STUDIES ON THE EFFECT OF STORAGE ON STABILITY AND PHYSICAL PROPERTIES OF SULPHUR PREVULCANISED NATURAL RUBBER LATEX

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BY

K.K SASIDHARAN

DEPARTMENT OF POLYMER SCIENCE & RUBBER TECHNOLOGY

COCHIN UNIVERSITY OF SCIENCE& TECHNOLOGY

COCHIN-682002

MAY 2002

PHONE: 578311 (7 Lines)
E-Mail: rrii@vsnl. com.

GRAMS: RUBRBOARD
TELEX: 888 285 RR II IN
FAX: 91-481 570303

रबड बोर्ड
(वाणिज्य मन्त्रालय, भारत सरकार)

THE RUBBER BOARD
(Ministry of Commerce, Government of India)

प्रशिक्षण और तकनीकी परामर्श विभाग
DEPARTMENT OF TRAINING & TECHNICAL CONSULTANCY

तकनीकी परामर्श विभाग
TECHNICAL CONSULTANCY DIVISION

कोट्टयम - केरल
KOTTAYAM - 686 009
KERALA STATE

Reply addressed to the
Director (T & TC)

Ref. No. TC/2/Gen/02

Date: 9th May 2002

CERTIFICATE

Certified that the thesis entitled "**STUDIES ON THE EFFECT OF STORAGE ON STABILITY AND PHYSICAL PROPERTIES OF SULPHUR PREVULCANISED NATURAL RUBBER LATEX**" being submitted by Sri.K.K.SASIDHARAN, in partial fulfillment for the award of the degree of MASTER OF TECHNOLOGY in Polymer Technology of Cochin University of Science and Technology, Cochin-22 is a record of bonafide work done by him under the guidance of **Smt. G Rajammal**, Rubber Technologist, Technical Consultancy Division, Rubber Board, Kottayam-9.

K.S.GOPALAKRISHNAN
DIRECTOR(T&TC)

Phone : 555723

DEPARTMENT OF POLYMER SCIENCE AND
RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022, KERALA, INDIA

Date

No.

CERTIFICATE

This is to certify that the project work entitled "**Studies on the effect of storage on stability and physical properties of sulphur prevulcanised natural rubber latex** " submitted by **Mr. K. K. Sasidharan** is an authentic record of the work done by him at Rubber Board, Kottayam under the guidance of Smt. G. Rajammal, Rubber Technologist, for the award of M.Tech Degree in Polymer Technology of Cochin University of Science and Technology.

Dr .K.E.George
Professor & Head

e-mail . kegeorge@cusat.ac.in Fax 0484 542747

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CONTENTS

CHAPTER I

INTRODUCTION

Introduction

Prevulcanised natural rubber latex is defined as one in which the rubber particles are chemically crosslinked so that on drying the latex , a vulcanised film is obtained without further heating[1].

The vulcanisation of latex was first proposed in the 1920's by Schidrowitz and subsequently developed by him and others[2]. Production of sulphur prevulcanised latex involves heating raw latex with various compounding ingredients such as sulphur and accelerator until the required degree of crosslinking is obtained. After being cooled, it is strained and sometimes clarified , and allowed to mature for a few days.

In this project the effect of storage on the stability and the physical properties of sulphur prevulcanised natural rubber latex is being investigated .

I.1. Natural Rubber Latex

Natural rubber latex is mainly obtained from the bark of the tree "Hevea brasiliensis" by the process of tapping. The freshly tapped latex is a whitish fluid of density between .975 - .980, pH from 6.5 to 7 and surface free energy from 40- 45 (ergs cm $^{-2}$). The rubber content of latex varies between 25 and 40% by weight and this variation is owing to factors such as clone, tapping intensity, soil condition, climatic conditions etc. In addition to the rubber hydrocarbon, a number of non rubber constituents such as proteins, carbohydrates, lipids, inorganic salts etc. are also present in latex[3]. The rubber hydrocarbon in latex is predominantly cis-1,4- poly isoprene and it occurs as molecular aggregates in the form of discrete particles which are usually spherical with diameter ranging from .02- 3.0 microns[4].

I.2. Preservation and concentration of Latex

Natural Rubber latex in vessels of rubber tree is sterile, but as it comes out, it gets contaminated by bacteria and yeasts[5]. The micro organisms metabolise the non rubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which lead to coagulation of latex[6]. Therefore, preservatives are added to latex immediately after collection, to prevent coagulation. Among the preservatives, ammonia is still widely used and it inhibits bacterial growth: acts as an alkaline buffer, raises the pH and neutralises free acid formed in latex[7]. But ammonia has the disadvantage that it is pungent smelling and prolonged exposure to the gas can cause discomfort to workers. Also high concentration of ammonia leads to processing problems. Therefore, attempts have been made to develop low ammonia preservation systems[8,,9,10]. A commonly used low ammonia system is LA-TZ which contains 0.2% Ammonia, 0.013% TMTD, 0.013% Zno and 0.05 % lauric acid[11,12].

Preserved field latex is unsuitable for most product applications as its rubber content is low. For the manufacture of most of the products, latex of 55-60 % rubber content is preferred. The important methods for concentration of preserved field latex are evaporation, creaming, centrifuging and electrodecantation. In India, only centrifuging and creaming are commercially used for the production of latex concentrates[13]. NR latex concentrate is a highly specified material. The significant properties of latex are dry rubber content

(DRC), non rubber solids (NRS), mechanical stability time(MST), volatile fatty acid number (VFA), Potassium hydroxide (KOH) number and alkalinity. The significance of these properties has been discussed by Blackley and Cockbain[14,15]. Latex concentrate is a non-Newtonian fluid and its viscosity decreases with increasing shear rate[16].

I.3. Latex Compounding

Latex products are manufactured from concentrated latex by mixing it with various compounding ingredients. The compounding ingredients are solids or liquids and may be water-soluble or water insoluble. They are added to latex as aqueous solutions, if they are water-soluble solids or liquids as dispersions if, they are water insoluble solids and as emulsions if they are water immissible liquids. General principles to be considered while addition of solutions, dispersions and emulsions to lattices [17]are

1. Particles size of dispersions and the droplet size of emulsions should be comparable to the particle size of the latex.
2. The colloid stability of dispersions and emulsion should be comparable to that of the latex.
3. The pH of solutions, dispersions and emulsions should be similar to that of latex.
4. It is desired that the ionic strength of the aqueous phase of the dispersion should be similar to that of the latex aqueous phase.

Dispersions of solid ingredients are prepared by first making a coarse slurry of the powered ingredient with water which contains the required amounts of dispersing agent and colloid stabiliser. The slurry is then ground in a suitable mill such as colloid mills, ball mill or attrition mills for an appropriate length of time so as to produce a dispersion of required small particle size[18].

Emulsions are prepared by first making a coarse suspension of oil droplets in water in the presence of a suitable emulsifying agent using a high speed stirrer and then subjecting this to a refining process.

I.4. Compounding Ingredients

The different ingredients used in latex compound are classified as

1 Surface active agents
2 Vulcanising agent
3 Accelerators
4 Activators
5 Antioxidants
6 Fillers
7 Viscosity Modifiers
8 Special additives

I.4.1. Surface active agents

These are substances which can bring about marked modifications in the surface properties of the aqueous media, eventhough they are present in small amounts of the order of 1% m /v or less. They have got great importance in latex technology and in this respect latex technology differs significantly from that of dry polymer or polymer solutions[19]. Their principle effect is to reduce significantly the surface free energy of aqueous medium. One part of its molecule is strongly hydrophilic and other part is strongly hydrophobic. As a result the molecule get s absorbed at the interface between the rubber and the aqueous media. Depending on function, they are classified as stabilising agents, dispersing agents, emulsifiers, wetting agents, viscosity modifiers and protective colloids.

Stabilisers are first added into latex during compounding to maintain the latex in the colloidal condition during compounding and further processing. The dispersing agents prevent the dispersed particles in dispersions from re-aggregating and alkyl sulphonates are used for this. The emulsifying agents are soaps, usually oleates formed 'insitu'. Wetting agents are used to reduce the interfacial tension between two surfaces. Proteins, alginates, polyvinyl alcohol and cellulose derivatives are used as protective agents and viscosity modifiers in the processing of latex compound [19,20,21,22].

Surface active substances are also classified broadly into ionic and non-ionic types. The ionic types are subclassified into anionic, cationic and amphoteric according as the surface active part of the molecule is anionic, cationic or amphoteric. According to the nature of the ionic groups the anionic types are sub classified as carboxylates, sulphonates and sulphates (e.g.: Potassium Oleate, Sodium naphthalene formaldehyde sulphonate etc.) Non- ionic surface active substances do not ionise in aqueous media. Important types used in latex technology are ethoxylates. They are less soluble in hot water than in cold water.

I.4.2. Vulcanising agents

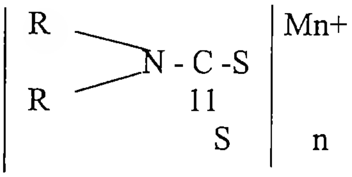
The normal vulcanising agent for NR latex is sulphur. Depending upon the particular property required for the product, sulphur is added at different levels ranging from 0.3-2.5 phr. Thiuram polysulphides (TMTD) along with Thiourea is used as Vulcanising agent for heat resistant products[23]. Dunn [24]reported that butyl Xanthogen disulphide in conjuction with a dithiocarbamate may be used to vulcanise latex film in the absence of sulphur. It has also been reported that organic peroxide and hydroperoxide may be used to vulcanise in latex films[21].

I.4.3. Accelerators

Accelerators are chemicals used in the latex compound to reduce the vulcanisation time and also to increase the technological properties of the vulcanised product. Their dosages vary from 0.5 to 3 phr depending on whether the vulcanisation system is high sulphur or low sulphur. Generally fast accelerators are used in latex technology because the vulcanisation temperatures are relatively low. The important classes used in latex compounding are the metallic and amine dialkyl dithiocarbamates[21]. The thiazoles and to a lesser extent, thiurams are of importance as secondary accelerators in conjunction with dithiocarbamates. Limited use has also been made of ' Xanthates" for room temperature vulcanisation of latex.

1.4.3a)Dithiocarbamates [21]

The salts of the dialkyl dithiocarbonic acid have the generic structure as shown below.

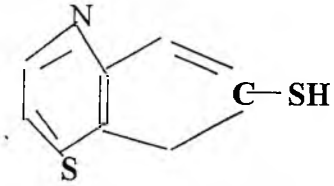


R - Alkyl or Aryl group

M- Metal

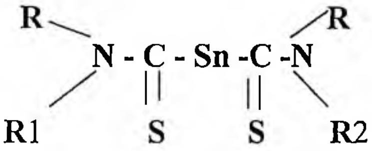
Although a considerable range of accelerators are available under this, zinc diethyl dithio carbamate (ZDC) and zinc dibutyl dithio carbamate (ZDBC) are most widely used. They are active in latex mixes in the absence of zinc oxide and activate thiazole accelerators[24].

I.4.3b. Thiozoles



Thiozoles are insufficiently active to be used on their own for latex work, but they function as secondary accelerators for the dithiocarbmate giving vulcanizate of high modules. The most common thiozole in latex compound is zinc salt of 2-mercaptobenzothiozole (ZMBT).

I.4.3c. Thiuram disulphide



As a class thiurams are insufficiently active to accelerate satisfactorily in latex compounding . The most commonly used thiuram in latex compounding as ultra accelerator and vulcanising agent. is tetra methyl thiuram disulphide(TMTD)[21].

I.4.4. Activators

Zinc oxide is used as activator in sulphur vulcanisation. It boosts up the cure time and also imparts additional heat resistance to latex products. Its dosage is 0.25 ~~-.5~~ to 0.5 phr for dipped products.

I.4.5. Antioxidants

~~The~~ Antioxidants protect~~s~~ rubber from deterioration by oxygen, heat, light, ozone etc. Styrenated phenol and poly merised 1,2 dihydro 2,2,4 trimethylquinoline are typical antioxidants used in latex compounds. Phenolic derivatives,are not much effective,but they have the advantage of non discolouration. BHT,Styrenated phenol and polymerised 1,2- dihydro 2,2,4-trimethyl quinoline ~~is~~ in small dosages (0.25 phr) are typical antioxidants used in latex products.

I.4.6. Fillers and pigments

Fillers are added to latex compound to modify the mechanical properties, and to cheapen the product. Pigments are used to colour the products. Usually used fillers are calcium carbonate,barium sulphate,Titanium dioxide,Chinaclay, silica etc. It is seen that no effect analogues to the reinforcement of dry rubber by fillers is observed when the same fillers are added to ~~the~~ latex.

I.4.7. Softeners

These are used to reduce the modulus of the product. One example is mineral oil which is used in the manufacture of balloons.

I.5. Preparation of latex compound[18]

Preparation of latex compound involves mixing of concentrated natural rubber latex with solutions/dispersions/emulsion of different compounding ingredients. High Ammonia or Low ammonia preserved lattices can be used for compounding. In the case of HA type of latex, for mixes containing higher amounts of Zinc oxide, deammoniation is done prior to compounding to avoid Zinc oxide thickening.

After each addition of chemical dispersion to latex, the compound is stirred slowly but thoroughly to get even distribution of the chemical in the latex. It is important to avoid contact between the stirrer and the container since latex may get coagulated by friction.

After the addition of all the compounding ingredients, the compound is allowed to mature for about 24-28 hrs and used for the manufacture of different latex products.

I.6. Prevulcanisation

There are three principal ways in which natural rubber latex can be prevulcanised.They are:[25]-

1) By allowing the latex particles to react with sulphur and one or more organic vulcanization accelerators,and possibly also with an inorganic vulcanisation activator.
2) By heating the latex with substances such as organic peroxides and hydroperoxides and possibly also with activator for those compounds.

3) By exposing the latex to high-energy radiation in the form of electron or electromagnetic waves.

Of these three ways of effecting latex prevulcanisation sulphur-prevulcanisation is by far the most important industrially. Almost all the prevulcanised natural rubber latex produced at present is by this method.

I.6.1. Sulphur-prevulcanization of Natural Rubber Latex[26]

Sulphur-prevulcanised natural rubber latex is invariably prepared by allowing the rubber molecules in the particles to react with sulphur under the influence of one or more organic accelerators, and possibility of an inorganic vulcanisation activator as well. These reagents are present in the aqueous phase of the latex.

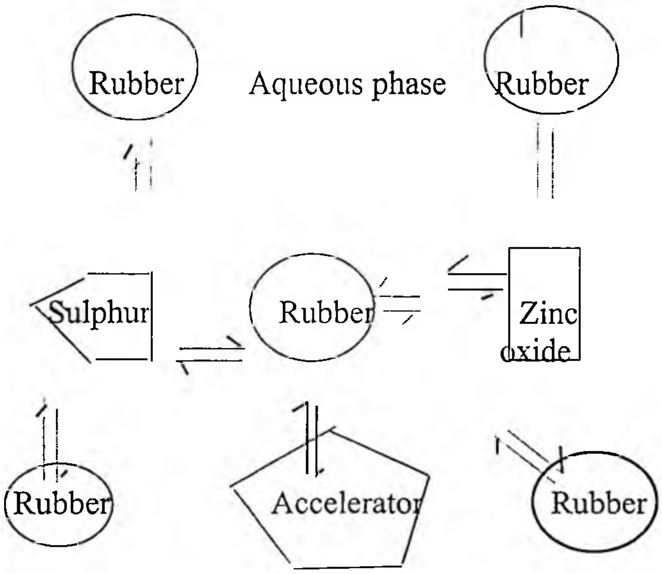
The chemistry of latex prevulcanisation has recently been reported. They explained the occurrence of prevulcanisation on the basis that both the accelerator & sulphur dissolve in the aqueous serum of latex before migration into the rubber phase and crosslink it.When the sulphur and accelerator reach the surface there are two possibilities, first the diffusion of these reactants into the rubber and then crosslinking.It`s also possible that crosslinking can take place faster than diffusion. In this case the core portion will not be crosslinked. If the latex particle is homogeneously crosslinked, the particle will coalesce well and form a film with optimal physical properties.

I.6.2. Kinetics and mechanism of sulphur-prevulcanisation of Natural Rubber Latex

We consider how the matter of the mechanism by which the sulphur prevulcanization of natural rubber occurs, together with the related matter of the kinetics of certain process which occur during the sulphur prevulcanization.The structure of the films dried from sulphur-prevulcanised natur~~e~~al rubber latex is considered in a subsequent section.The kinetics of the various processes which occur during sulphur-prevulcanisation are of interest not only in their own right but also because any satisfactory theory of the reaction mechanism must be consistant with such fact as have seen established in respect of kinetics [27,28].

Before proceeding to discuss the kinetics and mechanism of the sulphur-prevulcanization reaction, it is desirable to form a clear picture of the reaction system. The initial state of the reaction is illustrated schematically. The vulcanising ingredients are dispersed as sparingly-soluble particles in the aqueous phase of the latex, together with the rubber particles. It seems likely that the vulcanizing ingredients become absorbed into the rubber particles via the aqueous phase,and not by direct contact between the rubber particles and those of vulcanising ingredients. As the prevulcanization reaction proceeds it appears that the sulphur and organic accelerator become converted to form which do not cause opacity in films deposited from the latex. The ingredients have become almost entirely absorbed within the rubber particles in form which are rubber soluble[29].

In addition to consistency with the observed kinetics of the reaction ,the more obvious requirements which any satisfactory theory of the mechanism of sulphur-prevulcaniziation reaction must fulfil are as follows.



1) It must be consistent with reaction mechanisms which are generally accepted for the vulcanization of solid natural rubber using sulphur and organic vulcanization accelerators. This requirement implies that the sequence of reactions which is postulated to occur within the rubber particles must be of a similar nature to that which is believed to bring about sulphur-vulcanisation in dry natural rubber.

2) It must explain the processes by which vulcanising agents which are initially confined entirely to the aqueous phase of the latex rapidly become present in rubber particles in a form in which they are able to effect crosslinking of the rubber macromolecules by sulphur bridges.

3) It must explain the facility with which the reaction can occur at relatively low temperatures.

It has to be said at the out set of this discussion that,although considerable progress has been made in recent years in elucidating and understanding the principal features of the sulphur -prevulcanization reaction system,understanding of the distinctive chemistry of the reaction is still almost non-existent. The relative facility of the reaction is still essentially a mystery.

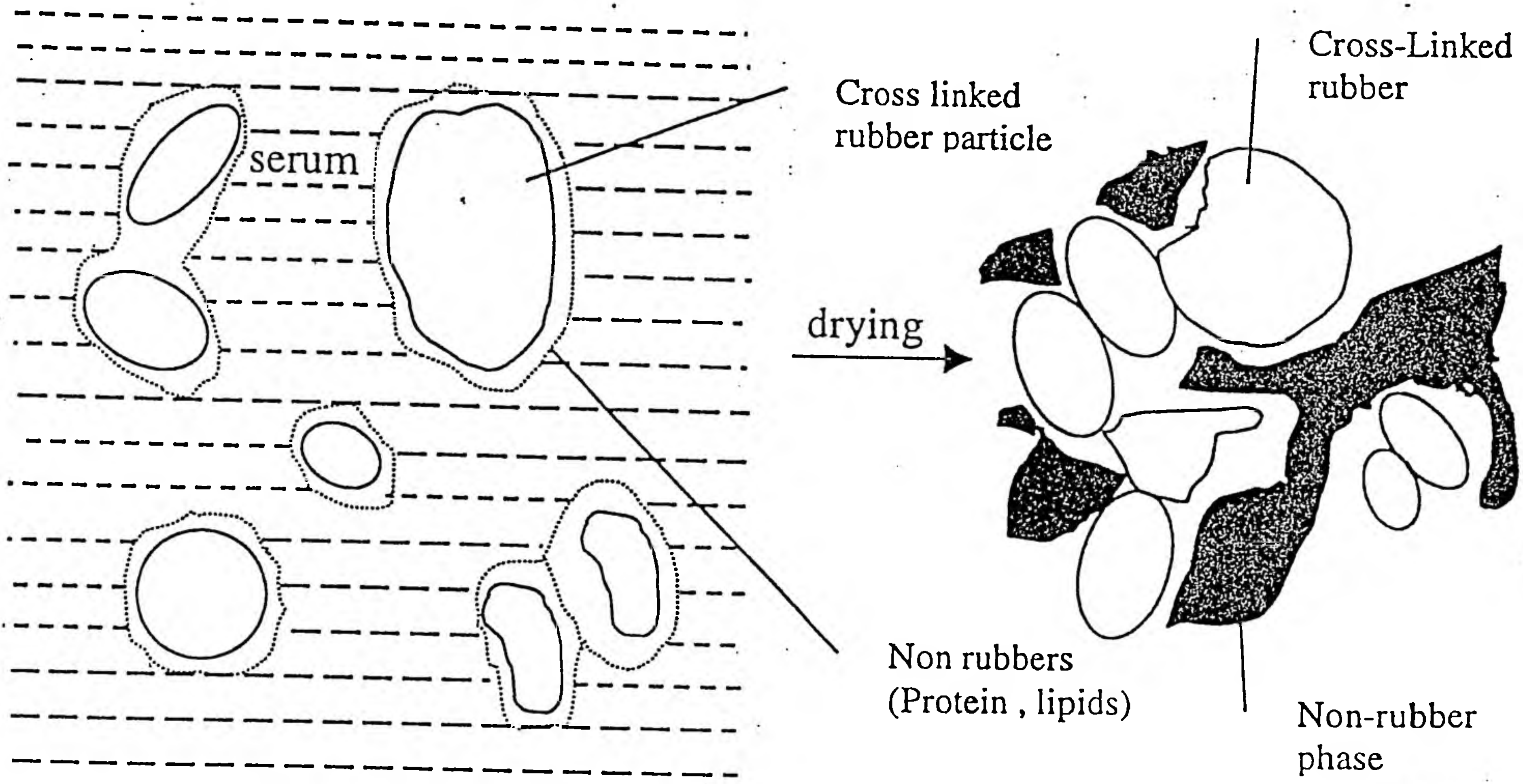
I.6.3. Structure of deposits from prevulcanized latex

Broadly speaking , three theories have been put forward to account for the strength of prevulcanised latex films [29].

1) The strength is attributed to primary valence bonds formed between the molecules of adjacent particles.
2) The film made up of discrete particles of vulcanized rubber cemented together by means of non -rubber constituents derived from the initial latex .
3) The strength of film is due to secondary valence bonds formed between the molecules of adjacent particles.

The last gives the best account of properties of the deposits. Film formation of prevulcanized rubber latex as given by Teik and Poh is shown in Figure. 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 of individual

FORMATION OF PREVULCANIZED NR LATEX FILM



rubber molecules.If the particle is 1μ 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 vulcanisation 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 net work. 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 prevulcanised 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 unvulcanised rubber,it being generally agreed that the coherence of unvulcanised 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 cross links. 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 strain curve can be explained in a convincing manner. The initial flat region of low modules is due to the molecules in the region of of overlap moving independently of one another, so that the behaviour is similar to that of unvulcanised rubber. The increasing stiffness observed after some 500 % extension is considered to be due to the increasing lack of independence of these molecules. Thus the ultimate tensile strength of a prevulcanised 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 valance 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.. 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 vulcanised latex and that, the strength determining bonds are predominantly of the vanderWaals type. Furthermore, the process of sulphur vulcanisation enhances significantly the polarity of the polymer which is contained within a vulcanised latex. This enhancement of polarity is an important factor in determining the strength of films deposited from sulphur vulcanised natural rubber latex.

I.6.4. Other methods of prevulcanisation

Various other curatives were investigated in connection with the vulcanisation of natural rubber latex. Philpott [31]discovered that prevulcanised latex can be prepared from compounds containing a sulphur donor such as tetra methyl thiuram disulphide accelerated with a nucleophile such as thiourea.

The crosslinking of latex by free radicals generated from peroxide [32,33] and hydroperoxide [34,35] 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 ionising radiations. Natural rubber latex when irradiated with gamma rays from a Co^{60} source,will become crosslinked and ~~from a~~ form prevulcanised latex. The degree of crosslinking relates to the dosage of radiation and the process may be enhanced by the use of sensitisers such as chloroform,carbon tetrachloride or monofunctional monomers. The cross links in irradiated latex are probably carbon- carbon type similar to those in peroxide cures. The attraction of radiation prevulcanised 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.

I.6.5. Advantages and disadvantages

Prevulcanised latex is a convenient form of material for the latex goods manufacturing industry especially the dipped goods industry. The latex doesnot require compounding and vulcanisation by the product manufacturer. It is especially suitable for products made by dipping because of the convenience of vulcanising 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 combing, carpet backing and cast rubber products. Better quality control can be achieved by the use of prevulcanised latex in product manufacture. Other advantages are shorter drying time and products of high clarity,particularly if prevulcanised latex is clarified before use.

Prevulcanised latex does not find application in latx foam manufacture mainly on account of its poor wet gel strength.(films prepared from prevulcanised latex exhibit lower tensile strength.) Films prepared from prevulcanised latex exhibit lower tensile strength,modulus and elongation at break as compared with postvulcanised films. Tear strength of prevulcanised latex films tends to be inferior to those of postvulcanised films,which restricts the application of prevulcanised latex to products of fairly thick wall section. When immersed in solvents such as benzene or carbontetrachloride,deposits from prevulcanised latex swell considerably to give gels which are mechanically rather weak. Prevulcanised latex films exhibit also inferior resistance to oils and greases. Thus a prevulcanised 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 prevulcanised latex are more readily damaged by oil and grease than are those which are produced by postvulcanisation.

I.6.6. Scope of the present work

Sulphur prevulcanised natural rubber latex is an Industrially important chemicaly modified form of latex which on drying gives vulcanised films of high physical properties. Production of this latex involves heating of 60 % centrifuged natural rubber latex with various compounding ingredients such as stabilizers, sulphur, accelerators,and activators until the required degree of crosslinking is obtained. It finds applications in many latex products such as dipped goods, latex backed carpets and coatings.

The chemical and physical properties of sulphur prevulcanised natural rubber latex may undergo changes during the storage of latex, due to the presence of surface active agents and residual vulcanising ingredients. A knowledge on the storage characterstics of sulphur prevulcanised latex is essential for the manufacture of latex product with consistent quality.

A perusal of literature shows that no much systematic investigation has been carried out on the effect of storage on the colloidal stability and physical properties of prevulcanised latex. N.M.Claramma[48] , Merril R.W.T[42], A.D.T. Gorton&T.D. Pendle[18] have studied the physical properties of prevulcanised latex on storage.

In this project work it is proposed to study the effect of storage on the colloidal stablity and physical properties of a typical sulphur pre vulcanised latex prepeared by giving different degree of vulcanisation. The following factors have been investigated.

I.Studies on colloidal stability of prevulcanised latex during storage

a) Mechanical Stability Time
b) Viscosity

II. Studies on crosslink density.

a) Swell Index
b) Chloroform number

III. Studies on Physical properties

CHAPTER 2

EXPERIMENTAL

EXPERIMENTAL

2.1. Raw Materials

2.1.1. Centrifuged Natural Rubber Latex

High Ammonia (HA) centrifuged natural rubber latex conforming to specifications (BIS-5430-1981) given in Table2.1 was used for the production of prevulcanized latex.

Table2-1
Properties of centrifuged Natural Rubber Latex used for the production of prevulcanized latex

Properties	Value	Requirements (BIS 5430-1981)	Test methods IS 9316.1987
Dry Rubber content(%)	60	60[a]	IS 3708(part 1) 1985
Non Rubber Solids (%)	1.5	2[b]	IS 9316 (part4) 1988
Sludge content by mass (%)	0.05	0.1[b]	IS 3708 (part2)1985
Ammonia content by mass(%)	0.8	0.6[a]	IS 3708 (part4) 1985
Potassium hydroxide number	0.5	1[b]	IS 3708 (part5) 1985
Mechanical stability time(sec)	1000	475[a]	IS 3708 (part6) 1985
Volatile fatty acid number	0.02	0.15[b]	IS 3708 (part7) 1986
Coagulam content (%) by mass	0.03	0.05[b]	IS 9316 (part3).1987
Copper content (ppm)	1	8[b]	IS 9316 (part8) 1987
Manganese content (ppm)	Traces	8[b]	IS 9316 (part9) 1987

[a] - minimum [b] – maximum

2.1.2. Zinc diethyldithiocarbomate (ZDC)

An ultra accelerator manufactured by M/S R.T.Vanderbuilt Company Inc, USA

2.1.3. Sulphur (Rhombic type)

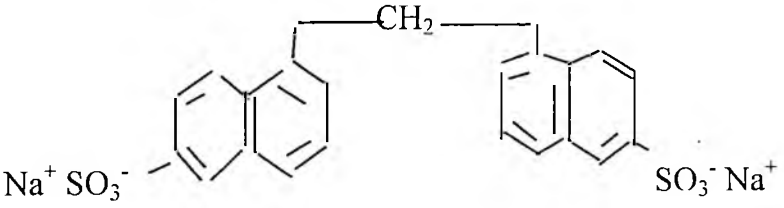
Industrial grade obtained from commercial source.

2.1.4. Zinc Oxide

Industrial grade (whiteseal) obtained from commercial source

2.1.5. Dispersol F

Dispersing agent manufactured by M/s ICI Ltd. Calcutta.Chemical name is sodium naphthalene formaldehyde sulphonate, also described as sodium methyline bis-(naphthalene sulphonate)



2.2. Preparation of Dispersions

Fifty percent dispersion of sulphur, zinc oxide, and zinc diethyldithiocarbomate were prepared separately by grinding in a ball mill using Dispersol F as the dispersing agent. The recipes used for making dispersions are given in Table 2-2.

Table 2.2 Formulation of dispersions

A. 50% Sulphur Dispersion

Ingredients	Parts by Weight	
Sulphur	100	
Dispersol F	3	
Water	97	Ball milled for 72h

B. 50% ZDC Dispersion

ZDC	100	
Dispersol F	2	
Water	98	Ball milled for48h

C 50% ZnO Dispersion

ZnO	100	
Dispersol F	2	
Water	98	Ball milled for 48h

2.3 Equipments Used

2.3.1 Prevulcanizer

It is a Liquid bath known as Insref Ultra Cryostat Circulator supplied by M/s Inlab Instruments Cochin. Fig 2-4-1 shows the photograph of Prevulcanizing Machine.

2.3.2 Brookefieid Viscometer

Brookefield Viscometer LVT Model supplied by M/s Brookefield Engineering Laboratories, Inc, Strongton MA 02072 USA.

2.3.3 Universal Tensile Tester

UTM model 4411 manufactured by M/s Instron England. was used for tensile testing.

2.3.4 Mechanical Stability Apparatus

Supplied by M/s Klaxon Signals, Birmingham,England.

2.3.5 pH meter

Digital pH meter 335 suplied by M/s Systronics,India.

2. 4 Test Methods

2. 4.1 Properties of centrifuged latex - The properties of centrifuged latex as given in Table 2.1 were determined as per IS 9316-1987.

2.4.2 Properties of prevulcanised latex

Chloroform Test [36]

This is probably the most rapid procedure for determining crosslink density in latex. A sample of the latex is coagulated by mixing with an equal volume of chloroform. After two to three minutes the coagulam is examined and graded. The following gradings are defined:

Number 1. The coagulum is a tacky mass and break in a stringy manner when stretched

Number 2. The coagulam is a weak lump which breaks short when stretched.

Number 3. The coagulam is in the form of non-tacky agglomerates.

Number 4. The coagulum is in the form of small dry crumbs.

2-4-3 Equilibrium Swelling [36]

The equilibrium swelling of a vulcanised rubber in a solvent is dependent on the density of cross links , the nature of the solvent, and the rubber. With a given rubber-solvent system, therefore, the equilibrium swelling value becomes a measure of the crosslink density of the vulcanizate.

Equilibrium swelling values are determined by immersing a thin film of the rubber in the solvent,usually toluene.and measuring the increase in weight, or in linear dimensions, at equilibrium.

Equilibrium swelling ratios are usually calculated in the following manner:

$$\text{Swell index, } Q = \frac{W_2 - W_1}{W_1}$$

Where W_1= Initial weight

and W_2= swollen weight

The variation of 'Q' with crosslink density, for conventionally-cured natural rubber in toluene, may be broadly described as follows:

Unvulcanised rubber, Q = >15

Lightly vulcanised, Q = 7-15

Moderately vulcanised,Q = 5-7

Fully Vulcanised, Q = <5

Advantages of the swelling test are that the results are directly related to crosslink density and are also quite reproducible.

2.4.4 Brookfield Viscosity (ASTM D 2526-229)

Viscosity of the latex was measured using Brookfield Viscometer. which is widely used for the measurement of latex viscosity. It consists of a rotating member,which is usually a cylinder driven by synchronous motor through a beryllium-copper torque spring. The viscous drag on the cylinder cause an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disk is rotating. The torque and therefore, the viscosity is indicated by means of a pointer and scale. The pointer is attached to the cylinder spindle and the scale of the drive spindle above the spring so that both pointer and scale rotate.

To measure the viscosity of the compound, 200ml latex compound was taken and placed it below the viscometer by fitting the spindle No .2 in correct position and placed it in such a position as to dip in the compound up to the cut mark of the spindle. Then allowed the spindle to rotate at a particular speed 60 rpm to obtain a reading. The pointer and scale are clamped tighter and the reading is noted and which is multiplied by a factor , 5 and the results is expressed in cps (mPa.s).

2.4.5 Determination of Tensile Properties

The tensile properties of the film, such as modulus, tensile strength, and elongation at break are tested using tensile tester (Instron model 4411) as per ASTM D3188. The machine consists of a load frame, an electronic control unit and a monitor, load measuring devices is load cell,fixed at the top of the load frame. Below the load cell is a moving -platform driven by a continuously variable speed motor. Grips suitable for the dumbbell specimens are fixed on to the load and the moving platform.

During testing the specimen is subjected to stretching at constant speed. Force and elongation are continuously monitored by the electronic circuit. As soon as the test specimens breaks, test results are displayed in the electronic circuit and printed as a table.

All tests were carried out at ambient temperature (28^0 C) Dumbbell specimens were cut from the dipped film for measuring tensile properties. The velocity of the moving cross head is adjusted to 500mm/ min. The specimen was elongated and the values of tensile strength, elongation at break and modulus were measured.

2.5 Experiments

Prevulcanisation : A base compound was first prepared as per formulation given in table 2.3

✓**Table 2.3 Formulation of Sulphur Prevulcanized NR Latex Compound**

Ingredients	Parts by weight	
	Dry Weight	Wet Weight
60% Centrifuged NR Latex (HA type)	100	167
10% KOH solution	0.25	2.5
10% Potassium Oleate solution	0.075	0.75
50% Sulphur dispersion	1.2	2.4
50% ZDC dispersion	0.8	1.6
50% ZnO dispersion	0.25	0.5

Fine ball-milled dispersion of the vulcanisation ingredients were added into centrifuged latex after the latter had attained the prevulcanisation temperature of 55^{0}C. Prevulcanisation was effected by heating the latex compound at 55°C in a water bath. Constant stirring of the latex was maintained throughout the course of the prevulcanisation. Rapid cooling of prevulcanised latex samples were carried out to arrest further pervulcanisation. Excess ingredients were allowed to settle for overnight and removed by decantation.

To study the effect of prevulcanisation time, samples were collected at different periods at constant temperature.

Sample A	Control-Unvulcanised
Sample B	Prevulcanised at 55^{0}C, 2h
Sample C	Prevulcanised at 55^{0}C, 4h
Sample D	Prevulcanised at 55^{0}C ,6h
Sample E	Prevulcanised at 55^{0}C, 8h
Sample F	Prevulcanised at 55^{0}C ,10h

Prevulcanised lattices were stored at room temperature (30^{0}C) for a peroid of 80 days for studying the storage characteristics. Properties of latices such as Total solids, MST, Brookefield Viscosity, Chloroform number, Swell index. pH and Tensile properties were determined at periods of 0,20,40,60and 80 days and the results are given in Table S1, S2,S3,S4,S5,S6 respectively..

I Studies on Colloidal stability of Prevulcanised Latex during Storage

a) Mechanical Stability Time

A graph is plotted with prevulcanisation time against MST (Fig -1).

The Mechanical Stability Time of prevulcanised latices B,C,D,E, &F at different peroids of storage viz. 0,20,40,60,&80 days are plotted in Fig 2.

b)Viscosity

The Brookfield viscosity of prevulcanised latex B to F were determind at different peroids of storage viz. 0,20,40,60&80 days and the results are plotted in infigure3.

II Studies on crosslink density

The swell index and chloroform number of prevulcanised latex B, C, D, E & F were determined at different periods of storage viz. 0,20,40,60,80 days. The effect of storage on variation of swell index and chloroform number are given in fig 4&5 respectively.

III Studies on Physical properties

A graph plotted with prevulcanisation time against tensile properties in Fig. 6. Variation of tensile strength modulus 700% ~~70%~~ and elongation at break at different periods of storage viz. 0, 20, 40, 60 and 80 are given in Fig. 7,8 and 9 respectively.

CHAPTER 3

RESULTS & DISCUSSION

RESULTS AND DISCUSSION

1 Studies on Colloidal Stability of Prevulcanised Latex during Storage

a) Mechanical Stability Time (MST)

Initial MSTof latices A to F is plotted against vulcanisation time(2-10 hr) in Fig.1. It is seen that as prevulcanisation time increases. the MST decreases, reaches a minimum at 4h and thereafter increases considerably up to 10 hr. . The colloid stability of prevulcanised latex, depends upon many factors, viz. the properties of NR latex, amount of potassium hydroxide and carboxylate soap,added, dosage of other vulcanising ingredients and prevulcanisation conditions such as time and temperature [39,40,41]

The colloidal stability of pre vulcanised latex is determined by two opposing factors. The presence of residual vulcanising ingradients especially ZnO and heating the latex may contribute for reducing the stability of latex due to zinc oxide thickening. Addition of alkalies and carboxylate soaps can increase the stability of latex by increasing the negative charge on the surface of the particles and by surface adsorption respectively. The initial drop in MST may be due to the fact that the former predominates during the initial period of vulcanisation but on prolonged heating the second factor predominates and MST increases. .

The increase in MST as vulcanisation time increases may be due to the fact that the presence of alkalies may accelerate the hydrolysis of proteins and phospho lipids adsorbed on the surface of the rubber particles, there by producing higher fatty acids soap. Similar results have been reported[46] for ammonia preserved centrifuged latex during heating under controlled conditions .

Mechanical stability of prevulcanised latices B,C,D,E &F measured at different periods of storage up to 80 days is given in figure2. It is seen that the MST of all the latices increase during storage for the period being studied. The increase in MST of prevulcanised latex during storage for 80 days may be due to some changes in the chemical constituents of the latex [39,41]. Hydrolysis of protein adsorbed on the surface of the rubber particles may continue leading to the formation of polypeptides and amino acids. Hydrolysis of lipids may lead to the formation of various substances such as glycerol,,long chain carboxylate anion, phosphate anion, organic bases etc. The increase in MST is the lowest for ~~the~~ latex B but it gradually increases for ~~the~~ latices from B to F. This shows that the changes in MST of prevulcanised latex during storage depend upon the extent of prevulcanisation. When the extent of prevulcanisation is low the amount of residual vulcanising ingredients may be higher. As vulcanisation time increaes more and more vulcanising ingredients might have been consumed and the amount of residual ingredients is reduced. . Lower increase in MST for latex B may be due to the presence of higher amount of vulcanising ingredients.

b) Effect of storage on Viscosity

Effect of storage for a period of 80 days on viscosity of prevulcanised latex is plotted in fig 3. It is seen that viscosity of latex B is almost constant at 50 mPa.s but for other latices C, D, E, &F, the viscosity slightly decreases during storage. This behaviour also supports the higher colloidal stability of prevulcanised latex [38] achieved during storage as discussed above.

II Studies on crosslinkdensity

a) Swell Index

Figure 4 depicts the effect of storage on swell index of pre vulcanised latex films.As the vulcanisation time increases swell index decreases . During storage , the swell index of latices B,C,D &E decreases and latex F remains almost constant .It shows that the vulcanisation is almost completed at 10 h and some extent of vulcanisation take place during storage for latices B,C,D&E.

b) Chloroform number

Figure 5 shows the effect of storage on Chloroform number. As the vulcanisation time increases chloroform number also increases . During storage of 80 days the chloroform number of latices B,C,D &E increases slightly and for latex F remains almost constant. It shows that the vulcanisation is completed at 10h and some extent of vulcanisation takes place during storage for latices B,C,D&E.

III Studies on Physical properties

In figure 6, the effect of variation of vulcanisation time on tensile properties is depicted. As vulcanisation time increases tensile strength and modulus increases and elongation at break decreases . Moderately higher tensile strength of 28.2 MPa is obtained even at prevulcanisation time of 2 h. Modulus increases from 6.456 to 9.488 [47].

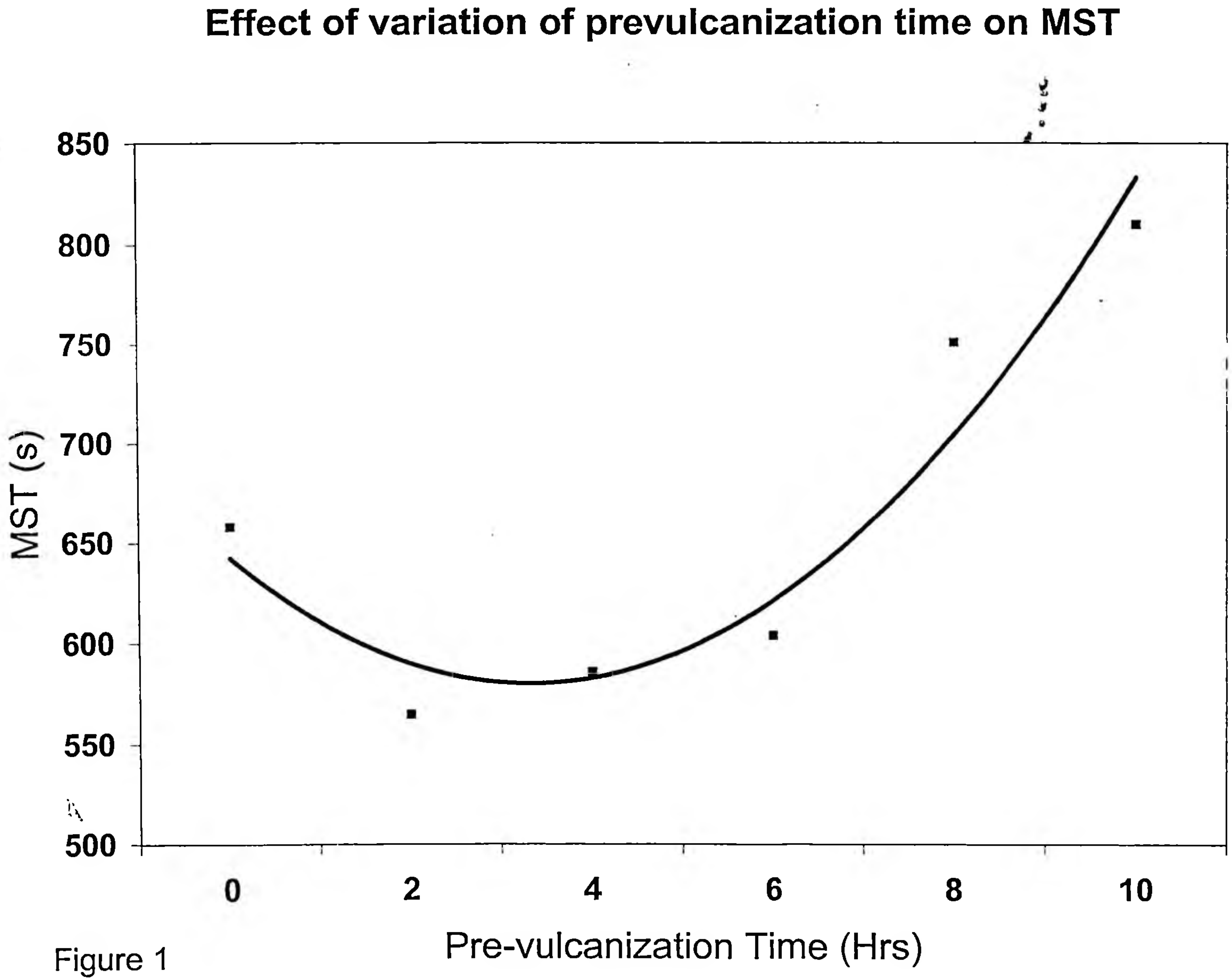
In figure 7 it is shown that as storage time increases tensile strength increase for latices B, C, D and E up to 20 days and thereafter decreases. But for latex F, the tensile strength decreases from 29.7 to 19.1.

The increase in tensile strength for the latices B, C ,D and E may be due to the increase in cross linking during storage of pre vulcanised latex. The decrease of tensile strength with increasing storage time may a consequence of decreasing ability of latex particles to coalesce and integrate fully as the concentration of the crosslinks in the particles increases.[42,44] Merril has reported that on prevulcanisation of NR latex, the modulus increases with crosslinking on storage and extension at break decreases somewhat on the storage of prevulcanised latex.[42,44] .It has been reported that the tensile strength of the films from prevulcanised natural rubber latex is depended upon the ability of the particles to coaleace and integrate when the film dries as well as upon the concentration of the crosslink in the rubber[38].

The variation of Modulus 700 % of prevulcanised latex on storage for a period of 80 days is given in figure 8. It is seen that Modulus 700% increases slightly during storage for B,C&D and remains almost constant for E&F.

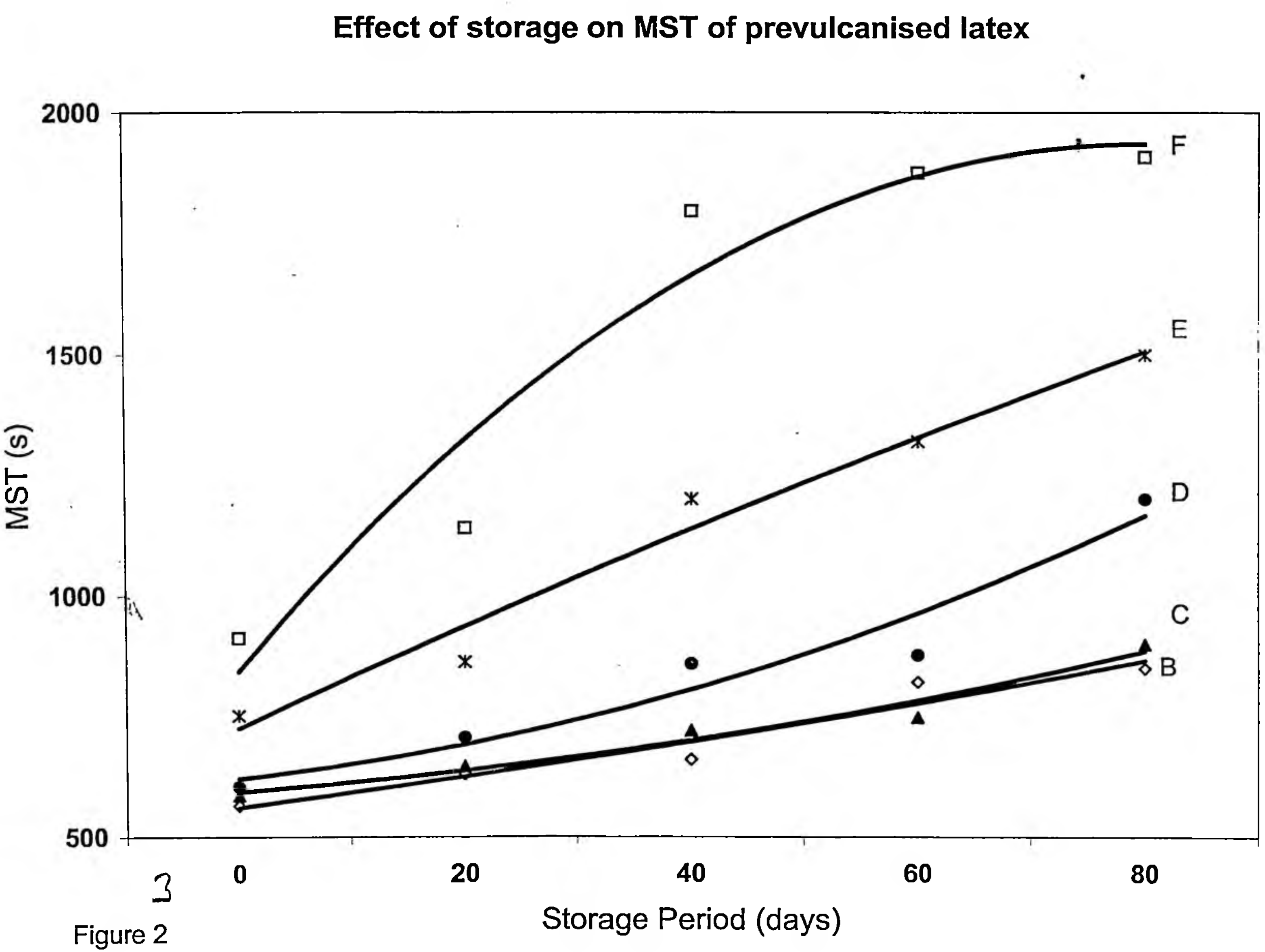
The effect of storage on elongation at break of latex film is given in figure9. It is seen that elongation at break decreases for all the samples but the decrease is higher for samples B & C. The change in EB and modulus may be due to the crosslinking of rubber particles during storage[47]

✓


Effect of variation of prevulcanization time on MST
850
800
750
700
650
600
550
500
MST (s)
0
2
4
6
8
10
Pre-vulcanization Time (Hrs)

✓

Figure 1



Effect of storage on MST of prevulcanised latex

3

Figure 2

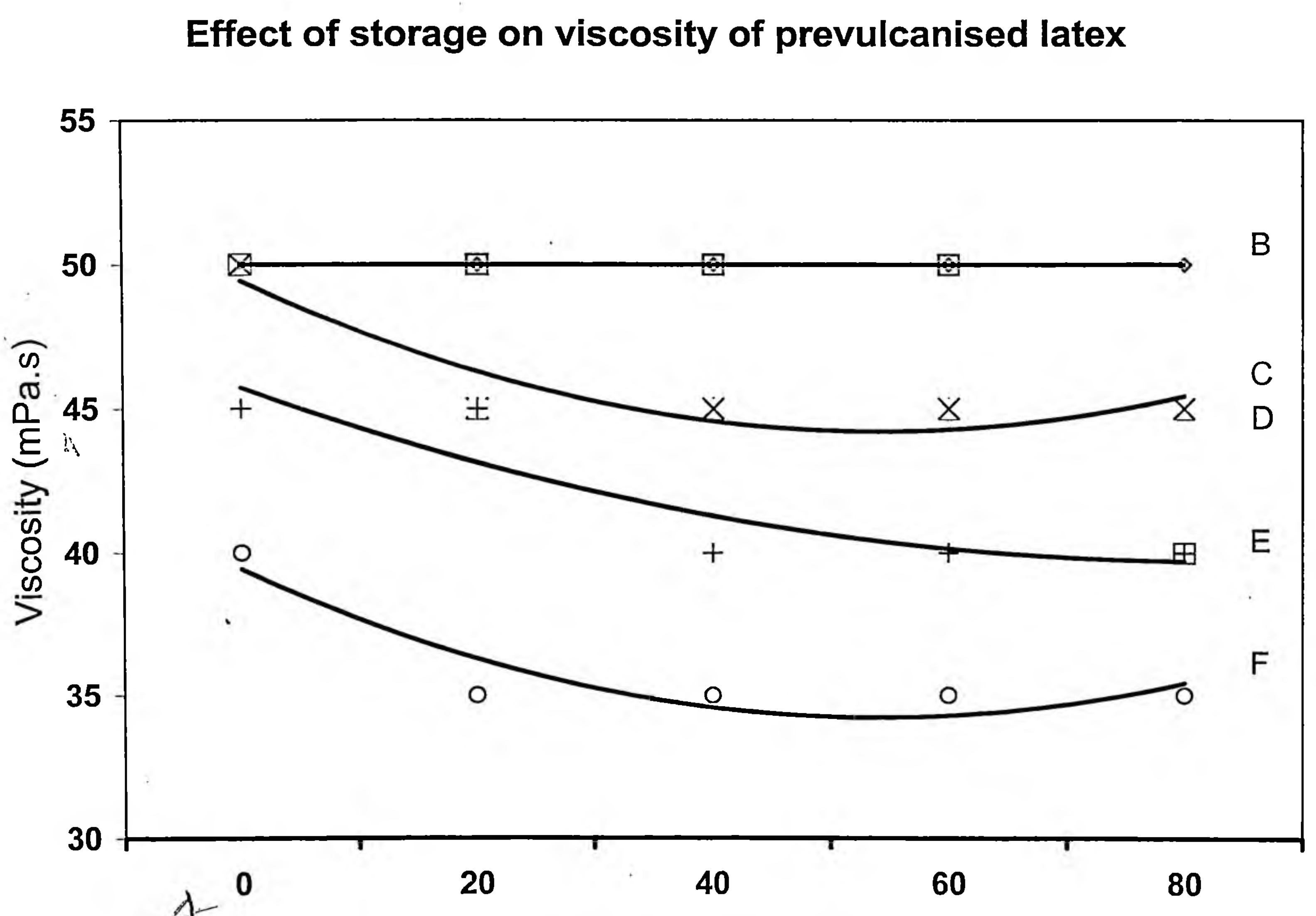

Effect of storage on viscosity of prevulcanised latex
Viscosity (mPa.s)
55
50
45
40
35
30
0
20
40
60
80
Storage Period (days)
B
C
D
E
F

Figure 3

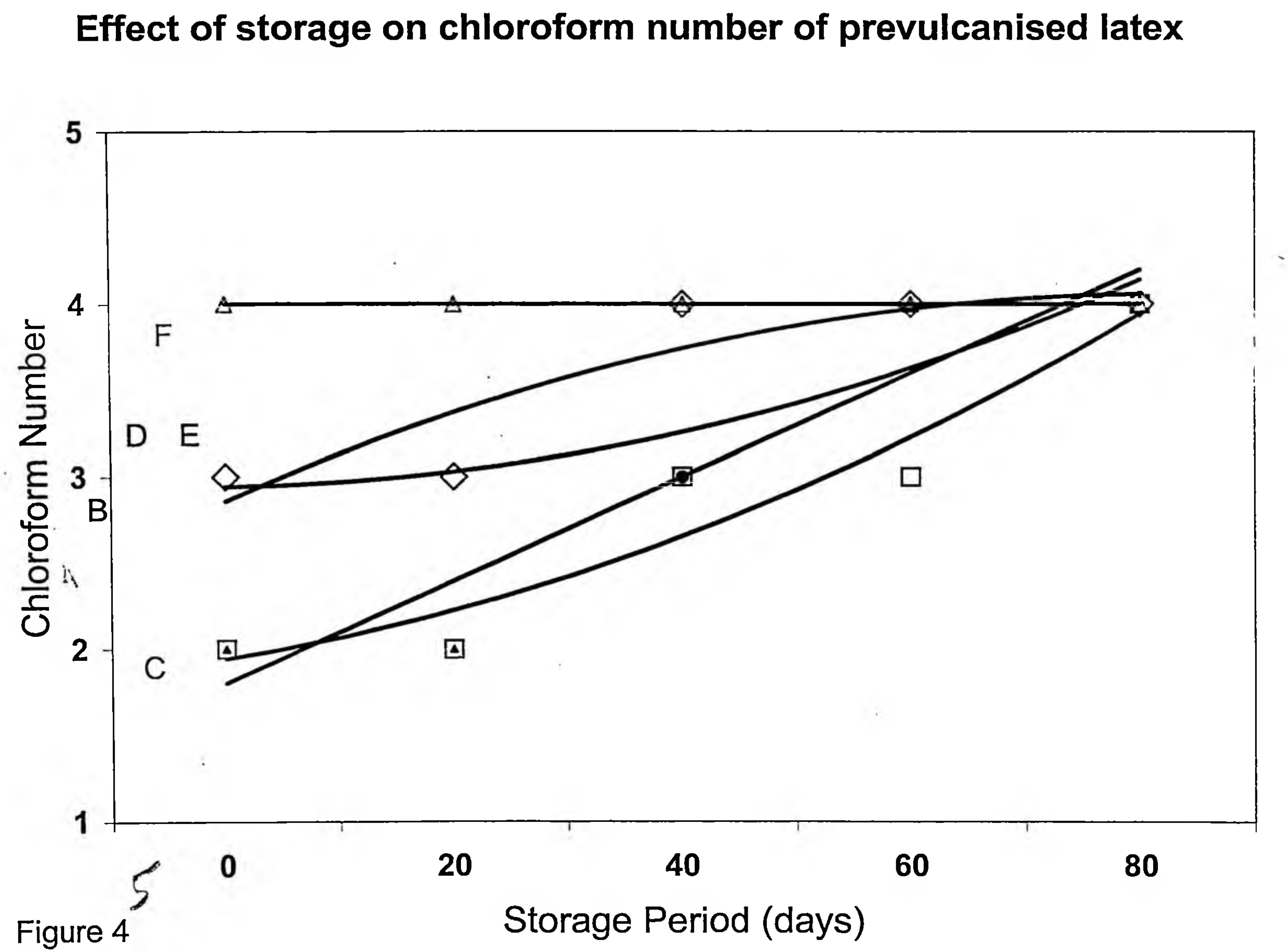

Effect of storage on chloroform number of prevulcanised latex
Chloroform Number
5
4
3
2
1
F
D
E
B
A
C
0
20
40
60
80
Storage Period (days)

Figure 4

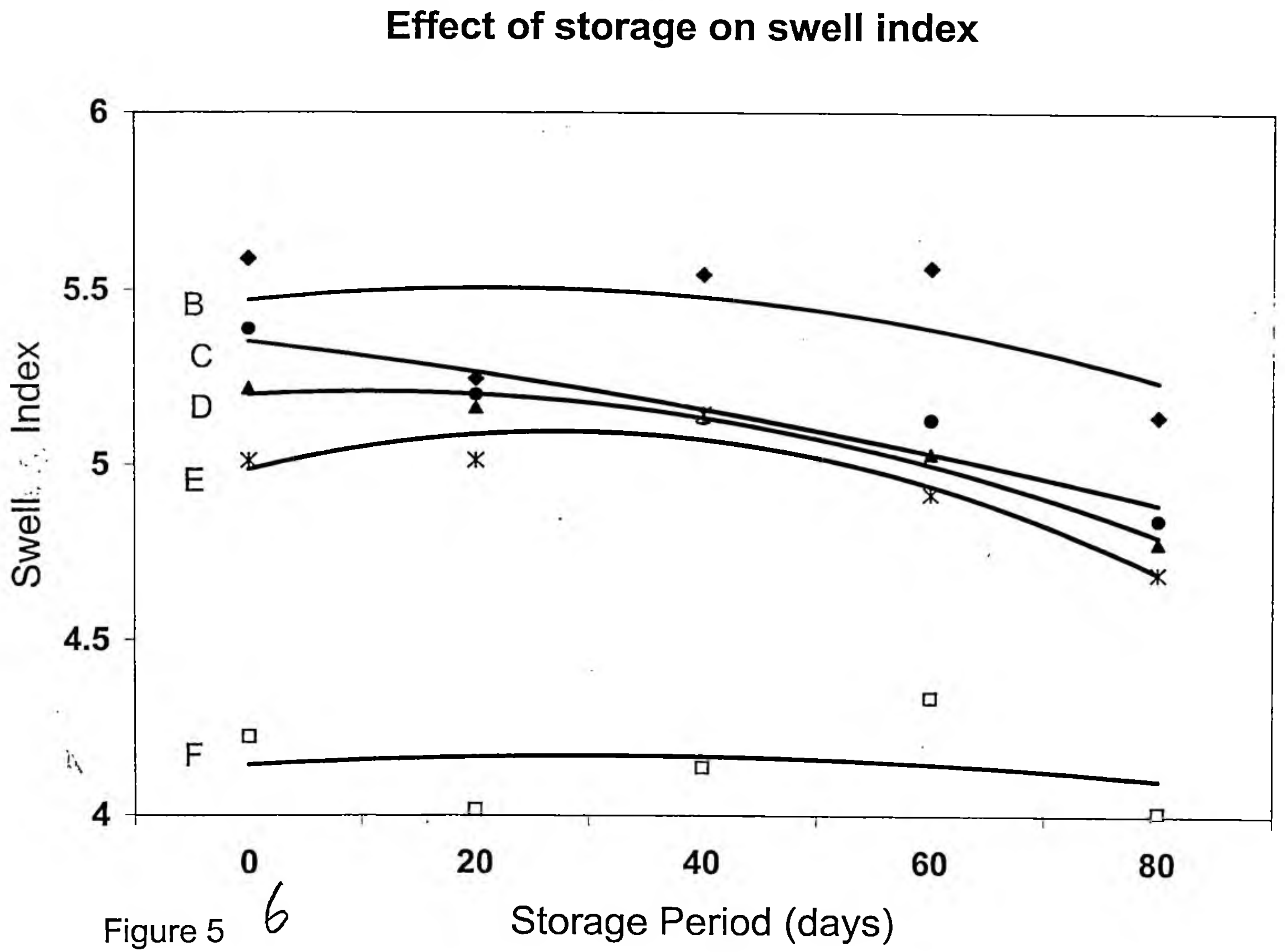

Effect of storage on swell index
Swell Index
6
5.5
5
4.5
4
B
C
D
E
F
0
20
40
60
80
Storage Period (days)

Figure 5 6

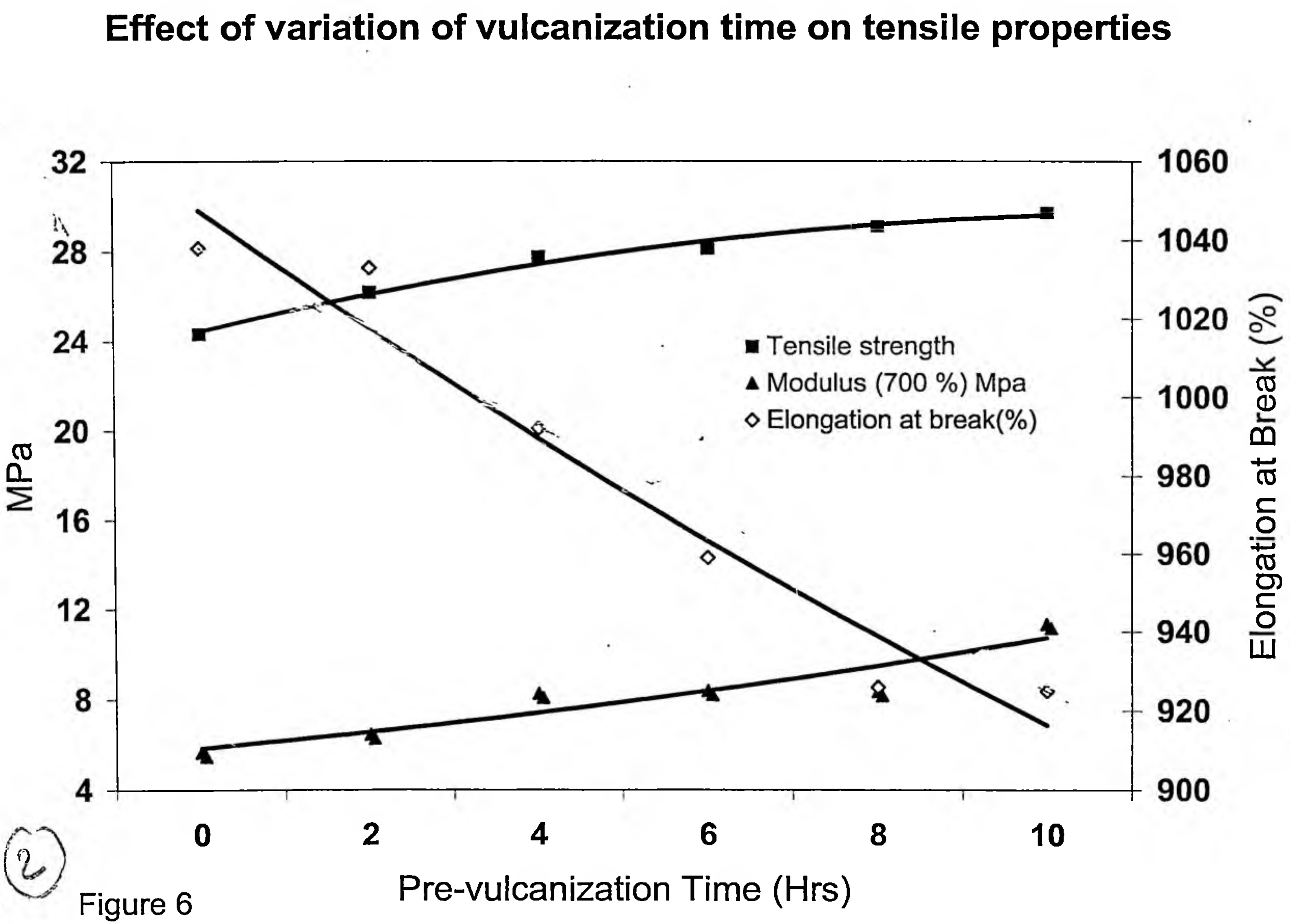


Fig ②

Figure 6

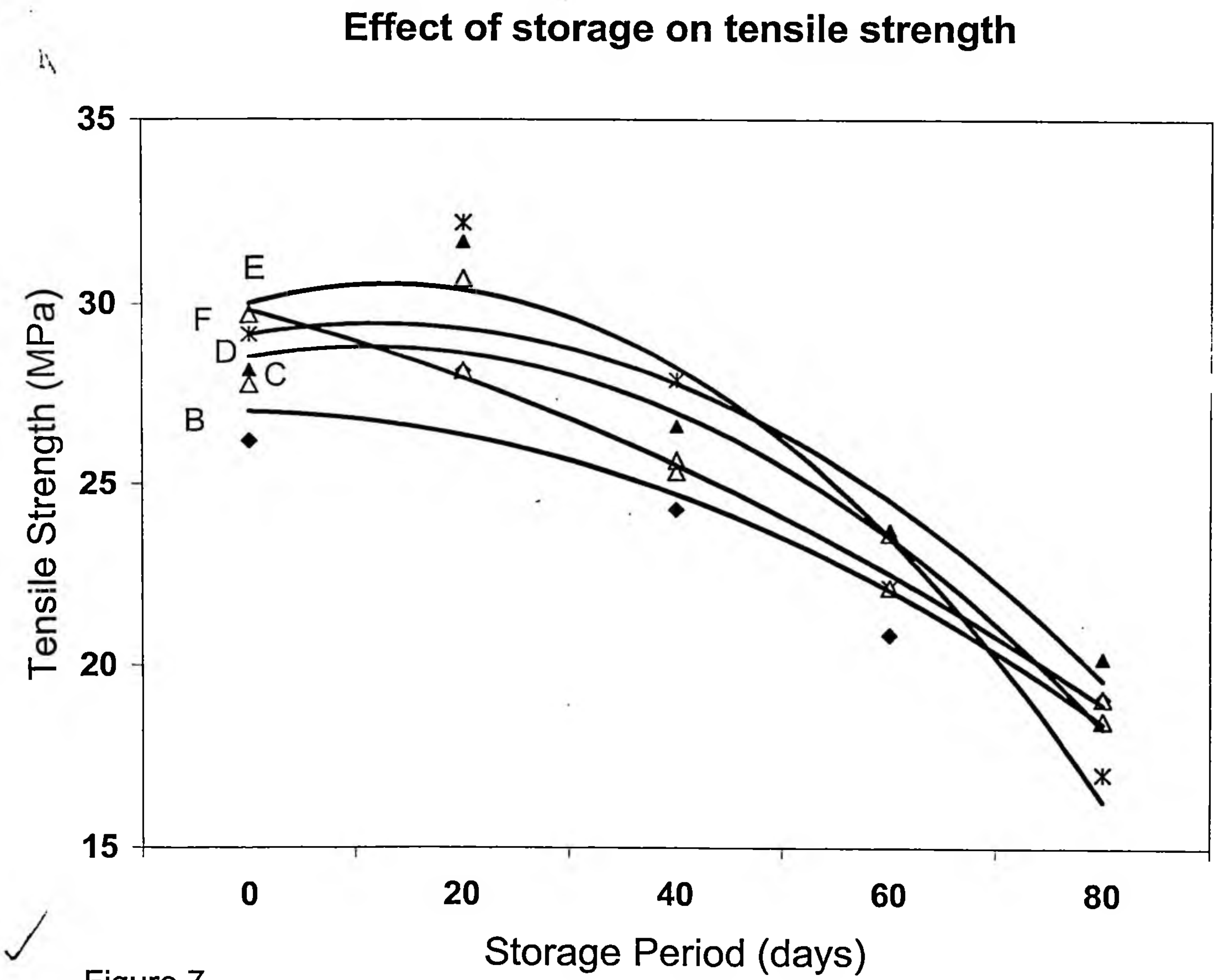

Effect of storage on tensile strength
Tensile Strength (MPa)
35
30
25
20
15
0
20
40
60
80
Storage Period (days)
E
F
D
C
B

Figure 7

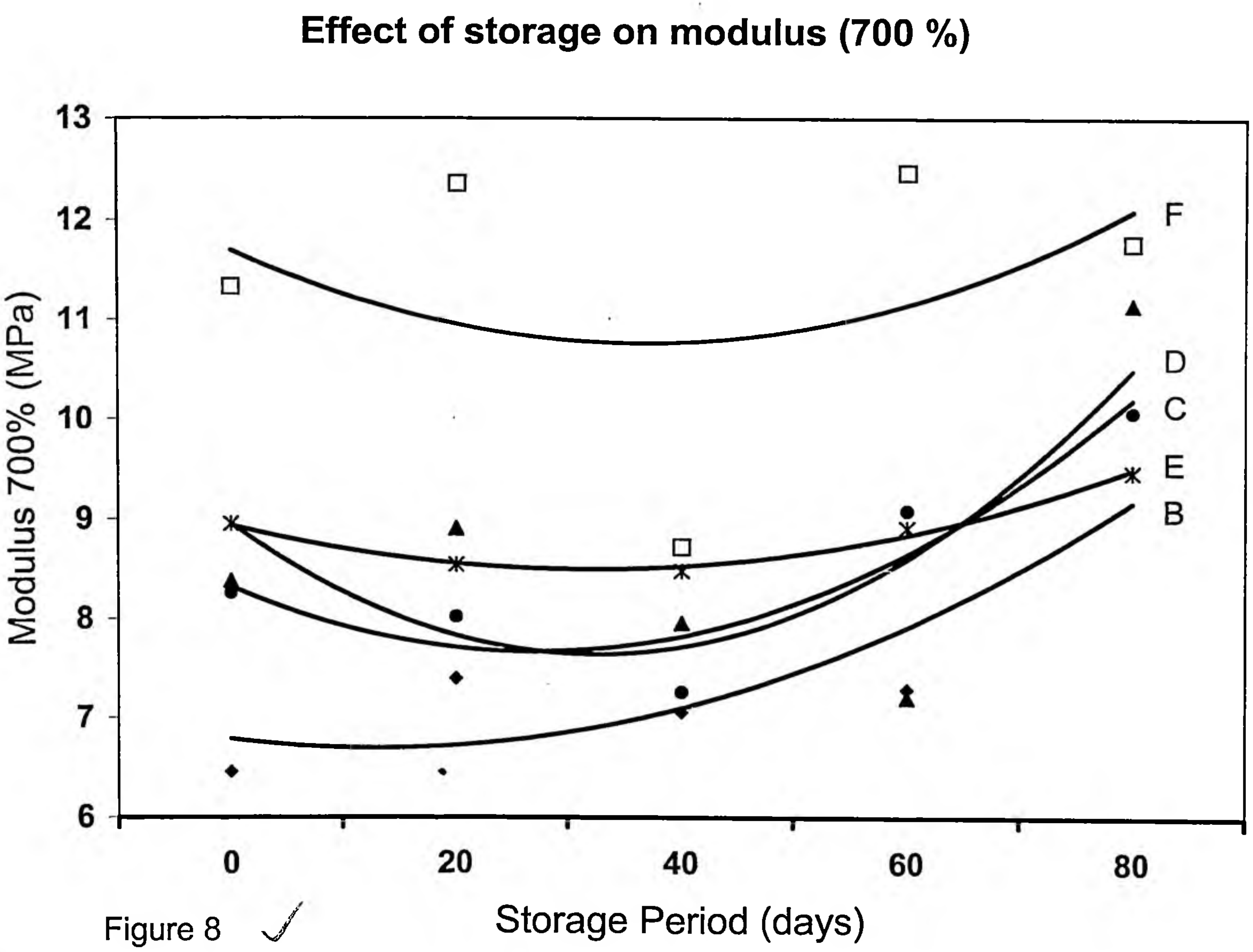

Effect of storage on modulus (700 %)
Modulus 700% (MPa)
13
12
11
10
9
8
7
6
0
20
40
60
80
Storage Period (days)
F
D
C
E
B

Figure 8

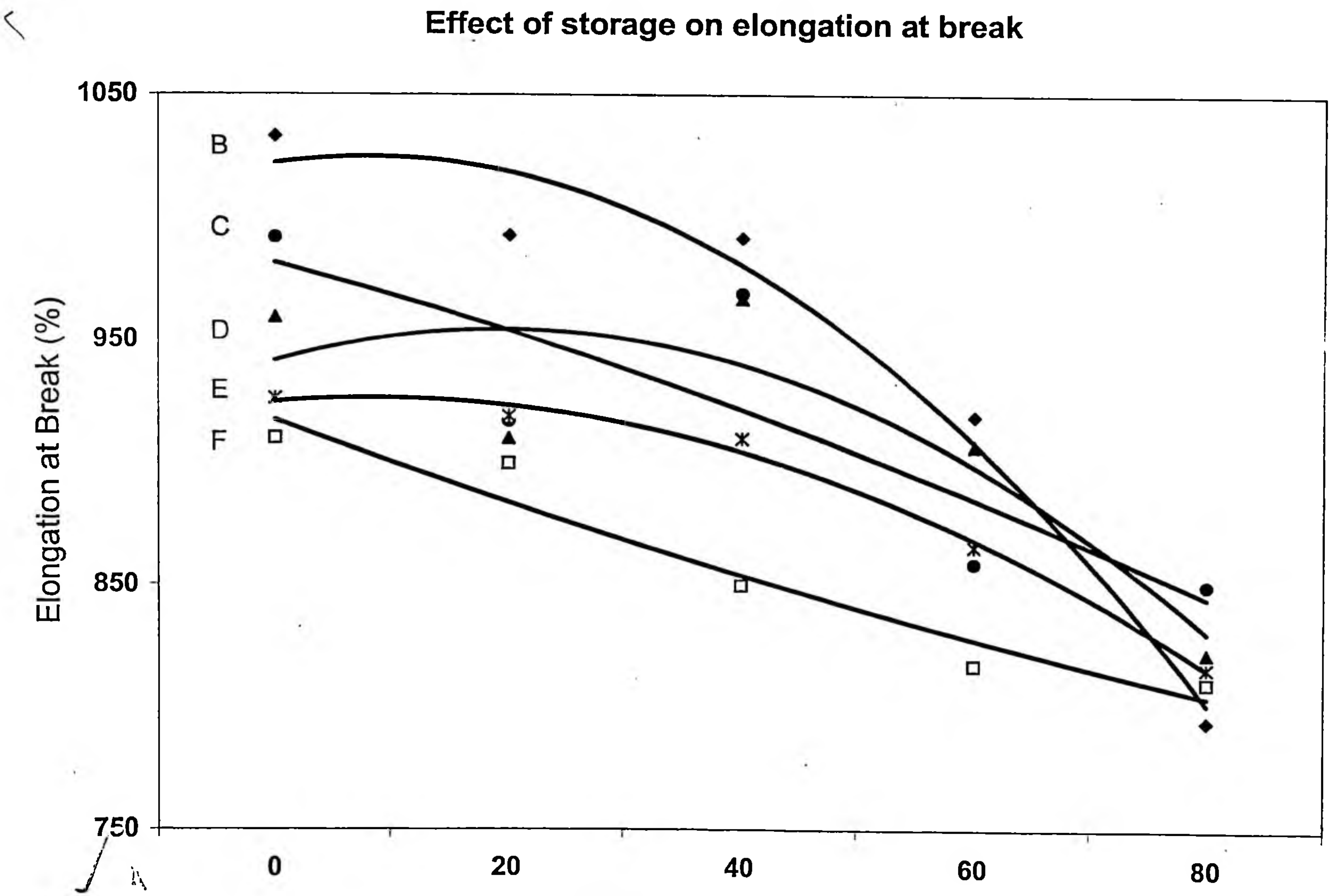

Effect of storage on elongation at break
Elongation at Break (%)
1050
950
850
750
B
C
D
E
F
0
20
40
60
80
Storage Period (days)

Figure 9

TableI a. Effect of variation of vulcanisation time on colloidal stability and Physical Properties of latex compound

Time of heating H/55^{0}C	Chloroform number	Toluene swelling (g/g)	MST (s)	Viscosity (mPa.s)	Tensile properties of casted film 70^{0}C 1Hr oven heating					
					Tensile strength (MPa)	MOD 100% (MPa)	MOD 300% (MPa)	MOD 500% (MPa)	MOD 700% (MPa)	Elongation (%)
0	1	6.71589	658	50	24.320	0.6474	0.0162	2.3316	5.665	1038
2	2	5.58850	565	50	26.175	0.6503	1.0595	2.5960	6.456	1033
4	2	5.38790	586	50	27.750	0.6898	1.0740	2.7330	8.260	992
6	3	5.21750	604	50	28.150	0.7017	1.1070	3.1740	8.380	959
8	3	5.01080	751	45	29.150	0.8189	1.2690	4.0710	8.950	926
10	4	4.22300	912	40	29.700	0.8546	1.3640	4.0870	11.330	925

Table S I. Storage properties of unvulcanised latex compound (Sample A)

Properties	Storage (Days)				
	0	**20**	**40**	**60**	**80**
Total solids content (%)	59	59	59	59	59
pH at 28^0C	10.5	10.5	10.5	10.5	10.5
MST (s)	658	660	720	802	1380
Viscosity (MPa.s)	50	50	50	50	45
Chloroform number	1	1	2	3	4
Swelling ratio	6.7158	6.2562	6.0574	5.7320	5.1380
Tensile strength (MPa)	24.32	25.65	23.12	23.00	18.70
Modulus 100% (MPa)	0.6474	0.7453	0.6510	0.6833	0.6756
Modulus 300% (MPa)	1.0162	1.1000	0.9873	1.0810	1.9200
Modulus 500% (MPa)	2.3316	2.5700	2.0110	2.2080	2.2840
Modulus 700% (MPa)	5.6650	6.0600	5.7560	7.3170	7.5640
Elongation at break (%)	1038	1026	1049	944	882

Table 5

TableS2. Storage properties of Pre-vulcanized latex (Sample B)

Properties	Storage (Days)				
	0	20	40	60	80
Total solids content (%)	59	59	59	59	59
pH at 28^{0}C	10.2	10.2	10.2	10.2	10.2
MST (s)	565	630	660	822	850
mPa.s Viscosity (MPa.s)	50	50	50	50	50
Chloroform number	2	2	3	3	4
Swelling ratio	5.5885	5.2450	5.5444	5.5630	5.1386
Tensile properties Before ageing					
Tensile strength (MPa)	26.17	28.15	24.30	20.84	19.11
Modulus 100% (MPa)	0.6503	0.7674	0.6828	0.7394	0.8252
Modulus 300% (MPa)	1.0162	1.1000	0.9873	1.1770	1.4020
Modulus 500% (MPa)	2.3316	2.5700	2.1100	2.3890	3.7920
Modulus 700% (MPa)	6.456	7.040	7.063	7.293	9.488
Elongation at break (%)	1033	993	992	919	794
Tensile properties After ageing (70^{0}C for 10 days)					
Tensile strength (MPa)	25.25	26.95	23.45	20.05	19.54
Modulus 700% (Mpa)	6.145	6.775	6.905	7.054	8.548
Elongation at break (%)	950	925	900	888	825

Table 7

Table S3. Storage properties of pre-vulcanized latex (Sample C)

Properties	**Storage (Days)**				
	0	**20**	**40**	**60**	**80**
Total solids content (%)	59	59	59	59	59
pH at 28^{0}C	10.2	10.2	10.2	10.2	10.2
MST (s)	586	646	720	748	900
Viscosity (MPa.s)	50	45	45	45	45
Chloroform number	2	2	3	4	4
Swelling ratio	5.3879	5.2010	5.1338	5.1286	4.8440
Tensile properties Before ageing					
Tensile strength (MPa)	27.75	30.70	25.35	23.64	18.51
Modulus 100% (MPa)	0.6898	0.7774	0.7246	0.7694	0.8319
Modulus 300% (MPa)	1.0740	1.2110	1.1460	1.2110	1.4360
Modulus 500% (MPa)	2.733	3.403	2.3510	2.6490	3.9290
Modulus 700% (MPa)	8.2600	8.0270	7.2650	9.0900	10.0700
Elongation at break (%)	992	917	969	859	850
TensileProperties After ageing (70^{0}C 10 days)					
Tensile strength (Mpa)	27.5	28.58	26.45	24.35	19.51
Modulus 700% (Mpa)	9.56	9.41	8.578	9.785	10.50
Elongation at break (%)	950	900	875	850	800

Table 8 Table [illegible]

Table S4. Storage properties of pre-vulcanized latex (Sample D)

Properties	Storage (Days)				
	0	**20**	**40**	**60**	**80**
Total solids content (%)	59	59	59	59	59
pH at 28^0C	10.2	10.2	10.2	10.2	10.2
MST (s)	604	706	760	878	1200
Viscosity (MPa.s)	50	45	45	45	45
Chloroform number	3	3	3	4	4
Swelling ratio	5.2175	5.1640	5.1386	5.0316	4.7800
Tensile properties Before ageing					
Tensile strength (MPa)	28.15	31.70	26.61	21.74	20.21
Modulus 100% (MPa)	0.7017	0.7844	0.7401	0.6191	0.8564
Modulus 300% (MPa)	1.1070	1.2480	1.1600	1.0250	1.4300
Modulus 500% (MPa)	3.1740	3.6480	2.7390	2.2940	3.3210
Modulus 700% (MPa)	8.380	8.912	7.962	7.209	11.15
Elongation at break (%)	959	910	967	907	822
Tensile properties After ageing (70^0C 10 days)					
Tensile strength (Mpa)	27	31.5	25.75	24.74	21.21
Modulus 700% (Mpa)	8.545	9.751	8.75	7.795	12.58
Elongation at break (%)	940	900	890	845	825

Tab # 9

Table S5. Storage properties of pre-vulcanized latex (Sample E)

Properties	**Storage (Days)**				
	0	**20**	**40**	**60**	**80**
Total solids content (%)	59	59	59	59	59
pH at 28^0C	10.2	10.2	10.2	10.2	10.2
MST (s)	751	863	1200	1320	1500
Viscosity (MPa.s)	45	45	40	40	40
Chloroform number	3	3	3	4	4
Swelling ratio	5.0108	5.0133	5.1456	4.9170	4.6900
Tensile properties Before Ageing					
Tensile strength (MPa)	29.15	32.22	27.90	22.42	17.04
Modulus 100% (MPa)	0.8189	0.7884	0.7547	0.7777	0.7922
Modulus 300% (MPa)	1.2690	1.4800	1.2230	1.2580	1.2670
Modulus 500% (MPa)	4.071	3.913	2.806	2.290	3.209
Modulus 700% (MPa)	8.950	8.550	8.488	8.920	9.741
Elongation at break (%)	926	919	900	866	816
Tensile Properties After Ageing (70^0C for 10 days)					
Tensile strength (MPa)	28.58	30.45	28.90	24.5	19.04
Modulus 700% (MPa)	9.25	9.55	9.05	9.35	9.48
Elongation at break (%)	950	915	980	985	800

Table S 6. Storage properties of pre-vulcanized latex (Sample F)

Properties	**Storage (Days)**				
	0	**20**	**40**	**60**	**80**
Total solids content (%)	59	59	59	59	59
pH at 28^0C	10.2	10.2	10.2	10.2	10.2
MST (s)	912	1140	1800	1878	1910
Viscosity (MPa.s)	40	35	35	35	35
Chloroform number	4	4	4	4	4
Swelling ratio	4.2230	4.0062	4.736	4.5361	4.209
Tensile properties Before Ageing					
Tensile strength (MPa)	29.70	28.15	25.66	22.15	19.11
Modulus 100% (MPa)	0.8546	0.9074	0.7747	0.9661	0.8168
Modulus 300% (MPa)	1.3640	1.525	1.348	1.525	1.410
Modulus 500% (MPa)	4.087	5.437	3.322	3.688	3.491
Modulus 700% (MPa)	11.330	12.360	8.729	12.470	11.770
Elongation at break (%)	925	831	889	817	830
Tensile Properties After Ageing (70^0C 10 days)					
Tensile strength (MPa)	28.548	28	24.75	21.75	20.12
Modulus 700% (MPa)	11.21	11.75	9.75	10.95	11.5
Elongation at break (%)	900	875	870	810	810

CHAPTER 4

SUMMARY& CONCLUSION

SUMMARY AND CONCLUSION

Sulphur prevulcanised NR latex was prepared using conventional vulcanisation system by heating at 55^{0}C for different periods namely 2,4,6,8 and 10 h. The changes in colloidal stability and physical properties were evaluated during the course of prevulcanisation.

The latices were stored for a period of 80 days and the changes in colloidal stability and physical properties were monitored at different intervals (0,20,40,60&80) days

During vulcanisation and storage, the MST of the prevulcanised latex increased and viscosity of latex remained almost unchanged.

The degree of crosslinking as measured by chloroform number, swell index and modulus 700% increased slightly for latices B & C during storage. There was no much change in crosslink density for lattices D,E & F.

For samples B, C, D and E, Tensile strength increases during storage for a period of 20 days and then decreases. But for sample F, the tensile strength decreases on storage.

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