions in water, except precipitated silica which was added as 25 per cent dispersion. Antioxidant SP and paraffinic oil were added as 50 per cent emulsions in water. Viscosity modifiers and coagulants were prepared as 5 per cent solutions in water.

The base formulation selected for the study is given in Table 6.1. After maturation for 24 h, films were prepared by casting the compound in glass cells. These were dried at room temperature and vulcanized at 100°C in an air oven for 1 h. These films were designated as 'postvulcanized films'.

Transparency measurement

Specimens, 5 x 1 x 0.05 cm in size, were cut from the vulcanizate and fixed on a glass strip of the same size, by means of two small strips of adhesive tape at both ends. The transparency of the film was measured using a Shimadzu UV-Visible Recording Spectrophotometer (UV-240) which gives values for light transmittance at wavelengths ranging from 300 to 900 nm. The transmittance values at a wavelength of 600 nm at which maximum light transmittance was obtained, were recorded. Absorbance of the supporting glass sheet was adjusted to zero in all measurements. The percentage transmittance is taken as a measure of the transparency of the films.

Latex films of thickness ranging from 0.2 to 1 mm were prepared using the base latex compound to study the effect of film thickness on transparency. In all other experiments the thickness of the film was adjusted to 0.5 mm. To study the effect of sulphur concentration on transparency, films were prepared by changing sulphur concentration from 0 to 2 phr in the base latex compound. Six different batches of the compound were made using 50 per cent zinc oxide dispersions prepared by ball milling for different periods, from 0 to 48 h. To study the effect of zinc oxide concentration the dosages tried varied from 0 to 5 phr. ZDC concentration in the base latex compound ranged from 0.5 to 2.0 phr to study the effect of different amounts of ZDC on transparency. Styrenated phenol based antioxidant was added to the base formulation at levels ranging from 0 to 1.5 phr to ascertain the influence of antioxidant concentration. Paraffininc oil at different levels from 0 to 5 phr was also tried in the base formulation. Viscosity modifiers employed in the study were polyvinyl alcohol, ammonium alginate, sodium carboxymethyl cellulose and casein at concentrations ranging from 0 to 1 phr. The fillers studied were precipitated silica, whiting, magnesium carbonate, china clay and titanium dioxide.

Latex compounds were also prepared by replacing centrifuged latex in the base formulation with creamed latex and field latex. Instead of casting, latex films from the base latex compound were prepared by coagulant dipping to study the effect of coagulants. Coagulants used were formic acid, acetic acid and calcium nitrate.

In another experiment a portion of the base latex compound was prevulcanized by heating at 70°C for 2 h. The prevulcanized latex was divided into two parts. One part was centrifuged at 3000 rpm for 10 minutes and then decanted. To study the effect of heating, films were prepared using base latex compound, prevulcanized latex and centrifugally clarified prevulvcanized latex and these films were heated at 100°C for 0 to 3 h. This treatment is inclusive of the time required for vulcanization in the case of postvulcanized films.

To study the effect of removing unreacted ingredients by sedimentation, the base latex compound was prevulcanized and divided into 6 parts and kept undisturbed for 0 to 5 days. After the period of storage, the latex samples were decanted and films prepared from it.

The effect of humidity on transparency, was studied by keeping prevulcanized latex films at different levels of humidity for 48 h before measuring transparency.

The effect of detackifiers on film transparency was also measured by applying detackifiers such as talc and silicone emulsion to the surface of latex vulcanizates before measuring transparency.

Based on the results, a formulation was selected for preparing transparent rubber band and the technological properties of the films prepared from it were compared with those prepared from a conventional formulation.

RESULTS AND DISCUSSION

Effect of thickness of film

The effect of thickness of latex film on transparency is shown in Figure 6.1. It is seen that as the thickness of the film increased, transparency has decreased. This is expected as rubber vulcanizates can never be fully transparent. As the thickness of a less transparent material increases light transmittance is bound to decrease. In all other experiments the thickness of the film was maintained at 0.5 mm.

The effect of heating of latex films on transparency, as shown in Figure 6.2, shows that heating increases transparency of latex films and the maximum transparency is obtained at a heating time of 1 h and thereafter the increase is not appreciable. Before heating, the latex films contain compounding ingredients like sulphur, in the free state. During the course of heating a major portion of these ingredients get used up in reactions with rubber, which improves transparency. Heating of the films also removes the final traces of moisture present in the film, further improving transparency. In all the other experiments, time of heating of the latex films was fixed as 1 h.

Effect of dosage of sulphur

The effect of adding sulphur on transparency is shown in Figure 6.3. As the dosage of sulphur increased, transparency increased initially and maximum transparency was obtained at a sulphur dosage of 1 phr. On further increasing the level of sulphur, a decrease in transparency was obtained. Therefore, for obtaining maximum transparency sulphur level should be maintained at 1 phr. It may be mentioned that when sulphur dosage is increased beyond the optimum level the quantity of free sulphur remaining in the vulcanized film increases resulting in the formation of crystals of free sulphur in the matrix and eventually in surface blooming.

Effect ball milling time of zinc oxide

Figure 6.4 shows the effect of ball milling time of zinc oxide on transparency. As the ball milling period is increased transparency also increases up to a period of 24 h and thereafter the change is not appreciable. This shows that transparency of latex vulcanizates is affected by the particle size of the solid ingredients and as the particle size is reduced transparency is increased. A ball milling period of 24 h reduces the particle size of zinc oxide to the optimum level for the purpose of transparency.

Effect of dosage of zinc oxide

The effect of adding different amounts of zinc oxide on transparency (Fig. 6.5) reveals that the addition of even small amounts of zinc oxide into the latex compound decreases transparency of the films considerably. The high tinting power of zinc oxide is responsible for the significant reduction in transparency. Indeed zinc oxide is not essential for latex vulcanization if zinc containing accelerators are employed. Therefore, for maximum transparency a formulation without zinc oxide will be desirable.

Effect of dosage of ZDC

The effect of ZDC concentration on transparency of the films is shown in Figure 6.6. It can be seen that as ZDC concentration increases from 0.5 to 2.0 phr transparency of the films decreases considerably.

Tables 6.2 and 6.3 shows the effect of ageing at 70°C of vulcanizates containing 0.5 to 2.0 phr of ZDC, on tensile strength and modulus respectively. It is evident that the ageing resistance of the vulcanizates improves as the concentration of ZDC increases.

The effect of ageing of the vulcanizates at 70°C on the Vr values are given in Table 6.4. The retention in Vr values on ageing is in line with the retention in tensile strength and modulus of the vulcanizates.

Combining ageing resistance with transparency of vulcanizates, for a product which requires transparency as well as reasonable ageing resistance, 1 phr of ZDC shall be used, while for that which requires good transparency irrespective of ageing resistance, ZDC concentration can be reduced to 0.5 phr.

Effect of process oil

Figure 6.7 shows the effect of adding paraffinic oil during compounding. It is seen that transparency of the latex films remains largely unaffected by the addition of paraffinic oil up to the level of 5 phr.

Effect of antioxidant

The results as depicted in Figure 6.8 show that transparency of the latex film is not significantly affected by the presence of styrenated phenol.

Effect of viscosity modifiers.

Figure 6.9 shows the effect of viscosity modifiers on transparency of latex films. Polyvinyl alcohol and ammonium alginate at 0.25 phr slightly improved transparency of the latex film and beyond this level transparency was found decreasing. But when casein was added, transparency of the film remained largely unaffected up to a concentration of 1 phr. However, in the case of sodium carboxymethyl cellulose, transparency decreased beyond 0.25 phr. The decrease in transparency is believed to be due to the difference in refractive indices of the materials and that of rubber.

Effect of fillers

Figure 6.10 shows the effect adding fillers on transparency. It is observed that all the fillers studied decreased transparency even at low concentrations, the maximum being in the case of titanium dioxide. The decrease was in the order, titanium dioxide > whiting > china clay > precipitated silica > magnesium carbonate. This decrease in transparency may be caused by the reflection and refraction of light by the filler particles. Transmission of light through a rubber compound will be decreased by fillers having a refractive index different from that of the rubber. If this difference is large, reflection and refraction will be larger and less light will be transmitted.

Effect of type of latex

The effects of using different latices such as centrifuged latex, creamed latex and field latex on transparency are shown in Figure 6.11. It is seen that films made out of creamed latex (prepared using either tamarind seed powder or ammonium alginate) and centrifuged latex have comparable transparency. Transparency was considerably reduced when field latex was used, indicating that the non-rubber constituents present in latex have a marked influence on the transparency of latex films.

Effect of methods of vulcanization and after-treatments

The effects of prevulcanization, centrifugal clarification of the prevulcanized latex and heat treatment of the films made therefrom, are shown in Figure 6.2. This shows that clarification of prevulcanized latex by centrifuging process improves transparency of the films and a further enhancement is possible by heat treatment of the films. For obtaining better transparency heating of the films for a minimum period of 30 min at 100°C is required. Heating is reported to improve the technological properties of prevulcanized latex film. Centrifuging of the prevulcanized latex effectively removes the unreacted ingredients and pieces of coagulum. Removal of these, from the prevulcanized latex enables it to form a homogeneous film having good clarity. During prevulcanization of latex, crosslinking takes place mostly within individual rubber particles. Additional crosslinks are introduced in the prevulcanized latex film during heating, linking the coalesced rubber particles together covalently[13]. This figure also shows that prevulcanized film is more transparent than postvulcanized film.

Figure 6.12 shows the effect of removing unreacted ingredients and other impurities by sedimentation under the influence of gravity, on transparency of films. It can be seen that the removal of sedimentable impurities in this way also improves transparency of prevulcanized latex. In small scale manufacturing units where a centrifugal clarifier is not available, it is possible to improve transparency by keeping the prevulcanized latex undisturbed for a sufficiently long period followed by decantation.

Effect of dipping techniques and coagulants

The effect of different methods of dipping and also the effect of different coagulants on transparency of vulcanizates are shown in Figure 6.13. The film made by straight dipping is more transparent than that made by coagulant dipping. Among the coagulants studied, all the coagulants decreased the transparency of films, the maximum effect being exhibited by calcium nitrate. The decrease was in the order, calcium nitrate > acetic acid > formic acid. When a coagulant is used it reacts with latex stabilizers, such as soap, resulting in the formation of either insoluble soap (in the case of calcium salts) or free fatty acid (in the case of acid coagulants). In either case transparency is reduced.

Effect of ambient humidity

Figure 6.14 shows the effect of atmospheric humidity on transparency of latex vulcanizates. It can be seen that the transparency is decreased by increase in humidity during storage. This is mainly due to the tendency of latex films to absorb moisture.

Effect of detackifiers

The effect of detackifiers such as talc and silicone emulsion is shown in Table 6.5. It is observed that when talc is applied the film is almost opaque. Better transparency and appearance are obtained with dilute silicone emulsion. It is reported[14] that liquid detackifiers maintain or improve the shine on the surface of the latex articles.

Based on the results obtained, a formulation for preparing transparent rubber band was selected. The formulation is given in Table 6.6. A conventional formulation is also given in Table 6.7. Films were prepared by casting based on the selected formulation and the conventional formulation and the properties compared.

Table 6.8 shows the physical properties of postvulcanized films, prepared based on the selected formulation and the conventional formulation, and also prevulcanized films, with and without clarification.

It is observed that all the films have comparable strength properties. Postvulcanized film and prevulcanized film prepared based on the selected formulations gave comparable transparency. Centrifugally clarified prevulcanized latex exhibited the maximum transparency, while the postvulcanized film prepared based on the conventional formulation was opaque. The retention of strength properties of these films after ageing at 70°C for 96 h are shown in Table 6.9. It can be seen that the retention of properties were also comparable for the films.

CONCLUSIONS

For obtaining maximum transparency sulphur at the level of 1 phr shall be used and zinc oxide omitted. For a product which requires transparency as well as reasonable ageing resistance, 1 phr of ZDC shall be used as acclerator. Fillers shall be avoided. A substantial increase in transparency is possible by clarification of prevulcanized latex preferably by centrifuging and by heat treatment of the films.

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Table 6.1

Formulation of the base compound

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Sulphur dispersion, 50%	4.0
Zinc diethyldithiocarbamate dispersion, 50%	2.0
Zinc oxide dispersion, 50%	0.4

Table 6.2

Effect of ZDC concentration on retention of tensile strength of the films after ageing at 70°C

Concentration of ZDC (phr)	Retention of tensile strenth after ageing for for different periods, days (%)		
	14	21	28
0.5	24.3	18.1	11.1
1.0	67.3	38.5	16.9
1.5	69.6	40.3	33.0
2.0	71.2	44.2	36.5

Table 6.3
Effect of ZDC concentration on retention of modulus of the films after ageing at 70°C

Concentration of ZDC (phr)	Retention of modulus, 100% after ageing for different periods, days (%)		
	14	21	28
0.5	59.2	49.0	38.8
1.0	93.8	89.5	43.8
1.5	96.9	93.8	91.7
2.0	97.0	93.9	91.8

Table 6.4
Effect of ZDC concentration on retention of Vr of the films after ageing at 70°C

Concentration of ZDC (phr)	Retention of Vr after ageing at 70°C for different periods, days (%)		
	14	21	28
0.5	76.8	65.4	56.4
1.0	98.0	95.4	82.7
1.5	99.1	98.5	96.5
2.0	99.8	98.0	97.2

Table 6.5
Effect of detackifier on film transparency

Detackifier	Transmittance (%)
Nil	40
Talc	0
Silicone emulsion	52

Table 6.6
Formulation for transparent rubber band

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Sulphur dispersion, 50%	2.0
Zinc diethyldithiocarbamate dispersion, 50%	2.0

Table 6.7
A conventional rubber band formulation

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Sulphur dispersion, 50%	2.4
Zinc diethyldithiocarbamate dispersion, 50%	2.0
Zinc oxide dispersion, 50%	0.4
Titanium dioxide dispersion, 33%	3.0

Table 6.8
Physical properties

Type of film	Modulus, 100% (MPa)	Modulus, 300% (MPa)	Modulus, 600% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Transmittance (%)
Postvulcanized (Table 6.6)	0.77	1.21	2.40	22.2	1240	48
Prevulcanized (Table 6.6)	0.74	1.20	2.37	20.9	949	51
Centrifugally clarified prevulcanized (Table 6.6)	0.71	1.05	2.29	20.1	931	91
Postvulcanized (Table 6.7)	0.79	1.32	2.58	21.6	1202	0

Table 6.9
Retention of properties after ageing at 70°C for 96 hours (%)

Type of film	Modulus 100%	Modulus 300%	Modulus 600%	Tensile strength	Elongation at break
Postvulcanized (Table 6.6)	97.4	95.0	82.5	82.2	105.0
Prevulcanized (Table 6.6)	97.2	93.3	80.5	95.6	110.0
Centrifugally clarified prevulcanized (Table 6.6)	97.1	97.1	82.0	102.4	112.0
Postvulcanized (Table 6.7)	93.6	94.6	89.5	82.0	97.2

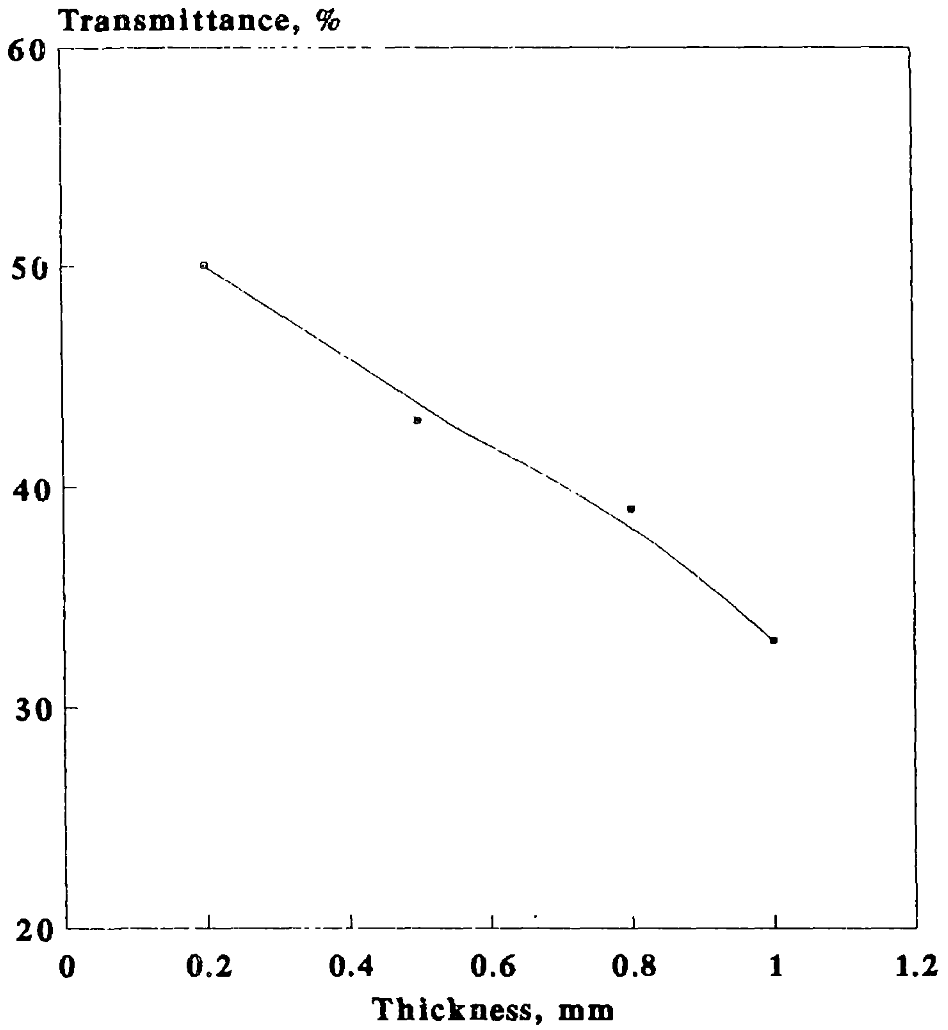

Fig.6.1. Effect of thickness of film on transparency

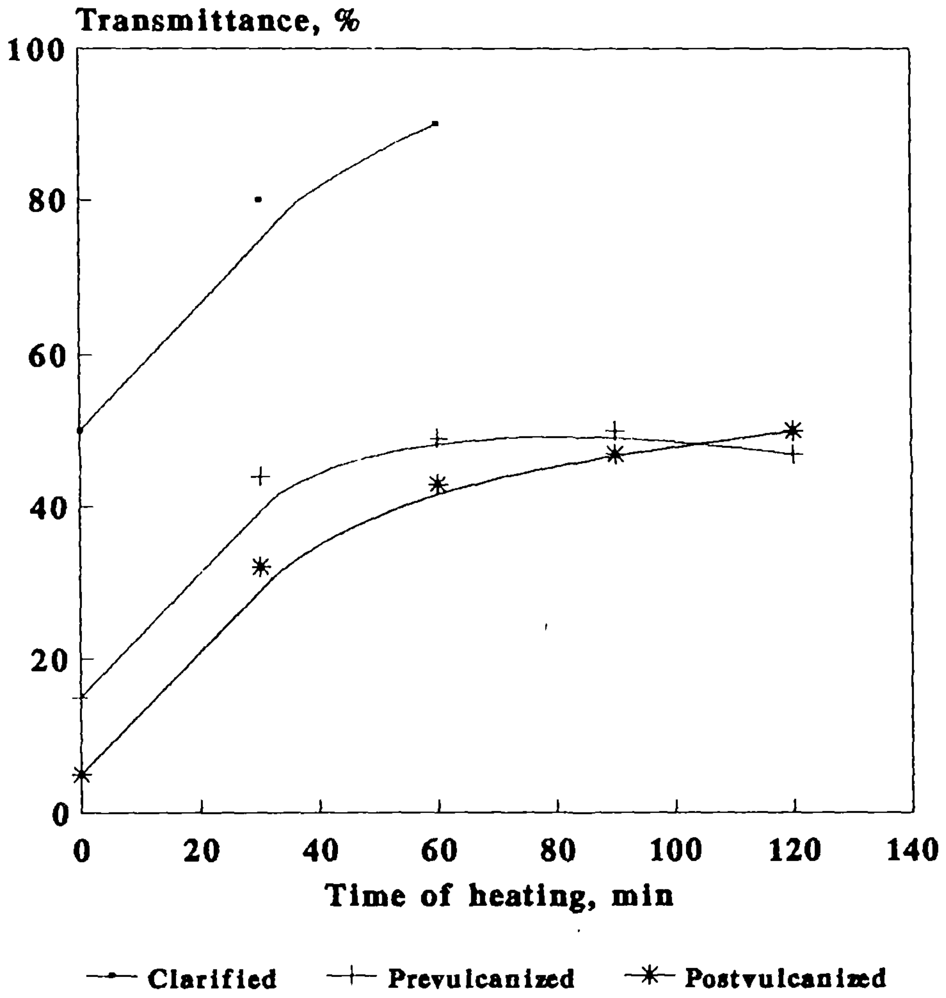

Fig.6.2. Effect of heating of latex film on transparency

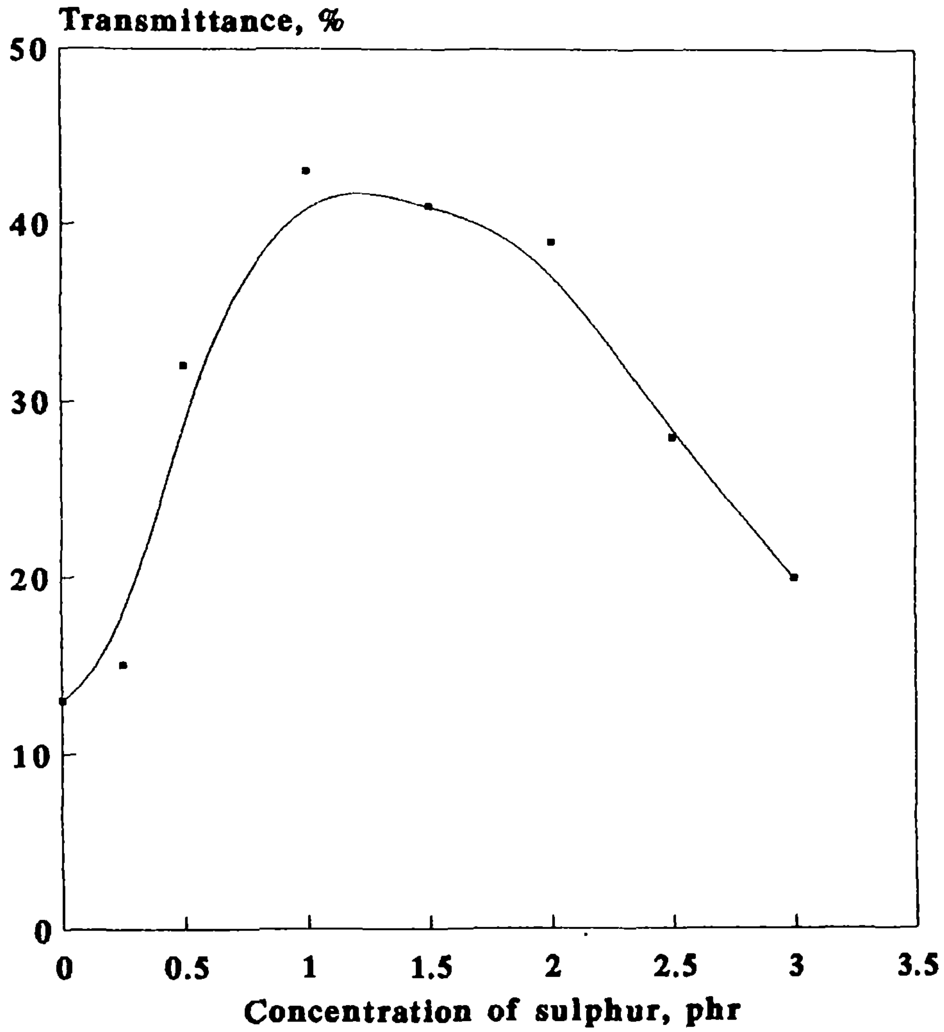

Fig.6.3. Effect of sulphur concentration on transparency

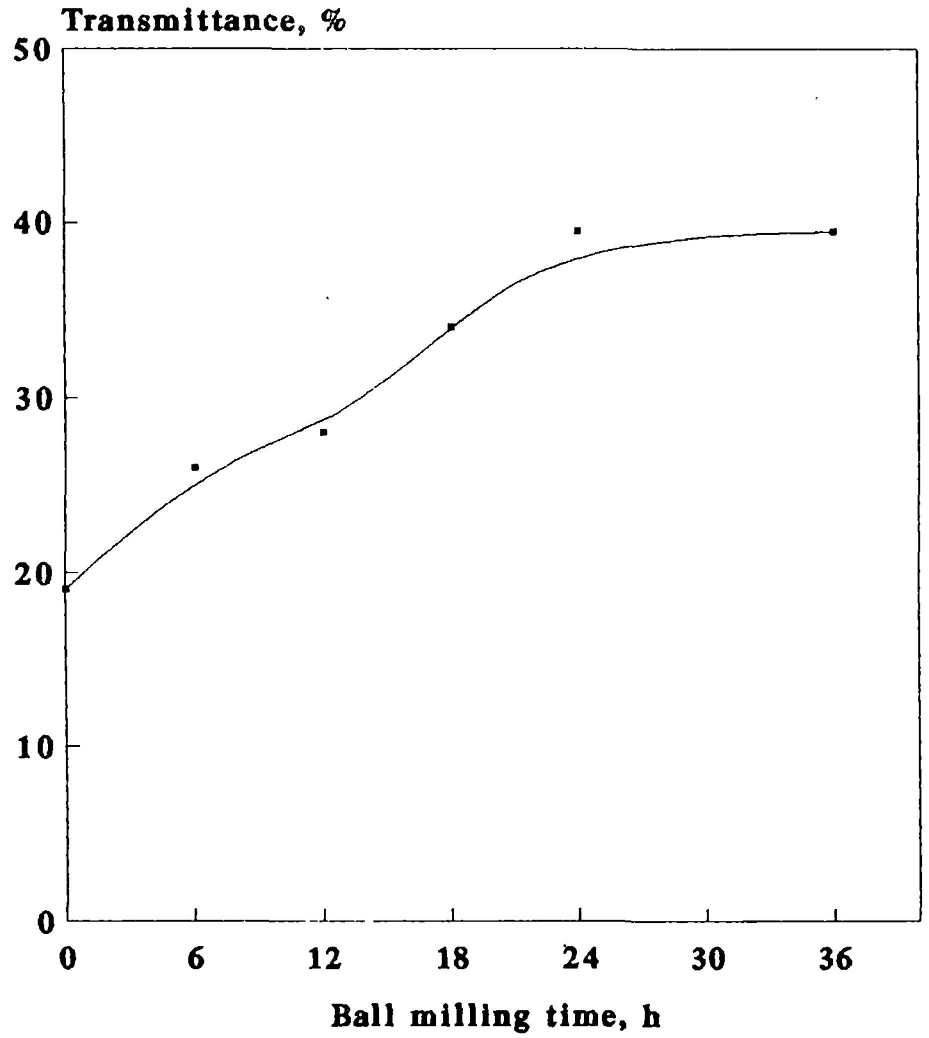

Fig.6.4. Effect of ball milling time of zinc oxide on transparency

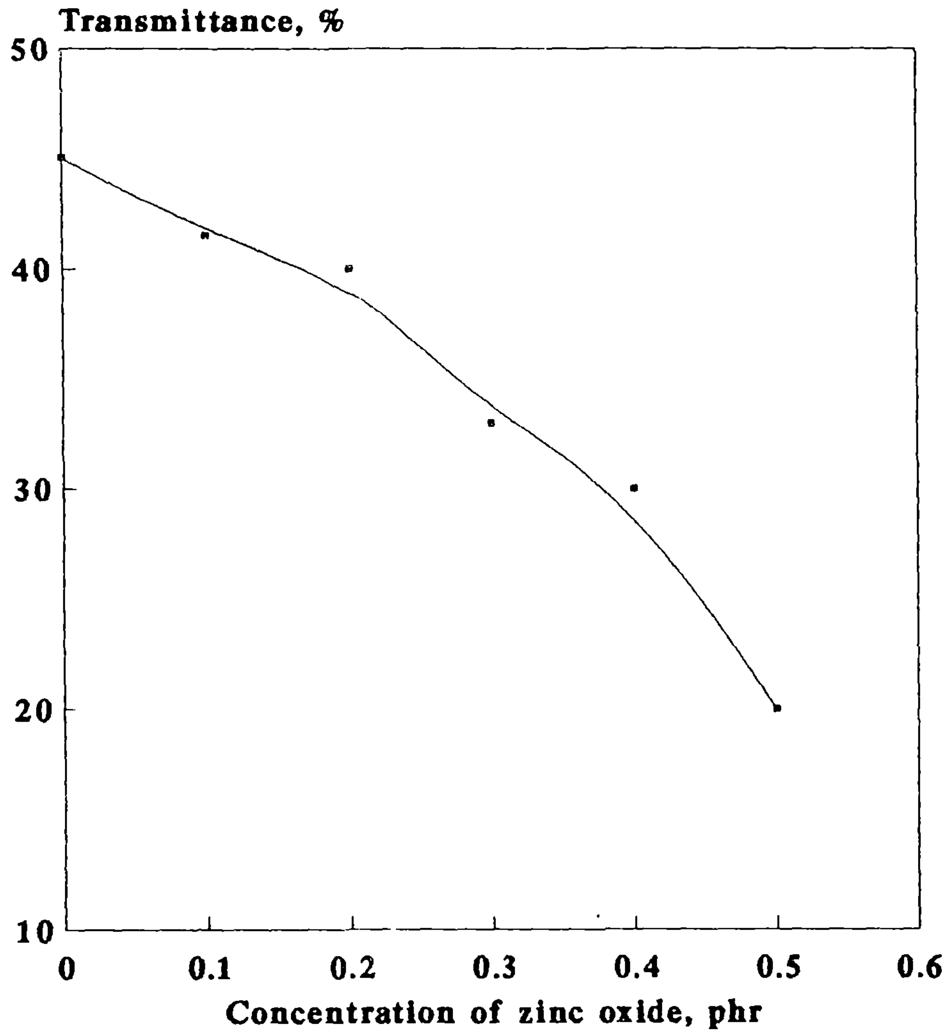

Fig.6.5. Effect of concentration of zinc oxide on transparency.

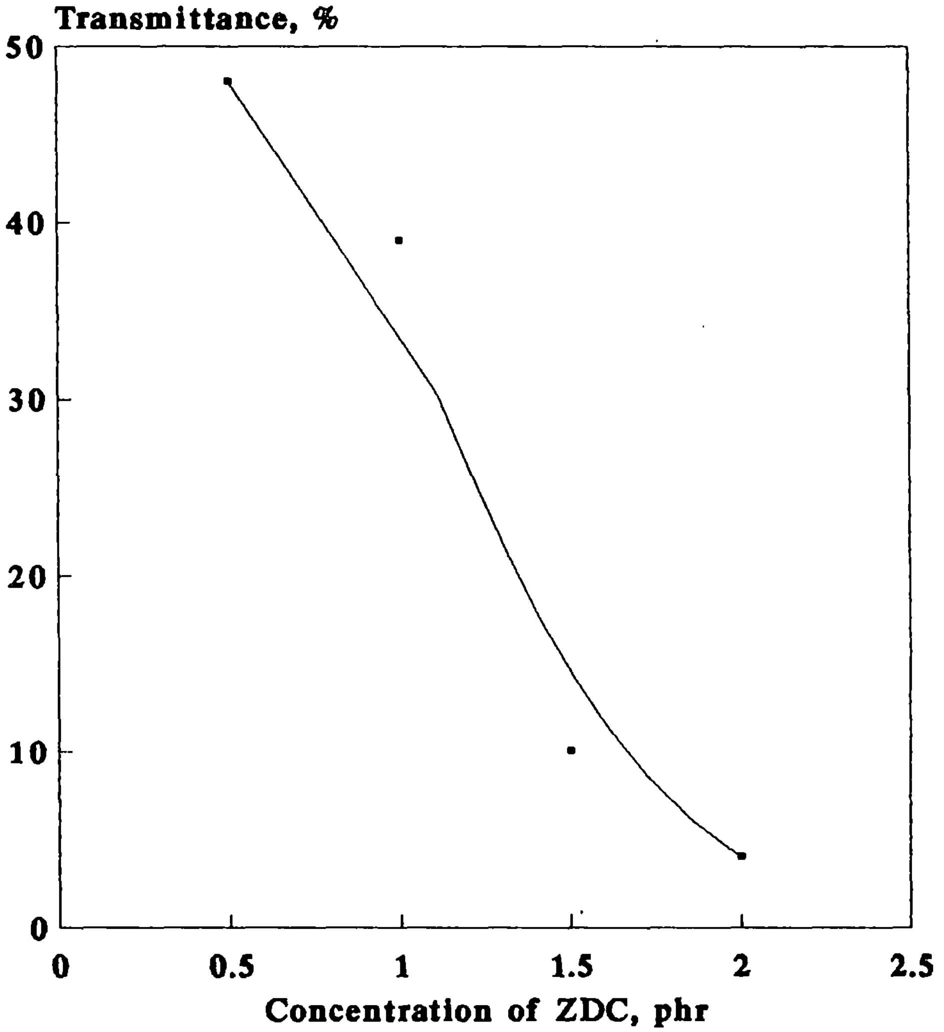

Fig.6.6. Effect of concentration of ZDC on transparency

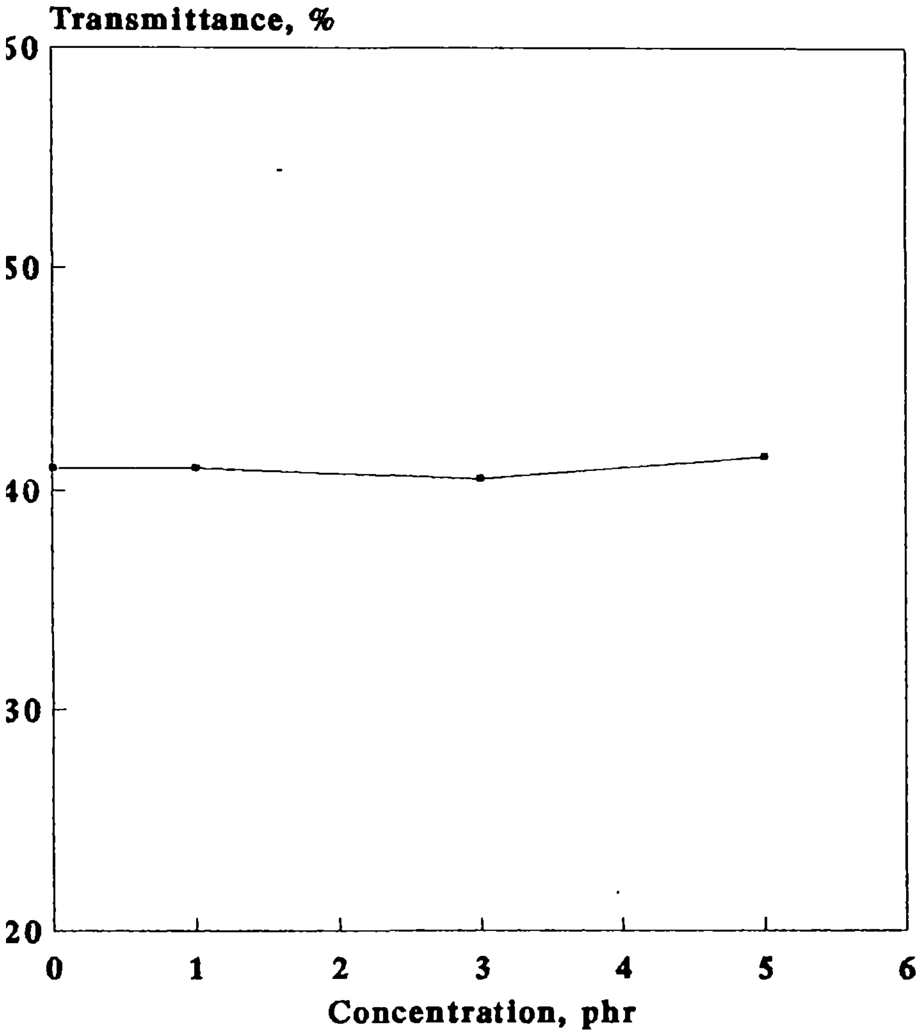

Fig.6.7. Effect of concentration of paraffinic oil on transparency.

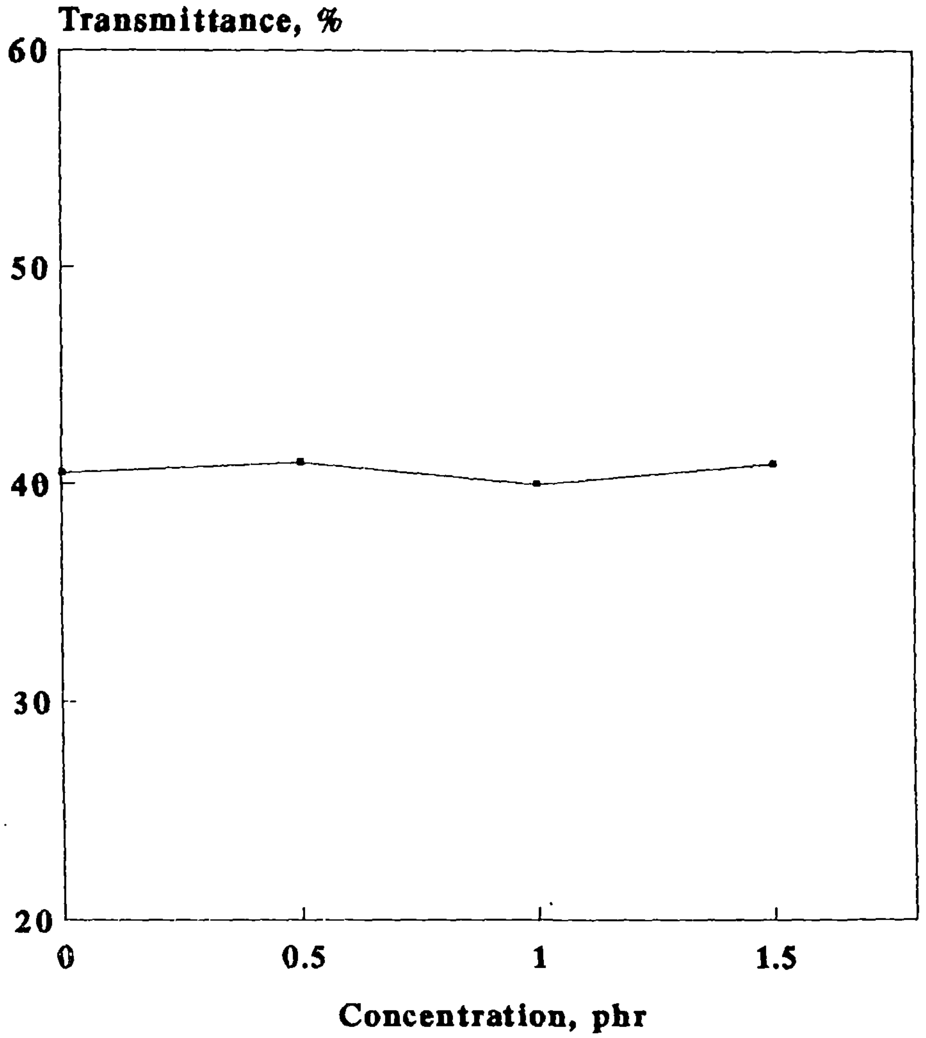

Fig.6.8. Effect of concentration of antioxidant on transparency

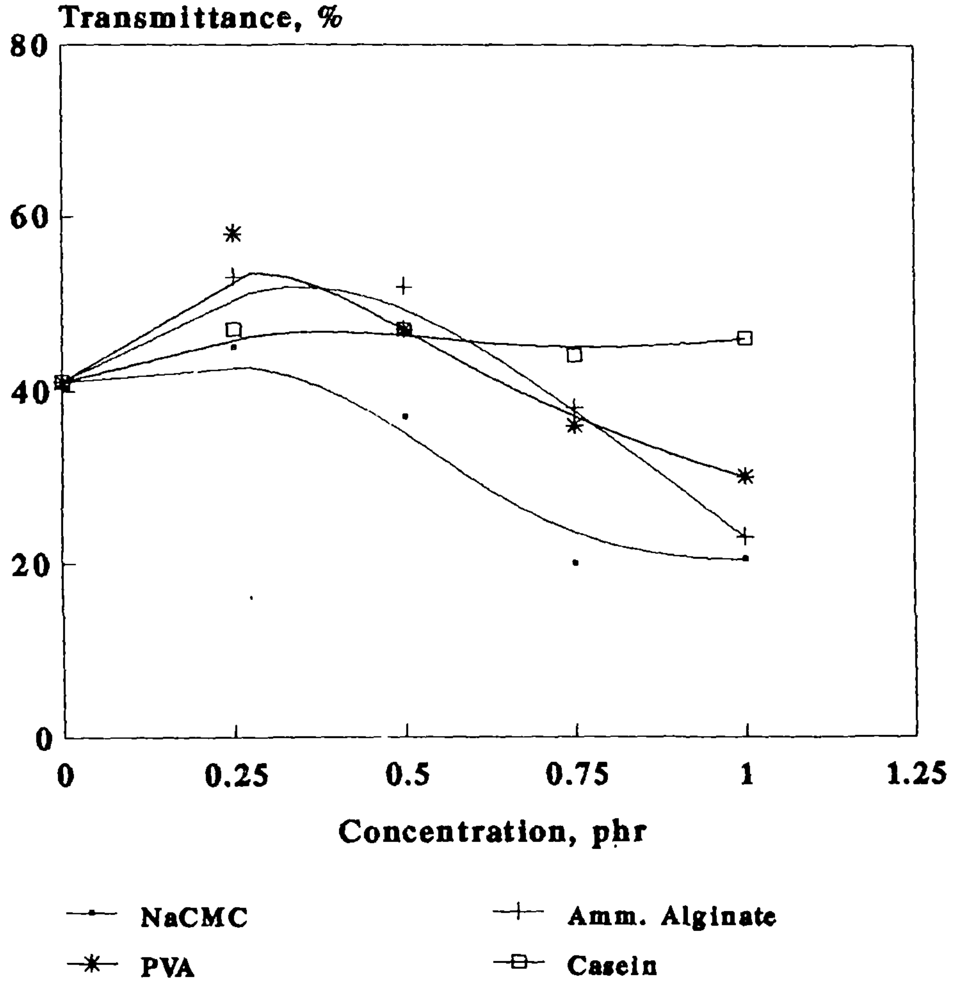

Fig.6.9. Effect of concentration of viscosity modifiers on transparency

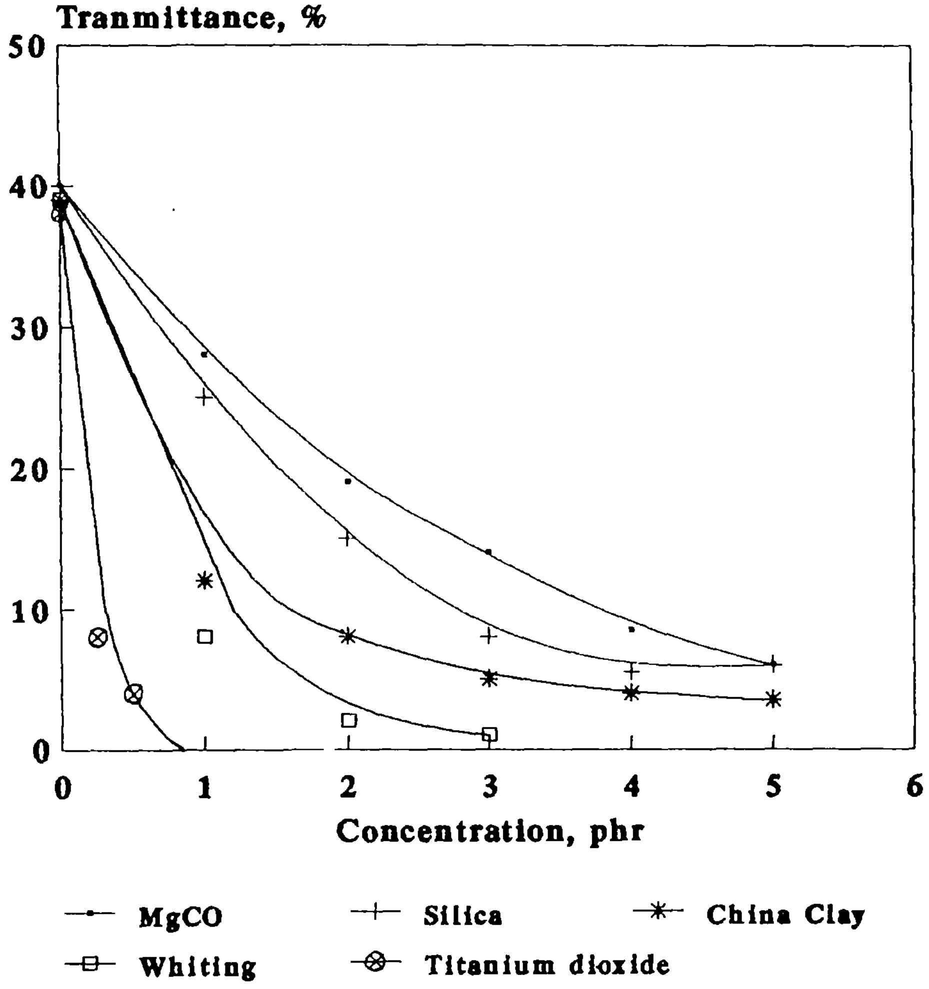

Fig.6.10. Effect of concentration of fillers on transparency.

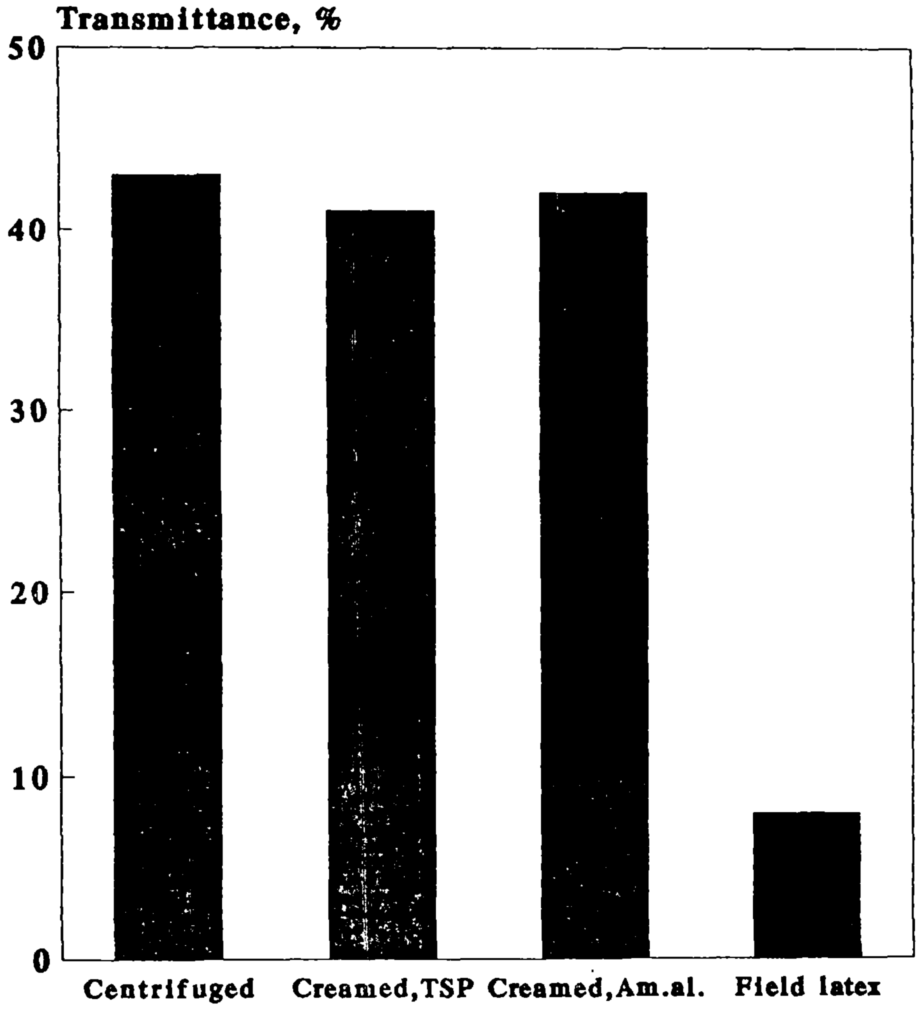

Fig.6.11. Effect of type of latex on transparency.

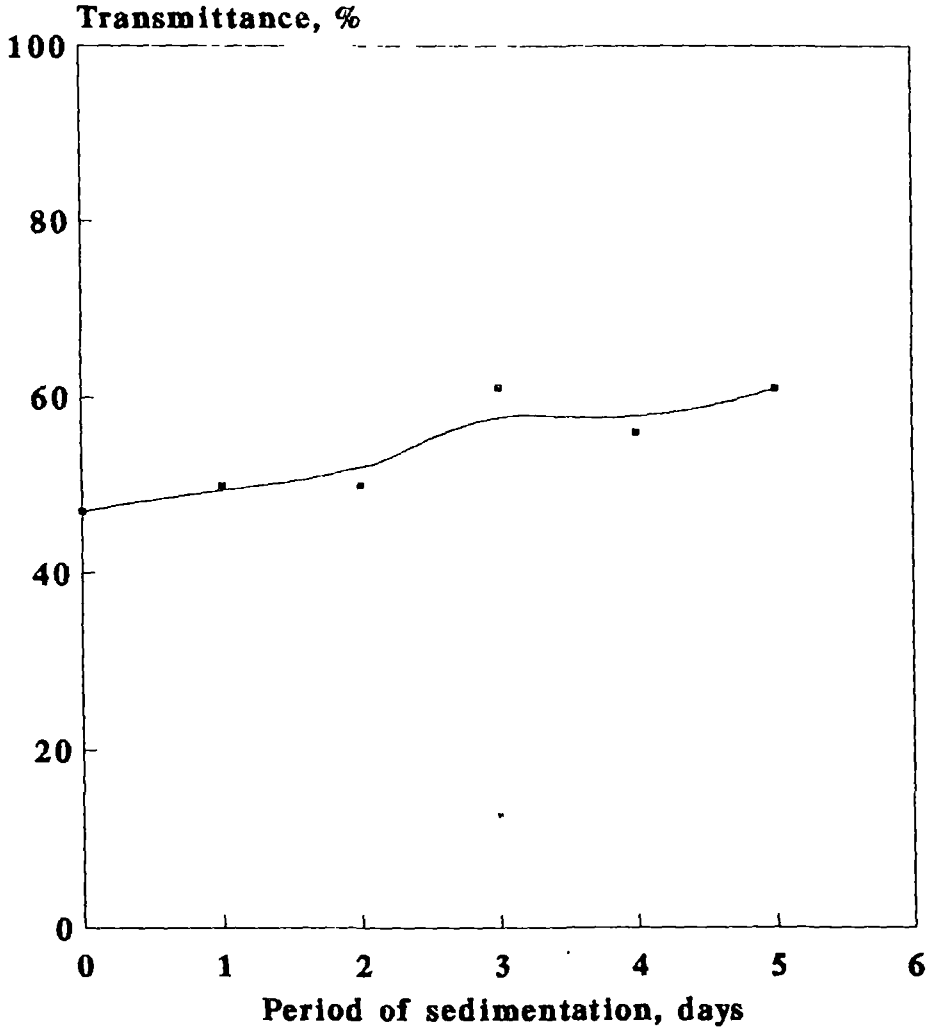

Fig.6.12. Effect of clarification of prevulcanized latex on transparency

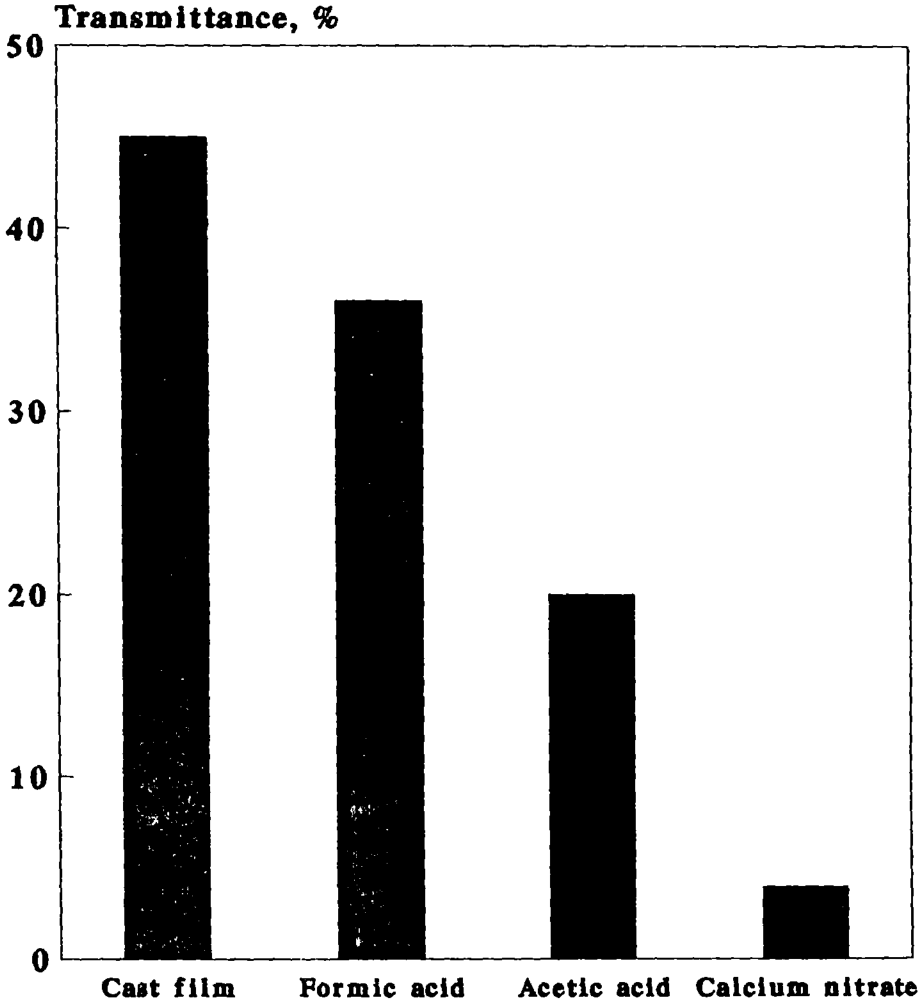

Fig.6.13. Effect of coagulants
on transparency

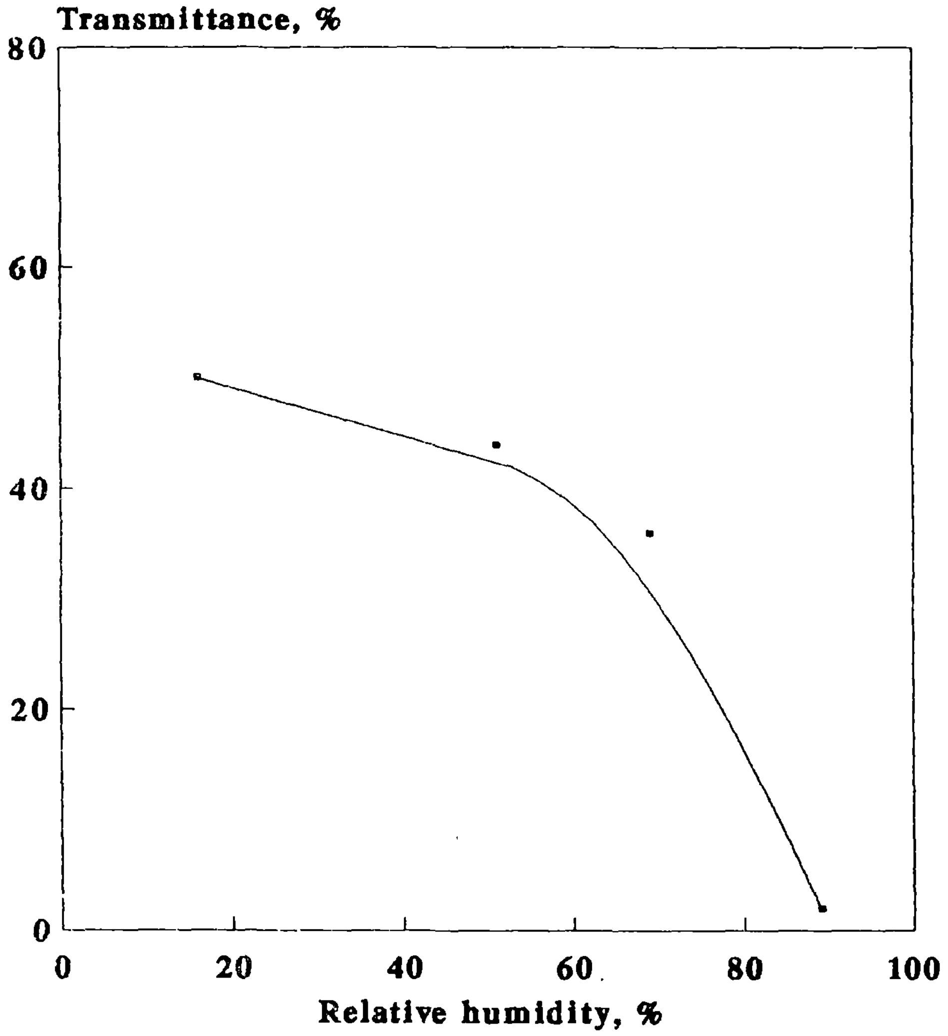

Fig.6.14. Effect of relative humidity on transparency.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Systematic investigations on prevulcanization of NR latex with special reference to the influence of storage of latex and after-treatments of films, have been carried out. The other aspects studied include the effect of temperature on sulphur prevulcanization, the extent of crosslinking, tensile properties, stress relaxation characteristics, water absorption and leaching characteristics of prevulcanized latex films.

As latex is stored for different periods before it is processed into finished products the influence of period of storage on various quality parameters, vulcanization characteristics and properties of prevulcanized and postvulcanized films has been studied. In this case a comparison has been made between high ammonia and low ammonia types of centrifuged latex.

Flow behaviour of latex is very important in determining its processability in the manufacture of finished products. The rheology of prevulcanized latex including the influence of added viscosity modifiers and fillers on flow properties were therefore investigated. The effect of fillers such as precipitated silica, china clay and whiting on strength properties and stress relaxation behaviour of PVL films was also attempted.

Transparency of latex film was another aspect chosen for systematic investigations, as transparency is considered a desirable attribute in certain types of latex products.

The effect of temperature of prevulcanization on properties of latex films is described in Chapter 3. The volume fraction of rubber (Vr), which is a measure of the crosslink density, showed a maximum, when prevulcanization was conducted at 80°C for 2 h or at 90°C for 1 h. At lower temperatures the rate of reaction was slow. At each temperature, tensile strength and elongation at break decreased when the prevulcanization time increased, whereas modulus increased up to maximum crosslinking and thereafter decreased. Water absorption and leaching were rapid as the extent of prevulcanization increased. The rate of stress relaxation slightly increased as the extent of prevulcanization increased. Based on overall balance of properties the optimum temperature and time for prevulcanization are 70°C and 2 h.

The second part of this Chapter deals with the rheological properties of prevulcanized latex (prepared at 70°C for 2 h) in the presence of viscosity modifiers and fillers. Prevulcanized latex exhibited pseudoplastic flow pattern. Pseudoplasticity and viscosity of the latex increased by the addition of viscosity modifiers and the effect varies with the type of viscosity modifier. Among the viscosity modifiers tried, sodium carboxymethyl cellulose (NaCMC) offered the highest viscosity at all shear rates (1 to 150 s^{-1}). Polyvinyl alcohol offered a higher viscosity than casein at low shear rates but as the shear rate increased PVA offered a lower viscosity than casein. The sensitivity to temperature was not affected by the addition of viscosity modifiers.

Pseudoplasticity and viscosity of latex were found to increase by the addition of precipitated silica and china clay, while the addition of whiting slightly decreased them. The sensitivity of latex towards temperature remained unaffected by the addition of fillers.

The fourth chapter deals with the effect of storage of HA and LATZ types of latex and after-treatments on the quality of films from prevulcanized latex. Storage period of latex concentrate affected the tensile properties of prevulcanized latex films. PVL film prepared from fresh latex showed low tensile properties. When prevulcanization was conducted using stored latex the film properties improved. After-treatment of the films substantially improved tensile properties irrespective of the storage period of latex. PVL films from fresh and stored latex exhibited comparable properties after the treatment. However, on storage of latex to beyond one year,properties were found to decrease. Out of the treatments studied, leaching in water gave better properties to the films than heat treatment. Storage of films at room temperature also improved the tensile properties. Optimum properties were obtained by leaching of films at 30°C for 4 h. Leaching time can be reduced by increase of temperature of the leach water. Increase in pH of water used for leaching slightly reduced the ageing resistance of the films. The effect of after-treatments on coagulant dipped films was comparable to that of cast films. The ageing resistance of the films decreased as the storage period of latex increased. The rate of decrease was more when the storage period was beyond one year. PVL films from HA and LATZ latices exhibited the same trend.

Storage of PVL up to three months did not significantly affect latex properties. The unreacted ingredients continue to vulcanize the latex during storage increasing modulus of the film and most of the vulcanization occurred within the first month of storage.

The second part of this chapter describes the effect of fillers on properties of PVL films. Addition of fillers such as precipitated silica, china clay and whiting decreased tensile strength and EB, but increased modulus. When the films were leached in water, tensile properties were improved. Addition of up to 10 phr each of china clay and whiting did not significantly affect the ageing resistance but addition of precipitated silica improved the ageing resistance. Tear strength was found to increase by the addition of precipitated silica followed china clay. Addition of whiting did not significantly affect tear strength. A low level of rubber-filler interaction was observed in the case of films containing precipitated silica. The rate of stress relaxation was slightly higher for films containing precipitated silica followed by those containing china clay and whiting. Optical microscopic observations showed a more uniform distribution of precipitated silica in the rubber matrix.

Chapter 5 presents the influence of storage on properties of HA and LATZ latices and vulcanizates (postvulcanization). DRC and TSC of HA and LATZ latices remained more or less unaffected by storage up to 18 months. Freshly prepared latices exhibited a slightly higher viscosity which decreased during one month and remained rather constant on further storage. Zinc oxide viscosity increased during storage. For LATZ latex the increase was very slow. However, HA latex showed a very rapid rise in ZOV as the latex ages. VFA number of HA and LATZ latices slightly increased on storage and LATZ latex exhibited a lower initial VFA number than HA latex. But on storage the difference narrowed down and after a period of 18 months, LATZ latex exhibited a higher VFA number, but within the permissible limits. KOH number of the latices also increased on storage. For fresh latex MST was very low and it rises during storage. Maximum MST was observed in 75 days of storage and afterwards a slow decrease has been noted. Because of the presence of added ammonium laurate during the preparation of LATZ latex, the change in its MST was observed only at 18 months of storage.

Physical properties of latex vulcaninzates were more or less unaffected by storage of latex up to six months. But beyond this period, a decrease in tensile properties was observed. Ageing resistance of the vulcanizates was also found to be affected by the storage period of latex.

Comparison of prevulcanized film with postvulcanized film showed that water absorption and leaching proceeded more rapidly in the former. Rate of drying was faster in the case of prevulcanized film than in the case of postvulcanized film. Morphological investigations confirmed the porous structure of prevulcanized latex film.

Chapter 6 deals with the influence of prevulcanization and compounding on transparency of NR latex films. For obtaining maximum transparency, sulphur at the level of 1 phr shall be used and zinc oxide omitted. For achieving good ageing resistance with transparency, 1 phr of ZDC shall be used, while for that which requires good transparency irrespective of ageing resistance ZDC concentration can be reduced to 0.5 phr. Solid ingredients shall be added as fine dispersions. Paraffinic oil and antioxidant SP do not influence transparency significantly. Viscosity modifiers at the level of 0.25 phr can be used, without any adverse effect on transparency. Fillers shall be avoided. Centrifuged latex and creamed latex gave films of comparable transparency. A substantial increase in transparency is possible by clarification of prevulcanized latex preferably by centrifuging and by heat treatment of the films. Ambient humidity decreases transparency. Products made by straight dipping are more transparent than those made by coagulant dipping.

List of Publications from this work

1. N.M. Claramma, L. Varghese and N.M.Mathew., " Effect of storage of natural rubber latex concentrate on properties of prevulcanized latex film", Kautschuk Gummi Kunststoffe (in press)

2. N.M. Claramma and N.M. Mathew., " Effect of temperature on sulphur prevulcanization of natural rubber latex". Journal of Applied Polymer Science (in press)

3. N.M.Claramma, L. Varghese and N.M. Mathew., " Influence of storage on properties of natural rubber latex concentrates and vulcanizates", Indian Journal of Natural Rubber Research., **8 (1)** : (1995), 1.

4. N.M.Claramma, K. Mariamma George and N.M Mathew., " Factors affecting transparency of natural rubber latex films", Indian Journal of Natural Rubber Research, **3 (2)**: (1990), 102

5. N.M.Claramma and N.M. Mathew., " Rheological behaviour of prevulcanized natural rubber latex", Kautschuk Gummi Kunststoffe (communicated)