STUDIES ON THE PRODUCTION, PROPERTIES AND PROCESSABILITY OF LOW PROTEIN LATEX

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CERTIFICATE

Certified that the thesis entitled ***"Studies on the Production, Properties and Processability of Low Protein Latex",*** being submitted by Mr. M. Sunney Sebastian M.Sc., M.Tech. 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 him under my supervision and guidance.

The results included in this thesis have not been submitted for the award of any other degree or diploma. It is also certified that Mr. M. Sunney Sebastian has fulfilled the necessary requirements for submission of thesis and has passed the qualifying examination.

Kottayam,
08.08.2005

E.V. Thomas.

DECLARATION

I hereby declare that the thesis entitled ***"Studies on the Production, Properties and Processability of Low Protein Latex"*** is the original research work carried out by me under the supervision and guidance of **Dr. E.V. Thomas**, Director (Rtd.), Rubber Board, Kottayam – 9 and no part of this thesis has been presented for any other degree or diploma from any other university or institution.

Kottayam – 9,
08/08/2005.

M. Sunney Sebastian.

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M. Sunney Sebastian.

LIST OF ABBREVIATIONS

NR	Natural rubber
HA	High ammonia
LA	Low ammonia
VFA	Volatile fatty acid
SPP	Sodium penta chlorophenate
ZDC	Zinc diethyl dithiocarbamate
ZMBT	Zinc mercapto benzothiazole
TMTD	Tetramethyl thiuram disulphide
BA	Boric acid
DRC	Dry rubber content
KOH	Potassium hydroxide
TNPP	Tris nonylated phenylphosphite
RVNRL	Radiation vulcanized natural rubber latex
nBA	Normal butyl acrylate
MFA	Monofunctional acrylate
PVME	Polyvinyl methyl ether
PPG	Poly propylene glycol
REF	Rubber elongation factor
kD	kilo Dalton
EP	Extractable protein
SCL	Single centrifuged latex
DCL	Double centrifuged latex
LPL	Low protein latex
ZST	Zinc stability time
MST	Mechnical stability time
EV	Efficient vulcanization
EB	Elongation at break
RVSCL	Radiation vulcanized single centrifuged latex
RVDCL	Radiation vulcanized double centrifuged latex
RVLPL	Radiation vulcanized low protein latex

Abstract of the Thesis

Latex protein allergy is a serious problem faced by users of natural rubber latex products. This is severe in health care workers, who are constantly using latex products like examination gloves, surgical gloves etc. Out of the total proteins only a small fraction is extractable and only these proteins cause allergic reactions in sensitized people. Enzymic deproteinisation of latex and leaching and chlorination of latex products are the common methods used to reduce the severity of the problem.Enzyme deproteinisation is a cubersome process involving high cost and process loss.Physical properties of such films are poor. Leaching is a lengthy process and in leached latex products presence of extractable proteins is observed on further storing. Chlorination causes yellowing of latex products and reduction in tensile properties.

In this context a more simple process of removal of extractable proteins from latex itself was investigated. This thesis reports the application of poly propylene glycol (PPG) to displace extractable proteins from natural latex. PPG is added to 60 % centrifuged natural latex to the extent of 0.2 % m/m, subssequently diluted to 30 % dry rubber content and again concentrated to obtain a low protein latex.

Dilution of concentrated latex and subsequent concentration lead to a total reduction in non - rubber solids in the concentrate, especially proteins and reduction in the ionic concentration in the aqueous phase of the latex. It has been reported that proteins in natural rubber / latex affect its behaviour in the vulcanisation process. Ionic concentration in the aqueous phase of latex influence the stability, viscosity and flow behaviour of natural latex. Hence, a detailed technological evaluation was carried out on this low protein latex.

In this study, low protein latex was compared with single centrifuged latex (the raw material to almost every latex product), double centrifuged latex (because dilution and second concentration of latex is accompanied by protein removal to some extent and reduction in the ionic concentration of the aqueous phase of latex.). Studies were conducted on Sulphur cure in conventional and EV systems under conditions of post - cure and prevulcanisation of latex. Studies were conducted on radiation cure in latex stage. Extractable protein content in vulcanised low protein latex films are observed to be very low. It is observed that this low protein latex is some what slower curing than single centrifuged latex, but faster than double centrifuged latex. Modulus of low protein latex films were slightly low. In general physical properties of vulcanised low protein latex films are only slightly lower than single centrifuged latex. Ageing properties of the low protein latex films were satisfactory. Viscosity and flow behaviour of low protein latex is much better than double centrifuged latex and almost comparable to single centrifuged latex.

On observing that the physical properties and flow behaviour of low protein latex was satisfactory, it was used for the preparation of examination gloves and the gloves were evaluated. It is observed that the properties are conforming to the Indian Standard Specifications.

It is thus observed that PPG treatment of natural latex is a simple process of preparing low protein latex. Extractable protein content in these films are very low.The physical properties of the films are comparable to ordinary centrifuged latex and better than conventionally deprotenized latex films. This latex can be used for the production of examination gloves.

CONTENTS

CHAPTER 1

INTRODUCTION

In the 1980's there was drastic increase in the use of examination gloves due to fear of AIDS. Examination gloves are once used and throw away materials. FDA has reported that during the five year period 1986–1991, use of examination gloves increased 15 fold. However, this drastic growth in the use of examination gloves and other latex products resulted in a new type of allergic reaction due to soluble proteins.

In the early years of glove manufacture, proper leaching was an essential step, to improve the physical properties. As the glove manufacturing industry could not cope up with the drastic increase in demand, leaching was either avoided or it's duration was reduced. During leaching, simultaneous to improvement in physical properties, soluble proteins were also removed.

The prolonged use of gloves by professionals in the medical field and availability of more proteins due to improper leaching aggravated the situation. Common symptoms of protein allergy were formation of weals and flares at the contact site with itching or stinging which usually disappear in about 0.5–2h (contact urticaria) or difficulty in breathing and fall in blood pressure. FDA has reported several casualties because of allergic reactions due to proteins in latex products. Thus latex protein allergy and its prevention or control necessitated detailed investigations.

Natural rubber (NR) is an important industrial raw material. Even though NR was known for many centuries, its potential as a versatile raw material was not fully understood, until the invention of the process of sulphur vulcanization by Charles Goodyear in 1839. Another important finding was that of the reinforcement of natural rubber by carbon black in the early years of the twentieth century. The introduction of organic accelerators and the development of pneumatic tyre were two other important developments.

Originally, rubber products like gloves were produced by dipping process using solutions of rubber in organic solvents, and not using latex, as being practiced now. The wide variability in properties of field latex and its low rubber content were two constraints that affected the advancement of latex technology in the early phase. As it was uneconomic to transport field latex, from tropical countries to Europe and N.America, methods for concentrating natural latex were introduced in the 1920's. The first patent for concentrating latex by creaming process was that of Traube(1). Concentration of field latex by centrifugal machines was developed in the early 1930's. The creaming and centrifugal processes of concentrating latex facilitated considerable blending of latex, so that concentrated latex of consistent quality was available to the industry.

The development of the Dunlop process for the production of latex foam, was a strong accelerating step for the development of latex technology. Even though the consumption of natural rubber as latex is much less than that of the dry forms, considerable progress has now been made in understanding the science and technology of latex and a variety of latex products like different types of gloves, balloons, catheters, teats, soothers, latex foam, elastic thread, adhesives etc. are now available.

CHAPTER 2

SURVEY OF LITERATURE

NATURAL LATEX

Blackley[1] has defined latex as a stable colloidal dispersion of a polymeric substance in an aqueous medium. Even though latex is available from many plant species, that obtained from Hevea brasiliensis alone is of commercial importance. Natural rubber latex is obtained from the rubber tree by the process of tapping. Latex that exudes from the tree is collected. This latex can be either coagulated to recover the solid rubber or preserved for subsequent concentration.

PHYSICAL PROPERTIES OF LATEX

Freshly tapped natural rubber latex is a white opaque fluid of specific gravity between 0.97–0.98 depending on the rubber content. It is almost neutral having pH in the range 6.5–7.0. Surface free energy varies from 40–45mJ m^{-2} (2). The viscosity of field latex is highly variable. Progressive dilution of fresh natural latex with water causes the viscosity to increase, reach a maximum and then suddenly decreases. These changes are attributed to the swelling and bursting of lutoid bodies in latex due to the disturbance of osmotic equilibrium between lutoid bodies and the aqueous serum(3).

COMPOSITION OF *HEVEA* LATEX

Hevea latex is a dispersion of very fine particles of rubber in an aqueous serum. The rubber hydrocarbon is mainly polyisoprene, having an average molecular weight of the order 10^6 (4). The rubber particles contribute about 30–40% of the total weight of latex. Besides rubber and water, fresh latex contains a number of organic substances and inorganic mineral matter. Being a natural product, the composition of latex varies between wide limits. Typical composition of fresh natural rubber latex(2) is given in Table 2.1.

TABLE 2.1

Typical composition of field latex

Constituent	***% (m/m) on whole latex***
Total solids	36
Dry rubber	33
Proteinaceous substances	1 – 1.5
Resinous matter	1 – 2.5
Ash	up to 1
Sugars	1
Water	add 100

Natural rubber latex contains about 1–1.5% m/m proteins. Out of the total protein content, about one half is dissolved in the aqueous phase, one quarter is adsorbed on the surface of rubber particles and the remaining is associated with larger particulate bodies such as lutoids(2).

COLLOIDAL STABILITY OF NATURAL LATEX

The term stability, as applied to a lyophobic colloid usually means the tendency for the system to remain unchanged as a colloidal disperson as time elapses(5). There is usually a thermodynamic tendency for a lyophobic colloid for phase separation, since aggregation and coalescence of the particles are accompanied by a loss of interphase between the two phases, and the interfacial free energy between the two phases is positive. Particle aggregation and coalescence are thermodynamically favoured processes, and these are accompanied by a reduction of the Gibbs interfacial free energy, thus providing thermodynamic motivation for these processes. In the case of a lyophobic colloid such as natural latex, there is a thermodynamic tendency for the particles to aggregate and coalsce and a mechanistic pathway by which these processes can occur. The sol is stable to the extent that other factors are present which prevent the occurrence of particle aggregation and coalescence over long periods of time. Such a stability of lyophobic sol is a consequence of the presence of barriers between the particles, which discourage the close approach of the particles. These barriers arise from the balance between various attractive and repulsive forces, which are operative between two particles as they approach each other closely. Colloidal stability is conferred if the balance between the attractive and repulsive forces is such that two particles are confronted by a potential energy barrier as they approach each other closely. The higher this barrier, the more stable the colloid.

The colloidal stability of natural latex is controlled by five basic forces of interaction between the particles(6). These are electrostatic forces, electromagnetic forces, Born forces, steric interactions and solvation.

PRESERVATION OF LATEX

Hevea latex, on coming out of the tree, gradually thickens and finally coagulates in a few hours. This is known as spontaneous coagulation.

Natural latex, when present in the latex vessel of the tree, is assumed to be sterile. As soon as it comes out, it is getting contaminated by different types of bacteria. These micro-organisms multiply rapidly at the expense of non-rubber constituents and by the time the latex arrives at the processing unit the microbial population is about 10^7 per ml(7). The microorganisms oxidise glucose to volatile fatty acids (VFA), mainly acetic acid(8). The VFA content of un-infected fresh latex is assumed to be zero(9). On keeping, the latex gradually thickens and coagulates. At a later stage, putrefaction sets in with the development of malodours. To prevent spontaneous coagulation and putrefaction, latex has to be preserved.

Ammonia is the first and the most popular preservative. It is generally added to field latex at about 1% concentration for long-term preservation; for concentrated latex, ammonia concentration is maintained at about 0.7% (HA latex).

However, ammonia when used at high concentrations has certain disadvantages. Hence several preservation systems containing lower levels of ammonia (about 0.2–0.3%) supplemented by secondary bactericides, known as low ammonia systems were introduced.

It was found that a combination of ammonia and tetramethyl thiuramdisulphide (TMTD) and zine oxide could function as an effective latex preservative and can maintain the latex for a considerable period with no rise in VFA number and ensure a good quality concentrate(10). Latex preserved with 0.2% ammonia and 0.0125% each of TMTD and zinc oxide was commercially accepted(11) and it is now popularly known as LATZ latex. LATZ latex shows good mechanical and chemical stability, accompanied by good processability characteristics(12). With the objective of reducing the emission of ammonia at the factory floor to a minimum, ultra low ammonia latices(13) and those free from dithio-carbamates and thiurams were introduced(14–16).

Despite the introduction of several preservation systems, belonging to low ammonia or ultra-low ammonia groups only HA and LATZ latices are commercially successful now.

CONCENTRATION OF NATURAL LATEX

Natural latex, as obtained from the tree, called field latex, has a dry rubber content (DRC) of only 30–35%. While making dipped articles, to attain a given thickness for the dry latex deposit, the number of dips to be performed is high if preserved field latex is used as such. Further it contains a high proportion of non-rubber materials(2). The proportion of very small particles also is high. The wet gel strength of deposit from field latex is very low. If the DRC of field latex is increased to about 50–60%, the above cited technical disadvantages can be eliminated to a great extent.

Concentrated latex will be more uniform in quality than field latex, as a good level of blending occurs at the latex concentrating factory. Moreover, it is uneconomic to transport latex of low DRC. For these reasons, field latex is processed into concentrated latex.

METHODS OF LATEX CONCENTRATION

The methods available for concentrating natural latex are:

- Centrifuging
- Creaming
- Evaporation and
- Electro-decantation

In India centrifugal process accounts for about 85% of the total concentrated latex and the remaining is produced by creaming process. Evaporated latex is processed in small quantities in other natural rubber producing countries like Malaysia, while electro-decantation is of accademic interest only.

In centrifugal process the rubber particles are separated into a cream fraction of DRC above 60% and skim fraction of DRC less than 5%, based on the difference in specific gravities of rubber and serum and by exerting high centrifugal forces over the dispersed rubber particles. A portion of the smaller particles in latex are led into the skim. The entry of rubber particles into skim is restricted in such a way that particles above a critical size are absent in the skim, whereas smaller particles can be found in centrifugally concentrated latex. Since the specific surface area of the small particles is very high compared to that of particles in cream, the proportion of adsorbed non-rubber materials in skim portion is substantially high. High proportion of water soluble materials are also removed in the aqueous phase of skim latex. Thus the cream portion is a cleaner fraction than field latex.

In the case of natural latex, specific gravity of rubber particles is less than that of the medium and hence it has tendency for creaming. The equilibrium rate of creaming is given by

$$\frac{dh}{dt} = - \frac{(\rho - \sigma) g}{18 \eta} x^2$$

where x is the diameter of the rubber particle, ρ it's density and σ and η are respectively the density and viscosity of the dispersion medium. However, natural creaming is a slow process and is of no practical use. The rate of creaming of natural latex can be increased by the addition of small quantities of water soluble hydrocolloids, called creaming agents. A typical example is ammonium alginate, added to the level of 0.08 to 0.1%m/m on the aqueous phase of ammoniated field latex. In India, the most commonly used creaming agent is the aqueous extract of tamarind seed powder, because of its low cost and easy availability. The creaming process is assisted by secondary creaming agents like higher fatty acid soaps, to the extent of about 0.05% m/m on the aqueous phase. Even this accelerated creaming process is rather slow and takes about 3–4 days to give cream of 55–60% DRC.

PROPERTIES OF CONCENTRATED LATEX

Quality parameters of single stage concentrated natural latex as specified by the International Organization for Standardization (ISO) are given in Table 2.2(17).

TABLE 2.2

ISO standards for concentrated natural latex

Properties	***Centrifuged***		***Creamed***	
	HA	***LA***	***HA***	***LA***
Total solids content (%m/m) min.	61.5	61.5	66.0	66.0
Dry rubber content (%m/m) min.	60.0	60.0	64.0	64.0
Non-rubber solids (%m/m) max.	2.0	2.0	2.0	2.0
Alkalinity as ammonia (%m/m)	0.60 min.	0.29 max.	0.55 min.	0.35 max.
Mechanical stability time(sec)min.	650	650	650	650
Coagulum content (%m/m) max.	0.05	0.05	0.05	0.05
Copper content (mg/kg) max.	8	8	8	8
Manganese content (mg/kg) max.	8	8	8	8
Sludge content (%m/m) max.	0.10	0.10	0.10	0.10
Volatile fatty acid number max.	0.20	0.20	0.20	0.20
KOH number max.	1.0	1.0	1.0	1.0

Further purified latices are obtained by second centrifuging or creaming. A second concentration process is accompanied by a fall in non-rubber solids content to about 0.6–0.8% m/m, KOH number to approximately 0.3–0.35 and VFA number in the range of 0.01–0.02. For standardising the quality of concentrated latex several national (including Indian Standards) and international standards are available(17-21).

LATEX COMPOUNDING

It is rather impossible to make useful rubber articles directly from latex unless it is vulcanized. The properties of vulcanized rubber can be modified by other chemicals. The process of mixing chemicals into latex to achieve some desired characteristics either for the latex mix or for the dry film is known as latex compounding. Major groups of compounding ingredients are stabilizers, vulcanizing agents, accelerators, activators, antioxidants, surface active agents, fillers and other special additives. Water soluble materials are added to latex as solutions, water insoluble solids as dispersions and water immiscible liquids as emulsions(22).

Rubber particles in natural latex are polydisperse and of colloidal size. The particle size of dispersions and droplet size of emulsions should, as far as possible be comparable to that of latex particles for getting uniform distribution in the latex compound(23-25). Because of the presence of alkali, the pH of latex is in the range 9–12. The colloidal stability and pH of the dispersions and emulsions to be added to latex shall be comparable to those of latex, for maintaining adequate colloidal stability to the final latex mix.

STABILISERS

Addition of certain chemicals to latex, generally decreases the colloidal stability. For example, by the addition of zinc oxide, latex thickens to some extent and the chemical stability of latex is very much affected. Hence latex has to be properly stabilized prior to the addition of chemicals. Stabilizers generally fall under three groups, viz. fixed alkali, surface active materials and protective colloids.

Potassium hydroxide is widely used as the fixed alkali. By adding KOH the pH of the latex is enhanced to about 12. The chemical stability of the latex is also enhanced.

Higher fatty acid soaps and synthetic organic sulphates and sulphonates, containing long hydrocarbon chains are used as anionic stabilizers. Protective colloids include casein, glue, gelatin etc.

Non-ionic stabilizers like polyethyleneoxide condensates (condensation product of ethyleneoxide with higher fatty acids, alcohols or phenols) are superior to natural products like casein due to less variability in product quality and non-putrefying nature.

SURFACE ACTIVE MATERIALS

Surface active substances, also known as surfactants, are substances which bring about a marked modification in the surface properties of aqueous media of latices, even when present in very small concentrations. Depending on the function they perform, they may be classified as wetting agents, dispersing agents, dispersion stabilizers, emulsifiers, foam promoters, foam stabilizers etc. Thus some of the latex stabilizers also function as surface active substances. For the majority of the surface active materials, the principal effect is lowering of the surface free energy against air and the inter-facial free energy against organic liquids.

Depending on the chemical nature, surface active substances can be classified as anionic, cationic, amphoteric and non-ionogenic types(26). The most commonly used are anionic surface active materials.

VULCANISING AGENTS

Elemental sulphur is the most commonly used vulcanizing agent for natural rubber latex and is used along with some accelerators. However, to achieve some specific properties for the vulcanized films, like heat resistance and to avoid staining of metal parts by sulphur, sulphur donors like thiuram polysulphides (eg. TMTD) are used in latex. But vulcanization with thiuram polysulphides and zinc oxide alone, in the absence of added sulphur proceeds at a useful rate, only at relatively high temperatures (say 140°C) whereas with latex products, vulcanization at about 100°C is the common practice. However, Philpott(27) has shown that certain sulphur containing compounds, notably thiourea, are able to activate vulcanization by thiuram polysulphides, so that well cured latex products could be produced rapidly at 100°C and the optimum mole ratio of thiourea to thiuram is 1:1. Dunn(28) has reported that butyl xanthogen disulphide in conjunction with a dithiocarbamate can be used to vulcanize natural rubber latex films; however, the level of each chemical to be used is appreciably high and hence this method is not adopted commercially.

Among the non-sulphur vulcanizing agents organic peroxides and hydroperoxides are the more important. During the 1990's peroxide vulcanization has gained some importance because of the possible liberation of nitrosamines and nitrosatable amines, derived from accelerators for sulpher vulcanization. t-Butyl hydroperoxide is the most important among the hydroperoxides(29). In the actual process, the organic hydroperoxide is added to latex in presence of a reducing agent like fructose. Peroxide prevulcanized latex would be particularly useful in the production of teats, soothers and catheters where the nitrosamine problem is most significant.

A new method of prevulcanizing natural latex, by the use of gamma radiation is dealt with later.

ACCELERATORS

Vulcanization of natural rubber with sulphur alone is a very slow process and physical properties of the vulcanizates are very poor(30). The group of chemicals known as vulcanization accelerators, when used along with sulphur impart high state and rate of cure. The most important class are dialkyl dithiocarbamates and the most widely used member is zinc diethyl dithiocarbamate (ZDC). Another member zinc dibutyldithiocarbamate is used when vulcanized films of higher clarity are needed and also when a higher level of prevulcanization is needed even during storage at ambient temperatures, during the maturation process(31). Dithiocarbamates are active even in the absence of zinc oxide. Thiazoles and to a lesser extent thiurams and guanidines are employed as secondary accelerators in conjunction with dithio-carbamates. Thiazoles are insufficiently active to be used on their own. The most widely used thiazole is zinc mercaptobenzthiazole (ZMBT). Replacement of one quarter to one half of ZDC by ZMBT results in much higher modulus being attained without any significant extension of the vulcanization time. ZMBT is activated by thiurams and dithiocarbamates(37).

Thiurams, as a class, are insufficiently active to accelerate satisfactorily sulphur vulcanization of diene rubbers in latex form. They are used as secondary accelerators along with dithiocarbamates. Most commonly used thiuram is TMTD.

ACTIVATORS

Activators assist in vulcanization by enhancing the reactivity of accelerator/accelerator-sulphur complex. The most commonly used activator in latex technology is zinc oxide. It is believed that zinc oxide reacts with the accelerator to produce an active accelerator complex which can react with sulphur to form the effective sulphurating agent. In the sulphur prevulcanization of natural latex, the state of cure is enhanced by addition of zinc oxide and the tendency for reversion is reduced(33). In a latex compound zinc oxide addition increases tensile strength and modulus of dry latex films.

ANTIOXIDANTS

Heat and oxygen, either separately or in combination can bring about the degradation of rubber molecules, resulting in deterioration of physical properties. The inherent ageing behaviour of rubber molecules in latex is good, as the molecules have not undergone any mechanical degradation, as brought about by mastication in dry rubber. However, antioxidants are commonly used in latex compounding, especially in products like dipped goods where the surface area to mass ratio is high. The commonly used antioxidants fall into two groups, viz.

- amine based antioxidants – they are powerful antioxidants, but can cause discoloration of the film.

- phenol based antioxidants – they are less active than amine antioxidants, but are non-discoloring and hence widely used in latex application. Styrenated phenol is a typical member.

A rather recent addition to the group of non-staining antioxidants is alkyl phosphites. Trisnonylated phenyl phosphite (TNPP) is very successfully used in radiation vulcanized natural rubber latex (RVNRL)(34). Alkyl phosphites do not cause the liberation of volatile nitrosamines.

FILLERS

Fillers are generally added to latex compound to modify its properties and to reduce cost(35). Fine particle carbon blacks and silicas, which are generally reinforcing fillers in dry rubber compounding do not reinforce the latex film by increasing tensile and tear strengths. It is believed that mastication of dry rubber generates rubber free radicals, which interact with the surface of filler particles and so unites the rubber particle to filler surface. In latex compounding this type of rubber-filler interaction is absent(23). Precipitated silica, china clay, whiting and precipitated calcium carbonate are the important mineral fillers used in latex compounding. Organic fillers (resins) can also be used as fillers in latex compounding.

SPECIAL ADDITIVES

Several types of substances fall in this group. Mineral oils and non-volatile esters find considerable application as polymer softeners and plasticizers. Certain petroleum gellies are used as cell wall lubricants and sodium silicofluoride as delayed action gelling agent for latex foam rubber. A number of viscous and resinous substances are used as tackifying resins in the formulation of latex adhesives. Other substances generally used are foaming agents, flame retardants, colours etc.

VULCANIZATION

Vulcanization or curing is an essential step in the manufacture of almost all rubber products. It is the process of crosslinking rubber molecules to transform them from a mainly viscous state to an elastic state by forming a three dimensional network. In terms of conventional physical properties this transformation enhances the modulus of the material and its resistance to rupture and tear.

Sulphur is being used as the most popular vulcanizing agent since its discovery by Goodyear, about 160 years ago. Although rubber can be cured by sulphur alone, the process is very slow and the properties obtained are not ideal(30). Today sulphur is used in conjunction with one or more accelerators. Accelerated sulphur vulcanization remains the crosslinking process for the overwhelming majority of rubber products both from dry rubber and latex. The three dimensional structure(36,37) produced by crosslink formation during vulcanization restricts the free mobility of the long polymeric molecules. The crosslinks have the effect of preventing the polymer chains moving bodily past each other when an external force is applied to the matrix. This is schematically represented in Figure 2.1(38).

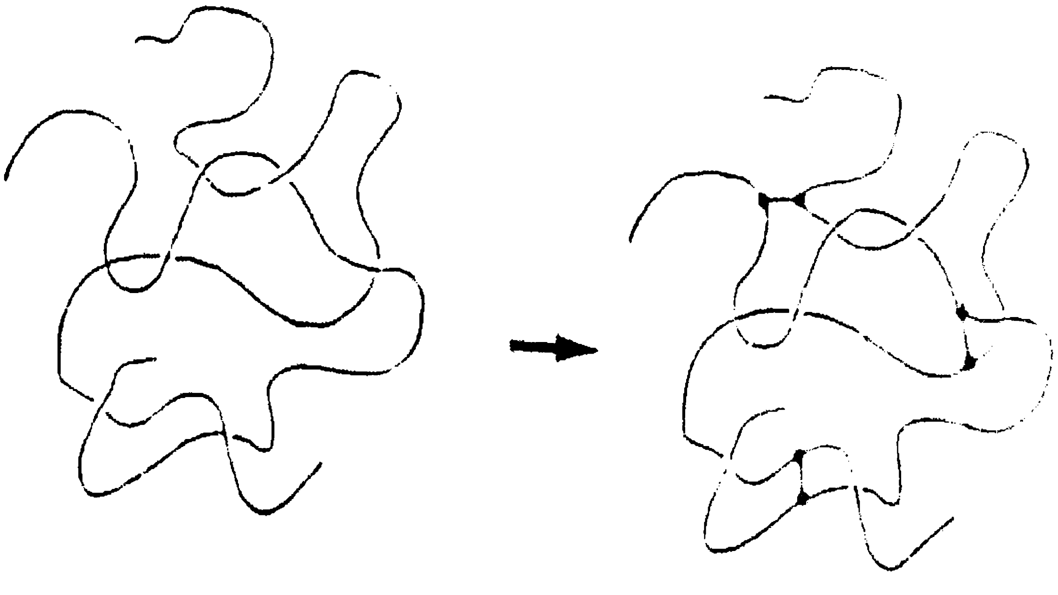
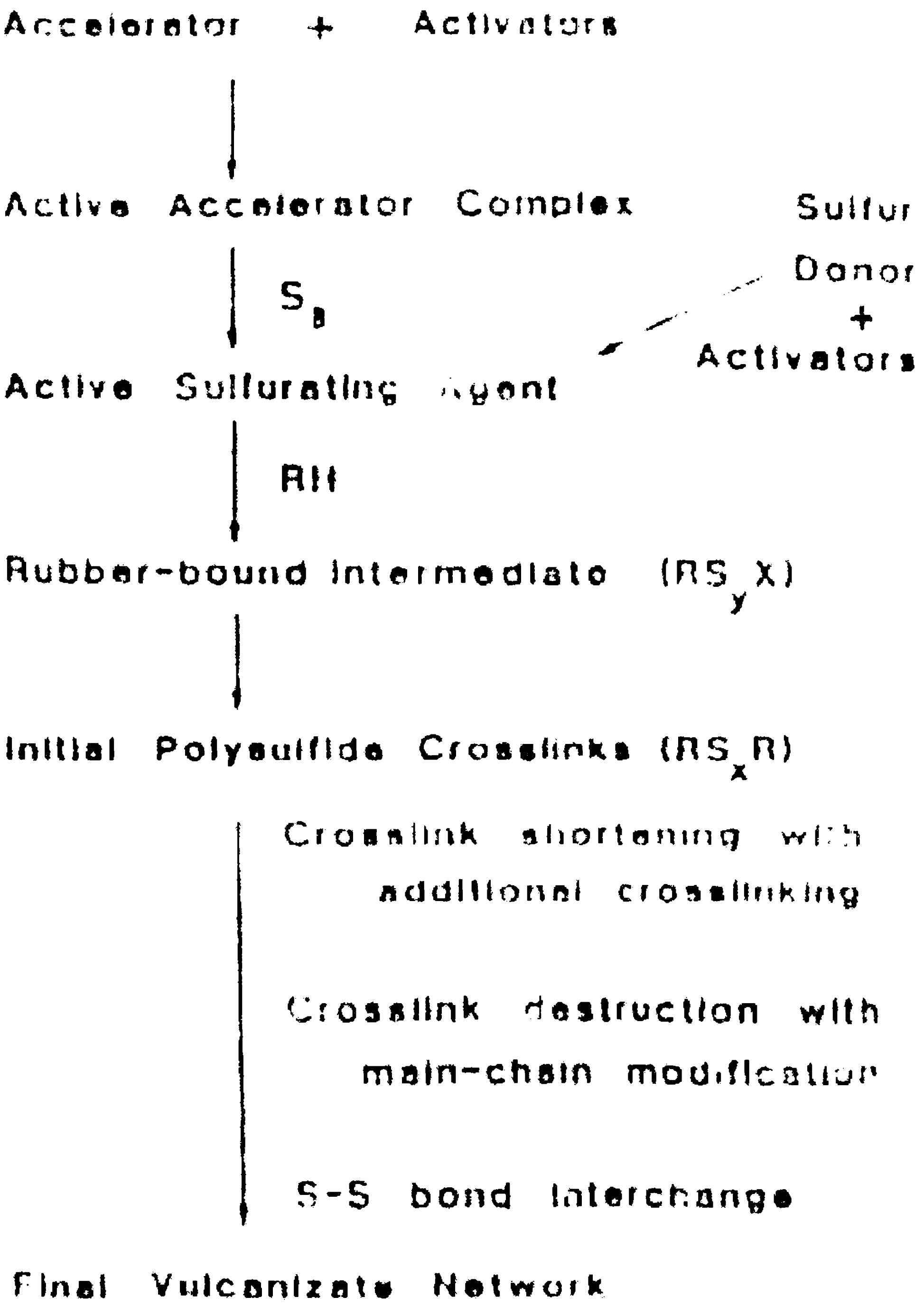


Figure 2.1. Crosslink formation

Sulphur vulcanization is an exceedingly complex chemical process, which is summarised in Scheme 2.1.



Scheme 2.1. Vulcanization reaction

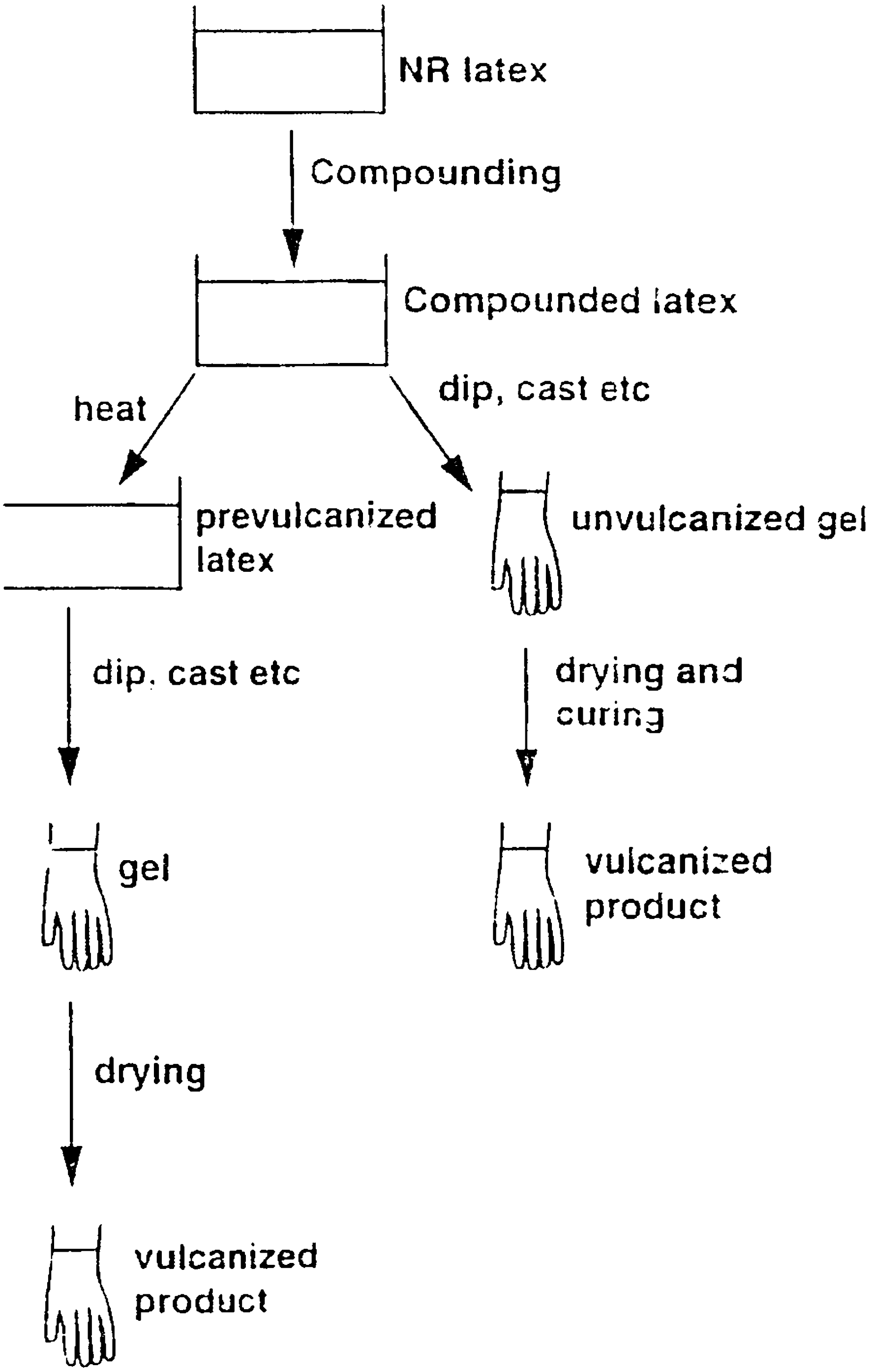
Crosslinks formed may be through a chain of sulphur atoms, or by a single sulphur atom or directly between carbon atoms. The vulcanizate properties are not functions of crosslink density alone. They are affected by the type of crosslink, nature of the polymer type, amount of filler etc(39). It is observed that modulus of latex films increases through a maximum and then decreases as vulcanizing time progresses(40). A similar effect has been reported for dry rubber vulcanizates also(41).

The mechanism of accelerated sulphur vulcanization has been extensively studied(42,43). It is believed that the mechanism of both pre-and post-vulcanization of latex will be the same, at least in outline. The first step is the combination of the accelerator with one or more activators, which has the effect of solubilising the accelerator in rubber. In latex compounds the most common activators are carboxylates, or naturally occurring amino compounds which are added as stabilizers. The active accelerator reacts with sulphur to produce active sulphurating agent, which, in turn, reacts with rubber hydrocarbon to give a pendant group consisting of a chain of sulphur atoms, terminated by the accelerator derivative. The pendant group can form a crosslink either by direct reaction with another polymer molecule or by disproportionation with another pendant group. In either case the initial crosslinks are polysulphidic. These crosslinks are chemically reactive and on continued heating undergo three parallel sets of reactions.

- desulphuration or crosslink shortening to disulphides and monosulphides, with the recycling of sulphur into additional crosslinks.
- decomposition or crosslink destruction, with the formation of non-crosslinking modifications along the polymer chain and
- exchange of sulphur-sulphur bonds, allowing rearrangement of chains and relaxation of stress within the net work.

VULCANIZATION METHODS FOR LATEX PRODUCTS

For the sulphur vulcanization of products made from latex, two alternatives exist (Scheme 2.2)[44].



Scheme 2.2. Methods of vulcanization

In the first method the chemicals required for vulcanization are mixed into the latex, then the mixture is formed into the required shape and dried. The dried rubber mix containing the chemicals is then heated to effect vulcanization. This is known as post-vulcanization since crosslinking occurs essentially after the product has been formed. The other alternative involves heating the latex at a suitable temperature with the vulcanization ingredients dispersed in it, until the required level of vulcanization has been achieved. This is called prevulcanization. The resulting prevulcanized latex can be formed into latex products in the normal way. Only drying is required to obtain the vulcanized rubber product.

Prevulcanization and post-vulcanization can be considered as two extreme cases. A latex compound prepared for post-vulcanization will generally undergo some degree of prevulcanization between the time it is compounded and the point at which it is used. On the other hand fully prevulcanized latex will generally contain some excess vulcanizing ingredients which can cause some post-vulcanization during and after drying of the product.

In post-vulcanized latex systems crosslink destruction is minimum because of the relatively low vulcanization temperatures; crosslink shortening and exchange of sulphur-sulphur bonds allowing rearrangement predominates, leading to a stable network containing some mono-and disulphidic crosslinks as well as polysulphidic ones. The relative proportions of the three types of crosslinks depend on the ratio of sulphur to accelerator in the original recipe and on the curing time and temperature, but in most latex systems di– and polysulphidic crosslinks predominate(45).

Zinc oxide is widely used in latex vulcanization systems, although zinc dialkyl dithiocarbamate accelerated vulcanization can successfully occur without it(4,22). Zinc Oxide prevents vulcanization to come to a premature halt due to depletion of accelerator and leads to a higher modulus.

PREVULCANIZATION OF NATURAL RUBBER LATEX

It is a special property of natural rubber latex, and also of some other types of diene latex, that it is possible to vulcanize the individual particles in latex without destroying its colloidal character(46). The product, prevulcanized latex, is colloidally stable, the dispersed polymer of which is crosslinked into networks of indefinite extent. In appearance, prevulcanized natural rubber latex is very similar to unvulcanized latex. The original fluidity of the latex is retained. The particles in prevulcanized natural rubber latex have essentially the same shape, size and size distribution as did those in the initial unvulcanized latex.

There are three principal ways in which natural rubber latex can be prevulcanized. They are:

- by reaction with sulphur and organic vulcanization accelerator(s),
- by heating latex with organic peroxides and hydroperoxides,
- by exposing latex to high energy gamma radiation or electron beam in the presence of sensitizers.

The possibility of vulcanizing the disperse phase of natural rubber latex without any concomitant colloidal destabilization was first investigated by Schidrowitz(47). Relatively high temperatures (about 140–145°C) were used, as very active organic accelerators were not available then. But now it is possible to prevulcanize latex to a high state of cure in about one hour at about 60–70°C.

Sulphur prevulcanized natural rubber latex is invariably prepared by allowing the rubber molecules in the latex particles to react with sulphur under the influence of one or more organic accelerators and possibly of an inorganic vulcanization activator as well. Compared to dry rubber vulcanization, prevulcanization of latex proceeds much more rapidly at the same temperature with the same vulcanizing ingredients(48). The speed of prevulcanization seems to be primarily associated with the presence of water(49). Recent investigations into sulphur prevulcanization of natural rubber latex have been summarized by Blackley(50). There are several features of the prevulcanization process which are subject to variation. These include(46)

- level of sulphur(31, 51-53)
- whether the vulcanization accelerators are water soluble or water insoluble, or a combination
- nature and levels of accelerators
- the particle size of the sulphur dispersion
- the particle size of dispersions of water-insoluble accelerators used
- whether or not an inorganic activator is used, if so the type and quantity
- the temperature-time profile which is imposed for the reaction
- the extent to which the reaction is allowed to continue

For a given level/type of accelerator, the modulus of the vulcanized films increases with an increase in sulphur content. Hamphreys and Wake(54) reported that no matter how much sulphur is included in the latex compound it is not possible to attain more than 1.8% combined sulphur with the rubber hydrocarbon. Dialkyl dithiocarbamates are the most commonly used accelerator. Water-insoluble accelerators, unless made into fine dispersions, may sediment during storage and the desired state of cure will not be attained. For equimolecular concentrations of sodium and zinc dialkyl dithio-carbamate the zinc derivatives give higher modulus(40). For equimolar levels of various dithiocarbamate accelerators, the state of cure attained during prevulcanization is affected by the alkyl chain length of dialkyl dithiocarbamate(48). The state of cure as well as modulus(40) increase as the number of carbon atoms on the alkyl group increases up to 4 (ie, butyl) and then again decreases. This is based on a balance between solubility in aqueous phase of latex and adsorption at rubber-serum interface(51).

A minimum of about 0.5phr accelerator is needed for reasonable level of vulcanization. It is seen that there is no appreciable change in tensile properties during the initial hours of prevulcanization as the concentration of the accelerator is increased(52). However, on prolonged heating, increase in modulus is observed at higher levels of accelerator concentration. For 1:1 ratio of sulphur to accelerator, tensile strength and modulus increases upto 1phr each of sulphur and zinc diethyl dithiocarbamate and further increase beyond this level has no appreciable effect(40). At higher times of prevulcanization a fall in tensile properties are however observed at higher concentrations of vulcanizing chemicals.

The particle size of sulphur and accelerator appeared to have no significant effect upon the tensile properties of films obtained from the latex(24). It indicates that the amount of vulcanizing ingredients which become available for reaction with rubber under these conditions is not significantly affected by the area of interface between sulphur or accelerator particles and the aqueous phase. Fine dispersions are essential to prevent sedimentation of ingredients during processing and thus to guarantee homogeneity of dispersion during the manufacturing process, but reaction can proceed from quite coarse dispersion if precautions are taken to prevent sedimentation. The rate of prevulcanization increases as the latex particle size decreases(55).

The effect of temperature on prevulcanization of natural latex has been studied by several authors(33,53,56). Increase in the temperature of prevulcanization was accompanied by an initial sharp increase in tensile strength and modulus(51). Claramma and Mathew(56) showed that the volume fraction of rubber in the dry film, which is a measure of crosslink density, exhibited a maximum when prevulcanization was conducted at 80°C for 2h or at 90°C for 1h. At each temperature, tensile strength and elongation at break decreased when prevulcanization time was increased, whereas modulus increased to a maximum and thereafter decreased.

The single most important factor in determining the tensile strength of film is the degree of chemical crosslinking(59). The degree of crosslinking in a vulcanizate film can be varied either by controlling the prevulcanization time, temperature or by changing the level of curatives. Irrespective of cure time and level of curative, the optimum tensile strength occurred when the degree of chemical crosslinking attained 1.0–2.2$\times10^{-5}$ gram mole of crosslink per gram of rubber hydrocarbon(40).

In the case of NR vulcanizates prepared by dry rubber compounding, it has been reported that the optimum tensile strength occurred when the crosslink density was in the range 4–7x10^{-5} gram mole per gram of rubber hydrocarbon(58,59). This range is significantly higher than that observed for the prevulcanized latex films. This difference suggests that a mechanism other than the degree of chemical crosslinking is operative in affecting the tensile strength of latex films.

It was believed that the presence of non-rubber constituents in natural rubber latex, especially proteins is essential for the occurrence of sulphur prevulcanization of natural latex. Ghazaly(60) has shown that it is possible to sulphur prevulcanize natural rubber latex from which most of the non-rubber materials have been removed; however the overall rate of crosslink insertion was found to be reduced.

MECHANISM OF SULPHUR PREVULCANIZATION

There are different schools of thought regarding the mechanism of sulphur prevulcanization of natural latex. Some authors have postulated that the reaction takes place as a result of direct contact between particles of reactants and rubber(61,62). Some other authors believe that the reactants must dissolve in the aqueous phase before diffusing into the rubber particles(48,61–63). van Gils(64) demonstrated that sulphur is appreciably soluble in the aqueous phase of ammonia preserved natural rubber latex where as it is not significantly soluble in dilute aqueous ammonia solution. Loh(48) found that zinc di-n-butyl dithiocarbamate is appreciably soluble in the aqueous phase of ammonia preserved natural rubber latex than in water or aqueous ammonia solution of pH 10.2. Enhanced solubility of sulphur and accelerator in the aqueous phase of latex, presumably facilitates sulphur prevulcanization. Recently it has been demonstrated that sulphur and zinc dialkyl dithiocarbamate accelerators are independently able to dissolve in ammonia preserved natural rubber latex which subsequently effect prevulcanization of latex when the other ingredient is even added as a solid phase(65).

It has been reported from qualitative observations that sulphur can transfer from sulphur particles originally present in the aqueous phase to the rubber particles remarkably rapidly. The zinc dialkyl dithiocarbamate accelerator by itself does not transfer from its particles to any significant extent. In the presence of sulphur, the accelerator can transfer, although more slowly than sulpher. It therefore, appears that the first major step of the reaction is the formation of a sulphur-accelerator species in the aqueous phase of the latex and that this species can get transferred to the rubber phase. If this species were surface active, then the most obvious mode of transfer would be adsorption from the aqueous phase onto the surface of the rubber particle. However, this sulphur-accelerator species has to be soluble in an aqueous medium. This is rendered soluble in water to a sufficient extent by interaction with some of the hydrophilic non-rubber substances, which are present in ammonia preserved natural rubber latex concentrate. The sulphur-accelerator species after adsorption loses by dissociation some or all of the hydrophilic moieties which have rendered it sufficiently water soluble for transfer to the surface of the rubber particles. The lost moieties would then return to the aqueous phase and be available for interaction with other molecules of the sulphur-accelerator species in due course whereas the residual sulphur-accelerator species at the particle surface would now be sufficiently hydrophobic in nature to migrate into the interior of the rubber particle. The sulphurating species that has thus entered the rubber particles bring about crosslinking reaction. When the active sulphurating species reach the surface two simultaneous processes can occur: diffusion of the active species and the crosslinking reaction. If the crosslinking reaction is faster than diffusion the particles are crosslinked preferentially near their surface and the reduced mobility of the rubber chains at the surface makes the effective fusion of the particles more difficult and the final properties will not be optimum.

Several authors have reported on different aspects of sulphur prevulcanization of natural latex(51,52). Porter(66) has compared the properties of pre-and post vulcanized latex films. He has also reported the effect of leaching and has examined the dependence of tensile strength on degree of crosslinking for pre- and post vulcanized films. Natural latex can be prevulcanized even at room temperature using zinc di-n-butyl dithiocarbamate(31). The effect of preservation system and quality of latex on prevulcanization characteristics have been studied by Low(51). According to Gazeley(67) the rate of extraction of water soluble materials is faster from prevulcanized films than from post-vulcanized films and increases with the degree of vulcanization. The easier extraction of water soluble materials from prevulcanized latex films is attributed to their higher porosity. Chong and Porter(68) have reported that the crosslinks formed in rubber particles during prevulcanization are predominantly polysulphidic. The proportion of mono- and disulphidic crosslinks was found to be less than 28% of the total crosslink concentration. A similar conclusion has been arrived at by Loh(48) and Peethambaran and George(69) also. Micro changes in the rubber particles during sulphur prevulcanization of natural latex have been studied(70). Also vulcanization was found to be continuing during storage(71).

PREVULCANIZATION WITH PEROXIDES

Prevulcanization of natural rubber latex, by heating in the presence of an organic peroxide has been known for many years(72,73). Peroxides can be used for vulcanizing dry rubber also. Organic peroxides are used in conjunction with activators, to facilitate decomposition. Even though peroxide vulcanization of latex was a simple process, there was little industrial interest, due to the relatively poor ageing behaviour of peroxide vulcanizates. Recently peroxide prevulcanization was reinvestigated(74-77) because of concern about the possible presence of carcinogenic nitrosamines in products made by conventional sulphur-accelerator reaction. It has been shown that hydro-peroxide prevulcanized latices can produce films with physical properties similar to those of sulphur vulcanized latex films. Also the possibility of allergic skin reactions due to accelerators can be avoided.

The basic mechanism of peroxide prevulcanization involves O—O cleavage of the peroxide producing alkoxy radicals. These radicals abstract hydrogen from polymer molecules principally from the α–methylene groups adjacent to the olefinic bonds to form polymer radicals which then crosslink together. A typical fructose activated t-butyl hydroperoxide mix is given in Table 2.3.

TABLE 2.3

Typical Peroxide Prevulcanization Mix

Ingredient	***Dry weight***	***Wet weight***
60% HA latex	100.0	166.67
68.1% t-Butyl hydroperoxide	0.85	1.25
20% Potassium laurate	0.25	1.25
20% Fructose	1.70	8.50
Water	—	22.40

For fructose-activated t-butyl hydro-peroxide system crosslink density of $5–6\times10^{-6}$ gram mole per gram of rubber hydrocarbon is required for optimum tensile strength. t-Butyl hydroperoxide concentration of about 9 milli mole/100 gram rubber and fructose/t-BHP mole ratio of 0.6 at 60°Cgives crosslink density of about $4–5 \times 10^{-6}$.

The ageing behaviour of films from peroxide prevulcanized natural rubber latex is generally poor. It has been recently reported that phenolic antioxidants like 2, 4 dioctyl phenyl sulphide-6-methyl phenol and 2, 2' methylene bis– [4 methyl-6-t-butyl] phenol are very effective anti-oxidants for peroxide prevulcanized latex films(78). The microstructure of peroxide prevulcanized latex films made from peroxide-water soluble activator combination is different from that made using a more rubber soluble thermally activated peroxide(79).

RADIATION VULCANIZATION OF NATURAL RUBBER LATEX

Radiation vulcanization of natural rubber latex has been investigated extensively since 1960's(80,81). However, the technique had not been used by the industry. The main reasons for the lack of interest were

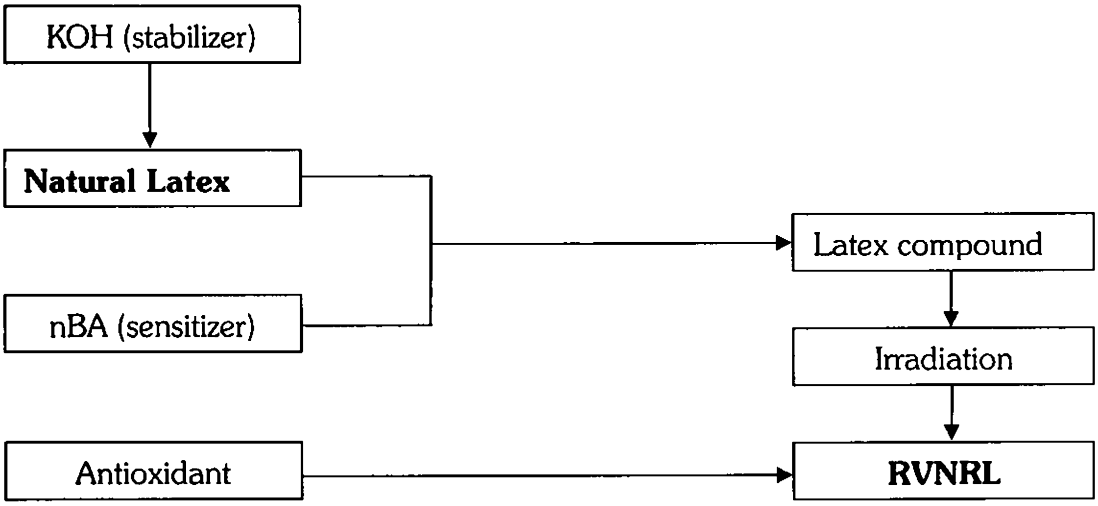
- high cost of irradiation for vulcanization
- low quality of the products from radiation vulcanized natural rubber latex (RVNRL)
- ambiguous advantages of the products

However, significant progress has been made in cost reduction and quality improvement of RVNRL mainly through the R&D support of the International Atomic Energy Agency and the U N Development Programme, known as the Regional Cooperative Agreement (RCA) in the Asia and Pacific Region(82). RVNRL films have the following advantages over conventional sulphur vulcanization(83).

- Absence of nitrosamines
- Very low cytotoxicity(84, 85)
- Low emission of sulphur dioxide and less formation of ashes on burning
- Transparency and softness
- Biodegradability

If natural latex alone is irradiated, the dose requirement to achieve reasonable level of crosslinking is very high, about 250–300kGy. Sensitizers are generally used to bring down the dose requirement. Monofunctional acrylates, such as 2-ethyl hexyl acrylate (2-EHA) or n-butyl acrylate (nBA) were found to accelerate radiation vulcanization(86,87). Thus with 5phr 2EHA or nBA, the dose requirement is 15kGy. However, the residual 2EHA monomer imparts objectionable smell to the film, as the residual monomer cannot be easily removed due to its low vapour pressure. n-Butylacrylate has high vapour pressure. However, it tends to destabilize latex. But latex can be stabilized by the addition of 0.2 phr potassium hydroxide(88).

The process of radiation prevulcanization is as shown in Scheme 2.3.



Scheme 2.3. RVNRL Processing

The mechanism of sensitizing action of nBA in RVNRL processing has been recently reported(89). The solvated electrons produced by the radiolysis of water forms a transient structure with nBA, capable of propagating the radical reaction with the monomer at high rates leading to crosslinking.

FILM FORMATION DURING DRYING OF PREVULCANIZED LATEX

Upon drying, some latices form transparent, tough continuous films where as others form friable, opaque, discontinuous films or powders. The form of film obtained depends upon the viscosity of the polymer particles and the conditions of drying. Differences in film characteristics, obvious from a casual macroscopical examination, have been correlated with submicroscopic morphology of the film(90). In continuous films the particles appear coalesced, but in discontinuous films they appear as spheres in juxtaposition. It has been postulated that the main contribution of energy for particle coalescence was provided by the polymer surface tension forces exerted as the total surface area of the latex polymer decreased very greatly(91). As the water evaporates, the particles are brought together so that their stabilizing layers are in contact and their further approach is hindered. The pressure forcing the particles together is increased by further evaporation of water (ie, by forces arising from the water-air interfacial tension) until the stabilizing layers are ruptured and a polymer-polymer contact is formed. Once this occurs, the pressure exerted upon the particles is increased further by the forces arising from the polymer-water interfacial tension. Numerical values of the pressure exerted upon the particles are functions of latex particle size, degree of coalescence and interfacial tension both of water against air and polymer against water(92).

During drying of prevulcanized natural rubber latex, the crosslinked latex particles coalesce or join together to form a continuous and homogenous phase. Film formation on drying of prevulcanized natural rubber latex is shown schematically in Figure 2.2(40).

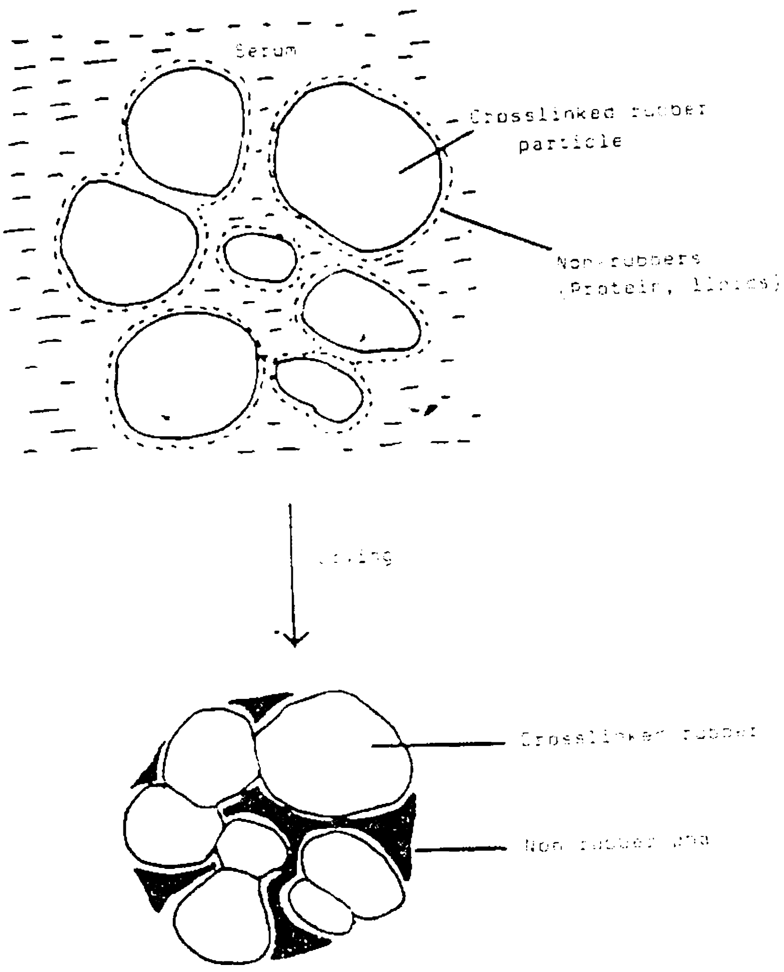


Fig. 2.2. Formation of latex film

However, the presence of hydrophylic non-rubbers such as proteins and lipids which are naturally present in natural rubber latex is likely to prevent the effective coalescence of rubber particles(93). Therefore, in order for the latex to obtain the best tensile strength, these hydrophylic non-rubbers must be removed as purported by water leaching treatment. On the other hand crosslinking in the rubber particles is essential so as to impart a higher tensile strength. But the latex particles must not be too highly crosslinked, since too high a modulus can hinder the effective fusion of latex particles to form a strong and coherent film.

Several theories have been put forward to explain the phenomenon of film formation. The major ones are primary valence bond theory, bonding adhesive theory and secondary valence bond theory. The secondary valence bond theory can account for the film formation in any type of prevulcanized latex.

MECHANICAL PROPERTIES OF PREVULCANIZED LATEX FILMS

Physical properties of sulphur prevulcanized natural rubber latex films, subjected to post-heating are comparable to those of post-vulcanized natural latex films. If precautions are taken to avoid post-vulcanization, then physical properties are intermediate between those for unvulcanized and post-vulcanized latex film. It is believed that during post-heating some amount of crosslinking also occurs due to the presence of residual vulcanizing ingredients, resulting in higher tensile strength. Dry prevulcanized latex films retain the original particulate structure, showing considerable inhomogenity and therefore zones of weakness which would yield low tensile strength. However, heating or leaching of the film improves in the degree of homogeneity. This partially accounts for the superior tensile properties. The surface active agent present on prevulcanized latex particles hinder the formation of a homogeneous film. During the leaching process these non-rubber materials are removed from the interface between the latex particles which comprise the film, with consequent improvement in the degree of interparticle integration. The effect of leaching on the modulus of prevulcanized latex films is critically dependent on the humidity at which the films are stored prior to testing(94). Films leached at low humidity levels give lower modulus than their unleached counterparts; but at moderate and higher levels of humidity this effect is reversed. This effect can be adequately explained in terms of a stiffening effect of natural non-rubbers under dry conditions and a softening effect of the same, which absorb moisture under humid conditions. Tear strength of prevulcanized latex films tends to be inferior to those of post-vulcanized deposits(95).

APPLICATIONS OF PREVULCANIZED LATEX

Prevulcanized latex is a very convenient form of latex for the dipping industry and has applications in other fields such as textile combining, carpet backing and cast rubber products. Prevulcanized latex is especially attractive for small dipping units since it can be used directly in the dipping operation thus eliminating latex compounding. Partially prevulcanized natural rubber latex has been found to be capable of yielding, thin films by dipping, which have very satisfactory mechanical properties, especially if those films are further vulcanized. Partially prevulcanized latex offers a considerable economic advantage over post-vulcanizable natural rubber latex, in that its use enables a large quantity of rubber to be partially vulcanized as bulk latex, instead of having to be entirely vulcanized when spreadout as thin films over the surface of innumerable formers. Better quality control and uniformity in products can be achieved by the use of prevulcanized latex. Prevulcanized latex can be clarified to remove the excess curatives, so that the films on drying exhibits higher clarity.

Despite the above stated advantages, prevulcanized latex is not without any disadvantage. The extent of cure in prevulcanized latex cannot be changed easily. Films prepared from prevulcanized latex have generally lower tensile properties and tear resistance, compared to post-vulcanized films. Prevulcanized latex films exhibit less resistance to oils, grease and solvents. Thus dipped gloves produced from prevulcanized latex are less resistant to oil and grease, than post-vulcanized films. Also prevulcanized latex does not find application in latex foam manufacture mainly on account of its poor wet-gel strength.

RHEOLOGICAL BEHAVIOUR OF LATICES.

The flow properties of a latex are of vital importance in engineering a latex to a given application(96). Latex rheology is concerned with the quantitative relationship between the shear stress to which the fluid may be subjected and the resultant shear rate thereby induced(97). The ratio of shear stress to shear rate is known as apparent viscosity. Theoretical treatment of the flow behaviour of latex is based on the assumption that latex contains two distinct flow units: a Newtonian solvent (in most cases water) and a polymer particle(98). Most latices behave in a pseudoplastic manner, namely, the apparent viscosity decreases as the rate of shear increases, to some limiting high shear viscosity from a low shear (zero shear) limiting viscosity, (first or initial Newtonian viscosity). Suitable mathematical equations have been developed to predict approximately the viscosity of monodisperse latices upto 55% solids content(99).

The graphical relationship between shear stress and shear rate is known as flow curve. Lenk has advanced a generalized flow curve(100). Natural rubber latex is a non-Newtonian fluid exhibiting pseudoplastic flow behaviour. While handling and under various stages of product manufacture, latex/latex compound is subjected to stress and flow/deformations. Proper understanding of the rheological behaviour of latices under different processing conditions is essential to evaluate the scope/limitations in any area of application. Flow behaviour encountered in foaming, extrusion, casting, spraying, dipping etc. differ considerably. Flow behaviour in a particular application change with temperature(101). In straight dipping the thickness of the dry deposit obtained depends on the viscosity of latex compound(102).

The rheological behaviour of latices can be modified to suit a specific manufacturing process by the use of viscosity modifiers. Generally the viscosity of latex compounds is increased by the use of water soluble hydrocolloids. In such cases they are referred to as thickener(103). Sodium polyacrylate(104) shows sharp, easily controlled increase in viscosity with most type of latices. The rheology and latex compounds has been discussed by Leaman(105).

The variation of viscosity with solids content has been studied in the case of natural latex(3,106) and styrene butadiene copolymer latices(107,108). Rheological behaviour of natural and synthetic latices in the presence of surface active agents has been investigated(109). The effect of various surface active agents on the rheological behaviour of centrifuged and creamed natural latex concentrate has been reported(110). The viscosity changes on blending of natural and styrene butadiene latices have been studied(111,112).

The viscosity temperature relationship of natural latex has been studied by Rhodes(113). The effect of temperature, viscosity modifiers and fillers on rheological behaviour of prevulcanized natural rubber latex has been reported by Claramma and Mathew(114).

REINFORCEMENT

In the development of rubber industry reinforcement of natural rubber by carbon black remains next to sulphur vulcanization in importance. The term reinforcement refers to improvement in one or more physical properties of a vulcanizate like tensile strength, modulus, hardness, abrasion resistance, tear resistance, fatigue resistance etc. Fine particle carbon blacks and silicas function as reinforcing fillers in vulcanizates based on dry rubber. However, they do not similarly reinforce when incorporated into rubber in latex. It is believed that working of dry rubber in processing machines (mixing mill or internal mixer) produces free radicals by mechanical breakdown of polymer molecules. These free radicals chemically combine with the reactive sites on filler particle surfaces, thus imparting reinforcement. Further, the rubber molecules in latex have low mobility due to higher size. Also the mechanical working forces rubber into the cavities on filler surfaces, causing physical binding. These two mechanisms are not operating in the case of latex-filler mixes.

When conventional reinforcing fillers are incorporated into latex, actually the vulcanizate is weakened. This is attributed to the poor rubber-filler interaction. The protective layer on rubber particles also reduces the rubber filler interaction.

However, these fillers stiffen the latex vulcanizate. Different techniques have been suggested to overcome the situation(115–117).

van Rossem and Plaizer(118) have found that small additions of bentonite clay to compounded latex increased the tensile properties of the dry vulcanized latex deposit. Fine particle hydrated silica has been described as a reinforcing filler for natural rubber latex films(119). Claramma, Varghese and Mathew(120) have studied the reinforcement of prevulcanized natural rubber latex films by precipitated silica, china clay and whiting.

For the production of filled latex compounds of high strength the following points have to be ensured(121)

- A high degree of dispersion of fillers and other ingredients added to the latex.
- Simultaneous precipitation of the particles from the latex mix, and
- Conditions which result in direct contact between the rubber and filler particles without intermediate layers of protective substances which lower the rubber-filler interaction energy.

LATEX PRODUCTS

Concentrated latex/prevulcanized latex finds application in several areas of product manufacture. The important classes of products are dipped goods, latex foam, extruded products, latex adhesives, latex paints etc.

TECHNIQUES IN LATEX INDUSTRY

DIPPING

Latex dipping is a process in which thin walled latex products are produced by first immersing a former in a latex, which is suitably compounded and then subsequently slowly withdrawing it from the latex in such a way as to leave a uniform deposit upon the former. Latex dipping processes are conveniently classified according to whether or not any colloid-destabilizing materials are used to assist in the formation of a polymer deposit upon the former. If no destabilizing material is used then the process is commonly known as simple or straight dipping. If a direct coacervant is used to promote the formation of a deposit, then the process is commonly known as coagulant dipping. A process in which the latex compound is formulated in such a way as to be heat-sensitive and the formation of a deposit is facilitated by heating the former, prior to immersion in the latex; it is known as heat-sensitized dipping. The formation of a coherent deposit depends upon two factors: uniform wetting of the former by the latex and adequate viscosity of the compounded latex to ensure that sufficient latex remains on the former during withdrawal from the latex bath and also during the subsequent drying step. Generally the thickness of deposit obtained from a single straight dip is very low, about 0.01–0.05 mm and such films are prone to defects, such as pinholes, which arises from the presence of grease spots and other imperfections on the surface of the former. For these reasons straight dipping is usually practised as a multi-dip process.

In coagulant dipping process, the formation of a deposit on the former is facilitated by the use of a direct coacervant. The main body of the latex film is produced by first coating the former with the coacervant. The former is then immersed in the latex compound and then allowed to dwell there for a specified period. During this period the latex in the vicinity of the former surface become colloidally destabilized to form a thin gelled layer around the former. At the end of the dwell period the former is slowly withdrawn from the latex. Gorton(122) has reported a quantitative relation between thickness of the dry latex deposit against dwell time in coagulant dipping process:

$$\theta^1 = \alpha + \beta\sqrt{(t \log q)}$$

Where θ^1 is thickness of the deposit excluding the contribution of straight dipping, t is dwell time and α and β are constants and q is the viscosity of latex compound. Where q is the viscosity of the latex compound. Blackley, Burgar and Shukri(123) have reported the variation of thickness of dry latex deposit against log (dwell time), for latex compounds of varying solids content. Typical dry deposit thickness in a single coagulant dip is 0.2–0.8mm.

In heat-sensitized dipping, the latex compound is formulated so as to be heat sensitive, and heating the former prior to immersion in the latex facilitates the formation of a deposit around the former. Heat sensitized latex dipping processes have found application in the manufacture of relatively thick walled rubber products, such as baby feeding teats and soothers by a single dip. The characteristics of an ideal heat sensitizer system has been described by Blackley(124). A number of heat sensitizing systems have been designed and the best known are systems containing

- zinc-ammine
- polyvinyl methyl ether (PVME) and
- polypropylene glycol (PPG)

The effect of potassium fatty acid soaps upon heat sensitivity of natural rubber latex containing zinc-ammine ions has been reported by Blackley and Asiah(125). The conditions under which PVME and PPG confer heat sensitivity has been described by Cockbain(126). The relationship between dwell time and thickness in heat sensitized dipping using PVME and PPG systems has been reported by Pendle and Gorton(127). According to Bratby(128) careful control of bath temperature is essential for successful production of baby teats and soothers by heat sensitized dipping.

FOAMING

Latex foam rubber is a cellular product, which has been made directly from liquid latex in which the cells are either all intercommunicating or only partially intercommunicating. The essential steps in the manufacture of latex foam rubber are foaming, shaping the product, setting the foam and vulcanizing(129,130).

Several methods are available for setting of the foam. Major ones are Dunlop process(131) and Talalay process(132). In Dunlop process then solidification of the foam is achieved by the action of a delayed action gelling agent (eg. Sodium silicofluoride). In Thalalay process solidification is achieved by bringing about a sol-gel transformation in the latex phase of the foam by first freezing the foam and then exposing the frozen foam to a chemical influence (eg. carbon dioxide) which causes the latex phase to gel.

EXTRUSION

Elastic thread is the most important product produced by extrusion process. In the process for the production of elastic thread, a latex compound is continuously extruded through appropriate nozzles into a coagulant solution(133). Latex tubing(134) is made by the extrusion of a heat sensitive latex compound through the annular space of two concentric polished tubes under a constant pressure head.

ADHESIVES

Natural latex is well known for its high cohesive strength and intrinsic tack. These properties make natural latex a basic raw material for adhesives. Also it has high solids content and low viscosity compared to solution adhesives. The performance of adhesives can be modified by addition of adhesion modifiers, curatives, thickeners and fillers. The technology underlying the development of latex based adhesives are described by Blackley(135).

SURFACE COATINGS

One of the most significant developments in the field of water-thinned paints is the introduction of polymers in latex form as film binders. The development of latex based paints has been described as the biggest advancement in paint technology, since the introduction of cellulose ether thickeners. Synthetic latices have been used extensively in emulsion paints. Initial experiments using natural rubber latex in such paints showed serious disadvantages in hardness, stability, brushability and pigment-binding capacity. Nadarajah and Ganeshasundaram(136) have reported that these properties can be improved by grafting styrene or methyl methacrylate, onto natural rubber, followed by vulcanization by cumene hydroperoxide.

ALLERGIC REACTIONS TO LATEX PRODUCTS

It has been established for several decades now that contact with latex products may produce dermatitic reactions in certain individuals. The most common condition is allergic contact eczema.

These skin allergies called type IV allergies are caused not by rubber itself, but by additives such as accelerators and antioxidants(137). However, in the past few years there have been increasing reports of another kind of allergy, referred to as type I allergy to dipped natural rubber latex products. The effects in allergic subjects can range from the localized skin response of contact urticaria, to the potentially life threatening anaphylactic shock. The allergy is caused by proteins native to *Hevea* latex and not by chemicals added during product manufacture.

LATEX PROTEIN ALLERGY

The first piece of evidence that latex itself should cause contact urticaria was provided by Nutter(138). Subsequent work implicated latex proteins as the eliciting factor of these allergic responses(139). The first report of anaphylactic shock from latex products (surgical gloves) came from Finland in 1984(140).

In certain individuals, exposure to protein allergens leads to a condition of hypersensitivity, whereupon further exposure causes immediate responses, such as contact urticaria or anaphylactic shock. In the case of anaphylactic shock, the state of hypersensitivity is known as anaphylaxis. Subsequent exposure to the protein antigens produces rapid responses, marked by a severe fall in blood pressure, difficulty in breathing and sudden collapse (anaphylactic shock). Other effects seen are conjunctivitis, rhinitis, urticaria and increased heart beat rate. These responses are directly due to the release of histamine and other substances from cells affected by the antibody-antigen reaction.

Contact urticaria and anaphylactic reactions, following exposure to gloves, balloons, contraceptives and dental cofferdams have been described in several papers(142-143). The seriousness of anaphylaxis has been demonstrated in the number of life threatening reactions which have occurred during medical examinations and surgery(144–147). During such procedures, items containing latex (gloves, tubings etc) are in close contact with body tissues and mucous membranes, with their moist environment providing ideal conditions for the elution and absorption of the protein allergens(148). In fact many of reported cases of severe anaphylactic reactions including shock, have been caused by latex gloves.

In the United States, fatalities following anaphylactic responses during barium enema examinations were reported(149,150). It was found that the deaths were due to latex proteins in the cuffs. The extent of this latex allergy among common population is not known exactly, although probably it is maximum among hospital workers.

IMPLICATION OF PROTEINS

Several tests have been used to implicate latex articles and more specifically the proteins as the eliciting factor of these allergic responses. Dermatological testing on sensitized individuals, for example skin prick and patch tests, indicate sensitivity to rubber article(s), whilst *in vitro* assays such as radioallergosorbent test (RAST), enzyme-linked immunosorbent assays (ELISA) and histamine release from white cells (basophils)(144,151,152) have been employed to demonstrate that the allergens are latex proteins. The reduction of allergenicity by treatment with proteolytic enzymes is also evidence that the allergens are proteinaceous. Thus several natural rubber latex proteins are allergenic. Allergy to these proteins is a prototype hypersensitivity reaction. Immediate hypersensitivity is a subset of antibody-mediated pathophysiological responses that are mediated by antibodies of the immunoglobulin E (IgE) class(153).

PROTEINS IN NATURAL LATEX

Fresh latex contains a number of proteins, and the total protein concentration is about 1% m/m(154). The polypeptides associated with the rubber particles constitute about 26% of the total latex polypeptides(155). A major protein which is strongly adsorbed on rubber particles has been identified by Dennis and Light(156), which is named as rubber elongation factor (REF). The amino acid sequence in REF has been elucidated(157). REF is 137 amino acid long, has a molecular mass of 14.6kD and lacks four amino acids, cysteine, methionine, histidine and tryptophan, which are generally found in other latex proteins. Another protein tightly bound to rubber particles is prenyltransferase, a 38kD protein, which also has been sequenced(158). The B and C serum fractions of fresh non-ammoniated latex when analysed by sodium dodecylsulphate polyacrylamide gel electrophorisis (SDS-PAGE) showed major protein bands at 46, 29 and 14kD and minor bands at 90, 55, 40, 36, 24, 20, and 18 kD(159–161).

Two other proteins identified in latex sera are hevein (5kD) and hevamine (29kD)(162,163). The amino-acid sequence in hevein also has been elucidated(164). Ammoniation of field latex alters the proteins. Ammoniation results in the release of lutoid proteins into the serum by partial and probably total hydrolysis of some proteins. Aggregation of proteins or protein fragments also occur. Antigenicity of a few proteins originally from both B and C sera are retained(165). REF partly decomposes on ammoniation to a fragment of slightly lower molecular mass (12kD) and unidentified products. This has been demonstrated in both HA and LATZ concentrates (166).

EXTRACTABLE PROTEINS

Out of the total proteins present in latex or latex film, only a small fraction is extractable(167) by water or artificial saliva. This is termed as extractable protein (EP). Thus EP content in HA latex films is about 0.04mg/g rubber, whereas the total protein content in HA latex is 20–26mg/g rubber. Subramaniam(168) has reported the changes in EP levels brought about by latex processing variables. Thus fresh natural latex has a total protein content of about 30–50mg/g rubber. However, on filming only about 8mg/g protein are extractable. In preserved field latex EP content is about 11–12mg/g. Centrifuged latex concentrate has a total protein content of about 16–20mg/g rubber. EP content in fresh centrifuged latex is about 0.5 mg/g, which on storage can reach about 1mg/g. The very low values of EP for centrifuged latex is believed to be due to the removal of ions from the system, thus making the proteins less soluble. EP content in double centrifuged latex is lower than that in single centrifuged latex by 25–30%.

On compounding latex concentrate, EP content nearly doubles, probably due to the presence of soaps, potassium hydroxide and other ionic species. Heating compounded latex to produce prevulcanized latex increases the EP content. During the drying of prevulcanized film by heating there is a further sharp increase in EP. Post-vulcanized film shows a similar rise in EP on heating.

HOW MUCH PROTEIN IS EXTRACTABLE?

Dipped natural latex products contain two types of proteins: those tightly bound to rubber particles(156) and any serum derived protein(169) remaining after the leaching/washing procedures during product manufacture. The latter probably gives rise to most of the extractable protein. The amount of water extractable protein from a latex film is very much lower than the actual amount of proteins present in the rubber(167). The ratio of EP to total protein was estimated by comparing protein levels in commercial examination gloves with that observed in a film with a minimum of non-protein nitrogen(166,170). Dalrymple and Audley have reported a maximum of 6% as EP in films from once centrifuged latex(171). A corresponding figure for double centrifuged latex film is 0.6%(171).

EP CONTENT IN PRE - AND POST-VULCANIZED DIPPED FILMS

EP content in latex films differ depending on whether the film was prepared from prevulcanized latex, or post-vulcanized after preparing the film. It is observed that films from prevulcanized latices generally have higher EP content(169,172). Prevulcanized latex films have a more open structure than post-vulcanized films(137). Hence it would be easier to extract proteins from prevulcanized latex films.

IDENTIFICATION OF LATEX PROTEIN ALLERGENS

Three allergenic proteins of molecular mass 2, 5 and 30kD have been identified by gel permeation chromatography of extracts of surgical gloves and cleaning gloves(173). Allergenic reactions were established by skin prick test. Similar work on condoms showed the presence of a protein allergen in the molecular weight range 3–10kD(174). Using sodium dodecylsulphate polyacrylamide gel electro-phoresis (SDS-PAGE), in which proteins are fractionated according to molecular mass, at least ten allergenic proteins have been identified by various groups working on fresh latex, ammoniated concentrate and extracts of gloves and condoms. Allergens were found with molecular masses ranging from 2–100kD. Proteins of molecular mass 14kD (probably REF) and 21kD have been suggested as major allergens(161,175). Several research groups have described REF as a potential latex allergen(176–179). REF is also named as Hev bI(161). Two B-serum proteins β-1, 3 glucanase (Hev bII) and a component of the microhelix (Hev bIV) have been shown to be allergic by virtue of their binding to immunoglobulin E (IgE) from the blood serum or plasma of latex allergic patients(180). Hev bII appears as a doublet of molecular mass 34 and 36kD under reducing conditions of SDS-PAGE. Hev bIV appears as a band of 50–57kD under reducing conditions. Yagamil *etal*(181) have reported plant defense related proteins as potential allergens. They have reported the existence of esterase chitinase, lysozyme and β-1, 3 glucanase in all latex product extracts. A 20kD protein suggested to be clinically the most significant allergen is shown to be prohevein (hevein preproprotein)(176). A 27kD protein, recognized characteristically by latex allergic patients with spina bifida or other congenital anomalies and a 36kD protein are proved to be latex allergens(176). A 30kD protein allergen is shown to be hevamine. Beezhold *etal*(182) have identified a 46kD protein as a latex allergen.

LEVEL OF EP AND ALLERGINICITY

There had been some speculations that total EP content was not correlated to their allergen content. However, good correlation between the two parameters have been shown by Yip *etal*(183) who assessed the skin prick test allergic response with EP content of gloves(174). Significant correlation is observed between EP content in gloves and their allergen levels as assessed by IgE-RAST inhibition immunoassay(184). Gloves with high EP contents were generally found to have high allergen contents and vice versa. Gloves with EP levels of 100μg/g or below always had very low allergen contents(185) (< 9AU/ml). AU/ml-allergen unit/ml, is an arbitrary unit and the ratings are given in Table 2.4.

TABLE 2.4

Correlation between allergen content and allerginicity.

Allergen level (AU/ml)	***Allerginicity.***
< 10	Low
10 – 100	Moderate
>100	High

METHODS OF REDUCING EP IN LATEX PRODUCTS

Several methods have been suggested to reduce the EP content in dipped latex products. Important among these are described briefly.

i. Leaching

Leaching is an important step in the manufacture of dipped latex products for the purpose of removing the water extractable non-rubber materials so as to enhance the physical properties of the films. Leaching of latex films can reduce EP content also(168,170,186), but the extent of reduction is dependent on the conditions used in leaching. Effect of wet gel Vs dry film leaching, effect of leaching time and temperature and effect of thickness of the films have been studied by several groups(186,187). For prevulcanized film, where the latex already has a high EP value, wet gel leaching is quite effective. More than 85% of EP was removed by leaching in water for 5min. However, for post-vulcanized films, where EP content increases during vulcanization, wet gel leaching for 5min. removes only about 60% EP. For both pre-and post-vulcanized films, leaching of dry films for 5min removes upto 90% EP. The rate of EP reduction for prevulcanized latex films was found to be higher than that of post-vulcanized latex films due to the larger surface area of prevulcanized latex films(53). In leaching out proteins, water at room temperature appears to be as effective as at higher temperatures (50–70°C). Kamath and Abraham have reported that leaching in flowing water is more effective than static water(186). The higher the flow rate of water in the leaching tank, the less is the EP remaining in the leached film. The effect of hardness of leaching water in reducing EP was reported by Dalrymple and Audley(170). Lower the hardness of the water used for leaching, the better is the protein removal. Sequential extraction of once extracted sample after storing for a period, again showed some EP in subsequent extractions(169). Presumably the initial extraction is of protein from or near the glove surface and further smaller amounts arise by slow penetration of the extractant into the glove. However, the largest amount of protein is extracted in the first extract. Leaching solution containing an enzyme Savinase^R can reduce the allergic antigen to 0.5–3.0% and EP to 40–70% of the untreated glove(188). It has been reported that reduction of water extractable proteins in dry natural rubber latex films could be accelerated by incorporating ultrasonic waves into the leaching system(189). In presence of ultrasonic waves, leach water at higher temperature was more effective. It was also observed that leaching of latex films in the presence of ultrasonic waves did not affect the tensile strength of films both before and after ageing. Leaching in other solutions such as ammonia, potassium hydroxide, acetic acid, hydrochloric acid, SDS, cetyl pyridinium chloride have shown no improvement or only marginal improvement in reducing EP compared to water. Leaching has been used as a means of reducing EP in films prepared from radiation vulcanized natural rubber latex (RVNRL) films also(190,191). But the duration of leaching is generally a few hours and hence leaching is to be carried out off-line, followed by drying.

ii. Autoclaving

A combination of wet gel leaching, water rinsing and steam sterilizing (1h at 120°C) of gloves reduced extractable protein and allerginicity(192). In the autoclaving process, prevulcanized films and films to be post-vulcanized are wet gel leached under static conditions for 2min at 60°C. The films on mould are then treated with hot air or steam in an autoclave for specified periods at the desired temperature. Autoclaving in steam was more effective than hot air, the residual EP level being near the limit of detection(169). Steam appeared less effective in removing protein from post-vulcanized than prevulcanized films. Steam autoclaving can affect physical properties unless precautionary measures are taken at the compounding stage. Also, it does not seem likely that autoclaving could be used on a large scale to produce articles of low allerginicity. It is possible that the switch over from the use of steam-sterilized to disposable gloves has partly contributed to the spread of allergy to latex proteins.

iii. Chlorination

Chlorination is one among the best available methods for reducing the extractable protein content in latex products(169,170,193). Initially chlorination was used as a method for providing a non-drag surface to dipped latex products(194). Aqueous chlorination of natural rubber surfaces involves the reaction of chlorine with natural rubber via an anionic mechanism to form carbonium ions(195). The carbonium ion formed can react by addition of chlorine, crosslinking with each other, cyclisation and oxidation depending on the pH of solution.

Chlorination of gloves and other latex products initially involves only a surface reaction. Depending on the thickness of the glove and time and concentration of the chlorinating solution, the reaction can proceed to the inside. Composition of a typical chlorinating solution(193) is given in Table 2.5.

TABLE 2.5

Composition of chlorinating solution

Ingredient	*Parts by weight*
Sodium hypochlorite (10%)	1.0
Conc. hydrochloric acid	0.3
Water	98.7

The proportion of glove to water is ideally 1:10 to 1:40. After chlorination, the films are properly washed and dried. By using chlorine concentration of 0.01 to 0.05, EP content can be reduced to about 10–20mg/kg.

However, strength and colour of the gloves tend to reduce upon chlorination, unless carried out at very low concentration. Prolonged chlorination results in the development of cracks on the surface.

iv. Use of proteolytic enzymes

The proteolytic enzymes function by hydrolyzing the peptide bonds of the proteins to produce smaller peptide units and amino acids(196). Commercially available and relatively cheap proteolytic enzymes Alcalase^R and Savinase^R have been examined for their effects on EP and the allerginicity of dipped goods(197). Alcalase^R has a destabilizing effect on latex. Hence natural latex is treated with this enzyme in presence of a suitable colloidal stabilizing system, followed by centrifugal concentration. Dipped films made from this enzyme treated latex show soluble protein levels of 5–65% of normal untreated films. However, protein allergen level as measured by histamine release, was reduced to 0.2 to 1.5% of the normal untreated latex film.

Savinase^R was used in on-line wet gel leaching before vulcanization and also to treat finished gloves. Latex gloves produced by Savinase^R leaching of latex gel showed soluble protein level of 40–70% of normal untreated glove, while the latex allergen level was only 0.5 to 3% of untreated glove. Off-line leaching of latex gloves with Savinase^R under controlled conditions for 30–300 sec reduces EP level to 6–44% of untreated glove and the allergen level of 0.2 to 1% of normal untreated glove.

Thus off-line leaching with Savinase^R is the best among the enzyme treatment. However, proteolytic enzymes are proteins and it is not unlikely that their use could possibly lead to a new allergy(191)

v. Use of low protein latex

An enzymically produced low protein latex concentrate, Loprol, has been developed at the Rubber Research Institute of Malaysia(198). Films prepared from Loprol, using different formulations show EP content in the range 30–100mg/kg.

A similar figure for ordinary HA cenex is in the range 400–800mg/kg and so far no reports are available on the allerginicity of articles made out of Loprol.

However, Loprol is generally higher in non-rubber solids and low in mechanical stability time compared to standard HA latex concentrate. Also, both in the case of pre-and post-vulcanized Loprol films, tensile properties are less, both before and after ageing compared to HA latex concentrate. Even though developed in 1993, Loprol is not yet available commercially, possibly because of its high cost and low physical properties of the films.

vi. Use of non-ionic surfactant

Another method of deproteinizing natural latex by displacement with a non-ionic surfactant has been reported(199). Latex is initially diluted to about 10% DRC, stabilized with 1%w/v of a non-ionic stabilizer (Triton X 100) and concentrated to 60% DRC. The process of dilution and concentration is repeated several times to achieve the desired level of deproteinization. It is observed that the tensile properties of deproteinized latex film is similar to that of ordinary HA latex film. However, repeated dilution to low DRC and concentration makes the process uneconomic. There has been a recent report from China also on the preparation and the properties of deproteinized natural rubber latex(200).

SCOPE OF THE PRESENT WORK

Widespread use of latex products has made a section of the people sensitive to latex proteins and cause allergic reaction like contact urticaria and anaphylaxis upon contact with latex products. Health-care workers as a group, are identified to be a high risk group, due to constant and prolonged use of latex products like gloves. The currently available methods of reducing extractable protein content in latex films and products are leaching, either as wet gel or dry film, autoclaving, chlorination, enzymic deproteinization etc. Generally, on-line leaching is very short and appreciable portion of extractable proteins is still retained in the article. Off-line leaching of dry vulcanized films is generally long and the product has to be again dried. This is an expensive step. Also prolonged leaching removes some of the antioxidants. This is an issue of great concern as the area to volume ratio is very high in dipped latex products. Dry latex films which are initially leached to remove soluble proteins, after storage for a period again show extractable proteins in them. This is believed to be due to the slow migration of soluble proteins from the inner layers to the surface. Thus leaching cannot ensure absence of EP at the user level. In the case of thick articles leaching is not very effective as a means of reducing EP. Autoclaving and chlorination can result in fall in tensile properties. Chlorination also results in yellowing of the latex film.

Removal of as much proteins as possible from the latex itself is a better solution to the present problem. This will result in a situation where soluble proteins are not available in the film in quantities sufficient to provide appreciable levels of EP for migration to the surface. The methods currently described in the literature for the production of deproteinized latex are rather expensive and cumbersome as the process involve treatment of latex with enzyme followed by dilution to 2-10% DRC and concentration by centrifuging. Further, dilution and concentration have to be repeated several times. Enzyme treatment at the latex stage also leads to some extent of colloidal destabilization. Also the tensile properties of films prepared from deproteinized latex are inferior compared to conventionally vulcanized ordinary HA latex films(198).

Availability of latex products which are free from extractable proteins (or atleast very low in extractable proteins), and having good tensile properties at reasonable prices, is now very much desired. In the light of the above, it was decided to investigate the development of a process of making modified natural latex from which much of soluble proteins have been removed. It will be an added advantage if the proposed method does not adversely affect the colloidal stability of latex. It has been reported that non-rubber substances such as proteins and lipids have significant effects on the behaviour of latex(201-203) and the physical properties of rubber(204). Proteins and amino acids have been inferred to be responsible for the branching and crosslinking of NR and also influence storage hardening, moisture absorption and dynamic properties(204,205). In this context the following investigations have been taken up.

- Identification of suitable chemical(s), having surfactant activity, capable of displacing at least the easily displaceable proteins from the rubber-serum interface to give a latex low in extractable proteins and to evaluate its raw latex properties.
- Behaviour of this latex in sulphur vulcanization (pre and post-vulcanization) as the vulcanization characteristics of natural latices are influenced by proteins.
- Radiation vulcanization of natural latex involves the diffusion of sensitizer into the latex particles, followed by crosslinking via hydrated electrons generated inside the latex particles. Removal of soluble proteins from rubber-serum interface may alter this crosslinking behaviour. Hence radiation vulcanization characteristics of this low protein latex were evaluated.
- Leaching of latex films, either at wet gel stage or as dry film is carried out for reducing type IV allergic reactions and improves physical properties. Leaching under different conditions were carried out to understand the changes in physical properties and extractable protein content in leached films.
- Generally the modulus of LPL films is low and in certain applications like medical tubing higher modulus is desirable. Hence, studies were undertaken on the reinforcement of low protein latex using silica.
- Introducing polypropylene glycol, alters the interface between rubber and water. Hence, the rheological behaviour of the latex was evaluated.
- Application of this modified latex in the production of examination gloves.

This thesis is divided into the following chapters.

Chapter 1 Introduction.

Chapter 2 Survey of literature.

Chapter 3 Materials compounding, sample preparation and testing procedures.

Chapter 4 Preparation and properties of low protein latex.

Chapter 5 Vulcanization characteristics of low protein latex.

  A. Vulcanization of low protein latex in conventional sulphur cure system.

  B. Vulcanization of low protein latex in EV (efficient vulcanization) cure system.

  C. Radiation prevulcanization of low protein latex.

Chapter 6 Rheological behaviour of low protein latex.

Chapter 7 Application of low protein latex in the production of examination gloves.

Chapter 8 Summary and Conclusions.

REFERENCES

1. D.C.Blackley. Polymer Latices: Science and Technology (Second Edn.), Chapman & Hall, London, Vol.1 Chapter 1, (1997).

2. D.C.Blackley. Polymer Latices: Science and Technology (Second Edn.), Chapman & Hall, London Vol.2 Chapter 9, (1997).

3. G. Verhaar. *Rubb. Chem. Technol.* **29**, 1484 (1956).

4. K.F.Gazeley, A.D.T.Gorton, T.D.Pendle, in Natural Rubber Science and Technology, A.D.Roberts (Ed.), Oxford University Press. Oxford Chapter.3, (1998).

5. D.C.Blackley. Ploymer Latices: Science and Technology (Second Edn.) Chapman & Hall. London, Vol.1, Chapter 3, (1997).

6. R.T.Davies. Proc. of Seminar on Latex Processing Technology: Understanding its Science. Hertford, p-1, (1991).

7. C.K.John. Proc. RRIM Planters' Conf., p-278, (1972).

8. J.S.Lowe. *Trans. Instn. Rub. Ind.* **36**, 202 (1960).

9. D.H.Taysum. Proc. Natural Rub. Res. Conf., Kuala Lumpur, p-834, (1960).

10. C.K.John, M.Nadrajah, P.S.R.Rao, C.M.Lan, C.S.Ng. Proc. Int. Rubber Conf., KualaLumpur, Vol. 4, p-339, (1975).

11. P.S.R.Rao, C.K.John, C.S.Ng, M.G.Smith, C.F.Robert. Proc. RRIM Planters' Conf. Kuala Lumpur, p-324, (1976).

12. N.P.Wong, C.K.John, H.C.Chin. *Planters' Bull.* **188**, 97(1986).

13. K.O.Calvert, T.Y.Tan, R.J.Prichards, P.Sundaram, *Plastics and Rubber Processing and Applications*. **3**, 137 (1983).

14. C.K.John. Proc. National Workshop on Latex and Latex Products. Kuala Lumpur, p-19, (1983).

15. C.Petri, G.Lottmann and T.D.Pendle. Proc. Int.Rubber Conf. Kuala Lumpur, p-71, (1997).

16. C.K.John, N.P.Wibg, H.C.Chin, A. Latiff and H.S.Lim. Proc. RRIM Rub. Growers' Conf. Kuala Lumpur, p-320, (1986).
17. ISO 2004-1997 (E), Rubber Latex, Natural Centrifuged or Creamed, ammonia preserved types-specification.
18. IS 5430-1981, Indian Standard Specifications for ammonia preserved concentrated natural rubber latex (first revision).
19. IS 11001-1984, Indian Standard Specifications for double centrifuged natural rubber latex.
20. IS 13101-1991, Indian Standard Specifications for ammonia preserved creamed natural rubber latex.
21. ASTM D 1070-97, Standard Specifications for Rubber–Concentrated, Ammonia preserved, Creamed and Centrifuged Natural Latex.
22. K.F.Gazeley, A.D.T.Gorton and T.D.Pendle. In Natural Rubber Science and Technology, A.D. Roberts (Ed), Oxford University Press, Oxford, Chapter 4, (1988).
23. D.C.Blackley. Polymer Latices, Science and Technology, Chapman & Hall, London, Vol.3, Chapter 15, (1997).
24. A.D.T.Gorton and T.D. Pendle, N.R.Technol. 12, 21 (1981).
25. C.Petri and T.D.Pendle. Proc. Int. Rub. Conf. Chennai, India, p-627, (1998).
26. D.C.Blackley, Polymer Latices: Science and Technology. Chapman & Hall, London, Vol.3, Chapter 16, (1997).
27. M.W.Philpott. Proc. Fourth Rub. Technol. Conf.London, p-470, (1962).
28. J.R.Dunn. *Trans. Instn. Rub. Ind.* **34**, 249 (1958).
29. R.T.Davis. Proc. Seminar on 'Latex Technology and Processing'. Hertford, p-79, (1992).
30. C.W.Evans. Practical Rubber Compounding and Processing. Applied Science Publishers London, Chapter 2, (1981).

31. N.P.Wong and C.T.Loo. Proc. Int. Rubber Conf. Kuala Lumpur, p-487, (1985).

32. G.A.Blokh. Organic Accelerators in Vulcanization of Rubber. IPST Jerusalem, Chapter 1, (1968).

33. R.W.T.Merril. M.Phil. Thesis. Polytechnique of N. London (1980).

34. A.M.D.Rosa, L.V.Abad, L.P.S.Ana-Rollerc, C.O.Tranquilar-Aranilla and C.L.Pascual Proc. Second Int. Sym. on RVNRL, Kuala Lumpur, p-15, (1996).

35. R.J.Noble. Latex in Industry, Rubber Age, New York, Chapter 8, (1953).

36. L.R.G.Treloar. Rep. Progr. Phys. (36), 755 (1973).

37. P.J.Flory. Principles of Polymer Chemistry. Cornel University Press, New York, Chapter 11, (1953).

38. D.S.Campbell. Proc. Seminar on Latex Processing Technology: Understanding its Science. Hertford, p-37, (1991).

39. B.A.Dogadkin, Z.N.Tarasora and I.I.Gol berg. Proc. Fourth Rubber Technol. Conf. London, p-65, (1962).

40. L.C.Teik and W.N.Poh. Developments in Plastics and Rubber Product Industries. Plastics and Rubber Institute of Malaysia, Kuala Lumpur, p-265, (1987).

41. E.R.Rodger. Developments in Rubber Technology. Vol.1, A.Whelan and K.S.Lee. (Ed) Applied Science Publishers. London, p-105, (1979).

42. L.Bateman, C.G.Moore, M.Porter and B.Saville. The Chemistry and Physics of Rubber-like Substances. Ed. L.Bateman. Mac Laren, Chapter15, (1963).

43. A.V.Chapman and M.Porter. Natural Rubber: Science and Technology A.D.Roberts (Ed). Oxford University Press Oxford, Chapter 12, (1988).

44. M.D.Morris. Proc. Seminar on Latex Processing and Technology. Hertford, p-41, (1992).

45. M.Porter. Proc. Int. Rub. Technol. Conf. Penang Malasia, p-26, (1988).

46. D.C.Blackley. Polymer Latices: Science and Technology. Vol. 2 chapter 13. Chapman & Hall, London, Vol. 2 Chapter 13, (1997).

47. P.Schidrowtiz. British Patent No. 193, 451 (1923).

48. A.C.P.Loh. Ph.D.Thesis. Ploytechnique of N. London, (1982).

49. D.C.Blackley. In *Encyclopedia of Polymer Science and Engineering*. John Wiley and Sons. New York. **8**, 665 (1987).

50. D.C.Blackley. Proc. Int. Rub.Technol. Conf. Kuala Lumpur, p-3, (1988).

51. E.H.Low. Proc.RRIM Planters' Conf. Kuala Lumpur, p-307, (1977).

52. A.D.T.Gorton. *N R Technol.* **10**, 9 (1979).

53. A.D.T.Gorton. Proc. Int. Rub. Technol. Conf. Kuala Lumpur, Penag, Malaysia, p-85, (1988).

54. N.C.H.Humphreys and W.C.Wake. *Trans. Instn. Rub. Ind.* **25**, 334 (1950).

55. O.Siswantoro. Ph.D.Thesis. Polytechnique of N. London (1985).

56. N.M.Claramma, N.M.Mathew. *J. Appl. Polym. Sci.* **65**, 1913 (1997).

57. N.J.Morrison and M.Porter. *Rub. Chem. Technol.* **57**, 63 (1984).

58. C.T.Loo. *Polymer* **15**, 357 (1974).

59. G.M.Bristow and R.F.Tiller. *Kautschuk Gummi* **23(2)**, 55 (1970).

60. H.M.Ghazaly. M.Phil Thesis. Polytechnique of N. London (1988).

61. T.I.Geller, D.M.Sandomirskii, Z.M.Ustinova, N.M.Fodiman and B.A.Dogadkin. *Koll. Zhur.* **25**, 291 (1963).

62. Z.M.Ustinova, N.M.Fodiman, T.I.Geller, D.M.Sandomirskii and B.A.Dogadkin. *Koll. Zhur.* **27**, 773 (1963).

63. J.W.van Dalfsen. *Rub. Chem. Technol.* **16**, 318 (1943).

64. G.E.van Gills. *Rub. Chem. Technol.* **50**, 144 (1977).

65. M.Porter, R.Rawi and S.A.Rahim. *J. nat. Rub. Res.* 7, 85 (1992).

66. M.Porter. In. Advances in Rubber Technology. Tata Mc Graw Hill Publishing Co. New Delhi, Chapter 23, (1989).

67. K.F.Gazeley. Polymer Latex II. Conf. The Plastics and Rubber Institute London, 18/1, (1985).

68. K.L.Chong and M.R.Porter. Int. Polymer Latex Conf. London (1978).

69. N.R.Peethambaran and T.K.George. *J. Appl. Polym. Sci.* **40**, 1627 (1990).

70. S.Hamzah, J.B.Gomez and P.S.R.Rao. *J. nat. Rub. Res.* **2**, 118 (1987).

71. S.Hamzah, J.B.Gomez and P.S.R.Rao. *J. nat. Rub. Res.* **4**, 41 (1989).

72. D.M.Stevens. British Patent No. 324 287 (1930).

73. G.Stott. British Patent No. 738 279 (1951).

74. R.T.Davis. Proc. Seminar on Latex Technology and Processing Herford, p-79, (1992).

75. R.T.Davis and K.F.Gazeley. *J nat. Rub. Res.* **8**, 176 (1993).

76. M.M.Said, T.D.Pendle and D.C.Blackley. *J. nat. Rub. Res.* **5**, 27 (1990).

77. M.M.Said, T.D.Pendle and D.C.Blackley. *J. nat. Rub. Res.* **6**, 158 (1991).

78. M.M.Said. Proc. Int. Rub. Conf. Kobe, Japan, p-43, (1985).

79. P.E.F Cudby and R.T. Davies. *J. nat. Rub. Res.* **12**, 67 (1997).

80. Y.Minoura and M. Asao. *J. Appl. Ploym. Sci.* **5**, 233 (1961).

81. Y.Minoura and M. Asao. *J. Appl. Ploym. Sci.* **5**, 401 (1961).

82. K.Makuuchi and V. Markoni. *IAEA Bull.* **33(1)**, 25(1991).

83. K.Makuuchi. Progress in Radiation Vulcanization of Natural Rubber Latex. RVNRL Consultant Meeting, Vienna (1995).

84. A.Nakamura, Y.Ikavashi, T.Tsuchiya and M.Kaniova. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex, JAERI-M 89, p-79, (1989).

85. T.Tsuchiya, Y.Ikarashi, K.Toyoda, T.Uchima, T.Miyahara, M.Takahashi and A. Nakamura. *Radiat. Polym. Chem.* **39**, 541 (1992).

86. K.Makuuchi and K.Tsushima.Proc. Int. Rub. Conf. Kuala Lumpur, p-502, (1985).

87. K.Makuuchi and K.Tsushima. *J. Soc. Rub. Ind. Japan*. **61**, 478 (1988).

88. C.Zhonghai and K.Makuuchi. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI - M-89-228, p-326, (1989).

89. S.Sabharwal, T.N.Das, C.V.Chaudhari, Y.K.Bhardwaj and A.B.Majali. *Radiat. Phys. Chem.* **51**, 309 (1998).

90. E.B.Bradford. *J. Appl. Phys.* **23**, 609 (1952).

91. R.E.Dillon, L.A.Matheson and E.B.Bradford. *J. Colloid Sci.* **6**, 108 (1951).

92. J.W.Vanderhoff, H.L.Tarkowski, M.C.Jenkins and E.B.Bradford. *J. Macromolecular Chem.* **1**, 361 (1966).

93. B.L.Archer, D.Barnad, E.G.Cockbain, P.D.Dickenson and A.I.Mac Mullen. In *The Chemistry and Physics of Rubber–like Substances*. L.Bateman (Ed.) Maclarn, London, Chapter 3 (1963).

94. M.Y.Amir-Hashim, M.D.Morris, M.G.O'brian and A.S.Farid. *Rub. Chem. Technol.* **70**, 560 (1997).

95. D.C.Balckley. High Polymer Latices. Maclaran & Sons Ltd. London, Vol. 1 Chapter 7, (1966).

96. E.A.Collins, C.A.Daniels and J.A.Davidson. *Elastomerics* **110(3)**, 31 (1978).

97. D.C.Blackey. Polymer Latices: Science and Technology.(second Edn.), Chapman & Hall. London, Vol.1.Chapter 6, (1997).

98. S.H.Maron and P.E.Pierce.*J.Colloid Sci.* **11**, 80 (1956).

99. R.V.Williamson.*J.Rheol.* **1**, 283 (1930).

100. R.S.Lenk.*J.Appl.Polymer Sci.***11**, 1033 (1967).

101. H.F.Smith.*J.Rubber Rs.Ins.Malaya* **11**, 44 (1941).

102. A.D.T.Gorton and P.E.Swinyard.*NR Technol.* **10**,73 (1979).

103. G.L.Brown and B.S.Garrett. *J.Appl. Polymer Sci.***1**, 283 (1959).

104. W.D.Schroeder and G.L.Brown. *Rub. Age* **69**, 433 (1951).

105. L.Leaman.*Rub. Age* **75**, 537 (1954).

106. E.Rhodes.*India-Rubber J.***97(1)**, 21 (1939).

107. S.H.Maron and S.M.Fok.*J.Coll.Sci.***10**, 482 (1955)

108. P.H.Johnson and R.H.Kelsey. *Rub. World.***138**, 877 (1958).

109. J.T.Varkey, S.Rao and S.Thomas. *Plastics Rubber and Composites Processing and Applications*. **23(4)**, 249 (1995).

110. N.R.Peethambaran, B.Kuriakose, M.Rajan and A.P.Kuriakose. *J.Appl. Polym. Sci.* **41**, 980 (1990).

111. D.C.Blackey and R.S.Charnock.*J.Instn.Rub. Ind.* **7**, 60 (1973).

112. J.T.Varkey, S.Thomas and S.Rao.*J.Appl.Polym. Sci.* **56**, 451 (1995)

113. E.Rhodes. *India-Rubber J.* **97 (2)**, 51 (1939)

114. N.M.Claramma and N.M.Mathew. *Kautschuk Gummi Kunststoffe* **51(2)**, 126 (1998).

115. N.R.Peethambaran and A.P.Kuriakose. *Indian J.Natural Rubber Res.* **1**, 1 (1988).

116. N.R.Peethambaran and A.P.Kuriakose. *Kautschule Gummi Kunststiffe* **42**, 1118 (1989).

117. L.Jose and R.Joseph. *Kautschuk Gummin Kunststoffe*. **46**, 220 (1993).

118. van Rossem and J.A.Plaizier.Proc. Rubber Technol. Conf. London, p-97, (1938).

119. S.Amdur, W.J.Hintz and R.Lancer/Carter Wallace Inc. International Patent Application No. WO 90/00890, 8 Feb. 1990.

120. N.M.Claramma, L.Varghese and N.M.Mathew, *J.Elastomers and Plastics*. **31**, 130 (1999).

121. B.A.Dogadkin, L.G.Senaatorskaya, V.I.Guseva, A.V.Sushyakov and P.I.Zakharchenko. *ColloidJ.(U.S.S.R)* **18**, 523 (1956).

122. A.D.T.Gorton. *J. Rub. Res. Inst. Malaya* **20**, 27 (1967).

123. D.C.Blackley, W.F.H.Burgar and B.A.W.Shukri. Preprints of Plastics and Rubber Institute Emulsion Polymers Conf. London, Paper no.9, (1982).

124. D.C.Blackley, Polymer Latices: Science and Technology. (Second Edn.). Chapman & Hall.London, Vol.1 Chapter 5, (1997).

125. D.C.Blackley and bt A.Asiah. *Plastics and Rubber. Materials and Applications* **4**, 103 (1979).

126. E.G.Cockbain. *Trans. Instn. Rub. Ind.* **32**, 97 (1956).

127. T.D.Pendle. Dipping with Natural Rubber Latex. NR Technical Bulletin. The Malaysian Rubber Producers Research Association Brickenbury, U.K.(1995)

128. D.M.Bratby. In 'Polymer Latices and their Applications'. K.O.Calvert (Ed.) Applied Science Publishers Ltd. London, Chapter 9, (1982).

129. D.C.Blackley. Polymer Latices: Science and Technology (Second Edn.) Chapman & Hall. London, Vol.3, Chapter 18, (1997).

130. E.W.Madge. Latex Foam Rubber. Maclaran, London, Chapter 7, (1962).

131. W.H.Chapman, D.W.Pounder and E.A.Murphy/Dunlop Rubber Co. Ltd. British Patent No. 332 525, (1930).

132. J.A.Talalay. British Patent No. 455 138. (1936).

133. D.C.Blackley. Polymer Latices: Science and Technology (Second Edn.), Chapman & Hall, London, Vol. 3, Chapter 23, (1997).

134. T.D.Pendle and A.D.T.Gorton. In 'Polymer Latices and their Applications'. K.O.Calvert (Ed.) Applied Science Publishers Ltd., London, Chapter 11, (1982).

135. D.C.Blackley. Polymer Latices: Science and Technology (Second Edn.) Chapman and Hall, London, Vol.3. Chapter 22, (1997).

136. M.Nadarajah and S.Ganeshasundaram. *J. Rub. Res. Inst. Malaya,* **22**, 423 (1969).

137. E.Cronin. Contact Dermatitis. Churchil Livingstone London (1980).

138. A.F.Nutter. *Brit. J. Dermatol.* **101**, 597 (1979).

139. K.Turjanmaa and T.Reunala. *Dermatological Clinics* **6**, 47 (1988).

140. K.Turjanmaa T.Reunala, R.Tuimala and T.Karkkainen. *Allergy* **39**, Suppliment 2, Abst. 35 (1984).

141. C.Morales, A.Basomba, J.Carreira and A.Sastre. *Clinical and Experimental Allergy.* **19**, 425 (1989).

142. J.S.Taylor, J.Cassettari, W.Wagner and T.Helm. *J. American Acad. Dermatol.* **21**, 874 (1989).

143. G.L.Sussonan, S.Tarlo and J.Dolovich. *J American Medical Association.* **265**, 2844 (1991).

144. J.E.Slater. New English *J. Medicine.* **320,** 1126 (1989).

145. K.Peequet, F.Laynadier and J.Dry. *J American Acad. Dermatol.* **22**, 631 (1990).

146. J.Swartz, B.M.Braude, R.F.Gilmour, B.Shandling and M.Gold. *Canadian J. Anaesth.* **37**, 589 (1990).

147. M.Gold, J.S.Swartz, B.M.Braude, J.Dolovich, B.Shandling and R.F.Gilmour. *J. Allergy Clin. Immunol.***87**, 662 (1991).

148. A.C.Garber, W.Jorg, S.Zbindon, R.A.Sajeev, P.H.Dangel *Anesthesiology.* **71**, 800 (1989).

149. D.W.Gelfand. *American J. Radiol.* **156**, 1 (1991).

150. D.K.Ownby, M.Tomlanovich, N.Sammons and J.Mc Cullough. *American J. Radiol* **156**, 903 (1991).

151. F.Leynadier, C.Pecquet and J.Dry. *Anasthesia.* **44**, 547 (1989).

152. K.Turjannama, L.Rasanen, M.Lelito, S.Makinan-Kiljunen and T.Reunala. *Allergy* **44**, 181 (1989).

153. D.A.Levy. Int. Conf. on Latex Protein Allergy: the present position. Amsterdam, p-33, (1993).

154. B.L.Archer and B.C.Sekhar. *Biochem. J.* **61**,503 (1955).

155. S.J.Tata. *J. Rub. Res. Inst. Malaysia* **28**, 77 (1980).

156. M.S.Dennis and D.R.Light. *J. Biol. Chem.* **264**, 18608 (1989).

157. M.S.Dennis, W.J.Hengel, J.Bell, W.Kohr and D.R.Light. *J. Biol. Chem.* **264**, 18618 (1989).

158. D.R.Light and M.S.Dennis. *J. Biol. Chem.* **264**, 18589 (1989).

159. B.Arreguin, P.Lara and R.Rodriquez. *Electrophoresis.* **9**, 323 (1988)

160. H.Hasma. *J.nat. Rub. Res.* **7**, 102 (1992).

161. J.E.Slater and S.K.Chhabra. *J. Allergy Clin. Immunol* **89**, 673 (1992).

162. H.I.Lee, W.F.Brockacrt and N.V.Raikhel. *J. Biol. Chem.* **256**, 15944 (1991).

163. P.A.Jekel, B.H.Hartmann and J.J.Beintema. *Eur. J. Biochem.* **200**, 123 (1991).

164. K.Walujono, R.A.Scholma, J.J.Beintema, A.Mariono and A.M.Hahn. Proc. Int. Rub. Conf. Kuala Lumpur 4, 518 (1975).

165. R.G.O.Kekwick. Int. Conf. on Latex Protein Allergy: the Latest Position. Amsterdam, p-21, (1993).

166. B.G.Audley. Proc. Seminar on Recent Advances in Latex Technology. Hertford, p-19, (1993).

167. H.Hasma. Proc. IRTC '93 Wkshop on Latex Proteins. Rubber Research Institute of Malaysia, Kuala Lumpur, p-27, (1994).

168. A.Subramaniam. Proc. Int. Latex Conf. Sensitivity to Latex in Medical Devices Baltimore, paper 51, (1992).

169. B.G.Audley and S.J.Dalrymple. Proc. Seminar on Latex Processing Technology: Understanding its Science Hertford, p-69, (1991).

170. S.J.Dalrymple and B.G.Audley. *Rub. Developments* **45 (2/3)**, 51 (1992).

171. K.F.Gazeley, A.D.T.Gorton and T.D.Pendle. In *Natural Rubber Science and Technology*. A.D.Roberts (Ed). Oxford University Press, p-99, (1988).

172. S.J.Dalrymple and B.G.Audley. Proc. Seminar on Latex Technology and processing. Hertford, p-63, (1992).

173. K.Turjanmma, K.Laurila, S.Makinen-Kiljunen and T.Renula. *Contact Dermatitis* **19**, 362 (1988).

174. K.Turjanmma and T.Renula. *Contact Dermatitis* **29**, 360 (1989).

175. H.Alenius, K.Turjanmma, T.Palosuo, S.Makinen-Kiljunen and T.Renuala. *Int. Arch. Allergy Appl. Immunol* **96,** 376 (1991).

176. T.Palosno. Proc. Int. Con. on Latex Protein Allergy: the Latest Positon. Paris, p-11, (1995).

177. X.Baur, Z.Chen and A.B.Czuppon. Proc. Int. Conf. on Latex Protein Allergy the Latest Position. Paris, p-17, (1995).

178. A.B.Czuppon, Z.Chen, S.Rennert, T.Engelke, H.E.Meyer, M.Herber and X.Baur. *J. Allergy Clin. Immunol.* **92**, 690 (1993).

179. D.P.S.T.G.Attanayaka, R.G.O.Kekwick, S.Herath and F.C.H.Franklin. Proc. Sym. on the Technology and End Uses of Natural Rubber. Beruwela, Sri Lanka, p-21, (1996).

180. R.Sunderesan, S.Hamzah, S.Hamid, M.A.Ward, H.Y.Yeang and M.J.Cadrosa. *J. nat. Rub. Res.* **10**, 82 (1995).

181. T.Yagami, M.Sato and A.Nakamura. *J. nat. Rub. Res.* **10**, 100 (1995).

182. D.H.Beezhold, G. Sussman, D.A.Kostyal and N.S.Chang. *Clin. Exp. Immunol.* **98**, 408 (1994).

183. E.Yip, N.K.Poon, M.K.Lang, K.Turjanmma. Proc. Int. Con. on Latex Protein Allergy : the Latest Position. Paris, p-33, (1995).

184. J.Yunginger, R.Jones, A.Fransway, J.Kelso, M.Warner, L.Hant and C.Reed. *J. Allergy Clin. Immunol.* **93,** 836 (1994).

185. E.Yip, T.Palosuo, H.Alenins and K.Turjanmaa. *J. nat. Rub. Res.* **12**, 120 (1997).

186. S.R.Kamath and M.S.Abraham. Proc. Int. Latex Conf. Sensitivity to Latex in Medical Devices. Baltimore, p-32, (1992).

187. A.H.M.Yatim. Proc. IRTC '93 Wkshop on Latex Proteins. Kuala Lumpnur, p-51, (1994).

188. E.Neils. Proc. Int. Latex Conf. Sensitivity to Latex in Medical Devices. Baltimore, p-34, (1992).

189. A.H.Eng, S.Kodama and H.Kawasaki. *J. Rub. Res.* **2**, 23 (1999).

190. W.M.W.Zin and N.Othman. Proc. Second Int. Sym. on RVNRL. Kuala Lumpur, p-115, (1996).

191. W.Bez. Pro. Second Int. Sym. on RVNRL. Kuala Lumpur, p-121, (1996).

192. F.Leynadier, T.T.Xuan and J.Dry. *Allergy* **46**, 619 (1991).

193. N.A.B.Aziz. Proc. IRTC '93 Wkshop on Latex Proteins. Rubber Research Institute of Malaysia, Kuala Lumpur, p-59, (1994).

194. Natural Rubber Technical Information Sheet. Latex Series. L17. Malaysian Rubber Producers Research Association, U.K. (1977).

195. T.C.K.Noakes. Proc. Int. Rub. Technol. Conf. Penang, p-288,(1988).

196. L.M.Barclay. Latex Protein Allergy: the Latest Position. Int. Conf. Paris, p-41, (1995).

197. E.Niels. Proc. Int. Latex Conf. Sensitivity to Latex in Medical Devices, Baltimore, p-34, (1992).

198. H.M.Ghazaly. Proc. IRTC '93 Wkshop on Latex Proteins, Kuala Lumpur, p-81, (1994).

199. N.Ichikawa, E.A.Hwee and Y.Tanaka. Proc. Int. Rub. Technol. Conf. Kuala Lumpur, p-101, (1993).

200. M.F.Huang, Y.Vhen, K.Xu, X.Yuan, X.Chen and G.Wang. Preprints of the International Rubber Research and Development Board Conference, China (1999).

201. T.Okita. *Rubber Chem. Technol.* **10,** 279, (1937).

202. R.J.Noble. *Rubber Chem.Technol.* **12**, 692 (1939).

203. S.Balruddin. M.Sc. Thesis, School of Industrial Technology, Sains University, Malaysia (1991).

204. S.Nair. *Rub. World* **198(4),** 27 (1988).

205. A.H.Eng, S.Kawahara and Y.Tanaka. *J.nat. Rub. Res.* **8**, 109 (1993).

CHAPTER 3

COMPOUNDING, SAMPLE PREPARATION AND TEST PROCEDURES

This chapter deals with the materials used in latex compounding methods, sample preparation and testing procedures adopted in the present investigations.

MATERIALS

FIELD LATEX

Field latex, collected from the experiment station of the Rubber Research Institute of India, was used in the study. After tapping, latex was collected before any tendency for precoagulation was observed. Field latex was sieved through 40 mesh sieve followed by 60 mesh to remove contaminants. The sieved latex was preserved with ammonia to the extent of about 1% by mass(1). This high ammonia (HA) preserved latex was used for preparing concentrated latex. Properties of field latex used in this investigation are given in Table 3.1.

TABLE 3.1

Properties of field latex

Property	*Value*
Dry rubber content, % m/m	32.15
Total solids content, % m/m	35.36
Non-rubber solids content, % m/m	3.21
Alkalinity as ammonia, % m/m	0.96
Magnesium content, % m/m	0.024
Volatile fatty acid number	0.022

CENTRIFUGED LATEX

High ammonia preserved field latex was treated with calculated amount of diammonium hydrogen phosphate(2) to precipitate almost completely the magnesium ions present in the latex. In the presence of ammonia, the added phosphate precipitates magnesium as insoluble magnesium ammonium phosphate.

$$Mg^{+2} + NH_3 + HPO_4^{-2} \rightarrow Mg(NH_4)PO_4$$

Sufficient time is allowed to sediment the sludge and the desludged field latex is concentrated using an Alpha Laval latex separator Model LRB 510. Concentrated latex obtained was ammoniated further as high ammonia centrifuged latex (HA cenex), which conformed to the specifications of the Bureau of Indian Standards, IS: 5430–1981. Properties of HA cenex used in the present study are given in Table 3.2.

TABLE 3.2

Properties of HA cenex

Property	*Value*
Dry rubber content, % m/m	60.04
Total solids content, % m/m	61.56
Non-rubber solids content, % m/m	1.52
Sludge content, % m/m	0.006
Coagulum content, % m/m	0.004
Alkalinity as ammonia, % m/m	0.80
Volatile fatty acid number	0.01
Potassium hydroxide number	0.56
Mechanical stability time* (sec)	840
Magnesium content, % m/m	0.004
Copper content, ppm on total solids	2.5
Manganese content, ppm on total solids	Nil

* tested after 20 days of concentration

CHEMICALS

The details of the chemicals used in this investigation are given in Table 3.3.

TABLE 3.3

Chemicals used in the investigation

Name of Chemical	*Description*
Ammonia	Liquefied ammonia gas : commercial grade
Diammonium hydrogen phosphate	Commercial grade
Lauric acid	Commercial grade
Potassium hydroxide	Laboratory reagent grade
Potassium laurate	Prepared in the laboratory using potassium hydroxide and lauric acid. Used as 20% aqueous solution
Potassium oleate	Prepared in the laboratory using potassium hydroxide and oleic acid. Used as 20% aqueous solution.
Polyvinyl alcohol	Laboratory reagent grade. Average molecular mass of 14000.
Polyproplylene glycol	Commercial grade. Average molecular mass 4000.
Sulphur	Sp. gravity 1.9. Standard Chemical Co., Chennai.
Zinc diethyldithiocarbamate	Sp. gravity 1.49. Product of ICI (India) Ltd.
Zinc mercaptobezothiazole	Sp. gravity 1.7. Product of ICI (India) Ltd.
Zinc oxide	Sp. gravity 5.5 Meta Zinc Ltd., Mumbai.
Dispersol F	Sodium salt of a sulphonic acid. ICI (India) Ltd.
n-Butyl acrylate	Commercial grade
Oleic acid	Laboratory reagent grade
Liquor ammonia	Laboratory reagent grade
Calcium chloride	Laboratory reagent grade
Calcium nitrate.	Laboratory reagent grade
Formic acid	Laboratory reagent grade
Acetic acid	Laboratory reagent grade
Benzene	Laboratory reagent grade
Toluene	Laboratory reagent grade
Thiourea	Laboratory reagent grade

PREPARATION OF LATEX COMPOUNDING CHEMICALS

Latex compounding ingredients were prepared as follows:

- Water soluble substances as aqueous solutions.
- Water insoluble solids as aqueous dispersions and
- Water insoluble liquids as aqueous emulsions

The general principles underlying the preparation of dispersions and emulsion are:

- The particle size of dispersions and droplet size of emulsions should, as far as possible, be comparable to the particle size of the latex to which they are to be added.
- The colloidal stability of the dispersions/emulsions should be comparable to that of the latex to which they are to be added. Also the stabilizing systems should be similar.
- The pH of solutions, dispersions and emulsions should not differ much from that of the latex to which they are added.
- The ionic strength of the aqueous phase of dispersions/emulsions should be similar to that of the aqueous phase of the latex.

PREPARATION OF SOLUTIONS

Water soluble chemicals were dissolved in deionized water at appropriate concentrations. Chemicals like polyvinyl alcohol are not readily soluble in water at ambient temperature. In cases where aqueous solutions were prepared in hot water, they were cooled before use. The chemicals were laboratory reagent grades and were used without further purification. The concentrations of the aqueous solutions of chemicals used in this study are given in Table 3.4.

TABLE 3.4

Concentration of solutions

Name of chemical	*Type and concentration of solution*
Potassium laurate	20% m/m aqueous solution
Potassium oleate	20% m/m aqueous solution
Potassium hydroxide	10% m/m aqueous solution
Polypropylene glycol	10% m/m aqueous solution
Thiourea	10% m/m aqueous solution
Formic acid	20% m/m aqueous solution
Calcium nitrate	5, 10, 15, 20% m/m aqueous solution
Calcium chloride	5, 10, 15, 20% m/m aqueous solution
Polyvinyl alcohol	5% m/m aqueous solution

PREPARATION OF DISPERSIONS

Water insoluble solid compounding ingredients were made into latex compatible aqueous dispersions by ball milling(3,4). Since natural latex is anionic, the surface active agent used in ball milling also was anionic-Dispersol F. The solids content of the dispersion, quantity of the dispersing agent to be used and duration of ball milling depends on the nature of the materials to be dispersed. The formulations of dispersions used in the present study are given in Table 3.5. Easily dispersible materials like zinc oxide, zinc diethyl dithiocarbamate, silica etc. require lower ball milling time compared to materials like sulphur and tetramethyl thiuramdisulphide which generally require longer periods. Before adding to latex, the quality of dispersions was checked by water miscibility test.

TABLE 3.5

Preparation of dispersions

Chemical dispersed and its solids content	*Ingredients*	*Parts by weight*	*Ball milling time (h)*
Sulphur (50% m/m)	Sulphur	100	72
	Dispersol F	3	
	Deionized water	97	
Zinc oxide (50% m/m)	Zinc oxide	100	24
	Dispersol F	2	
	Deionized water	98	
Zinc diethyldithiocarbamate (ZDC) (50% m/m)	ZDC	100	24
	Dispersol F	2	
	Deionized water	98	
Zinc mercaptobenzothiazole (ZMBT) (50%m/m)	ZMBT	100	24
	Dispersol F	2	
	Deionized water	98	
Tetramethyl thiuramdisulphide (TMTD) (33%m/m)	TMTD	100	48
	Dispersol F	2	
	Deionized water	198	
Precipitated silica (25%m/m)	Precipitated silica	100	24
	Dispersol F	2	
	Deionized water	298	

40% Zinc oxide dispersion is prepared by diluting 50% dispersion with water.

PREPARATION OF EMULSIONS

To prevent destabilization and improve compatibility, water immiscible liquids were emulsified before being added to latex[3,4]. The emulsions used in latex applications are generally of the oil-in-water type, consisting of the insoluble material, an emulsifying agent and water. The emulsifying agent used in the present study was ammonium oleate, a higher fatty acid soap formed *in-situ*.

The water-immiscible liquid to be emulsified was mixed with oleic acid (part A). Deionized water and ammonia water were separately mixed (part B). Part A was warmed to 60°Cand added to B as a thin stream, under high speed stirring to get a stable emulsion.

The formulations of emulsions used in the present study are given in Table 3.6.

TABLE 3.6

Preparation of emulsions

Chemicals emulsified		***Ingredients***	***Parts by weight***
n-Butylacrylate (n-BA, 50%m/m)	Part A	nBA	100
		Oleic acid	3
	Part B	25% Ammonia solution	3
		Deionized water	94
Trisnonylated phenyl phosphite (TNPP, 50%m/m)	Part A	TNPP	100
		Oleic acid	3
	Part B	25% Ammonia solution	3
		Deionized water	94

RAW LATEX PROPERTIES

The routine quality parameters of raw latex/latex compound were measured as described below; References to the relevant Indian Standards are given in Table 3.7.

TABLE 3.7

Latex property measurement

Property	***Test Method***
Dry rubber content	IS 3708 (part 1) : 1985
Total solids content	IS 9316 (part 4) : 1988
Sludge content	IS 3708 (part 2) : 1985
Coagulum content	IS 9316 (part 3) : 1987
Alkalinity	IS 3708 (part 4) : 1985
Volatile fatty acid number	IS 3708 (part 7) : 1986
Potassium hydroxide number	IS 3708 (part 5) : 1985
Mechanical stability time	IS 3708 (part 6) : 1985
Magnesium content	IS 3708 (part 11) : 1986
Copper content	IS 9316 (part 7) : 1987
Manganese content	IS 9316 (part 9) : 1987

Details of the test methods are described below

Dry Rubber Content

The dry rubber content (DRC) of a latex is defined on the percentage by weight of the whole which is precipitated by acetic acid under closely defined conditions. The DRC of NR latices slightly exceeds the rubber hydrocarbon content since small quantities of various non-rubber constituents are co-precipitated with rubber.

For DRC determination, a known weight (W_1 gm) latex is diluted to about 12.5% DRC by adding water. It is coagulated by slow addition of 2% acetic acid. The coagulam is pressed into a thin sheet, about 1 mm in thickness. It is leached in water, dried at 70°C and weighed (W_2 gm).

$$\text{DRC\%} = \frac{W_2}{W_1} \times 100$$

Total solids content

Total solids content (TSC) is defined as the percentage by weight of the whole which is non–volatile at a definite temperature. TSC is usually determined for assessing the non-rubber solids (NRS) content in latex.

$$\textbf{\% NRS = \% TSC - \% DRC}$$

A known weight of latex W_1 gm is weighed into a clean petridish of known weight (W_2 gm). The latex is allowed to evaporate at 70°C. The weight of the petridish with dry film is taken (W_3 gm).

$$\text{TSC\%} = \frac{(W_3 - W_2)}{W_1} \times 100$$

Sludge content

Sludge content in latex is the non-polymer impurities in latex, which sediment under the influence of gravity. In natural latex, the major component in sludge is magnesium ammonium phosphate.

The determination of sludge involves centrifuging a known weight of latex (W_1 gm) so as to effect a preliminary separation of rubber particles and sediments.

After removal of the rubber fraction, the residue is repeatedly centrifuged with ethanol-water-ammonia mixture, until the supernatant liquid is clear. The sediment is then quantitatively transferred to a beaker and dried to constant weight (W_2).

$$\text{Sludge content \%} = \frac{W_2 \times 100}{W_1}$$

Coagulam content

The term coagulum refers to the material retained on a 180 micron IS sieve under conditions of the test. It comprises of pieces of polymer coagulum skin and course foreign matter.

About 200gm of latex (W_1 gm) is mixed with an equal volume of 5% potassium oleate soap solution. An 80 mesh stainless steel sieve is cleaned, dried and weighed (W_2 gm). The diluted latex is filtered through the sieve. The coagulum retained on the sieve is washed with soap solution until free from latex and finally with water, until the washings are free from soap. The sieve, with coagulum is dried at 70°C and weighed (W_3 gm).

$$\text{Coagulum content \%} = \frac{(W_3 - W_2)}{W_1} \times 100$$

Alkalinity

Ammonia is generally added to latex as a preservative. In special cases, fixed alkali like potassium hydroxide also may be added to latex. Thus by alkalinity is meant the free alkali content of latex.

In the actual practice about 2gm of latex is added to about 200ml distilled water containing few drops of bromothymol blue solution as indicator. This diluted latex is titrated against approximately 0.1N standard HCL, until the colour changes to yellow at the end point. The volume of acid consumed is noted and alkalinity is calculated as ammonia.

$$\text{Alkalinity as ammonia, \%} = \frac{1.7\,NV}{W}$$

Where

N = Normality of HCl.
V = Volume of HCl in ml.
W = Weight of latex in gm.

Volatile fatty acid number

Volatile fatty acid (VFA) number test measures the content of steam volatile fatty acids in latex like acetic, formic and propionic acids. At various stages of latex handling several microorganisms enter into latex. These act on glucose present in latex, producing mainly acetic acid. Hence VFA number is defined as the number of grams of potassium hydroxide equivalent to the volatile fatty acids present in latex of 100gm of total solids.

In the actual procedure 50gm latex is mixed with 50ml 30% ammonium sulphate solution and warmed on a water bath. The latex coagulates. The coagulum is squeezed and 25ml serum acidified with 5ml 50% sulphuric acid. 10ml of this mixture is steam distilled in a Markham still. About 100ml distillate is collected. The distillate containing volatile fatty acids is titrated against approximately 0.01N standard barium hydroxide solution. The titre volume is noted and VFA number calculated.

$$\text{VFA No.} = \frac{561NV\,(50+(100\text{-}DRC)\,W/\,100\,D)}{25\,W \times TS \times 1/3}$$

Where

N = Normality of barium hydroxide solution.
V = Volume of barium hydroxide solution (ml).
DRC = % of dry rubber in latex.
W = Weight of latex in gm.
D = Density of serum, gm/ml.
TS = % total solids in latex.

KOH number

Natural latex contains minor amounts of anions like volatile fatty acid anions, carbonate/bicarbonates, phosphate, citrate, oxalate, sulphate, sulphide, higher fatty acid anions etc. KOH number is defined as the number of grams of potassium hydroxide required to neutralise the acid radicals present in latex of 100gm of total solids.

In practice, to 50gm of latex, 5% formaldehyde solution is added to reduce its ammonia content to 0.5N in the aqueous phase and enough water to dilute it to 50% TSC. Using a pH meter the latex is potentiometrically titrated against 0.5N KOH solution. The end point of the titration is the point of inflection of the pH – ml (KOH) titration curve.

$$\text{KOH No.} = \frac{561\ NV}{TS \times W}$$

Where

N = Normality of KOH solution
V = Volume of KOH solution in ml
TS = % total solids content of latex
W = Weight of latex in gm.

Mechanical stability time

Mechanical stability of a latex measures its resistance towards mechanical forces which tend to increase the number and violence of collisions between latex particles and walls of the containing vessel so as to destabilise the latex.

The equipment used is Klaxson Mechanical Stability Tester. The latex is diluted to 55% TSC and equilibrated to 35°C. The rotor of the mechanical stability tester is introduced into latex and stirred at 14000 ± 200rpm. The kinetic energy acquired by the particles from the rotor leads to increased frequency of collisions leading to particle aggregation. The time that elapses before signs of incipent destabilisation appear, expressed in seconds, is the mechanical stability time of latex.

Magnesium content

The stability of natural latex as a colloid is due to the repulsive forces between negative charges on the latex particles derived from adsorbed proteins or higher fatty acids. Mg^{+2} can neutralise the negative charges to some extent, leading to a reduction in the stability of latex.

A known weight of latex (about 2gm) is diluted to about 100ml and it is titrated against standard EDTA solution (about 0.005M) using Solochrome Black T indicator, until the wine-red color changes to sky-blue.

$$\text{Magnesium content \%} = \frac{2.432\ MV}{W}$$

Where

M = Molarity of EDTA solution.
V = Volume of EDTA solution (ml).
W = Weight of latex in (gm).

Copper content

Copper is present in latex in minor amounts and can function as a pro-oxidant leading to polymer degradation.

The estimation is carried on dried latex solids. A known weight (about 5gm) latex solids is ashed at 550°C. It is extracted with an acid mixture (2 volumes of HCL : 1 volume of HNO_3 : 3 Volumes of water) and made alkaline with ammonia. Iron is precipitated off as citrate. Copper in the solution is made into yellow coloured copper diethyldithiocarbamate and extracted into chloroform. The optical density of the solution is measured photometrically. Using the optical density, concentration of copper is derived from a calibration curve.

Manganese content

Like copper, manganese also is a pro-oxidant in rubber.

About 10gm of the dried latex solids are ashed. The ash is treated with potassium hydrogen sulphate and sulphuric acid. After dissolving the ash in dilute sulphuric acid, iron is complexed with orthophosporic acid and manganese is oxidised to permanganate by boiling with potassium periodate. The optical density of the solution is measured photometrically. Using optical density; the concentration of manganese is derived from a calibration curve.

Viscosity

Viscosity of raw latex/latex compound was determined by a Brookfield viscometer (Model LVT) using spindle number 2(5). It consists of a rotating cylinder, driven by a synchronous motor through a beryllium-copper torque spring. 200gm of latex of 60% total solids content is weighed into a 250ml beaker and the cylinder is inserted into the latex. The cylinder can be rotated at different desired speeds depending on the viscosity to be measured. (60rpm in the present case). 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 a pointer and scale. The scale reading is converted to viscosity values using conversion factors, depending on the speed of rotation of motor. For spindle number 2 and 60rpm the conversion factor is 5.

ZINC OXIDE VISCOSITY OF LATEX(6)

Zinc oxide dispersion causes destabilization and thickening of latex. Latex to which zinc oxide has been added as dispersion normally has a higher viscosity than one without zinc oxide. The chemical stability of latex is inversely proportional to the viscosity at a given time after addition of zinc oxide. Sufficient latex of known solids content, equivalent to 100gm solids was taken in a beaker. To this one part of potassium oleate was added as 20% aqueous solution and the latex mixture diluted to 57% total solids by adding distilled water. The temperature of the latex was maintained at 25°C. 0.5 parts of ammonium sulphate as 10% aqueous solution and 5 parts of zinc oxide as 40% dispersion were added. The viscosity of the latex was determined using Brookfield viscometer with spindle number 2 at 60rpm at the end of 5 minutes after the addition of zinc oxide(5).

ZINC STABILITY TIME(7)

The chemical stability of latex was measured by determining the mechanical stability of latex in the presence of zinc oxide. To a 500ml beaker, sufficient latex containing 100gm total solids was weighed. 10gm of 50% zinc oxide dispersion was added to latex with stirring in a period of 5 minutes. Latex was diluted to

55% total solids using 1.6% aqueous ammonia. 80gm of the latex was transferred to the latex container of Klaxons' mechanical stability tester and its MST determined. The time in seconds required to initiate flocculation was measured as zinc stability time.

ZINC HEAT STABILITY TIME(7)

Zinc oxide dispersion was added to latex as in ZST test. Latex was then diluted to 55% TSC and introduced in a water bath maintained at 90°C. Latex is manually stirred until coagulation. This time, expressed in seconds is the zinc heat stability time (ZHST).

RHEOLOGICAL PROPERTIES

Natural latex is pseudoplastic in nature. Its viscosity and flow behaviour are affected by shear rate and temperature. A Haake Viscotester VT 550 was used to study the effect of shear rate and temperature on viscosity of latices. This equipment is capable of operating in the temperature range –30 to 150°C and shear rate can be varied from 1 to $200s^{-1}$. Different sensor systems are available with the equipment. In this study sensor system NV was used. The equipment measures the variation of shear stress τ or apparent viscosity η with shear rate γ.

The Haake viscotester belongs to the coaxial cylinder viscometers(8). The rotor speed and temperature of measurement are previously set. The latex is sheared in the annular space between the two cylinders and one is forcibly rotated. The latex exerts a resistance to the rotational movement. The torque transmitted to the other cylinder was measured. The data obtained were analyzed by a computer.

The rheological behaviour of latices were analyzed using the Power Law equation (also known as Ostwald-de-Wack equation).

$$\tau = \kappa \gamma^n$$

where

τ = shear stress (Pa)

κ = viscosity index

γ = shear rate (s^{-1})

n = flow index

In logarithmic form, Power Law equation gives

$$\log \tau = \log \kappa + n \log \gamma$$

A plot of log γ Vs log τ gives a straight line, whose slope is n and y-intercept as log κ. The apparent viscosity of latex η is the ratio of shear stress to shear rate. Thus,

$$\eta = \frac{\tau}{\gamma} = \frac{\kappa \gamma^{n}}{\gamma}$$

ie,

$$\eta = \kappa \gamma^{n-1}$$

In logarithmic form,

$$\log \eta = \log \kappa + (n-1) \log \gamma$$

A plot of log γ Vs log η gives a straight line, whose slope is (n-1) and y-intercept is log κ.

DETERMINATION OF NITROGEN

Nitrogen in latex films originates from proteins present in latex. Determination of nitrogen was carried out by semi-micro Kjeldahl method(5). Determination of nitrogen content involves the oxidation of rubber hydrocarbon in the latex film while nitrogen in proteins is converted to ammonium salts. The oxidant mixture used consisted of potassium sulphate, copper sulphate and selenium metal powder. After oxidation the mixture was made alkaline and was steam distilled in a semi-micro Kjeldahl apparatus to remove the liberated ammonia. The liberated ammonia was absorbed in boric acid and titrated against standard sulphuric acid. From the titre volume nitrogen content was calculated.

PREPRATION OF LATEX COMPOUND(9)

The required amount of latex was strained through cheese- cloth into a container. Suitably prepared compounding ingredients were weighed into tared containers. Then these materials were added according to the following schedule, while the latex was being thoroughly stirred without vortexing

(a). Colloidal stabilizers:

pH adjusters, soaps, synthetic surfactants, protective colloids

(b). Elastomer phase modifiers:
Zinc oxide, sulphur, accelerators, antioxidants

(c). Fillers, colour pigments, plasticizers

(d). Thickeners

(if highly viscous, dilute the unthickened compound before adding to batch)

Low viscosity compounds were stirred at high speeds. High viscosity compounds required larger propellers and slower speeds. The latex compound thus prepared was allowed to mature, say for 24h, under slow stirring. During maturation some extent of prevulcanization occurred to latex.

PREVULCANIZATION

The matured latex compound was heated on a water bath in a covered container at the desired temperature, under constant stirring at low speed. Covered container minimised loss of ammonia and stirring prevented skin formation at the surface. Samples of the mix were withdrawn at appropriate time intervals for testing. Samples withdrawn were immediately cooled to room temperature to arrest further prevulcanization(9). The prevulcanized latex samples were sieved through 100 mesh sieve before subsequent processing/testing.

POST-VULCANIZATION

Latex compound was prepared and matured usually for 24h as described earlier. Films were prepared by casting or coagulant dipping (as described later). Dried films were vulcanized by heating in air at any desired temperature for a given period. The vulcanized films were leached in water for appropriate time and dried.

RADIATION VULCANIZATION

Latex was compounded as per the formulation given in Table 3.8(11). Compounded latex was matured for 24h and irradiated by high energy gamma radiation from a cobalt 60 source in a Gamma Chamber 5000 installed by the Board of Radiation and Isotope Technology (BRIT), Mumbai, Department of

Atomic Energy, Government of India. The dose of radiation was changed by varying the period of irradiation and dose rate is varied by using attenuators (lead vessels which holds the latex container), of suitable thickness. After irradiation vulcanized latex films were prepared by casting.

TABLE 3.8

Latex compound for radiation vulcanization

Ingredient	*Parts by weight*	
	Dry	*Wet*
60% HA latex	100	167
10% Potassium hydroxide solution	0.3	3
50% n-Butyl acrylate	5	10
Water	—	to dilute to the desired solids

PREPARATION OF CAST FILMS

Cast films were prepared by the method described by Flint and Naunton(12). Strips of glass about 1–2mm thickness were fixed on edges of glass plate, approximately 20cm x 20cm to form shallow trays of about 15cm x 15cm. A suitable quantity of latex was poured on to each of the plates and was distributed as evenly as possible by tilting the plates. The quantity of latex, initially poured on to the glass plate, was determined in such a way that the thickness of the dry film was about 0.5 to 0.75mm or any other desired thickness. The glass plates were placed on leveled Tables and the compound allowed to dry slowly at ambient temperature.

PREPERATION OF DIPPED FILMS(13)

In coagulant dipping process, the formation of the deposit on the former was facilitated by the use of a direct coacervant. The main body of the latex film was produced by first coating the former by the coacervant. The former was then immersed in the latex compound and allowed to dwell for a specified period. During this period, the latex in the vicinity of the former surface became sufficiently destabilized to form a thin gelled layer around the former. At the end of the dwell period, the former was slowly withdrawn from the latex. The film which coated the former at the withdrawal stage was usually only partly gelled, the outer layer being still more or less fluid. Hence the former was tilted/rotated in appropriate directions so that the ungelled latex was uniformly distributed over the former surface. Both wet coagulant dipping and dry coagulant dipping processes were adopted in this study. Formic acid was used as the wet coagulant and calcium chloride and calcium nitrate as dry coagulants.

LEACHING OF LATEX FILMS

Latex films, prepared by casting or dipping were leached to remove non-rubber materials in the film and any residual coagulant. Leaching of dried latex films was carried out in deionized water using film to water ratio of 1:400. The temperature of leach water and duration of leaching were carefully controlled. After leaching the films were dried in air.

DETERMINATION OF CROSSLINK DENSITY

The extent of cure of latex film is directly proportional to the number of crosslinks formed within the rubber matrix. Crosslink density was determined by solvent swelling method(14). The higher the swelling lower is the number of crosslinks. About 0.1–0.2gm of latex film was accurately weighed and it was soaked in about 25ml of toluene for 48h, by which time the latex film swells by imbibing the solvent. The swollen film was taken out, gently wiped to free it from toluene absorbed on the surface and immediately weighed. Crosslink density was calculated by using the Flory-Rhener equation(15).

$$\mathbf{Vo = \kappa Q^{-5/3}}$$

Where

Vo = crosslink density (= number of crosslinks/gm.)
κ = a constant = 4.71×10^{20} for natural rubber-toluene system
Q = Swelling ratio

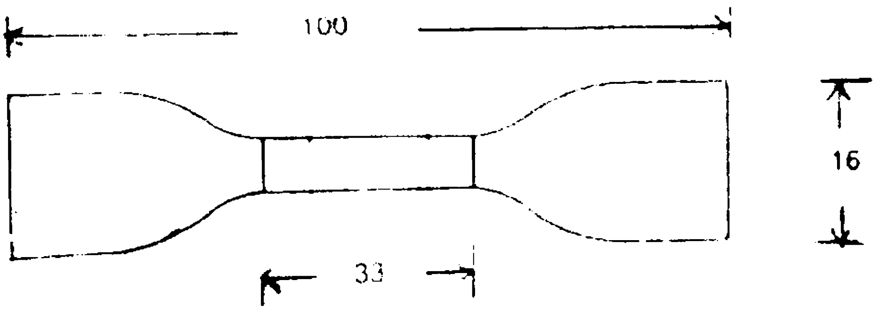
ESTIMATION OF EXTRACTABLE PROTEINS IN LATEX FILMS

Extractable protein content in latex films were estimated by Lowry method(16) as modified by RRIM(17). The extractant used was distilled water. About 2gm of latex film was accurately weighed into 250ml beaker containing 50ml distilled water.

The beaker was swirled at intervals. Water soluble proteins in the film were extracted into the aqueous phase and extraction was continued for 3h. The extracted protein being very dilute was concentrated by precipitation reaction with trichloroacetic acid and phosphotungstic acid. The precipitated protein was dissolved in 2.6ml 0.1M sodium hydroxide and estimated colourimetrically by using Phenol Folin reagent against bovine serum albumin as standard and measuring the absorbance at 750nm.

TENSILE STRESS-STRAIN BEHAVIOUR

Tensile properties of vulcanized latex films were determined as per IS 3400(Part1):1987[(18)] using type D dumb–bell specimens on a Hounsfield Universal Testing Machine. The dimensions of the dumb–bell specimen is given below.



Dumb-bell specimens were cut by stamping from latex films using a die having sharp edges to avoid any imperfections on the cut edge. Dumb-bell specimens were mounted on the testing machine by pneumatic grips. The test piece was stretched smoothly at substantially constant cross-head speed of 500mm/minute. The stress–strain behaviour of the films were recorded until the film breaks. Modulus of the films at different elongations, tensile strength and elongation at break are determined from the stress-strain curve. Modulus at a given elongation is the force per unit area of cross section of the test specimen, required to elongate the sample to a given elongation. Tensile strength is the force per unit area of the specimen required to break the specimen by stretching. Elongation at break is the maximum elongation (expressed as percentage) at which specimen breaks by application of tensile force. The results reported are the mean values for five measurements.

ACCELERATED AGEING TEST

Latex films on heating, in the presence of air or oxygen undergo thermal and oxidative degradation. The accelerated ageing of latex films was carried out as per IS 3400(Part 4):1987(19). Dumb-bell specimens were subjected to accelerated ageing in a tubular oven maintained at 70°C for a period of 168h. After ageing the specimens were taken out, kept at ambient conditions for a period of not less than 16h in a strain free condition. The aged films were tested for tensile properties. Testing of aged films was completed within 96h after accelerated ageing.

REFERENCES

1. D.C.Blackley. Polymer Latices: Science and Technology. (Second Edn.) Chapman & Hall. London, Vol.2, Chapter 9, (1997).

2. E.W.Madge, H.M. Collier and J.D.Peel. *Trans. Instn. Rub. Ind.* **26**, 305 (1950).

3. The Vanderbilt Latex Handbook (Third Edn.) E.F.Mausser (Ed.) R.T.Vanderbilt Company, Inc., Chapter 5, (1987).

4. D.C.Blackley. Polymer Latices: Science and Technology. (Second Edn.). Chapman & Hall, London, Vol.3, Chapter 15, (1997).

5. D.C.Backley. High Polymer Latices. Maclaran and Sons Ltd. London, Vol.2, Chapter 8, (1966).

6. E.A.Murphy. Proc. Rubber Technol. Conf. London, p-151, (1938).

7. J.L.M.Newnham and D.J.Simcox. Proc.Int.Rubber Technol. Conf. Washington, p-323, (1959).

8. The Vanderbilt Latex Handbook (Third Edn.). E.I.Mausser (Ed.). R.T.Vanderbilt Company Inc., Chapter 14, (1987).

9. D.C.Blackley. Polymer Latices: Science and Technology. (Second Edn.). Chapman & Hall, London, Vol.1, Chapter 8, (1997).

10. E.H.Low. Proc. RRIM Planters' Conf. Kuala Lumpur, p-308, (1977).

11. C.Zhoghai and K.Makuuchi. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex JAERI. M89-228, p-326, (1989).

12. C.F.Flint and W.J.S.Naunton. *Trans.Instn.Rub.Ind.* **12**, 367 (1937).

13. D.C.Blackley. Polymer Latices: Science and Technology. (Second Edn.). Chapman & Hall, London, Vol.3, Chapter 17, (1997).

14. R.M.Panich, N.M.Fodiman and S.S.Voyutski. *Soviet Rub. Technol.* **18(2)**, 14 (1959).

15. P.J.Flory and J.Rhener. Jr. *J. Chem. Phys.* **11**, 521 (1943).

16. O.H.Lowry, N.J.Rosebrough, A.L.Farr and R.J.Randall. *J. Biol. Chem.* **193**, 265 (1951).

17. F.Yusof and H.Y.Yeang. *J.nat. Rub. Res.* **7**, 206 (1992).

18. IS 3400 (Part 1): 1987 Methods of Test for vulcanized rubbers–Tensile stress-strain properties (second revision).

19. IS 3400 (Part 4): 1987 Methods of Test for vulcanized rubbers–Accelerated ageing (second revision).

CHAPTER 4

PREPARATION AND PROPERTIES OF LOW PROTEIN LATEX

Allergic reactions due to the prolonged use of latex products are currently discussed in length(1-4). Nutter(5) has attributed these allergic reactions to the presence extractable proteins (EP) in latex products. Proteins cause contact urticaria and anaphylaxis in sensitized people(6). Leaching(7,8) and chlorination(9) are the most commonly used methods for reducing EP. Very long on-line leaching is impossible in a commercial dipping plant. Chlorination reduces the physical properties of latex films(10) and imparts an yellow colour at high chlorine concentration. Well leached latex films on storage, again show the presence of EP on the surface. This is believed to be due to the migration of soluble proteins from inner layers to the surface. Reducing extractable protein content in latex itself can probably solve the problem to a great extent.

A method for deproteinizing latex(11) was reported earlier. The method is based on enzymic process. This method is rather expensive as latex has to be diluted to 10% dry rubber content (DRC) and again concentrated to 60% DRC. Dilution and concentration have to be repeated several times depending on the level of deproteinization required. Another approach is production of 'Loprol'(12) which is also based on an enzymic process(13). The content of non-rubber materials in this latex is higher, compared to conventional concentrated HA latex and physical properties of the films are lower. Also there are reports that it is not unlikely that the enzymes themselves may prove to be allergic(14) as the enzymes are some type of proteins. There are many chemicals, including surfactants which are reported to be capable of modifying proteins on the surface of rubber particles in latex. One of the major problems associated with chemical modification is that often high levels of these agents are needed and these may have severe adverse effects on the colloidal properties of latex(15). Another approach into displace proteins from rubber-serum interface in latex. Several chemicals/chemical combinations were screened initially in their ability to reduce EP in latex films. The results of studies to produce natural latex low in EP using a non-enzymic process and the evaluation of this low protein latex (LPL) are reported in this chapter. Based on the results obtained in this study, a process was standardized for the preparation of low protein latex (LPL) which is described at the end of this chapter.

EXPERIMENTAL

Screening of chemicals

Two higher fatty acid soaps (potassium laurate and potassium oleate) and two non-ionic surface active substances (polyvinyl alcohol, PVA average molecular mass 14000 and polypropylene glycol, PPG average molecular mass 4000) were examined for their ability to displace proteins from rubber-serum interface. Each of these chemical was added to 60% high ammonia (HA) latex at 0.1%m/m concentration and allowed to equilibrate for about 20h. The treated latex was diluted to 30% DRC by adding 1.6% aqueous ammonia and then centrifugally concentrated to 60% DRC after a total of 24h. Cast films of thickness 0.1–0.2mm were prepared using levelled glass plate(16), dried in air, leached in water for one hour at ambient temperature and the residual EP contents were estimated by Lowry method(17) of color development as modified by RRIM(18).

Preparation of low protein latex using polypropylene glycol

Preliminary screening indicated Polypropylene glycol (PPG) as the most effective among the chemicals screened. PPG was added to commercial high ammonia preserved 60% natural rubber latex at different concentrations. Since this process is based on protein displacement from the surface of latex particles, a portion of the latex was stirred for one hour to evaluate the effect of stirring. After 24 hours the diluted latex was centrifugally concentrated to low protein latex (LPL) of 60% DRC. To evaluate the effect of second centrifugal concentration on protein removal from latex, double centrifuged latex (DCL) was also prepared from the initial standard single centrifuged latex (SCL) after dilution with 1.6% ammonia water followed by centrifugal concentration without adding any chemicals. The properties of SCL, DCL and LPL were evaluated.

Testing of latices

The general quality parameters of latices as described in IS:5430–1981 for ammonia preserved concentrated natural rubber latex were evaluated as per the relevant parts of Indian Standards, IS:3708 and IS:9316. Viscosity of latices were determined using Brookfield viscometer (spindle number 2 at 60rpm(19)). Zinc oxide viscosity was determined by Newnham and Simcox method(20)

Infra red studies on raw latex films

For characterising the latex films, IR spectra of the films were scanned. IR spectra were scanned for raw SCL, DCL and LPL films as well as films leached in water for 5 minutes.

Preparation of vulcanized latex films

Latices were compounded using sulphur and accelerator following the conventional cure system as per the formulation given in Table 4.1. Compounded latex was matured for 24h and cast films were prepared using levelled glass plate(16). Dipped films were prepared by coagulant dipping(21). Films were vulcanized by heating for one hour at 100°C in air. Leaching of vulcanized latex films is an accepted procedure as a means to improve the physical properties of films. Hence vulcanized films were leached for 5 minutes in water at 30°C using rubber to water ratio 1:400. Leached films were air dried.

Testing of latex films

EP content in the films were determined by RRIM modified Lowry method(17). Nitrogen content in the films were estimated by semimicro Kjeldahl method(22) and crosslink density by solvent swelling method(23), using Flory-Rhener equation(24). Tensile properties of the vulcanized films were determined using the relevant Indian Standards.

Effect of storage of low protein latex

Shelf life is an important characteristic of latex. To study the effect of long-term storage, latices were stored in polyethylene containers and raw latex properties were evaluated after different periods of storage.

Effect of surface active substances on extractable protein content

Table 4.2 shows the effect of four different surface active materials in reducing EP in leached latex films when used at 0.1%m/m of latex. It is believed that reduction in EP is achieved by displacement of soluble proteins by the added surface active substance. PPG exhibits the best performance among the four chemicals. The presence of high concentrations of carboxylic acid soaps adversely affects the colloidal stability of compounded latex in the presence of zinc oxide(25) which liberates small amounts Zn^{+2} ions in the aqueous phase which subsequently form insoluble zinc soaps, leading to a reduction in colloidal stability of latex. The addition of PVA resulted in thickening of latex to some extent. Addition of PPG was not accompanied by any visual adverse effect on colloidal stability, even after storing for 24h. Hence further detailed evaluation was limited to PPG only.

Effect of concentration of PPG on EP content

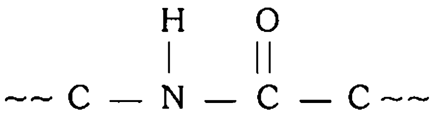
Figure 4.1 shows the variation of EP content in cast films against concentration of PPG, and also the effect of stirring. There is a progressive reduction in EP content in the films along with an increase in concentration of PPG. Initially there is considerable fall in EP content and the rate of fall decreases at higher concentrations of PPG. It was expected that mechanical stirring would facilitate protein removal from the surface of rubber particles. However, contrary to expectation, at higher concentrations of PPG, EP content in films prepared from stirred latex showed slightly higher values, even though the increase is only small. EP is only a small fraction of the total proteins in latex film(6). Reduction in the rate of fall in EP content with increasing concentration of PPG may be probably due to the preferential removal of less tightly bound proteins at the rubber-serum interface. A possible explanation for the slightly lesser EP content in films from latex which was not stirred is as follows. In presence of PPG, part of the least firmly absorbed proteins are displaced by surface active molecules of PPG. Also PPG can get adsorbed over the rubber particles carrying proteins, making the latter less extractable. During stirring the equilibrium,

proteins at rubber- serum interface ⇌ proteins in aqueous phase

will be shifted towards the right. Simultaneously aqueous phase also contains PPG. When stirring is stopped proteins and PPG can get adsorbed at the surface of rubber particles, small quantities of proteins probably forming an outer layer. These proteins became easily extractable. Also it is observed that the optimum concentration of PPG is 0.2% on the wet weight of latex and this concentration is used for the subsequent work.

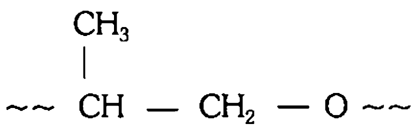
Infrared absorption of latex films

Proteins are polypeptides and have the characteristic grouping



$$\sim\sim C - \overset{\overset{\displaystyle H}{|}}{N} - \overset{\overset{\displaystyle O}{||}}{C} - C \sim\sim$$

The repeat unit in polypropylene glycol is



$$\sim\sim \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - O \sim\sim$$

In NR, the N—H bonds belong proteins Characteristic IR absorption frequencies for N—H bond is in the range 3300–3500.

The absorption peaks at 3421.38 in Figure 4.2 (SCL film) 3422.63 in Figure 4.3 (DCL film) and 3412.39 in Figure 4.4 (LPL film) are due to N—H stretching. The intensity of these peaks are in the order

SCL > DCL > LPL.

The other absorptions due to C—N, C==O and C—O are considered as the peak positions and intensities over lap and cannot be identified with respect to the bond type, since there are several non-rubber constituents in NR latex film.

The IR spectra of the leached films (Figures 4.5, 4.6 and 4.7) show that intensity of the N—H peaks are considerably reduced. This is due to removal of proteins by leaching. In the leached films, intensity of N—H peak in the order

SCL > DCL > LPL.

This finding strengthen the observation that LPL films show very low levels of EP, (as described in the following paragraph)

Protein content in raw latex films and residual EP in vulcanized latex films

Table 4.3 shows the total nitrogen content and approximate content of total proteins in raw latex films prepared from the three types of latices. Protein contents are evaluated by multiplying the percentage nitrogen content by 6.25. Total protein content in LPL is slightly above half of that present in SCL. Nitrogen content in the dry LPL film, and thus its total protein content is not much less than that of DCL. Table 4.4 gives a comparison of EP content in latex films prepared from SCL, DCL prepared out of it, and LPL prepared from this SCL using 0.2%m/m PPG. Even though a second centrifuging is accompanied by a fall in EP as shown by less EP content in DCL compared to SCL, this fall is mainly due to removal of soluble proteins available in the aqueous phase. During LPL processing PPG displays some of the adsorbed proteins from the rubber-serum interface. However PPG effectively displaces only the weakly adsorbed proteins, which are finally observed as EP. This is in agreement with earlier reports that only a small fraction of total proteins is extractable(6). EP content in these LPL films are comparable to those reported for chlorinated gloves(10).

Raw latex properties

Table 4.5 shows the raw latex properties of LPL and a comparison is made with SCL and DCL also. Low non-rubber solids, VFA number and KOH number in DCL and LPL, compared to SCL are due to recentrifuging of SCL. The aqueous phase of SCL contains some dissolved substances and inorganic ions. Dilution of latex allows some absorbed materials from the rubber-serum interface to go to the aqueous phase. During the subsequent concentration process, water removed as skim latex carries proportionate quantities of dissolved substances. Non-rubber content in LPL is somewhat lower than that reported previously for enzyme deproteinized low protein latex(12). The viscosity of DCL is higher than that of SCL. The presence of electrolytes in latex system can affect its flow characteristics(26). During the second stage of centrifugal concentration, the ionic concentration of the aqueous phase of DCL is reduced in comparison to SCL. In general it is found that removal of the electrolytes causes a large increase in viscosity. The generally accepted explanation for this behaviour is that the removal of the electrolytes causes an expansion of the electrical double layer surrounding the latex particles, thereby effectively increasing its volume. However, the viscosity of LPL is comparable to SCL, even though the ionic concentration in its aqueous phase is similar to that of DCL. It is believed that the bound electrical charges at the surface of the LPL particles are less than DCL as indicated by their lower protein content compared to DCL. Thus the electro viscous effects, associated with LPL particles are lower. The expansion of the electrical double layer surrounding the latex particles are less, thus keeping their effective volume less. Further, PPG being a non-ionic surface active material would have facilitated some extent of particle agglomeration, which also contributes to reduction in viscosity. For a given solids content of the latex, the higher size of the dispersed particles, lowers the viscosity of the system(27) . Also a fraction of the smaller dispersed rubber particles are removed as skim latex during the second stage centrifugal concentration. The viscosity of LPL being comparable to SCL, makes LPL to be a material suitable for making thin walled dipped articles like examination gloves and condoms.

ZST is an important property of latex, as colloidal stability of compounded latex during maturation and product manufacturing process is very important. Latex when compounded with zinc oxide, a small fraction of the added zinc oxide, in presence of ammonia and ammonium ions dissolves in the aqueous phase of latex forming zinc amine complexes(28) of the general formula $(Zn(NH_3)_n)^{+2}$, where $n = 1$ to 4. These complexes have low stability constants and easily liberate Zn^{+2} ions, which in turn form insoluble zinc soaps, by robbing the surface active anions at the rubber serum interface. Removal of dissolved Zn^{+2} facilitate dissolution of more zinc oxide. However, LPL shows high chemical stability as evidenced by low zinc oxide thickening and high zinc stability time (ZST). This is because of the reduced availability of surface active anions on the surface of latex particles in LPL. This is partly due to displacement of adsorbed protective anions by PPG and partly due non-ionic PPG functioning as a protective coating over the latex particles there by attracting a layer of dipolar water molecules. The data on protein content in Table 4.3 suggests that the latter factor makes appreciable contribution to the high chemical stability of LPL. According to Newnham and Simcox(20) ZST values between 300–500 seconds imply high zinc oxide stability. Thus high ZST of LPL is due to the lower availability of anionic surface active materials on rubber particles in LPL and adsorption of PPG at the rubber–serum interface. Even though LPL has good ZST values, its ZHST values are lower than SCL and DCL, despite the availability of lower levels of anions. This behaviour is due to the heat sensitizing action of PPG, when the temperature of the compounded latex is kept at 90°C.

Effect of storage on properties of latices

Major raw latex properties that undergo variation during storage are mechanical stability, colloidal stability (as measured by zinc stability time), viscosity and KOH number. Figure 4.8 shows the variation of mechanical stability time (MST) of latices during storage for six months period. It is observed that for[all latex samples MST increases initially during storage, reaches a maximum and then slowly declines. Two major hydrolytic changes occur in ammoniated latex during storage: hydrolysis of proteins and of phospholipids. Hydrolysis of proteins lead to the formation of polypeptides and amino acids and hydrolysis of phospholipids leads to the formation of glycerol, higher fatty acid anions, phosphate anions and organic bases(27). The adsorption of the ammonium salts of these fatty acids-particularly the oleates and linoleates–at the particle interface would produce an increase in mechanical stability due to the higher surface charge and, therefore, a higher repulsive energy between approaching particles(29). The liberation of amino acids from protein hydrolysis and generation of volatile fatty acids, by the activity of micro organisms on sugars, (especially glucose) tend to destabilize latex; the anions of the above acids increase the over all ionic concentration in the aqueous phase. The overall stability of latex is a net result of stabilizing action of higher fatty acid anions and the destabilizing action of other anions. In natural latices, initially the generation of higher fatty acid anions by phospholipid hydrolysis is much faster than the hydrolysis of proteins and the maximum MST is achieved in about 30 days. However, simultaneously protein hydrolysis liberates destabiliz anions. In latices of about 2–3 months age, the stabilizing and destabilizing contributions more or less balance, and MST remains somewhat constant. Due to the higher rate of phospholipid hydrolysis, the availability of phospholipids is almost exhausted in about 3–4 months hence the contribution of stabilizing component decreases, while the role of destabilizing anions still increase, resulting in fall in MST of latex. The higher stability of DCL and LPL over SCL is probably due to the lower availability of proteins in them. Further, in LPL the PPG adsorbed on the rubber particle will attract water molecules around them preventing close approach of the particles. Thus among the three lattices LPL exhibits highest mechanical stability during storage.

Figure 4.9 represents the variation of chemical stability of latices, as measured by zinc stability time (ZST). It is observed that, within the period covered by this study, ZST of the three types of latices is in the order.

SCL < DCL < LPL

It is further observed that for each latex, chemical stability increases gradually during storage upto about 30–60 days and then gradually decreases. The reduction in colloid stability is mainly a consequence of increase in ionic strength of latex, the principal mechanism being ion-pair formation with anions generated and the ammonium ions present in latex serum(29) and the zinc ions dissolving in the aqueous phase as zinc amines, which ultimately lead to the formation of insoluble zinc soaps(30,31).

It is believed that higher ZST of DCL and LPL over SCL in due to reduced ionic concentration and lower level of proteins, achieved by dilution and subsequent concentration. During the second centrifugal concentration process, a portion of the non-rubber materials, which would subsequently liberate destabilizing anions in the aqueous phase of the latex, are removed so that ionic concentration in DCL and LPL are not increased up to the level of SCL. In the case of LPL, nonionic PPG further improves chemical stability by way of 'steric stabilization' which may be explained as arising from excess osmotic pressure in the interaction zone of the two approaching particles (32) or from elastic compression of the adsorbed layers(33).

Viscosity of latex/latex compounds is a very important factor controlling processability. Viscosity is the outcome of the resistance offered to the relative motion of rubber particles and serum. Figure 4.10 shows the variation of viscosity of latices during storage. It is observed that for a given age of latex, viscosity is in the order

DCL > SCL > LPL

Viscosity increases progressively during storage. Also with increasing age of latex, the rate of increase in viscosity increases with the three types of latices.

The occurrence of structural viscosity is, in general caused by two factors: first the formation of a structure in the sol and second the hydrodynamic influence on the orientation of the dispersed particles in relation to their shape and size(34). In natural latex, one of the factors contributing to its viscosity is the orientation of a number of water molecules around each rubber particle in a water mantle with a structure that prevents free Brownian movement of these molecules. When the latex is at rest an appreciable amount of water will be immobilised in this way, giving the system a very high intrinsic viscosity. Proteins adsorbed at the rubber-serum interface are highly dipolar and hence the content of immobilised water is high in SCL and DCL. But the ionic concentration in the aqueous phase is higher in SCL than in DCL due to the higher level of hydrolysis occurred to proteins and phospholipids. Also the concentration of metallic ions like K^+ and Mg^{+2} are less in the aqueous phase of DCL. Thus the electrical double layer associated with the particles in SCL are more compressed so that the effective number of water molecules immobilized is less in SCL than DCL. Thus SCL exhibits lower viscosity on storage also when compared to DCL. As in the case of DCL, the ionic concentration in the aqueous phase of LPL is lower. However, this is more than compensated for by the possible agglomeration of particles, suggested earlier. Thus LPL exhibits lower viscosity than SCL and DCL.

Figure 4.11 shows the variation of KOH number of latex during storage. KOH number is a measure of the total anionic concentration in latex. Carbonates and bicarbonates mainly formed by dissolution of carbon dioxide into the aqueous phase of latex make the highest contribution to KOH number. Different types anions are liberated in latex by the hydrolysis of phospholipids and proteins. The concentration of these anions increases with the age of latex. For a given age of latex, among the three type of lattices, KOH number is highest for SCL, and in DCL and LPL it is almost similar. This is attributed to the lower phospholipid and protein content in DCL and LPL, which undergo hydrolysis during storage. The slightly lower KOH number of LPL over DCL is attributed to the slightly lower protein contact and by some protection offered to proteins towards hydrolysis by adsorbed PPG molecules.

Properties of cast films

Table 4.6 shows the tensile properties of sulphur vulcanized cast films of SCL, DCL and LPL, both before and after ageing. The physical properties of DCL are generally lower compared to SCL. This is attributed to the reduction of non-rubber materials, especially proteins. Proteins are believed to contribute to the tensile strength of vulcanized natural rubber through hydrogen bonding. Proteins have also been shown to influence the stress-strain and modulus of vulcanized latex film(35). A similar result on the role of proteins on radiation vulcanized of natural latex has been reported(36). However, LPL showed tensile properties similar to SCL even though protein content is less than that in DCL. This is attributed to the better inter-particle interaction via the possible hydrogen bonding ability exhibited by PPG which compensates for the protein removal. The physical properties of LPL films are found to be better than those reported for enzyme deproteinized low protein latex films(13). The reduction is tensile properties, usually accompanied in deprotenization is thus overcome with the present LPL.

Ageing of latex films is generally accompanied by molecular breakdown, leading reduction in tensile properties. The changes in tensile properties of LPL films by heat ageing at 70°C for seven days also are similar to those of SCL films. The high retention of tensile properties is due to the antioxidant activity of accelerator residues from zinc diethyl dithiocarbamates. For DCL, improvements in physical properties are observed on heat aging. This is probably due to the increased state of cure on continued heating and also due to the antioxidant activity of dithiocarbamate residues.

Dipping with low protein latex

Coagulant dipped films were prepared from latex compounded as per the formulation given in Table 4.1. Table 4.7 gives the results of coagulant dipping with the three types of latices using different coagulants for a dwell time of 30 seconds. It is seen that for a given coagulant, thickness of dry latex films are in the order.

SCL>DCL>LPL

Destabilization of anionic lattices occurs when cations reach the surface of latex particles. Proteins are one among the major components in imparting negative charges to latex particles. Its content is the lowest in LPL. It is also observed that higher thickness is obtained when salts of divalent cations like calcium are used. It is believed that dipositive cations of calcium are more able to destabilize anionic natural latex (though LPL is less anionic than SCL) than mono-positive H^+ ions. Between 20% calcium chloride and calcium nitrate the former gives higher thickness, under similar dipping conditions. This is due to the higher Ca^{+2} content in a given quantity of calcium chloride compared to nitrate.

Lower thickness of dry film with LPL is a disadvantage in dipping thick articles. However, LPL is aimed for making thin articles like examination gloves and condoms. Hence lower thickness is of advantage in making more number of articles from a given weight of latex. The effect of concentration of coagulant on thickness of dry films LPL is given in Figure 4.12 in the case of calcium nitrate and chloride as coagulants. It is seen that in the range of concentration of coagulant studied, in both cases, film thickness increases linearly with increasing concentration of coagulant, the chloride giving higher thickness.

Tensile properties of dipped LPL films

Tensile properties of coagulant dipped latex films are shown in Table 4.8. Among the three coagulants, formic acid gives the highest modulus and calcium chloride the lowest. Tensile strength shows the reverse order. A similar result in the case of radiation vulcanized natural rubber latex has been reported by Makuuchi(37). The elongation at break of the dipped films is highest when calcium chloride is used as coagulant It is believed that one Ca^{+2} ion need not neutralize both its positive charges by negative charges on same latex particle. It is equally able to bridge between two latex particles. This type of inter-particle crosslinking results in higher tensile strength when calcium salts are used as coagulants.

The data on EP content in LPL films (Table 4.3) and of the tensile properties (Table 4.8) of LPL films evaluated in this study are promising enough. The detailed procedure adopted in its processing is described below.

PROCEDURE FOR LPL PROCESSING

Field latex, obtained from rubber plantation was preserved with 0.8% ammonia and stored for 8 days. This preserved field latex was transferred to a bulking tank of a latex centrifuging factory. Mg^{+2} ions present in latex will adversely affect the colloidal stability of the latex and had to be removed. Hence the content of Mg^{+2} ions was evaluated by complexometric EDTA titration and calculated quantity of diammonium hydrogen phosphate was added to latex as 10% aqueous solution to precipitate Mg^{+2} ions, as magnesium ammonium phosphate

$$Mg^{+2} + NH_3 + HPO_4^{-2} \rightarrow Mg\ (NH^4)\ PO_4$$

This is allowed to sediment as sludge. The desludged field latex is fed to the bowl of latex separator, rotating at about 7000rpm. The latex gets distributed between the separator discs, where it is separated into two components, the cream fraction and skim fraction. The skim regulating screw of the latex separator is so adjusted that the cream fraction has DRC of 60–61%. The cream fraction had ammonia content of 0.46%. This was further ammoniated to 0.8%. This is the SCL.

To a known weight of SCL, 0.2%m/m PPG (average molecular mass of 4000) was added as 10% aqueous solution and well mixed. After 22h, this SCL was diluted to 30% DRC by adding 1.6% aqueous ammonia solution and well mixed. After 2h this latex was again centrifugally concentrated to 60% DRC to get LPL. Its ammonia content was maintained at 0.8%.

CONCLUSION

Low protein latex, produced by non-enzymic process exhibits very low levels of extractable proteins in vulcanized films compared to ordinary natural latex films. Low protein latex exhibits high mechanical and chemical stability and low viscosity. LPL exhibits good retention of physical properties during long-term storage. The behaviour of LPL in coagulant dipping is similar to SCL. Vulcanized low protein latex films exhibits high tensile properties comparable to conventional sulphur vulcanized films of SCL. Retention of physical properties on heat ageing is good. These characteristics make LPL a suitable raw material for the production of thin articles like examination gloves, condoms, toy balloons, teats and other medical and pharmaceutical products.

REFERENCES

1. K.Turjanmaa. *Contact Dermatitis* **17**,270 (1987).

2. F.Leynadier and J.Dry. *Clinical Reviews in Allergy* **9**,371 (1991).

3. C.P.Hamann. *American.J. Contact Dermatitis* **4**, 1 (1993).

4. K.Ellis. Latex Protein Allergy: the latest position. Int. Conf. Paris, p-29 (1995).

5. A.F.Nutter. *Brit .J.Dermatol.* **101**,597 (1979).

6. B.G.Audley and S.J.Dalrymple. Latex Processing Technology: Understanding its Science, Hertford, p-69 (1991).

7. S.J.Dalrymple and B.G Audley. *Rub. Developments* **45(2/3)**, 51 (1992).

8. A.H.Muhammad Yatim, Proc. IRTC '93 Wkshop on Latex Proteins, Kuala Lumpur, p-51 (1994).

9. S.J.Dalrymple and B.G Audley. Latex Technology and Processing, Hertford, p-63 (1993).

10. N.A.Abd. Aziz Proc. IRTC '93 Wkshop on Latex Proteins, Kuala Lumpur, p-59 (1994).

11. N.Ichikawa, E.A.Hwee and Y.Thanaka. Proc. Int. Rubber Technol. Conf. Kuala Lumpur, p-101 (1993).

12. H.M.Ghazaly, Proc. IRTC '93 Wkshop on Latex Proteins, Kuala Lumpur, p-81 (1994).

13. H.M.Ghazaly, *J.nat. Rub. Res.* **9**, 96 (1994).

14. W.Bez. Proc. Second Int. Sym. RVNRL Kuala Lumpur, p-121 (1996).

15. L.M.Barclay. Latex Protein Allergy: the Latest Position. Int. Conf. Paris, p-41 (1995).

16. C.F.Flint and W.J.S. Naunton. *Trans. Instn. Rub. Ind.* **12**, 367 (1937).

17. O.H.Lowry, N.J.Rosebrough, A.L.Farr and R.J.Randall. *J.Biol. Chem.* **193**,265 (1951).

18. F.Yusof and H.Y.Yeang. *J. nat. Rub. Res.* **7**, 206 (1992).

19. D.C.Blackey. High Polymer Latices, Maclaaran and Sons Ltd. London, Vol.2, Chapter 8 (1966).

20. J.L.M.Newnham and D.J.Simcox. Proc.Int. Rubber Technology Conference, Washington, p-323 (1959).

21. D.C.Blackely. Polymer Latices Science and Technology (Second Edn.) Chapman & Hall, London, Vol.3, Chapter 17 (1997).

22. D.C.Blackley. High Polymer Latices. Maclaram and Sons Ltd, London, Vol-2, Chapter 8 (1966).

23. R.M.Panich, N.M.Fodiman and S.S.Voyutski. *Soviet Rub. Technol.* **18(2),** 14 (1959).

24. P.J.Flory and J.Rehner Jr. *J.Chem. Phys.* **11**, 521 (1943).

25. D.C.Blackely. Polymer Latices Science and Technology (Second Edn.) Chapman & Hall London, Vol. 1, Chapter 5 (1997).

26. E.A.Collins, C.A.Daniels and J.A.Davidson. *Elastomerics* **110(3)**, 31 (1978).

27. P.H.Johnson and R.H.Kelsey. *Rub. World* **138**, 877 (1958).

28. E.W.Medge, H.M.Collier and J.L.M.Newnham. Proc. Third Rub. Technol. Conf. London, p-67 (1954).

29. D.C.Blackley. Polymer Latices Science and Technology (Second Edn.) Chapman & Hall, London, Vol.2, Chapter 9 (1997).

30. T.D.Pendle and A.D.T.Gorton. *Rub. Chem. Technol.* **51**, 986 (1978).

31. G.M.Kray and M.van den Temple. *Trans. Instn. Rub. Ind.* **28**, 144 (1952).

32. E.W.Fischer. *Kolloidzeitchrifto.* **60**, 120 (1958).

33. P.Bagchi. *J.Colloid Interface. Sci.* **47**, 86 (1974).

34. G.Verhaar. Proc. Third Rubber Technol. Conf. London, p-77, (1954).

35. K.L.Chong and M.Porter. Int. Conf. Polymer Latex. Plastics and Rubber Institute, London (1978).

36. N.Mohid, K.Makuuchi, F.Yoshi and I.Ishigaki, Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex JAERI-M 89-228, p-157, (1989).

37. K.Makuuchi. Radiation Vulcanization of Natural Rubber Latex. RCA Regional Training Course: Quality Control of RVNRL, Indonesia (1997).

TABLE 4.1

Latex compound used for preparing vulcanized films

Ingredient	*Dry weight*	*Wet weight*
60% Natural latex	100	167
10% Potassium hydroxide	0.1	1.0
50% Zinc diethyldithiocarbamate	1.0	2.0
50% Sulphur	1.75	3.5
50% Zinc oxide	0.25	0.5

TABLE 4.2

Effect of surface–active substances in reducing EP content in latex films

Surface-active substance (0.1% m/m of latex)	*EP content (mg/kg) of dry vulcanized latex films after leaching*
Nil (DCL)	451.0
Potassium laurate	224.0
Potassium oleate	238.0
PVA	142.0
PPG	62.1

TABLE 4.3

Total nitrogen and approximate protein content in cast films of raw latex

Type of Latex	*Nitrogen content (% m/m)*	*Approximate protein content (=% of nitrogen x 6.25)*
SCL	0.28	1.750
DCL	0.18	1.125
LPL	0.15	0.938

TABLE 4.4

Residual EP content in latex films

Type of Latex	*EP content (mg/kg)*
SCL	780.2
DCL	451.0
LPL	4.0

TABLE 4.5

Raw latex properties

Parameter	SCL	DCL	LPL*
Dry rubber content (%)	60.06	60.10	60.08
Total solids (%)	61.60	60.67	60.86
Non-rubber solids (%)	1.54	0.57	0.78
Coagulum (%)	0.006	0.004	0.004
VFA number	0.064	0.018	0.017
KOH number	0.45	0.26	0.26
Mechanical stability time (sec)	936	>1200	>1200
Viscosity (cps)	65.0	90.0	62.5
Zinc oxide viscosity (cps)	145.0	72.5	62.5
Zinc stability time (sec)	112	172	362
Zinc heat stability time (sec)	438	496	244

* prepared using 0.2% PPG

TABLE 4.6

Physical properties of sulphur vulcanized latex films

Property			SCL	DCL	LPL
Before Ageing	Modulus (MPa)	M 100	0.76	0.64	0.75
		M 300	1.24	1.02	1.42
		M 500	1.92	1.64	2.08
	Tensile strength (MPa)		30.32	28.59	29.11
	Elongation at break (%)		1352	1384	1409
After Ageing*	Modulus (MPa)	M 100	0.72	0.65	0.70
		M 300	1.16	1.19	1.36
		M 500	1.76	1.82	2.07
	Tensile strength (MPa)		31.44	31.57	30.02
	Elongation at break (%)		1328	1331	1370

* aged at 70°Cfor seven days.

TABLE 4. 7

Thickness of dry LPL films obtained by coagulant dipping

Coagulant	***Thickness of dry film(mm)***		
	SCL	***DCL***	***LPL***
20% aqueous formic acid	0.152	0.136	0.124
20% aqueous calcium nitrate	0.295	0.256	0.210
20% aqueous calcium chloride	0.332	0.294	0.234

TABLE 4. 8

Tensile properties of coagulant dipped Latex films

Type of latex	***Property***	***Coagulant***		
		20% Formic acid	***20% Calcium nitrate***	***20% Calcium chloride***
SCL	Modulus M500 (MPa)	2.05	1.96	1.99
	Tensile Strength (MPa)	27.45	29.94	30.51
	Elongation at break (%)	1196	1274	1346
DCL	Modulus M500 (MPa)	1.86	1.80	1.78
	Tensile Strength (MPa)	25.88	27.62	27.54
	Elongation at break (%)	1102	1148	1150
LPL	Modulus M500 (MPa)	2.01	1.95	1.92
	Tensile Strength (MPa)	26.93	28.41	29.68
	Elongation at break (%)	1148	1245	1378

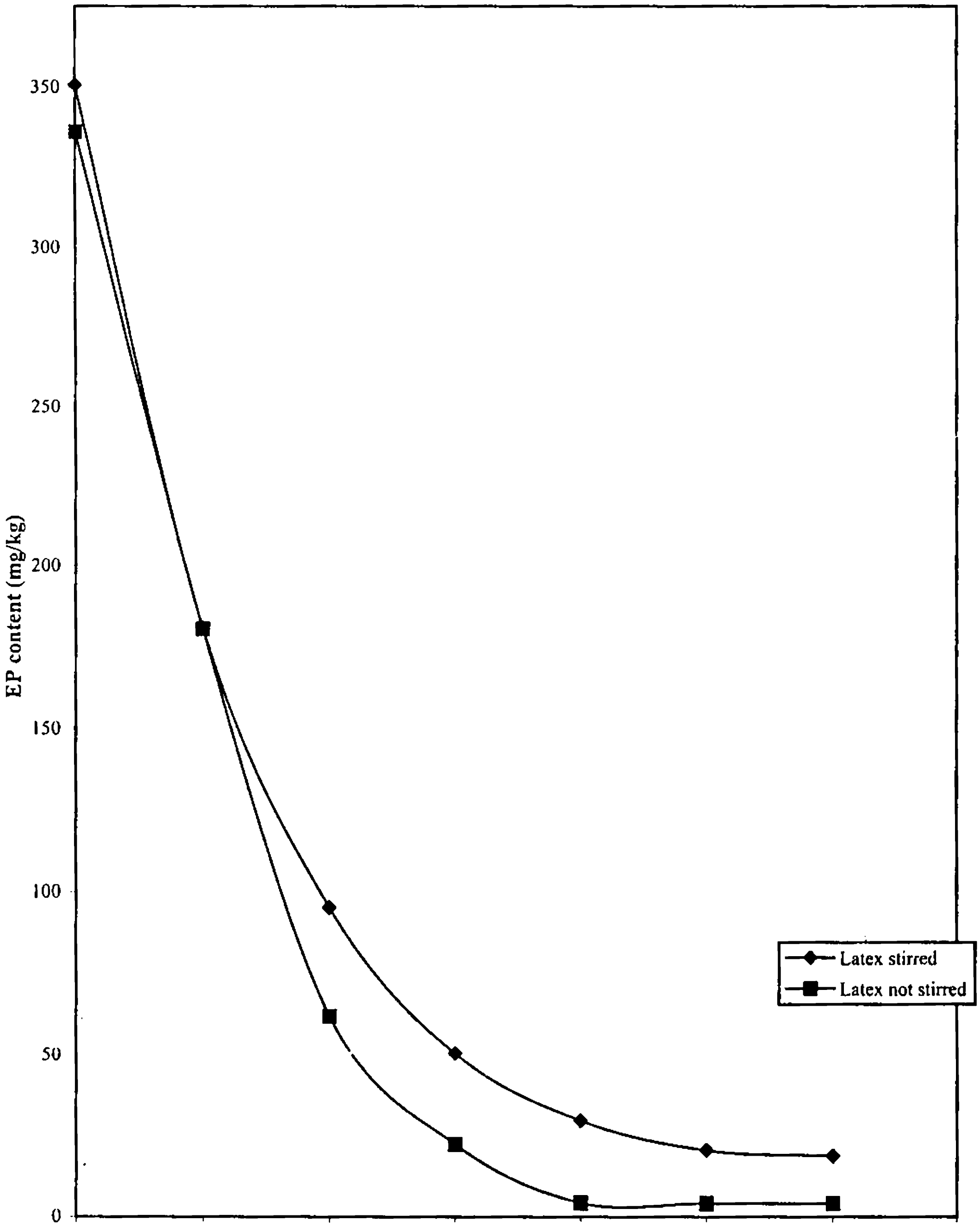


Fig 4.1. Effect of concentration of poly propylene glycol and mechanical stirring on extractable protein content in cast films.

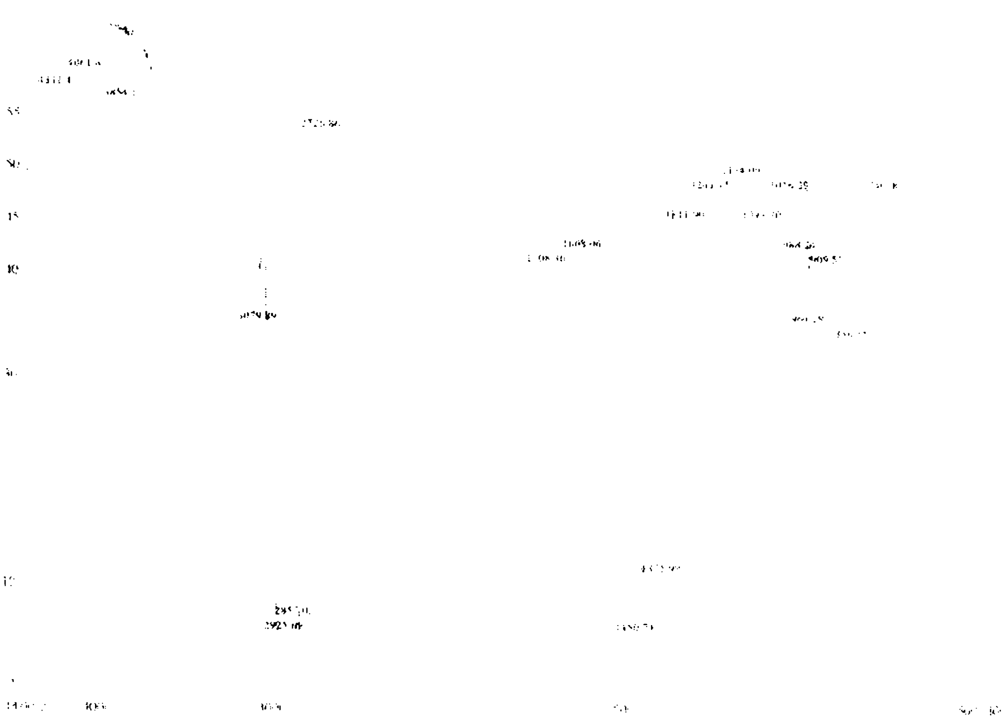


Fig. 4.2. IR spectrum of SCL film before leaching

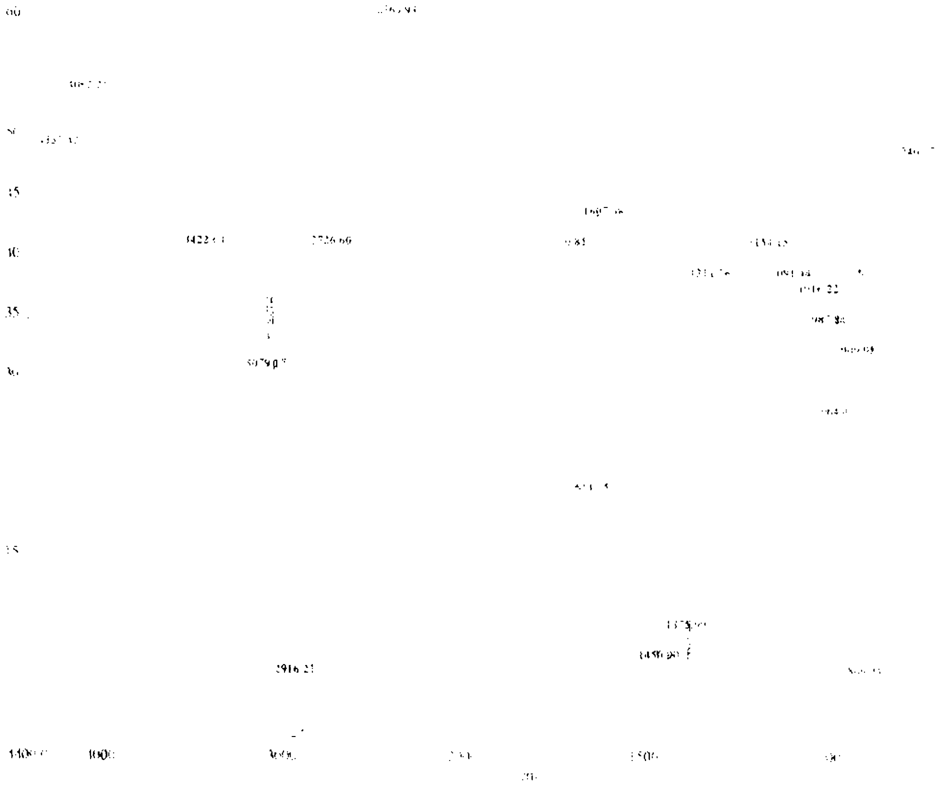


Fig. 4.3. IR spectrum of DCL film before leaching

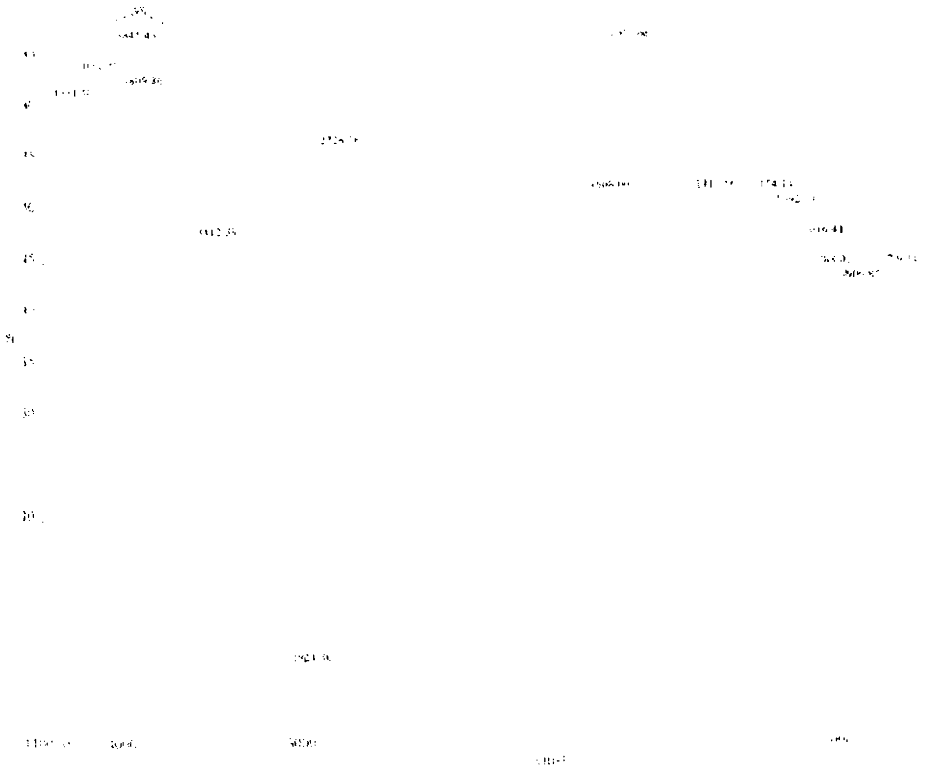


Fig. 4.4. IR spectrum of LPL film before leaching

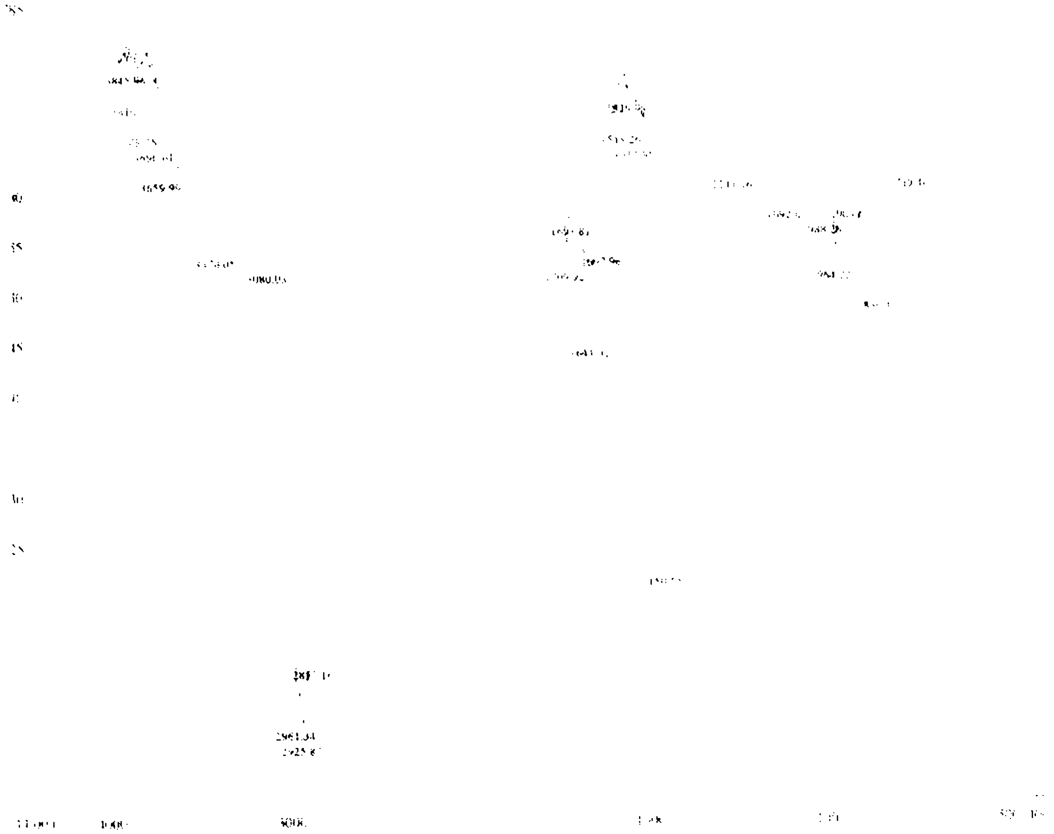


Fig. 4.5. IR spectrum of SCL film after leaching

Fig. 4.6. IR spectrum of DCL film after leaching

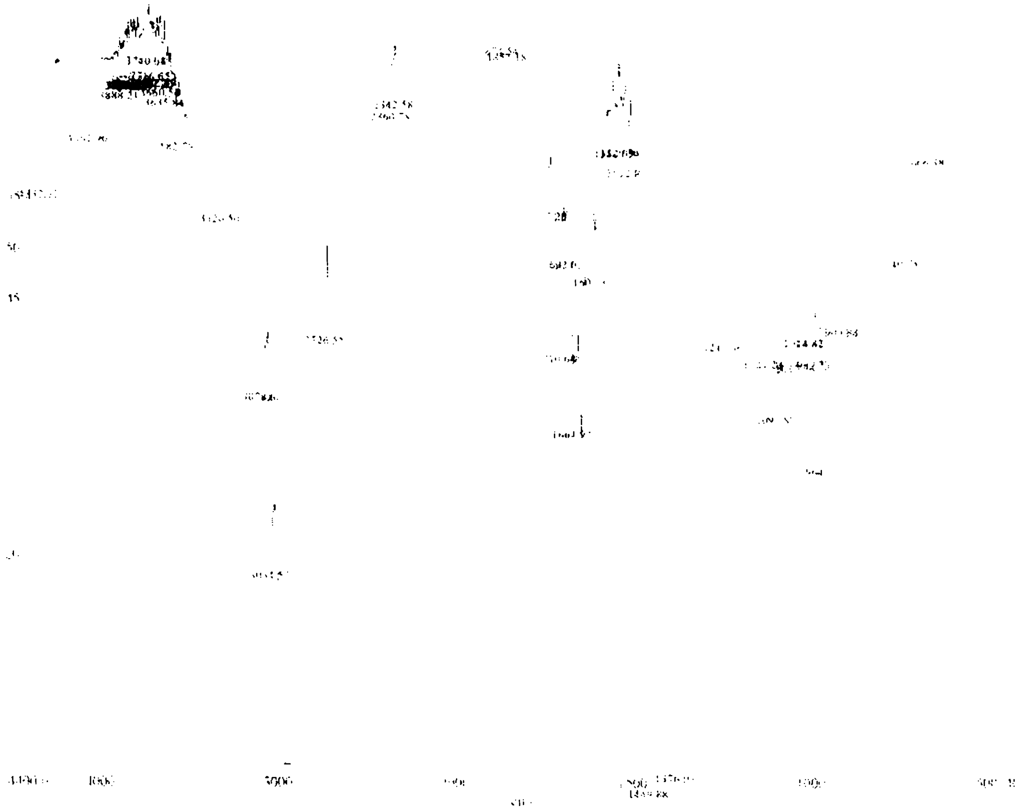


Fig. 4.7. IR spectrum of LPL film after leaching

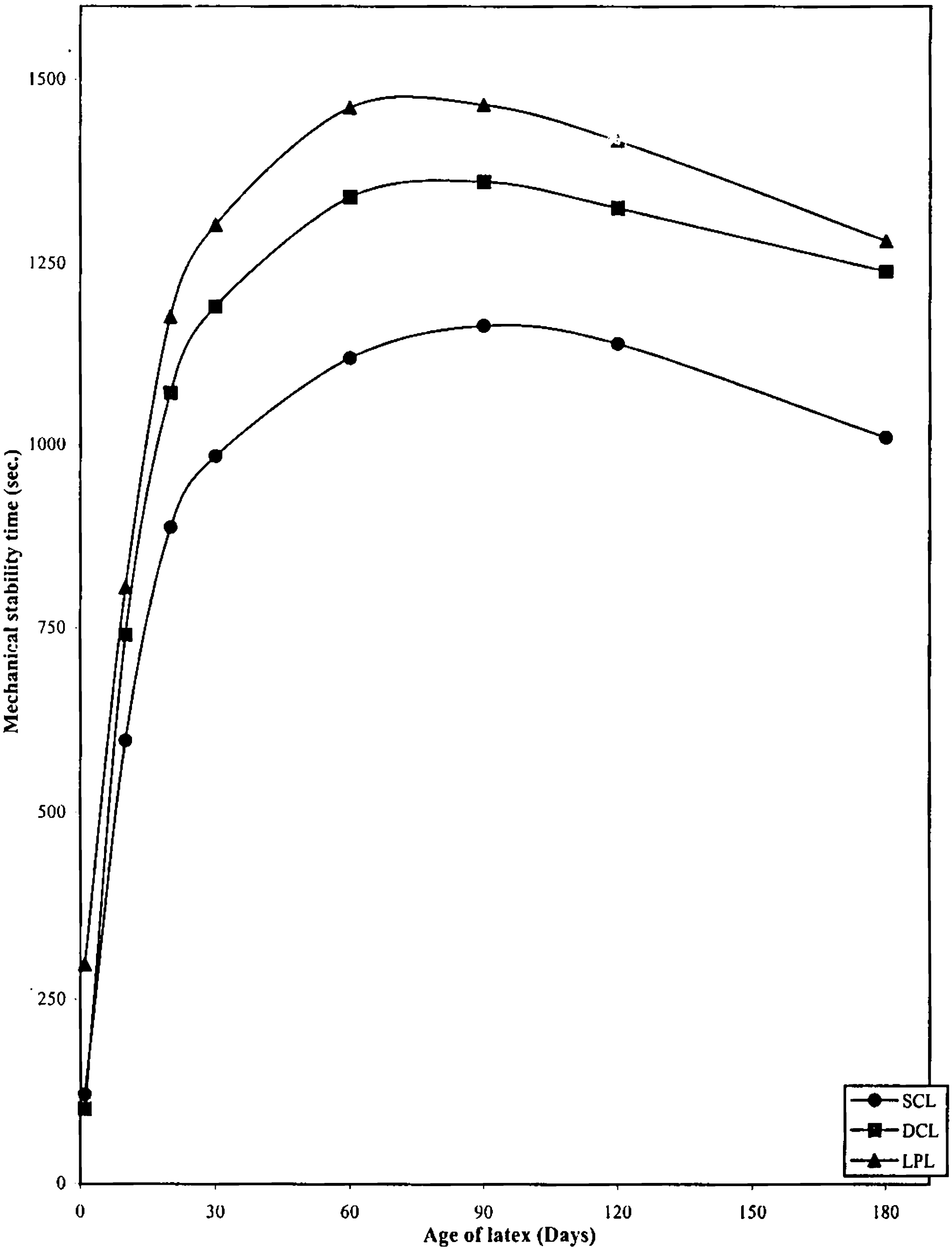


Fig 4.8. Effect of age of latex on mechanical stability time.

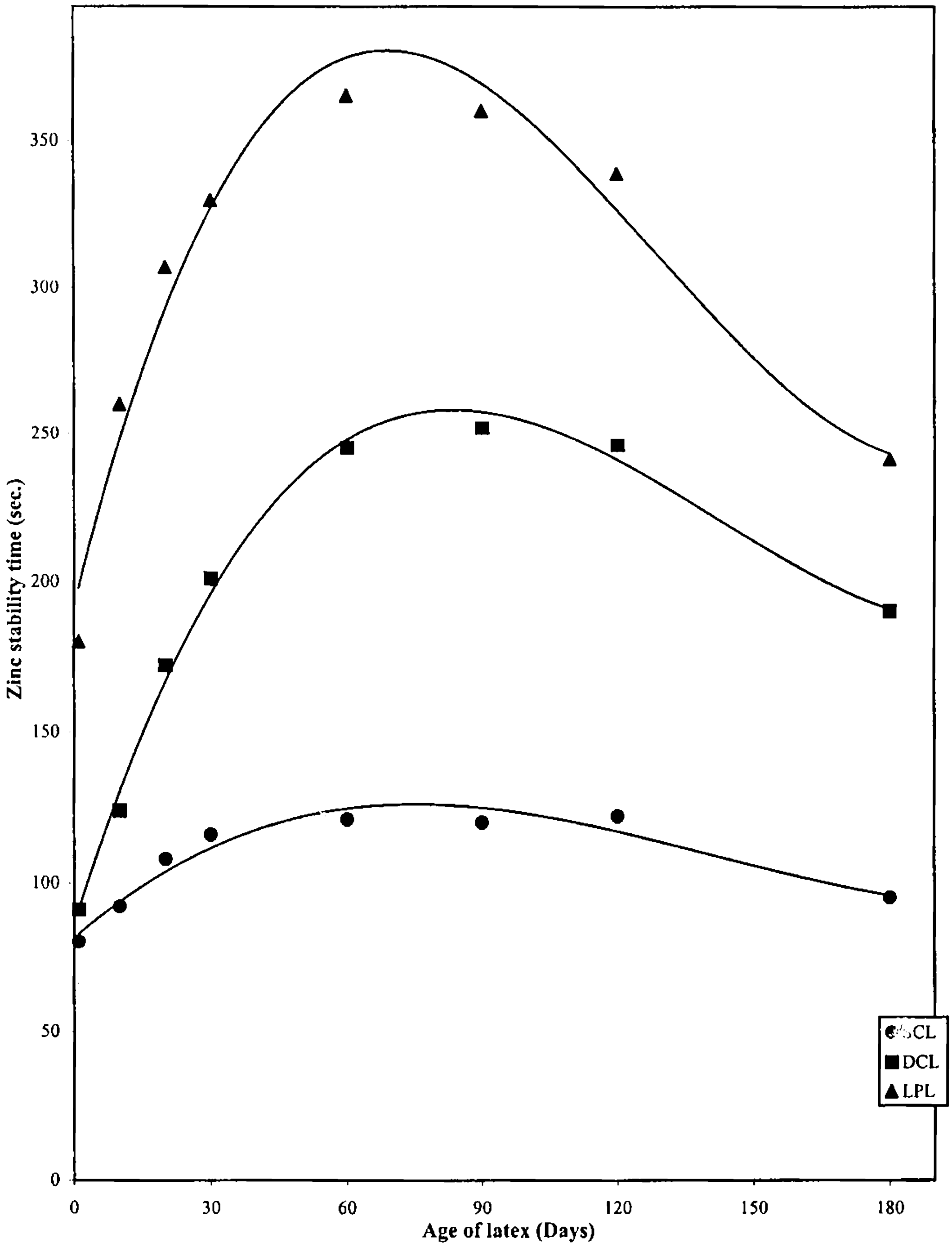


Fig 4.9. Effect of age of latex on zinc stability time.

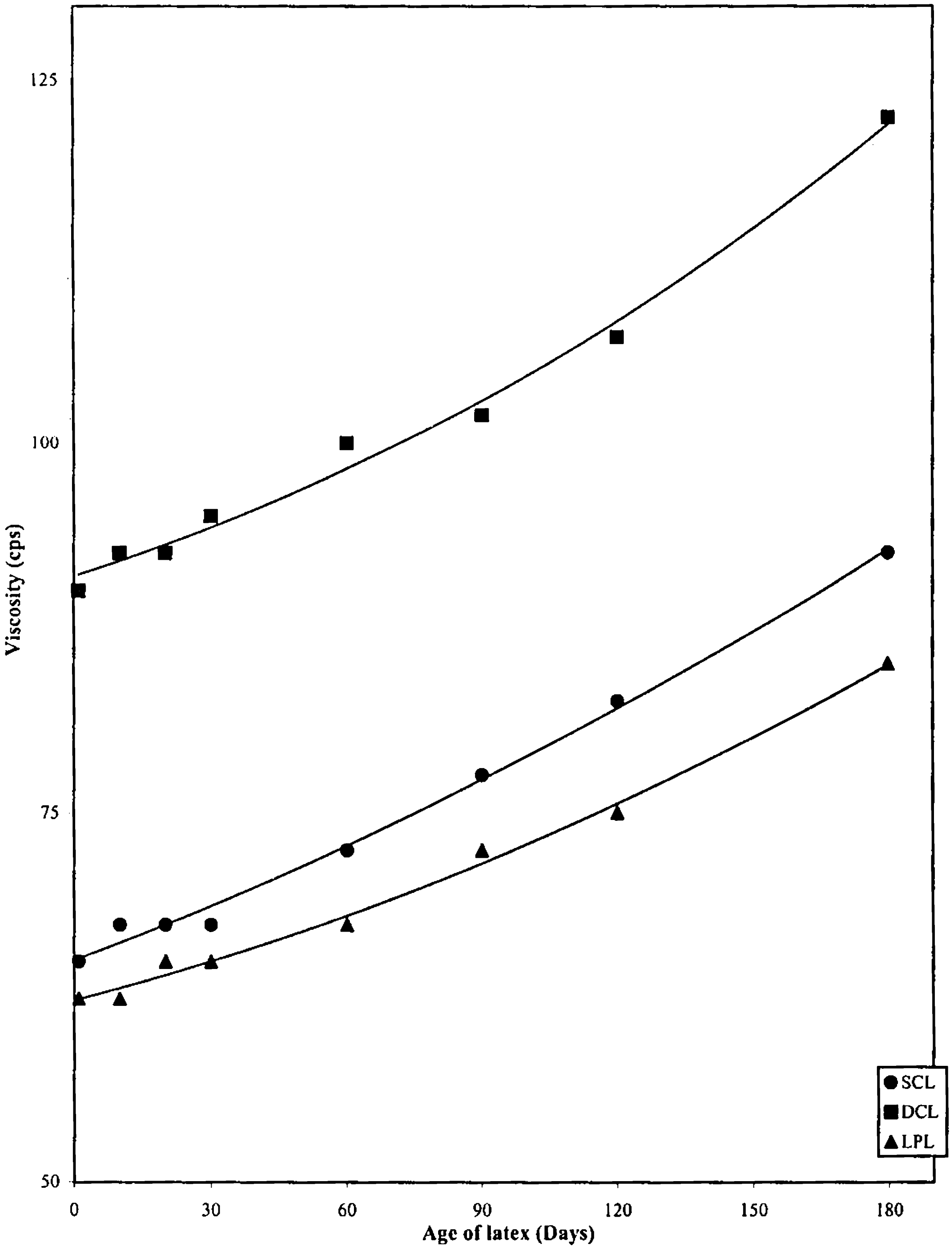


Fig 4.10. Effect of age of latex on viscosity.

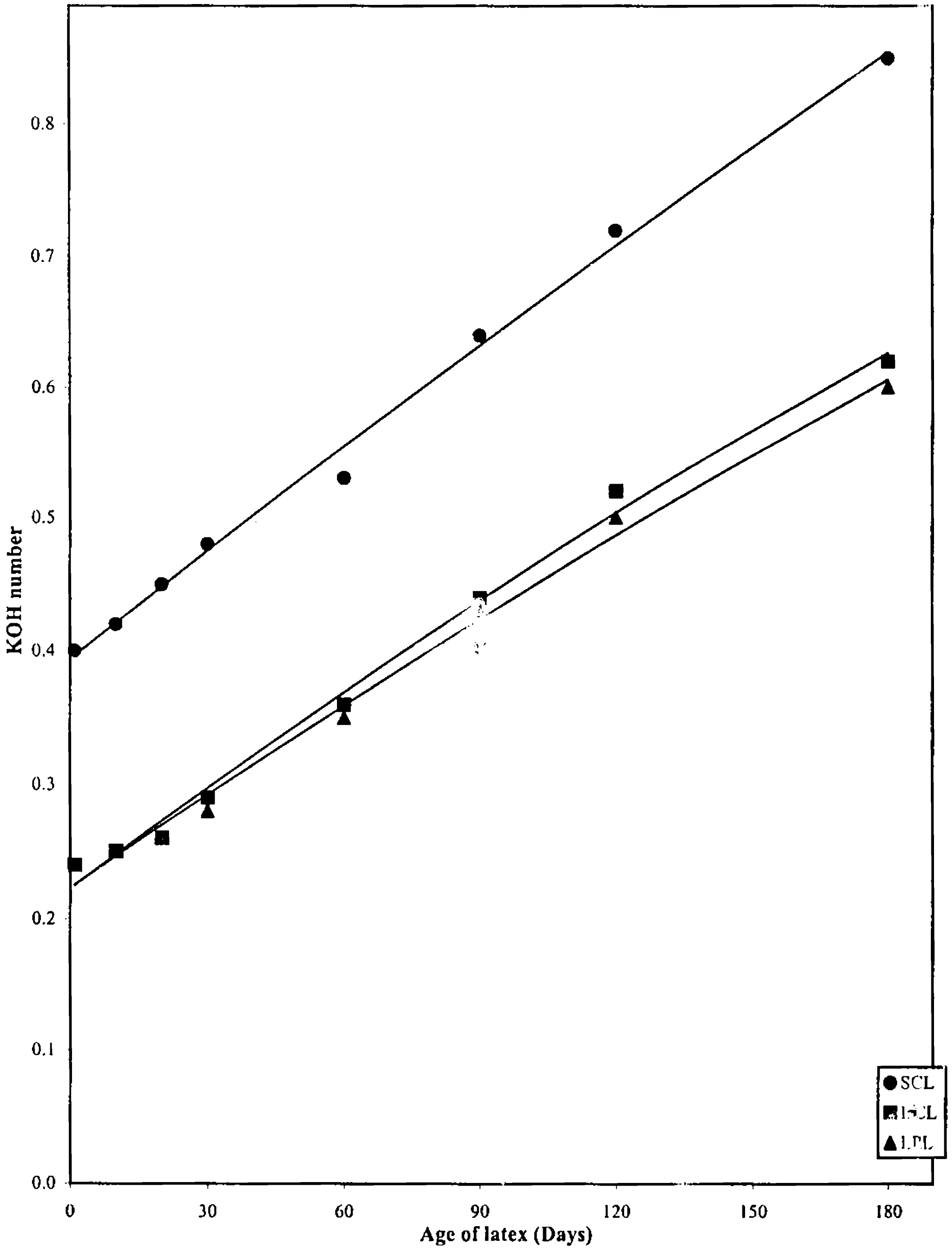


Fig 4.11. Effect of age of latex on KOH number.

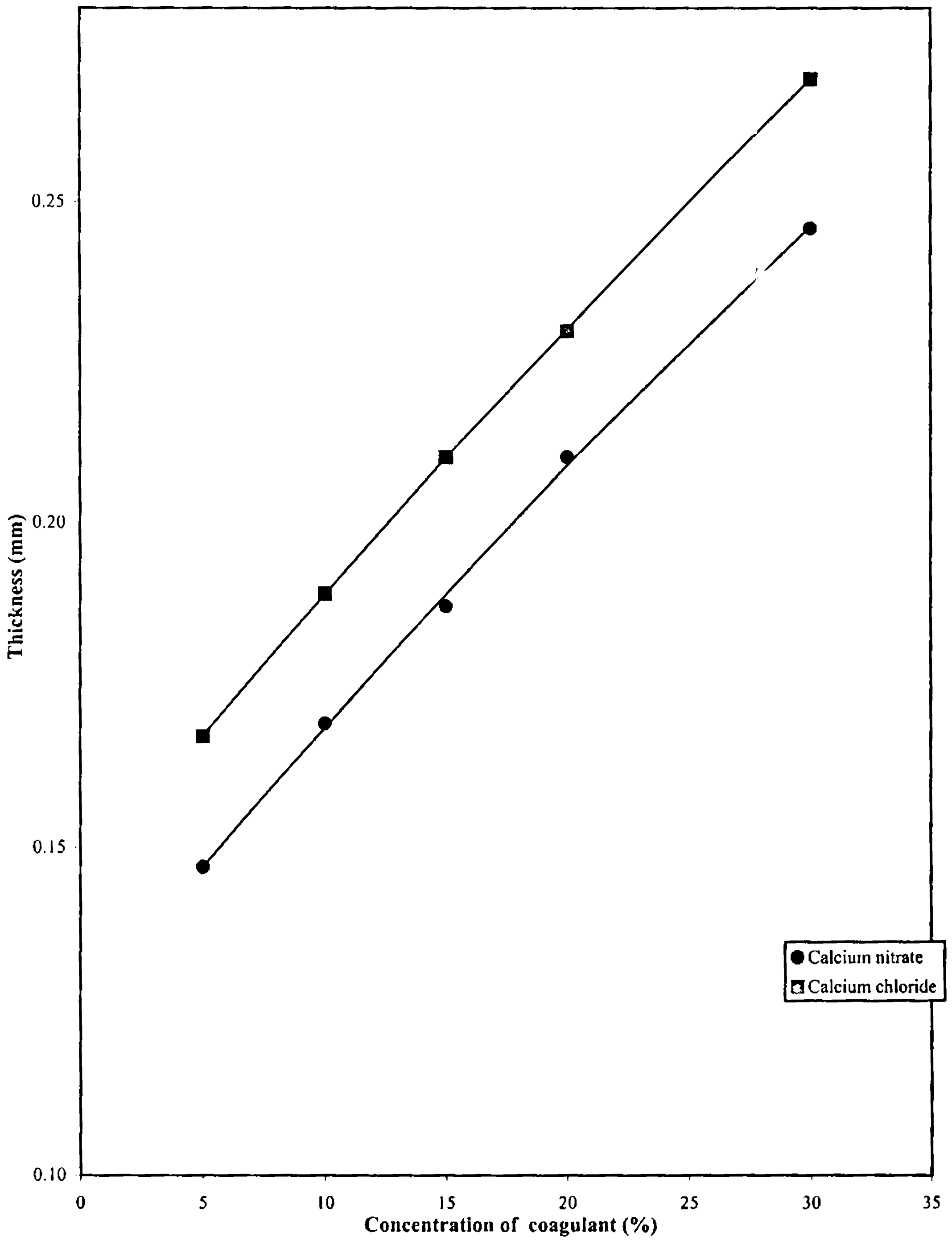


Fig 4.12. Effect of variation of thickness dry LPL films against concentration

CHAPTER 5

VULCANIZATION CHARACTERISTICS OF LOW PROTEIN LATEX

Extractable proteins (EP) in natural rubber latex products can cause allergic reactions in sensitized people(1-4). A form of natural rubber latex which can result in very low EP in latex products, has been developed by a non-enzymic deproteinization process(5). This low protein latex (LPL) contains low level of non-rubber materials, especially proteins. The sulphur vulcanization characteristics of natural latex are, to a certain extent, controlled by the level of non-rubber materials especially proteins(6–8). Since LPL is low in total proteins also, its vulcanization behaviour is likely to be different from that of standard centrifuged latex (SCL).

LPL can find application in the production of medical and pharmaceutical products like catheters, examination gloves, teats, soothers, condoms etc, which make intimate contact with human body. Another area of application is medical tubing. Latex products made from LPL will be of advantage to persons sensitive to latex proteins. For achieving desirable properties for the vulcanizates, the vulcanization conditions have to be standardized. The basic objective of the development of a vulcanization system for an elastomer is to transform essentially linear polymer molecules into a three dimensional network by the insertion of crosslinks.

Crosslinking have the effect of preventing the polymer chains moving bodily past each other when an external force is applied to the matrix. Vulcanization of NR is generally brought about by heating with sulphur and accelerator(s). The amount of sulphur and accelerator determine the crosslink density and type of crosslink, which in turn control the physical properties. Vulcanization can be achieved by peroxides or high energy gamma radiation also. This chapter, dealing with vulcanization of LPL is divided into three parts:

A. Vulcanization of low protein latex in conventional sulphur cure system.

B. Vulcanization of low protein latex in EV (efficient vulcanization) cure system.

C. Radiation prevulcanization of low protein latex.

REFERENCES

1. A.F.Nutter. *Brit.J. Dermatol.* **101**, 597 (1979).

2. K.Turjanmaa and T.Reunala. *Dermatologic Clinics.* **6**, 47 (1988).

3. K.Wrangsjo, J.E.Wahlberg, I.G.K.Axelsson, *Contact Dermatitis.* **19**, 264 (1988).

4. F.Leynadier, C.Pecquet and J.Dry. *Anaesthesia.* **44**, 547 (1989).

5. M.S.Sebastian,V.George and E.V.Thomas. Proc. 18th Rub. Conf. Indian Rubber Manufaturer's Research Association, Mumbai, p-105, (2000).

6. G.E.van Gills. *Rub. Chem. Technol.* **50**, 141 (1977).

7. D.C.Blackley. Proc. Int. Rubber Technol. Conf., Kuala Lumpur, p-3 (1988).

8. A.D.T Gorton, *NR Technol.* **6**, 52 (1975).

CHAPTER 5A

VULCANIZATION OF LOW PROTEIN LATEX IN CONVENTIONAL SULPHUR CURE SYSTEM

Traditionally crosslinking reaction in natural rubber is brought about by using sulphur and organic accelerators. From an economic point of view, the most widely used cure system is the one employing low levels of accelerator (about 0.4–1.2phr) along with high levels of sulphur (about 2.0–3.5phr). This is known as conventional sulphur cure system.

The ratio of the amount of any given accelerator to sulphur largely determines the type of sulphur crosslinks formed and the amount of sulphur which combines with the rubber in non-crosslink structures such as cyclic sulphides(1). Low ratios favour polysulphidic crosslinks with a relatively high level of cyclic sulphides.

For the sulphur vulcanization of products made from latex two alternate methods exist(2). The first is that the chemicals required for vulcanization are mixed into the latex then the latex mixture (compound) is formed into the required shape and dried. The dried rubber matrix containing the chemicals is then heated to effect vulcanization. This is known as post-vulcanization since crosslinking occurs essentially after the product has been formed. The other alternative involves heating the latex with the vulcanization ingredients dispersed in it. This is called prevulcanization and the resulting prevulcanized latex can be formed into latex products in the normal way. Only drying is required to obtain the vulcanized rubber product.

Post-vulcanization of latex products is fundamentally the same as that of vulcanization of dry rubber compounds. The main difference between the two processes is that in latex products the ingredients are incorporated into latex as aqueous dispersion/emulsions, then removing water. In dry rubber the chemicals are added as powders using an open mill or internal mixer.

The mechanism of accelerated sulphur vulcanization has been extensively studied(3-5). The first step in the combination of accelerator with activator, forming an active accelerator, soluble in rubber. The active accelerator reacts with sulphur to produce an active sulphurating agent which reacts with the rubber hydrocarbon to give a pendent group of chain of sulphur atoms terminated with the accelerator derivative. The pendent group can form a crosslink.

Sulphur prevulcanization of concentrated natural latex has been studied by several authors. Recent developments in the prevulcanization of natural latex have been described by Blackley(6). Low(7) has studied the prevulcanization rates of natural latices from different sources and age and also the effect of storage on the properties of prevulcanized latex/latex films after clarification of the prevulcanized latex. Teik and Poh(8) and Wong and Loo(9) have studied the room temperature prevulcanization of natural latex as a means of reducing cost of production. Various general purpose and special purpose formulations for prevulcanizing natural latex have been described by Gorton(10). The kinetics and mechanism of sulphur prevulcanization has been described by Merrill(11) and Loh(12). Compounding formulations suitable for the production of special medical/food items such as teats and soothers are also described by Gorton(13). The effect of temperature on prevulcanization of latex has been reported by Claramma and Mathew(14). The effect of leaching on properties of prevulcanized latex films has been described by several authors(6,8,10). Sulphur prevulcanization of double centrifuged natural latex also has been studied recently(15).

It has been believed that the presence of various non-rubber constituents, especially proteins are essential for the occurrence of sulphur prevulcanization reaction(16). Also there are reports that tensile properties of prevulcanized latex films are considerably affected by the level of proteins in the films. Hence it seemed worthwhile to study the post-vulcanization and prevulcanization characteristics of LPL using conventional sulphur system.

The extent of crosslink formation depends on temperature of vulcanization and duration of heating. This chapter reports the results of studies on the effect of duration of post-vulcanization on crosslink density of the film, its tensile properties, behaviour of the films on accelerated heat ageing and the synergestic effect of accelerator combinations. Prevulcanization studies include effect of temperature and duration of heating on crosslink density and tensile properties of latex films, effect of leaching of films and accelerated ageing. The extractable protein content in these latex films also were determined.

Materials and methods

From a batch of SCL preserved in HA system, DCL and LPL were prepared by the method described in Chapter 4. Potassium hydroxide used as stabilizer in latex compounding was prepared as 10% aqueous solution. Vulcanizing chemicals, sulphur, ZDC and Zinc oxide each were prepared as 50% dispersion by ball milling.

The formulation of the latex compound for post-vulcanization and prevulcanization in conventional sulphur cure system is shown in Table 5A.1. The latex compound after preparation was matured for 24h. For post-cure studies, cast films were prepared on levelled glass plate(17) and heated at 100°C for various intervals, and leached in water at room temperature.

To study the synergestic effect of accelerators in conventional system and also for improving the modulus of vulcanized films, a combination of ZDC and ZMBT (total quantity of accelerator was 1phr) was used as per the formulation in Table 5A.2. Cast films were vulcanized by heating at 100°Cin air for predetermined periods and leached in water at room temperature.

For prevulcanization, the matured latex compound was heated on a water bath at a given temperature under constant slow stirring. Samples were withdrawn at constant intervals and cooled immediately to arrest further crosslinking. To study the effect of temperature on prevulcanization, the latex compound was heated at 50, 60 and 70°C. Attempt to prevulcanize LPL at 70°C was not successful, as the latex compound was getting destabilized, due to the heat sensitizing activity of PPG.

Cast films were prepared by pouring enough latex on levelled glass plates and dried in air. Leaching of the films was carried out in water at 30°Cfor 1h except in cases where duration of leaching was a variable. The leached films were dried in air at room temperature. The state of cure of the films was assessed by solvent swelling method(18) and crosslink density was evaluated by using Flory-Rhener equation(19). Tensile properties were determined on a Hounsfield Universal Testing Machine following the Indian Standard procedure(20). Ageing of latex films was done at 70°Cfor 7 days. Extractable protein contents in latex films were estimated by RRIM modified Lowry method(21) using distilled water as the extractant and laboratory grade reagents were used for these estimations.

RESULTS AND DISCUSSION

POST-VULCANIZATION

Effect of duration of post-vulcanization in conventional cure system on crosslink density and effect of accelerated heat ageing

Variations in crosslink density of SCL, DCL and LPL films with time of post-vulcanization and the effect of heat ageing are shown in Figure 5A.1. For all the three types of latex films crosslink density increases with time of vulcanization, reach a maximum and then declines; however, the maximum crosslink density, and the duration of heating to achieve the state of cure differ. In general, at all durations of post-vulcanization, SCL films have higher crosslink density than DCL and LPL films. Thus DCL and LPL are slow curing than SCL and this difference in cure rate may be primarily due to difference in protein content. The three types of latex films post-vulcanized for short intervals, on ageing, show higher crosslink density due to further crosslink formation. Crosslink densities in DCL and LPL films are almost similar and are lower than that of SCL films. Higher crosslink density in aged SCL films, over DCL and LPL films, is due to the higher initial value for SCL films and antioxidant activity provided by accelerator residues(1) and naturally occurring antioxidants(22). Natural antioxidants are less in DCL and LPL compared to SCL films because of their removal during second centrifugal concentration. It is observed that crosslink densities in aged films of the three types of latices decrease with duration of post-vulcanization. In conventional cure system the crosslinks are mainly polysulphidic. The decline in crosslink density is believed to be due to main chain modifications occurring as a result of breakdown of polysulphidic crosslinks with the insertion of liberated sulphur in cyclic sulphides(13). Reduction in crosslink density is thus due to molecular rearrangement. It is observed that in vulcanized LPL films maximum crosslink density is achieved when duration of post-vulcanization is 1h. However, maximum crosslink density in aged film is observed when initial duration of post-vulcanization was about 45 minutes at 100°C, prepared as per the formulation given in Table 5A.1.

Effect of duration of post vulcanization in conventional cure system on tensile properties of latex films and effect of accelerated heat ageing

Figure 5A.2 shows the effect of variation of modulus of latex films against duration of post-vulcanization at 100°C, both before and after ageing. Modulus of all the latex films increase initially with duration of post-vulcanization. SCL films show maximum modulus at about 1.2h of vulcanization while DCL and LPL have maximum at 1.1h of vulcanization. Beyond this state of cure modulus decline. For a given period of post-vulcanization, SCL films have higher modulus than DCL or LPL films. Higher crosslink density of SCL films is the major factor contributing to the higher modulus. It is observed that LPL films have higher modulus than DCL films, even though crosslink densities are similar in these films. This is probably due to higher forces of attraction between latex particle of LPL films due to high Hydrogen bonding originating from adsorbed PPG molecules on particles surface. Ageing of latex films is accompanied by increase in modulus, when the period of post-vulcanization is below the period corresponding to maximum modulus. It is observed that the modulus of SCL and LPL films post-vulcanized for 1h remain more or less constant even after ageing. This is probably because the molecular rupture occurring during ageing is compensated by additional crosslink formation. Films vulcanized beyond this period are accompanied by reduction in modulus. Reduction in crosslink density of the aged films is mainly responsible for reduced modulus on ageing. However, both SCL and LPL latex films vulcanized to the optimum level show high retention of modulus, probably due to the antioxidant activity of dithiocarbamate accelerator residues(1) and naturally occurring antioxidants(22). However in the case of DCL films beyond a period of 1h of post-vulcanization accelerated ageing is accompanied by fall in modulus. This is primarily a result of low crosslink density in the aged film.

As seen from Figure 5A.3 post-vulcanized SCL and LPL films show high tensile strength and the gradation is

SCL > LPL > DCL

Before ageing, for the three types of films maximum tensile strength is achieved when post-vulcanized for about 1h at 100°Cwhich is considered to be the optimum period of vulcanization. Slightly higher tensile strength is exhibited by SCL films over LPL. Higher tensile strength of SCL and LPL films is primarily due to high crosslink density. Attractive forces due to Hydrogen bonding between proteins and/or PPG adsorbed on the surface of coalesed latex particles in the film make a secondary contribution. However, in DCL films, crosslink density is least among the three latices. Contribution due to Hydrogen bonding is low due to reduced level of proteins and absence of PPG. On ageing, under-cured SCL, DCL and LPL films show a slight improvement in tensile strength followed by a fall. In the case of DCL and LPL films tensile strength after ageing reduce linearly with increase in vulcanization time. On heat ageing, there is net reduction in crosslink density for optimum and over-cured films. After ageing, retention of tensile strength is higher for SCL film, even though crosslink density in aged SCL and LPL films vulcanized for 1h are almost equal. Thus in addition to crosslink density, effectiveness of interparticle coalescence during film formation also contributes to higher tensile strength of SCL films after ageing. LPL films post-cured for 0.5h showed considerable improvement in tensile strength after ageing. Formation of additional crosslinks on ageing makes substantial contribution to this improvement. Other LPL films initially cured for longer duration show lower retention. Retention of tensile strength on ageing is lowest for DCL films. This may be due to the rupture of crosslinks on ageing and removal of naturally occurring antioxidants, during the second centrifugal concentration, involved in the production of DCL and LPL.

Elongation at break of the SCL, DCL and LPL films vulcanized in the conventional system are shown in Figure 5A.4. The data show that for both SCL and LPL films elongation at break decreases with increase in cure time, reaches minimum value and then increase. However DCL films show a constant decrease. Ultimate elongation os lowest for DCL films. This reduction is attributed to the increase in crosslink density and modulus of the films. However, over-cured films of SCL and LPL show slightly higher elongation. This is probably due to the reduction in crosslink density and modulus of the over-cured films. Also ageing of the films reduces ultimate elongation. The reduction in elongation is probably due to the thermal and oxidative degradations that have occurred to the polymeric chains and/or crosslinks in all films.

Synergestic effect of accelerator combination on tensile properties post-vulcanized latex films

It is a common practice in the technology of natural latex to replace a portion of dithiocarbamate accelerator by thiazole for improving the modulus of latex films(23-25). The results obtained by replacing different portions of zinc diethyldithiocarbamate (ZDC) by zinc salt of mercaptobenzothiazole (ZMBT) in post vulcnizaion of LPL films is given in Figure 5A.5 (to limit the volume of data, this study is confined to LPL films alone). It is seen that replacement of 20% ZDC by ZMBT improves the modulus for all samples studied except where the film is under-cured. However, ZMBT addition above 20% reduces the modulus in the case of films cured beyond the optimum period of vulcanization.

However, it is seen from Figure 5A.6 that partial replacement of ZDC by ZMBT is accompanied by a reduction in tensile strength for all the combinations and the extent of reduction increases with increasing content of ZMBT in the vulcanizate.

Figure 5A.7 shows the effect of accelerator combinations on elongation at break (EB) of LPL films. It is seen that for a given duration of vulcanization, up to about 25% content of ZMBT in the accelerator combination, EB reduces, is minimum at about 25-30% ZMBT and increases for higher ZMBT content. The initial reduction in EB is due to higher modulus and subsequent increase in ultimate elongation is probably because of the lower state of cure due to the slow curing nature of ZMBT.

The effect of heat ageing on modulus of LPL films post-vulcanized for 1h at 100°C using different combinations of ZDC/ZMBT is shown in Figure 5A.8. It is seen that for all combinations of ZDC and ZMBT under study, modulus of the films increases on ageing. The extent of increase is least for ZDC/ZMBT combination 1.0/0 and maximum for 0.5/0.5. As ZMBT is not a fast accelerator as ZDC, by 1h heating at 100°Cthe films have not cured to the optimum. Hence, further curing occurs during heat ageing, leading to increase in modulus. It is seen that for maximum modulus after ageing, replacement of 0.25 parts of ZDC by ZMBT is necessary.

Heat ageing of LPL films is accompanied by fall in tensile strength for all combinations of ZDC/ZMBT. The results obtained are shown in Figure 5A.9. Tensile strength decreases slightly with increase in the content of ZMBT. It is believed that the reduction in tensile strength is due to thermal degradation of the rubber molecules. However, the overall retention of tensile strength on ageing is good. Ageing of the vulcanized latex films, containing various levels of ZDC and ZMBT is accompanied by reduction in elongation at break, as seen from Figure 5A.10. As in the case of tensile strength the reduction in ultimate elongation is attributed to thermal degradation of molecular chains. It does not appear that a rational explanation in terms of the chemistry of accelerated sulphur vulcanization reaction has ever been proposed(25).

Effect of duration of post-vulcanization on physical properties of latex films containing different levels of ZDC/ZMBT combinations

Figure 5A.11 shows the variation in modulus of LPL films post-vulcanized for different durations and containing different levels of ZDC and ZMBT, the total content of accelerators being 1phr. It is seen that the time required to achieve a given modulus slightly reduces with increasing content of ZMBT. For all accelerator combinations, modulus increases from a low value, reaches a maximum and then declines. The fall in modulus on continued heating beyond the optimum is possibly due to the thermal degradation occurring during continued heating.

The variation in tensile strength is shown in Figure 5A.12. The highest tensile strength is observed at about 1h of post-vulcanization for all ZDC/ZMBT combinations and maximum tensile strength is achieved when ZDC alone is used as accelerator. For each of the accelerator combinations investigated, tensile strength increases from a low initial value, reaches a maximum at about 1h and then declines.

The variation of elongation at break with duration of post-vulcanization is shown in Figure 5A.13. EB initially decreases and is minimum at about 1h of vulcanization and then increases. For a given duration of vulcanization the lowest EB is shown by ZDC/ZMBT combination of 0.6/0.4.

PREVULCANIZATION

Swelling index and crosslink density of pre-vulcanized latex films

Natural latex films absorb hydrocarbon solvents and swell. The extent of solvent absorption and swelling are inversely proportional to extent of cure(25). Table 5A.4 shows the variation of weight swelling index for three types of latex films at 60°Cand also at LPL films at 50°C which are prepared from latex prevulcanized for different intervals. The values obtained for DCL and LPL films are almost similar, indicating that their states of cure are almost comparable. Swelling Index for LPL at 50°Cshows a progressive fall, while the data at 60°Cfor SCL, DCL and LPL films initially decreases with prevulcanization time, passes through a minimum value and then increase. But the minimum value for SCL films at 60°C is appreciably lower than that of DCL and LPL films. This indicates that the state of cure of SCL is much higher than that of DCL and LPL films. According to Gorton and Pendle(17) weight swelling index values between 15–7 corresponds to lightly vulcanized film, 7–5 for moderately vulcanized and less than 5 for fully vulcanized film. Thus it is seen that DCL and LPL are slow in vulcanizing compared to SCL and do not achieve a fully cured state.

Figure 5A.14 gives the variation of crosslink density with time of prevulcanization. In the case of LPL at 50°C, crosslink density steadily increases during 5h of heating and does not show a maximum. Generally prevulcanization times are of the order of 2–3h and the crosslink density achieved during this period is about $2.5–3.0\times10^{19}$ per gram of rubber hydrocarbon. However, crosslink density in rubber particles of LPL at 50°C in 2–3h is too low. Thus for practical application, prevulcanization temperature of 50°C is of no use for LPL. The three types of latices when prevulcanized at 60°C, crosslink density increases initially with time, reaches a maximum and then slowly declines on continued heating. For SCL maximum crosslink density is observed at about 3.5h while DCL and LPL show maximum at 3h heating. The maximum value exhibited by DCL and LPL are much lower than that of SCL. Moderate levels of crosslinks are formed in LPL at 60°C, while SCL under similar conditions are crosslinked to a higher state. Since the crosslink density achieved at 60°C in LPL was low, prevulcanization at 70°C was tried. However, attempts to prevulcanize LPL at 70°C failed, as the latex was destabilized after 1h of heating due to the presence of polypropylene glycol in latex, which can function as a heat sensitizing chemical.

It is observed that sulphur can transfer from sulphur particles originally present in the aqueous phase of latex to the rubber particles remarkably rapidly, while zinc dialkyl dithiocarbamate accelerator by itself does not transfer from its particles to any significant extent(23). However, in presence of sulphur, the accelerator can transfer more rapidly, although more slowly than does sulphur on its own(23). The first major step in vulcanization of latex particles is the formation of a sulphur-accelerator species in the aqueous phase of the latex. During prevulcanization of latices, sulphur and sulphur-accelerator species can independently dissolve in the serum, with the assistance of some serum constituents and form a loose complex having some surface activity and get adsorbed at the rubber-serum interface(3,26). However, after adsorption, the hydrophilic component of the adsorbed species is somehow lost, thus becoming hydrophobic. The hydrophobic species dissolves in rubber and migrates to the interior of the latex rubber particle where they react with rubber molecules thus leading to the formation of crosslinks. The hydrophilic component of the sulphur-accelerator complex returns to the aqueous phase facilitating further complex formation and adsorption at the rubber-serum interface. Some non-rubber components in latex assist in the dissolution and adsorption of sulphur/accelerators(27). In DCL and LPL the non-rubber materials are less and hence the amount of sulphur and accelerator entering rubber particles are believed to be less. Thus the degree of vulcanization is low in DCL and LPL. In LPL at 50°C, initially crosslink insertion is very slow; after 3–3.5h, there is a rapid increase as shown in Figure 5A.14. This in turn, may be probably due to the slow transfer of vulcanizing ingredients into the rubber phase. This slow entry of curatives to LPL particles at 50°C may be due to some hindrance made by polar hydroxyl groups of adsorbed polypropylene glycol molecules at the rubber particle surface. At 60°C, crosslink insertion is more rapid in three types of latices, probably due to higher rate of activity of sulphurating species. However, this individual rate is highest for SCL. The decrease in crosslink density on continued heating at 60°C in the case of SCL, DCL and LPL is probably due to the breakdown of effective crosslinks, which are mostly polysulphide in conventional cure system(28,29). Crosslinks and pendent groups undergo a variety of further reactions; these are considered 'side reactions' in sulphur vulcanization. These take place at the same time as crosslinking, during over-cure and in the service life of the vulcanizate. Consequently their relative rates determine the efficiency of vulcanization. Desulphuration and decomposition are the two most important types of reactions occurring after crosslinking. These side reactions predominate beyond optimum cure(30), leading to an overall reduction in crosslnk density, on continued heating.

Tensile Properties of prevulcanized latex films

Figure 5A.15 shows the variation of modulus (at 500% elongation) of cast films against time of prevulcanization of latex. At 50°C for LPL, there is a gradual increase in modulus initially; but modulus increases more rapidly beyond 3h of prevulcanization. The observed variation in modulus is in agreement with the formation of crosslinks at 50°C as shown in Figure 5A.14.

When prevulcanization is carried out at 60°C, SCL, DCL and LPL films exhibit increasing modulus with increase in duration of prevulcanization. In the whole interval of prevulcanization modulus of SCL film is higher than that of DCL and LPL films and exhibit the order

SCL > LPL > DCL

ie, LPL gives softer vulcanizates. The lower modulus of LPL films compared to SCL films is mainly due to the lower crosslink density. Even though crosslink density in DCL and LPL films are more or less similar, modulus is higher for LPL films. This observation suggests that in addition to crosslink density some secondary factors are also involved in the overall modulus. At about 3h of prevulcanization, the observed modulus of 1.45 to 1.50MPa in the case of LPL films is sufficient enough to meet the modulus requirement for examination and surgical gloves. Also, low modulus of vulcanized LPL films is a desirable characteristic in the manufacture of products like examination gloves, as the wearer will not feel uneasy, on prolonged usage.

For a given duration of prevulcanization, the difference in modulus between LPL and SCL films remains somewhat constant initially and the difference increases marginally as prevulcanization proceeds. However, this observed difference is not in line with the difference in crosslink density between LPL and SCL films. The wide difference in crosslink density observed in Figure 5A.14 as prevulcanization proceeds is not reflected in modulus. This may probably be due to better inter-particle integration in LPL films via increased van der Waals attraction and Hydrogen bonding caused by adsorbed surface-active molecules. Eventhough crosslink density in DCL and LPL films are more or less equal, for a given duration of prevulcanization lower modulus of DCL films is attributed to reduced inter particle attractive forces.

Figure 5A.16 shows the variation of tensile strength of latex films with respect to prevulcanization period at different temperatures. The tensile strength observed for LPL films even after 4h of prevulcanization at 50°C is less than that achieved in 0.5h at 60°C. This is in line with the extent of crosslink formation at 50°C.

However, after 4.5h of prevulcanization at 50°C, the crosslink density of LPL films exceeds that of the LPL film prepared from latex prevulcanized at 60°C for 0.5h. However, the tensile strength of the latter film is higher. This is probably because a portion of crosslinks may be interamolecular, and do not contribute to tensile strength. This is in agreement with the results reported earlier(31) in the case of dry rubber products. It is also observed that DCL films exhibit lower tensile strength than LPL films even though crosslink densities are almost similar in both types of latex films. This is also in agreement with observation that crosslink density is not the only factor controlling tensile strength of latex film(6). In addition to crosslink formation, tensile strength is controlled to some extent by the effectiveness in the fusion of individual latex particles during film formation. At 60°C, the highest tensile strength is exhibited in about 2.5 to 3h of prevulcanization for the three types of latex films. This time interval does not coincide with the maximum of crosslink density Vs prevulcanization time curve (Figure 5A.14). Prevulcanization beyond a period of 3h is accompanied by a fall in tensile strength in the case of films made from three types of latices. The fall in tensile strength may be partly due to modification of crosslinks on continued heating(31) and also due to less effective fusion when they become more crosslinked(8). From the data presented in Figures 5A.15 and 5A.16 it can be seen that at moderate temperatures for a given crosslink density, the higher the temperature of prevulcanization, the higher the tensile strength of cast films. It is believed that at moderate temperatures, the crosslinks are more of an intermolecular nature, rather than main chain modifications.

Figure 5A.17 shows the variation of elongation at break of latex films against time of prevulcanization. LPL films at 50°C show lower elongation than that at 60°C. This is due to lower crosslink density and modulus of the former film. Further, LPL films show higher elongation compared to SCL and DCL films, even though LPL film has lower crosslink density. This observation suggests that effective inter particle fusion during film formation is a more important factor in deciding the tensile properties of latex films, than degree of crosslinking itself.

Effect of heat ageing on crosslink densities of prevulcanized latex films

Since latex films prepared from LPL prevulcanized at 50°C was low in crosslink density and tensile properties, ageing studies were not conducted on these films. The variation in crosslink densities of latex films on heat ageing at 70°C for 7 days is presented in Figure 5A.18. In the case of SCL films there was initially an increase in crosslink density on ageing, followed by a net fall as prevulcanization advanced. The maximum in the aged crosslink density occurred at about 2h of prevulcanization. DCL films prepared from latex prevulcanized for 0.5h melted, while 1h film showed a small increase in crosslink density on heat ageing and with other films, there was a net decline. In the case of DCL films, crosslink density after ageing was highest in the film prepared from latex prevulcanized for 2h. With LPL films, a trend similar to DCL was observed. In LPL films the highest crosslink density after ageing was observed in films which were prevulcanized for 2–2.5h among the three types of films the reduction in crosslink density due to ageing was highest in SCL films as prevulcanization time increased. In under-cured SCL and LPL films, there was a net increase in crosslink density due to the formation of additional crosslinks, by utilising the residual curatives. In conventionally cured latex films, the crosslinks are polysulphidic and the fall in crosslink density on heat ageing is attributed to breakdown of polysulphidic crosslinks with the inscrtion of liberated sulpher in cyclic sulphides.

Effect of heat ageing on tensile properties of prevulcanized latex films

The effect of heat ageing on modulus of prevulcanized latex films is given in Figure 5A.19. Cast films prepared from DCL and LPL, prevulcanized for half an hour, on ageing at 70°C for 7 days melted due to severe degradation. The modulus of three types of films decreases on ageing. This decrease in modulus roughly corresponds to fall in crosslink density of latex films. The major difference between the unaged and heat aged latex films is that for all the three types of latex films modulus of unaged films steadily increase throughout the course of prevulcanization, while a peak is observed in the aged modulus of films of the three types of latices. The aged modulus of DCL, and LPL films increased up to a prevulcanization period of 2–2.5h, and thereafter gradually decreased, while the maximum in the aged SCL curve was at about 3h of prevulcanization. The observed modulus values after heat ageing is the net result of two processes:

- further crosslink formation due to residual curatives available in the films
- thermal and oxidative degradation of the polymer network.

It is believed that some naturally occurring antioxidants in latex, residual ZDC or its fragments available in the film function as antioxidants, thus protecting the film to some extent in the ageing process. However, the net fall in modulus indicates that contribution of degradative process is more in determining the modulus of the films on ageing.

Variation in tensile strength of the three types of latex films, before and after ageing against duration of prevulcanization are given in figure 5A.20. Films of LPL exhibit reasonably good retention of tensile strength on heat aging at 70°C for 7 days. Upto a period of 3h of prevulcanization, the aged tensile strength of LPL films were better than those of SCL, even though the tensile strength before ageing was higher for SCL. After ageing DCL films had lowest tensile strength among the three types. At prevulcanization times beyond 3h aged SCL films were slightly better in tensile strength than LPL films. However, this observation is not much significant, as optimum prevulcanization time for SCL was 3h at 60°C.

One of the major factors contributing to tensile strength of latex films is crosslink density. After ageing crosslink densities of SCL films were higher than those of LPL films. But LPL films after ageing had higher tensile strength up to prevulcnization period of about 3h. It is therefore suggested that the forces of attraction due to Hydrogen bonding, originating from adsorbed PPG contributes to the tensile strength.

The results of elongation at break after ageing are given in Figure 5A.21. The under-cured LPL films show a slight increase in elongation at break, whereas those cured beyond optimum, show reduced elongation. The longer the duration of prevulcanization, the lower the ultimate elongation. Reduction in crosslink density is the main factor contributing to this behaviour. SCL and DCL films prevulcanized for various durations show decrease in elongation.

In general the tensile properties of prevulcanized LPL films after ageing are reasonably good. Forces of attraction via Hydrogen bonding plays an important role. The residual dithiocarbamate accelerator or its fragments functioning as antioxidants also have contributed to the good retention of tensile properties on heat ageing.

Effect of leaching on properties of sulphur prevulcanized latex films

Leaching of dipped latex products, either as wet gel or as dry film is beneficial for several reasons(32,33). The most important is improvement in physical properties. In medical products, accelerator residues causing skin irritation and dermatitis (type IV allergy) and naturally occurring proteins causing contact eczema and anaphylactic shock (type I allergy) are reduced by leaching. In products like electrician's gloves, the ionic components are removed by leaching, thereby improving electrical resistance. Also the appearance of latex products are improved by leaching.

The improvement in physical properties of latex films can be due to either increase in crosslink density or better fusion of latex particles during film formation(8) or both. To assess the separate contributions of each of the above factors, crosslink densities of LPL films prepared from conventionally sulphur prevulcanized LPL were leached for different intervals and the physical properties of the leached films were evaluated. To limit the volume of data, the effect of leaching is limited to LPL films alone. The data obtained on crosslink density are given in Figure 5A.22. It is observed that leaching of LPL films imoroves crosslink density. Water at room temperature followed by room temperature drying has no effect on crosslink density. This is in line with earlier reports(29).

The variation in the modulus of unleached and leached latex films are given in Figure 5A.23. It is observed that for a given state of vulcanization (as determined by the time of prevulcanization), modulus of unleached films is the least and it progressively increases with time of leaching. However, as indicated by the position of curves in Figure 5A.23 it is further observed that rate of increase in modulus decreases with increase in leaching period and beyond a period of 2h, there is practically no increase in modulus of dry LPL film. It is also observed that for a given duration of leaching, effect of leaching on modulus is high, when films are prepared from LPL prevulcanized for short periods, and the improvement is decreasing with duration of prevulcanization. It is believed that during leaching, some of the adsorbed non-rubber materials on the surface of the rubber particles are removed(14), thus permitting better inter-particle fusion.

The tensile strength of sulphur prevulcanized LPL films are affected by leaching. The data obtained are presented in Figure 5A.24. As in the case of modulus, the tensile strength of leached films increase with increase in the duration of leaching. Again this increase in tensile strength by leaching of the film is believed to be due to better inter-particle integration. However, a decrease in tensile strength is observed for long leaching periods (eg. 2h leaching). It is believed that in addition to increased inter-particle fusion, the contribution from Hydrogen bonding and van der Waals forces of attraction due to adsorbed polypropylene glycol and remaining proteins would have contributed to tensile strength. Prolonged leaching in water remove a portion of these adsorbed materials, causing reduction in Hydrogen bonding and van der Waals attractive forces between the adjacent particles, net result being a reduction in tensile strength.

Effect of leaching on the ultimate elongation of sulphur prevulcanized LPL films prevulcanized for different intervals is given in Figure 5A.25. Elongation figures for the unleached film also are given for comparison. The variation in elongation at break decreases with leaching time. This is almost in line with the inverse relation between modulus and ultimate elongation of latex films.

Effect of leaching on tensile properties of sulphur prevulcanized LPL films after accelerated ageing

The tensile properties of LPL films after heat ageing are appreciably affected by their leaching history. The data on the effect of duration of leaching in water on aged modulus of LPL films are presented in Figure 5A.26. A comparison of Figure 5A.26 with Figure 5A.23 shows that in the case of unleached films, modulus of films increases slightly on ageing upto about 2.5h of prevulcanization, which is the optimum period of prevulcanization and then decreases. However, the observed maximum modulus of unleached LPL films is slightly lower than those of the leached films prevulcanized for the same period. It is further observed that the best retention of aged modulus is observed for those films, which previously were leached for half an hour and longer leaching reduces the aged modulus.

The aged modulus of latex films are the net result of several factors:

- Crosslink density of the films before and after ageing
- The extent of inter-particle integration during film formation and its modification by leaching
- Role of ZDC and its fragments functioning as antioxidants
- Role of naturally occurring antioxidants(34,35).

Major naturally occurring antioxidants in natural latex are tocotrienols(36), tocopherols(37), betaines, amino and phenolic compounds(38).

Ageing of prevulcanized latex films is accompanied by a reduction in crosslink density (except those which were highly under-cured). However, leaching or its duration have practically no effect on crosslink density(33). Longer leaching effectively removes the non-rubber materials facilitating better inter-particle integration(8). However, residual ZDC/its fragments and the naturally occurring antioxidants are removed by long leaching. Thus it is observed that for maximum retention of modulus of LPL films after ageing, duration of leaching has to be restricted to less than half an hour. However, even the 2h leached film, after ageing shows higher modulus than the unleached one, which still retains all the naturally occurring or added antioxidants. This observation suggests that effective inter-particle fasion makes lower contribution to the modulus of aged films.

Maximum tensile strength for leached films is observed when films are leached for 1h (Figure 5A.24). However, long leaching reduces aged tensile strength as seen from Figure 5A.27. It is observed that for achieving maximum tensile strength for aged films, optimum leaching period is half an hour. As in the case of aged modulus, the reduction in aged tensile strength of leached films is attributed to removal of added (dithiocarbamate residues) and naturally occurring antioxidants, thus promoting degradation. Tensile strength of aged films, which were initially leached for short intervals were higher than that of unleached film, while the 2h leached film is only marginally higher than that of unleached film. This suggests that tensile strength of aged latex film depend on the presence of antioxidants more than that in the case of modulus.

From Figure 5A.28 it is observed that short leaching improves elongation at break; lowest elongation at break after ageing is observed when latex was prevulcanized for about 2.5h and films previously leached for 2h. However, for films prepared from latex cured beyond optimum, unleached films had the lowest elongation at break.

Extractable protein content in prevulcanized latex films

Extractable protein content of SCL, DCL and LPL films of different states of vulcanization, both before and after leaching for 5min in static water, at film to water ratio of 1:400 are given in Figure 5A.29. Even though a definite trend cannot be observed for the EP content, the following general conclusion can be made.

- EP content in unleached latex films in the order

  SCL > DCL > LPL

- EP content in the three types of unleached latex films increase with the duration of prevulcaization.
- The same order in seen in the above films after leaching for 5min.
- Leaching for a short period of 5min is accompanied by a drastic fall in EP content.

Processing of DCL and LPL from SCL is accompanied by dilution of latex, followed by centrifugal concentration. Generation of second stage of skim latex in the process, facilitates removal of proteins. Thus DCL and LPL are lower in EP. Use of PPG in LPL processing facilitates protein displacement from rubber-serum inter face, so that LPL had least EP content. For prevulcanization, latices are heated at 60°C for various intervals. During this heating process some of the strongly observed proteins are degraded and made water soluble, so that unleached films show increased – EP and EP content increases with duration of prevulcanization(39).

EP content increases with increase in duration of prevulcanization. It is believed that, during prolonged heating, some of the strongly adsorbed proteins are degraded and made water extractable. During the short period of leaching (as in online leaching) they are removed. Thus all the three types of leached films show low EP contents in comparison with their unleached counterparts. The residual EP contents in LPL films leached for even 5 minutes are generally very low, in the range of 30–60mg/kg. This is lower than the EP content reported for LOPROL. Thus Figure 5A.29 clearly indicates the superiority of LPL, over SCL and DCL with respect to residual extractable protein content in leached film.

The effect of duration of leaching on residual EP content in LPL films is shown in Figure 5A.30. As seen from Figure 5A.29, even very short leaching is enough to reduce EP in LPL films to low levels. From Figure 5A.30 it is seen that prolonged leaching reduces residual EP still further. It is believed that during the prolonged leaching the degraded proteins in the interior layers of the films migrate to the surface and are removed. However, the reduction brought in by further leaching is only marginal. This is because the degradation that has occurred to proteins in LPL film is sufficiently high so that they are easily removed even by a short leaching period, so that very little is retained.

CONCLUSIONS

Following conclusions are derived from the above study:

- LPL, like SCL can be compounded and post-vulcanized in the conventional sulphur cure system. The physical properties of LPL films are slightly lower than that of SCL films; however, they are sufficiently high to meet the specifications of common dipped latex articles. The ageing behaviour of post-vulcanized LPL films are good.
- In post-cured LPL films, this modulus of LPL films can be improved by replacing a portion of dithiocarbamate accelerator by thiazole and the physical properties are optimum when ZDC/ZMBT ratio is 75:25. Physical properties of films after ageing are satisfactory.
- LPL can be sulphur prevulcanized to a reasonably high degree of crosslinking by using conventional cure system. However, rate and state of prevulcanization are less compared to SCL. The highest crosslink density is achieved in 3h of prevulcanization at 60°C. Reasonably good tensile properties are exhibited by prevulcanized LPL films, even though little lower than that of SCL. The highest tensile strength is achieved after 2.5h of prevulcanization. However, modulus continuously increases with time of prevulcanization. Ageing behaviour of LPL films are reasonably good and comparable to those of SCL films.
- The physical properties of LPL films are influenced by leaching. For maximum physical properties, leaching for a minimum period of 1h is essential. However, for achieving best combination of physical properties after ageing leaching has to be limited to less than half an hour.
- During the course of prevulcanization, more of proteins are becoming soluble and can be removed by leaching. LPL films leached for even 5min show EP content in the range of 30–60mg/kg only. Prolonged leaching still reduces residual EP, but the decrease is only marginal.

REFERENCES

1. D.J.Elliott, in Developments in Rubber Technology Vol.1, Chapter 1. Ed. A.Whelan and K,S.Lee. Applied Science Publishers Ltd., London (1979).

2. M.D.Morris. Proc.Seminar on Latex Technology and processing, Hert fort, UK p-41 (1992).

3. L.Bateman, C.G.Moore, M.Porter and B.Saville in the chemistry and physicas of Rubber like substances. Ed. Bateman, Macharu and Sons Ltd., London (1963).

4. A.V.Chapman and M.Porter, in Natural Rubber science and Technology. Ed. A.D.Roberts, oxford University Press, Oxford, Chapter 12, (1988).

5. A.V.Coran, Vulcanization in Encyclopedia of Polymer science and Engineering, John Wiley, New York (1989).

6. D.C.Blackley. Proc Int. Rub. Technol. Conf., Kuala Lumpur, p–3, (1988).

7. E.H.Low. Proc. RRIM Planters' Conf., Kuala Lumpur, p–307 (1977).

8. L.C.Teik and W.N.Poh. Developments in the Plastics and Rubber Product Industries. Plastics and Rubber Institute of Malaysia, Kuala Lumpur, p-265, (1987).

9. N.P.Wong and C.T.Loo. Proc. Int. Rub. Conf. Kuala Lumpur, p–487, (1985).

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

11. R.W.T.Merrill. Prevulcanization of Natural Rubbber Latex. M.Phil. Thesis. U.K. Council for National Academic Awards (1980).

12. A.C.P.Loh. Further Investigations on the Prevulcanization of Natural Rubber Latex. Ph.D Thesis. U.K. Council for National Academic Awards, (1982).

13. A.D.T.Gorton. Proc. Int. Rub. Technol. Conf., Kuala Lumpur, p–85, (1988).

14. N.M.Claramma and N.M.Mathew. *J. Appl. Polym. Sei.* **65**, 1913 (1997).

15. V.George, M.S.Sebastian and E.V.Thomas. *Rub. India,* **52 (12)**, 9 (2000).

16. D.C.Blackley. Polymer Latices: Science and Technology. Second Edn. Chapman & Hall, London, Vol.2, Chapter 13, (1997).

17. C.F.Flint and W.J.S.Nauton. *Trans. Instn. Rub. Ind.* **12**, 367 (1937).

18. R.M.Panich, N.M.Fodiman and N.M.Voyatski. *Soviet Rub. Technol.* **18 (2)**, 14 (1959).

19. P.J.Flory and J.Rehner Jr. *J. Chem. Phys.* **11**, 521 (1943).

20. IS 3400 (Part 1): 1987 Methods of Test for vulcanized rubbers–Tensile stress-strain properties (second revision).

21. F.Yusof and H.Y.Yeang. *J. nat. Rub. Res.* **7**, 206 (1992).

22. M.Nadarajah, A.Coomaraswamy, S.Kasinathan and A.S.L. Tirimanne. *J. Instn. Rub. Ind.* **6**, 26(1972).

23. 'Vulca for ZMBT' in Latex Manual, Imperial Chemical Industries, London (1953).

24. E.W.Madge. Latex Foam Rubber, Chapter 9. Maclaren & Sons Ltd., London (1962).

25. A.D.T.Gorton, *NR Technol.* **6**, 52 (1975).

26. M.Porter, R.Rawi and S.A.Rahim. *J. nat. Rub. Res.* **7**, 85 (1992).

27. G.E.van Gils, *Rub. Chem. Technol.* **50**, 141 (1977).

28. D.C.Blackley. Polymer Latices:Science and Technology. Vol. 3, Chapter 16, Second Edn. Chapman & Hall, London (1997).

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

30. A.V.Chapman and M.Porter. In 'Natural Rubber Science and Technology. A.D.Roberts (Ed), Oxford University Press, Chapter 12, (1997).

31. E.R.Rodger, in Developments in Rubber Technology-1. Ed. A.Whelan and K.S.Lee. Applied Science Publishers Ltd., London, Chapter 3, (1979).

32. M.Porter. Proc. Int. Rub. Conf., London, p–1, (1996).

33. M.D.Morris. Proc. Seminar on Latex Technology and Processing, Hertford, U.K, p–41, (1992).

34. M.Y.Amir-Hashim, M.D.Morris, M.G.O.Brien and A.S.Farid. *Rub. Chem. Technol.* **70**,560 (1997).

35. M.Nadarajah, A.Coomarasamy, S.Kasinathan and A.S.L.Tirimanne. *J. Instn. Rub. Ind.* **6**, 26 (1972).

36. P.J.Dunphy, K.J.Whittle, J.F.Pennock and R.A.Morton; *Nature* **207**, 521 (1965).

37. J.R.Davies and F.W.Kam. *J. Instn. Rub. Ind.* **2**, 86 (1968).

38. R.F.A.Altman. *Rub. Chem. Technol.* **14**, 664 (1941).

39. H.M.Ghazaly Proc. Int.Rubber Technology Conf. 1993, workshop Latex Proteins. Rubber Research Inst. Malaysia, p-8 (1994).

TABLE 5A.1

Formulation of latex compound for post- and prevulcanization in conventional cure system

Ingredient	*Parts by weight*	
	Dry	*Wet*
60% Natural latex	100	167
10% Potassium hydroxide	0.1	1.0
50% Sulphur	1.75	3.50
50% Zinc diethyldithiocarbamate	1.0	2.0
50% Zinc oxide	0.25	0.50

TABLE 5A.2

Formulation of latex compound for post-vulcanization in conventional cure system using accelerator combinations

Ingredient	*Parts by weight*	
	Dry	*Wet*
60% Natural latex	100	167
10% Potassium hydroxide	0.1	1.0
50% Sulphur	1.75	3.50
50% Accelerators (ZDC + ZMBT)	1.0	2.0
50% Zinc oxide	0.25	0.50

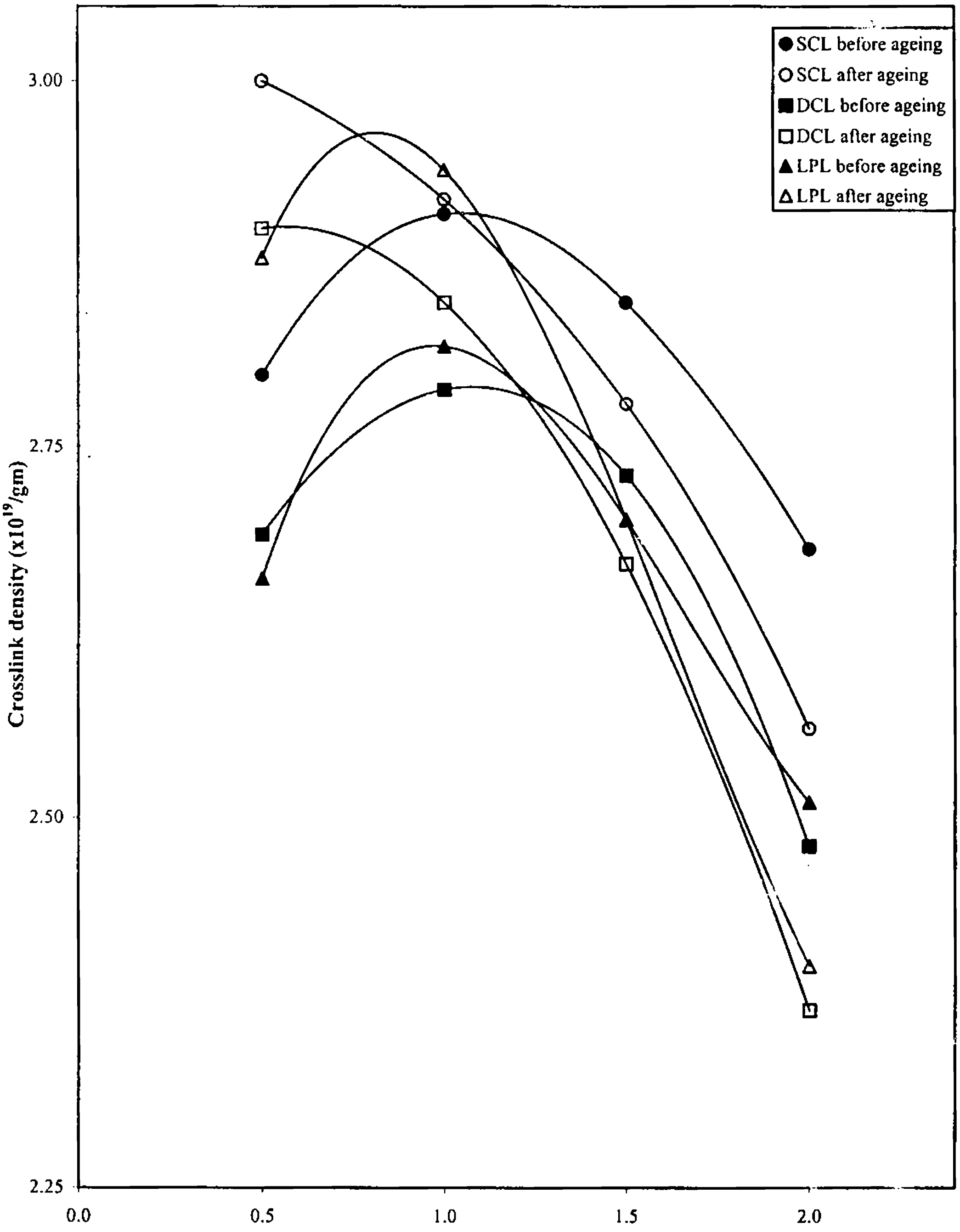


Fig 5A.1. Effect of duration of post-cure in conventional system at 100°C on crosslink density of latex films and the effect of heat ageing

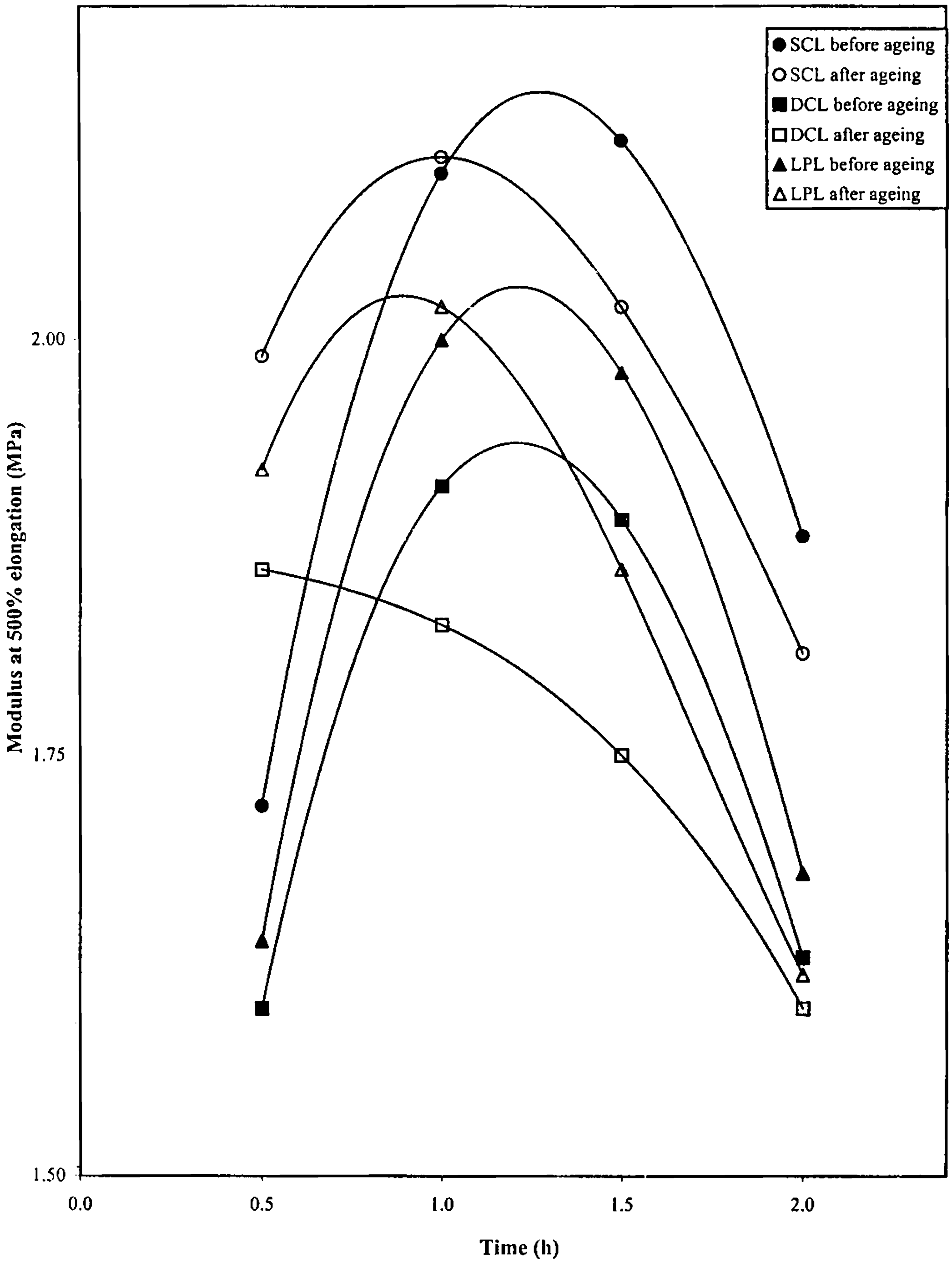


Fig 5A.2. Effect of duration of post-cure in conventional system at 100°C on modulus of latex films and the effect of heat ageing

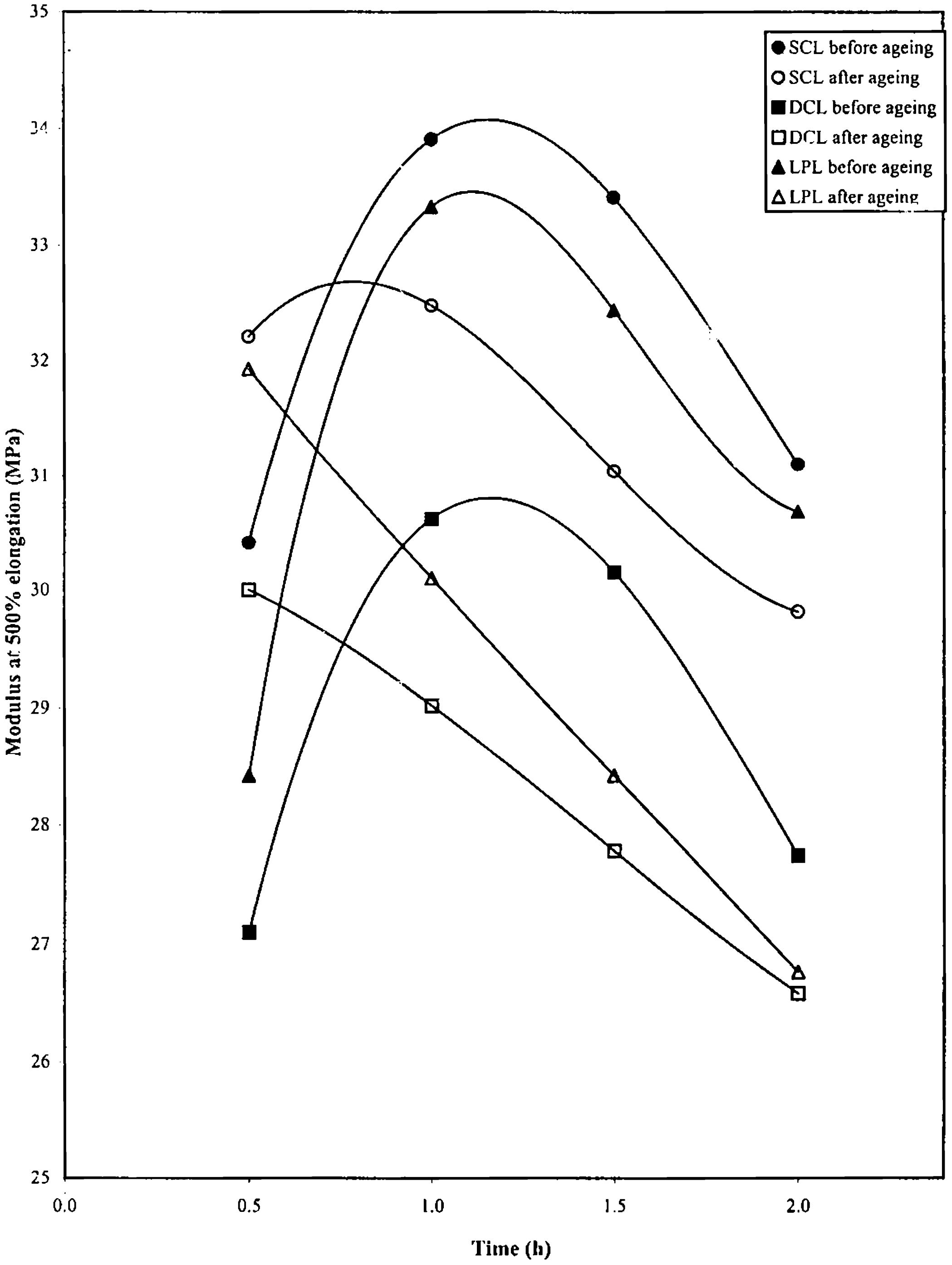


Fig 5A.3. Effect of duration of post-cure in conventional system at 100°C on tensile strength of latex films and the effect of heat ageing

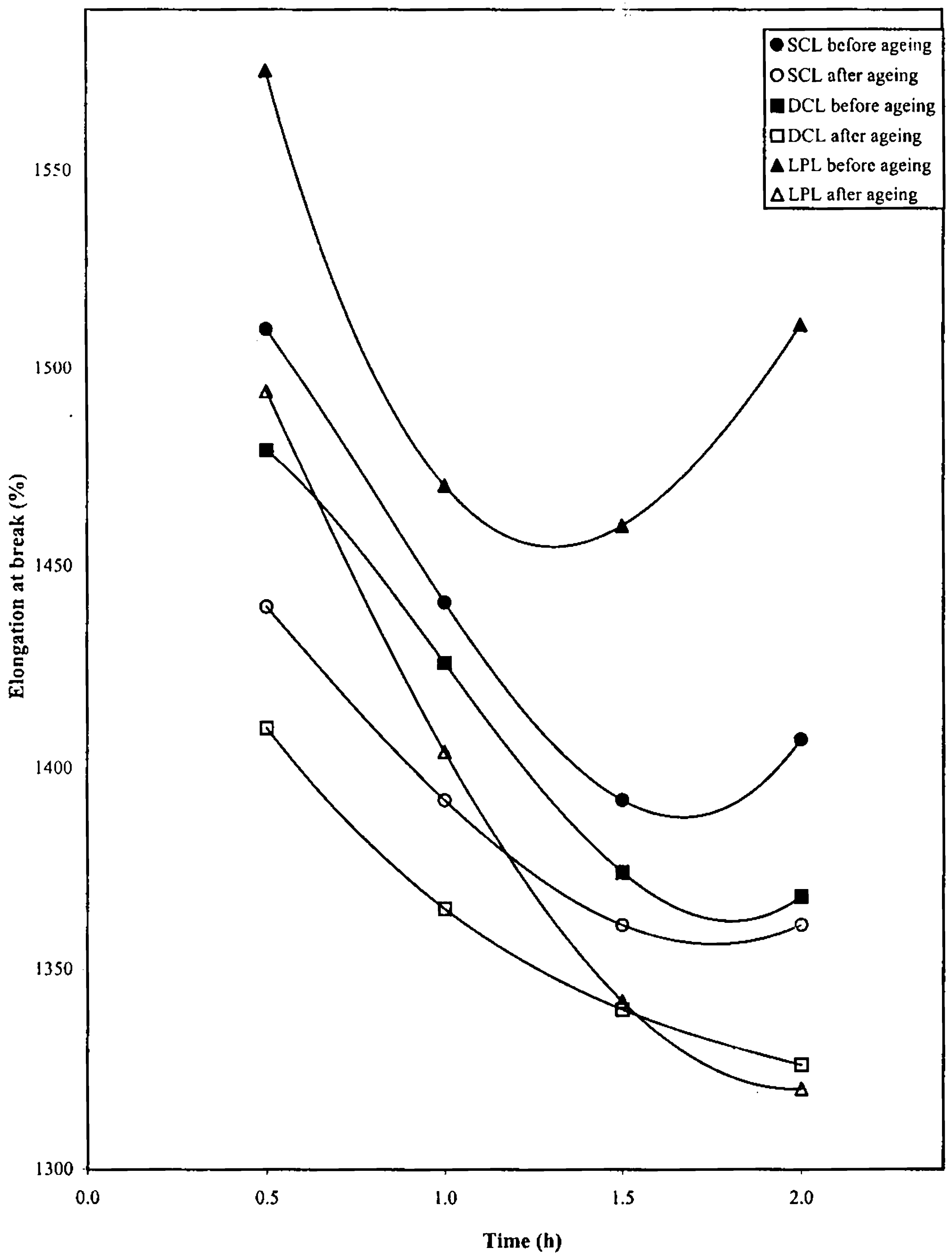


Fig 5A.4. Effect of duration of post-cure in conventional system at 100°C on elongation at break of latex films and the effect of heat ageing

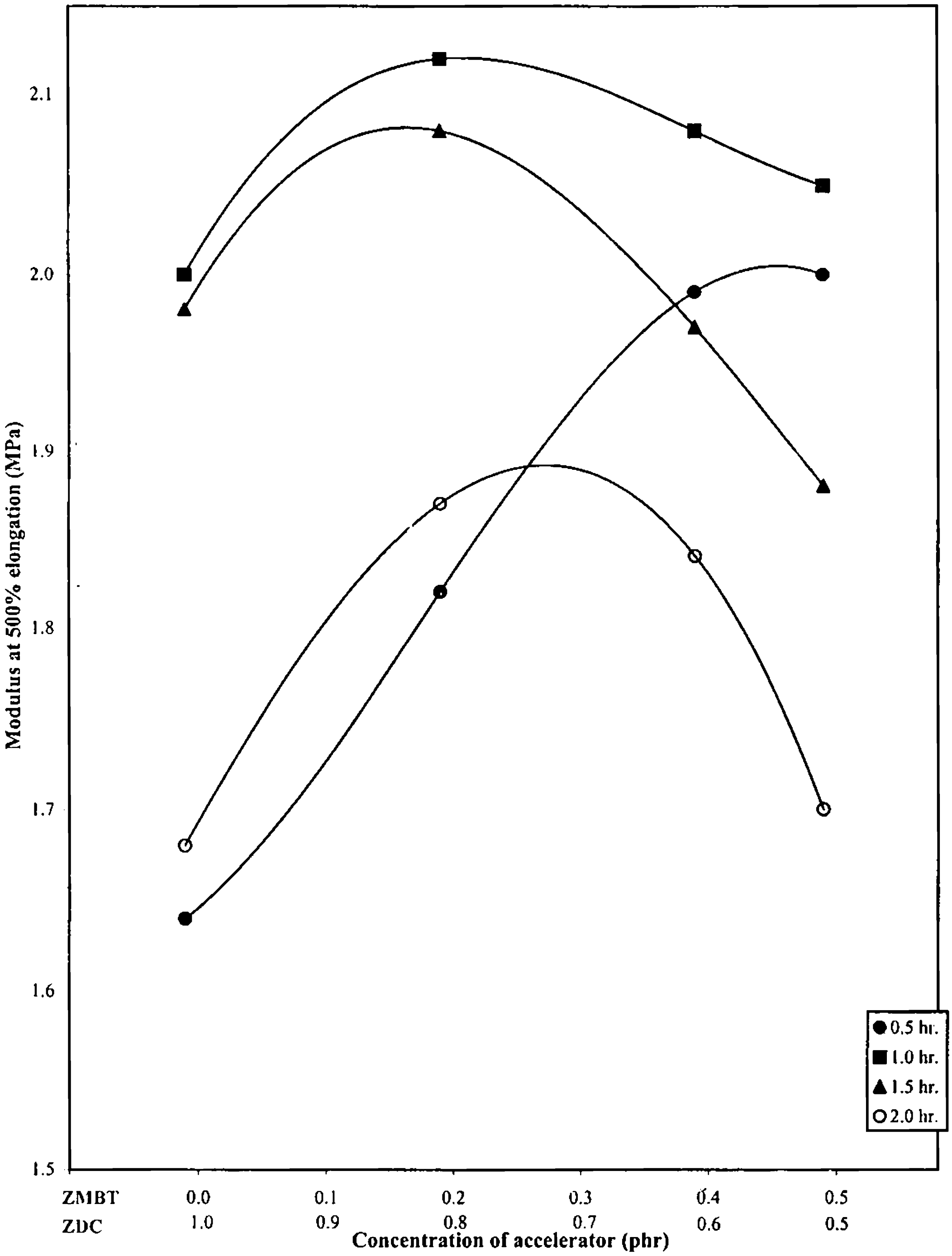


Fig 5A.5. Effect of accelerator combination on modulus of LPL films vulcanized for various intervals

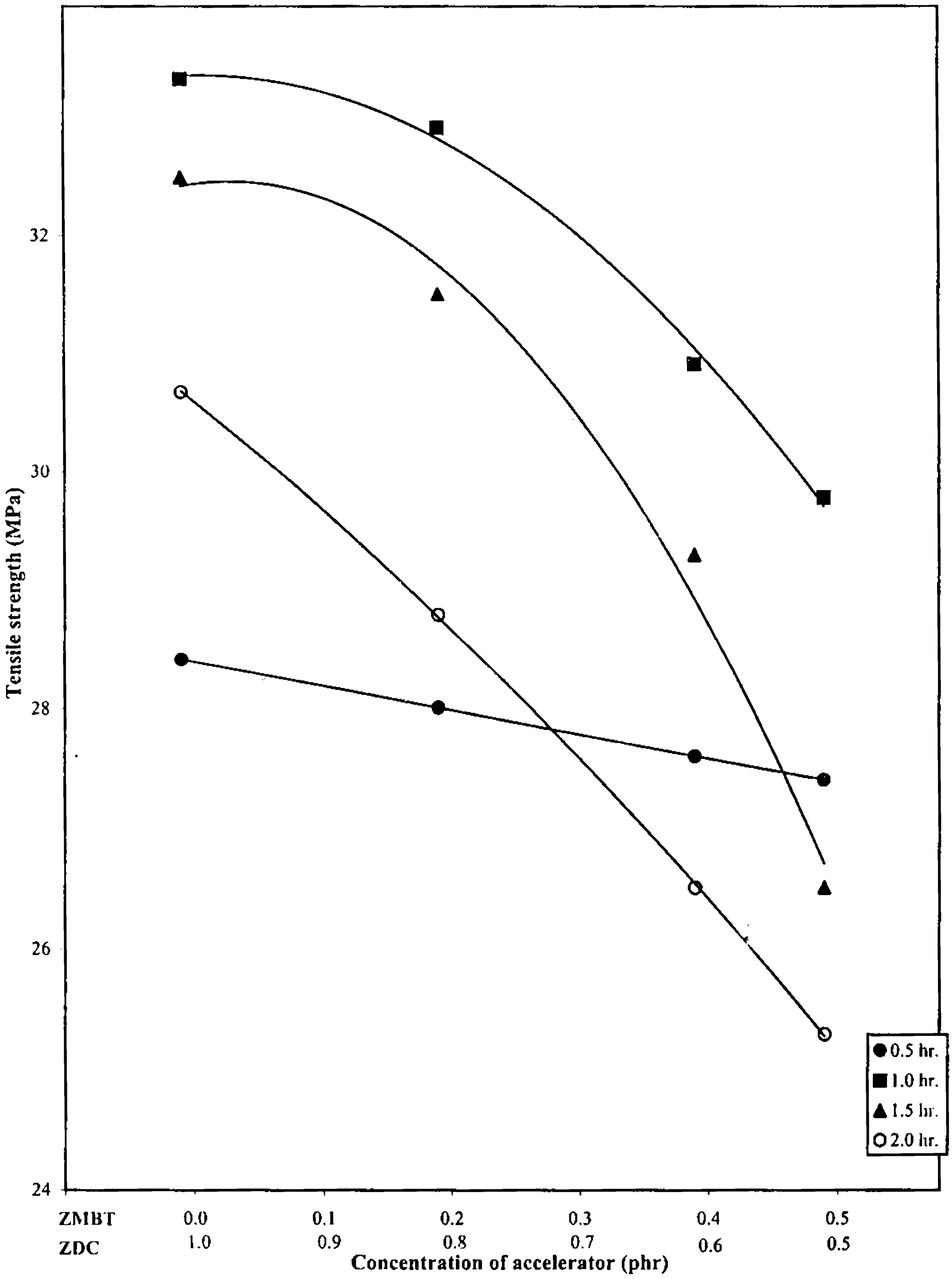


Fig 5A.6. Effect of accelerator combination on tensile strength of LPL films vulcanized for various intervals

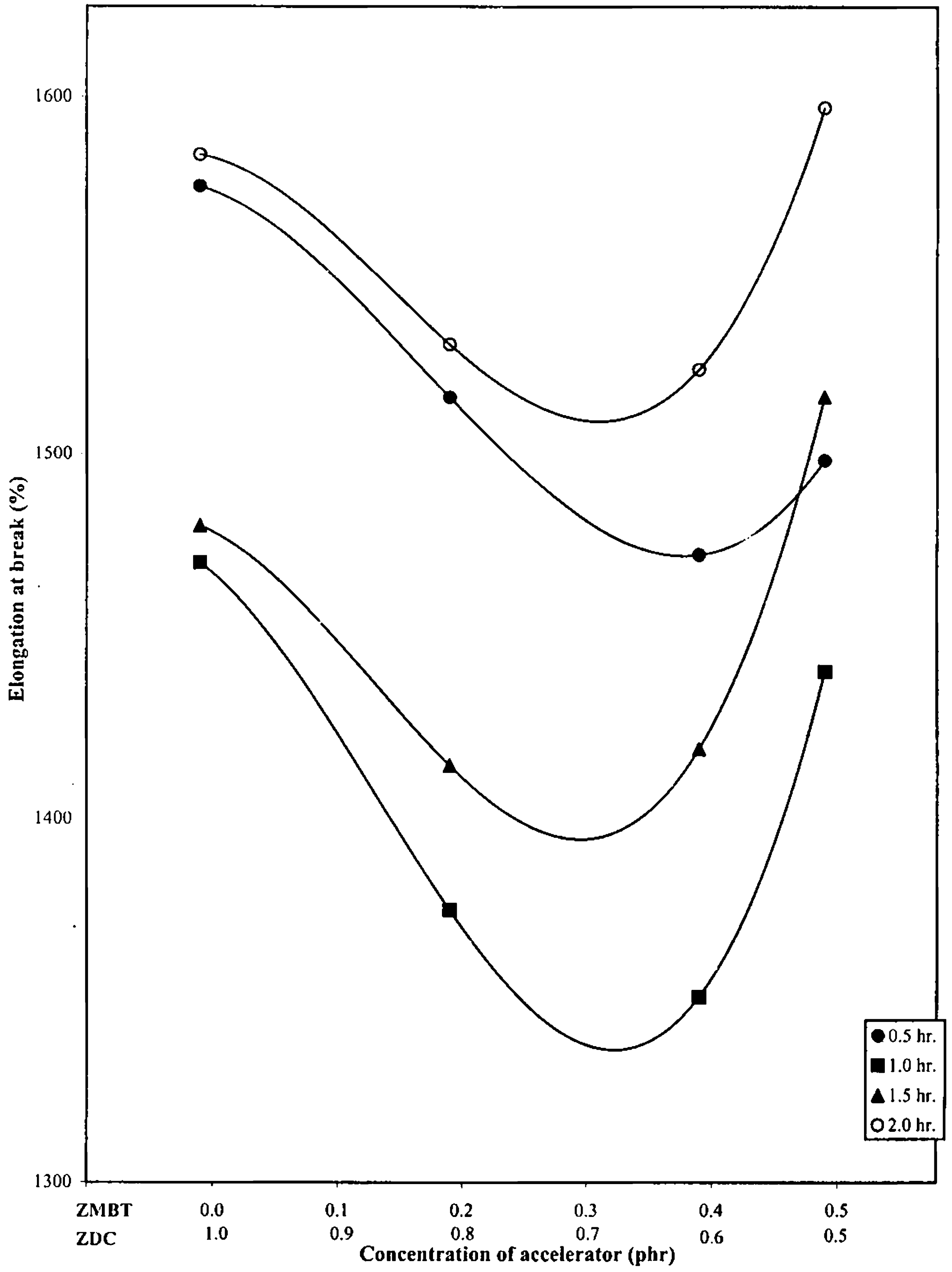


Fig 5A.7. Effect of accelerator combination on elongation at break of LPL films vulcanized for various intervals

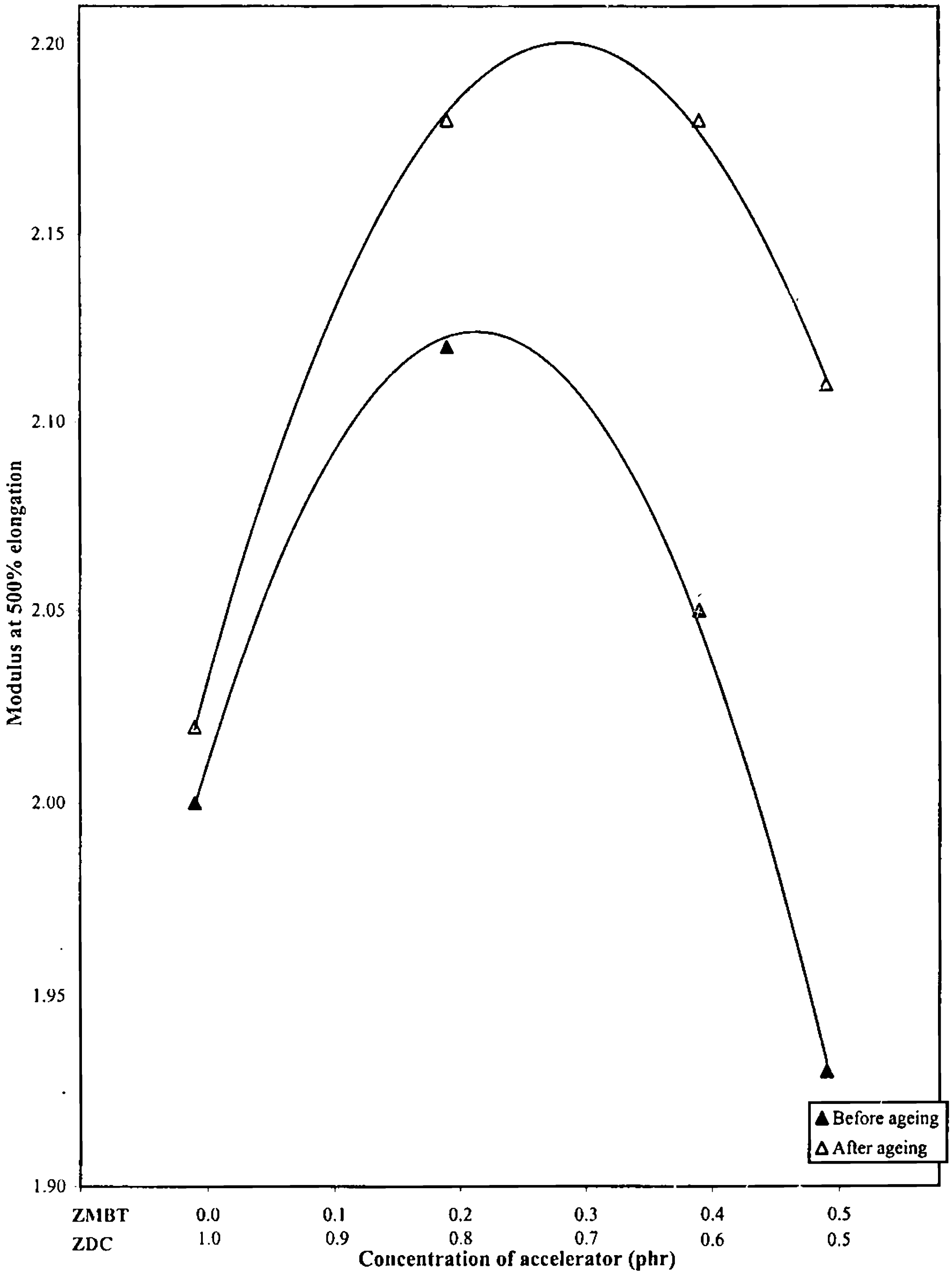


Fig 5A.8. Effect of accelerator combination on aged modulus of vulcanized LPL films

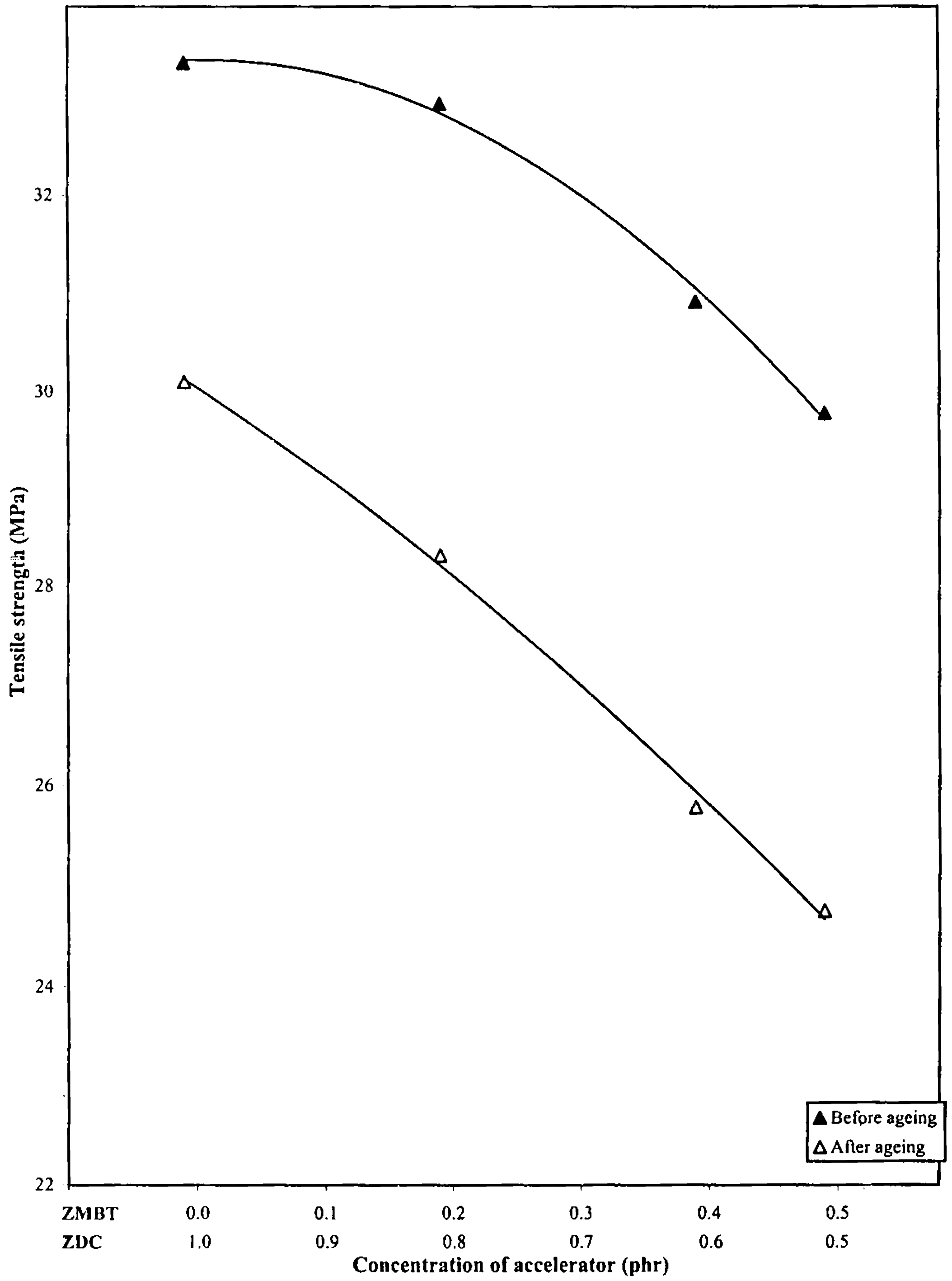


Fig 5A.9. Effect of accelerator combination on aged tensile strength of vulcanized LPL films

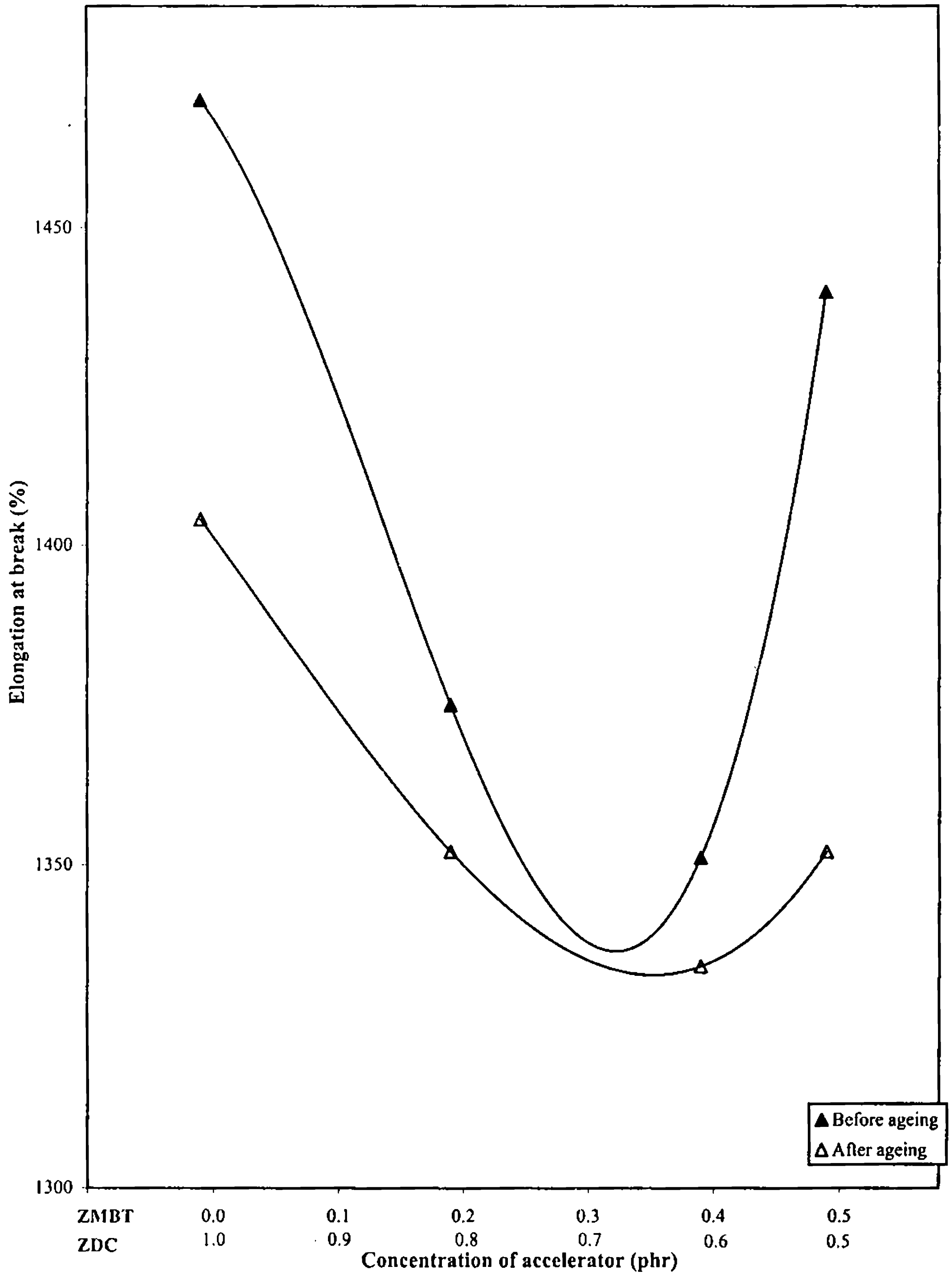


Fig 5A.10. Effect of accelerator combination on elongation at break of vulcanized LPL films after ageing

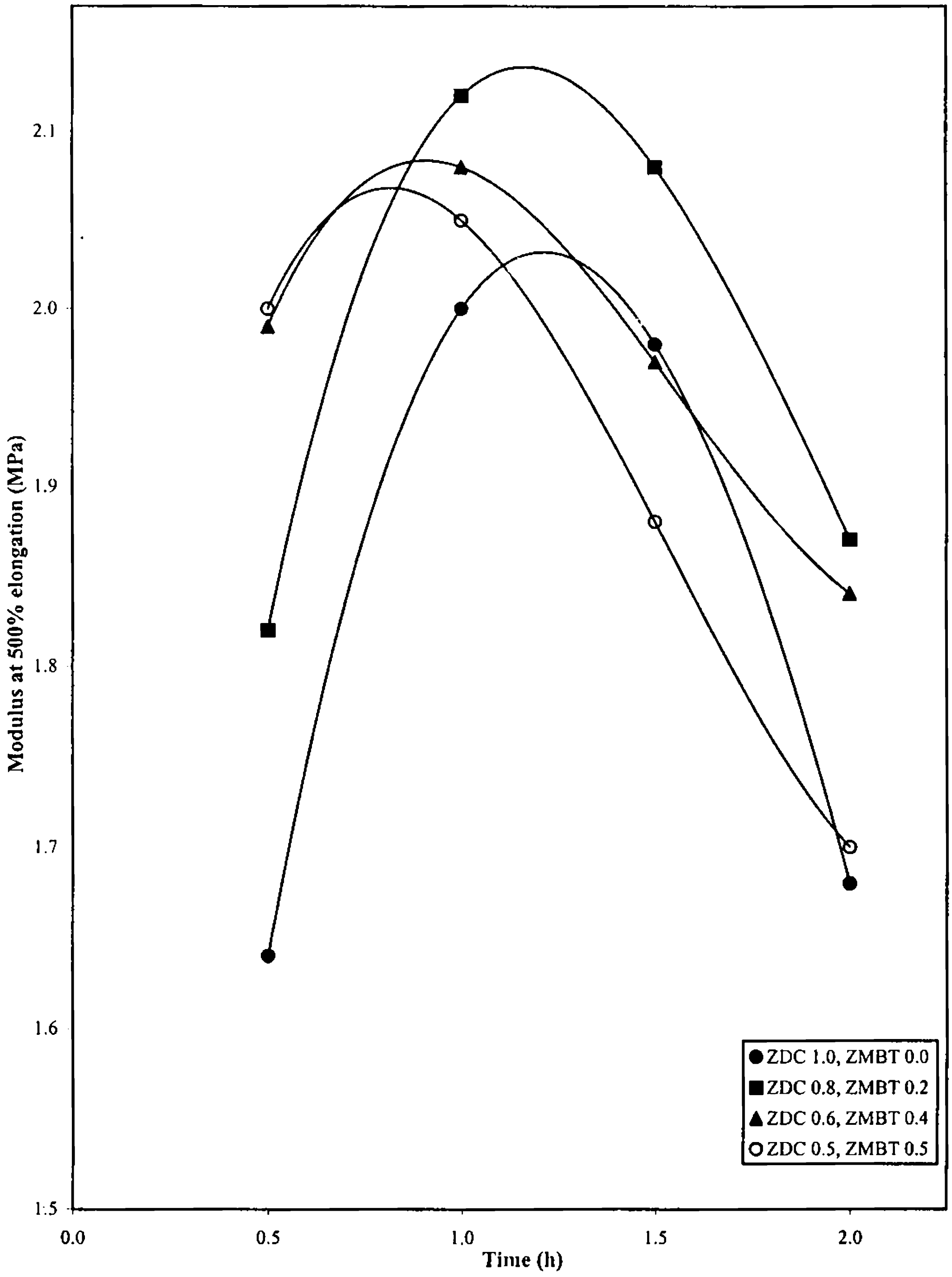


Fig 5A.11. Effect of duration of post-cure on modulus of LPL films using different accelerator combinations.

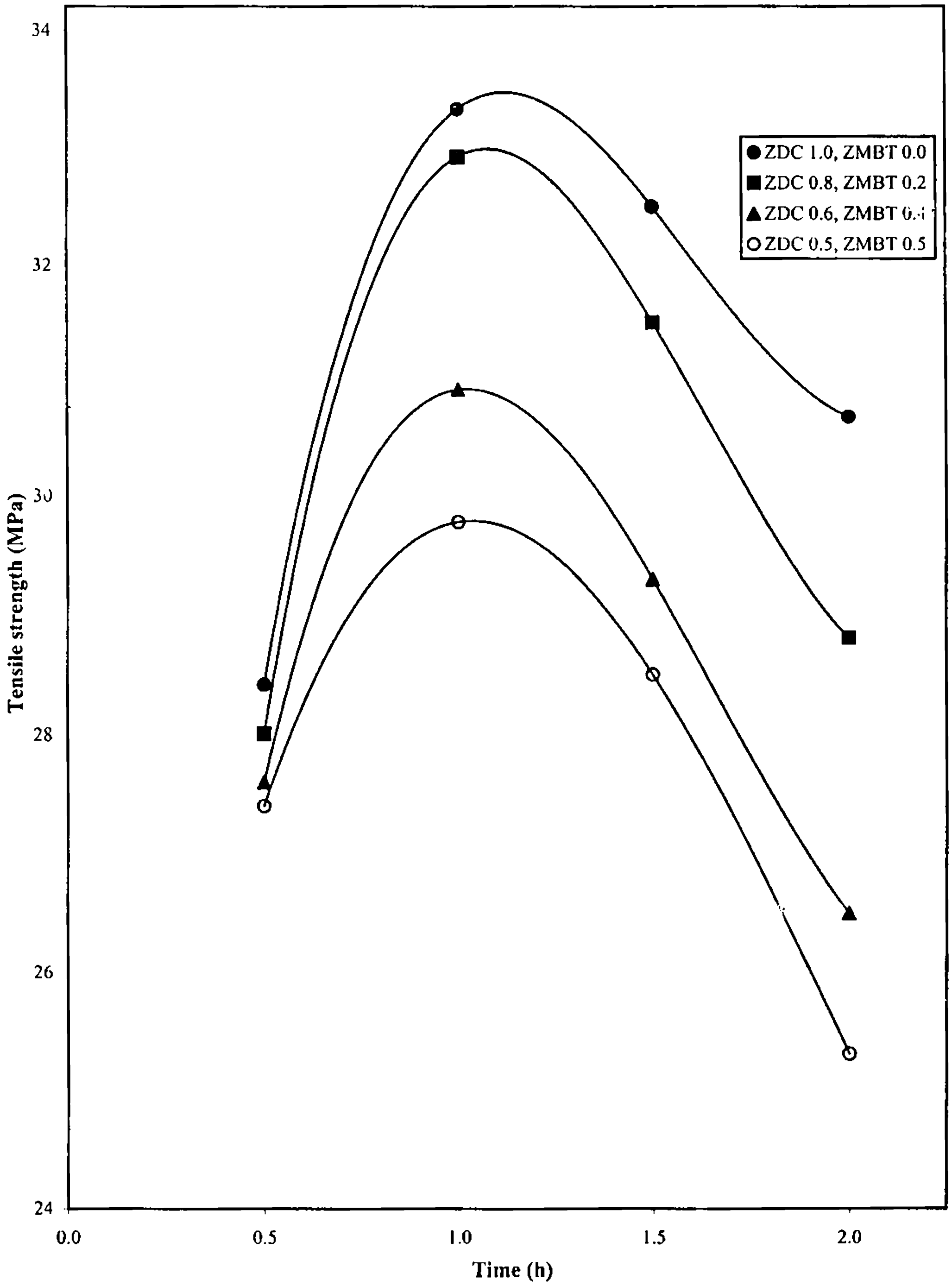


Fig 5A.12. Effect of duration of post-cure on tensile strength of LPL films using different accelerator combinations.

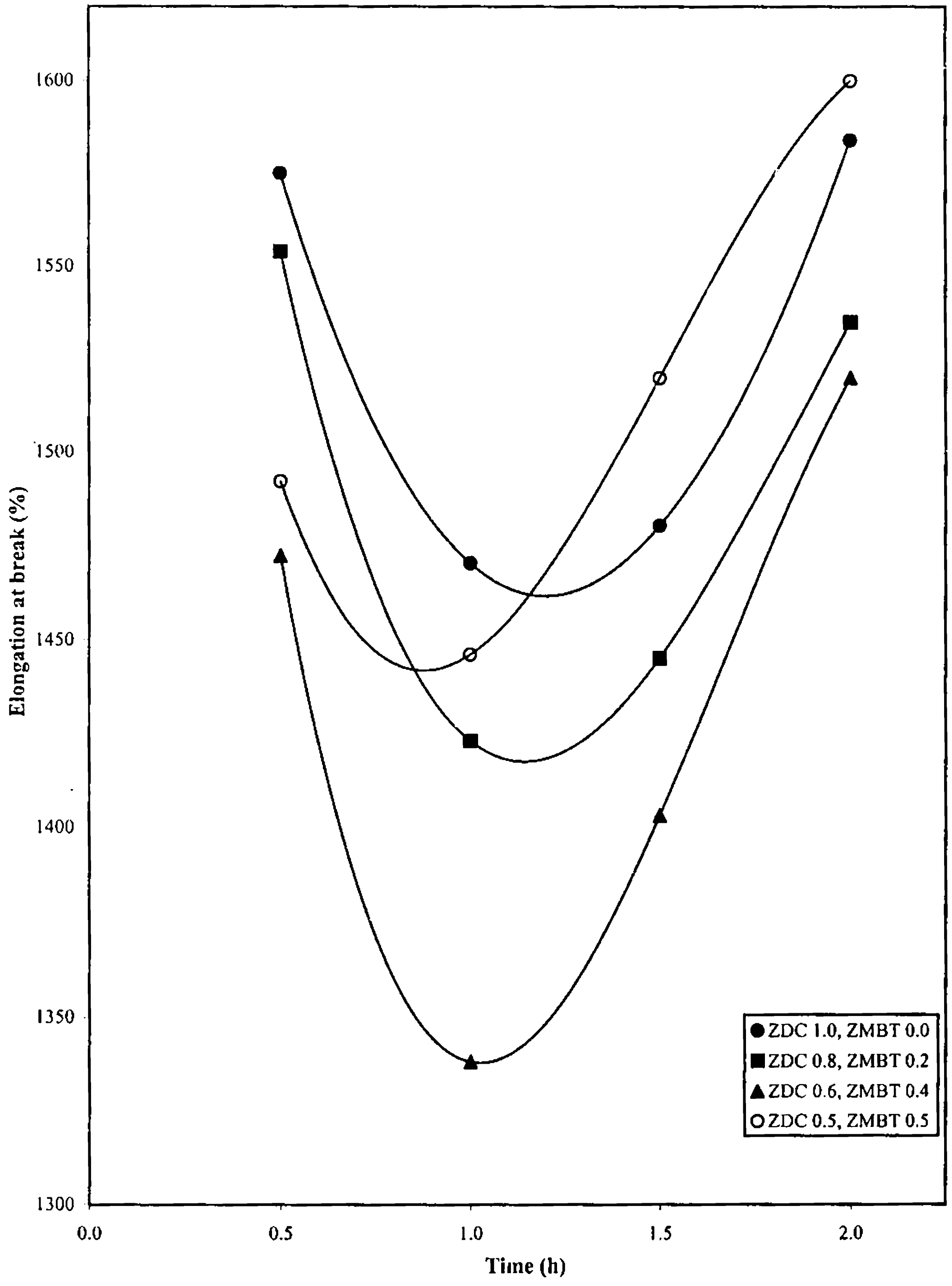


Fig 5A.13. Effect of duration of post-cure on elongation at break of LPL films using different accelerator combinations.

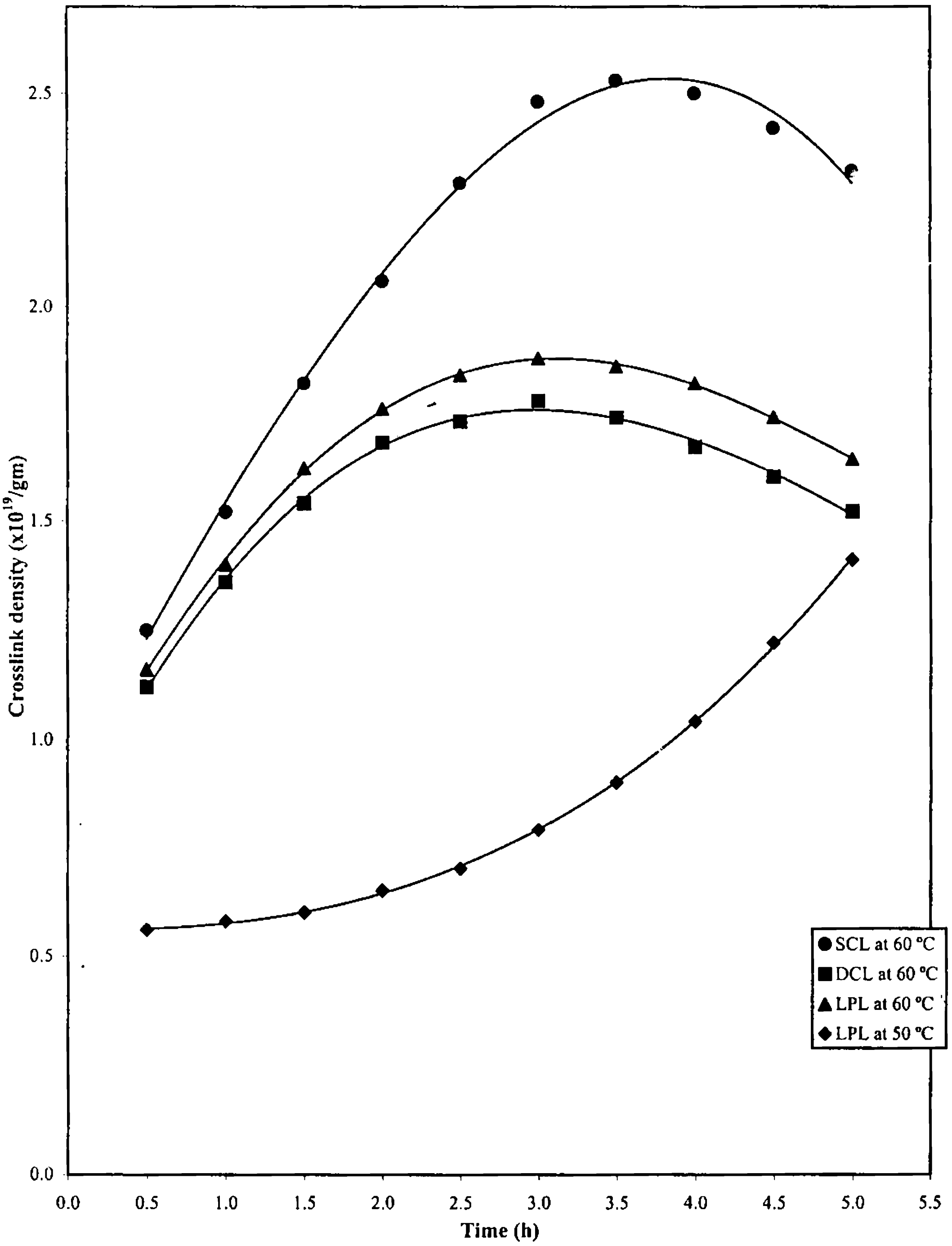


Fig 5A.14. Effect of duration of prevulcanization on crosslink formation in latex films.

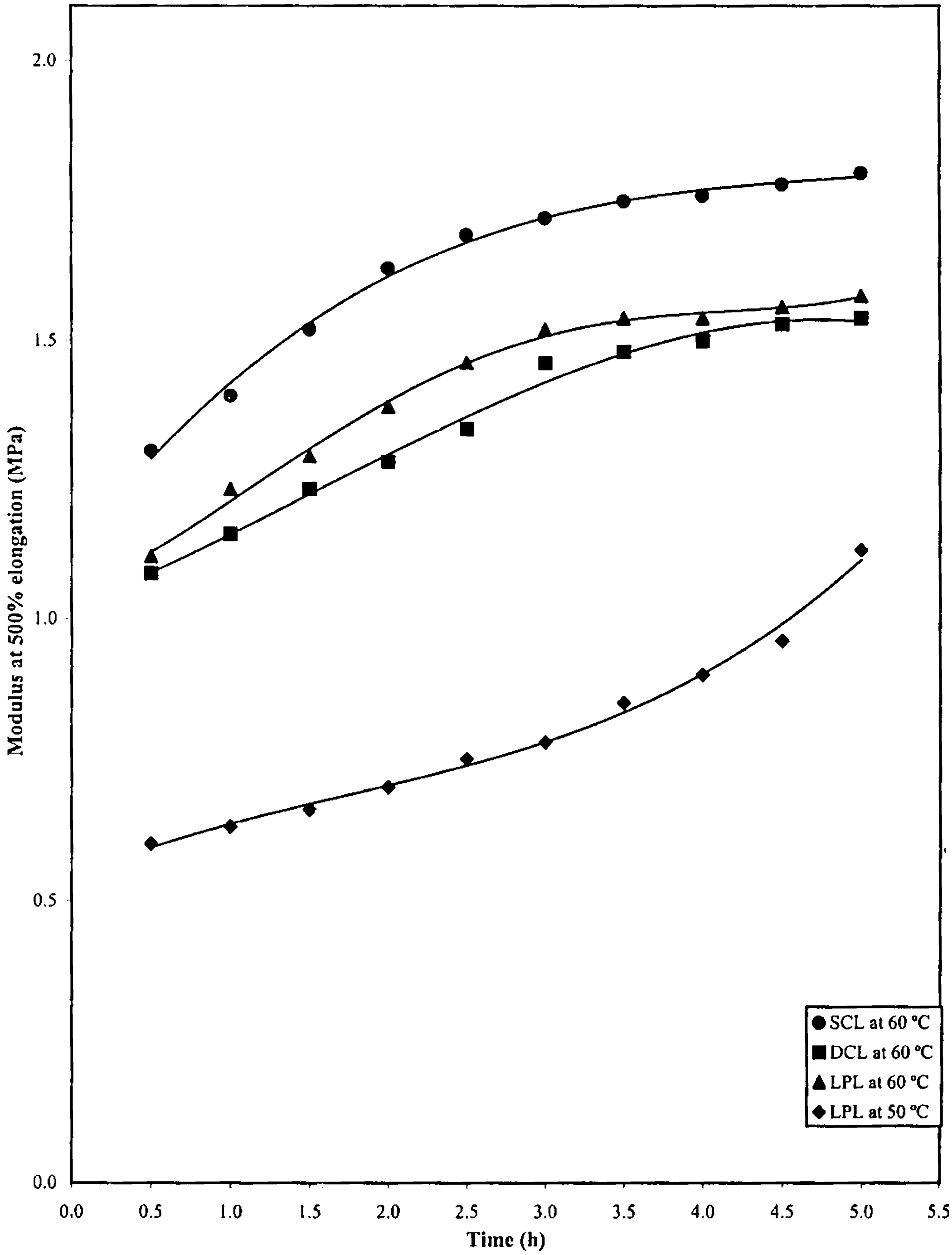


Fig 5A.15. Effect of duration of prevulcanization on modulus of latex films.

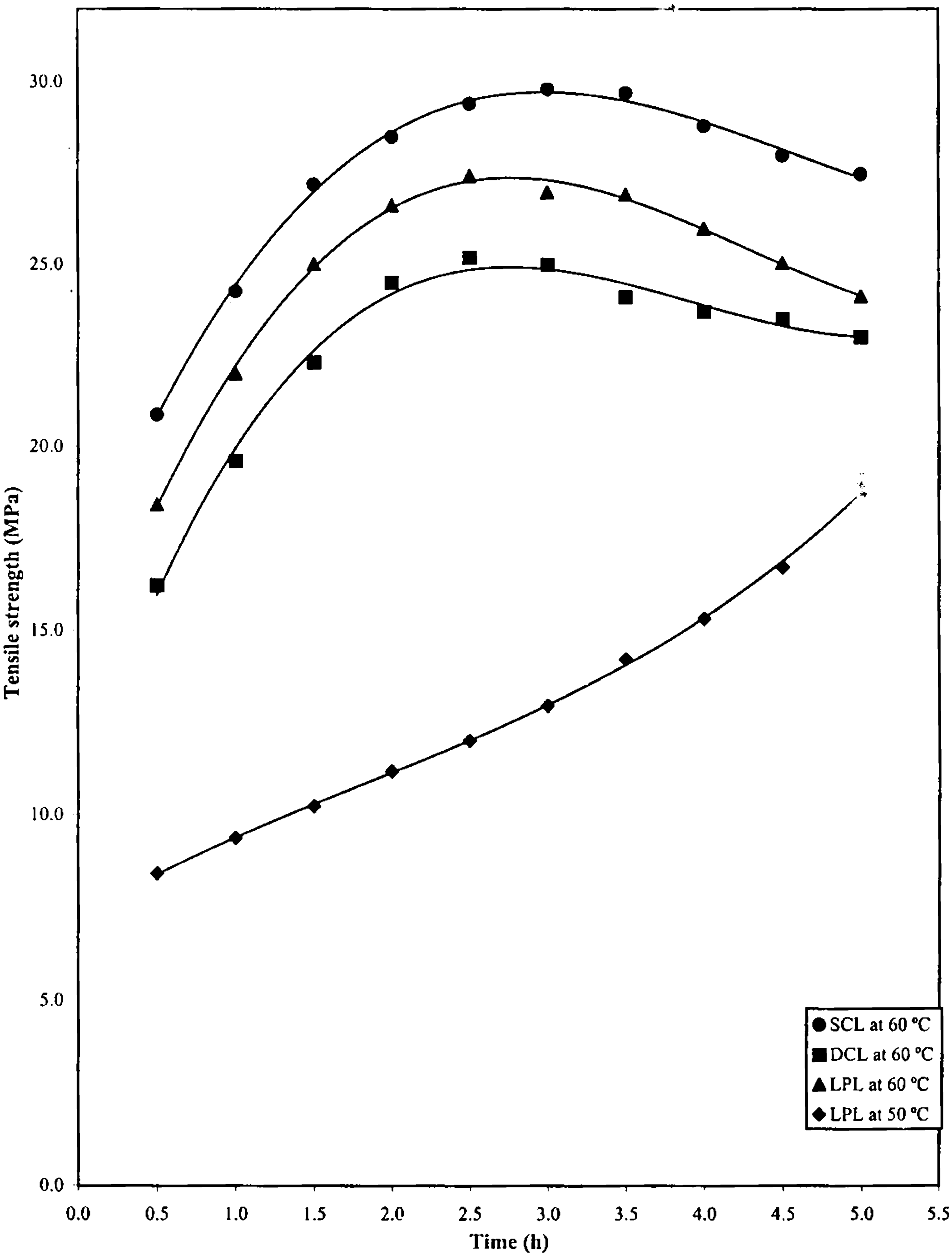


Fig 5A.16. Effect of duration of prevulcanization on tensile strength of latex films.

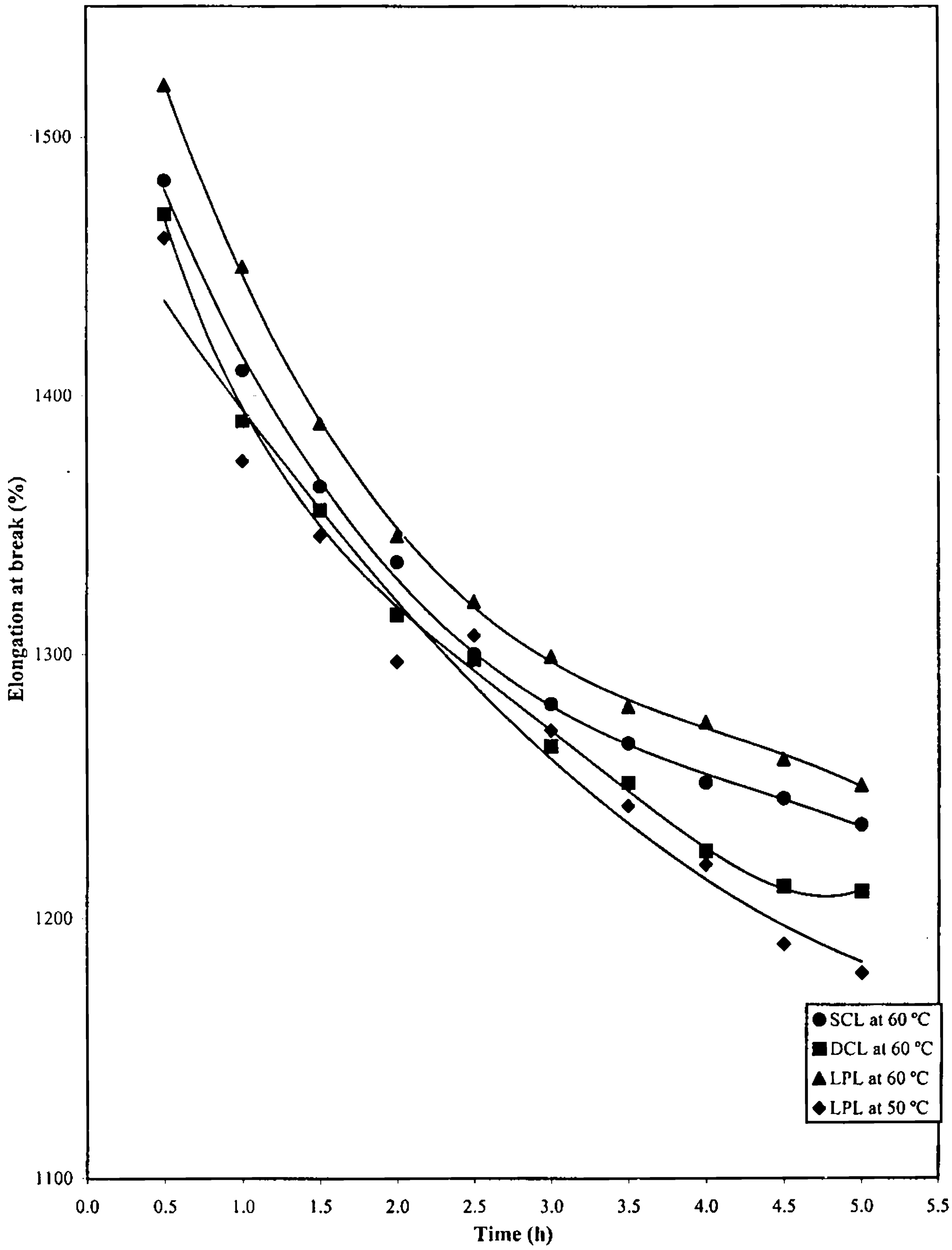


Fig 5A.17. Effect of duration of prevulcanization on elongation at break of latex films.

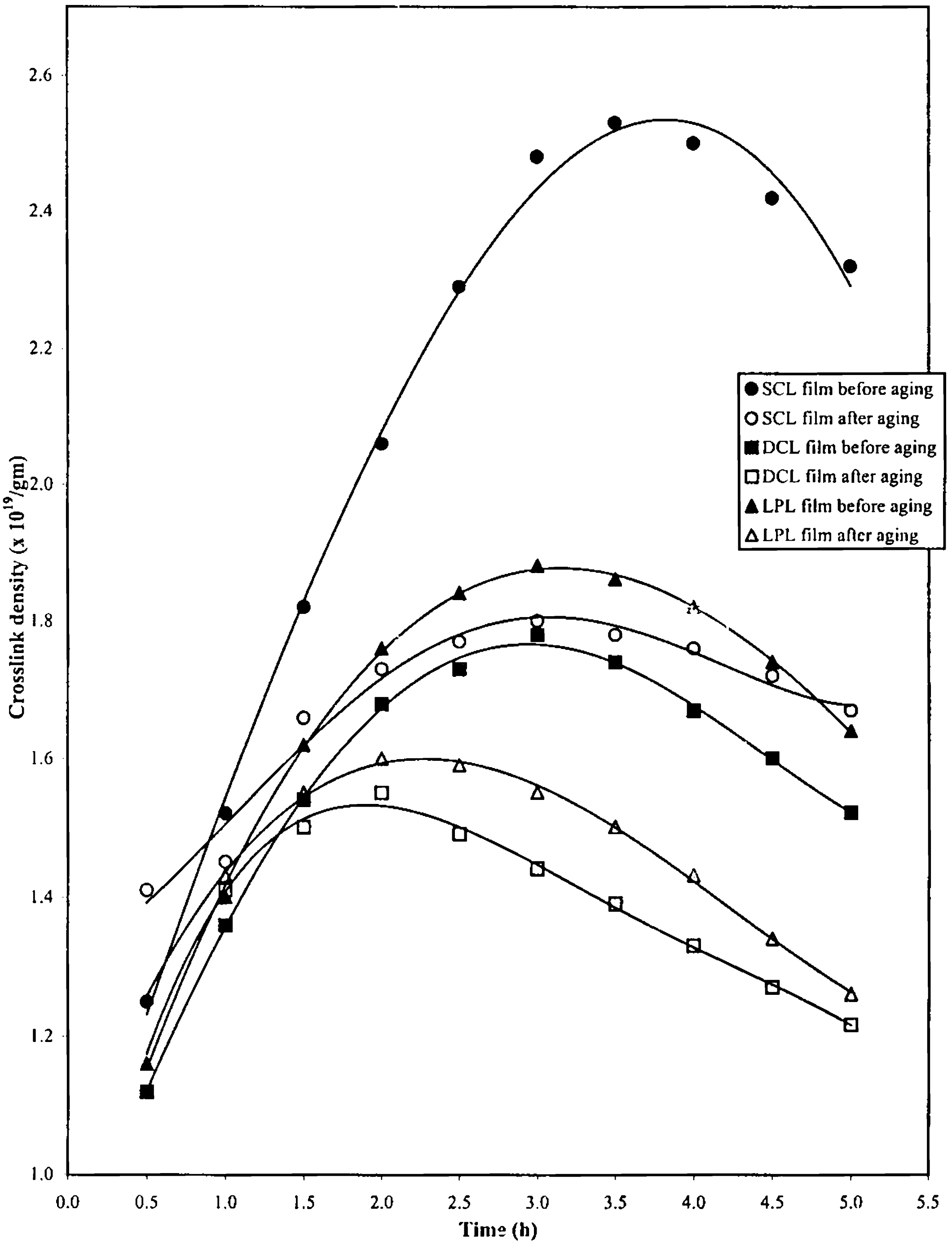


Fig 5A.18. Effect of heat ageing on crosslink density of prevulcanized latex films.

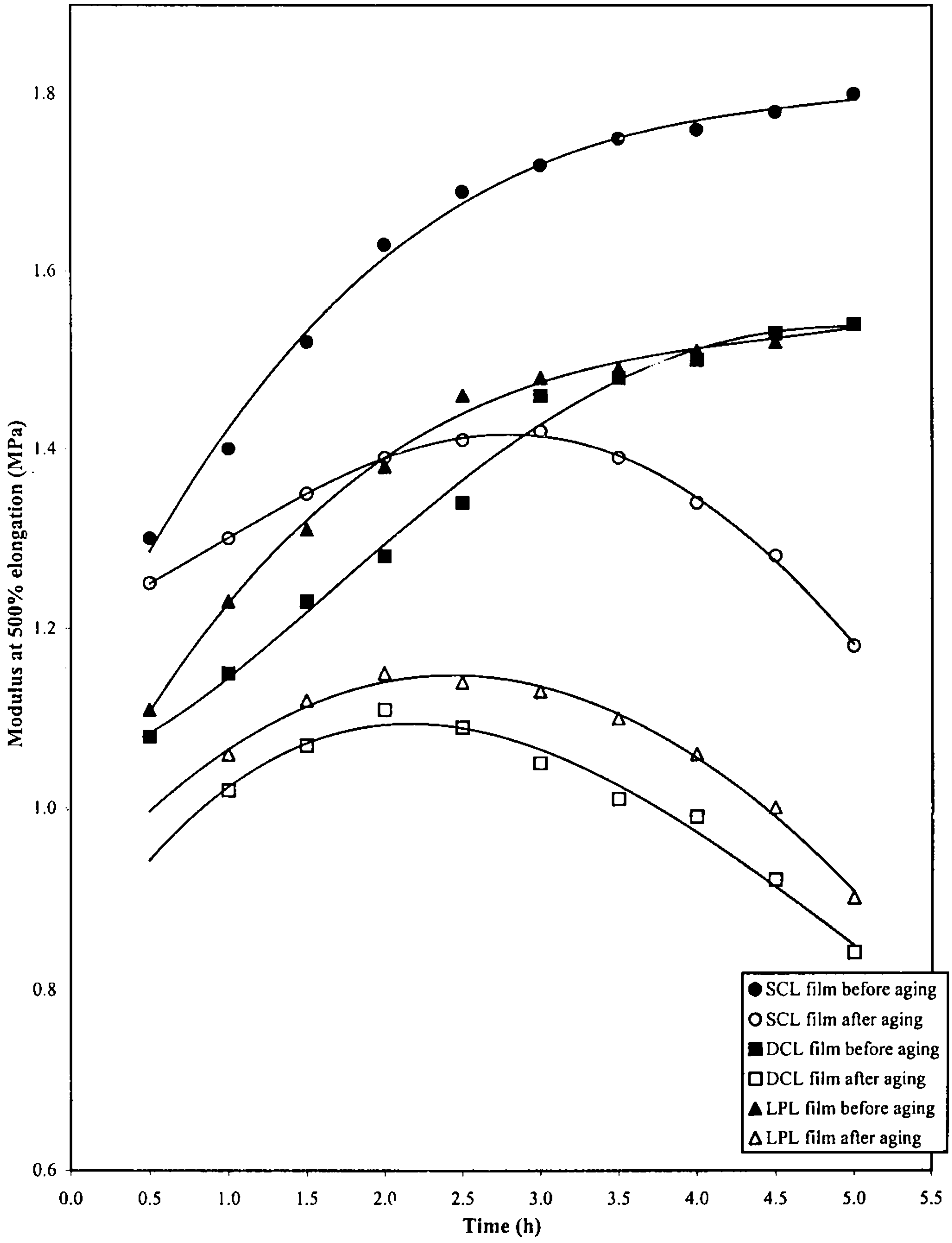


Fig 5A.19. Effect of heat ageing on modulus of prevulcanized latex films.

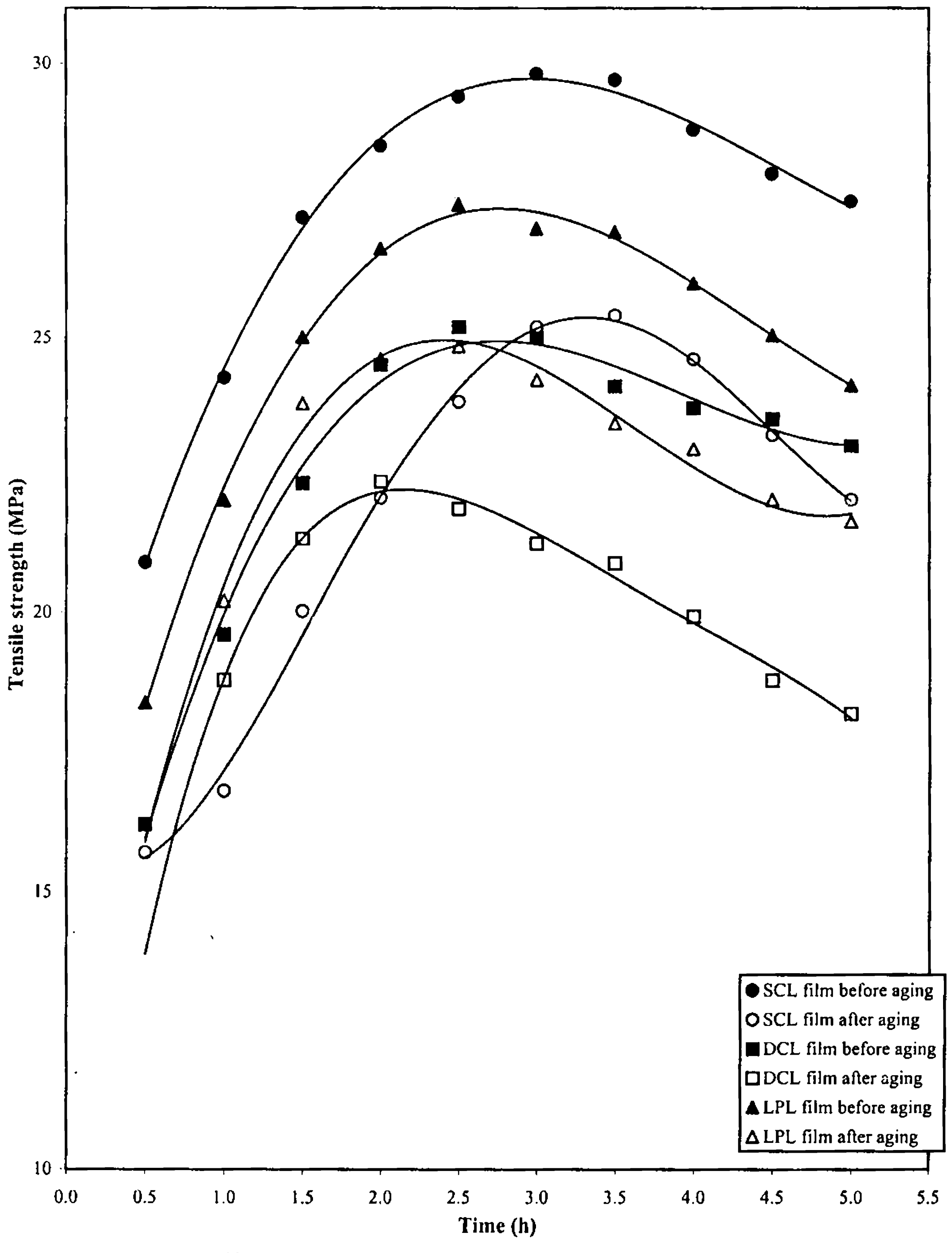


Fig 5A.20. Effect of heat ageing on tensile strength of prevulcanized latex films.

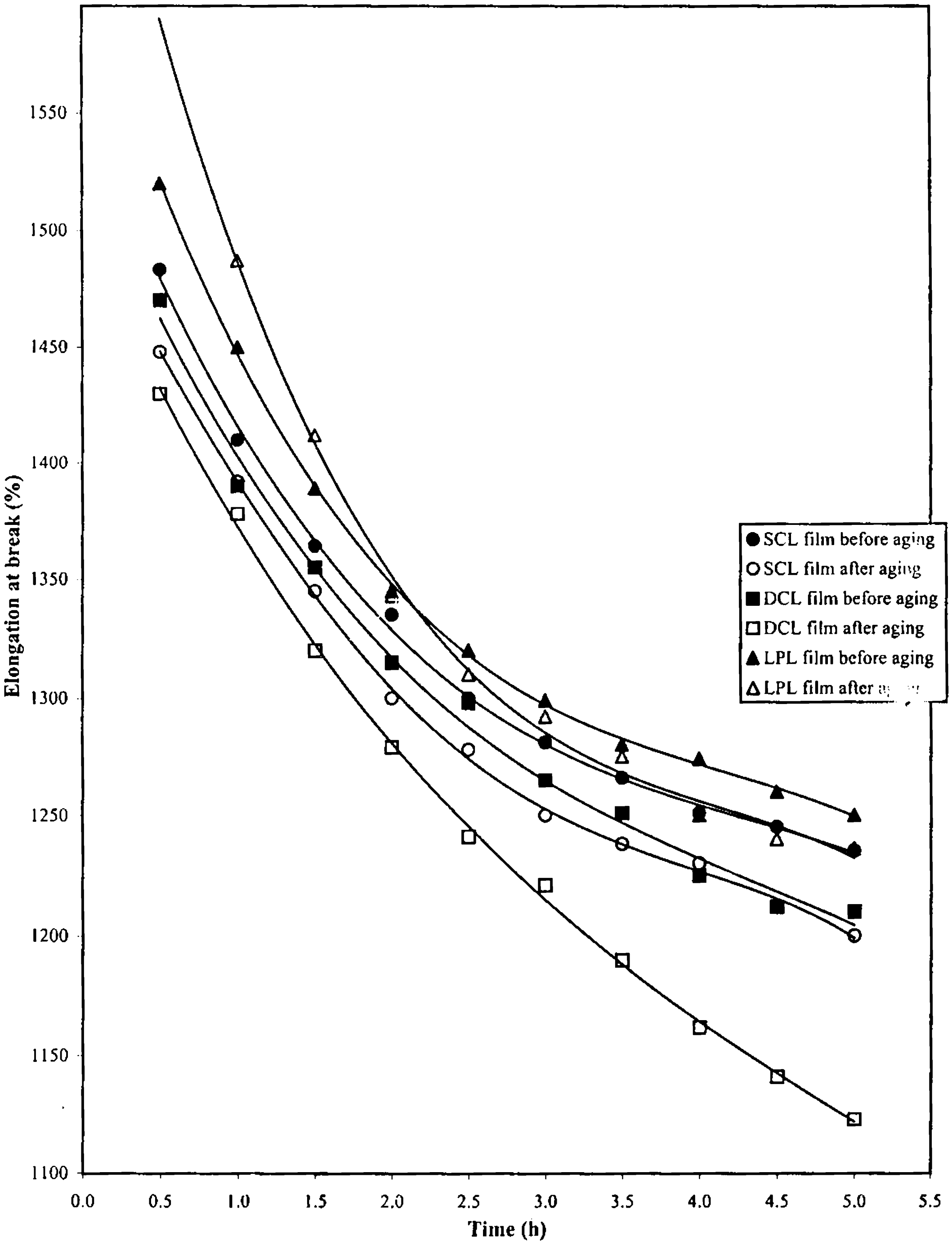


Fig 5A.21. Effect of heat aging on elongation at break of prevulcanized latex films.

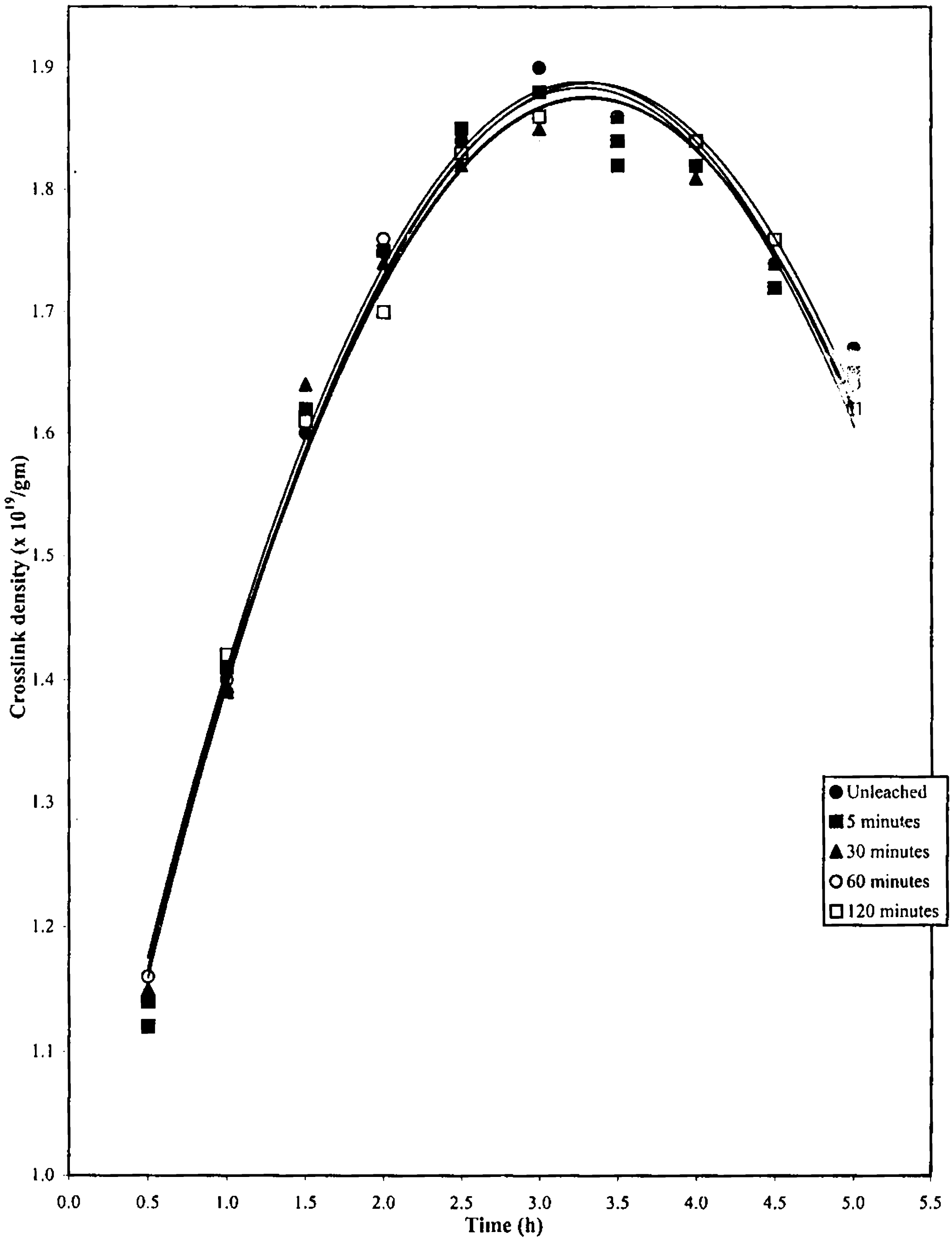


Fig 5A.22. Effect of leaching on crosslink density in LPL films.

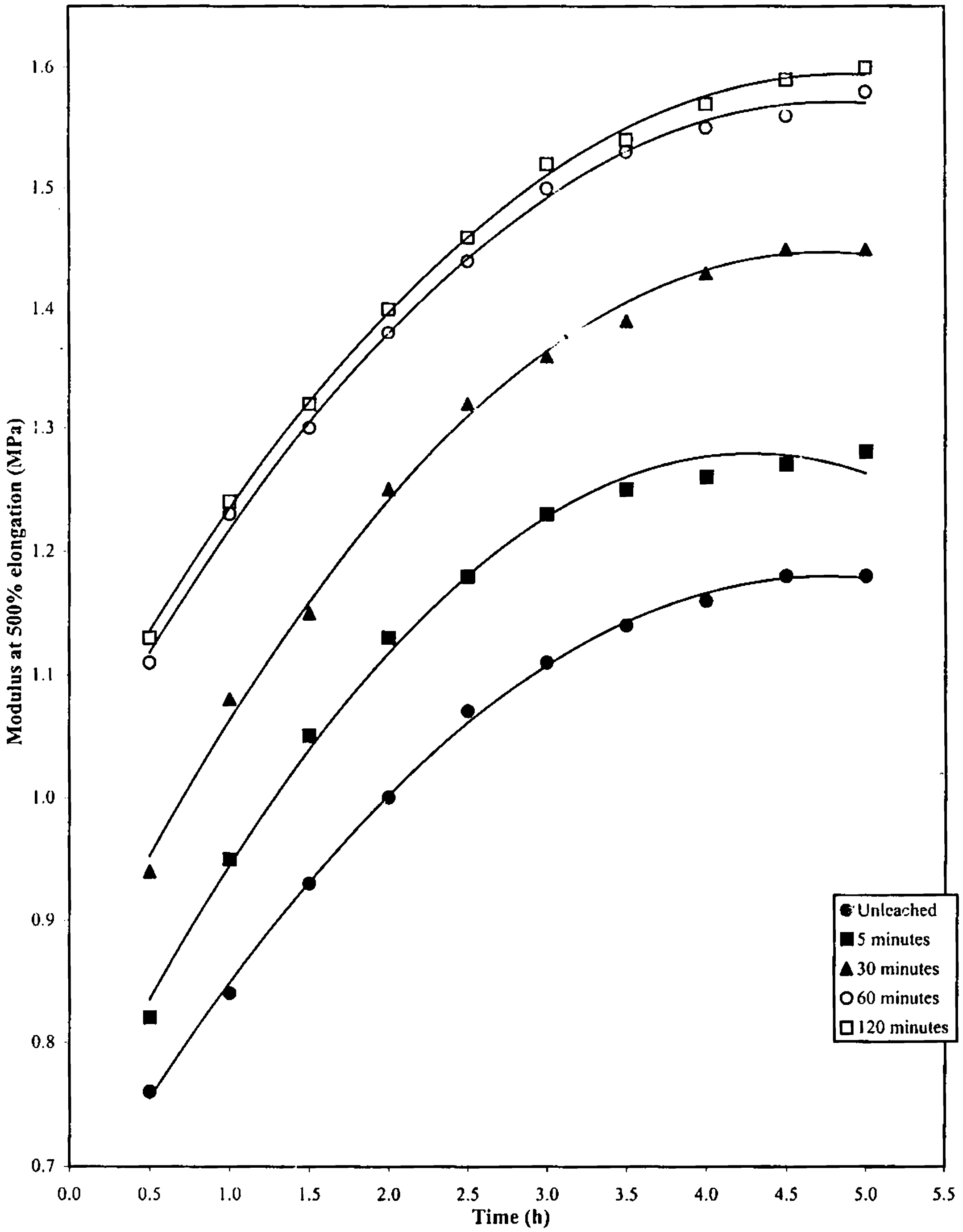


Fig 5A.23. Effect of leaching on modulus of LPL films.

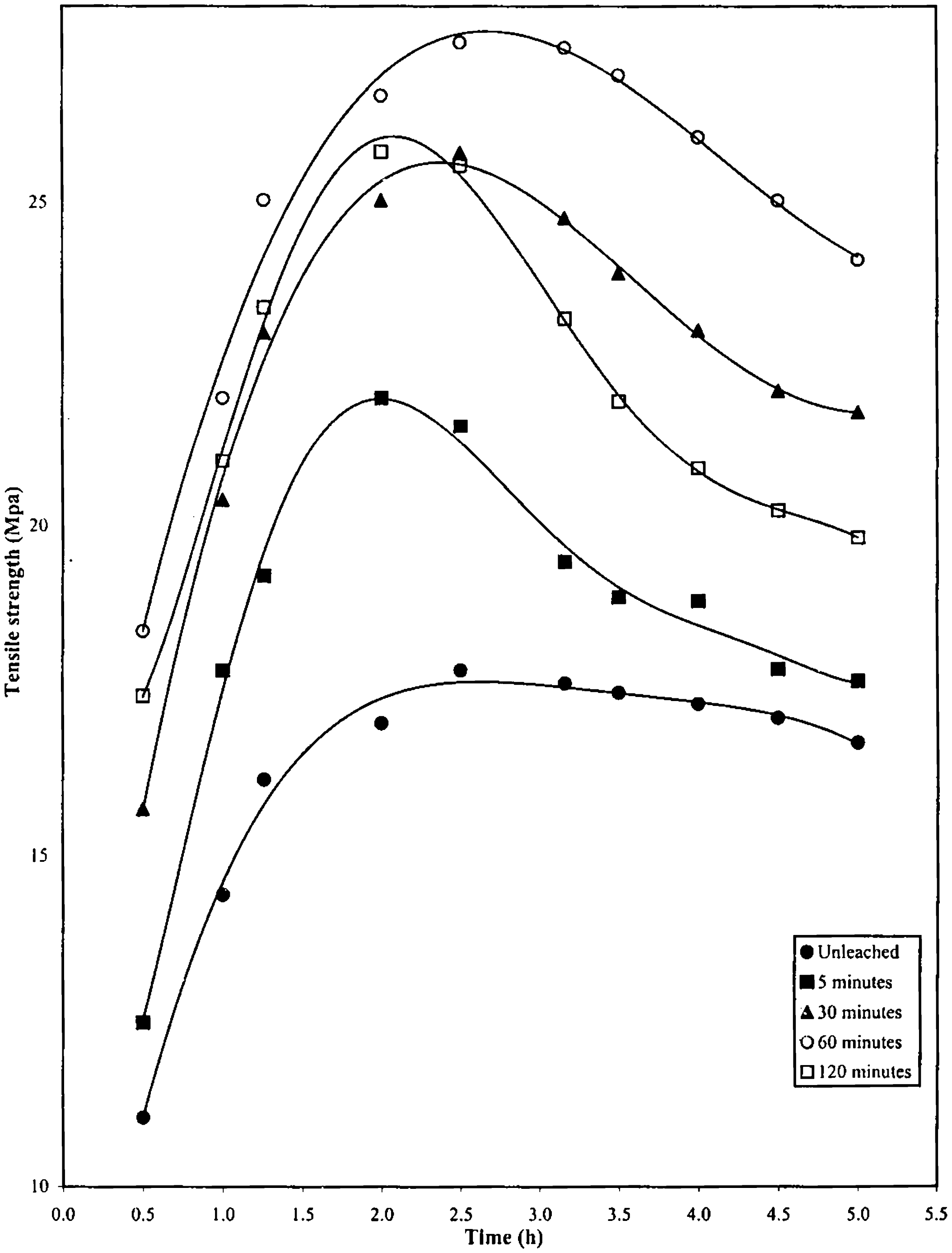


Fig 5A.24. Effect of leaching on tensile strength of LPL films.

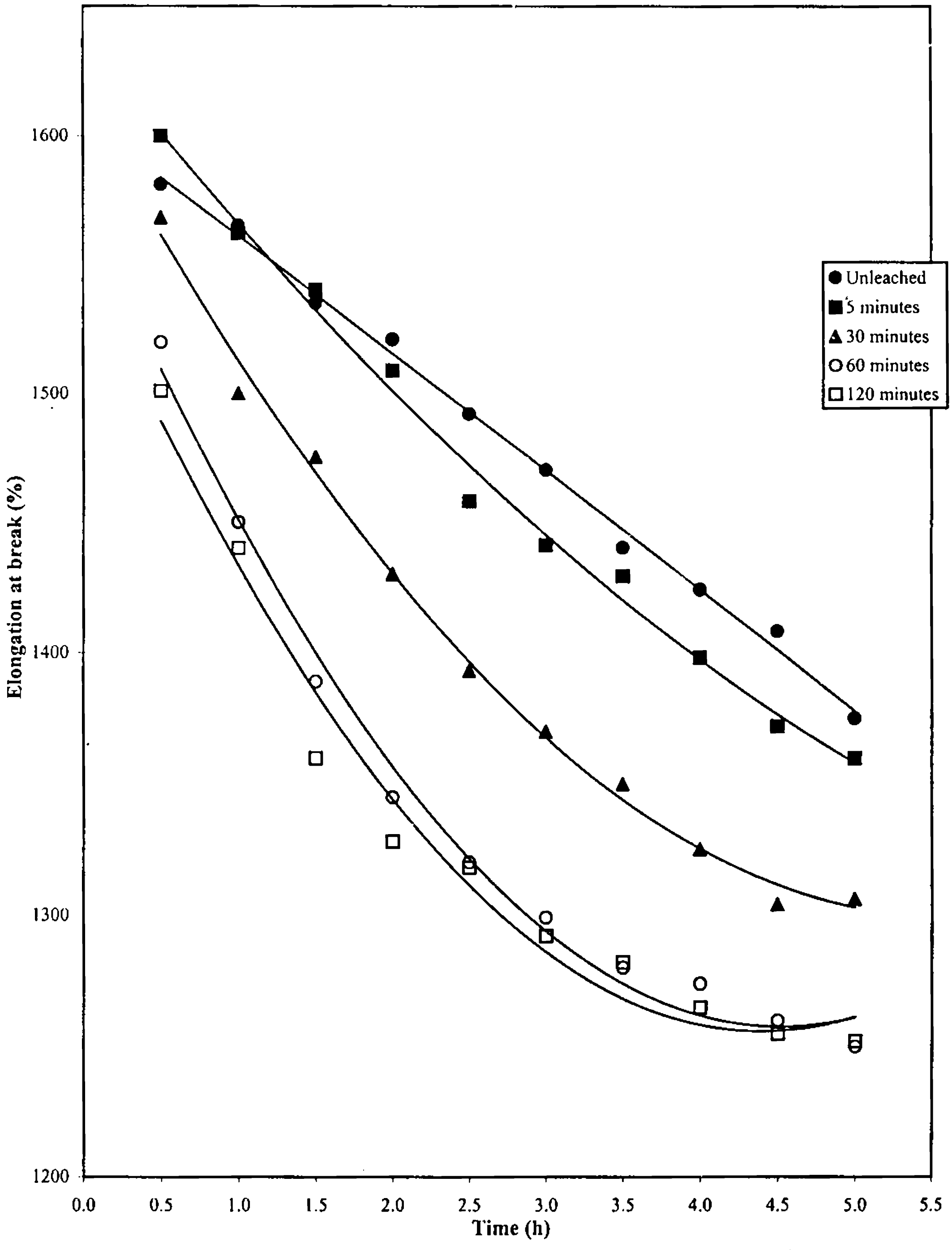


Fig 5A.25. Effect of leaching on elongation at break of LPL films.

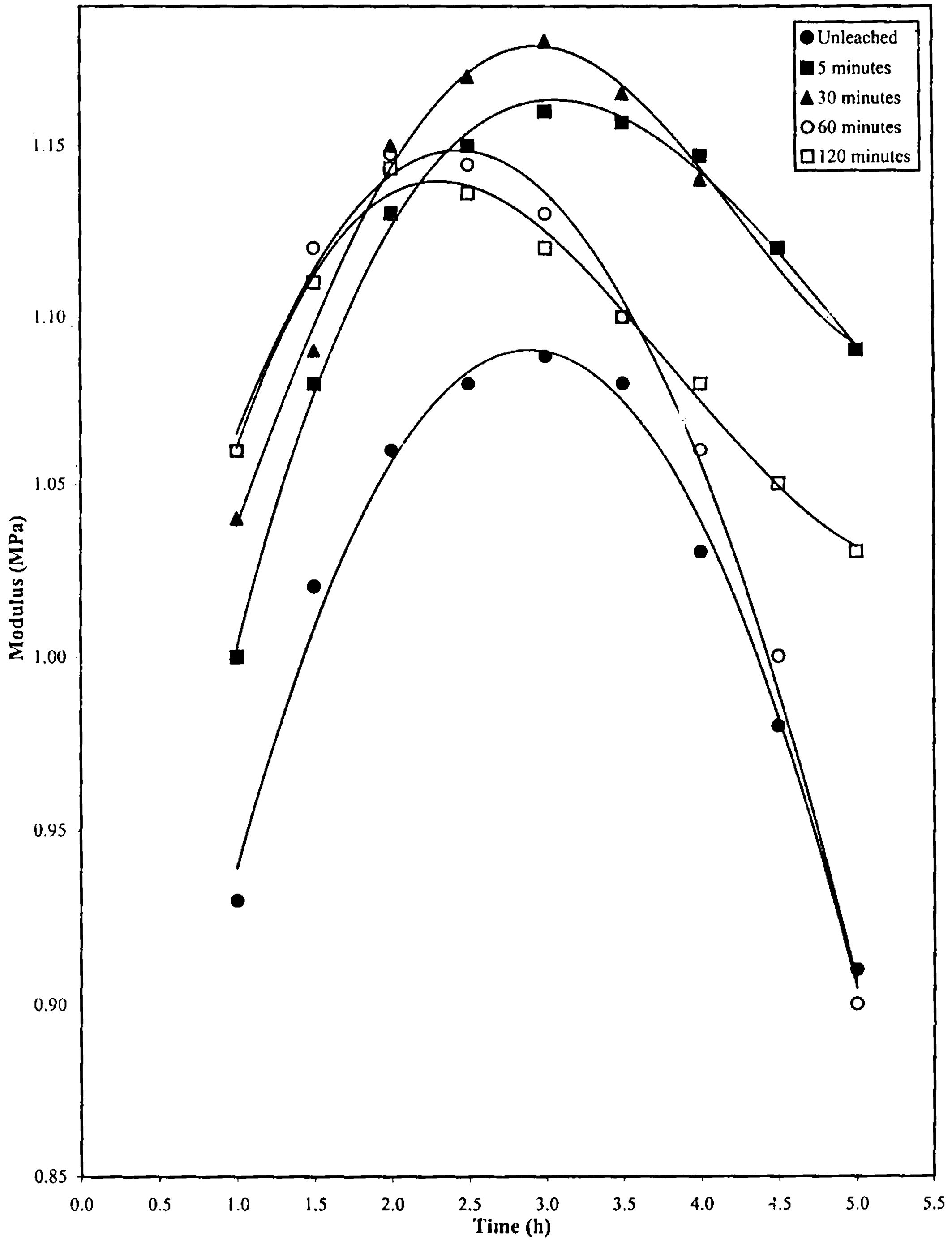


Fig 5A.26. Effect of leaching on modulus of LPL films after ageing.

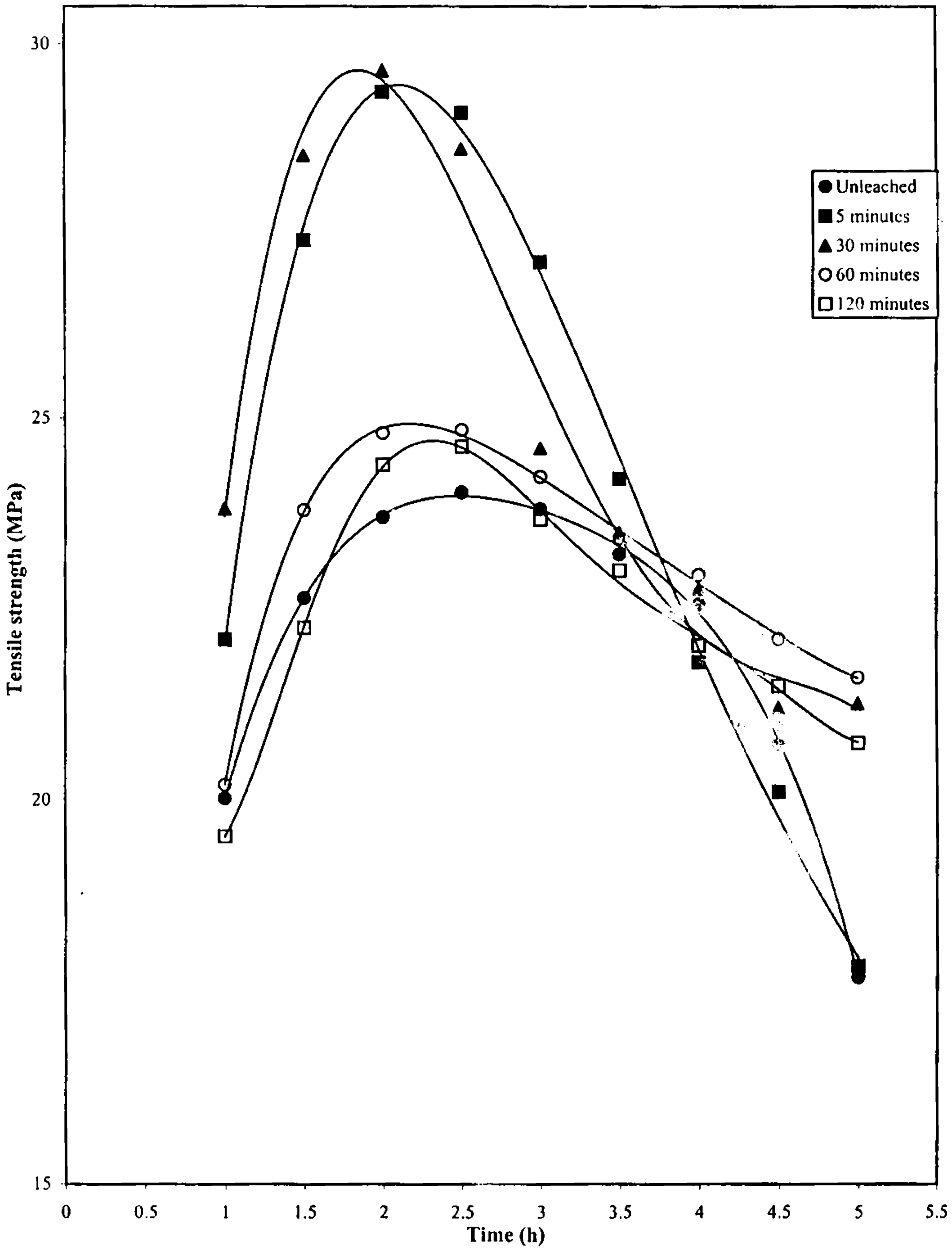


Fig 5A.27. Effect of leaching on tensile strength of LPL films after ageing.

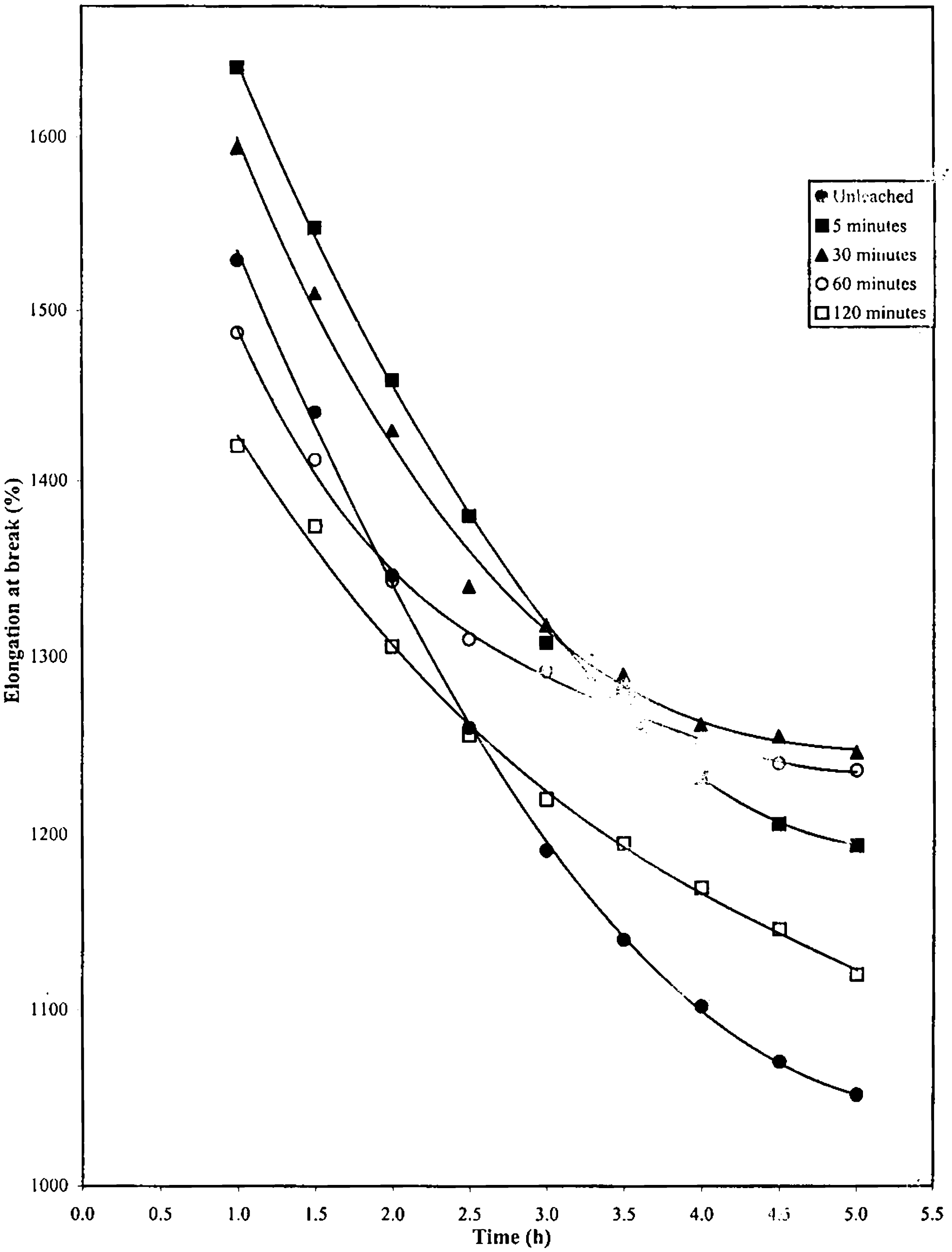


Fig 5A.28. Effect of leaching on elongation at break of LPL films after ageing.

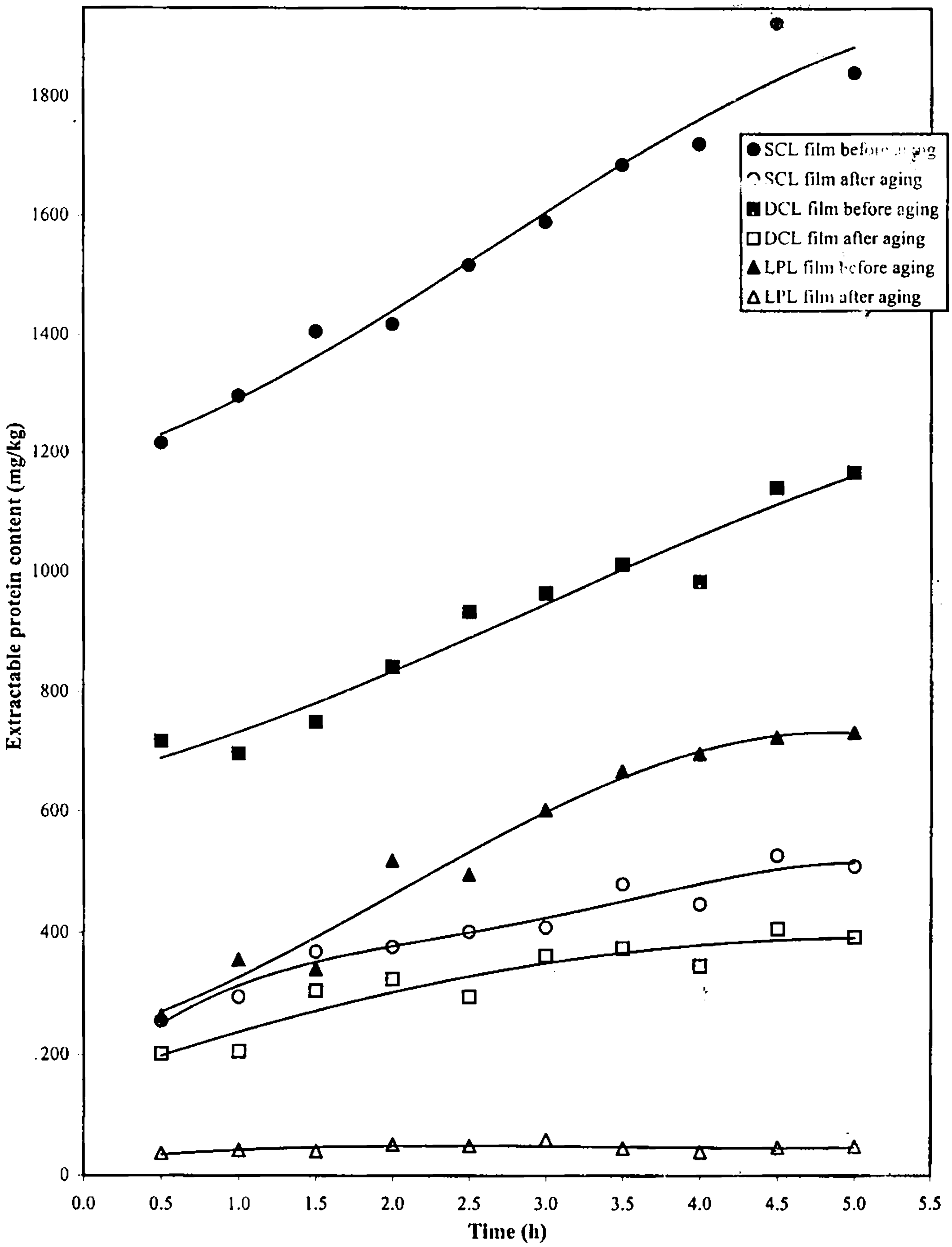


Fig 5A.29. Effect of heating time and leaching on EP content in prevulcanized latex films.

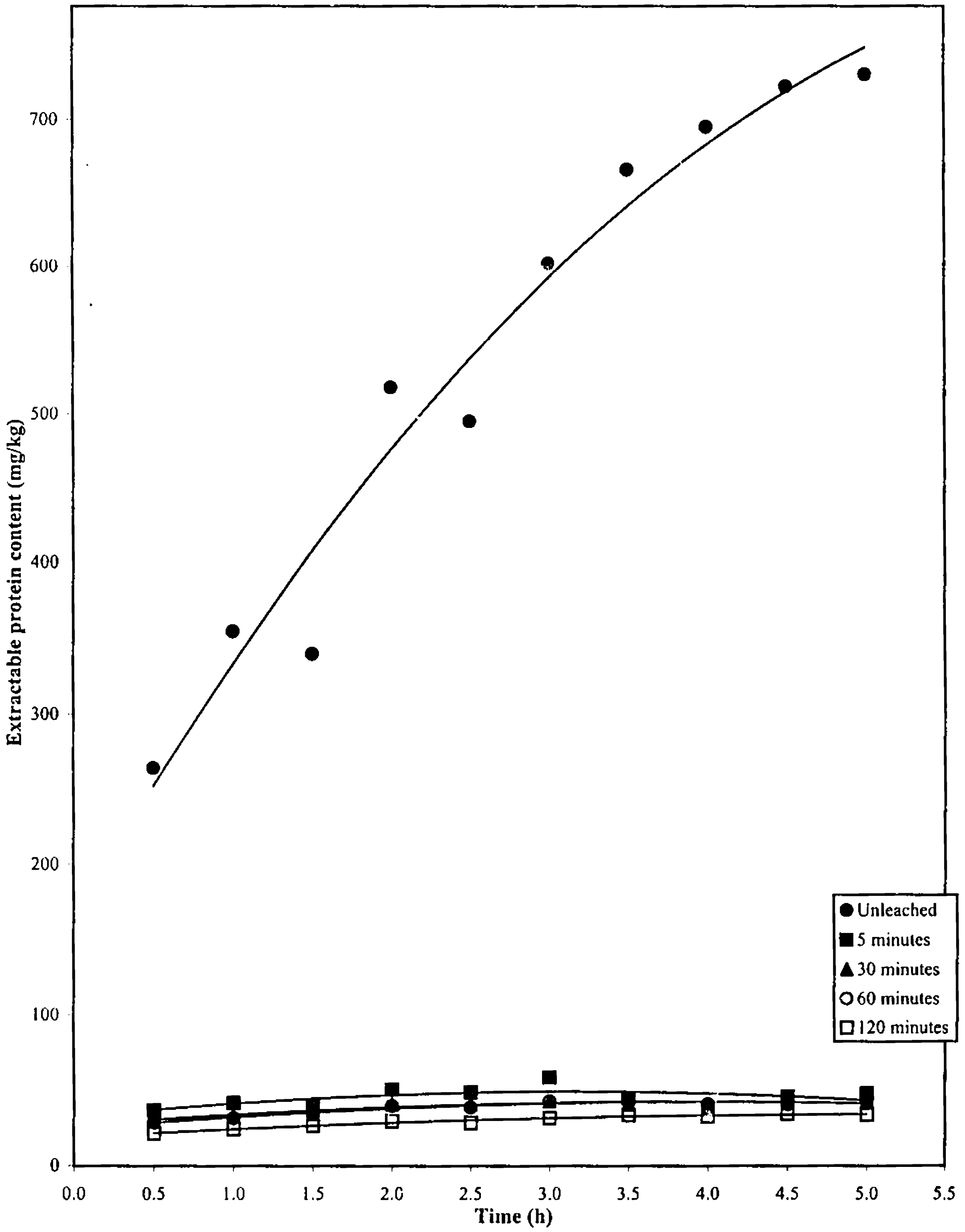


Fig 5A.30. Effect of leaching on residual EP content in LPL films.

CHAPTER 5B

VULCANIZATION OF LOW PROTEIN LATEX IN EV CURE SYSTEM

Natural rubber being an olefinic polymer is generally susceptible to rapid ageing and oxidation. The situation becomes all the more acute if the rubber articles have to function at relatively higher temperature or have to undergo any type of repeated heat treatment at elevated temperatures. The situation is further aggrevated, if the article has high surface area to volume ratio. For example, surgical gloves, a natural rubber product has to undergo repeated sterilization at about 120°C. To retain high mechanical properties after each heat treatment the inherently poor oxidation resistance of natural rubber has to be improved.

Chemical antidegradants are widely used to confer ageing and oxidation resistance to rubber products. A second approach involves modifying the cure system(1). It is generally accepted that EV (efficient vulcanization) cure system, employing a higher proportion of accelerator and low level of sulphur is useful in such situations(2). The ratio of any given accelerator to sulphur largely determines the type of sulphur crosslinks formed and also the amount of sulphur which combines with the rubber in non-crosslink structures such as cyclic sulphides. In EV system the crosslinks are mainly monosulphidic along with some disulphidic ones which have higher thermal stability than polysulphidic crosslinks and main chain modifications, common to conventionally sulphur cured vulcanizates. Monosulphidic crosslinks are more stable to heat than polysulphidic crosslinks, because the energy to rupture the C–S bond is higher than that of the S-S bond(3). In EV cured vulcanizates high concentration of accelerator residues are available which function an antioxidants probably by deactivating the hydroperoxides and behave synergestically with added antioxidants of the phenolic or amine type(4). Since LPL can find application in products like surgical gloves, which requires high heat resistance, curing of LPL in EV system seems worth studying. However, curing of NR latex in EV system has not been much extensively studied. Peethambaran and George(5) have studied the prevulcanization of NR latex in EV system and the application of this prevulcanized latex in elastic thread production. This chapter reports the results of studies on pre- and post-vulcanization of LPL in

EV system, properties of the films obtained from it and their behaviour on accelerated ageing. The results are compared with SCL and DCL.

EXPERIMENTAL

LPL was processed out of centrifuged latex by following the method described in Chapter 4. For post – and prevulcanization in EV system, latex compounding was carried out as per the formulation given in Table 5B.1. For post-vulcanization studies in EV system, the compounded latices were matured for 24h, cast films were prepared on leveled glass plates(6) and vulcanized at 100°C for predetermined duration. Dried films were leached in water for 60 minutes at room temperature and dried in air.

For prevulcanization studies also compounded latices were matured for 24h. For effecting prevulcanization, latex compounds were heated on water bath at 60°C for predetermined intervals. For determining the effect of extent of cure on physical properties, samples were withdrawn at definite intervals and cooled immediately to arrest any further crosslinking. Films were prepared by casting and dried in air. The air dried films were leached in water for 1h and dried at room temperature.

The state of cure of the latex films was assessed by determining crosslink density by solvent swelling method(7) using Flory-Rhener equation(8). Physical properties of the films were determined by as per Indian Standard procedures(9). Ageing of latex films was carried out by heating at 70°C for 7 days(10).

RSESULTS AND DISCUSSIONS

Effect of duration of post-vulcanization in EV system and accelerated heat ageing on crosslink density of latex films

Figure 5B.1 shows the variation of crosslink density of SCL, DCL and LPL films with duration of post-vulcanization in EV system. The data indicate that for the three types of latex films crosslink density increases with duration of post-vulcanization. DCL and LPL films are slow curing than SCL films, as seen from

Figure 5B.1. It has been postulated that sulphur(11) and sulphur accelerator complex(12) are able to dissolve in the aqueous phase of latex with the assistance of some of the non-rubber substances present in latex, forming some loose complex having some surface activity and get adsorbed at the rubber-serum interface. After adsorption, the hydrophilic component is some how lost and the hydrophobic species containing sulphur-accelerator complex migrates into rubber and form crosslinks on heating. In DCL and LPL, due to the second stage of centrifugal concentration and also by displacement by PPG to some extent in the case of LPL, the level of active non-rubber substances are low, ultimately leading to a net reduction in crosslink density.

Figure 5B.1 also shows the variation in crosslink density after ageing of the films at 70°C for 7 days. On ageing there is an overall increase in crosslink density. This is partly due to absence of poly sulphide crosslinks, which on rupture give main modifications and the additional crosslink formation during ageing, utilizing the residual curatives in the film. Due to the high thermal stability of the predominantly mono-and disulphidic crosslinks in the films cured by EV system, crosslink rupture is minimum. The high concentration of accelerator residues also function as antioxidants. Films that were initially under-cured showed the highest crosslink density after ageing. This shows that crosslink formation is a predominant reaction during the accelerated ageing process. However, the films which were initially vulcanized beyond the optimum, on ageing, show a reduction in crosslink density. However, the crosslink density of all the aged films were higher than those of the unaged ones. This is again due to high thermal stability of mono and disulphidic crosslinks, which resists rupture.

Effect of duration of post-vulcanization in EV system and accelerated heat ageing on tensile properties of latex films

The variation of modulus of latex films with duration of post-vulcanization in EV system is given in Figure 5B.2. It is observed that modulus of all the latex films increases with duration of post-vulcanization and DCL and LPL films show lower modulus than SCL films for a given period of vulcanization. This is probably due to the lower rate of cure in DCL and LPL film, as observed from crosslink density data. Even though crosslink density data are almost similar for DCL and LPL, modulus of LPL film is slightly higher than DCL films. This is attributed to the attractive forces originating from PPG molecules on the surface of rubber particles.

The data on the variation of modulus of aged films also is given in Figure 5B.2. It is observed that ageing of the three types of under-cured films result in increase of modulus and the aged modulus decrease as the duration of post-vulcanization increases. The fall in aged modulus along with duration of post-vulcanization is partly in agreement with crosslink density of the aged films. Even though crosslink density value is highest on ageing in LPL film post-vulcanized for 1h, a maximum is not observed in the modulus curve. This observation suggests that factors other than crosslink density are involved in determining the modulus of LPL film. It is suggested that as the latex particles become more crosslinked they became harder and the inter particle fusion became less effective.

Figure 5B.3 shows the variation of tensile strength with duration of post-vulcanization in EV system. Tensile strength increases with increase in duration of vulcanization, reaches a maximum and then decreases. Both SCL and LPL films show almost the same maximum tensile strength. However, the time required to achieve the maximum tensile strength is slightly more for LPL films. This is due to the lower rate of cure of LPL films. Tensile strength of DCL film is the lowest for any duration of post-vulcanization. This is mainly due to the lower crosslink density in DCL films. The maximum tensile strengths of the three types of films in EV system are lower than those of films cured in conventional system (when compared with Figure 5A.3). This observed reduction in tensile strength in EV system is attributed to the lower crosslink density in the EV cured films and reduced flexibility of mono- or disulphidic crosslinks when compared to polysulphidic crosslinks.

The variation of tensile strength of aged films also is presented in Figure 5B.3. The three types of films, initially under-cured, show high increase in tensile strength after ageing. This is primarily due to increase in crosslink density on heating. However, DCL and LPL films vulcanized beyond optimum are accompanied by reduction in tensile strength on accelerated ageing. This may be due to the thermal degradation occurring in the molecular networks. However, with SCL films tensile strength increases after ageing. A probable factor contributing to higher tensile strength is increased crosslink density.

The effect of post-vulcanization time on elongation at break of latex films cured in EV system both before and after ageing is shown in Figure 5B.4. It is seen that elongation at break of the three types of films is maximum at the optimum cure time and then decrease with increase in cure time. This reduction in ultimate elongation is due to increase in crosslink density and modulus of the film. On accelerated ageing, all the tree types of films show decrease in ultimate elongation for increase in cure time.

Effect of duration of prevulcanization in EV system on crosslink density of latex films.

The variation of crosslink density in SCL, DCL and LPL films with respect to duration of prevulcanization at 60°C in EV system is shown in Figure 5B 5. Crosslink density of rubber particles in three types of latices prevulcanized in EV system increased from a low initial value along with duration of prevulcanization. For a given duration of prevulcanzation, SCL films showed higher rate of cure than DCL and LPL. From the slope of the cure curve for SCL it is seen that rate of vulcanization is high initially and reduces with duration of prevulcanization. However, the slopes of the cure curves for DCL and LPL increase continuously with duration of prevulcanization and achieve a high state of cure on continued heating. Thus there is marked difference in the prevulcanization characteristics of SCL, DCL and LPL in EV system.

The basic mechanism of sulpher prevulcanization of NR latex suggests that sulphur and accelerator can independently dissolve in the aqueous phase of latex with the assistance of some hydrophilic serum constituents, leading to the formation of some loose complex, having some surface activity. They get adsorbed at the rubber serum interface(11,12). However, after adsorption, the hydrophilic component of the adsorbed species is somehow lost and it becomes hydrophobic. The hydrophobic species migrates to the interior of rubber hydrocarbon particles and form crosslinks. The hydrophilic component returned to the aqueous phase form new complexes and facilitates further transfer of curatives into rubber particles in latex. However, in latex serum the solubility of accelerator is much less, compared to that of sulphur and thus the rate of transfer of accelerator is much lower compared to that of sulphur(11). In EV cure systems the proportion of accelerator in the aqueous phase is very high compared to sulphur. However, the availability of curatives within the latex particles is limited, leading to the formation of mono and disulphidic crosslinks in the film with the assistance of available accelerator and sulphur.

It is also observed that for any given duration of prevulcanization state of cure in SCL film is much higher than in DCL and LPL films. The rate of entry of curatives into latex particles is determined by the concentration of the non-rubber substances which form surface-active loose complexes with sulpher and accelerator. In processing of DCL and LPL from SCL, portion of the dissolved non-rubber serum constituents and surface active substances, including proteins at the rubber-serum interface are removed. In SCL, the components that facilitate the entry of curatives into the latex particles are higher, while in DCL and LPL, their availability is much reduced. This accounts for the lower crosslink density in DCL and LPL films, compared to SCL films when prevulcanized in EV system. The crosslink density in LPL films are slightly higher that DCL. It is believed that proteins have some influences on the transfer of curatives in aqueous phase to rubber particles in latex. In LPL, even though protein content is slightly lower, crosslink density is higher than in latex particles of DCL. This observation suggests that adsorbed PPG assists the curatives in entering the latex particles in LPL.

Effect of duration of prevulcanization in EV system on tensile properties of latex films

Figure 5B.6. shows the variation of modulus of latex films against duration of heating for prevulcanization in EV system. For a given period of heating, modulus of films are in the order

SCL > LPL > DCL

This is an agreement with the crosslink density data. It can be noted that in EV system, modulus of three types latex films increase with cure time. But the rate of increase in modulus reduces with cure time. However, the observed rate of crosslink formation in DCL and LPL particles and rate of increase in modulus of these films are not in agreement. Further, LPL films have slightly higher modulus than DCL films even though their crosslink densities are more or less comparable. Thus it can be seen that variation in crosslink density alone cannot fully explain the variation in modulus of latex films. In about 5h of heating, the three types of films do not show any signs of reversion. This is attributed to the high thermal stability of monosulphidic workslinks formed during EV cure. During film formation, modulus of the films are determined both by crosslink density and the extent of inter-particle integration(13). In the case of leached SCL film, the inter-particle attractive forces are stronger due to the availability of more residual proteins on particle surface. It has been reported that proteins and aminoacids like 3-aminopropionic acid, generated from degraded proteins accelerate crosslink formation(14). These factors contribute to the higher modulus of SCL films. Higher modulus of LPL films compared to DCL films may be partly due to slightly higher crosslink density and partly due to forces of attraction via Hydrogen bonding generated from adsorbed PPG molecules on the surface of LPL particles.

The variation of tensile strength with respect to duration of heating is given in Figure 5B.7. SCL, DCL and LPL films vulcanized in EV system show increase in tensile strength with duration of heating; however, the rate of increase in tensile strength decreases with increase in duration of vulcanization. The three types of film attain maximum tensile strength in about 5h at 60°C. Tensile strength follow the order

SCL > LPL > DCL

as in the case of modulus. The increasing tensile strength with time of heating of the three latex films in EV system is almost in line with their crosslink density. The tensile strength of EV cured latex films is generally low. This is probably due to the low flexibility of the mono- and disulphidic crosslinks in the EV system. Even though crosslink densities of DCL and LPL films are more or less similar, the tensile strength of LPL films are slightly higher than those of DCL films. As in the case of modulus, this is attributed to higher forces of attraction between latex particles in LPL film via Hydrogen bonding due to PPG molecules adsorbed on rubber particles.

Data on elongation at break of vulcanized latex films can be seen from Figure 5B.8. The elongation at break of the three types of latex films is in the order

SCL > LPL > DCL

Further, ultimate elongation decreases with increase in duration of prevulcanization.

Effect of accelerated heat ageing on crosslink density of prevulcanized latex films in EV system

The effect of accelerated heat ageing at 70°C for 7 days on crosslink density of latex films prevulcanized in EV system for different duration is given in Figure 5B.9. For comparison, crosslink density data of the films before ageing are also provided in the figure. In the case of SCL films, as stated earlier crosslink formation before ageing initially increase rapidly with duration of heating. Beyond 3h rate of crosslink formation is somewhat low and reaches about 2.5×10^{19} per gram in 5h. However, after ageing the highest crosslink density is exhibited by films prevulcanized for half an hour. The lower the initial state of cure the higher the crosslink density in the aged film. The crosslink density of the film, prevulcanized for 3h remained almost constant. Beyond 3h of prevulcanization, the crosslink density of films after ageing was lower than that before ageing and the difference increased as duration of prevulcanization increased.

Accelerated ageing of DCL films prevulcanized for various duration are accompanied by increase in crosslink density. The crosslink density of LPL films before ageing increases with time of heating. However, the crosslink densities of these films after ageing remain more or less constant at about 2.05×10^{19} per gram. This observation suggests that even in the under-cured films, curatives were available in sufficient quantity to generate additional crosslink during the accelerated ageing process, irrespective of the initial duration of prevulcanization. However, even the lowest crosslink density in SCL films after ageing is higher than the maximum of heat aged LPL films. The observed increase in crosslink density of various latex films after accelerated ageing clearly indicates that more crosslinks are formed during the ageing process utilizing residual curatives and not due to crosslink modification as the crosslinks in EV system are of high thermal stability. High thermal stability is attributed to the high proportions of mono- and disulphidic crosslinks and low proportion of polysulphidic ones in the EV films, as against high proportion of polysulphidic crosslinks in the conventional cure system.

The above data on crosslink density clearly indicates that films prepared from latex heated for only half an hour give the highest state of cure after ageing. This shows that sufficient quantity of curatives have entered the latex particles during maturation period. The rate of entry of accelerator particles into latex particles is slower than that of sulphur(11). Thus during prevulcanization more and more crosslinks are formed with the available accelerator as prevulcanization progresses. The data on crosslink density indicates that the reduction in protein content in DCL and LPL reduce the quantity of curatives that enter the latex particles. Thus DCL and LPL has lower crosslink density than SCL, both before and after ageing and at all durations of prevulcanization. The reduction in crosslink density in aged SCL films prepared from latices prevulcanized for longer durations indicates some breakage of existing crosslinks. Considering the high thermal stability of mono- and disulphidic crosslinks, the crosslinks that break may probably be some physically effective crosslinks formed due to the poor fusion of highly crosslinked latex particles.

Aged LPL film has some what higher crosslink density than DCL films. This is attributed to the entry of more curatives to latex particles in LPL during maturation of latex compound and during its heating period.

Effect of accelerated heat ageing on tensile properties of latex films prevulcanized in EV system

Heat ageing has profound influence on modulus, tensile strength and ultimate elongation of latex films cured by EV system. The effect of accelerated heat ageing on modulus of SCL, DCL and LPL films is provided in Figure 5B.10. Modulus of aged films of the three latex types increases after ageing. The aged modulus increases with duration of prevulcanization, show a maximum at about 3h of prevulcanization and gradually decreases for all the three types. Also at all durations of prevulcanization, SCL films have higher modulus compared to DCL and LPL films, both before and after ageing. The higher modulus of SCL film is attributed to the higher state of cure and better interparticle attraction through Hydrogen bonding and van der Waals forces due to the presence of higher levels of proteins on their surface than in DCL and LPL films.

Films prepared from DCL and LPL prevulcanized for short intervals, after ageing show considerable increase in modulus and a maximum is observed for films prepared from latex prevulcanized for about 2.5h. Increase in crosslink density on heat ageing makes substantial contribution to increase in aged modulus. Since crosslink density after ageing is more or less constant for LPL films prevulcanized for different durations, the increase in aged modulus from 0.5–2.5h of prevulcanization is attributed to better interparticle integration and molecular chain entanglements. However, the decrease in aged modulus of three latex types beyond 2.5h of prevulcanization is probably due to less effective fusion of particles which were initially crosslinked to a high state of cure(13). The aged modulus of DCL and LPL films is lower than those of SCL films. Low crosslink density in aged LPL films is a major contributing factor. Even though crosslink densities of DCL and LPL films, both before and after accelerated ageing are more or less similar, slightly higher modulus exhited by LPL films after ageing. This is attributed to force of attraction due to Hydrogen bonding in LPL films due to PPG molecules.

Data on variation of tensile strength of prevulcanized latex film before and after ageing with respect to duration of prevulcanization is provided in Figure 5B.11. Irrespective of the time of prevulcanization, tensile strength of aged LPL films remains more or less constant at a high value of approximately 36MPa. Increase in crosslink density in the aged films and the thermal stability of predominantly mono- and disulphidic crosslinks in latex particles prevulcanized by EV system primarily contribute to high tensile strength after ageing of LPL films. Further because of the low level of non-rubber solids content, fusion between the particles during film formation would be better. This also contributes to increase in tensile strength. Tensile strength of SCL and DCL films also increases on ageing and the maximum value is reached for those films which were initially prevulcanized for a minimum of 2.5h. However, this maximum tensile strength of SCL film is lower than that of aged LPL films. This is probably due to the less effective fusion of crosslinked latex particles due to the presence of non-rubber substances adsorbed on latex particles. DCL films, which had lower tensile strength on accelerated ageing showed tensile strength similar to SCL films, even though crosslink density in aged DCL films were lower than those in SCL. This also in attributed to better particle fusion, due to lower non-rubber substances with DCL films.

At all duration of prevulcanization elongation at break decreases after ageing for the three types of latex films as shown in Figure 5B.12 Elongation at break after ageing is lower in SCL films than in LPL films and DCL film show the lowest values. This behaviour of SCL film is partly due to higher modulus of aged SCL films. Higher crosslink density and increased modulus of LPL films on ageing contribute to higher ultimate elongation. High elongation indicates that the molecular chains have become more flexible on ageing. van der Waals forces of attraction between adsorbed PPG and residual proteins on rubber particle surface also contribute to the high ultimate elongation in the LPL films.

CONCLUSIONS

Following conclusions are derived from the above study:

- LPL films can be post-vulcanized in EV system. It is slightly slow curing than SCL, but more or less comparable to DCL films. Accelerated ageing of LPL films is accompanied by increase in crosslink density.
- Physical properties of post-vulcanised LPL films are slightly lower than SCL films, however, it is sufficiently high to meet the specifications for common latex products. Post-cured LPL films in EV System show good retension of physical properties.
- LPL can be prevulcanized using sulphur and accelerator in EV system for a given duration of prevulcanization the state of cure is slightly lower than that of SCL films, but slightly above DCL films. The rate of cure is almost comparable for SCL and LPL films. Accelerated heat ageing of LPL films is acoompanied by increase in crosslink density. Physical properties of prevulcanized LPL in EV system are good, eventhough slightly lower than SCL film. LPL films show good retension of physical properties on accelerated ageing.

REFERENCES

1. B.H. To, in Rubber Technology: Compounding and Testing for performance, J.S. Dick (ED), Hanser Publishers Munich Chapter 15, (2001).
2. W.J.Cooper, *Polym. Sci.* **28**,195 (1958).
3. L.B.Bateman, J.Icunneen, G.J.Moore, L.Mullins and A.G.Thomas in the Chemistry of Physics of Rubber-like Substances, L.Bateman (Ed.), Macleran & Sons Ltd., London.
4. D.J.Elliott, in Developments in Rubber Technology–1. A Whelan and K.S.Lee (Ed.) Chapter 1. Applied science Publishers, London (1979).
5. N.R.Peethambaran and T.K.George. *J. Appl. Polym. Sci.* **40**, 1627 (1990).
6. C.F.Flint and W.J.S.Naunton, *Trans. Instn. Rubber Ind.* **12**, 367 (1937).
7. R.M.Panich, N.M.Fodiman and N.M.Voyatski. *Soviet Rub. Technol.* **18(2)**, 14 (1959).
8. P.J.Flory and J.Rehner *Jr. J.Chem. Phys.* **11**, 521(1943).
9. IS 3400 (Part 1) 1987:Methods of Test for Vulcanized rubbers tensile stress–strain properties (second revision).
10. IS 3400 (part 4) 1987:Methods of Test for vulcanized rubbers- Accelerated ageing (second revision).
11. G.E.van Gills. *Rub. Chem. Technol.* **50**. 141 (1977).
12. M.Porter, R.Rawi and S.A.Rahim. *J. nat. Rub. Res.* **7**, 85 (1992).
13. L.C.Teik and W.N.Poh Developments in the Plastics and Rubber product Industries, Plastics and Rubber Institute of Malaysia, p-265 (1987).
14. A.D.T.Gorton, D.C.Blakley and H.M.Ghazaly. Polym. Latex III. Int. Conf. 24/1, London (1989).

TABLE 5B. 1

Formation of Latex compound for post and prevulcanization in EV system

Ingredient	*Parts by weight*	
	Dry	*Wet*
60% Natural latex	100	167
10% Potassium hydroxide	0.1	1.0
10% Potassium laurate	0.2	2.0
50% Sulphur	0.25	0.50
33%TMTD	3.0	9.0
10% Thiourea	1.0	10.0
50% Zinc oxide	0.4	0.8

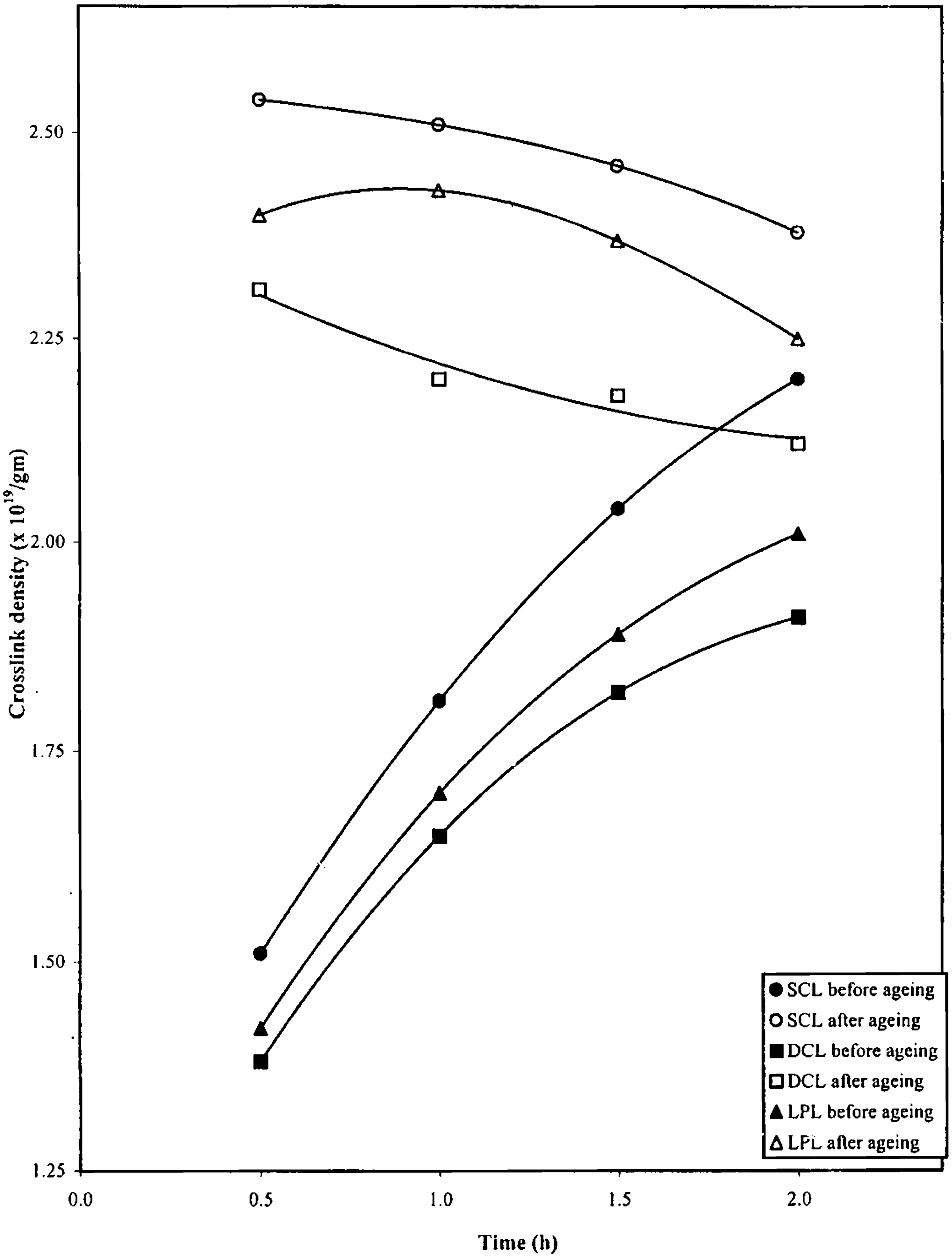


Fig 5B.1. Effect of duration of post-cure in EV system at 100°C on crosslink density of latex films and effect of heat ageing

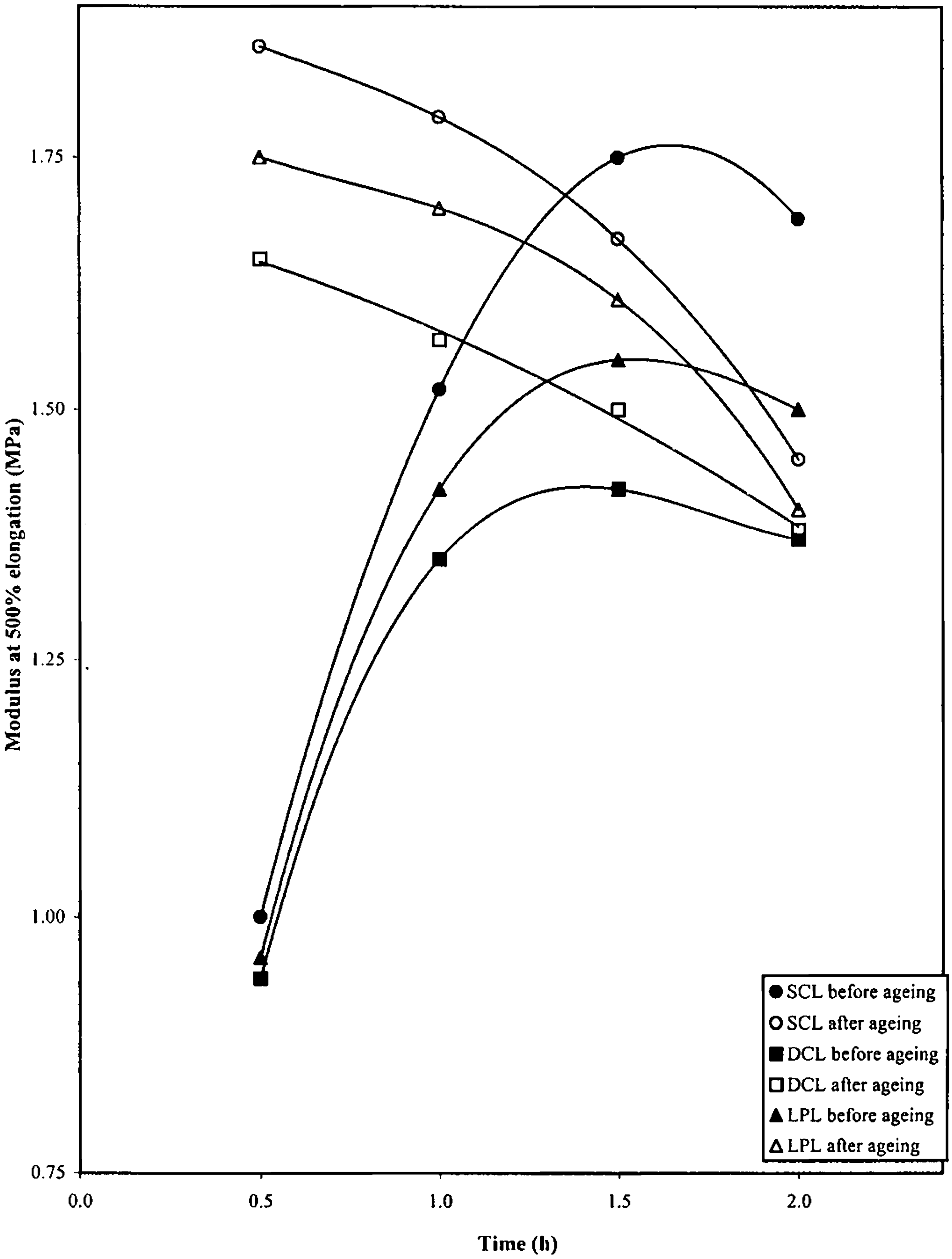


Fig 5B.2. Effect of duration of post-cure in EV system at 100°C on modulus of latex films and effect of heat ageing

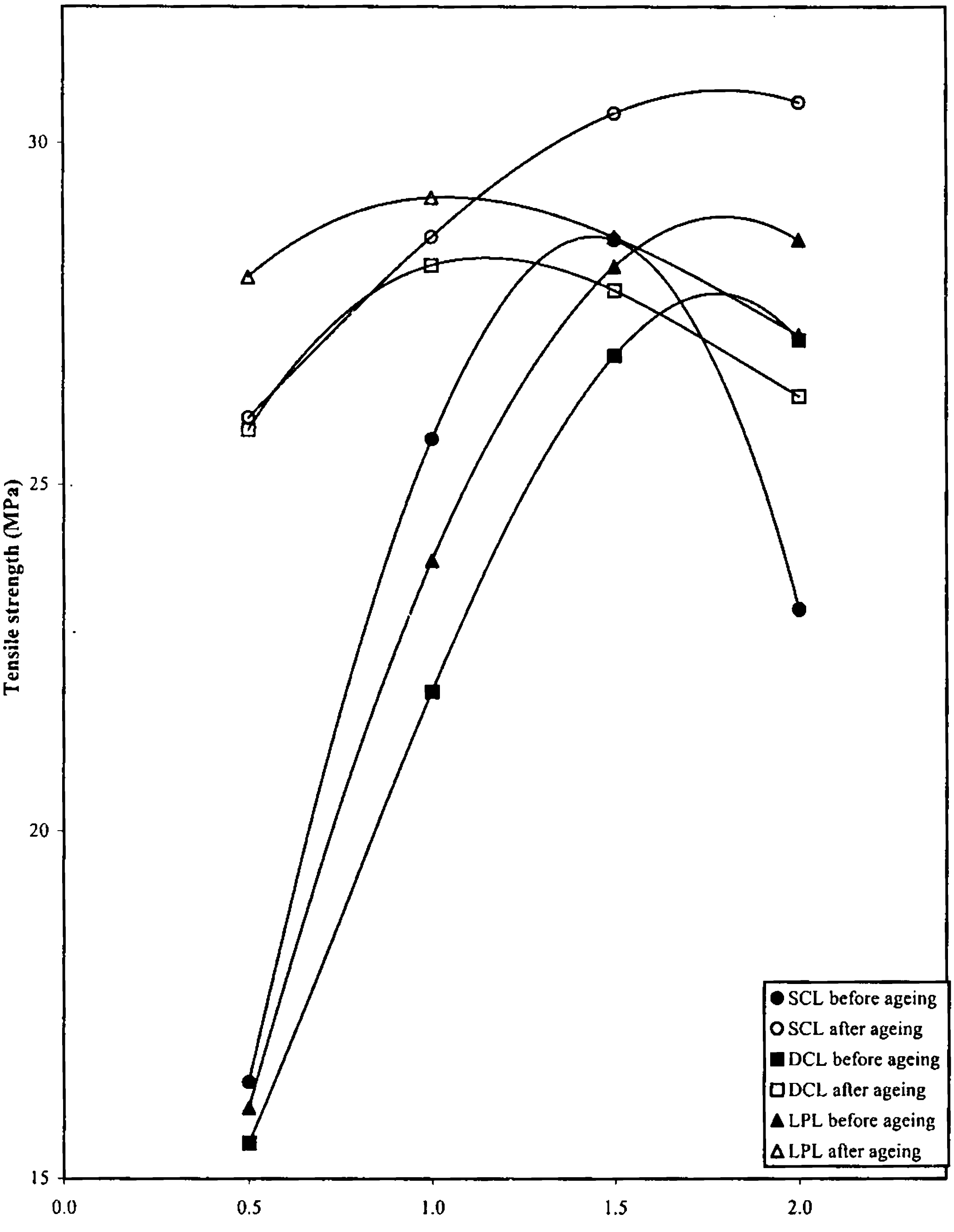


Fig 5B.3. Effect of duration of post-cure in EV system at 100°C on tensile strength of latex films and effect of heat ageing

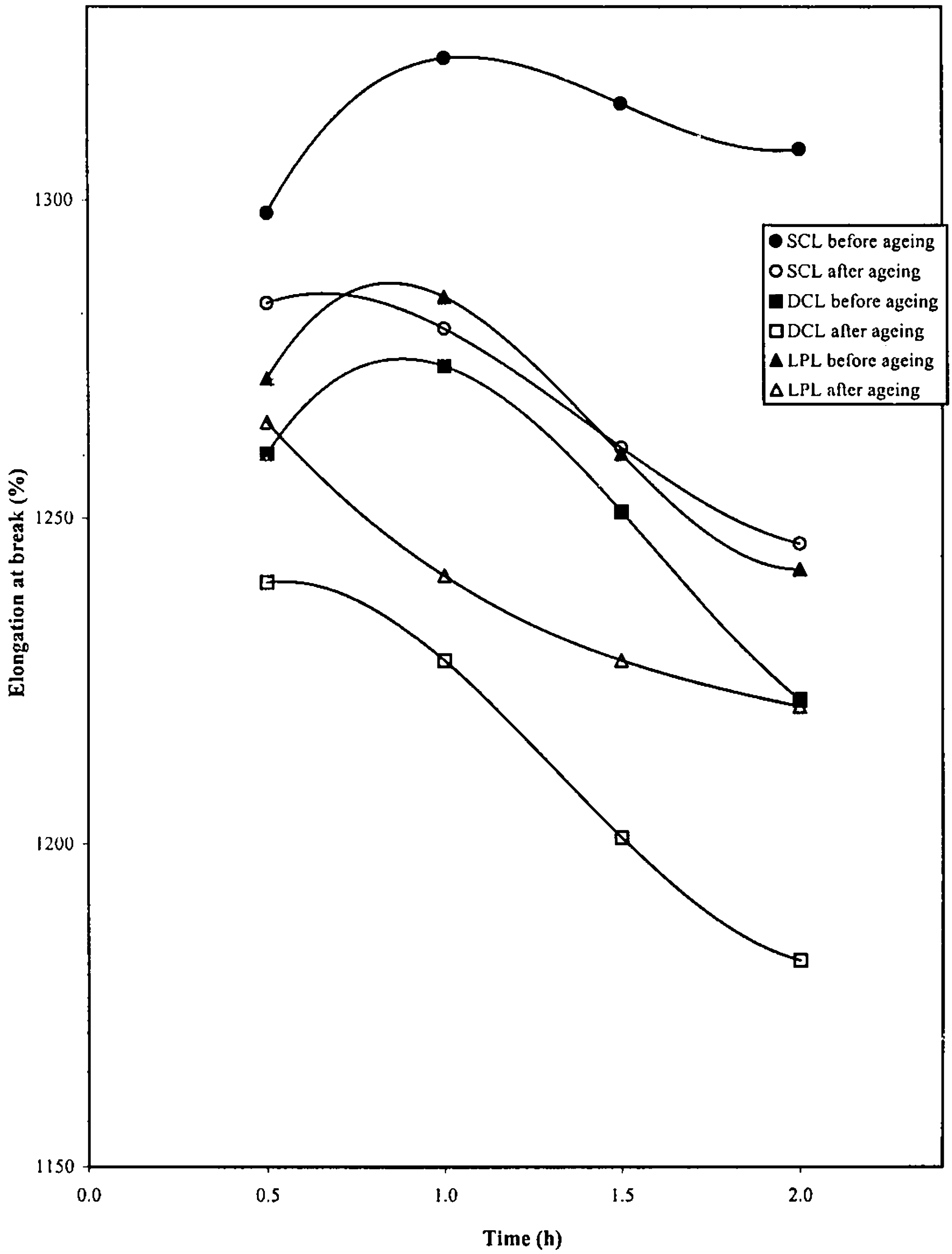


Fig 5B.4. Effect of duration of post-cure in EV system at 100°C on elongation at break of latex films and effect of heat ageing

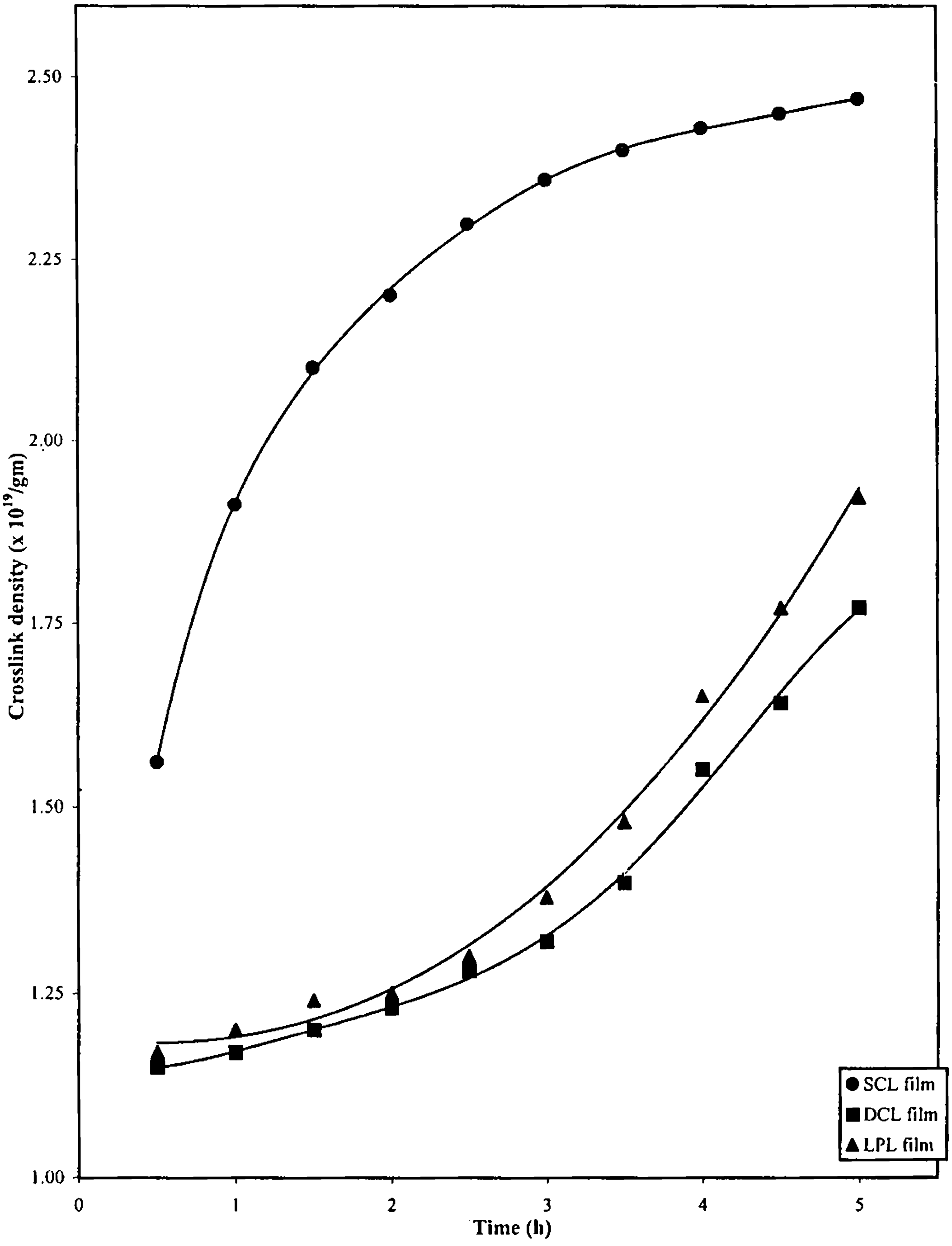


Fig 5B.5. Effect of heating time on crosslink density of prevulcanized latex films in EV system.

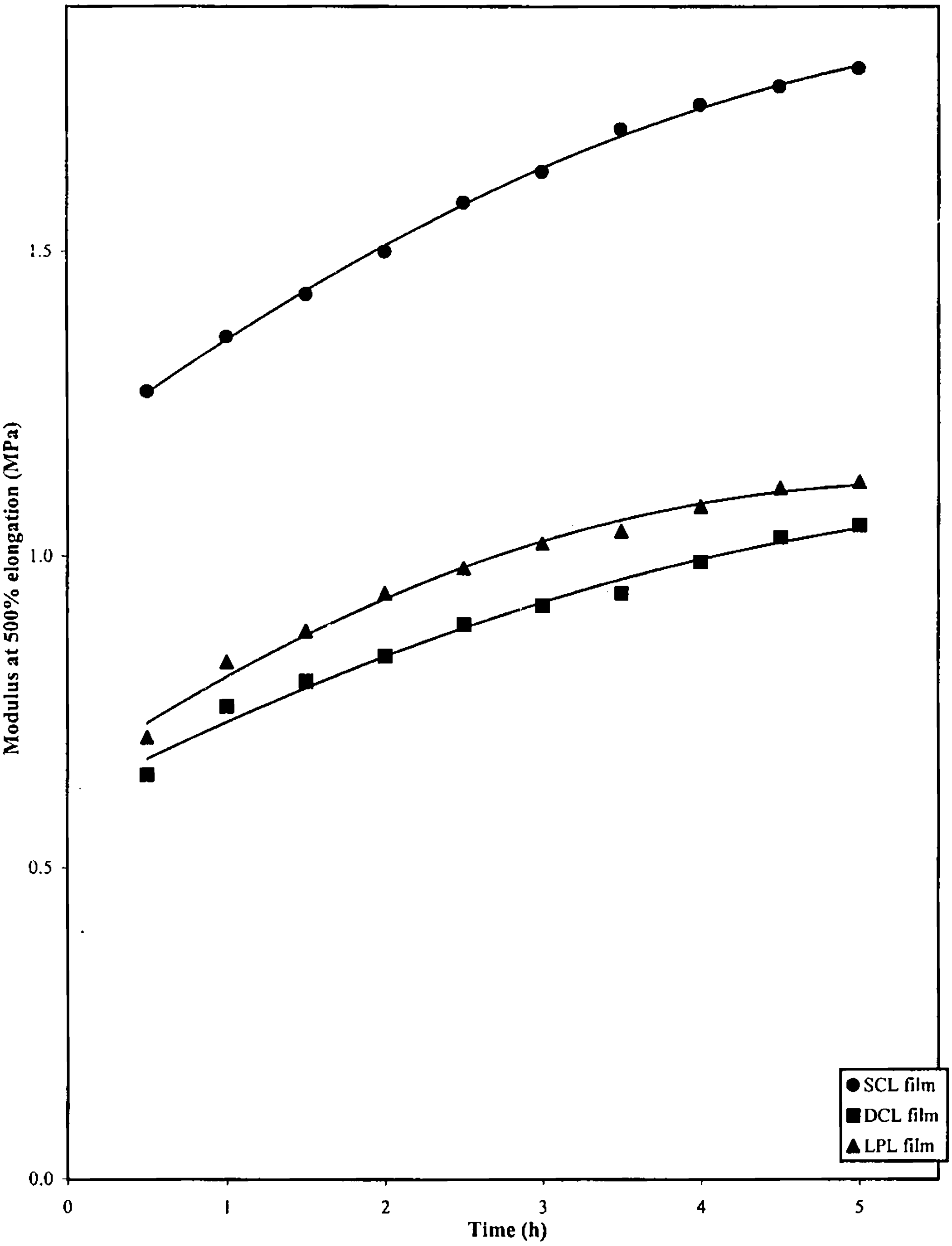


Fig 5B.6. Effect of heating time on modulus of prevulcanized latex films in EV system.

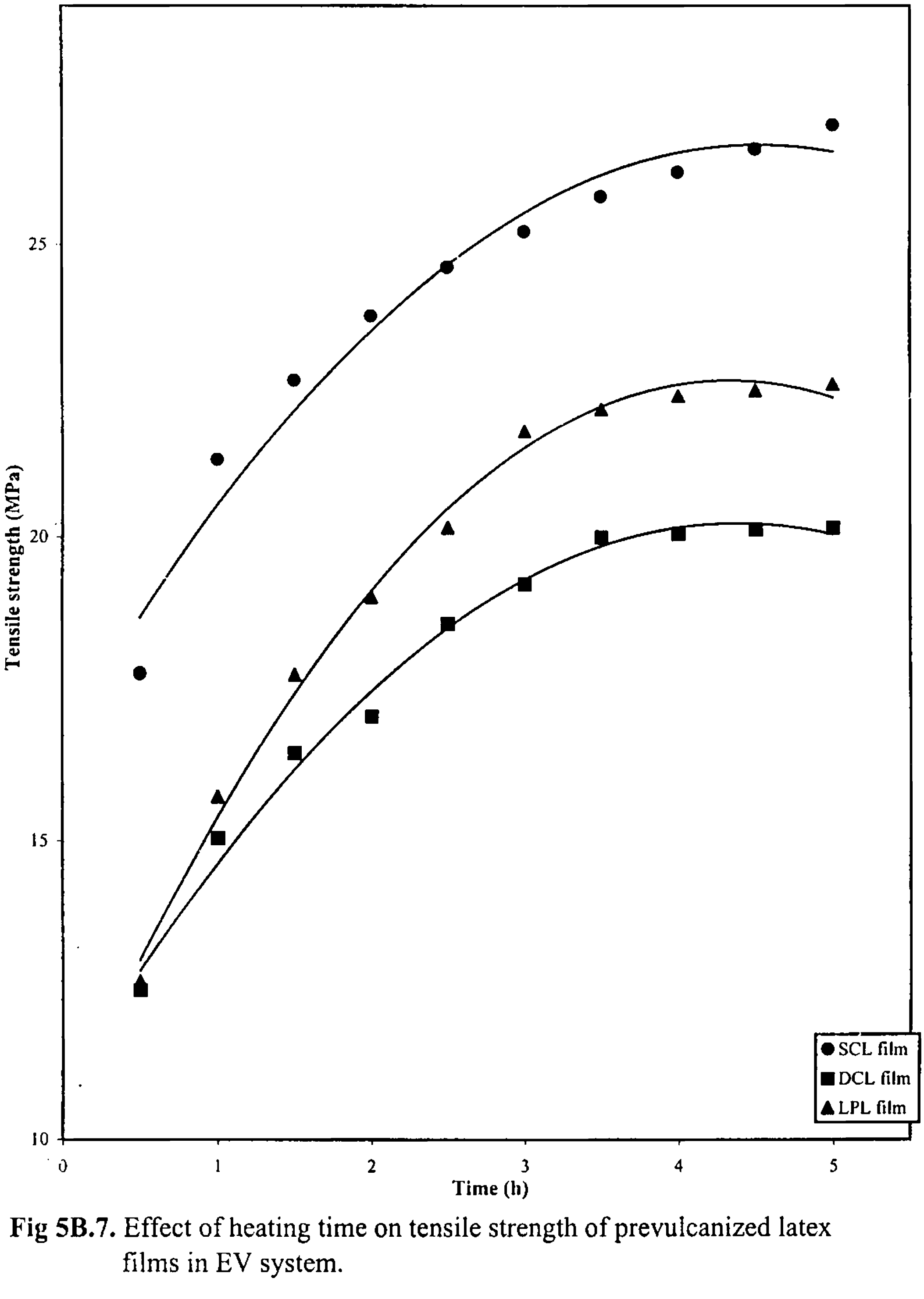


Fig 5B.7. Effect of heating time on tensile strength of prevulcanized latex films in EV system.

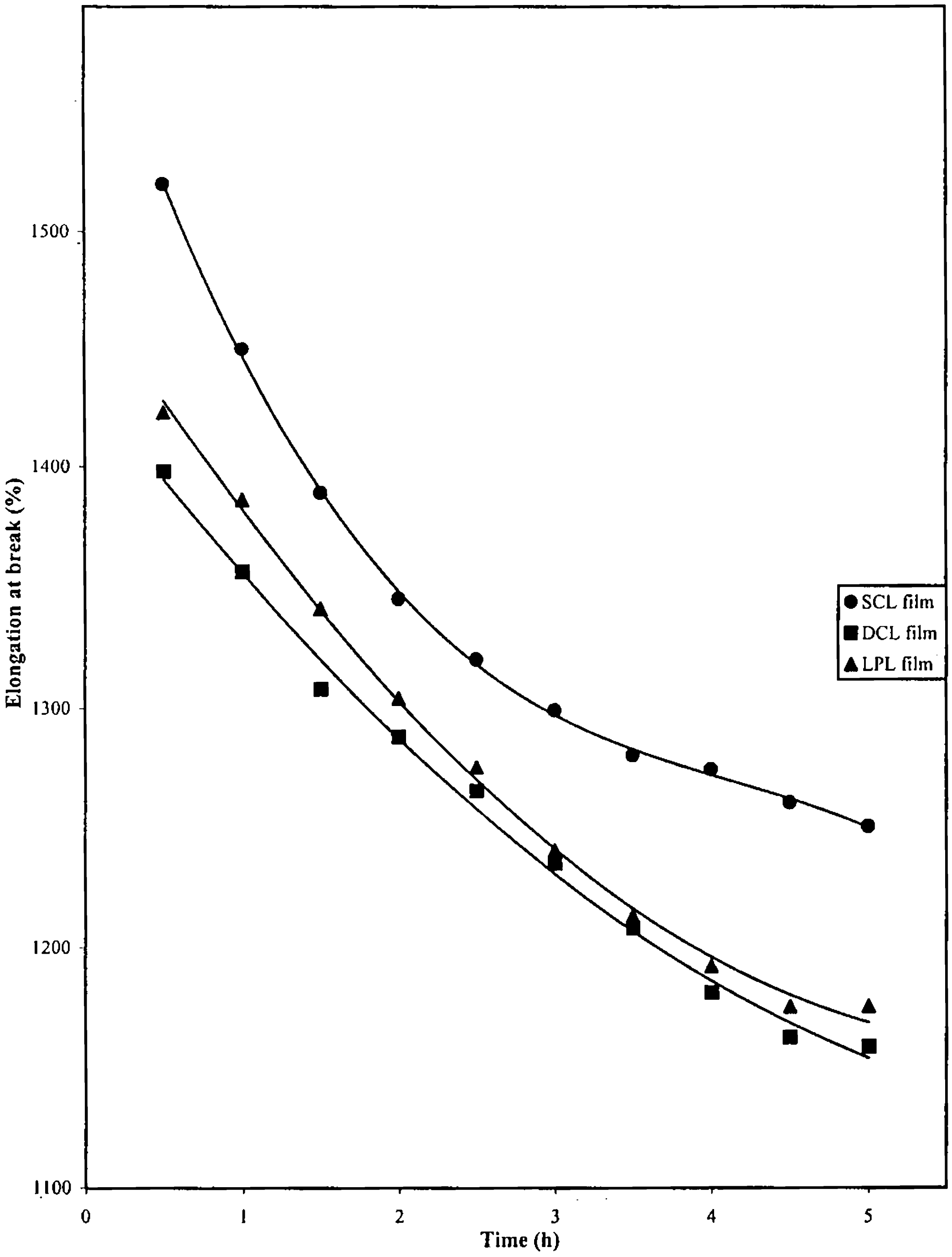


Fig 5B.8. Effect of heating time on elongation at break of prevulcanized latex films in EV system.

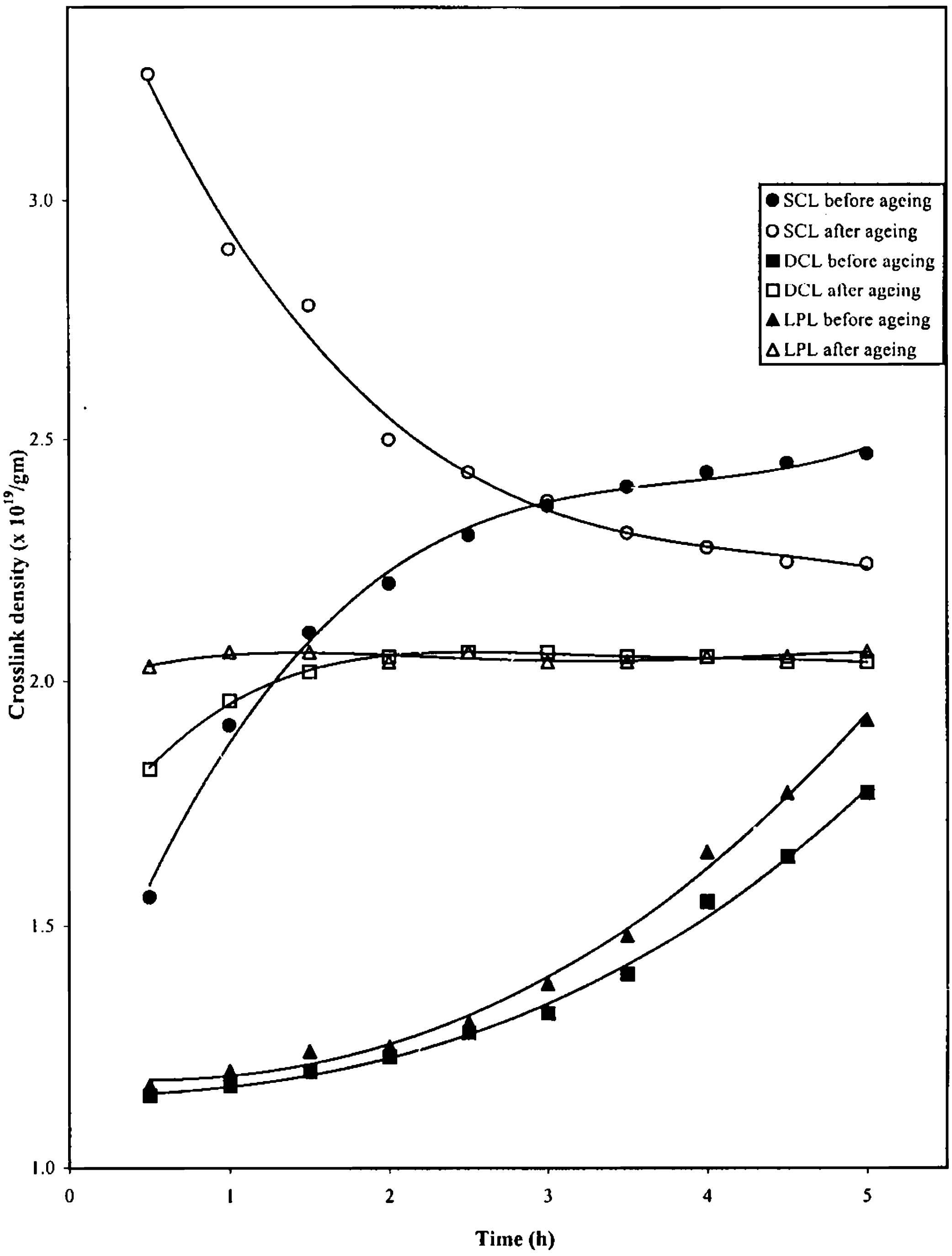


Fig 5B.9. Effect of accelerated heat ageing on crosslink density of latex films in EV system

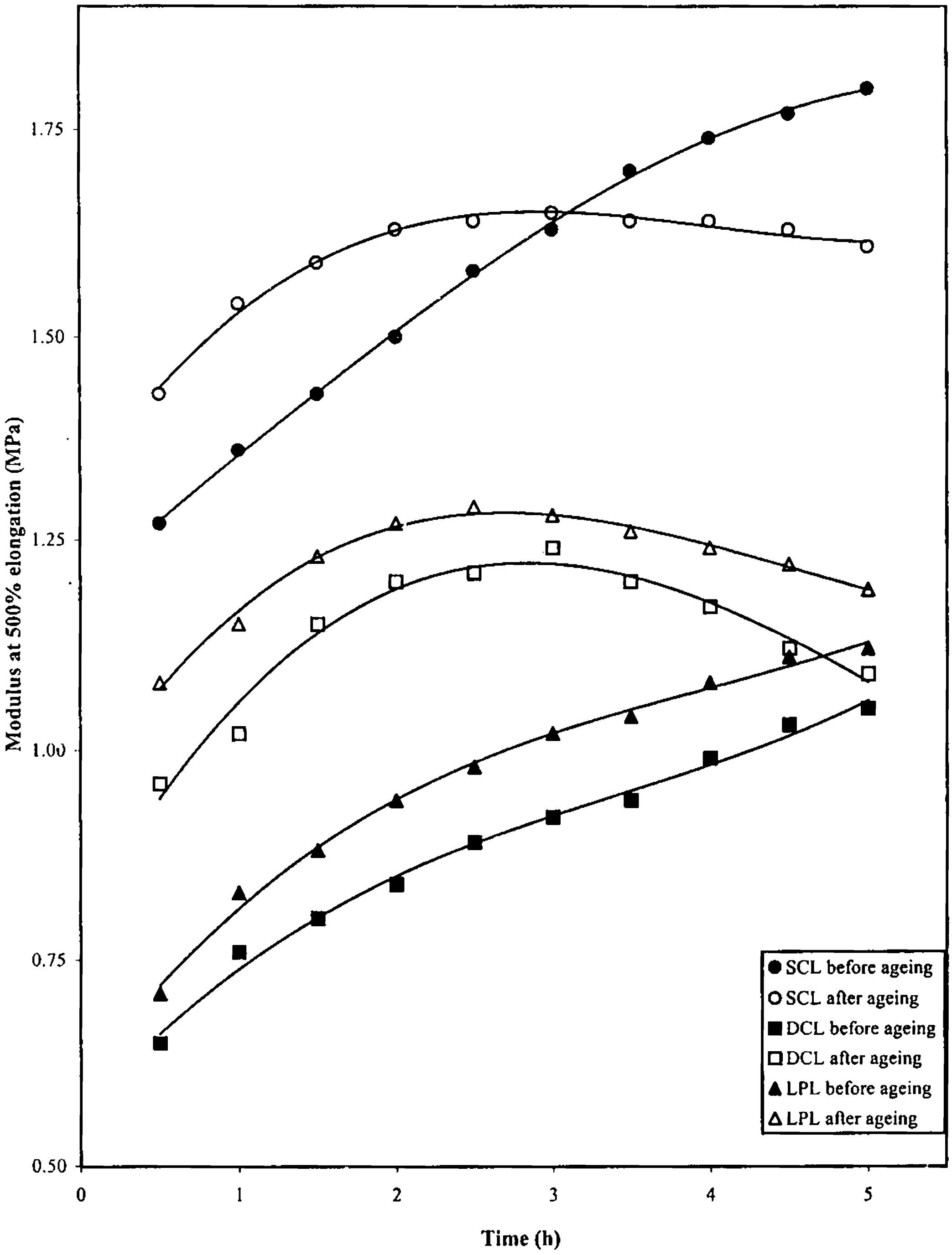


Fig 5B.10. Effect of accelerated heat ageing on modulus of latex films in EV system.

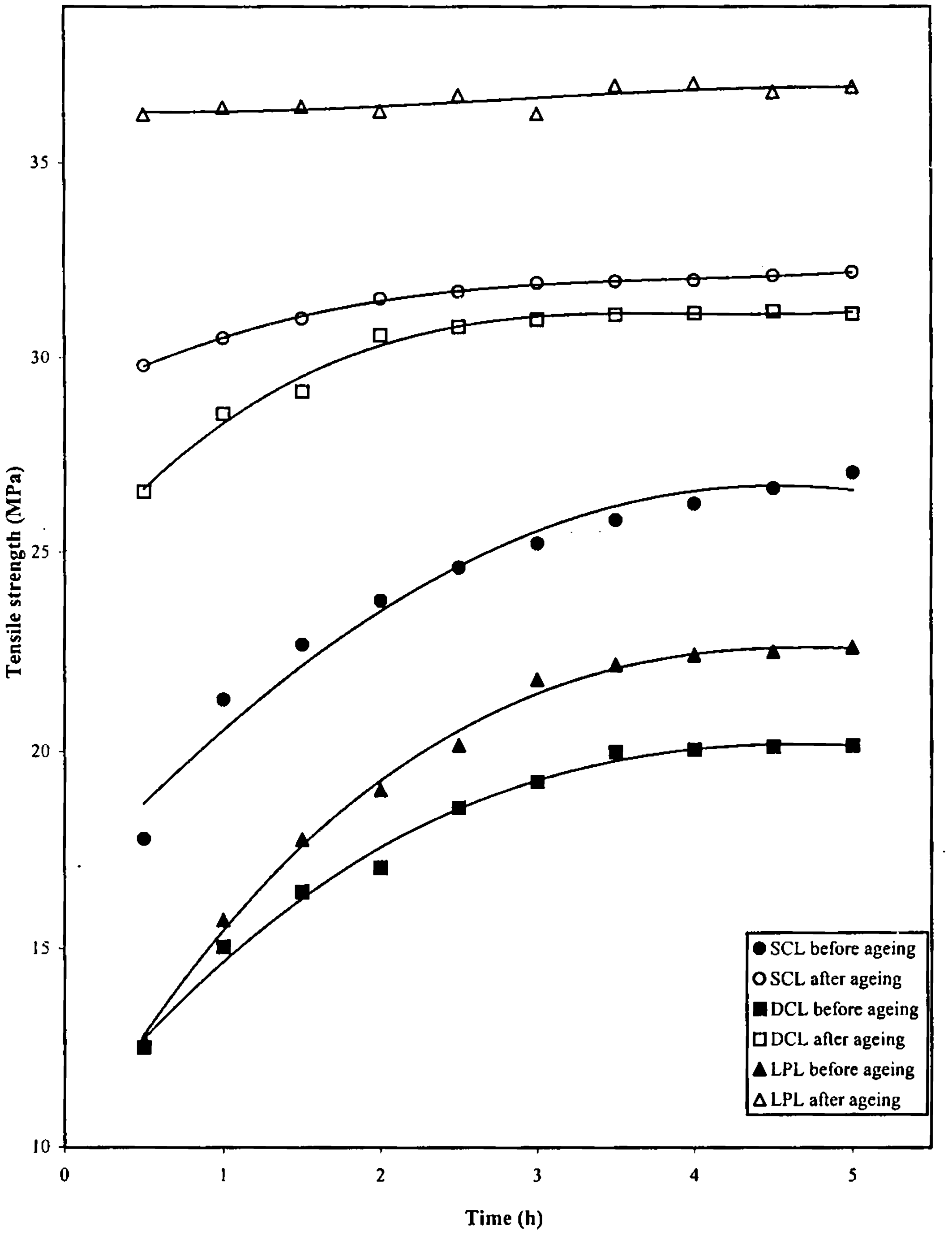


Fig 5B.11. Effect of accelerated heat ageing on tensile strength of latex films in EV system.

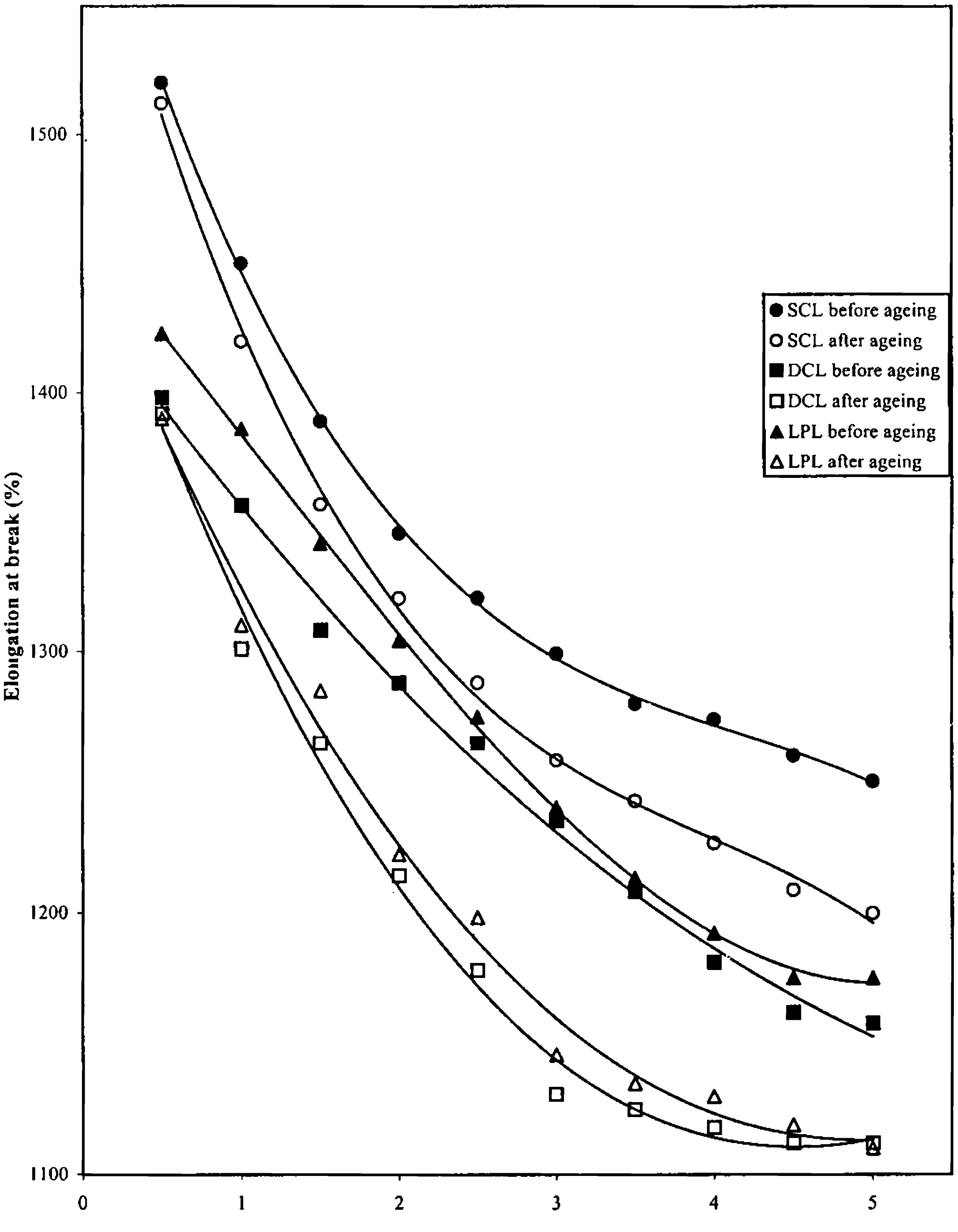


Fig 5B.12. Effect of accelerated heat ageing on elongation at break of latex films in EV system.

CHAPTER 5C

RADIATION PREVULCANIZATION OF LOW PROTEIN LATEX

Natural rubber in dry form or as latex is usually vulcanized by sulphur and accelerators. Crosslinking can be brought about by organic peroxides or high energy radiations also. Radiation vulcanization is the process of crosslinking rubbery molecules in latex using high energy radiation(1), either gamma rays or electron beams. However, the dose requirement is high, about 250–300kGy(2). Hence the process is carried out in the presence of a sensitizer to reduce the dose required to impart adequate level of prevulcanization. n-Butylacrylate (nBA) is commonly used as sensitzer and the dose requirement is only about 15kGy(3). Radiation vulcanization process does not involve the use of organic accelerators that can liberate carcinogenic nitrosamines and nitrosaTable amines, whereas in conventional sulphur vulcanization organic accelerators are used. During irradiation of latex, proteins are partly degraded and can be removed by leaching(4,5). Thus radiation vulcanization provides clean products, free from type IV allergic reactions(6) originating from added chemicals. Varghese *etal*(7) have reported that addition of water soluble polymers like polyvinaylalcohol and polyethylene oxide to radiation vulcanized latex, makes protein removal from latex films more fast by leaching.

It has been proved that extractable proteins in latex products can cause immediate type I allergies in sensitized people(8-10). Low protein latex (LPL) is a form of natural rubber latex which shows very low levels of extractable proteins in leached films(11). Irradiation of a latex, inherently low in extractable proteins is likely to provide latex products still lower in extractable proteins. Hence it is believed that radiation crosslinking of LPL will provide vulcanized films free from type IV allergic reactions arising from rubber chemicals, carcinogenic nitrosamines and nitrosatables originating from residues of dithiocarbamate and thiuram based accelerators and very low in extractable proteins.

However, it is observed that radiation vulcanized natural rubber latex films generally are low in modulus. Even though low modulus is an advantage in products like examination gloves, it is a disadvantage in the case of articles like latex tubing, catheters, feeding bottle nipples, soothers etc. where increased modulus is desirable. In such situations radiation vulcanized latex films require reinforcement. Further the extent of crosslinking brought about in rubber molecules depends on how effectively high energy radiations are utilized. To some extent this is influenced by the rubber content in the latex being irradiation and the dose rate if irradiation. This chapter reports the effect of dose and dose rate of gamma radiation, rubber content in irradiated latex, the effect of leaching and post-drying of leached films on crosslink density, physical properties, extractable protein content of the films and reinforcement of radiation vulcanized LPL films using silica.

EXPERIMENTAL

Low protein latex was produced by the method described in chapter-4(11). Gamma irradiation was carried out using Gamma Chamber 5000, developed by the Board of Radiation and Isotope Technology (BRIT), (Department of Atomic Energy, Government of India), Mumbai, which is loaded with Cobalt-60. Latex compound used for irradiation is prepared according to the formulation given in Table 5C.1 and allowed to mature for 6h before irradiation. Irradiation at different doses is achieved by varying the duration of exposure and dose rate is varied by the use of attenuators. Cast films were prepared on levelled glass plates(12) and dried in air at room temperature until the films became transparent. Dry films were leached in distilled water for predetermined periods. Crosslink density of vulcanized films were measured using solvent swelling method(13) following Flory–Rhener equation(14). Tensile properties were evaluated on a Hounsfield Universal Testing machine using ASTM test methods. Extractable proteins in latex films were estimated by the RRIM modified Lowry method(15).

Silica, used for improving the modulus, was prepared as 25% dispersion by ball milling. Silica dispersion was blended with radiation vulcanized LPL in various proportions and cast films were prepared for testing.

RESULTS AND DISCUSSION

Effect of dose of irradiation on crosslink density in vulcanized latex films

Radiation can interact with rubber in latex to form free radicals either by hydrogen abstraction or by chain scission(16). Two such radicals can undergo addition reaction to form a crosslinked structure. Free radicals can also undergo transfer reaction and the newly formed radicals also can form crosslinked structure. The dose requirement for achieving adequate level of crosslinking reaction in the absence of sensitizers is about 300kGy(2). By the use of acrylic monomers(3,17) the dose requirement has been reduced to about 15kGy. By gamma ray irradiation acrylic monomers undergo hydrogen abstraction leading to the formation of $^{\bullet}CH{=}CH{-}COOR$ free radicals(18,19). As this acrylic free radical is more mobile than the rubber chain, it attacks a double bond in an adjacent chain, forming a rubber free radical. The newly formed free radicals form crosslinked structures.

When an aqueous emulsion of nBA is irradiated, radicals like $^{\bullet}OH$, $H^{\bullet}$ and hydrated electrons e^{-}_{hy} are generated by the radiolysis of water(20). The radiation polymerization of nBA in an aqueous matrix involves only hydrated electrons, e^{-}_{hy}(21) and the reactions can be represented as

$$nBA + e^{-}_{hy} \longrightarrow nBA^{-\bullet}$$

$$nBA^{-\bullet} + nBA \longrightarrow (nBA)_2^{-\bullet}$$

The mechanism of sensitization by nBA is via the transient produced by the reaction of e^{-}_{hy} with nBA, capable of propagating the radical reaction with the monomer at high rates leading to polymerization/ vulcanization. The solubility of nBA in natural rubber is high(17) and $nBA^{-\bullet}$ radicals formed in the rubber phase alone contribute to crosslinking reaction(21).

Figure 5C.1 shows the effect dose of irradiation on the number of crosslinks formed per gm of dry film of LPL. The behaviour of the single centrifuged latex

(SCL) from which LPL was prepared also is given for reference. Data is also presented in respect of the double centrifuged latex (DCL) processed out of this SCL, since LPL processing involves a second stage of latex concentration by centrifuging. Data presented in Figure 5C.1 indicate that for the three types of latices, crosslink density increases with dose. However, the rate of increase in crosslink density decreases with increase in dose. As the dose of irradiation increases, the concentration of e^{-}_{hy} within the rubber particles increase thus more nBA$^{-\bullet}$ radicals are formed resulting in the formation of more number of crosslinks. The decrease in the rate of formation of crosslinks at higher doses may probably be due to the decreasing concentration of free nBA available within the latex particles. Further, it is likely that simultaneous to crosslink formation, some extent of crosslink rupture also may occur, contributing to the reduction in the overall rate of crosslink formation.

It is also observed from Figure 5C.1 that at low doses of irradiation crosslink density in LPL films is intermediate between DCL and SCL films. However, at higher doses of irradiation, LPL films exhibit crosslink densities comparable to SCL films. The low crosslink density in DCL may probably be due to the lower availability of nBA within latex particles. Availability of adsorbed proteins at the rubber-serum interface is more in SCL compared to DCL or LPL. Proteins are likely to form weak hydrogen bonds with the oxygen atoms of nBA, thus facilitating the entry of nBA into rubber particles and then move into the rubber phase, because of its solubility in(17) rubber phase. Among the three types of lattices, protein content in highest in SCL, permitting the entry of more nBA In DCL, content of proteins is less, thus restricting the entry of nBA. In the case of LPL, the reduction of proteins is compensated by the presence of surface active polypropylene glycol (PPG), which also can form hydrogen bonds with nBA molecules. This explains the comparable crosslink density in SCL and LPL films.

Effect of dose of irradiation on tensile properties of latex films

Figure 5C.2 shows the variation of modulus of latex films at 500% elongation with dose of irradiation. It is seen that modulus of SCL and LPL are almost similar at all doses of irradiation, while DCL film is lower in modulus. For the three latex films, modulus increases with dose. However, the rate of increase in modulus decreases with increasing dose.

The modulus of prevulcanized latex films is contributed mainly by two factors: degree of crosslinking within individual latex particles and the degree of interparticle coalescence of latex particles during drying and film formation(22). From Figures 5C.1 and 5C.2 it is seen that the pattern of variation in crosslinks and modulus with dose of irradiation is more or less similar. This suggests that the nature of interparticle coalescence during film formation is more or less similar with the three types of latices, which in turn, is attributed to the removal of non-rubber materials during leaching. Thus the major reason for variation of modulus with dose of irradiation between the three latices is the variation in crosslink density.

From Figure 5C.3 it can be seen that for the three types of films, tensile strength initially increases with dose, reaches a maximum and then decreases. The initial increase in tensile strength with dose of irradiation is attributed to progressive increase in crosslink formation. In the case of natural latex highest tensile strength is centred around dose of 15kGy(3). For DCL and LPL films also maximum tensile strength is observed at about 15kGy. Further increase in dose is accompanied by fall in tensile strength. It is believed that high modulus of highly crosslinked latex particles prevent their effective fusion to form a strong and coherent film(22) during drying.

Tensile strength of latex films prepared from latices irradiated to 15kGy the optimum dose of irradiation, is in the order

SCL > LPL > DCL.

At 15kGy, eventhough SCL and LPL films have almost the same crosslink density, tensile strength is slightly higher for SCL film. This is attributed to the higher forces of attraction between latex particles in the film via Hydrogen bonding originating from absorbed proteins, which is highest in SCL film. DCL films exhibits the least tensile strength. This is due to low crosslink density and low attractive forces via Hydrogen bonding, due to low protein content.

The variation of elongation at break with dose of irradiation is presented in Figure 5C.4. For the three types of films, ultimate elongation reduces with increase in dose of irradiation. For various doses of irradiation elongation at break is slightly lower for LPL films than SCL films and DCL films the lowest. As the dose irradiation increase, the crosslink density in crease. Crosslinking restricts the movement of molecular chains when a streaching force is applied. Further, the effectiveness of fusion of latex particles are reduced, when they become more hard due to increased crosslink density.

Effect of dose of irradiation on extracTable protein content in latex films

Out of the total proteins present in a vulcanized natural latex film only a small portion of it is extractable(23). Figure 5C.5 shows the variation of residual extractable proteins (EP) in radiation vulcanized SCL, DCL and LPL films, both before and after leaching. It is seen that in the case of the three types of unleached films, EP content is in the order

SCL > DCL > LPL

This observation is in agreement with the initial EP content of the three latex types, before irradiation. Further EP content increases with radiation dose. Similar observations were made by other workers also(7,8). However, after leaching residual protein content in latex film is substantially reduced. It is believed that proteins in natural latex are decomposed by gamma irradiation, resulting in substantial reduction in molecular weight, making them water soluble. A comparison between EP content in SCL and LPL films before leaching indicates that during LPL processing, easily degradable and/or extractable proteins were effectively displaced. At low doses of irradiation, leached LPL films contain practically no EP and films prepared from LPL irradiated at higher doses contain very low levels of EP. Even radiation crosslinked SCL films after leaching have EP content in the range 30–60mg/kg. It is reported that EP content below

100mg/kg does not generally cause allergic reactions(24). However, there is no line of demarcation between allergic and non-allergic levels of EP. Even very minute levels of EP may be sufficient enough to cause allergic reactions in highly sensitized persons. Thus vulcanized LPL films containing almost nil EP can be safely used by even highly sensitized people.

Effect of dose rate of irradiation on crosslink density in latex films

Results on the effect of dose rate on crosslink density of latex films are presented in Figure 5C.6. For the three types of latices, there is only very small increase in crosslink density when a given dose (here 15kGy) is delivered at higher dose rates. Practically, the dose delivered, and not the rate at which it is delivered determines the number of crosslinks formed. The number of hydrated electrons e^-_{hy} generated within latex particles during irradiation determine the number of crosslinks formed(21) and it is believed that their number is controlled by the total energy supplied, and not by the rate at which it is delivered. In addition to crosslinking reactions, e^-_{hy} can undergo certain side reactions with some impurities(21). At low dose rate of generation of e^-_{hy} is also low and hence the ratio of the concentration of impurity to e^-_{hy} is high. This ratio is low when high concentrations of e^-_{hy} are generated at higher dose rates, leading to lower proportion of side reactions ie, more crosslinks are formed. This explains the slightly higher crosslink formation at higher dose rates.

The slope of the DCL and LPL curves are almost similar, while the SCL curve is little more steep, suggesting that some other factors are also involved in crosslink formation. It is suggested that some non-rubber components in the aqueous phase of SCL, which are removed during the second centrifugal concentration for processing DCL and LPL have contributed to increased crosslink formation with increase in dose rate of irradiation.

Effect of dose rate on tensile properties of latex films

The variations of modulus, tensile strength and elongation at break of dry latex film with dose rate are given in Figures 5C.7, 5C.8 and 5C.9 respectively. Figure 5C.7 shows that for the three types of latices, modulus increases to some extent with dose rate. This increase in modulus closely parallels the slight increase in crosslink density at higher dose rates. The tensile strength decrease by irradiation at higher dose rates, even though crosslink density has increased slightly. This fall in tensile strength is believed to be due to the less effective fusion of well crosslinked latex particles(22). From Figure 5C.9, it seems that increase in dose rate is accompanied by a reduction in ultimate elongation. This is partly due to increased crosslinking restricting the relative movement of molecular chains and partly due to increase in modulus. In short, on increasing the dose rate of irradiation, the modulus is slightly increased and elongation at break is reduced by increasing dose rate, while tensile strength shows appreciable fall.

Effect of dose rate on residual extractable protein content in latex films

The data on the effect of dose rate during irradiation of latex on residual extractable protein content in latex films are presented in Figure 5C.10. Only slight variations are observed in the total EP in the unleached films. Thus dose rate has practically no effect on EP content in vulcanized films. This is probably because the protein degradation is mainly controlled by the total dose and not by dose rate. The films were leached for 5min. and it is found that residual EP in leached films remains more or less constant at very low values. This observation suggests that irrespective of the dose rate, the proteins are so highly degraded that they are easily leached off over short leaching periods.

Effect of rubber content in irradiated latex on crosslink density of latex films

It has been reported that it natural rubber latex irradiated in the absence of a sensitizer, the vulcanization rate increases with decreasing concentration of rubber in latex(25). However, Makkuchi has reported that in presence of an irradiation sensitizer the effect is not remarkable(1). The extent of crosslink formation, when latex particles are irradiated at 15kGy at varying dry rubber contents of latices is shown in Figure 5C.11. For the three types of lattices crosslink density in the films increases gradually with increasing DRC of irradiated latex, reaches a maximum at 50% and then decreases. This is in agreement with previous reports(26). SCL films exhibit highest crosslink densities. However, the crosslink densities observed in LPL films at various DRCs are almost comparable to SCL. While DCL films show lower values. However, the fall in crosslink density beyond the optimum DRC of 50% is slightly higher for LPL films. As stated earlier the $nBA^{-\bullet}$ radicals formed within the latex particles by the action of nBA and e^{-}_{hy} contribute to crosslinking reactions. In a latex of low DRC, the ratio of water within the rubber phase to those in the aqueous phase of latex is very low and hence the e^{-}_{hy} generated within latex particles are comparatively less and thus the extent of crosslink formation is less within the latex particles. In higher DRC latex the concentration of nBA in the aqueous phase is high, thus allowing more nBA to diffuse into the rubber particles. Also the relative proportion of water within the rubber particles is higher leading generation of larger of e^{-}_{hy}. This inter facilities the formation of more nBA^{-} free radicals and hence increased number of crosslinks are formed. However, above 50% DRC, crosslink density is observed to be decreasing. In latex of any rubber content, compounded with nBA, the available free space with in latex particles, initially occupied by water are now partially occupied by nBA and its content increases with increase in DRC of latex, and the availability of water in latex particles decreases. This leads to decreasing concentration of e^{-}_{hy} formed by the radiolysis water in rubber particles. Thus DRC of latex above 50%, crosslink densities in their latex particles are lower. Thus the relative availability of nBA and water with in latex particles determine the crosslink densities, when exposed to given dose.

Effect of rubber content in irradiated latex on tensile properties of latex films

The tensile properties of radiation vulcanized latices are affected by the rubber content in the latex irradiated. The variations in modulus at 500% elongation, tensile strength and elongation at break against the rubber content of the latex being irradiated are given in Figures 5C.12, 5C.13 and 5C.14 respectively. From Figure 5C.12 it is seen that modulus of the films initially increases with increase in DRC of latex, maximum modulus is observed at 50% DRC and then decreases.

As stated earlier, modulus of latex films is depending on the degree of crosslinking within latex particles and their effective coalescence during film formation. A comparison with Figure 5C.11 and 5C.12 shows that below the optimum DRC of 50%, the rate of increase in modulus is higher than the rate of increase in crosslink density. For any given DRC, the general trend in variation of modulus is

SCL > LPL > DCL

Even though crosslink densities of DCL and LPL films are almost comparable. Further, modulus of LPL films are not much below SCL films, even though crosslink densities are higher for the latter film. Thus it is evident that below 50% DRC, inter-particle integration during film formation has a more important role in determining the modulus, than that above 50% DRC.

Figure 5C.13 shows that the effect of tensile strength of films on DRC of irradiated latex. Even though tensile strength depends on DRC of irradiated latex, it is more dependent on DRC in the case of SCL. Maximum tensile strength is exhibited at 50% DRC for three types of laticies. In the case of LPL its irradiation below about 42% DRC shows tensile strength above that of SCL, but in all other situations tensile strengths of films prepared from irradiated lattices are again in the order

SCL > LPL > DCL

The maximum tensile strength for 50% DRC of SCL films is slightly higher than that of LPL. This is partly contributed by increased crosslink density of SCL films and partly because of the contribution of proteins to tensile strength via van der Waals forces(1) of attraction and H–bonding.

Data on elongation at break presented in Figure 5C.14 shows that decrease with increase in DRC of irradiated latex upto 50% DRC. For SCL and LPL films EB passes through a minimum, at 50% DRC while DCL films do not show a minimum. Elongation at break is slightly low for LPL films than SCL films. This is also attributed to the effect of proteins where the individual particles are held together by strong van der Waals forces and H–bonding.

Effect of leaching on tensile properties of radiation vulcanized latex films

Leaching is an important processing step in the production of dipped latex articles for improving physical properties(27-29). Figures 5C.15, 5C.16 and 5C.17 show respectively the variation of modulus, tensile strength and elongation at break of radiation vulcanized latex films, against duration of leaching in water at room temperature. It is observed that for the three types of latex films modulus tensile strength and elongation at break increase along with an increase in duration of leaching. The modulus of SCL and LPL films are comparable at all periods of leaching, even though the former has a slightly higher modulus and DCL films shows lower values. Tensile strength is higher for SCL films at all periods of leaching, again DCL films showing lower values. Values of elongation at break are not much different for SCL and LPL films. These improvements in physical properties on prolonged leaching are attributed to the removal of non-rubber materials from the films, thus facilitating better inter-particle integration(22,27). From Figure 5C.15 it can be seen that the improvement in modulus diminishes with increase in duration of leaching. This is because by initial leaching substantial portion of non-rubber materials are removed from the thin latex films and the quantity left behind for subsequent removal decreases and thus the rate of removal of non-rubber materials diminishes with longer leaching period. Thus it can be seen that even though there is improvement in modulus with increase in duration of leaching, the rate of improvement decreases. A similar behaviour is observed from Figure 5C.16 for tensile strength also. It can further be seen from Figure 5C.16 that the improvement in tensile strength of films on leaching initially is higher for SCL than LPL and least for DCL films. However, after long leaching as the difference in tensile strength between the SCL and LPL films decreases. It is believed that during irradiation of latices various non-rubber substances including proteins undergo degradation and the degraded products are removed by leaching. This degradation of non-rubber substances is believed to be highest in SCL, which contains the highest level of non-rubber materials. After removal of these components, the differences between the characteristics of SCL and LPL films became more narrow, leading to a lower difference in tensile strength between the two. For the three types of latex films, elongation at break slightly increases with duration of leaching. Increase in elongation is associated with increase in interparticle integration and homogeneity in the film(30). However, the increase in elongation is slightly lower for SCL films than LPL films.

Effect of leaching on residual EP content in radiation vulcanized latex films

Figure 5C.18 shows the effect of leaching on residual extractable protein content in radiation vulcanized SCL, DCL and LPL films leached for various intervals. The latices were vulcanized by irradiating to a dose of 15kGy at the rate of 1.333kGy/h. SCL film shows high EP content due to degradation of the proteins and residual EP is progressively reduced by continued leaching. A similar phenomenon is observed in DCL and LPL also. But the total EP content even in the unleached LPL film is very low compared to SCL film and in radiation vulcanized LPL films leached for one hour and above residual EP content is practically nil. This indicates that treatment of latex with PPG replaces easily displaceable and degradable proteins and during the second centrifugal concentration they are carried away into the skim portion.

It is observed that in general longer leaching period is associated with reduction in EP content in the films. However, even after 2h of leaching SCL and DCL film still show some EP. This is believed to be due to migration degraded proteins from the inner layers of the latex films to the surface.

Effect of post-cure heating of radiation vulcanized latex films on crosslink density

Post-cure heating is an important after treatment adopted for latex films for improvement in physical properties(29). Figure 5C.19 shows the effect of post-cure heating at 80°C of radiation vulcanized latex films irradiated to a dose of 15kGy. It is seen that crosslink density of three types of latex films increase on heating at 80°C for short periods. In the case of SCL and LPL films, maximum in the crosslink density curve is attained in about 1h heating, while for DCL films it is

2h. The improvement in crosslink density is higher for LPL and DCL films than SCL films. However, on continued heating crosslink density decreases for the three types of films. Heating of sulphur prevulcanized latex films can result in the formation of higher number of crosslinks by continued vulcanization by utilizing the residual curatives in the films(31). However, such a situation is not present in radiation vulcanized latex films as no curatives are used. The increase in crosslink density, even though small, may be probably due to rearrangement/modification of already formed crosslinks via bound nBA molecules. Continued heating causes more crosslink rupture, leading to net reduction in crosslink density. Hence for achieving maximum crosslink density, for radiation vulcanized latex films, the optimum period of heating is found to be 1h for LPL films. Crosslink density is some what higher in post-heated SCL films and the order is

SCL > LPL > DCL

films. However, improvement in crosslink density by post-heating is the highest in LPL films, compared to SCL and DCL films.

Effect of post-cure heating on tensile properties of radiation vulcanized latex films

Post-cure heating of sulpher vulcanized latex films is generally accompanied by improvement in physical properties. Post-cure heating of radiation vulcanized SCL, DCL and LPL films are also accompanied by improvement in physical properties. Variation of modulus, tensile strength and elongation at break with respect to duration of post-heating are shown in Figures 5C.20, 5C.21 and 5C.22 respectively. Modulus of SCL films increases upto a heating period of 2h while for DCL and LPL films, maximum modulus is observed at 3h of post-heating. Continued heating decreases modulus. Change in crosslink density has some influence on change in modulus. However, change in crosslink density cannot fully explain this observed variation in modulus on post-heating. Crosslink density increases on heating for 1h; however, modulus increases upto 2h heating for SCL and 3h heating for DCL and LPL films. This increase in modulus is believed to be due to better fusion of latex particles in the film.

Similarly tensile strength increases upto 2.5h of heating in the case of SCL films and 3h of heating for DCL and LPL films. Thus the maximum of tensile strength curves do not coincide with the maximum of crosslink density curve. This shows that inter-particle integration, resulting from a homogenous structure is also responsible for the improvement in tensile strength on post-cure heating. The elongation at break of the three types of latex films decrease on post-cure heating.

Thus it is seen that tensile properties of radiation vulcanized LPL films are improved by heating and the duration of heating is about 3h at 80°C for achieving maximum modulus and tensile strength.

Effect of addition of silica to radiation vulcanized latex on tensile properties

Reinforcing fillers such as carbon blacks and silicas are generally added to dry rubber vulcanizates for improving tensile properties. However, these fillers do not behave as truly reinforcing fillers in latex compounds. This abnormal behaviour of reinforcing fillers in latex vulcanizates is due to poor rubber-filler interaction(32). However, modulus of the latex film is improved(33).

Figure 5C.23 shows the effect of addition of silica to radiation vulcanized latex on modulus of dry films, both before and after ageing. It is seen that for a given content of silica in the vulcanizate, modulus of LPL films is slightly lower than that of SCL films. DCL films have lowest modulus. It is further observed that by addition of silica to radiation vulcanized SCL and LPL there is a linear increase in modulus with respect to the content of silica and both the curves are almost parallel ie; the extent of increase in modulus for a given filler content is almost the same in both the latices. However, with DCL films the modulus curve is not linear. The magnitude of increase in modulus decreases on increasing silica content. This observation suggests that silica-rubber interaction is better in SCL and LPL films than in DCL film. This is probably due to increased availability of polar materials in SCL and LPL films (proteins alone in SCL films and proteins and PPG in LPL films). On ageing, modulus of DCL and LPL films decrease and the reduction in modulus is more when silica content is higher. This reduction is attributed mainly to polymer degradation. However, in the case of SCL films, modulus increases slightly on ageing for small additions of silica upto about 5phr and then decreases below that of the unaged films. This improvement in modulus at low silica levels is believed to be due to better rubber filler interaction on heating. However, this interaction becomes less effective at high silica levels.

The variation of tensile strength with silica content is shown in Figure 5C.24. In the case of SCL and LPL films there is almost a linear reduction in tensile strength on incorporation of silica while with DCL films reduction is higher at higher levels of filler additions. This also is believed to be due to poor rubber-filler interaction. This poor rubber-filler interaction in latex rubber vulcanizates is partly due to the absence of mechanical forces driving rubber into the surface cavities/ imperfections on silica particles and partly due to the presence of a protective layer of surface active materials on both rubber particles and dispersed filler particles preventing direct contact between the two particles(32). The extent of reduction in tensile strength of the films is in the order

SCL < LPL < DCL

at higher levels of filler addition.

Ageing of the three types of silica-filled radiation vulcanized latex films is accompanied by reduction in tensile strength. The aged tensile strength of LPL films are lower compared to SCL films and that of DCL films are the lowest. The extent of reduction in tensile strength with increasing silica content follows almost a linear relation. The fall in the tensile strength of the films on accelerated ageing is attributed to polymer degradation.

Addition of silica to the three types of radiation vulcanized latices reduces elongation at break of the dry films (Figure 5C.25). The reduction in EB varies linearly with silica content. The observed variations are in agreement with the modulus of the films. EB values are in the order

SCL < LPL < DCL

It is believed that addition of more silica imparts greater restriction to the relative movement of rubber molecular chains, leading to a reduction in elongation at break. On ageing, three types of vulcanized films show slightly lower EB and at all levels of silica, EB of aged films follows the same order as that the unaged films. The reduction in EB on accelerated ageing is believed to be due to thermal degradation of rubber molecules.

CONCLUSIONS

Like ordinary centrifuged latex low protein latex also can be prevulcanized by gamma radiation, in presence of a sensitizer and the optimum dose is found to be 15kGy. Crosslink density of LPL films is only slightly lower than SCL films. Radiation-cured low protein latex films show good tensile properties, though slightly lower than that of standard centrifuged natural latex films. Optimum cured low protein latex films after extraction with water for 1h contains practically no residual extractable protein. Hence radiation vulcanized LPL films can provide high protection against latex protein allergy problem. Physical properties of radiation-cured low protein latex films are dependent on dry rubber content of the irradiated latex and the optimum properties are achieved when irradiated at 50% DRC. However, reasonably good physical properties are obtained for radiation-cured low protein latex films prepared from vulcanized latex irradiated at 58% DRC also. Leaching and post-cure heating of radiation cured low protein latex films improve their physical properties.

Since radiation vulcanized low protein latex films after leaching is almost free from residual extractable proteins, and exhibits good tensile properties it can be used for the production of articles like examination gloves, teats, soothers, balloons, condoms etc. which are almost free from type I allergic reactions.

Modulus of radiation vulcanized low protein latex films can be improved by incorporation of silica and the extent of increase is proportional to the silica content. This behaviour of LPL enables it to find application in products like catheter requiring high modulus.

REFERENCES

1. K.Makuuchi. Radiation Vulcanization of Natural Rubber Latex. RCA Regional Training Course. Quality Control of RVNRL, Indonesia (1997).

2. K.Makuuchi. Progress in Radiation Vulcanization of Natural Rubber Latex. RVNRL Consultant Meeting, Vienna (1995).

3. C.Zhonghai and K.Makuuchi. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI – M89-228, p-326 (1989).

4. K.Makkuchi, F.Yoshii. K.Hyukutake and T.Kume, *Int. Polym. Sci. Technol,* **23(2)**, T 28 (1996).

5. W.M.W.Zin and N.Othaman. Proc. Second Int. Sym. on RVNRL. Kuala Lumpur p–115 (1996).

6. K.F.Gazeley and T.D.Pendle. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI – M 89-228. p-79 (1989).

7. S.Varghese, K.Makuuchi, F.Yoshii, Y.Katsumura and E.V.Thomas. Proc. Int. Rubber Conf. Chennai. p–641 (1998).

8. A.F.Nutter. *Brit. J. Dermatol.* **101**, 597 (1979).

9. K.Turjanmaa and R.Rennala. *Dermatological Clinic* **6**, 47(1988).

10. K.Wrangsjo, J.E.Wahlberg and I.G.K.Axelsson, *Contact Dermatitis*, **19**, 264 (1988).

11. M.S.Sebastian, V.George and E.V.Thomas. Proc. 18th Rub. Conf. Indian Rubber Manufactures' Research Association. Mumbai. p–105 (2000).

12. C.F.Flint and W.J.S.Naunton. *Trans. Instn. Rub. Ind.* **12**, 367 (1937).

13. R.M.Panich, N.M.Fodiman, N.M.Voyatski. *Soviet Rub. Technol.* **18(2)**, 14 (1959).

14. P.J.Flory and J.Rehner.Jr. *J. Chem. Phys.* **11**, 521 (1943).

15. IS 3400 (Part 1) 1987:Methods of Test for vulcanized rubbers – tensile stress-strain properties.

16. F.Yusof and H.Y.Yeang. *J. nat. Rub. Res.* **7**, 206 (1992).

17. S.Sbharwal, Y.K.Bharadwaj, C.V.Chaudhary, B.R.Dhanwade and A.B.Majali. Proc. National Seminar on Radiation Vulcanized Natural Rubber Latex, Kottayam (1992).

18. K.Makuuchi and T.Tsushima. Proc. Int. Rub. Conf. Kuala Lumpur. p–502 (1985).

19. M.H.Rao and K.N.Rao. *Radiat. Phys. Chem*, **26**,6 (1985).

20. C.Siri-Upathum, K.Makuuchi and I.Ishigaki. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI – M 89-228, p–336 (1989).

21. J.W.T.Spinks and R.JWood. An Introduction to Radiation Chemistry. p–315. Wiley, New York (1990).

22. S.Sabharwal, T.N.Das, C.V.Chaudhari, Y.K.Bhardwaj and A.B.Majali. *Radiat. Phys. Chem.* **51**,309 (1998).

23. L.C.Teik and W.N.Poh. Developments in the Plastics and Rubber Product Industries. The Plastics and Rubber Institute, Kuala Lumpur p–265 (1989).

24. B.G.Audley and S.J.Dalrymple. Proc. Seminar on Latex Processing Technology : Understanding its Science. Hertford, U.K. p–69 (1991).

25. E.Yip, T.Palosuo, H.Alemins and K.Turjanmaa *J. nat, Rub. Res.***12**, 120 (1997).

26. Y.Minoura and M.Asao. *J. Appl. Polym. Sci.* **5**, 233 (1961).

27. V.Geroge, M.S.Sebastian, I.J.Britto and E.V.Thomas. *Rubber India*, **53 (5)**, 7 (2001).

28. M.Portor. Proc.Int. Rub. Conf. London p–1 (1996).

29. S.B.H.Wahab, K.Makuuchi, R.Devendra and C.P.Pausa. Proc. Int. Sym. Radiation vulcanization of Natural Rubber Latex. JAERI, M 89-228, p–216 (1989).

30. D.C.Blackley. Proc. Int Rub. Technol. Conf. Kuala Lumpur. p–3, (1988).

31. A.D.T.Gorton. Proc. Int, Rub. Technol. Conf. Kuala Lumpur p–85, (1988).

32. B.A.Dogadkin, I.G.Senatorskaya, V.I.Guseva, A.V.Suslyakov and P.I.Zakharachenko. *Colloid. J.(USSR)* **18**,523 (1956).

33. N.M.Claramma, L.Varghese and N.M.Mathew. *J. Elastomers and Plastics.* **31**,130 (1999).

TABLE 5C.1

Latex compound for radiation vulcanization

Ingredient	*Parts by weight*	
	Dry	*Wet*
60% Natural Latex	100	167
10% Potassium hydroxide	0.3	3.0
50% n-Butyl acrylate	5	10
Water	—	To 50%

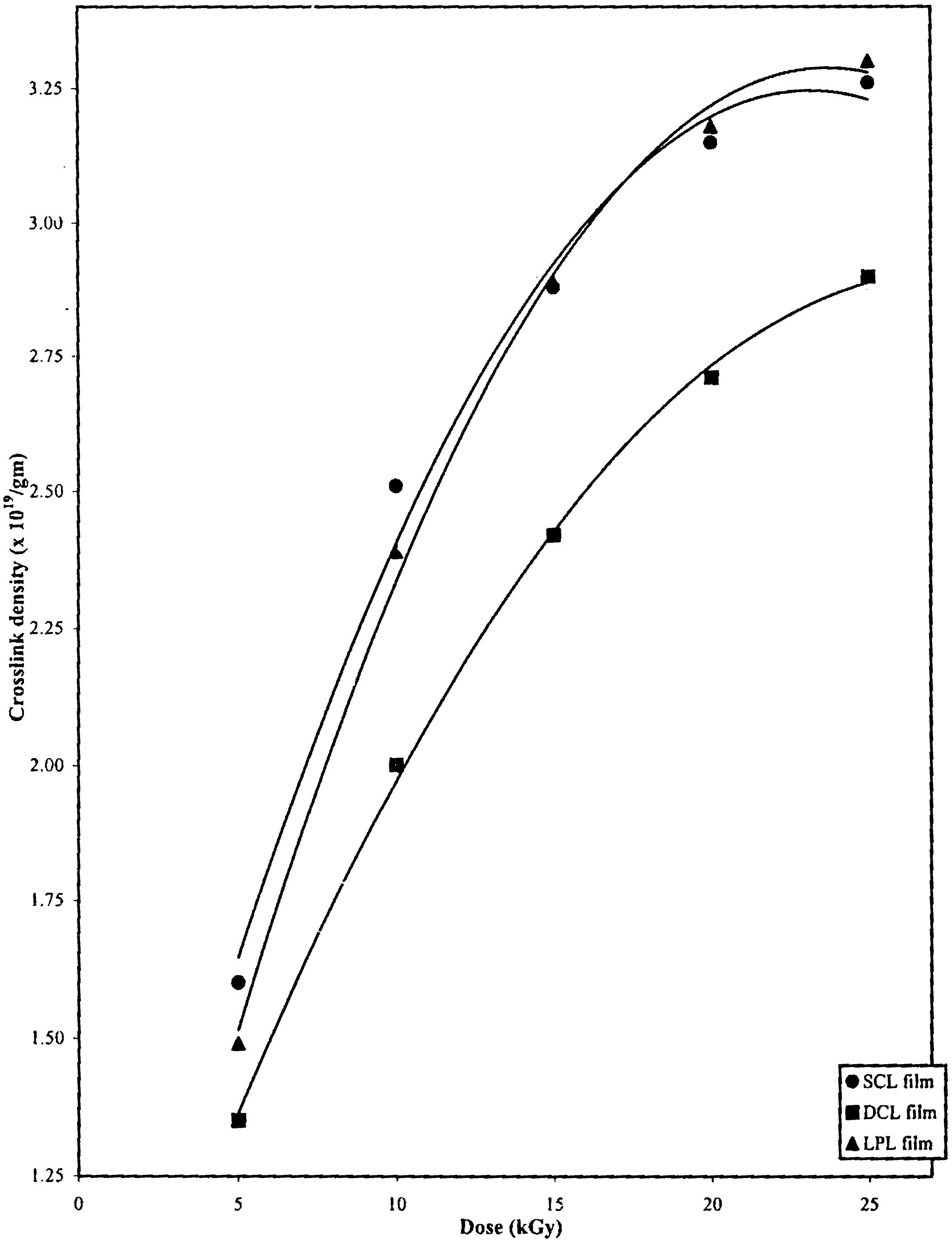


Fig 5C.1. Effect of dose of radiation on crosslink density in radiation vulcanized latex films.

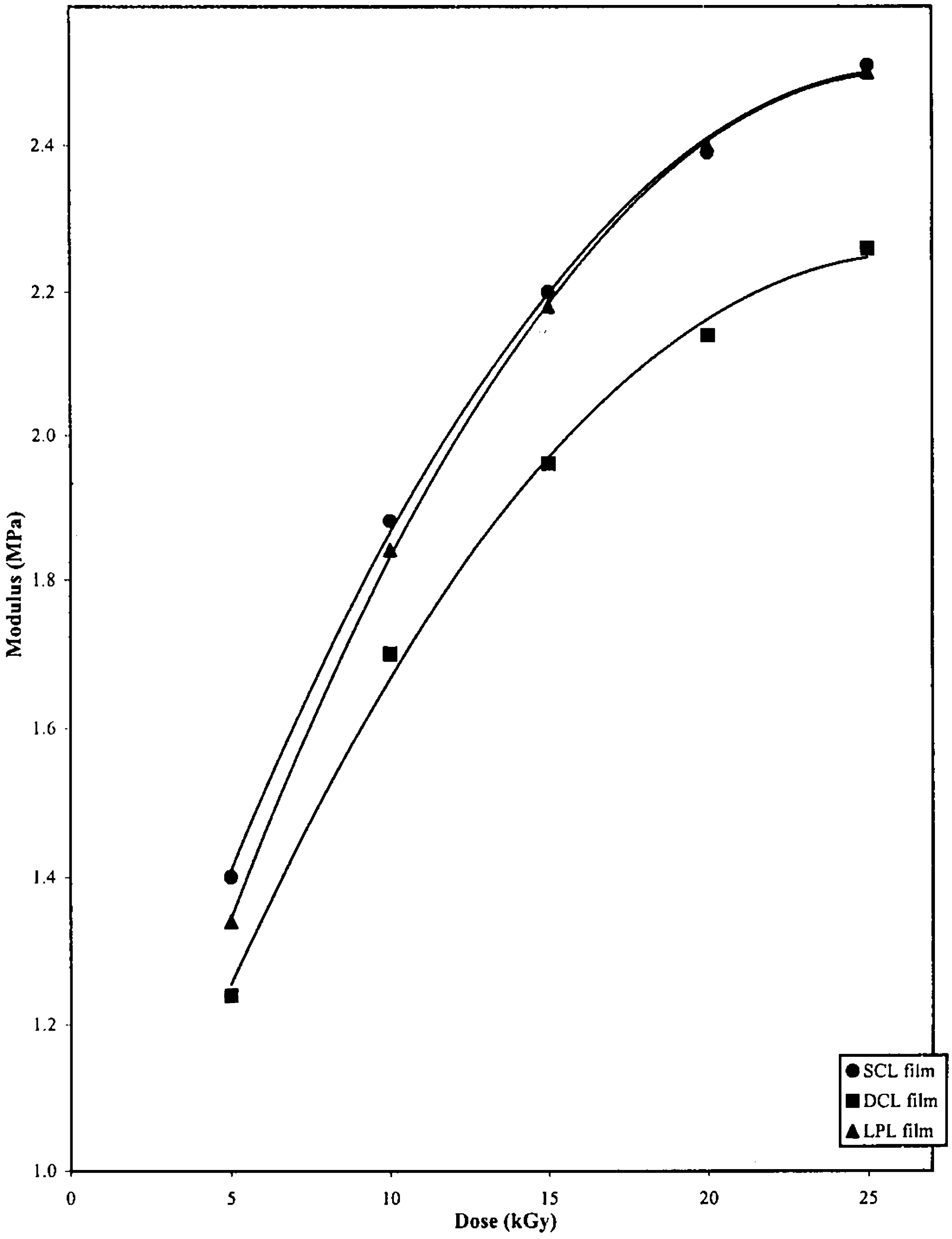


Fig 5C.2. Effect of dose of radiation on modulus of radiation vulcanized latex films.

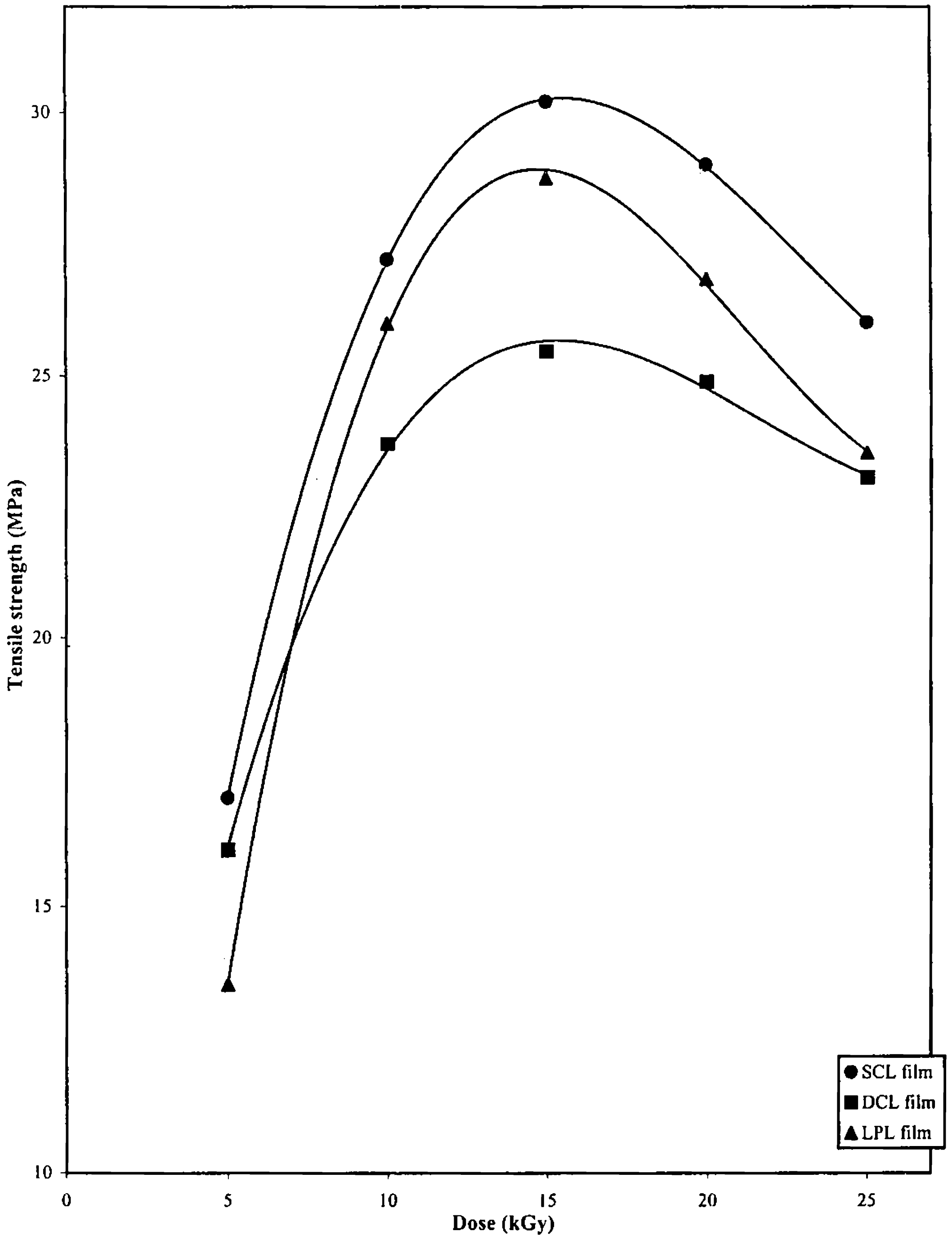


Fig 5C.3. Effect of dose of radiation on tensile strength of radiation vulcanized latex films.

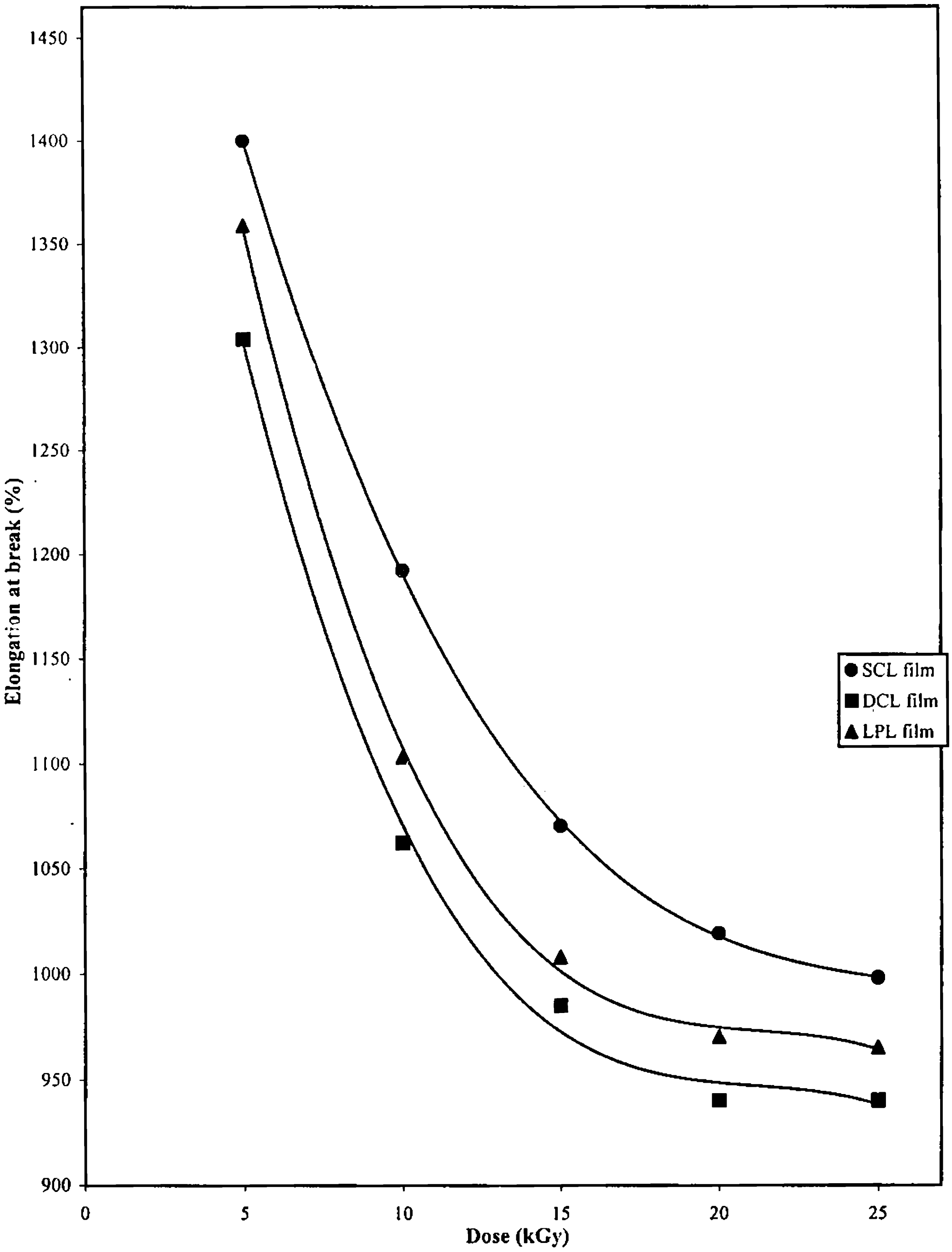


Fig 5C.4. Effect of dose of radiation on elongation at break of radiation vulcanized latex films.

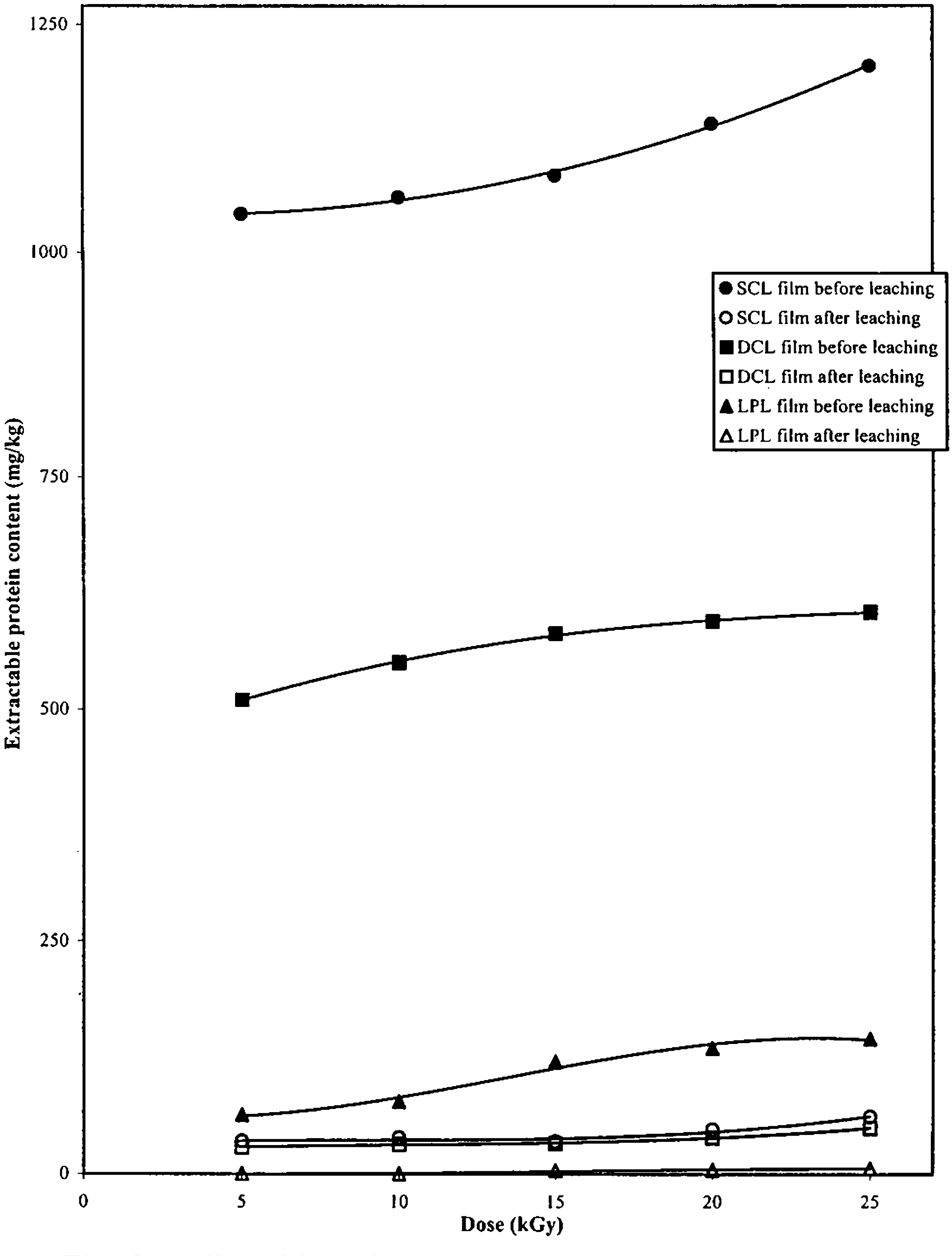


Fig 5C.5. Effect of dose of radiation on extractable protein content in latex films before and after leaching.

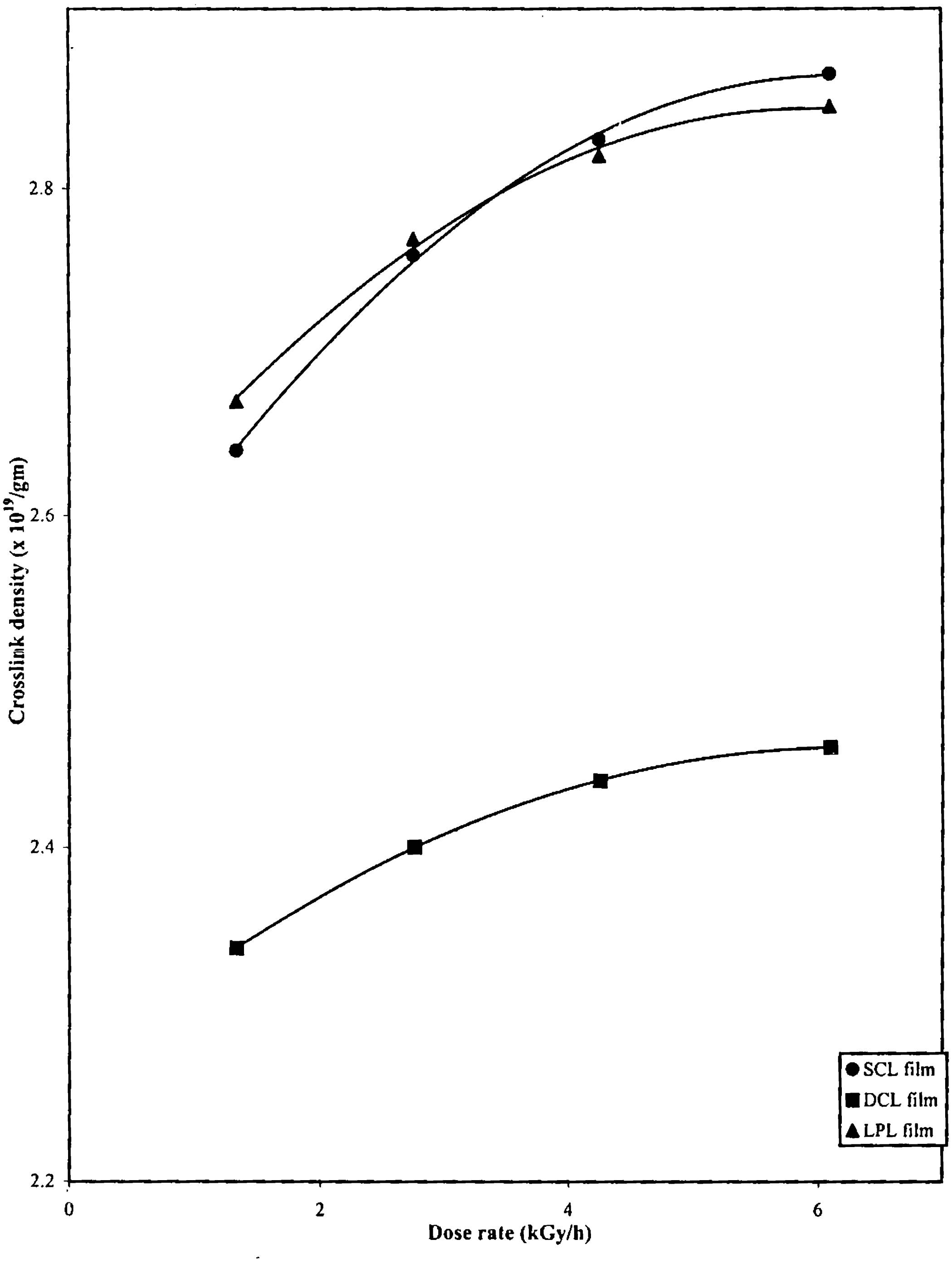


Fig 5C.6. Effect of dose rate of radiation on crosslink density in latex films. (Dose 15 kGy)

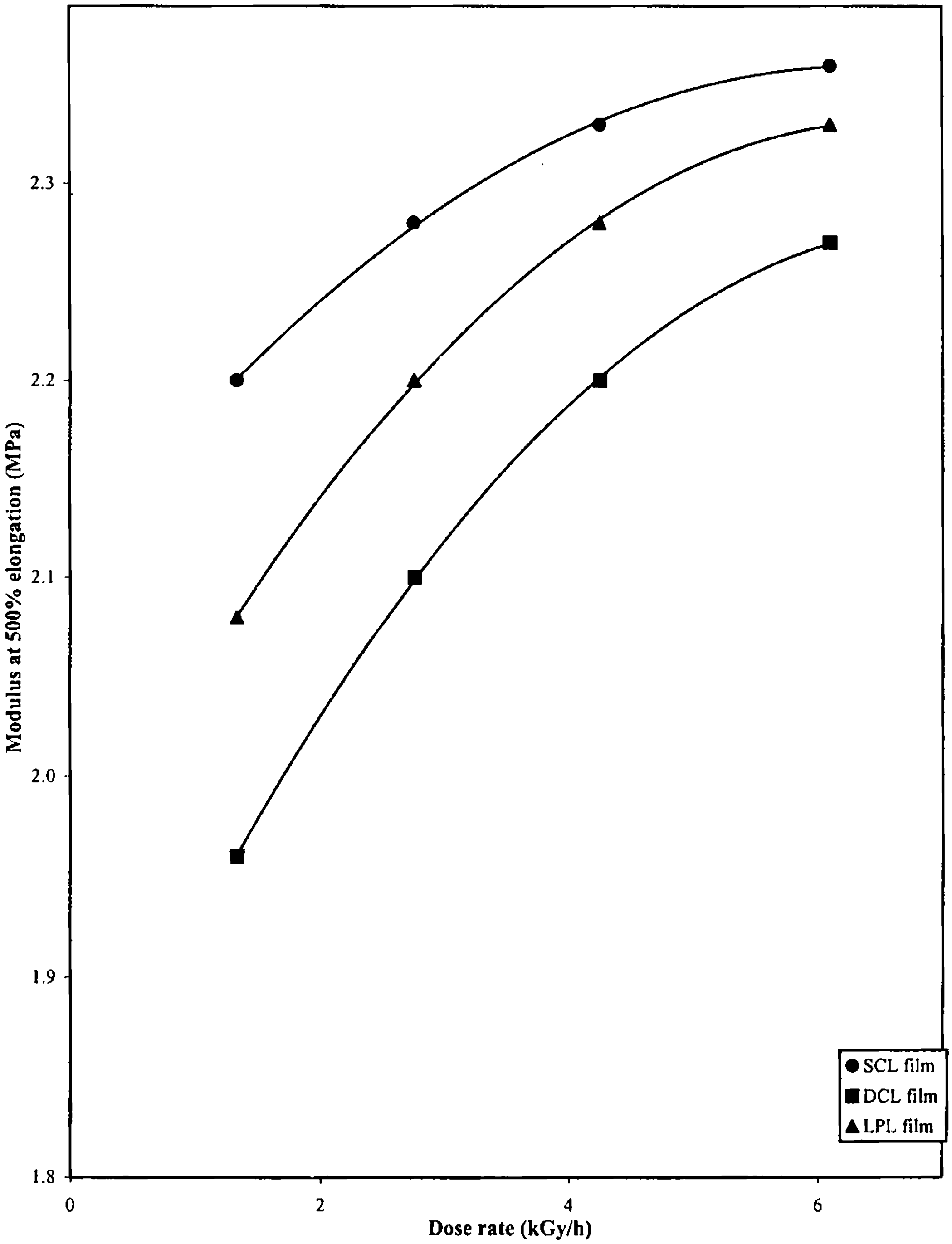


Fig 5C.7. Effect of dose rate of radiation on modulus of latex films. (Dose 15 kGy)

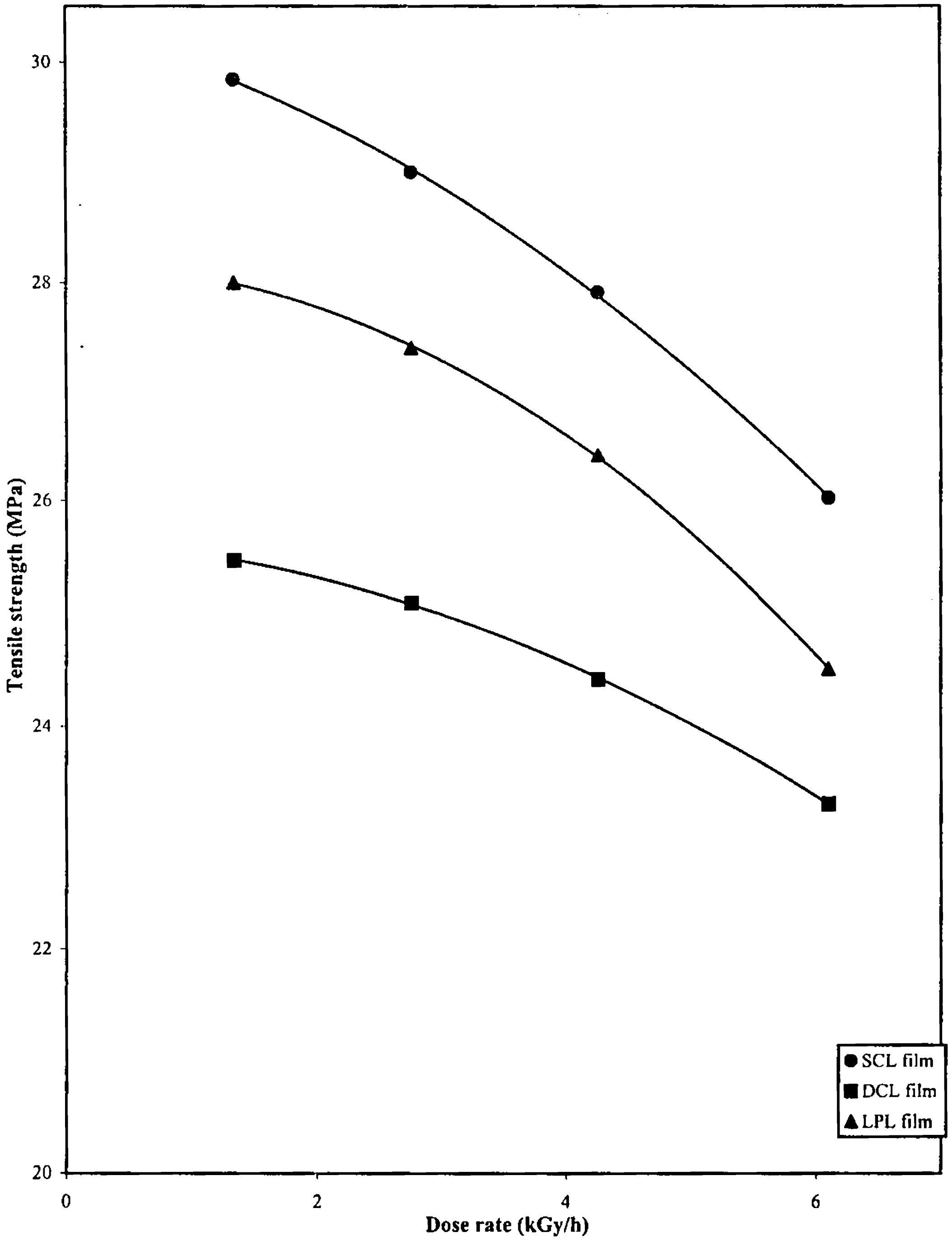


Fig 5C.8. Effect of dose rate of radiation on tensile strength of latex films. (Dose 15 kGy)

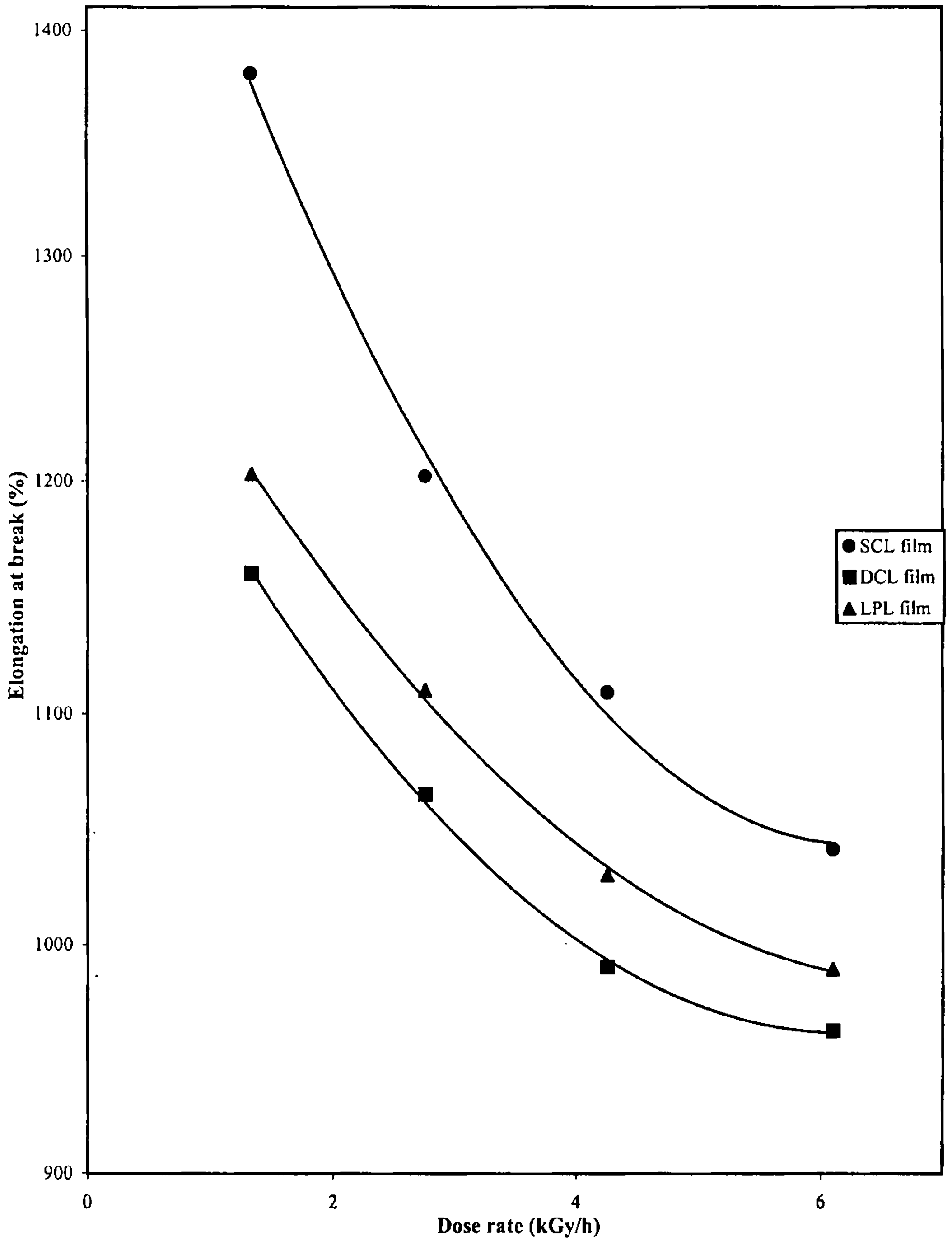


Fig 5C.9. Effect of dose rate of radiation on elongation at break of latex films (Dose 15kGy)

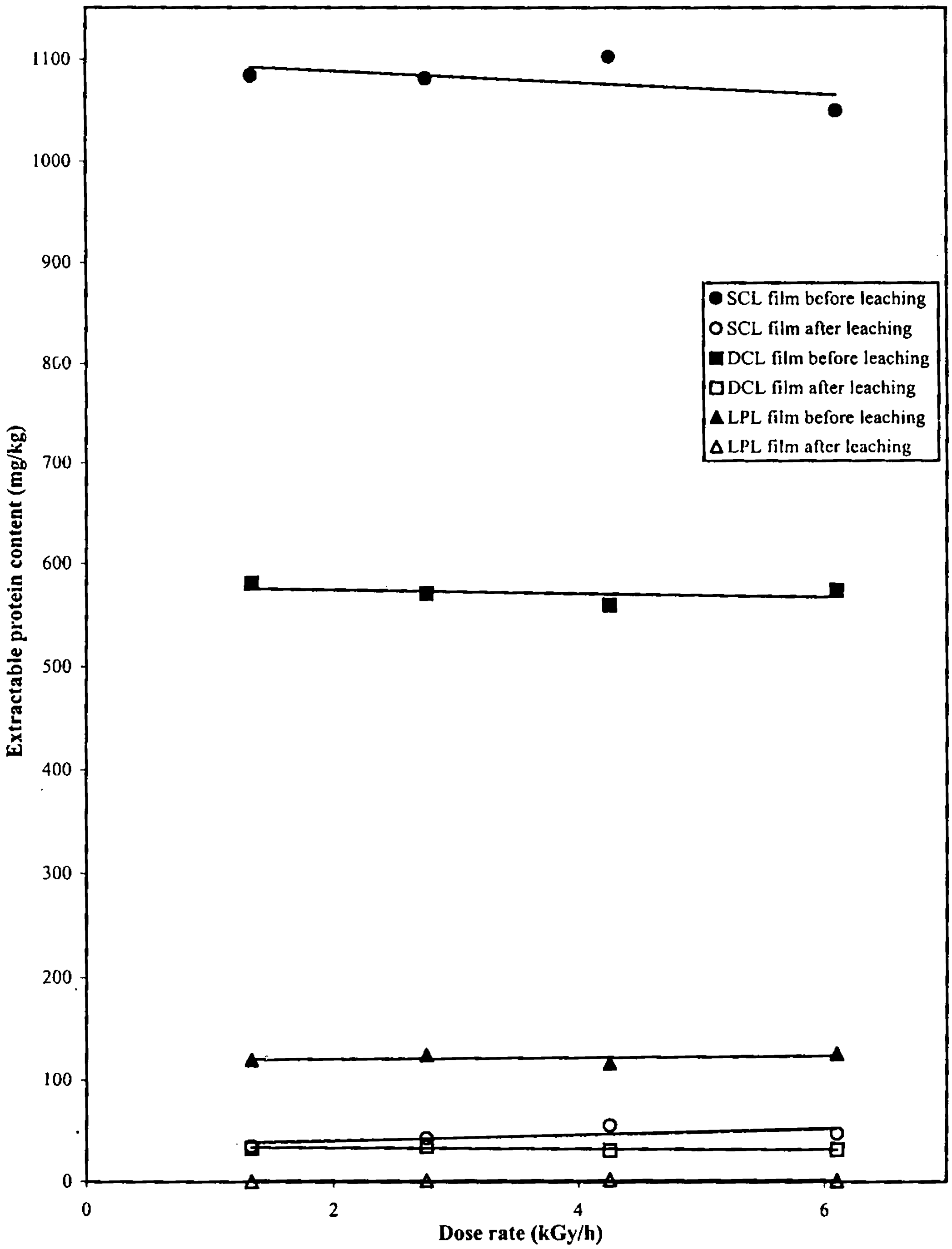


Fig 5C.10. Effect of dose rate of radiation on EP content in latex films. (Dose 15 kGy)

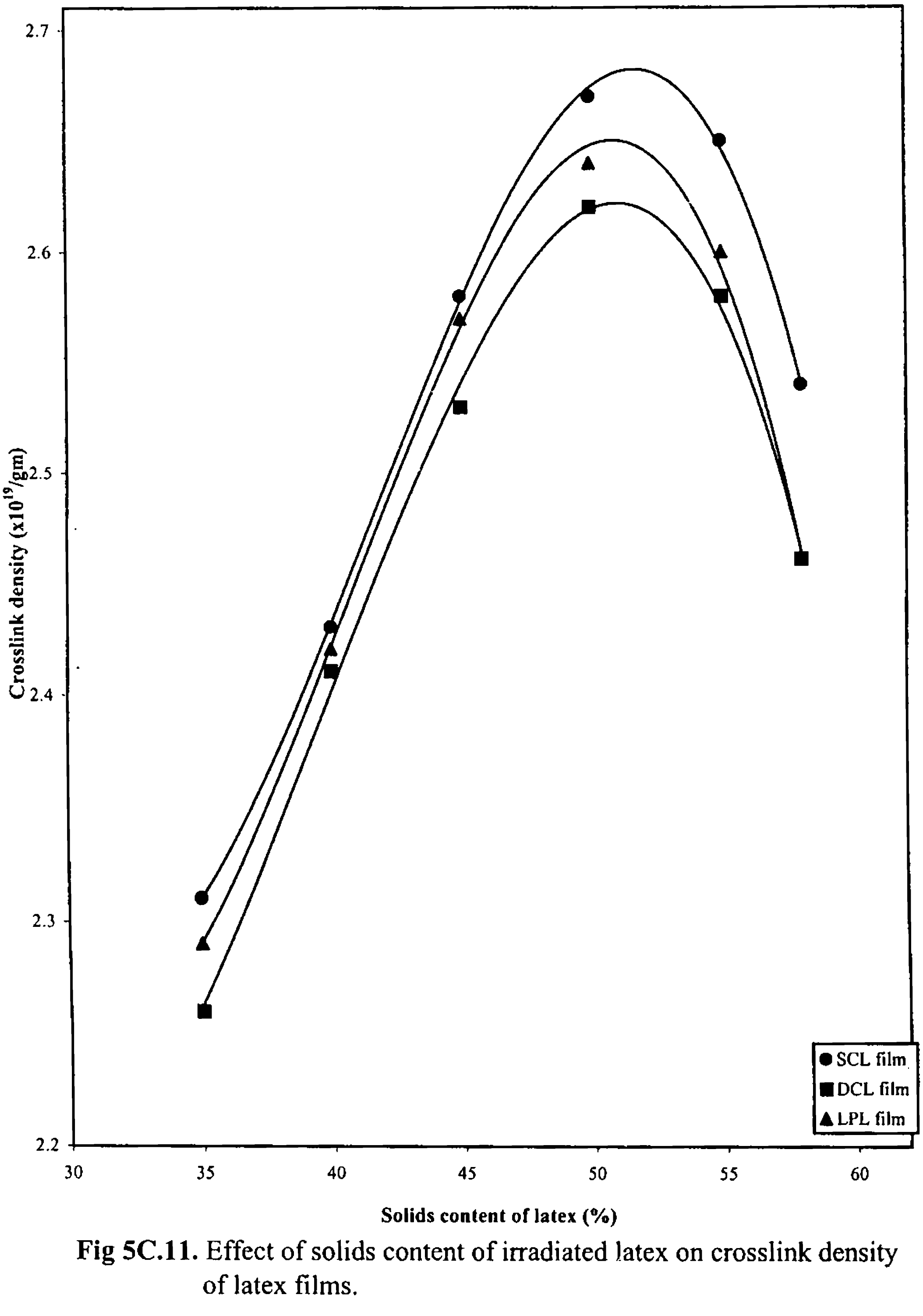


Fig 5C.11. Effect of solids content of irradiated latex on crosslink density of latex films.

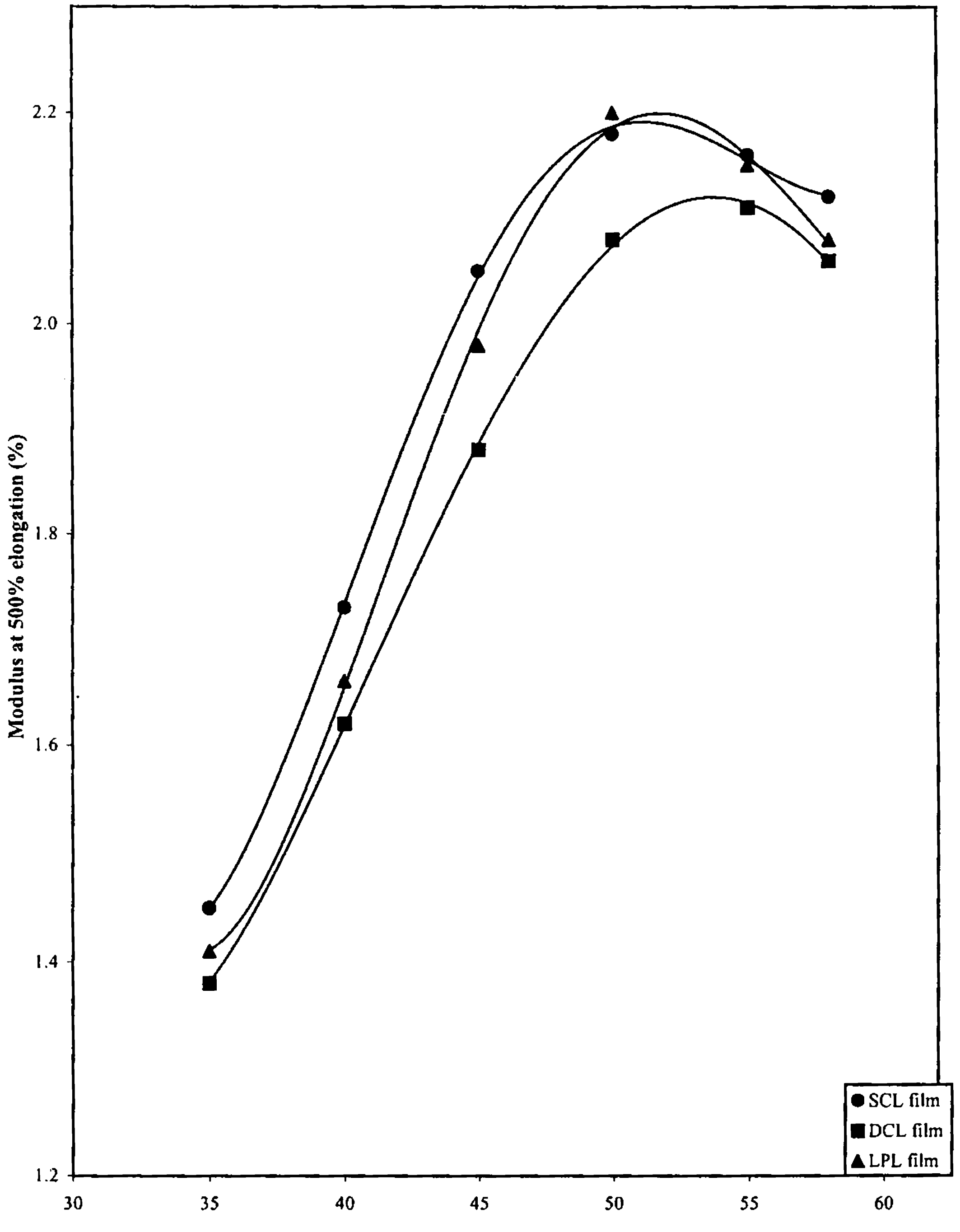


Fig 5C.12. Effect of solids content of irradiated latex on modulus of latex films.

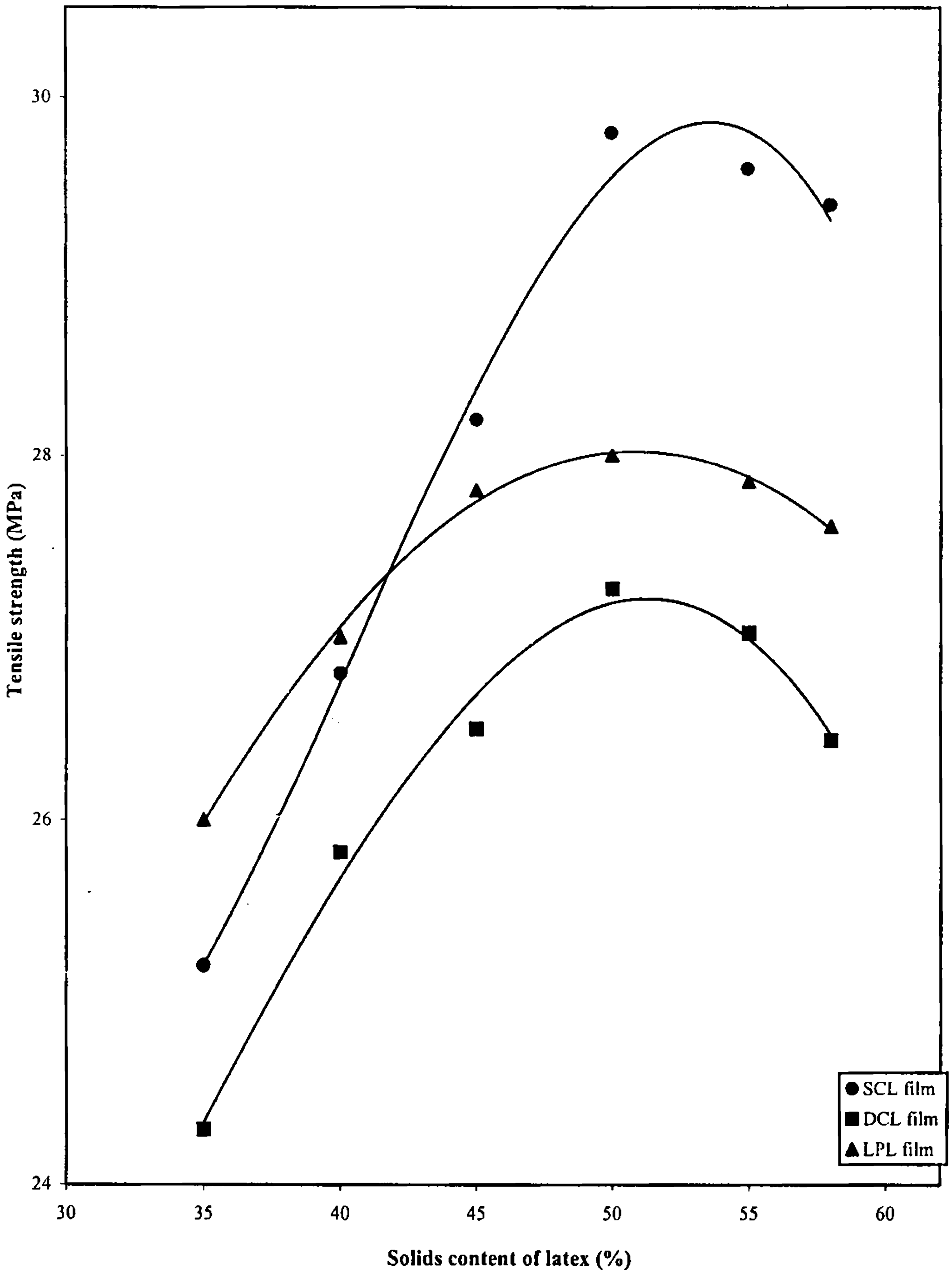


Fig 5C.13. Effect of solids content of irradiated latex on tensile strength of latex films.

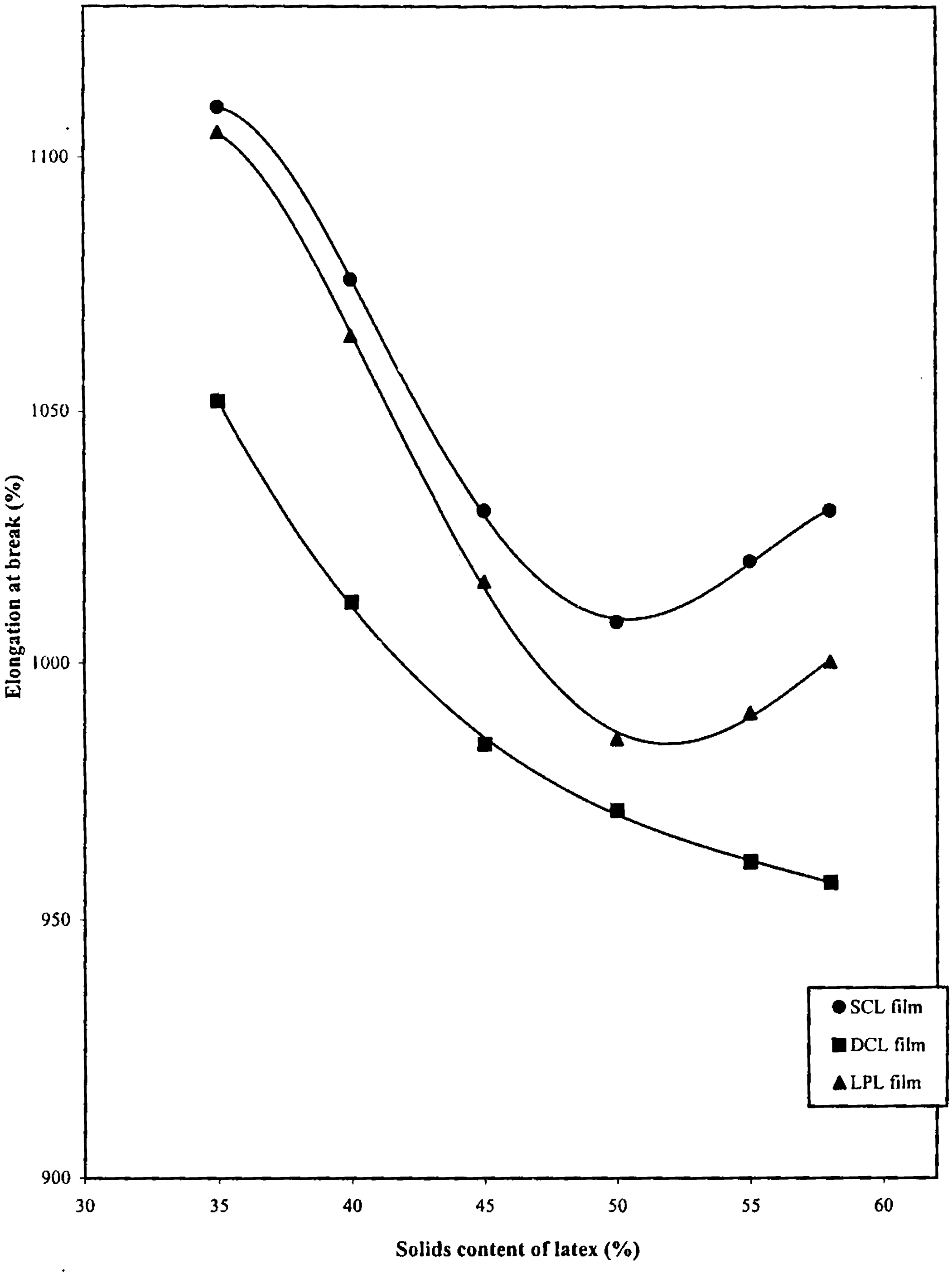


Fig 5C.14. Effect of solids content of irradiated latex on elongation at break

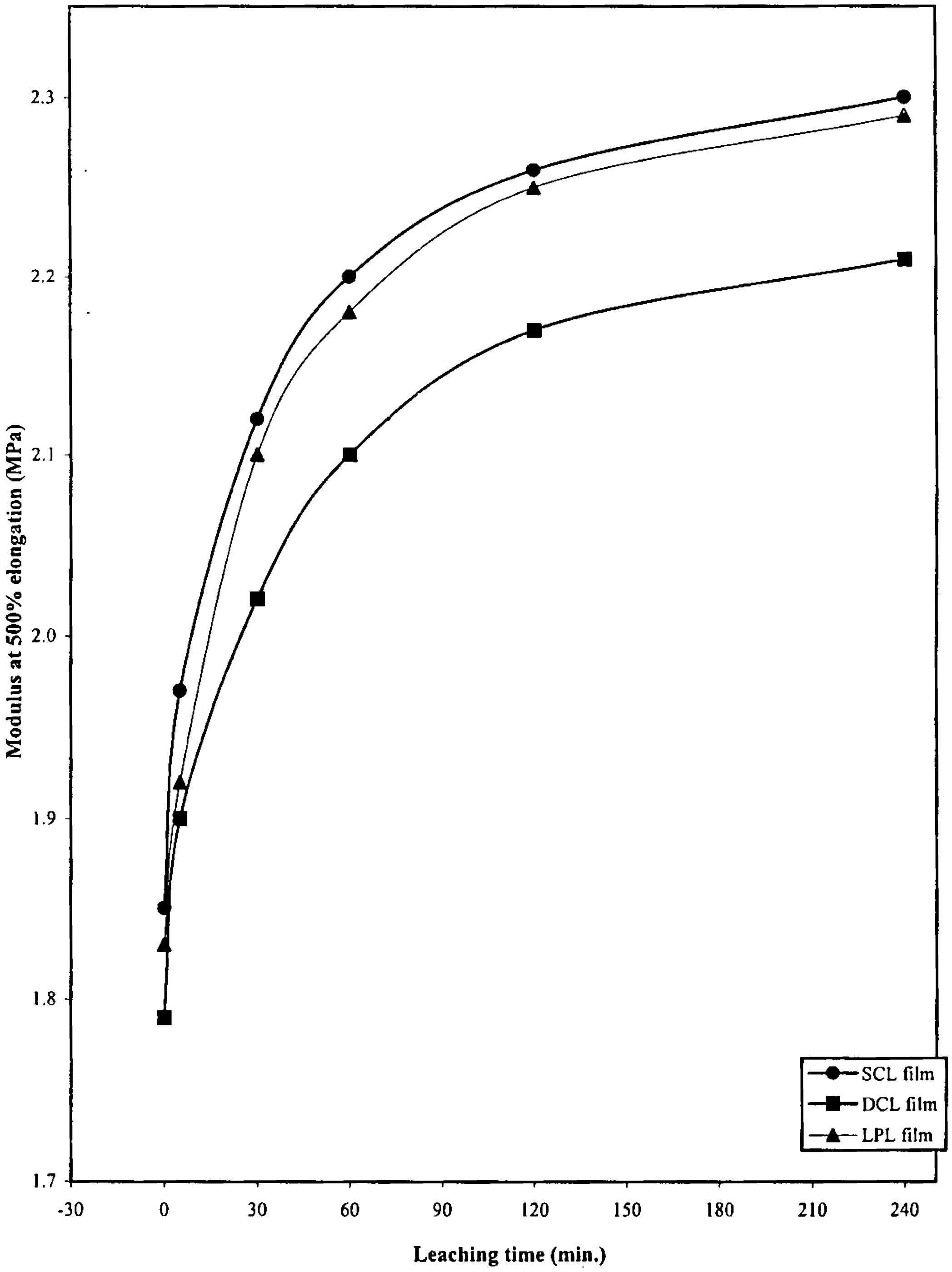


Fig 5C.15. Effect of leaching on modulus of radiation vulcanized latex films.

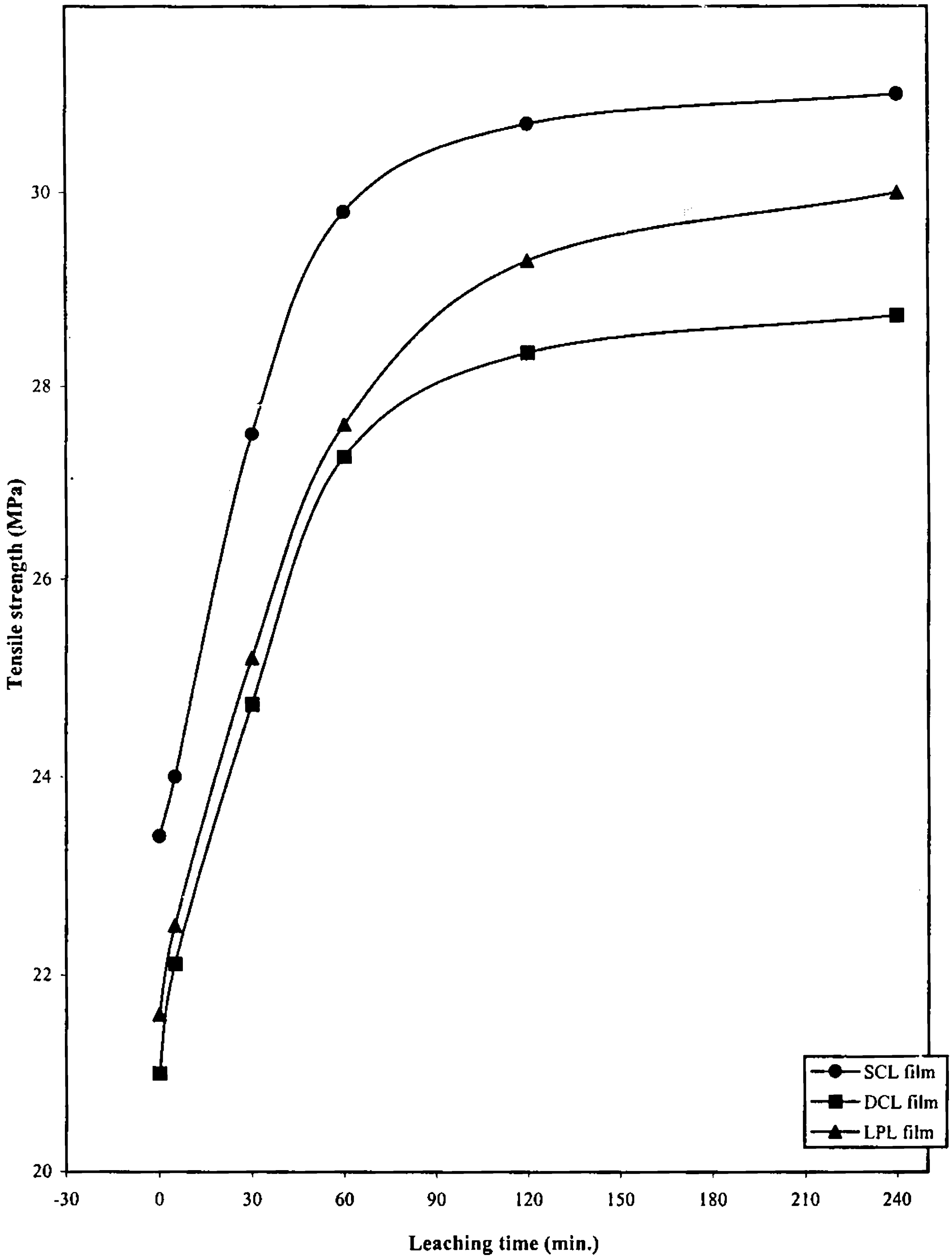


Fig 5C.16. Effect of leaching on tensile strength of radiation vulcanized latex films.

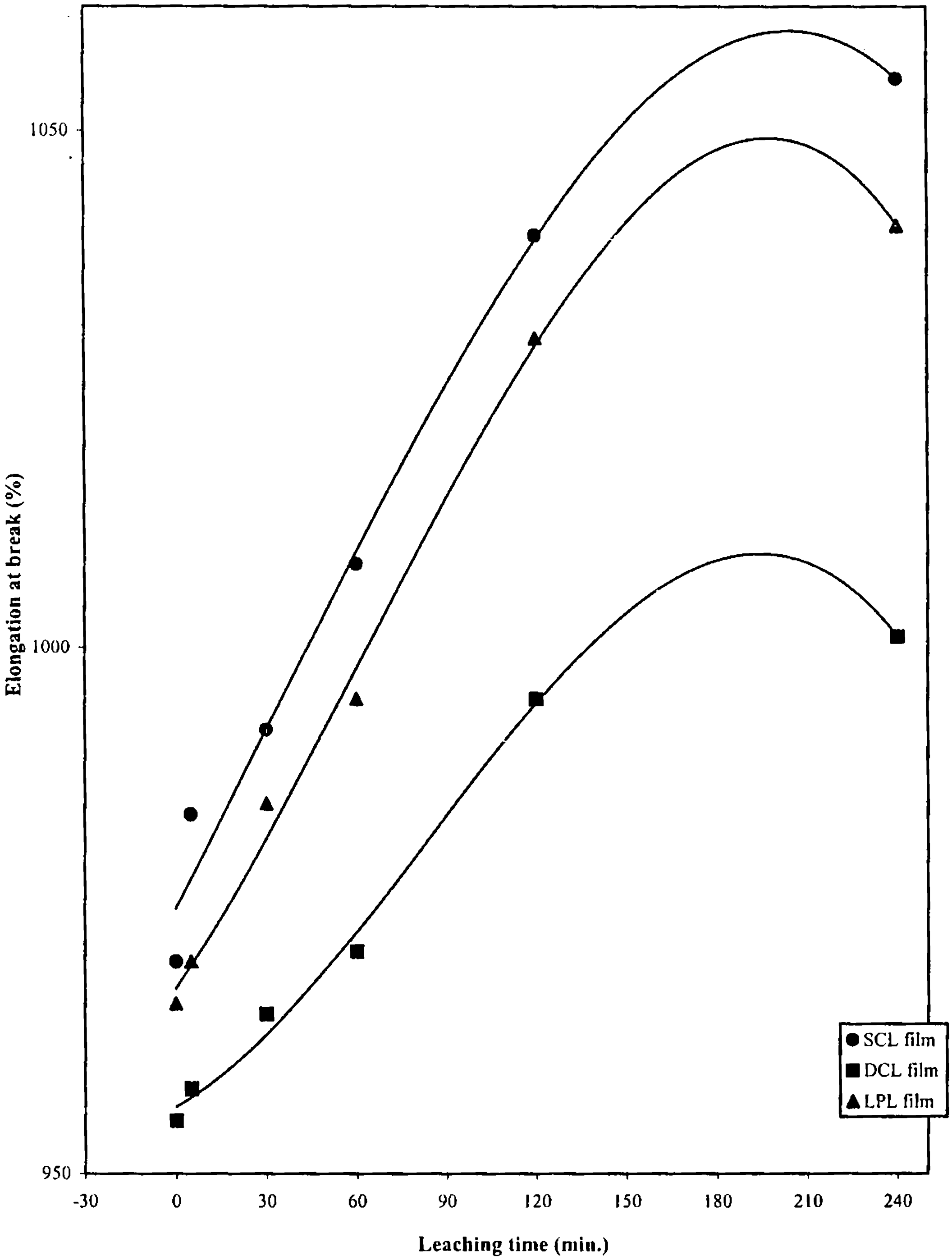


Fig 5C.17. Effect of leaching on elongation at break of radiation vulcanized

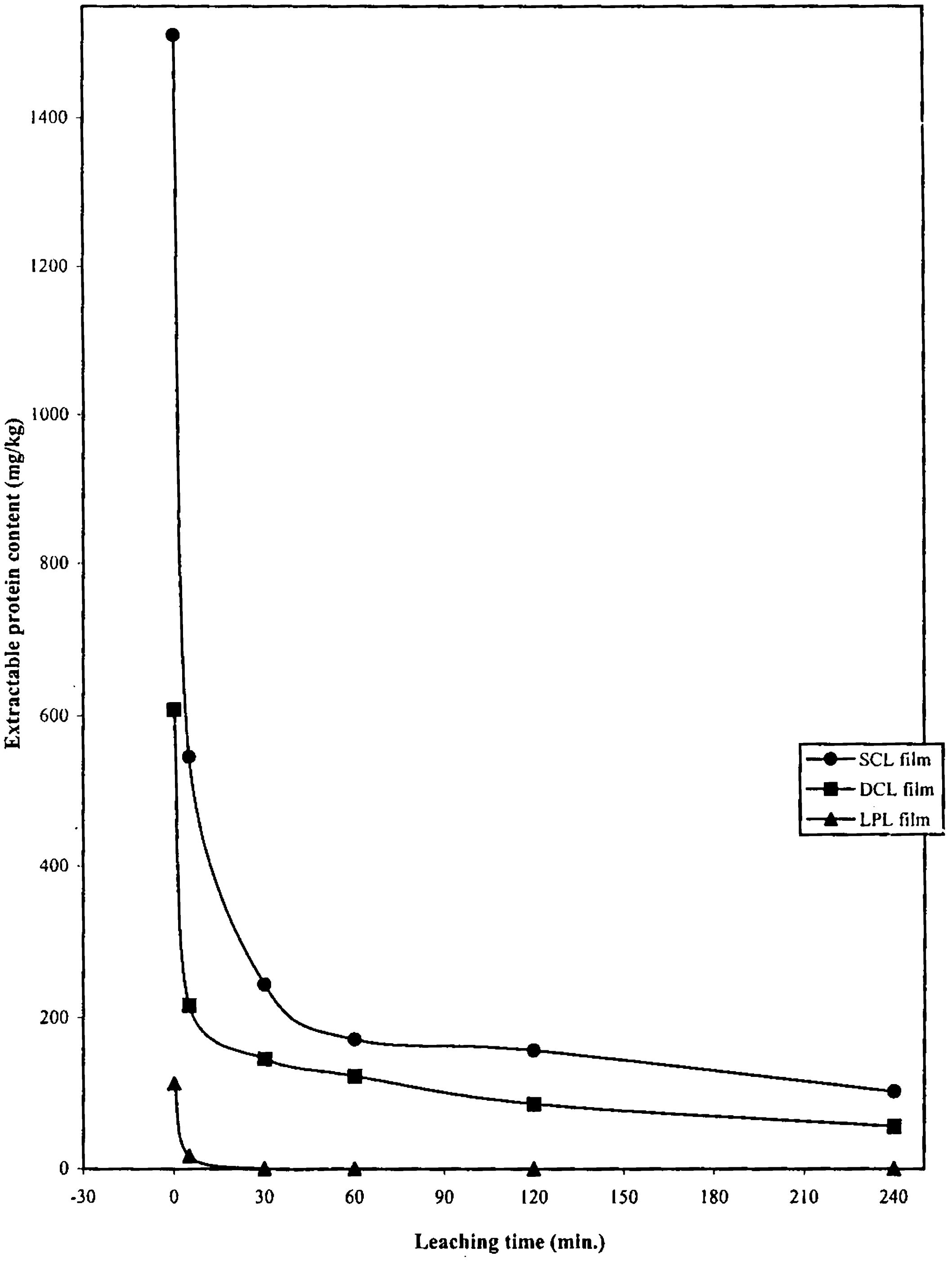


Fig 5C.18. Effect of leaching on extractable protein content in radiation vulcanized latex films.

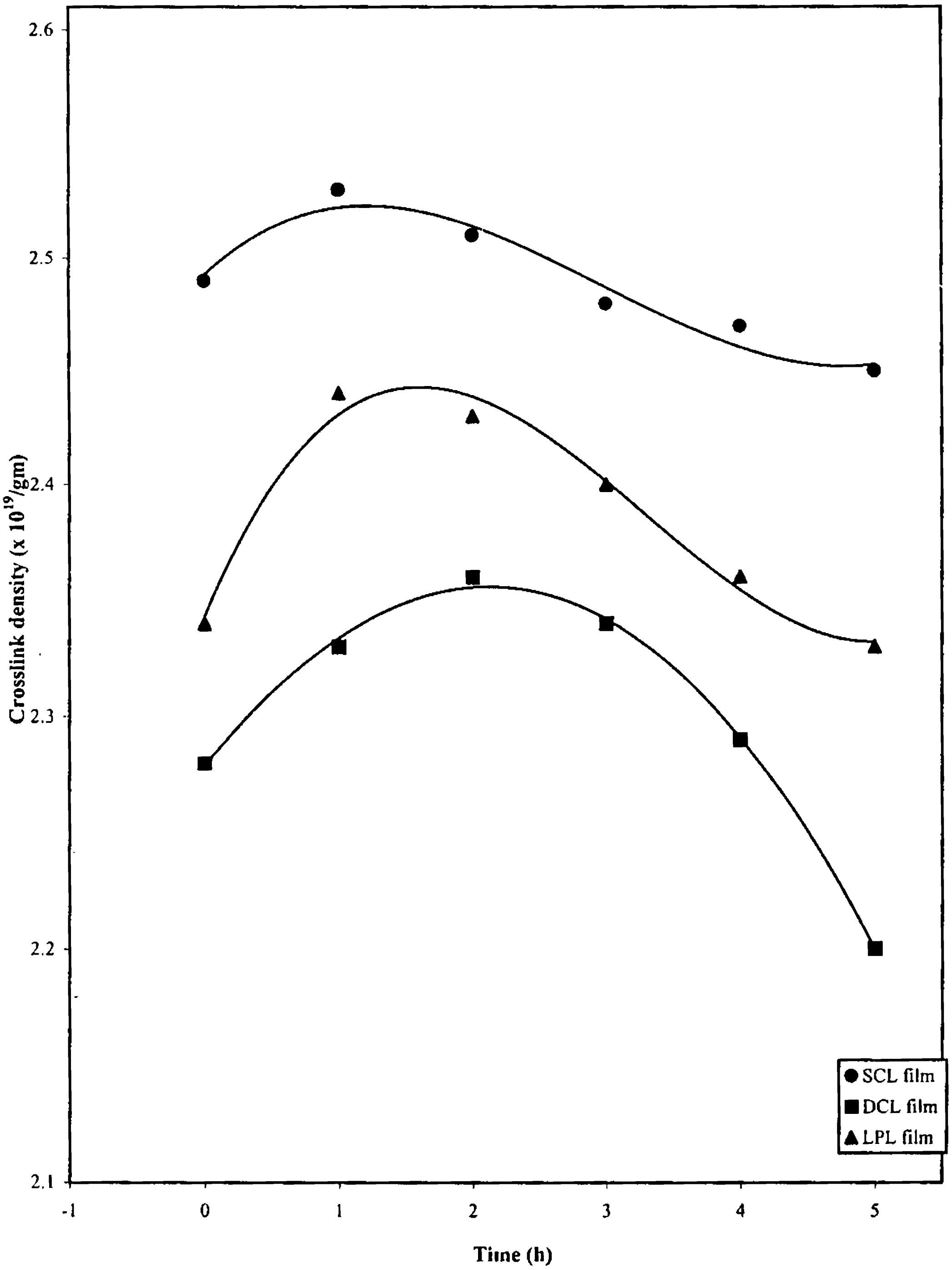


Fig 5C.19. Effect of post-cure heating at 80°C on crosslink density of radiation vulcanized latex films.

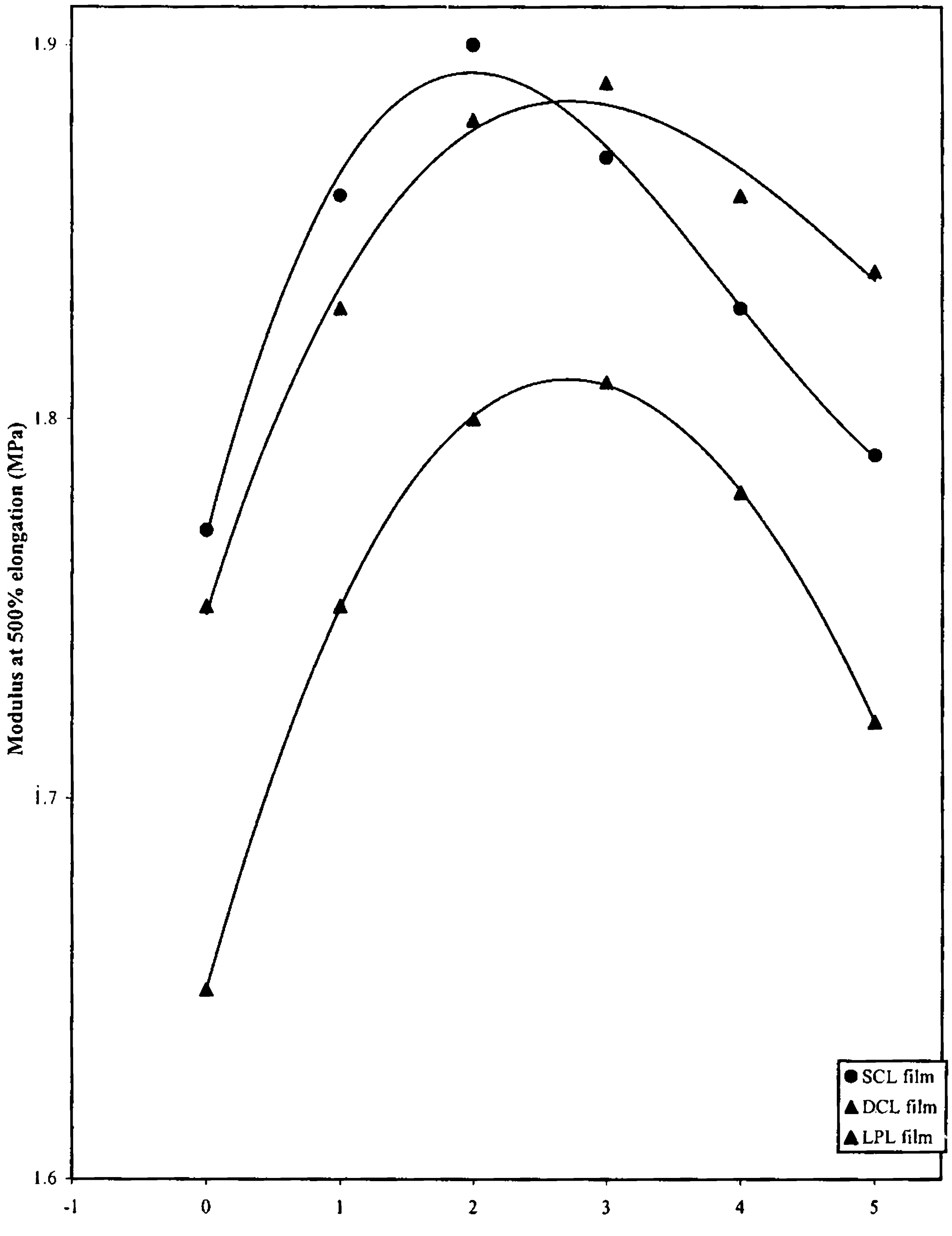


Fig 5C.20. Effect of post-cure heating at 80°C on modulus of radiation vulcanized latex films.

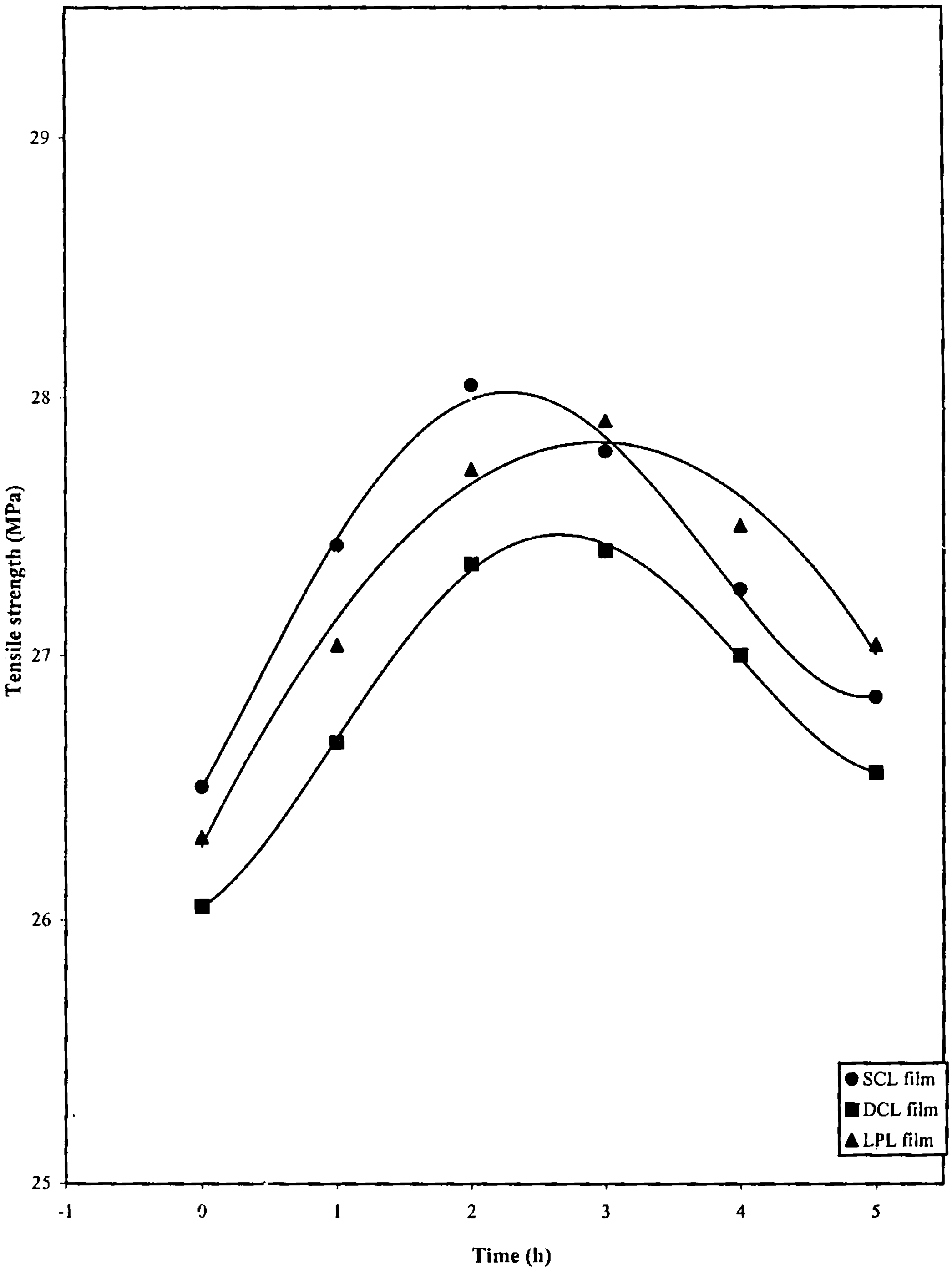


Fig 5C.21. Effect of post-cure heating at 80°C on tensile strength of radiation vulcanized latex films.

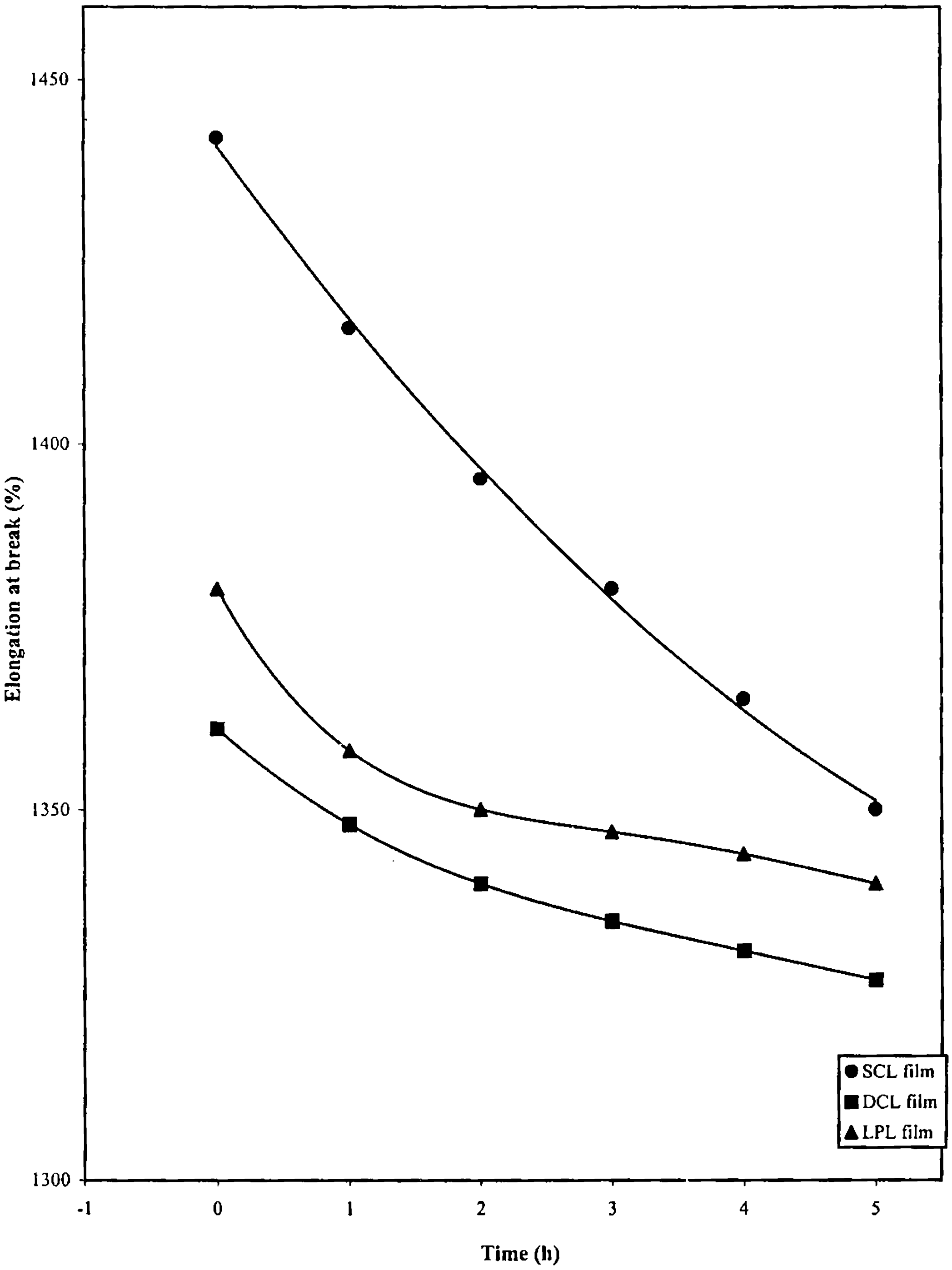


Fig 5C.22. Effect of post-cure heating at 80°C on elongation at break of radiation vulcanized latex films.

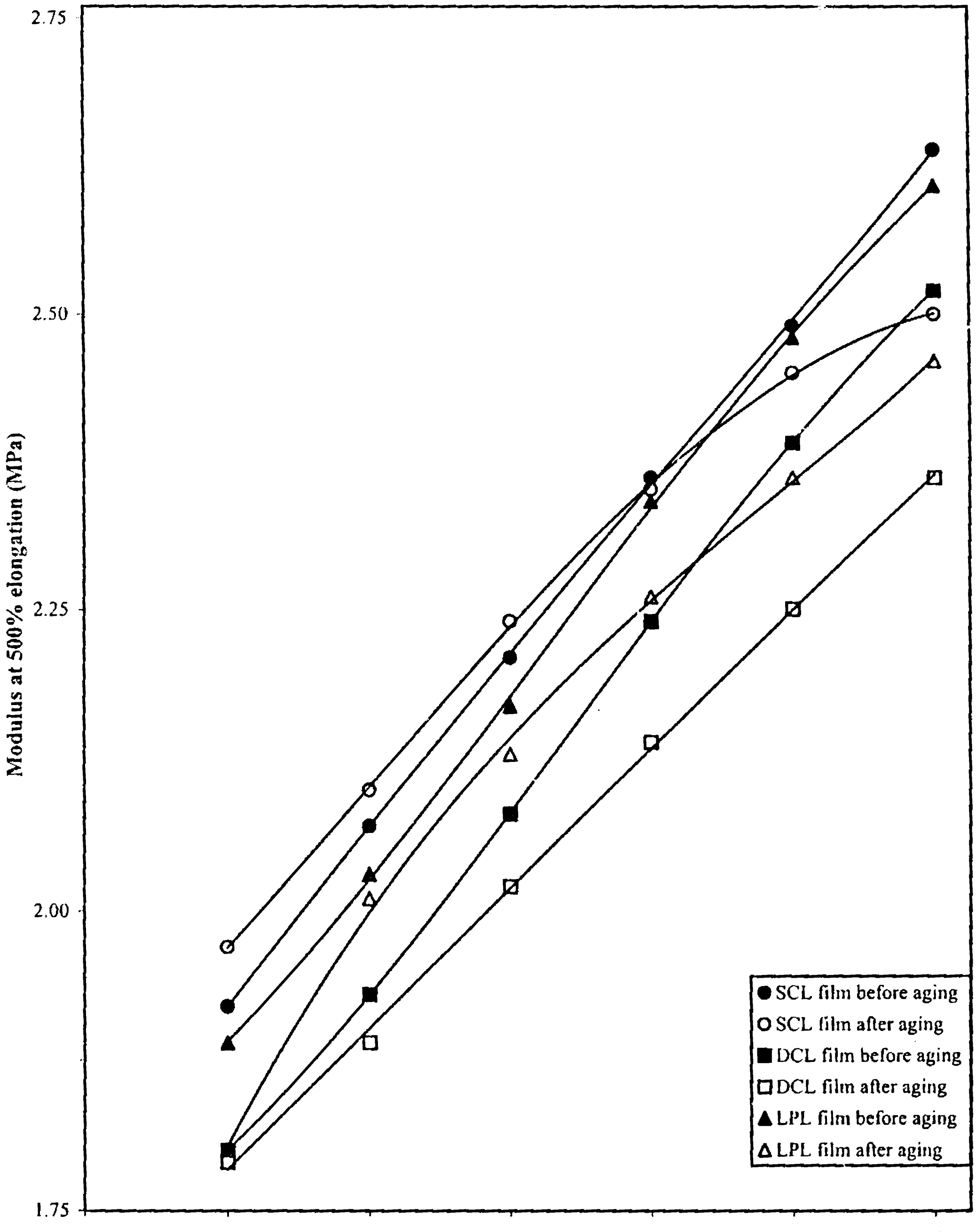


Fig 5C.23. Effect of addition of silica on modulus of radiation vulcanized latex films.

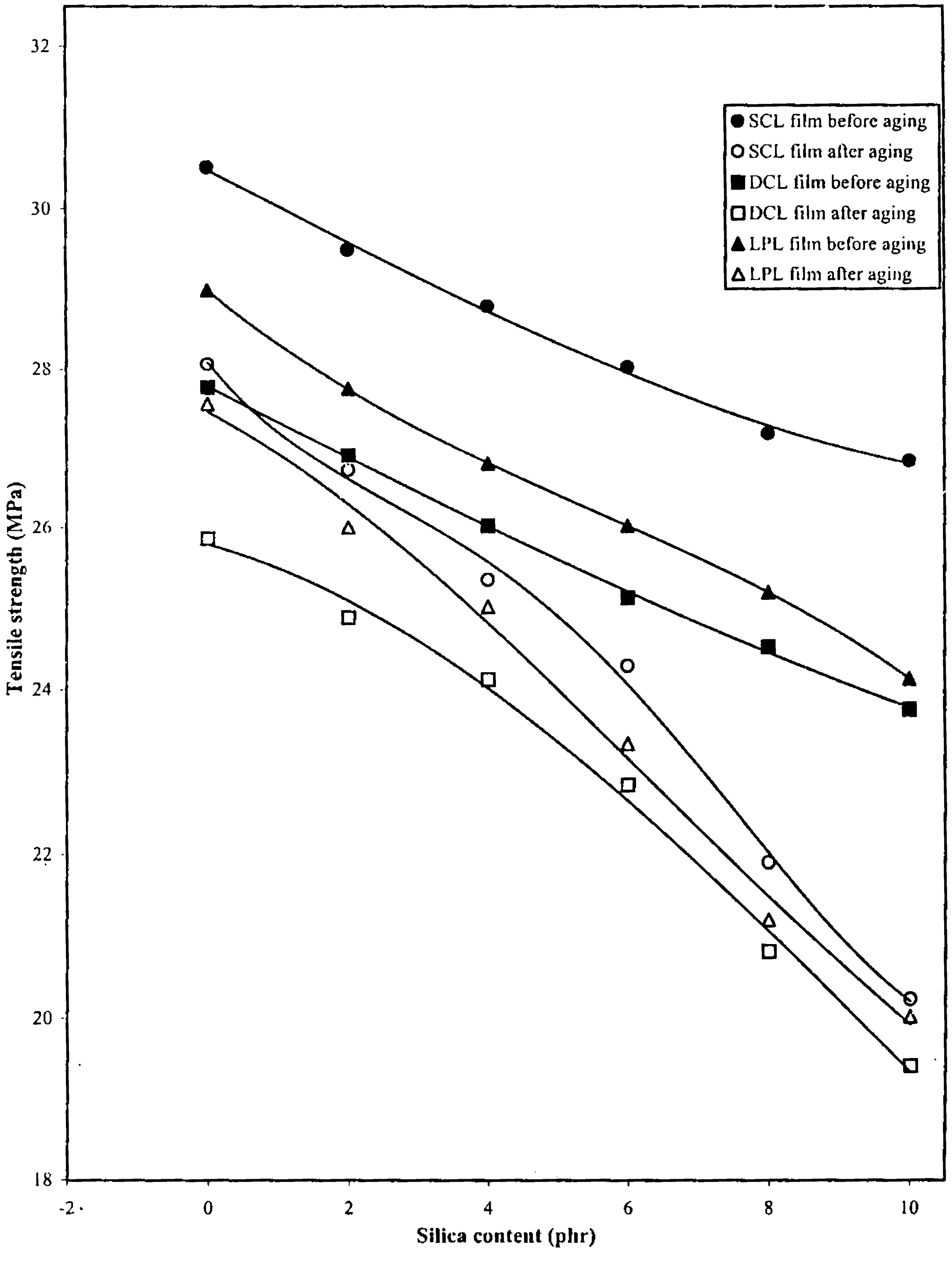


Fig 5C.24. Effect of addition of silica on tensile strength of radiation vulcanized latex films.

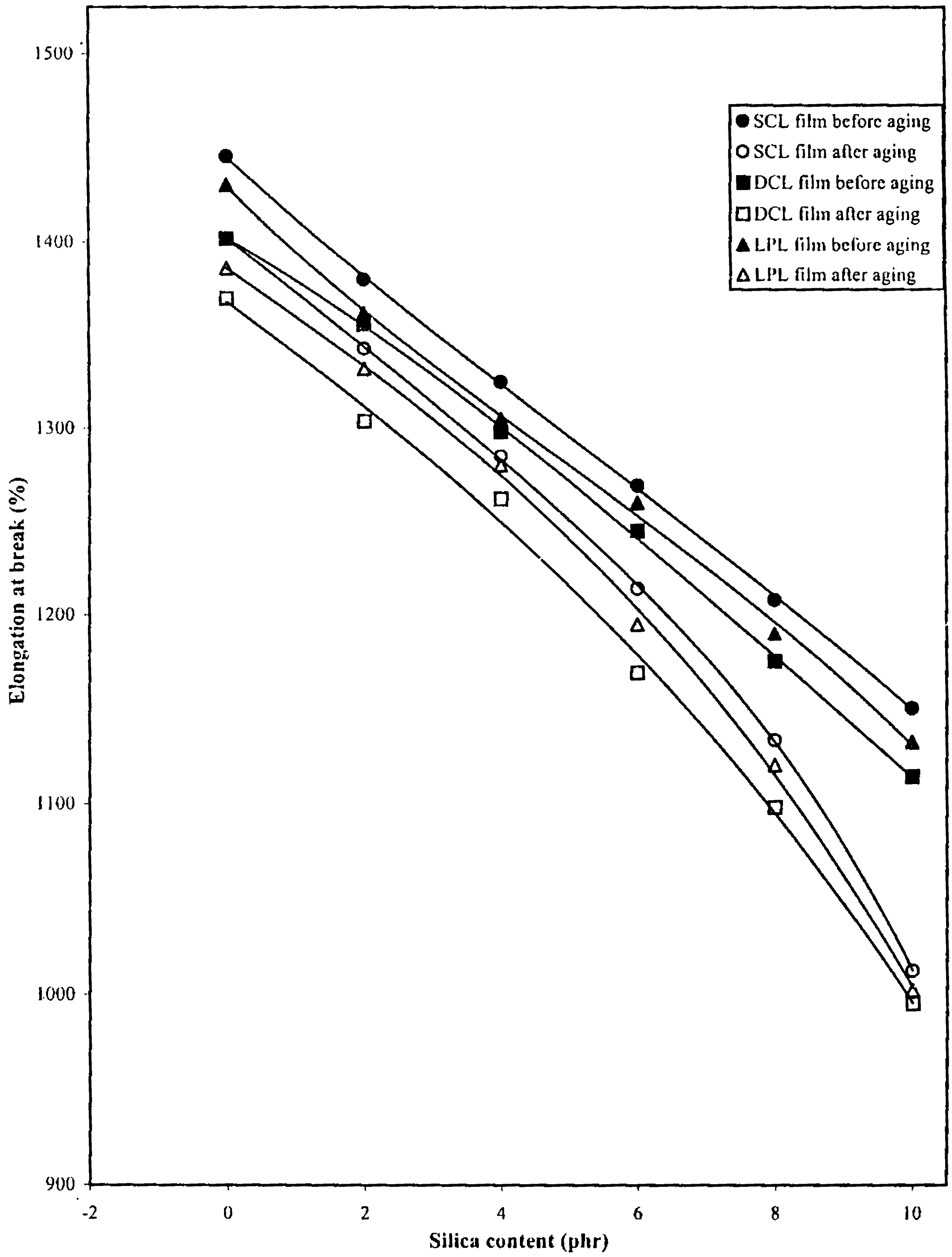


Fig 5C.25. Effect of addition of silica on elongation at break of radiation vulcanized latex films.

CHAPTER 6

RHEOLOGICAL BEHAVIOUR OF LOW PROTEIN LATEX

The rheological behaviour of latices are of both practical and theoretical interest. The raw latex, natural or synthetic is subjected to lot of stresses and flow during processing. Major areas of application of latices are dipped products, latex foam, rubberized coir/hair, surface coatings, extruded products etc. The viscosity of latices and latex compounds are of much concern in latex product manufacturing operations like dipping, foaming, casting, spraying etc. In these processes, compounded latex is subjected to different types of flow, accompanied by varying shear stresses. The control of undesirable viscosity increase in sulphur vulcanizable latex compounds have been studied long back(1). A fundamental knowledge of the viscosity of latices is essential for trouble free operation of the above techniques.

The factors which affect the flow properties of latices are volume fraction of the dispersed polymer, size and size distribution of the dispersed particles, absorption of dispersion medium by polymer particles, presence of lyophilic macromolecules, presence of surface active substances, and presence of bound electric charges at the surface of latex particles(2). The viscosity of latices is very much dependant on concentration. With respect to rheology of latices, three concentration regions can be distinguished(3).

- Extremely low concentration when an individual latex particle is not influenced by its neighbours ie; no particle-particle interaction and the viscosity contributions from individual particles are purely additive. ie; flow is Newtonian.
- An intermediate concentration range where particle interactions play a significant role. Contributions from individual particles are no longer additive and viscosity-concentration relation is non-linear, but flow is Newtonian.
- Higher concentrations where the rheology is dominated by particle interactions ie; viscosity is a function of both concentration and shear rate and the flow is non-Newtonian.

Particle-particle interactions become highly important in determining the flow characterstics of latex, especially at high solids content(4). Latex viscosity is also affected by electrolyte type and level in dispersion medium, shear rate, shear history and temperature(4). Most experimental work on latex rheology has been concerned with their viscosity-concentration relationship and pseudoplastic behaviour. The well-known Einstein equation(5) deals with the low concentration region.

$$\eta_r = \frac{\eta}{\eta_0} = 1 + 2.5\,\emptyset$$

where

η_r = relative viscosity

η = viscosity of dispersion

η_0 = viscosity of dispersion medium

$\emptyset$ = volume fraction of dispersed phase

Einstein equation was subsequently modified by several workers(6-10) mainly to account for the inter-particle interactions of the dispersed particles and the resultant non-Newtonian flow. Marron and Pierce(11) treat the flow behaviour of latex using the assumption that latex contain two distinct flow units : a Newtonian solvent (mostly water) and polymer particles.

The viscosity of latex at any total solids content decreases with increasing particle size(12). Also the viscosity of a blend of two or more relatively monodisperse latices of different particle sizes will be less than that of any of the individual latices at the same volume fraction of dispersed polymer(12).

The rheological behaviour of latices can be modified by the use of viscosity modifiers. Leaman(12) has studied the rheological behaviour of natural and different synthetic latices and latex compounds/latex paints in presence of thickening agents/fillers. Sodium polyacrylate shows sharp and easily controlled viscosity increase with most type of latices(14). The effect of solids content and temperature on viscosity of natural rubber latex has been reported(15,16). The rheological behaviour of concentrated natural latex in the presence of surface-active agents has been studied by Peethambaran *etal*(17). The effect of temperature, viscosity modifiers and fillers on the rheological behaviour of prevulcanized natural latex has been reported by Claramma and Mathew(18).

It is well known that the flow behaviour of latices can be considerably modified by the addition of lyophilic macromolecules which are soluble in the dispersion medium(2). A water soluble polymer PPG is used in the processing of LPL. Also during a second stage of latex centrifuging a portion of the smaller particles are also removed. Further in LPL, the electrolyte content in the aqueous phase of latex is reduced by second stage of latex concentration. Hence it seemed worth while to study the rheological behaviour of LPL. This study reports the rheological behaviour of raw LPL, sulphur prevulcanized LPL and radiation vulcanized LPL at different solid contents at varying shear rates and at different temperatures. Comparison is made with SCL and DCL.

EXPERIMENTAL

LPL was prepared from single centrifuged latex (SCL), conforming to Indian Standard specifications IS 5430-1981, by the method reported earlier(19). To study the effect of second stage centrifugal concentration, a batch of double centrifuged latex (DCL) also was prepared from the same SCL. Rheological evaluation of LPL was made in comparison with SCL and DCL. Rheological measurements were made on raw latices, sulphur prevulcanized latices and radiation vulcanized latices.

For the prepartion of sulphur prevulcanized latices latex was compounded as per formulation given in Table 6.1. Water immiscible solid chemicals were added as dispersions. Compounded latex was matured for 24h and then prevulcanized by heating at 60°c for 2.5h, under constant stirring. For the purpose of radiation crosslinking, latices were compounded as per the formulation given in Table 6.2. Water immiscible nBA was prepared as 50% aqueous emulsion. Latices were irradiated by gamma rays from a cobalt 60 source in Gamma Chamber 5000, to a total dose of 15 kGy at the rate of 1.331 kGy/h.

Viscosity of latices were measured with Brook field viscometer using spindle number 2 at room temperature. To study the effect of solids content of latex on viscosity, 60% DRC latex was diluted with 1.6% aqueous ammonia. Other rheological evaluations were made using a Haake Viscotester VT 550 using NV Sensor System for measurements. Shear rate was varied in the range 1–200 s^{-1}. Viscosity measurements were made on raw latices at 60% solids content. In the case of sulphur prevulcanized latices viscosity measurements were made at 57% solids content and for radiation vulcanized latices measurements were made at 52% solids content. The effect of temperature on flow behaviour was studied at four different temperature 30°, 35°, 40°, and 45°C.

RESULTS AND DISCUSSION

Effect of solids content on the viscosity of raw latices

This study was conducted in the solids content range 30-60%. Latices with solids content below 30% do not have much practical application and at above 60%, viscosity increase to very high values.

Figure 6.1 shows the variation of viscosity of the three types of latices with its solids content. From the figure it is observed that viscosity of the three types of latices increase with increase in solids content. However, the increase is not linear. Rate of increase in viscosity also increase with increase in solids content.

In latex, the surface of each rubber particle is adsorbed by a layer of naturally occurring proteins and phospholipids or any externally added surface active materials. These are polar in nature and dipolar water molecules crowd around each particle. Thus each rubber particles is solvated to some extent. Rutgers(20) suggests that the effective volume of dispersed phase in latex is grater than the volume fraction of dispersed rubber, because the molecules of the dispersion medium are tightly associated with the particle surface. The non-linear increase in viscosity of latices with increase in solids content is attributed to this solvation factor.

It is observed that for a given solids content the viscosity of SCL and LPL are almost similar (LPL being slightly lower) while DCL shows higher viscosity. DCL differs from SCL in the following respects.

- A slight increase in the average particle size.
- Reduction in the electrolyte concentration in the aqueous phase.

When DCL is processed out of SCL a portion of the smaller particles and a substantial portion of the aqueous phase of diluted SCL are removed as skim latex during the second stage of concentration. Removal of smaller particle causes an increase in average particle size slightly and this reduces viscosity slightly. Removal of ionic substances leads to a reduction in electrolyte concentration and this leads to expansion of the electrical double layer associated with latex particles.

The effects of surface bound electrical charges and the associated electrical double layers upon flow behaviour of latices are collectively known as electro viscous effect(4,21). Distortion of the electrical double layer under shear leads to increase in viscosity (primary electroviscous effect)(3,21).

Coulombic interactions between the double layers of different particles lead to increase in viscosity (secondary electroviscous effects). During shear, distortion of the particles of solids may occur as a result of the electrostatic forces, arising from the presence of charges on the particle (tertiary electroviscous effects). In the case of DCL the contribution of the three types of electroviscous effects more than compensates the small increase in average particle size. Thus DCL shows higher viscosity than SCL.

Particles size distribution and electrolyte concentration in the aqueous phase of LPL are almost comparable to DCL. However, viscosity of LPL is lower than that of DCL Data presented in Chapter 4 shows that approximate protein content in LPL is 0.938%, while that in DCL is 1.125%. Thus contributions from electro viscous effects are believed to be lower in LPL and these account for lower viscosity of LPL compared to DCL.

Effect shear rate on apparent viscosity of raw latices

According to Power Law equation(22)

$$\tau = \kappa \gamma^{n} \quad \text{.................................(1)}$$

where

τ = shear stress (Pa)

κ = viscosity index

γ = shear rate (s^{-1})

n = flow index

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

$$\eta = \frac{\tau}{\gamma} \quad \text{.......................................(2)}$$

Combining equations (1) and (2)

$$\eta = \kappa \gamma^{n-1}$$

Taking logarithms

$$\log \eta = \log \kappa + (n-1) \log \gamma$$

The plot of log η against log γ gives a straight line, whose slope is (n-1), from which the flow index n can be calculated.

Figure 6.2 gives the variation of apparent viscosity against shear rate for SCL, DCL and LPL at 60% rubber content and Figure 6.3 gives the log-log plot. It has been reported earlier that the rheology of natural rubber latex at higher concentration is dominated by particle interactions and the flow is non-Newtonian(23). From Figure 6.2 it is seen that the three types latices are pseudoplastic fluids ie, their apparent viscosities decrease with increasing shear rates. Two explanation are offered for pseudoplastic behaviour(22).

- Asymmetric latex particles are extensively entangled and/or randomly oriented at rest. Under shear, the particles become oriented and points of entanglement are reduced. The orientation may be opposed by disorienting effects of Brownian motion. At very high shear rates orientation may be complete and in this range near Newtonian behaviour may be observed.
- In natural latex, the dispersed particles are highly solvated. With increase of shear rate, solvated layers may be sheared away resulting in decreased interaction between the particles and consequent reduction in apparent viscosity.

From Figures 6.2 and 6.3 it is seen that at all shear rates DCL had higher viscosity and the the order of viscosity is

DCL > SCL > LPL

The aqueous phase of natural latex contains several dissolved ions. As stated earlier, during second centrifugal concentration of SCL, a portion of the aqueous phase is removed. Removal of aqueous phase is accompanied by removal of the ions dissolved in it. Hence the ionic concentration in the aqueous phase of DCL and LPL is less than that in SCL. Removal of electrolyte from the aqueous phase of latex causes a large increase in viscosity and a marked shear thinning characteristic (pseudoplastic behaviour) results(24). As stated earlier, generally accepted mechanism for this behaviour is that removal of the electrolyte causes an expansion of the electrical double layer surrounding the latex particles thereby effectively increasing their diameter and thus their volume. This immobilizes a layer of solvent molecules. Despite the reduction in ionic concentration in the aqueous phase of LPL, a reduction in viscosity is observed for LPL at all shear rates. In the present study no anionic surface-active materials were added to LPL. Thus the electrical charges on latex particles are contributed by naturally occurring non-rubber materials like proteins and phospholiphids only. It has been found that in LPL protein content is less. It is believed that in LPL, the increase in viscosity which ought to have accompanied the reduction in ionic concentration is probably more than compensated for by the fall in electrical charges on the latex particles. This situation leads to a fall in viscosity of LPL over that of SCL. From Figure 6.2 and 6.3 it is further observed that as shear rate increases, the extent of shear thinning is reduced. It is believed that the orientation effects brought in by shearing are opposed by disording effects of Brownian motion (22).

Zero shear viscosity of raw latices

The value of instantaneous viscosity of a latex at vanishingly small values of shear is known as its zero-shear viscosity. Zero-shear viscosities of three types of latices are given in Table 6.3. It is seen that zero-shear viscosity is the highest for DCL and least for SCL, even though LPL shows lower viscosity at all other shear rates. This is probably due to the crowding of water molecules around rubber particles over whose surface PPG molecules are adsorbed leading to an increase in the effective size of the particles. These water molecules are sheared off at higher shear rates, accompanied by a fall in viscosity. At very low shear rates, the water molecules crowding around the rubber particles in LPL cause higher viscosity.

Flow index of raw latices

The flow index `n' in Power Law equation is obtained from the slope of curves in Figure 6.3. The flow index of an ideal Newtonian fluid is assumed to be unity. How far a real fluid deviates from ideal behaviour is judged by observing the deviation of n from unity. A value of $n>1$ indicates dilatant behaviour while $n<1$ indicates pseudoplastic behaviour. The lower the value of n below unity, the more pseudoplastic the latex. The flow index values of the three latices also are given Table 6.3. Thus pseudoplasticity of the latices differs slightly and is in the order

SCL > LPL > DCL

This order suggests that the envelope of water molecules surrounding latex particles in DCL are sheared off very easily

Effect of shear rate on apparent viscosity of sulphur prevulcanized latices

The variation of viscosity of the three types of sulphur prevulcanized latices are given Figure 6.4 and its log-log plot is given in Figure 6.5. Viscosity measurements were made at 57% solids content. Viscosity of sulphur prevulcanized latices are in the order

SVLPL > SVDCL > SVSCL

Highest viscosity is shown by LPL as against DCL in the case of raw latex. It is believed that PPG was adsorbed at the surface of rubber particles in raw LPL. PPG has inverse solubility in water and behaves as a heat sensitizing agent. During prevulcanization at 60°C at least partial precipitation of PPG occurs. Thus the following factors contribute to the increases viscosity of sulphur prevulcanized LPL over the other two:

- Lower ionic concentration in the aqueous phase (due to second stage latex concentration)
- Partial removal of PPG from rubber serum inter phase, contributing to a reduction in steric stabilization.
- Precipitated PPG molecules cause an increase the number of dispersed particles per unit volume of the aqueous phase of LPL.

Between sulphur vulcanized SCL and DCL, the latter shows slightly higher viscosity. This is mainly due to the reduced ionic concentration in the aqueous phase of DCL and the resultant expansion of the electrical double layer surrounding the latex particles.

Figures 6.4 and 6.5 also show that viscosity of the three vulcanized latices decrease with increasing shear rate ie, their behaviour is pseudoplastic.

Zero shear viscosity of sulphur prevulcanized latices

Table 6.4 gives the zero-shear viscosity of the three types of sulphur vulcanized latices. It is in the order

SVLPL > SVDCL > SVSCL

Zero shear viscosity is highest for SVLPL and this is believed to be due to the precipitation of PPG and also due to the reduced ionic concentration in the aqueous phase of LPL.

Flow index of sulphur prevulcanized latices

Table 6.4 also gives the flow index of sulphur vulcanized latices. Compared to raw latices, the value of 'n' has increased slightly on sulphur vulcanization in the case of SCL at 57% solids content showing it has become less pseudoplastic. However, 'n' values have decreased appreciably in the case of SVDCL and slightly for SVSCL. Among the sulphur prevulcanized latices, psedoplasticity is in the order

SVDCL > SVLPL > SVSCL

The variation in pseudoplasticity is related the ease with which water molecules surrounding latex particles can be sheared off on increasing the shear rate.

Effect of shear rate on apparent viscosities of radiation vulcanized latices

The variation of viscosity against shear rate of the three types of latices after radiation vulcanization measured at room temperature and at 52% solids content is given in Figure 6.6 and its log-log plot in Figure 6.7. The three types of latices exhibit pseudoplastic behaviour. LPL which exhibited the lowest viscosity among the three raw latices now again shows higher viscosities at all shear rates as in the case of sulphur vulcanization. The difference in viscosity between radiation vulcanized SCL and DCL is only small. All the three types of latices contain 0.3phr KOH as stabilizer, so that ionic concentration of the aqueous phase is sufficiently high and hence the difference in viscosity between SCL and DCL disappears. The higher viscosity of radiation vulcanized LPL is believed to be due to the heat-sensitizing action and inverse solubility of PPG. During irradiation, the temperature of latex rises to about 50–55°C. At this temperature, PPG precipitates to some extent, so that the effective number of particles per unit volume increases leading to increase in viscosity.

Zero shear viscosity of radiation vulcanized latices

Table 6.5 gives the zero shear viscosity of three types of radiation vulcanized latices. Zero shear viscosity is in the order

RVLPL > RVDCL > RVSCL

which is again the same order for sulphur vulcanized latices.

Flow index of radiation vulcanized lattices

The flow index values are obtained from log-log plot provided in Figure 6.7. Compared to the unvulcanized latex, the flow index values of radiation vulcanized latices are higher, showing that they have become less pseudoplastic as with sulphur vulcanized latices and among the three vulcanized lattices, RVLPL is the most pseudoplastic.

Effect of temperature on apparent viscosity of low protein latex

The variation of apparent viscosity of raw LPL with shear rate at different temperature is shown in Figure 6.8 and the corresponding log-log plot is given in Figure 6.9. It is seen that at all shear rates, apparent viscosity decreases with increase in temperature. Similar results on the drop in viscosity of natural field latex and concentrated latices with increasing shear rates have been reported(25,26). Also at any shear rate apparent viscosity decreases with increase of temperature. The effect of temperature on viscosity of a dispersion of a solid is mainly related to the change in viscosity of the medium(27) and viscosity at any temperature is provided by Arrhenius type equations(28,29). The apparent volume V of a dispersed polymer mass at any temperature consists of two portions – that part which is contributed by the molecules themselves, V_0 and free volume V_f. Viscosity decreases with increasing temperature because free volume increases. When free volume increases the flow units become less restricted and with increasing temperature they become more highly energized, less highly organized thus resulting in decreased viscosity(30). As done previously, 'n' values are obtained from the log-log plot of shear rate against apparent viscosity as given in Figure 6.9.

The zero shear viscosity and flow index values of raw LPL at temperatures in the range 30° to 45°C are presented in Table 6.6. The zero shear viscosity decreases with increase in temperature and flow index slightly increases with increase in temperature. Thus increase in temperature makes the latex slightly less pseudoplastic.

Figure 6.10 shows the variation of apparent viscosity with temperature of latex at various shear rates and Figure 6.11 represents the corresponding curves for log (viscosity) against temperature. It is seen from Figure 6.10 that at each shear rate viscosity decreases with increase in temperature and the extent of decrease in viscosity narrows down with increase in shear rate. As stated earlier the decrease in viscosity on increasing temperature is attributed to the increase in free volume. At higher shear rates, the water molecules immobilized around the latex particles by van der Waals forces have already been sheared away, so that subsequent increase in temperature has only small effect.

Effect temperature on apparent viscosity of sulphur prevulcanized low protein latex

The variation of apparent viscosity of sulphur vulcanized LPL (SVLPL) at 57% solids content against shear rate at different temperatures is shown in Figure 6.12 and the corresponding log-log plot is shown in Figure 6.13. It is observed that viscosity of SVLPL decreases with shear rates at all temperatures ie, the behaviour is pseudoplastic at all temperatures. The magnitude of reduction in viscosity with increasing shear rate decreases with increase in temperature. From the log-log plot it is seen that zero shear viscosity decreases with increase in temperature while the flow index value increases slightly; ie, SVLPL becomes less pseudoplastic with increase in temperature. This is believed to be due to the less dense envelope of water molecules surrounding vulcanized latex particles, as the molecules of dispersion medium acquire more kinetic energy with increase in temperature.

The variation of zero shear viscosity and flow index of SVLPL at various temperatures are given in Table 6.7. Zero shear viscosity reduces with increase in temperature. This is believed to be mainly due to the fall in viscosity of the dispersion medium. Values of flow index, n increases slightly ie; SVLPL becomes less pseudoplastic with increase in temperature.

A comparison of Figure 6.12 with Figure 6.10 shows that the viscosity of SVLPL at 57% solids content is slightly higher than that of raw LPL at 60% solids content. This is believed to be due to the precipitation of PPG during heating for imparting prevulcanization.

The variation of viscosity of SVLPL with temperature at different shear rates is shown in Figure 6.14 and a plot of log (viscosity) against temperature is shown in Figure 6.15. It is observed that at any shear rate, increase in temperature is accompanied by fall in viscosity. This is believed to be partly due to removal of water molecules around latex particles held by van der Waals forces on increasing shear rates and partly due to the fall in viscosity of the dispersion medium with increase in temperature.

From Figure 6.15, it is also observed that the extent of fall in viscosity with temperature reduces as shear rate increase. It is assumed that at high shear rates, reduction in viscosity with temperature is mainly due to fall in viscosity of the dispersion medium.

Effect of temperature on apparent viscosity of radiation vulcanized low protein latex

The effect of shear rate on apparent viscosity of radiation vulcanized LPL (RVLPL) at different temperatures at 52% solids content is given in Figure 6.16 and the corresponding log-log plot is shown in Figure 6.17. As in the case of raw LPL, viscosity decreases with shear rate at all temperatures ie; RVLPL also shows pseudoplastic behaviour and the rate of fall in viscosity decreases with increasing shear rates. The extent of reduction in viscosity with shear rate decreases with rise in temperature. The log-log plots of Figure 6.17 in the temperature range 30–45°C are all straight lines and the flow index values are determined. The results of zero shear viscosity and flow index values are given in Table 6.8. The zero shear viscosity also decreases with increase in temperature. This is mainly due to reduction in viscosity of the dispersion medium on increasing temperature. The flow index values slightly increase with temperature. Thus on increasing temperature RVLPL becomes less pseudoplastic. As in the case of SVLPL, RVLPL particles are surrounded by lower number of water molecules, due to their higher kinetic energy on increasing temperature.

The variation of viscosity with temperature at different shear rates are given in Figure 6.18 and log (viscosity) is plotted against temperature in Figure 6.19. At a given shear rate an increase in temperature of RVLPL is accompanied by a reduction in viscosity. However, the extent of reduction in viscosity reduces with increasing shear rate and above shear rate of $150s^{-1}$ the decrease is almost constant. This observed reduction of about 5 Pas is exclusively due to increase in free volume. It is believed that some water molecules are immobilized around each latex particle by van der Waals forces and this 'structure' is almost completely destroyed at higher shear rates.

The curves in Figure 6.19 show a rather steep fall in viscosity when the temperature changes from 30 to 35°C, while subsequent decrease of log (viscosity) is rather uniform. This steep fall in log (viscosity) was not observed in the case of raw LPL when temperature is gradually increased. This is believed to be partly due to change viscosity of the dispersion medium(15). Further, some water molecules, which were immobilized around suspended latex particles are removed during shearing on increasing the temperature, since water molecule acquire higher kinetic energy.

Effect of storage on viscosity and flow behaviour of LPL

The changes in flow behaviour of a latex during long term storage is very important from a commercial point of view. It is observed that the viscosity of LPL increases on storage. Figure 6.20 gives the variation of viscosity of LPL immediately on production and after storage for 60 days with increasing shear rates and Figure 6.21 provides the log-log plot. From Figure 6.20 it is seen that viscosity of LPL increases on storage at all shear rates. The reduction in viscosity on increasing shear rate is higher for LPL immediately on production than after storage. As the latex becomes more viscous, the zero shear viscosity also increases on storage.

Some proteins and phospholiphids adsorbed at the rubber-serum interface attract water molecules and the effective size of the particles increases. On increasing shear rates, these immobilized water molecules are sheared off resulting in viscosity reduction.

During storage, a part of the adsorbed non-rubber materials are hydrolyzed and become water soluble(31). Hydrolysis of proteins lead to the formation of polypeptides and amino acids. Hydrolysis of the phospholipids lead to the formation of various substances such as glycerol, long chain carboxylate anions, phosphate anions and organic bases. Thus the overall concentration of dissolved substances in the aqueous phase increases leading to the increase in viscosity of LPL.

As the content of adsorbed polar materials is reduced at the rubber-serum interface, the content of immobilized water molecules around the rubber particles decreases, thus making the latex less pseudoplastic. This is again observed from the plot of log (viscosity) against log (shear rate) given in Figure 6.21. The slope of the lines indicates that LPL becomes less pseudoplastic during storage.

The changes in zero shear viscosity and flow index arrived at from Figures 6.20 and 6.21 respectively are given in Table 6.9. It can thus be seen that, even though LPL becomes more viscous on storage, it also becomes less pseudoplastic.

CONCLUSIONS

- Viscosity of the three types of latices increase with rubber content and the observed increase is nonlinear. Among the three latices, double centrifuged latex is the highest in viscosity.

- The viscosity of low protein latex is slightly less than that of standard centrifuged latex and appreciably lower than double centrifuged latex. Low protein latex is pseudoplastic like the other two.

- Sulphur prevulcanized and radiation vulcanized low protein latices show higher viscosity and pseudoplasticity compared to respectively sulpur vulcanized and radiation vulcanized standard centrifuged latices.

- In the temperature range under study (30–45°C) increase in temperature of low protein latex is accompanied by reduction in viscosity at all shear rates. Reduction in viscosity becomes less significant at higher shear rates.

- Storage of low protein latex is accompanied by increase in viscosity. However the latex becomes less pseudoplastic.

REFERENCES

1. C.F.Flint. Proc. Rubber Technol. Conf. London, p-312 (1938).
2. D.C.Blackely Polymer Latices: Science and Technology, (Second Edn.) Chapman & Hall, London, Vol.1. Chapter 6 (1997).
3. F.L.Saunders. Advances in Polymerization and Latex Technology, 18th Annual Short Course, American Chemical Society. Vol.3. Lecture No.14 (1987).
4. E.A.Collins, C.A.Daniels and J.A.Davidson.*Elastomerics* **110(3)**, 31 (1978).
5. A.Einstein. *Ann.Physik.* **17**,459 (1905).
6. W.Vand, *Nature* **155**,364 (1945).
7. H.C.Brinkman. *J.Chem.Phys.* **20**, 571 (1952).
8. R.Roscoe. *Brit. J. Appl. Phys.* **3**, 267 (1952).
9. M.Mooney. *J.Colloid Sci.* **6**, 162 (1951).
10. I.M.Krieger and T.J.Dougherty. *Trans.Soc.Rheol.* **3**, 137 (1959).
11. S.H.Marron and P.E. Pierce. *J.Colloid Sci.* **11**, 80 (1956).
12. P.H.Johnson and R.H.Kelsey. *Rub.World* **138**,877 (1958).
13. L.Leaman. *Rub.Age* **75**, 537 (1954).
14. W.D.Schroeder and G.L.Brown. *Rub.Age* **69**, 433 (1951).
15. E.W.Madge. *Rubber Chem. Technol.* **8**, 501 (1935).
16. H.F.Smit. *J.Rub.Res.Inst.Malaya*, **11**,44 (1941).
17. N.R.Peethambaran, B.Kuriakose, M.Rajan and A.P.Kuriakose. *J.Appl.Polym.Sci.* **41**, 980 (1990).
18. N.M.Claramma and N.M.Mathew. *Kautschuk Gummi Kunstsoffe* **51(2)**, 126 (1988).
19. M.S.Sebastian, V.George and E.V.Thomas. Proc.18th Rub.Conf. Indian Rubber Manufacturers' Research Association, Mumbai. p-105 (2000).

20. R. Rutgers. *Rheologica Acta.* **2(4)**, 305 (1962).

21. R.J.Hunder, Zeta Potencial in Colloid Science : Principles and Applications, Chapter 5, Academic Press, London (1981).

22. J.A.Brydson. Flow Properties of Polymer Melts. The Plastics and Rubber Institute. London. Chapter 1 (1981).

23. H.F.Gazeley, A.D.T.Gorton and T.D.Pendle. Natural Rubber Science and Technology, A.D.Roberts (Ed.) Oxford University Press. Oxford. Chapter 4 (1988).

24. J.G.Brondyan and E.L.Kelly. *J.Kolloid Sci.* **20**, 7 (1965).

25. O.Bachele. *Rubber Chem. Technol.* **10**, 675 (1937).

26. E.Rhodes *Rubber Chem. Technol.* **12**, 655 (1939).

27. E.T.Severs. Rheology of Polymers. Reinhold Publishing Corporation, New York, Chapter 5, (1962).

28. E.N.dac Amdrade. *Nature* **125**, 309 (1930).

29. J.de Guzman. *Anales Soc. Espan. Fos.y.quim.* **11**, 353 (1913).

30. R.S.Lenk. Polymer Rheology. Applied Science publishers Ltd; London, Chapter 3, (1978).

31. D.C.Blackley. Polymer Latices : Science and Technology. Second Edn. Chapter 9, (1997).

TABLE 6.1

Formulation of latex compound for sulpur prevulcanization

Ingredient	***Parts by weight***	
	Dry	***Wet***
60% Natural latex	100	167
10% Potassium hydroxide	0.1	1.0
50% Sulphur	1.75	3.50
50% Zinc diethyldithiocarbamate	1.0	2.0
50% Zinc oxide	0.25	0.50

TABLE 6.2

Latex compound for radiation prevulcanization

Ingredient	***Parts by weight.***	
	Dry	***Wet***
60% Natural Latex	100	167
10% Potassium hydroxide	0.3	3.0
50% n-Butyl acrylate	5	10
Water	—	To 50%.

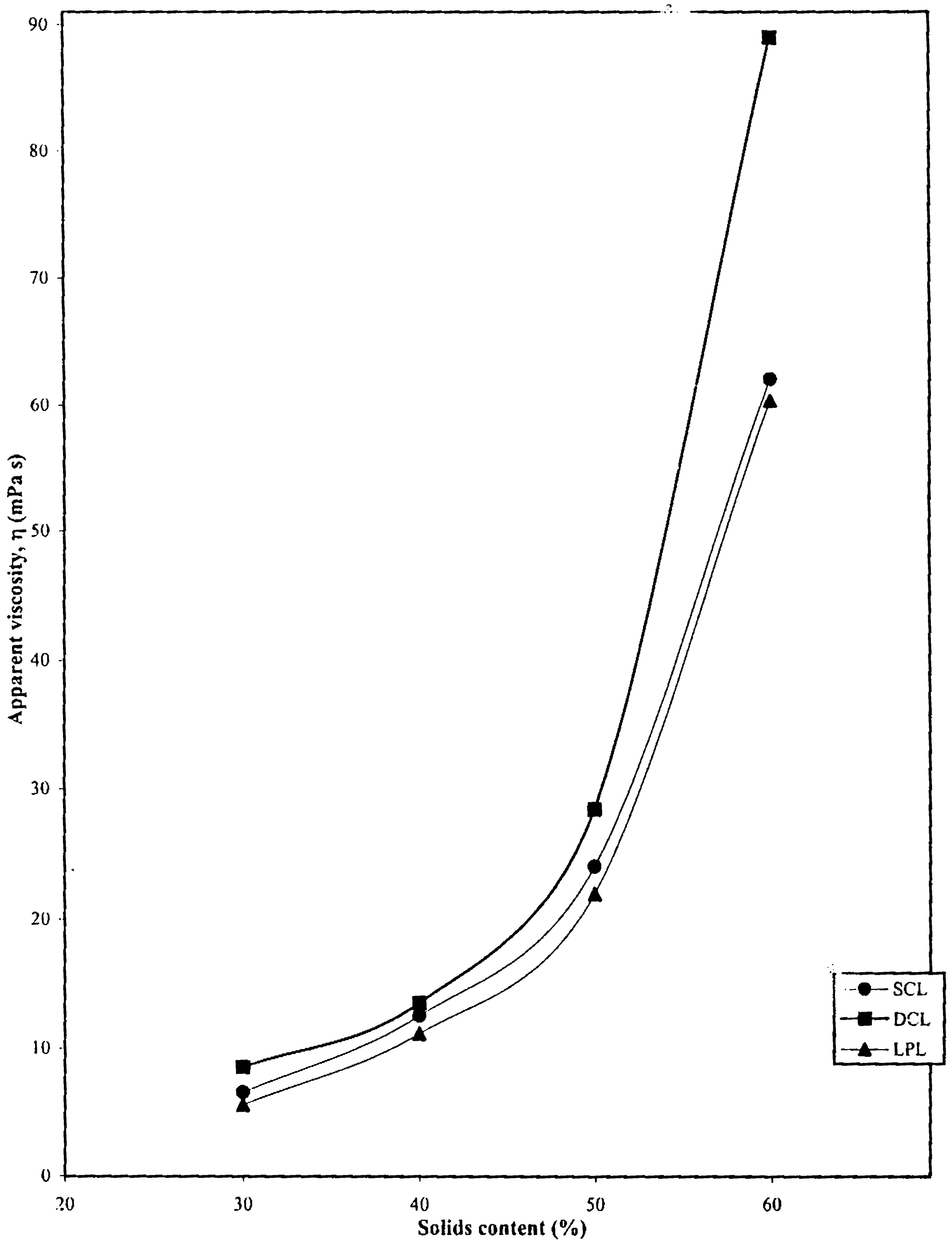


Fig 6.1. Effect of solids content on apparent viscosity of latices at 30°C.

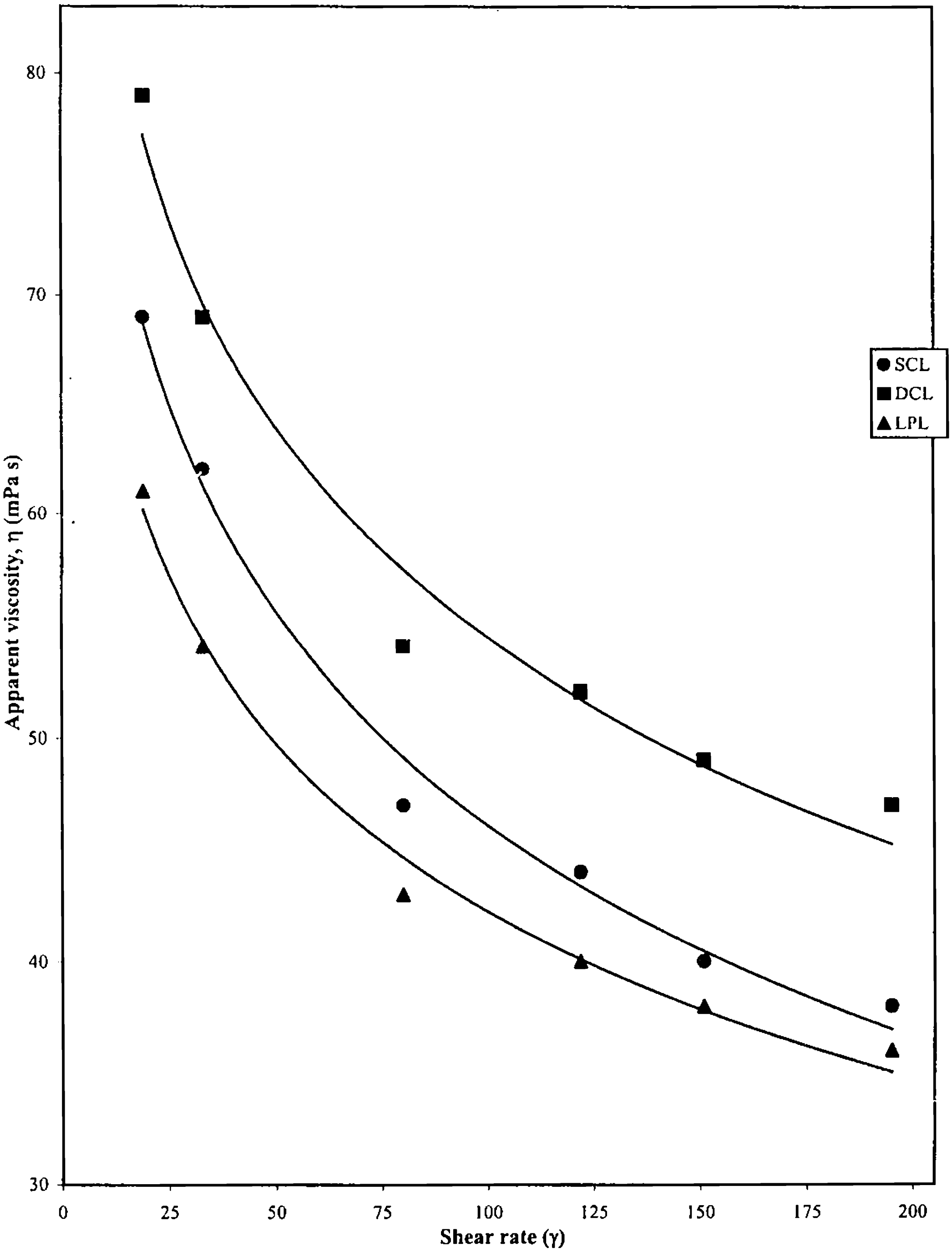


Fig 6.2. Effect of shear rate on apparent viscosity of latices at 30°C. (solids content 60%)

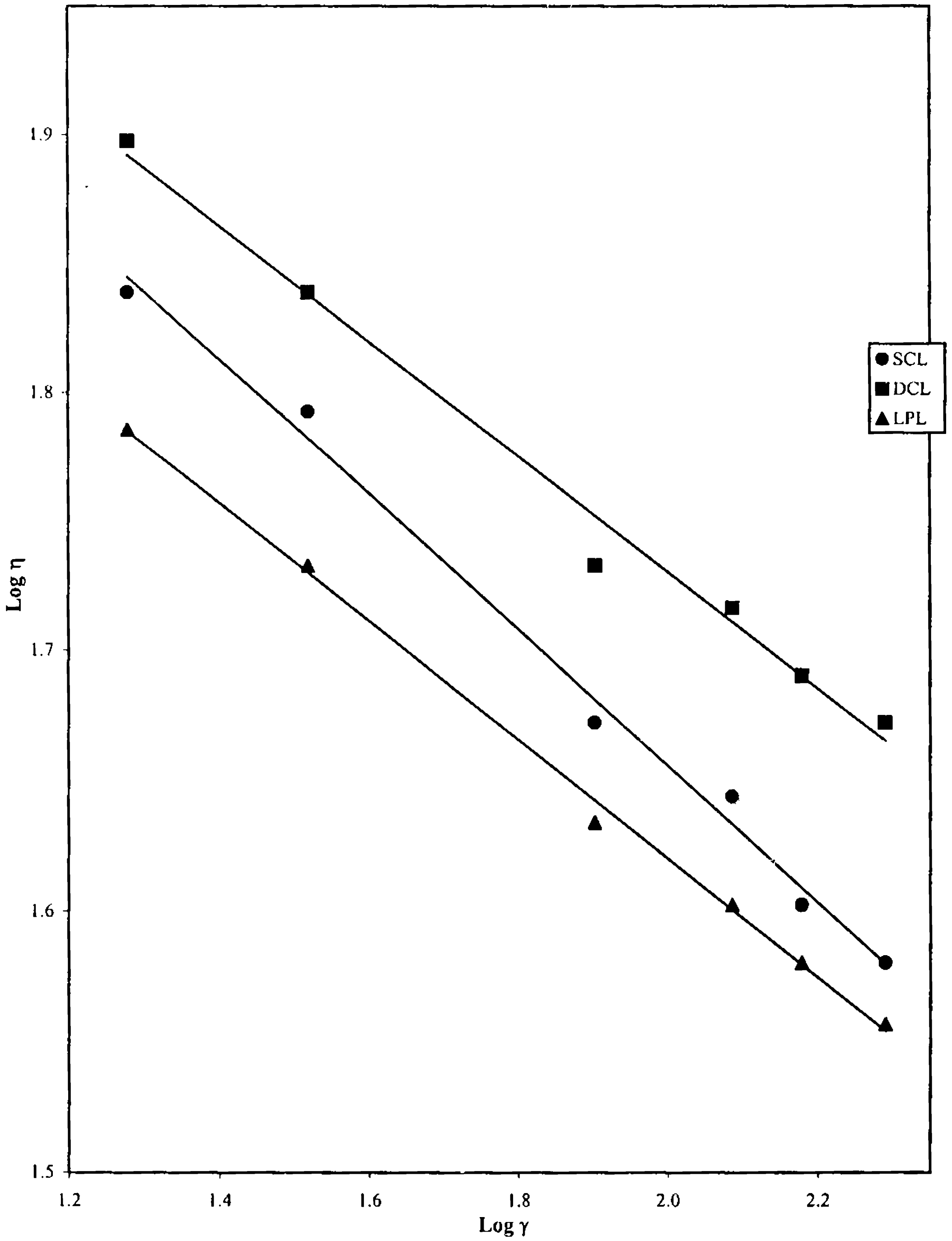


Fig 6.3. Log-log plot of variation of shear rate on apparent viscosity of latices at 30°C (solids content 60%).

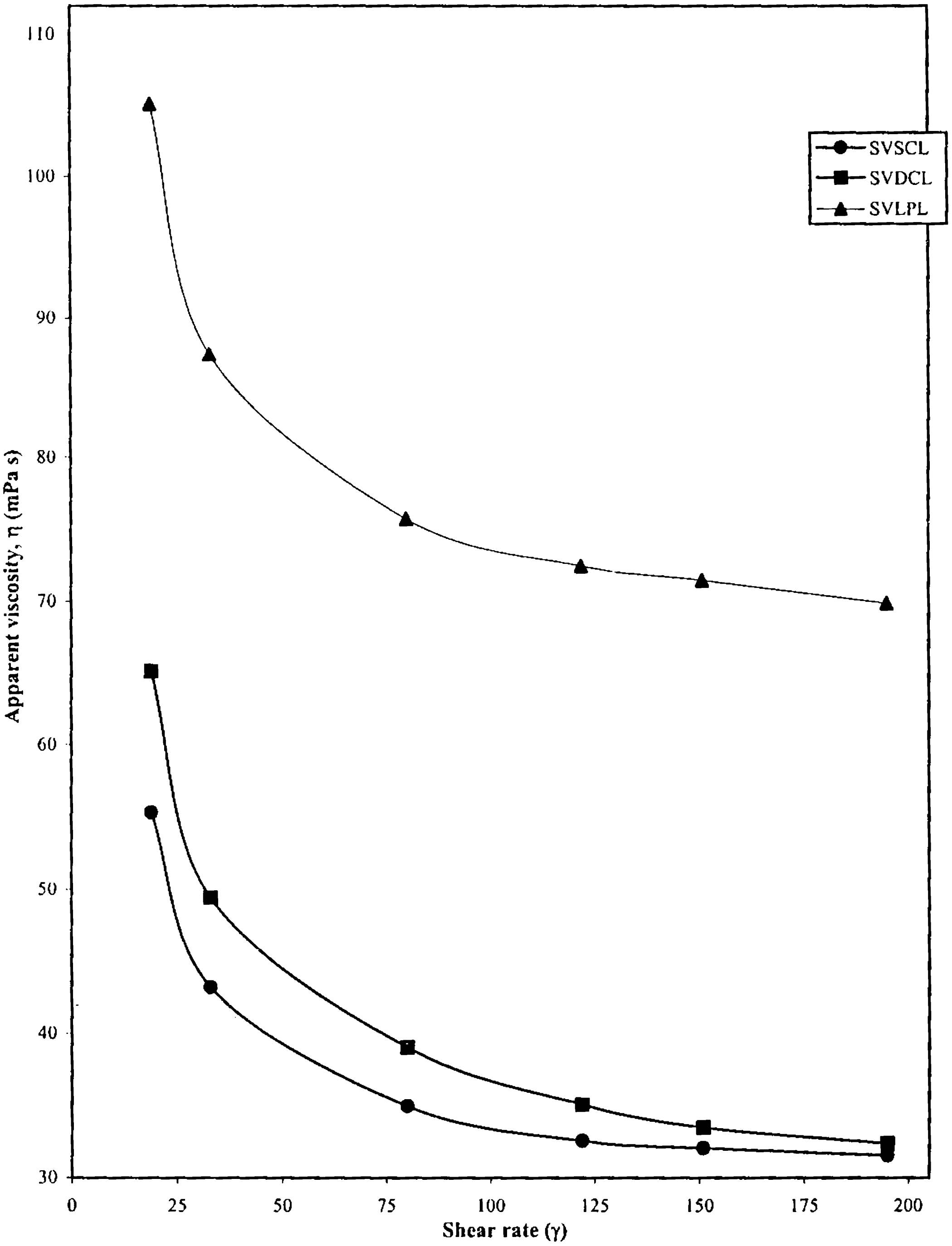


Fig 6.4. Effect of shear rate on apparent viscosity of sulphur prevulcanized latices at 30°C (solids content 58%).

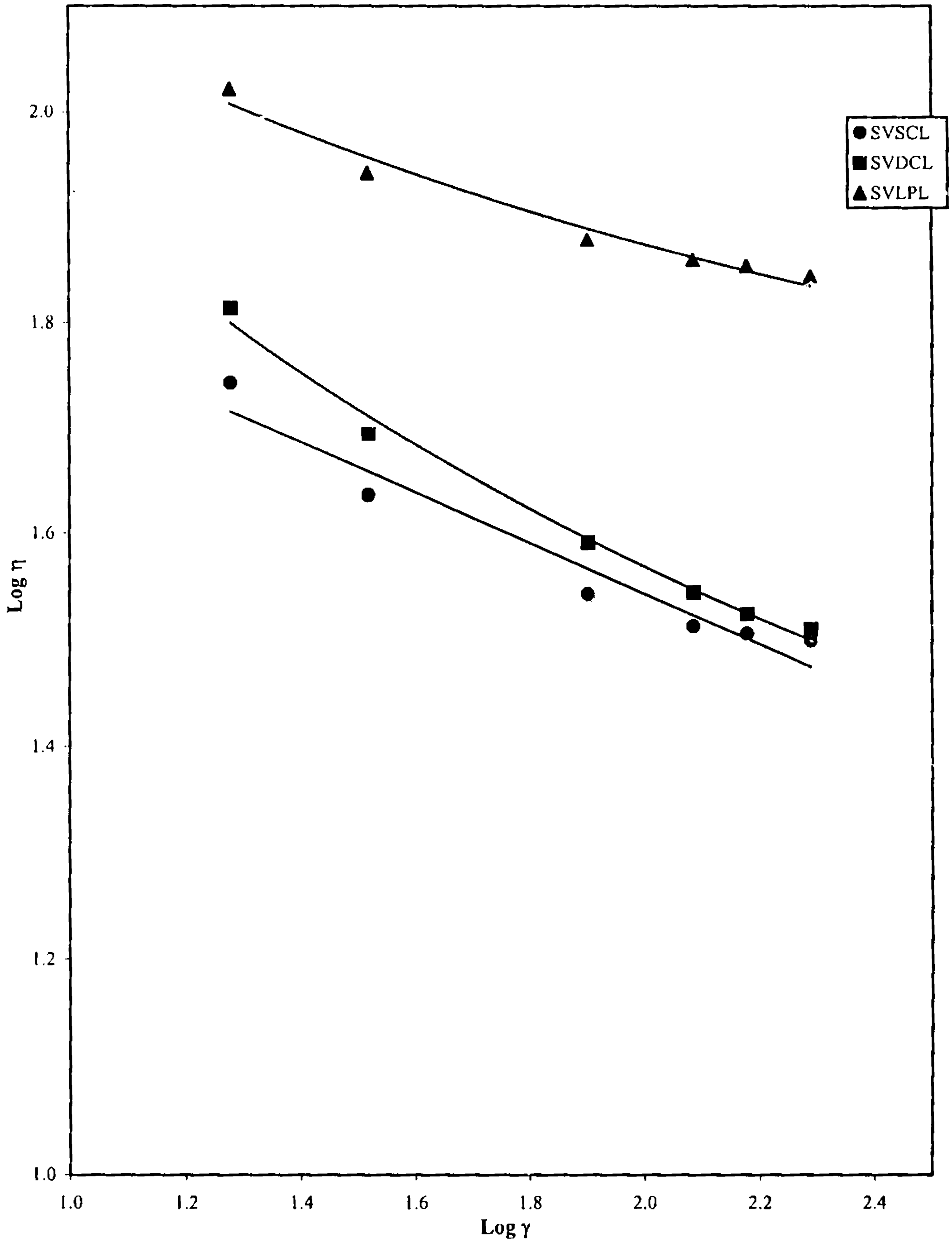


Fig 6.5. Log-log plot of variation of shear rate on apparent viscosity of sulphur prevulcanized latices at 30°C (solids content 58%).

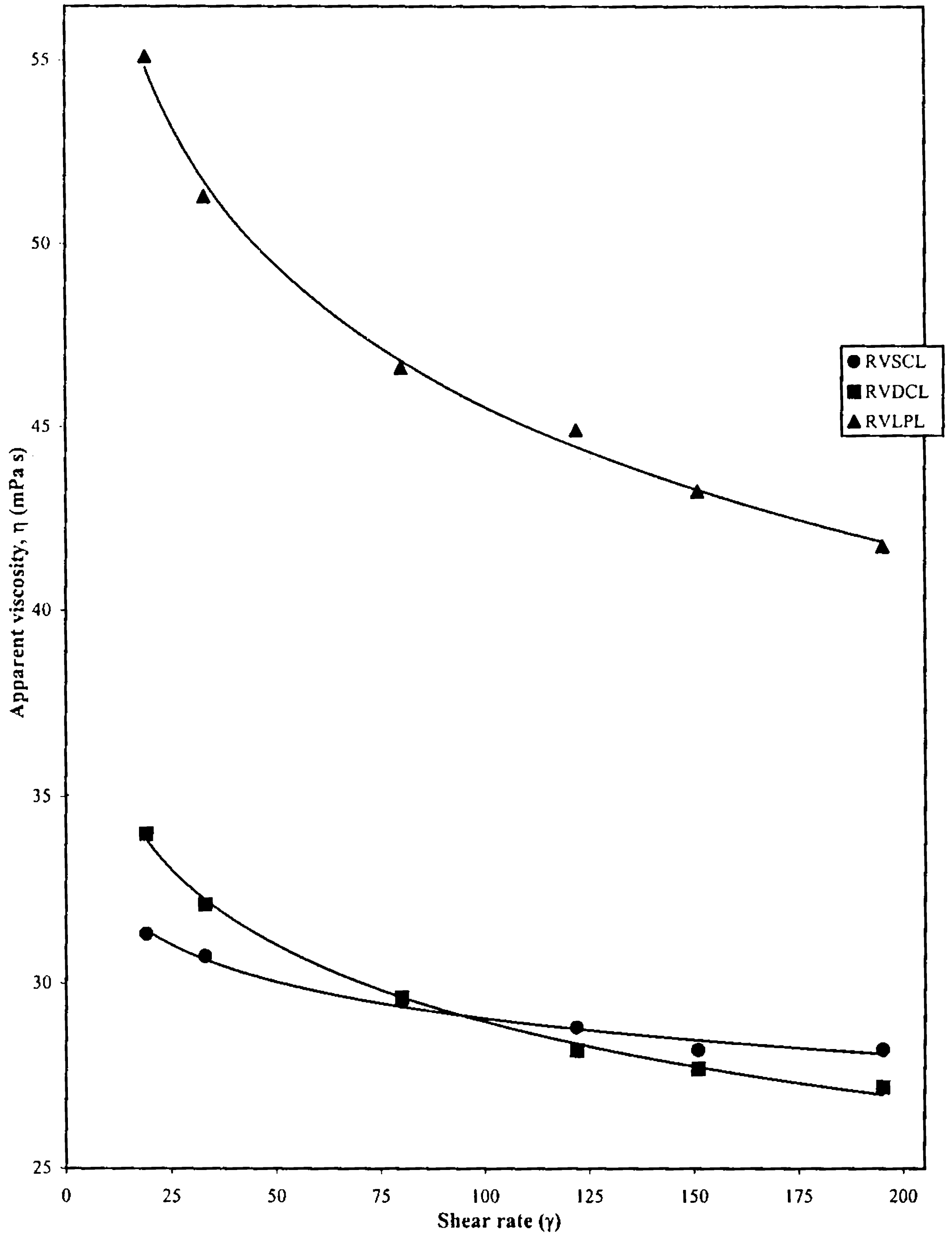


Fig 6.6. Effect of shear rate on apparent viscosity of radiation vulcanized latices at 30°C (solids content 52%).

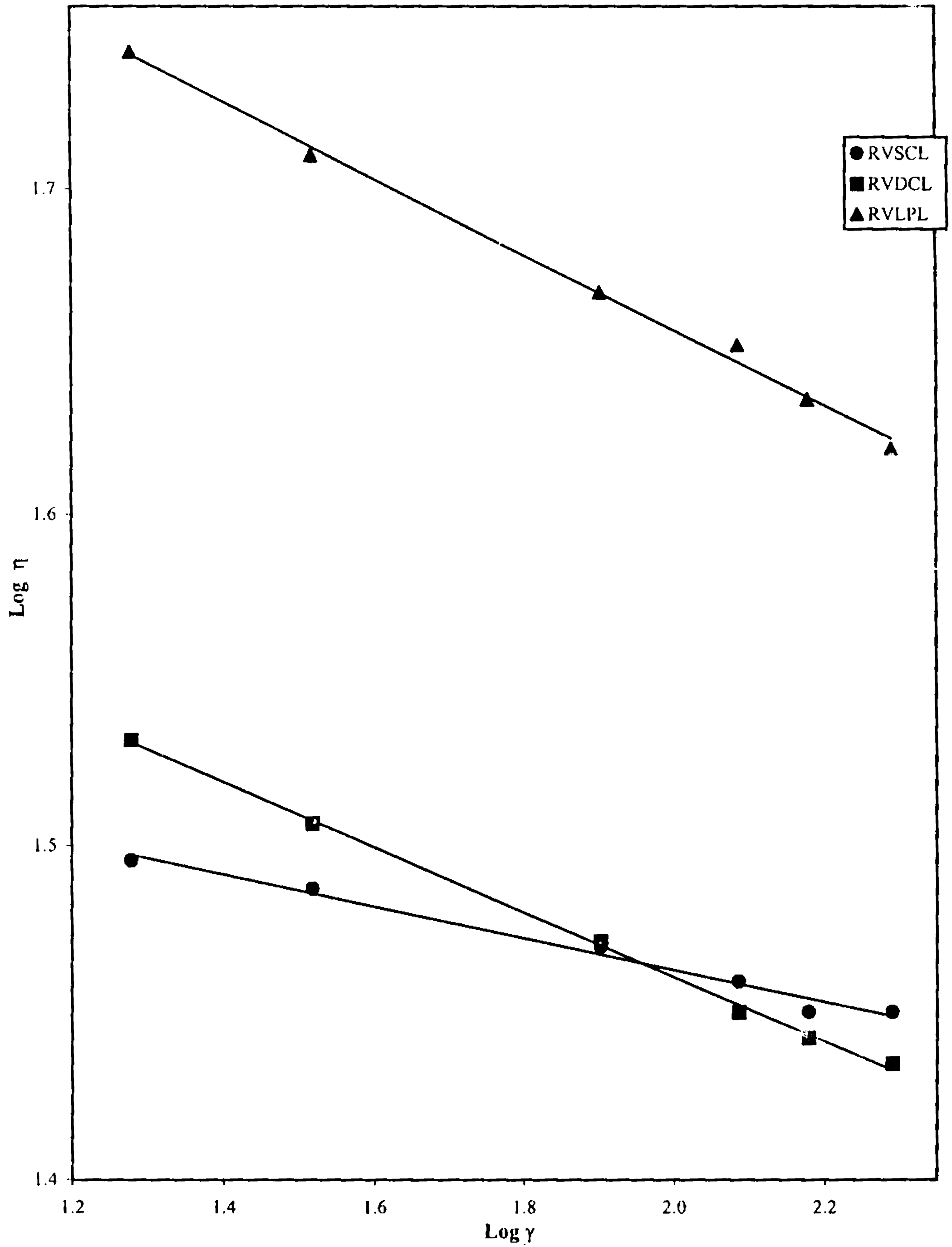


Fig 6.7. Log-log plot of variation of shear rate on apparent viscosity of radiation vulcanized latices at 30°C (solids content 52%).

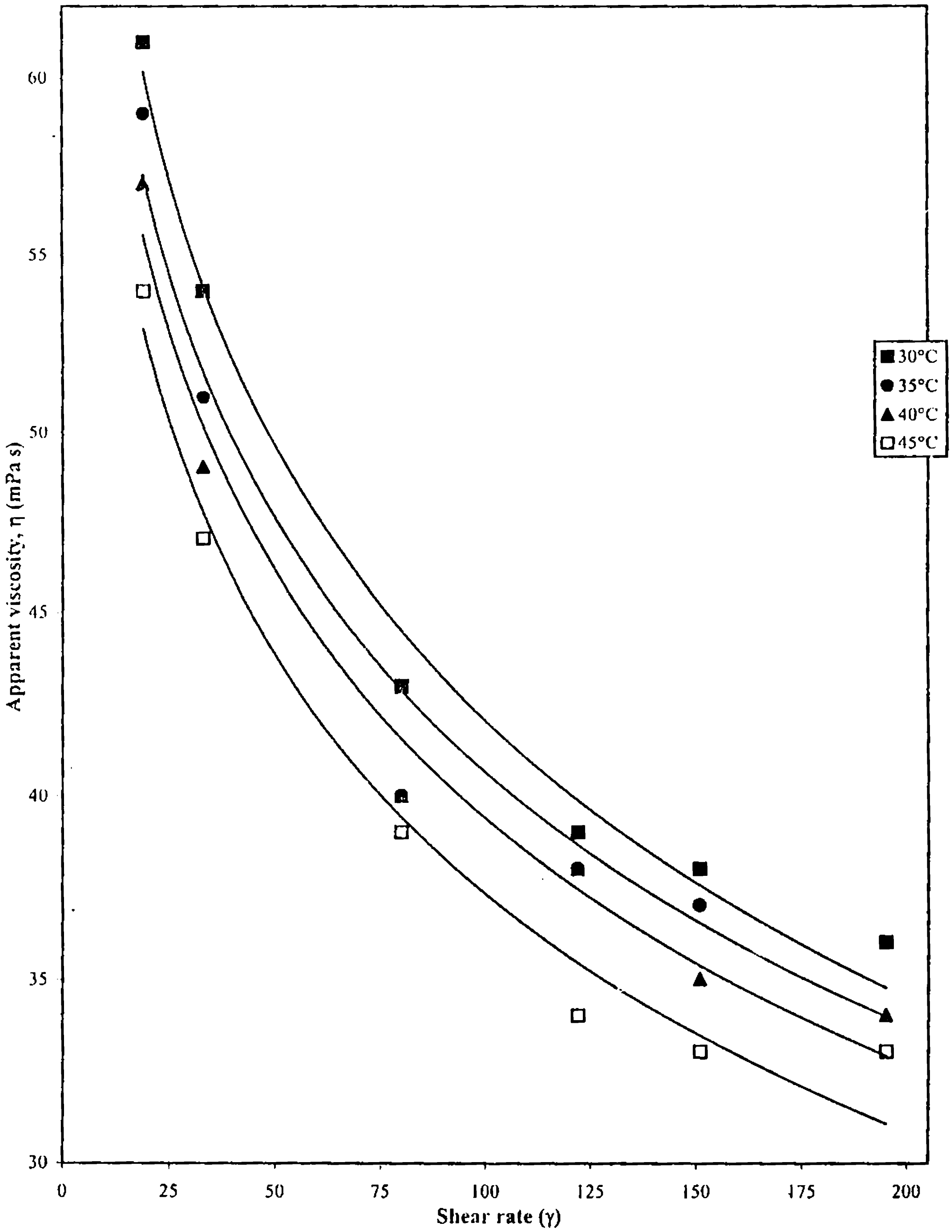


Fig 6.8. Effect of shear rate on apparent viscosity of LPL at different temperatures (solids content 60%).

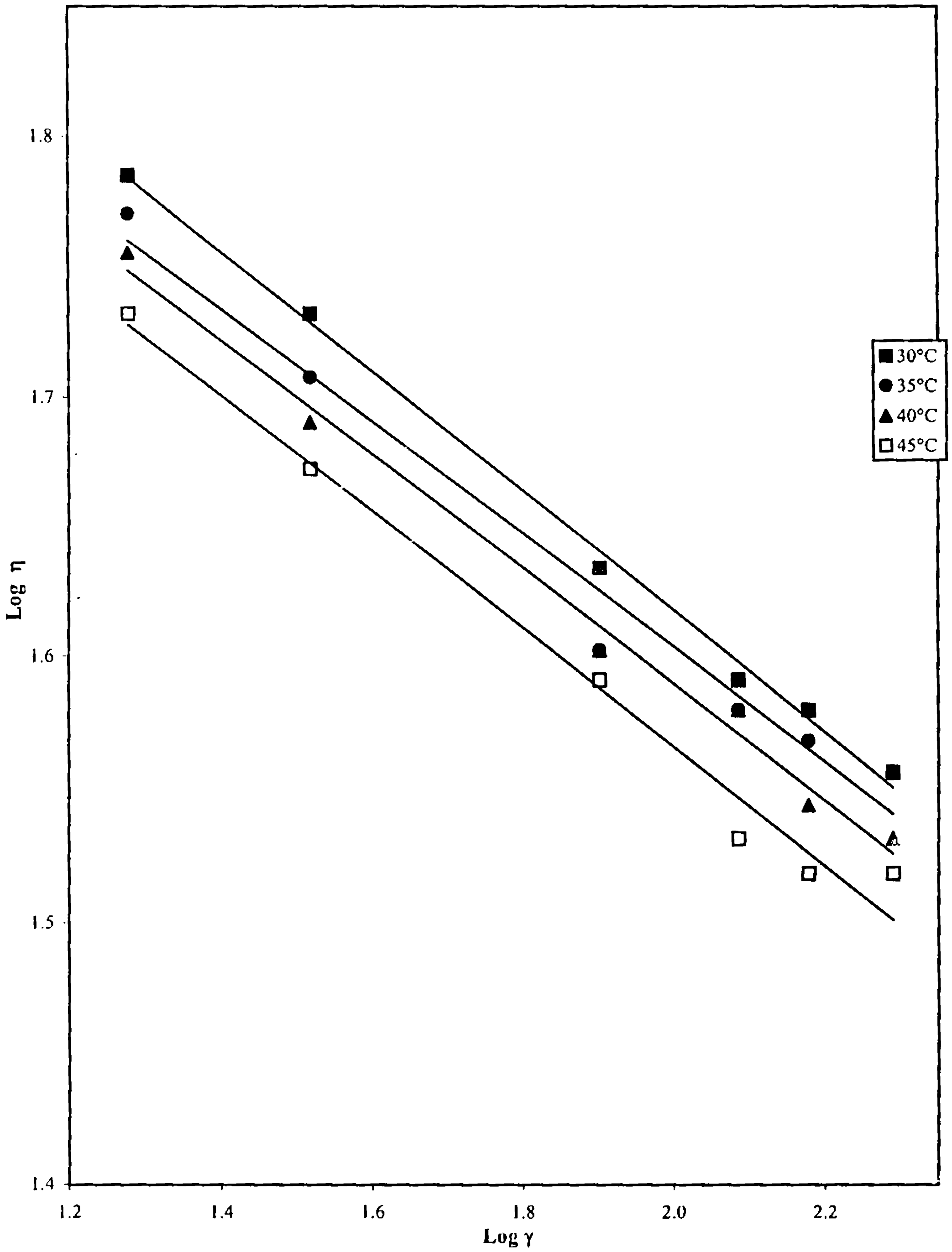


Fig 6.9. Log-log plot of variation of shear rate on apparent viscosity of LPL at different temperatures (solids content 60%).

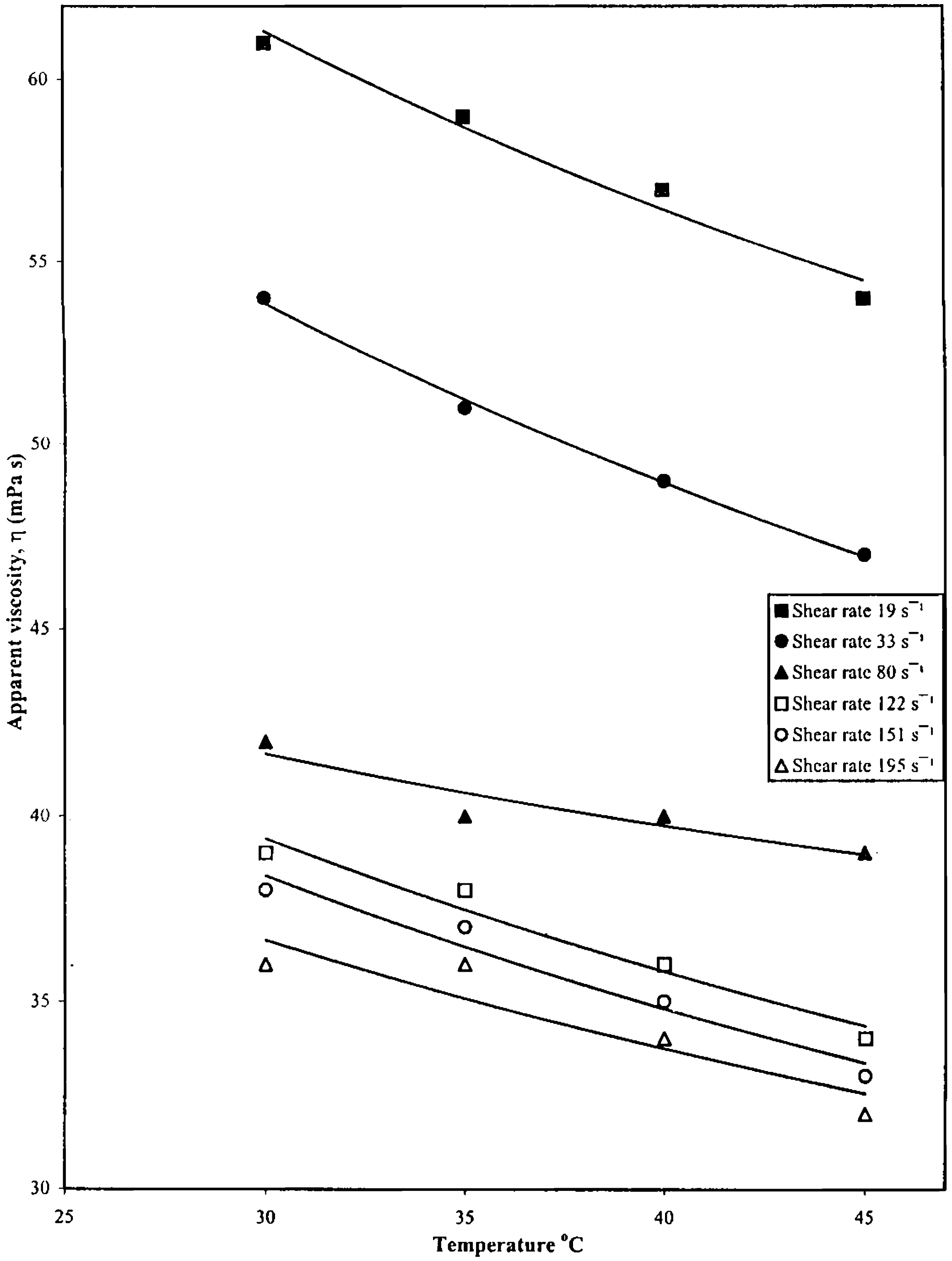


Fig 6.10. Effect of temperature on apparent viscosity of LPL at different shear rates (solids content 60%).

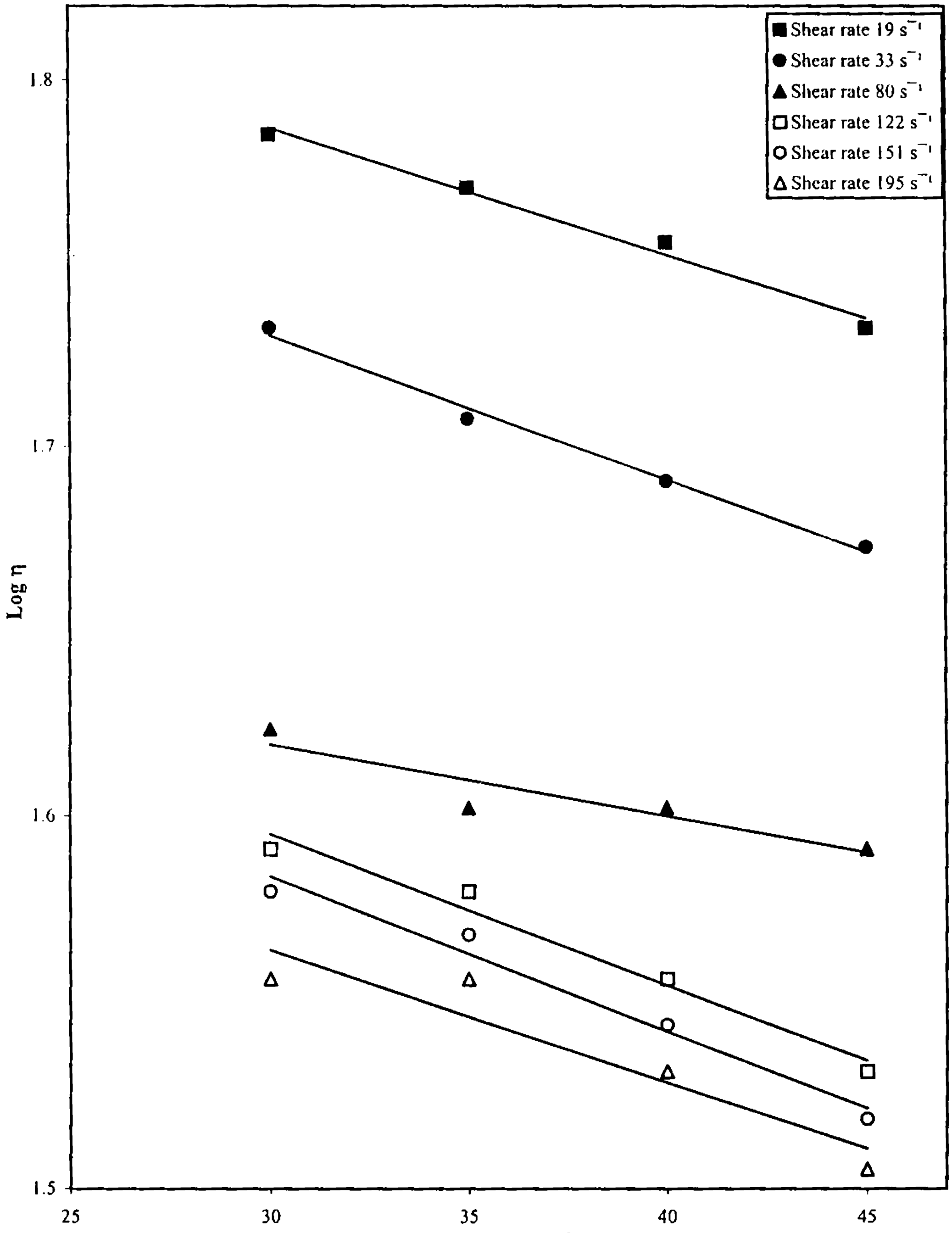


Fig 6.11. Effect of temperature on log (apparent viscosity) of LPL at different shear rates (solids content 60%).

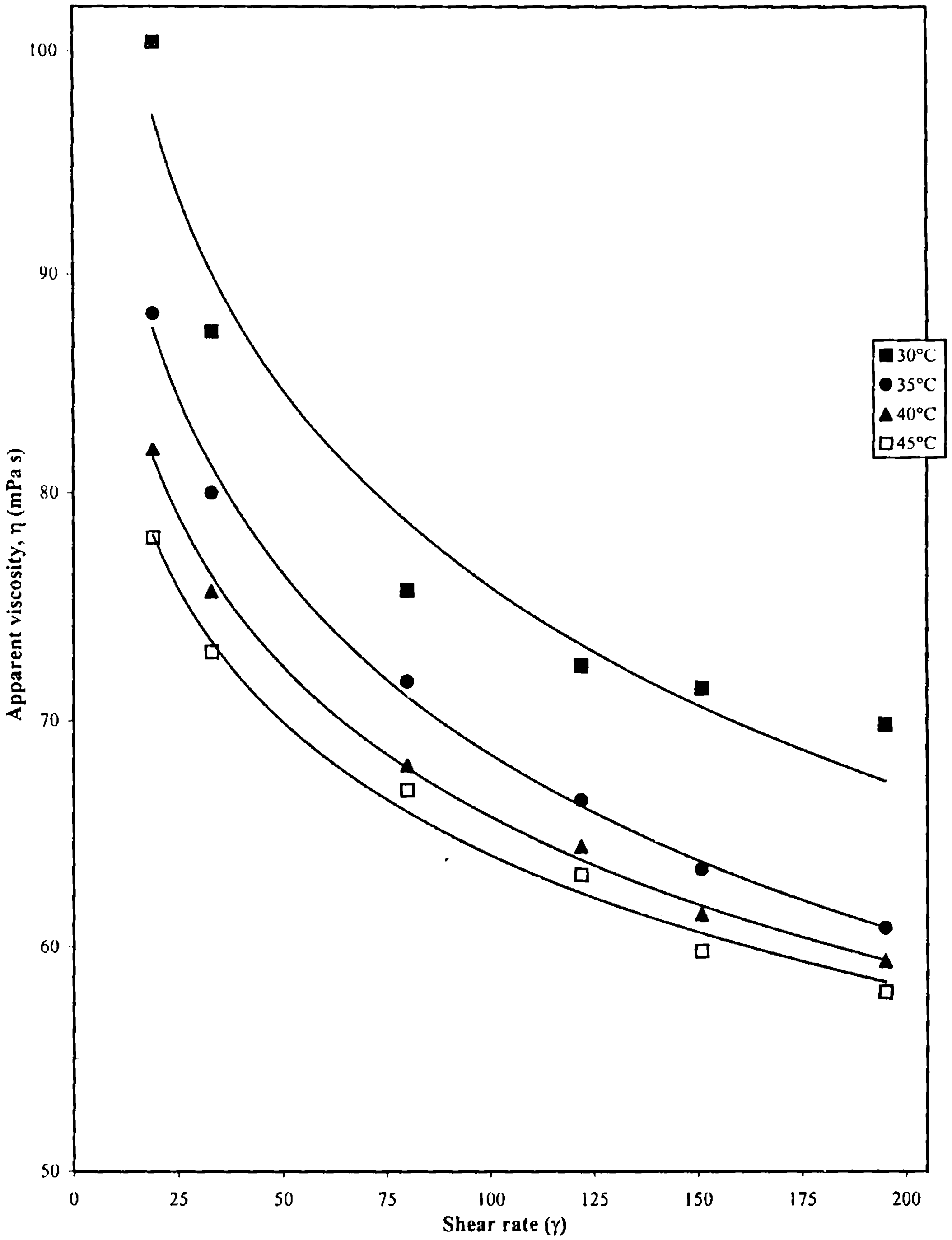


Fig 6.12. Effect of shear rate on apparent viscosity of sulphur prevulcanized LPL at different temperatures (solids content 57%).

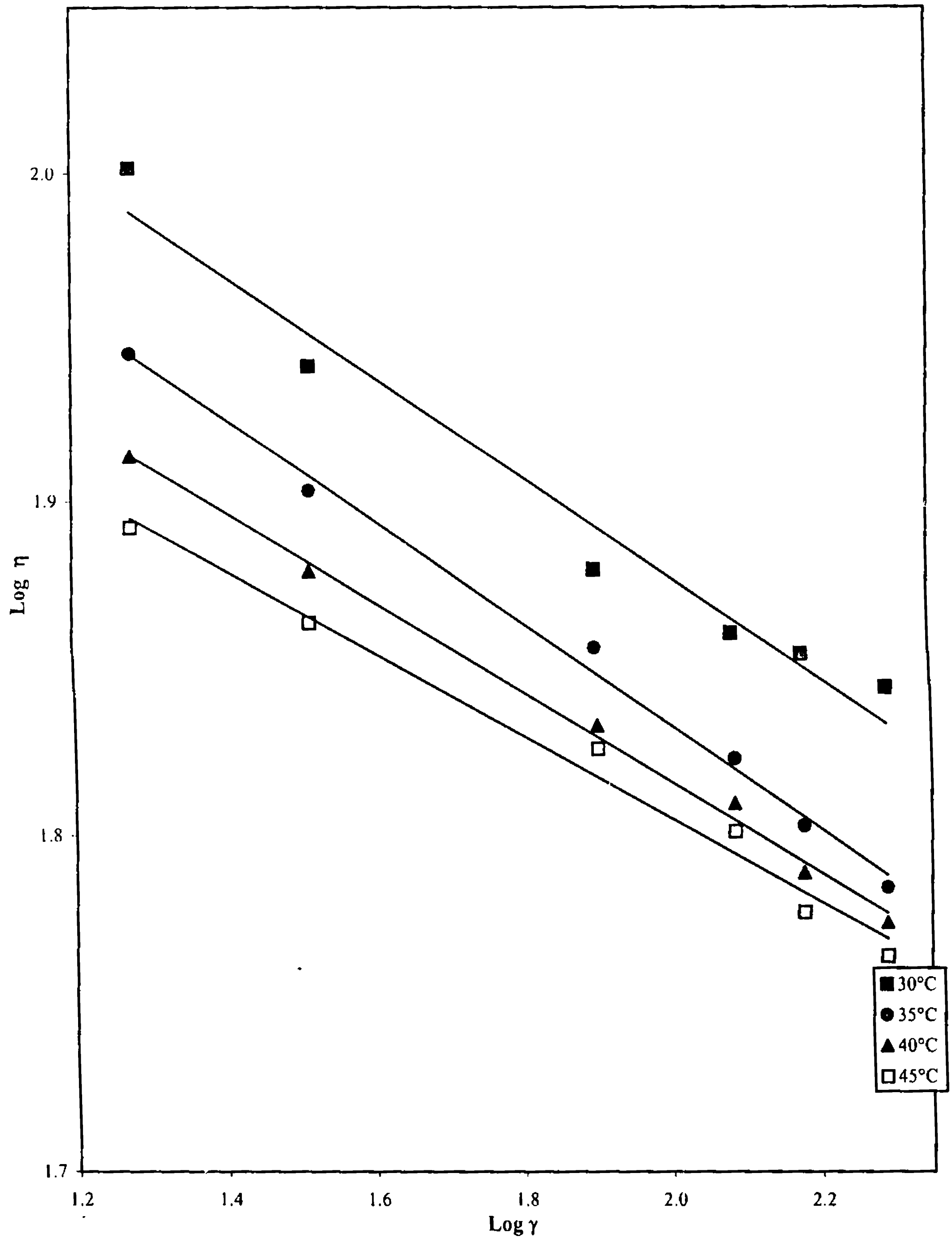


Fig 6.13. Log-log plot of variation of shear rate on apparent viscosity of sulphur prevulcanized LPL at different temperatures (solids content 57%).

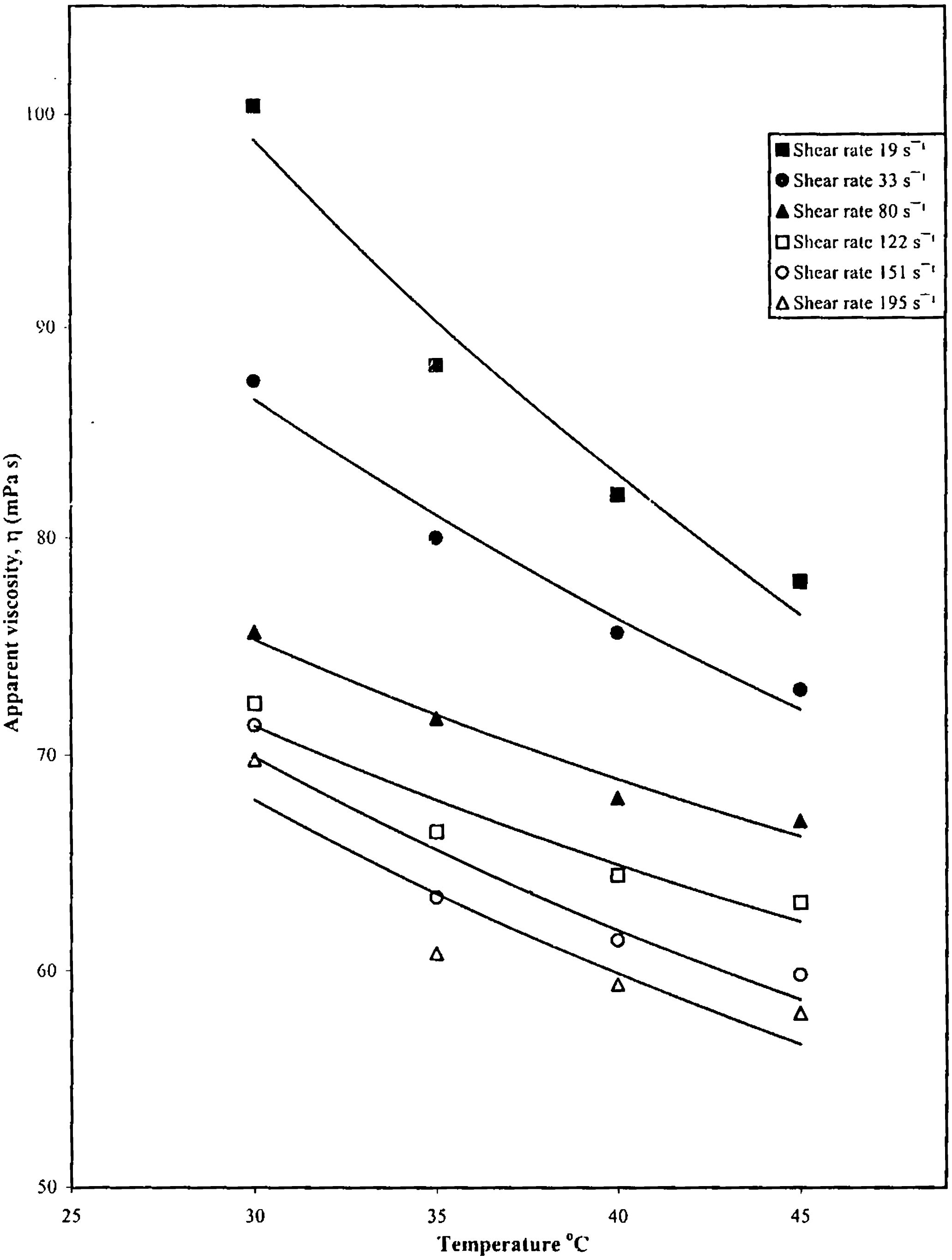


Fig 6.14. Effect of temperature on apparent viscosity of sulphur prevulcanized LPL at different shear rates (solids content 57%).

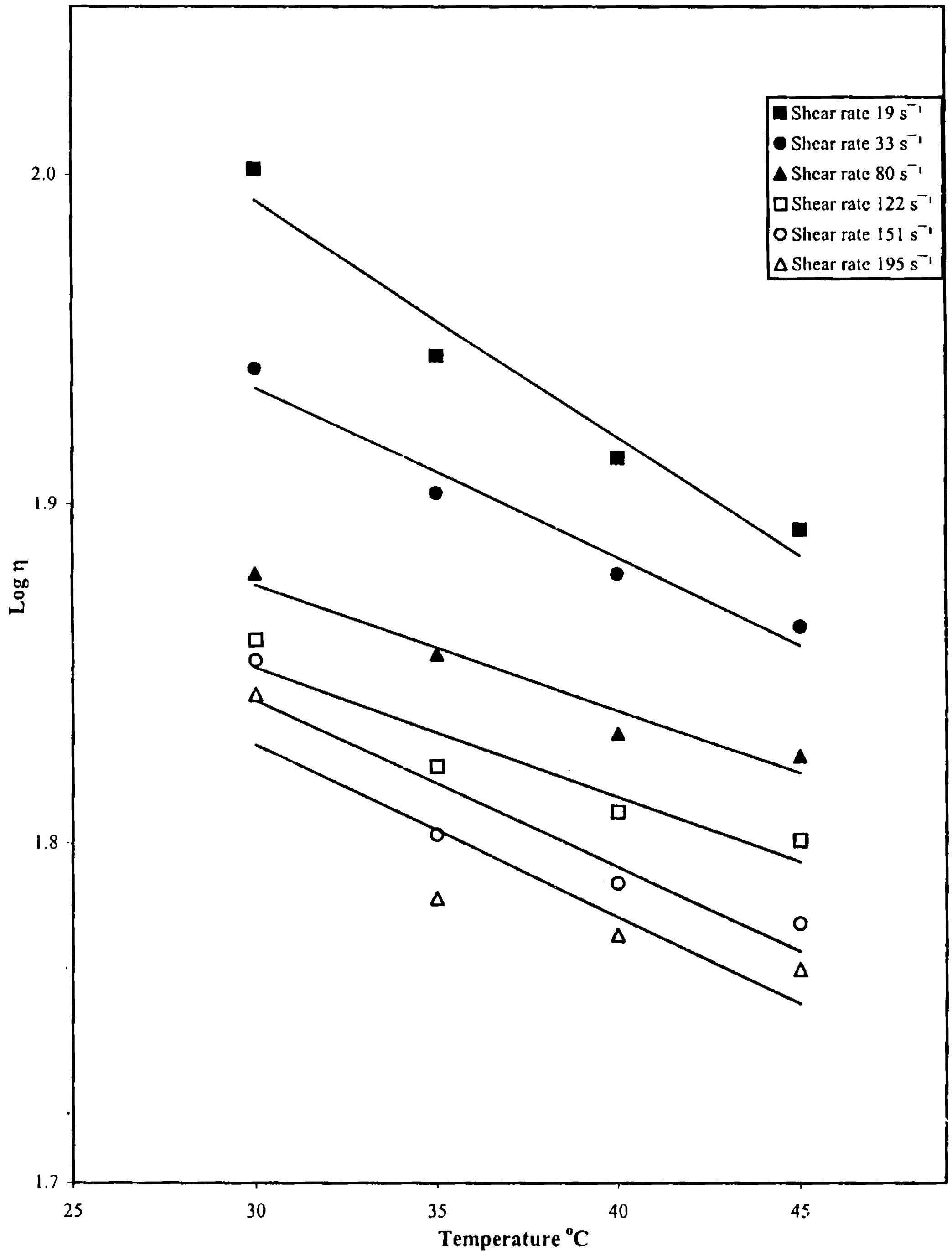


Fig 6.15. Effect of temperature on log (apparent viscosity) of sulphur prevulcanized LPL at different shear rates (solids content 57%).

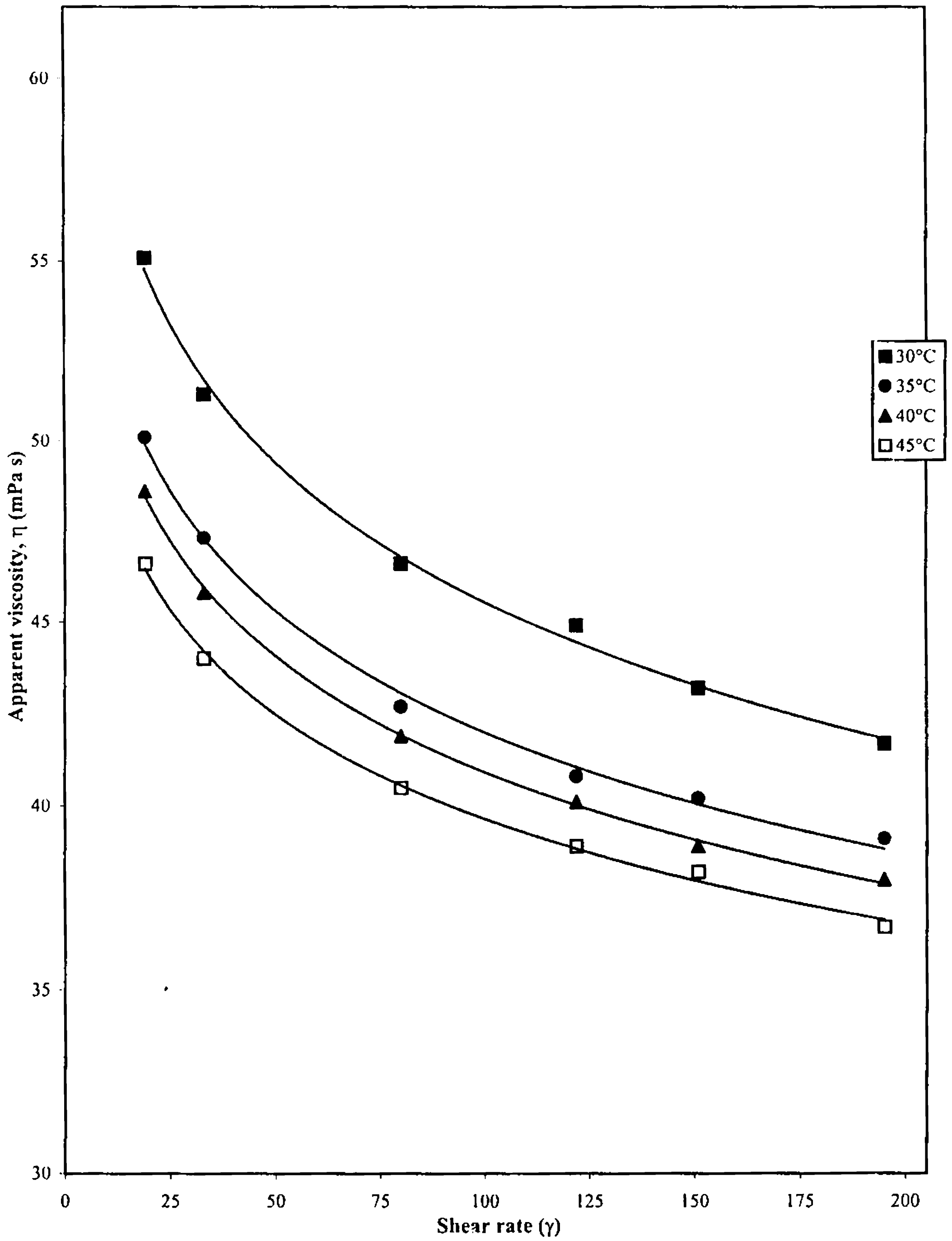


Fig 6.16. Effect of shear rate on apparent viscosity of radiation vulcanized LPL at different temperatures (solids content 52%).

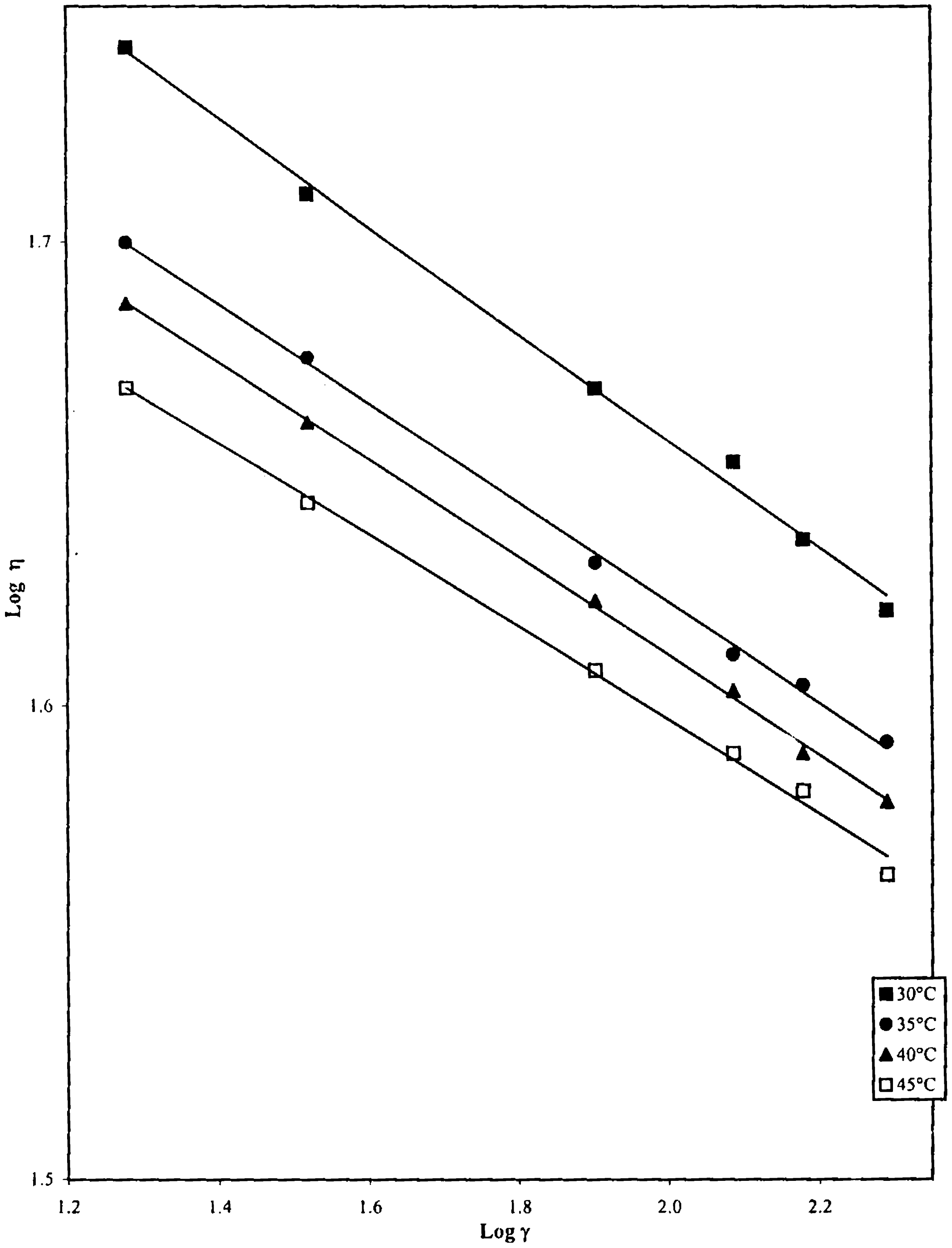


Fig 6.17. Log-log plot of variation of shear rate on apparent viscosity of radiation vulcanized LPL at different temperatures (solids content 52%).

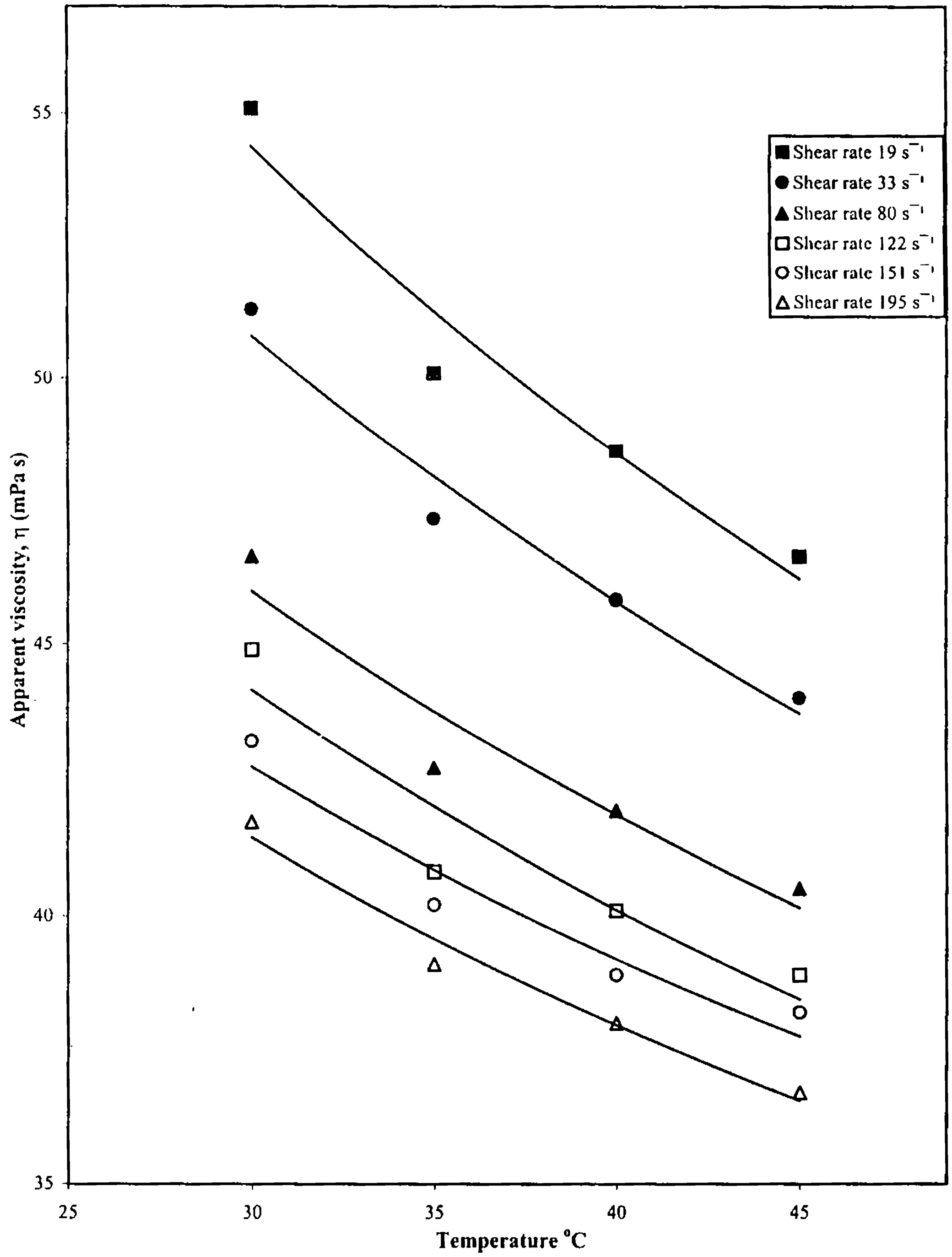


Fig 6.18. Effect of temperature on apparent viscosity of radiation vulcanized LPL at different shear rates (solids content 52%).

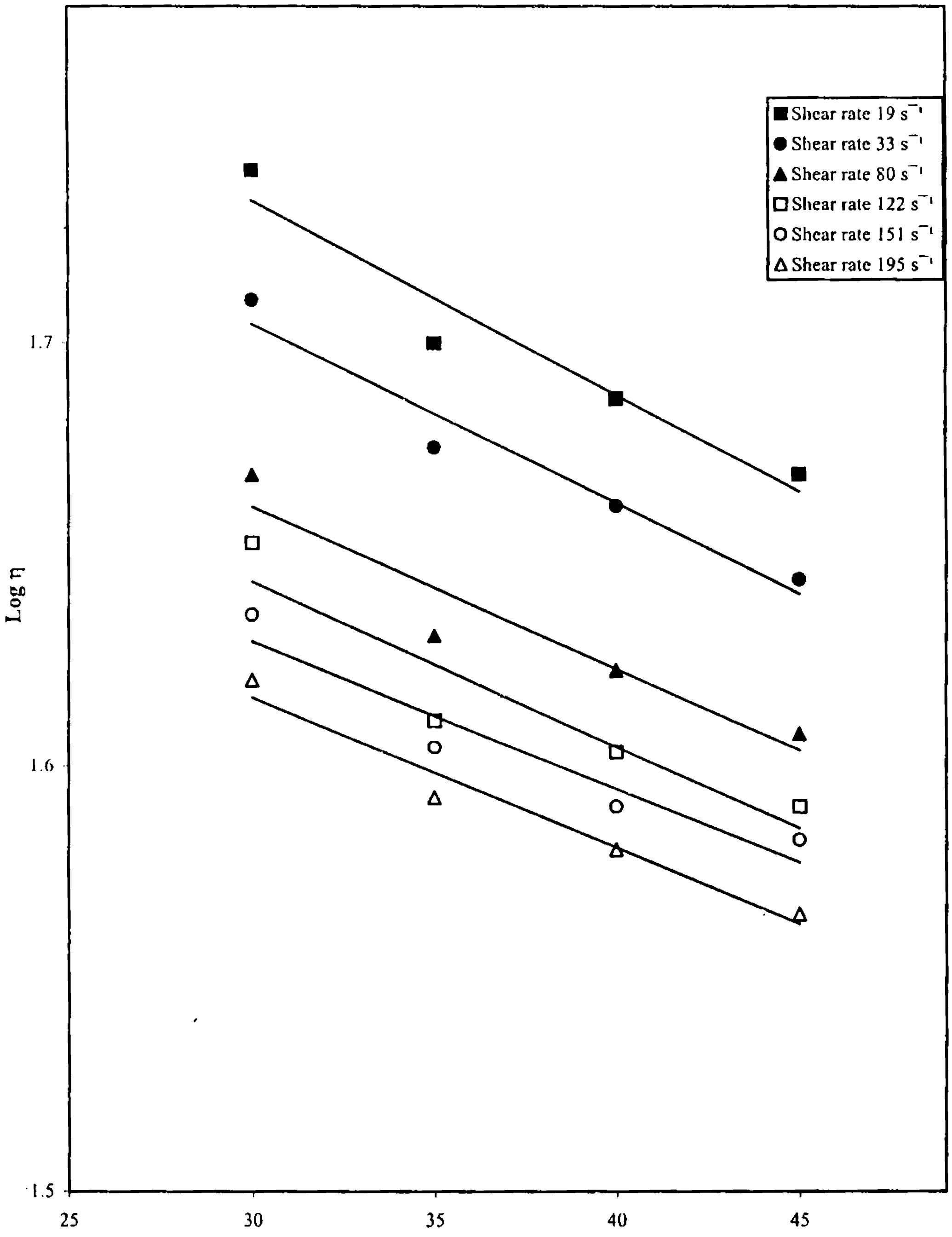


Fig 6.19. Effect of temperature on log (apparent viscosity) of radiation vulcanized LPL at different shear rates (solids content 60%).

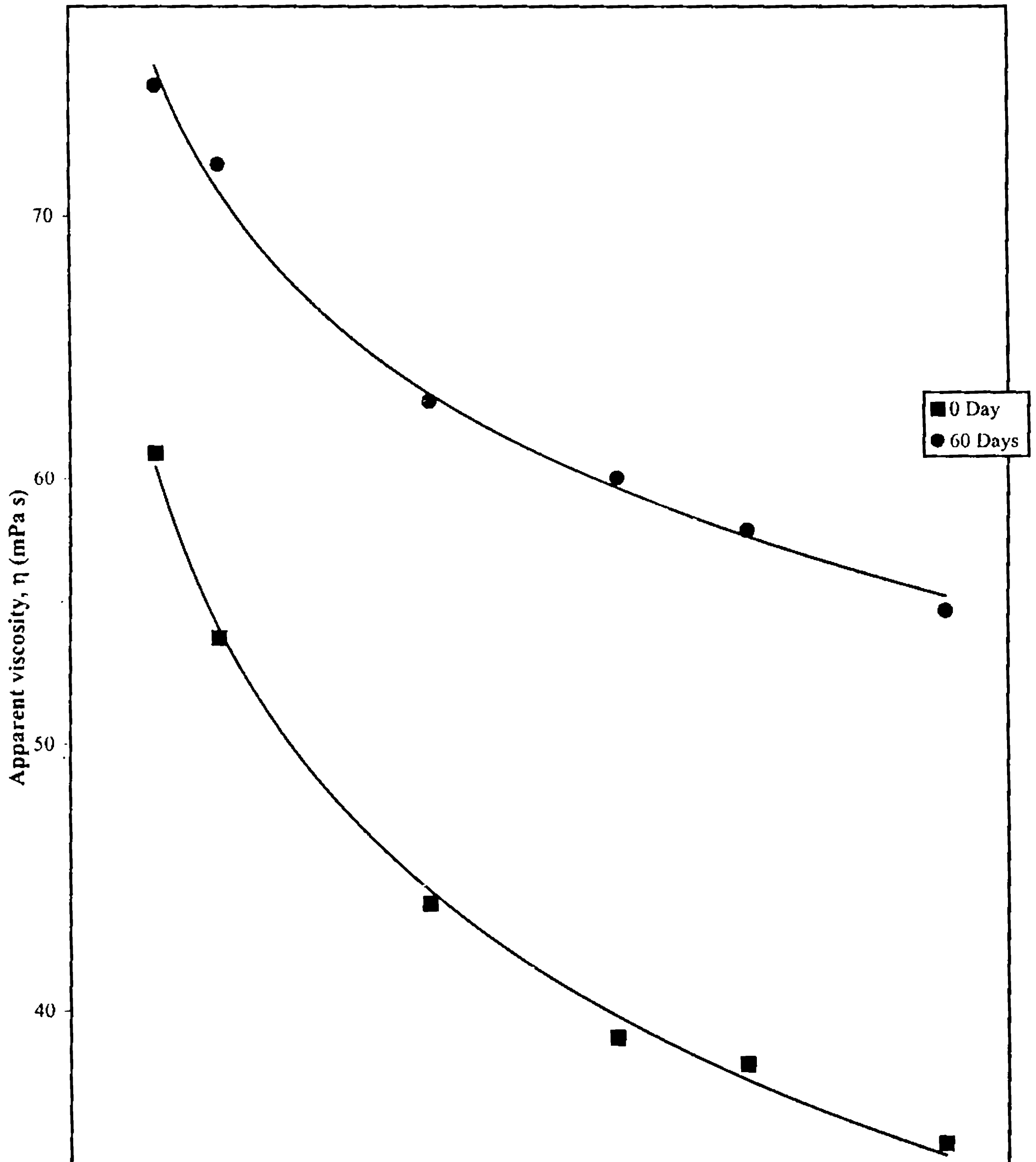


Fig 6.20. Effect of storage on apparent viscosity of LPL at different shear rates at 30°C (solids content 60%).

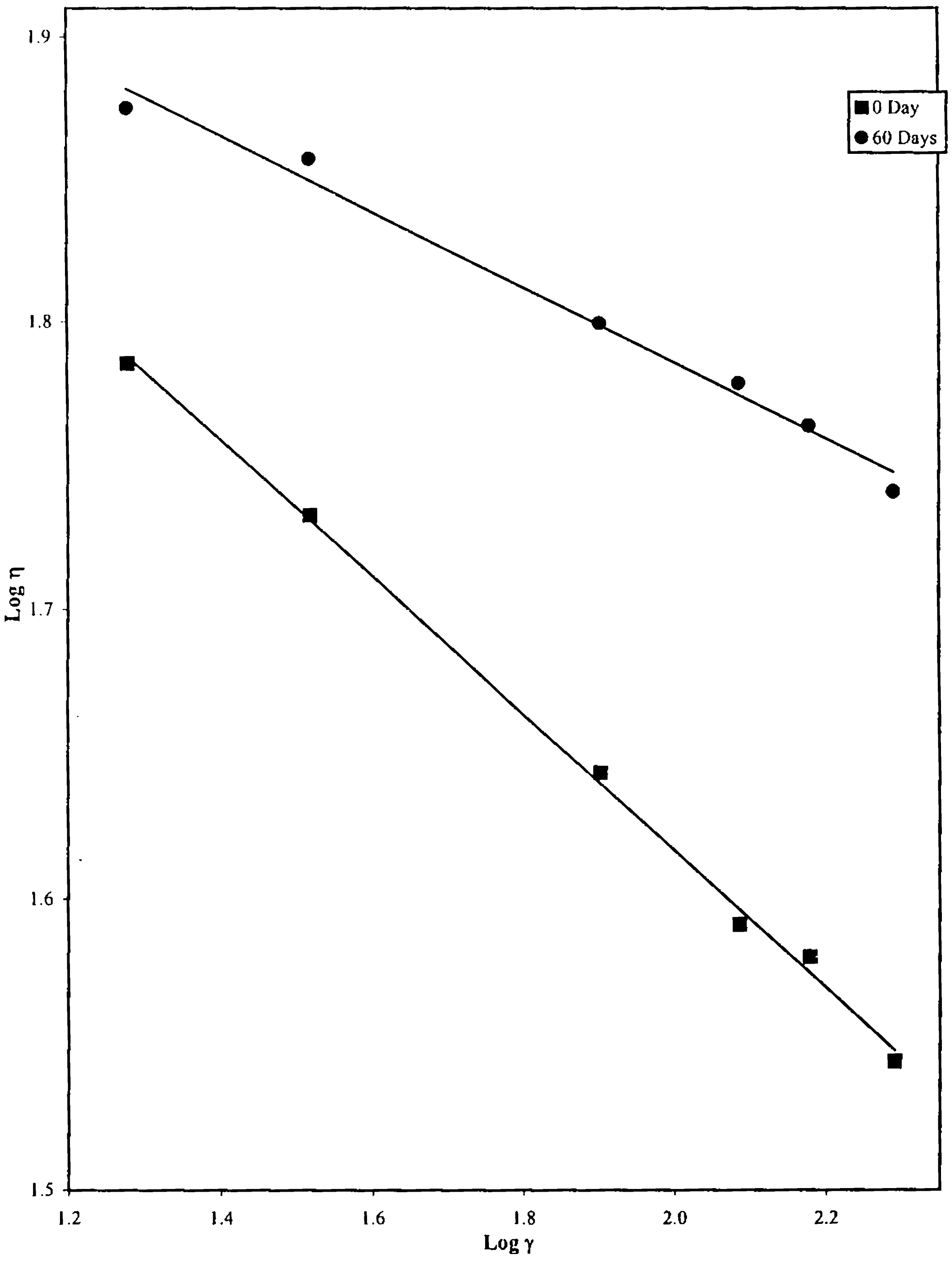


Fig 6.21. Log-log plot of shear rate on apparent viscosity at 30°C of LPL on storage (solids content 60%).

CHAPTER 7

APPLICATION OF LOW PROTEIN LATEX FOR LABORATORY SCALE PRODUCTION OF EXAMINATION GLOVES

Dipped latex products consume more than 50% of the concentrated natural latex produced in the world. Dipped latex products include various types of gloves, condoms, medical tubing's, balloons, rubber band etc. Major types among gloves are surgical gloves, examination gloves, house hold gloves, industrial gloves, electrician gloves etc. The fear of AIDS has caused drastic increase in the use of examination gloves. FDA has reported that during the period 1986–1995 the import of medical gloves to the United States increased from 1 billion to 15.4 billion(1). This drastic increase was mainly on the anticipation that latex gloves could prevent the transmission of Hepatitis B Virus (HBV) and Human Immunodeficiency Virus (HIV) and other blood-borne pathogens. Morris and Pendle(2) have reported that latex films can function on barriers to viruses. However, wide spread use of latex products has given rise to a new type of allergic reaction to the user (type I allergy) different from type IV allergy originating from the chemicals used in product manufacture. Nutter(3) has identified this new allergic reaction to be due to proteins in latex products. Out of the total proteins only a small fraction is extractable(4) and these extractable proteins (EP) cause allergic reactions is sensitized people. Protein allergic reactions are characterized by the formation of weals or flares at the contact site and in high sensitized persons fall in blood pressure, difficulty in breathing, speeding heart rate etc(5). FDA has also reported some causalities due to latex protein allergy(6). Convening two world conferences (Latex Protein Allergy : the present position, Amstardam 1993 and Latex Protein Allergy : the Latest Position, Paris 1995) is sufficient to bring out the importance of the problem. Health care workers are identified as a risk group for latex protein allergy(7,8).

Several Methods have been suggested to reduce the severity of the protein allergy problem. Important among them are leaching(9,10) and chlorination(11) of latex film. Latex films leached for long periods after storing for few days again show the presence of EP(4). This is believed to be due to the migration of EP from the interior layers or due to the breakdown of proteins on the surface of the film, which were not initially extractable. Further, long on line leaching is impractical. Chlorination is an effective method in reducing EP in latex films. However, at slightly higher concentration of chlorine, the gloves undergo yellowing and cracks are formed on the surface of the film, leading to reduction in tensile properties.

Low protein latex (LPL) is inherently low in EP and hence the chances of migration of proteins to the surface during storage of leached LPL films is low. This is important when the time interval between the production and use of examination gloves is considered.

This chapter describes the application of LPL in the laboratory scale production of examination gloves. Dipping studies were carried out in conventional sulphur cure system, followed by evaluation of technological properties and EP content in the films. The effect of storage on EP content of gloves also was evaluated. Comparison has also been made with gloves prepared from single centrifuged latex (SCL) and double centrifuged latex (DCL).

EXPERIMENTAL

From a batch of high ammonia preserved natural rubber latex, SCL was prepared by centrifugal concentration process. A portion of SCL was diluted with 1.6% aqueous ammonia solution and concentrated after 24h to get DCL. Another portion of SCL was mixed with aqueous polypropylene glycol (PPG) to the extent of 0.2% (dry weight) on the wet weight latex. It was diluted and concentrated as in the case DCL to get LPL.

The three types of latices were compounded in the conventional sulphur cure system, as per formulation given in Table 1. Latex compounds were matured for 24h, under constant slow speed stirring. Portions of compounded latices were diluted to the desired solids content. Viscosity of the latices were measured using Brookfield viscometer (spindle No.2). Using clean ceramic moulds, examination gloves were prepared by straight dipping process. Dipping conditions were standardized so that the gloves produced had thickness about 0.1mm. The gloves were vulcanized by heating in air at 100°C for 1h. Keeping the gloves on the moulds, they were leached for 5mins in water at room temp.

The gloves were tested to verify conformity with IS 13422:1992(9). The physical property requirements of examination gloves prepared from natural latex as per this Indian standard are given in Table 7.2. Physical properties of the gloves were measured as per IS 3400 (part 1):1987(10). The gloves were subjected to accelerated heat ageing studies at 70°C for 168h, as per IS 3400 (part 4):1987(11). Residual extractable protein content in the gloves were determined by the RRIM modified Lowry method(12). EP content of gloves were estimated after 3 months also, to evaluate the changes in EP content on storage. Gloves made from LPL have been compared with those made out of SCL and DCL.

RESULTS AND DISCUSSION

Effect of solids content of latex compound on viscosity

Figure 7.1 gives the variation of viscosity at room temperature of compounded and matured latices against solids content. At any solids content viscosity is in the order

DCL > SCL ~ LPL

The high viscosity of compounded DCL is mainly due to the reduced ionic concentration in the aqueous phase, due to the second stage of centrifugal concentration. For the three types of latex compounds, viscosity increase with solids content. This is in agreement with the results reported earlier(13,14). For the three latex compounds increase in viscosity against solids content is non-linear and is higher at higher solids contents. This is in agreement with previous reports on natural and synthetic lattices(15). The high viscosity of compounded DCL is mainly due to reduced ionic concentration in the aqueous phase due to second stage of centrifugal concentration. From the data it is further evident that the basic nature of the latex is not changed by compounding.

Even though the ionic concentration in the aqueous phase of DCL and LPL are similar, compounded LPL has viscosity, similar to that of compounded SCL. It is believed that the reduced protein content in LPL and the presence of PPG in it contribute to this behaviour.

Figure 7.2 shows the variation of log (viscosity) Vs solids content. The curves obtained are almost linear. Curves for compounded SCL and LPL almost coincide, while compounded DCL curve is different. Gorton(15) has reported that for different natural latex compounds at equal solids content, the log (viscosity) curves are almost coincident. Thus the deviation of compounded DCL is believed to be due to reduced ionic concentration in the aqueous phase.

Effect of solids content and viscosity on thickness of dry deposit in straight dipping

Figure 7.3 shows the variation of viscosity of compounded latices against thickness of deposit in straight dipping. It is observed that thickness varies linearly with log (viscosity). The behaviour of compounded SCL and LPL are almost identical, however, for a given viscosity compounded DCL gives higher thickness. It is believed that the higher viscosity and lower flow behaviour contribute to higher thickness.

Figure 7.4 shows the variation of thickness of dry deposit is straight dipping against solids content of compounded latices. It is observed that for the three compounded latices, the relation is almost linear. Compounded SCL and LPL give almost similar thickness while DCL has higher deposit thickness. The higher thickness of DCL films is attributed to higher compound viscosity.

Production of examination gloves with LPL

As per Indian standard specification(9), the minimum thickness of examination gloves is 0.1 mm. It has been reported that in making latex products by straight dipping, it is advisable to give two dips to reduce the chances pin holes(16). Hence two straight dips were employed.

From the data obtained in Figure 7.4 compounded SCL and LPL were prepared at 53% solids content and DCL at 50% solids content. After 24h maturation, examination gloves were prepared by two dips. After the first dip, the deposit was partially dried before second dip to avoid any problem in adhesion between the two deposits. The deposits were vulcanized at 100°C for 1h. By keeping the vulcanized gloves on the mould, they were leached in water for 5min. and dried at 70°C for 0.5h.

Physical properties of examination gloves

The gloves were tested to assess conformity to IS 13422:1992. Results obtained are given in Table 7.3. The results obtained indicate that the three types of gloves conform to Indian standards.

Extractable protein content in examination gloves

The residual extractable protein content in the three types of gloves were estimated. The results obtained are given in Table 7.4. It is observed that EP content in LPL gloves are very low compared to others.

Effect of storage on EP content in examination gloves

Gloves were kept at room temperature in sealed polythene covers for 3 months. The EP content in the gloves were evaluated. The results obtained are given in Table 7.5. The results indicate that increase in EP content in gloves made out of LPL is very small.

CONCLUSIONS

- The data obtained from the study indicate that LPL can be used for the production of examination gloves.
- Physical properties of gloves meet Indian standard specifications for examination gloves.
- Extractable protein content in the LPL glove is very low compared to SCL and DCL gloves.
- Storage of LPL gloves is accompanied by only a small increase in EP.
- Conditions are standardized for production of examination gloves from LPL.

REFERENCES

1. J.Stigi and A.Lowery. Guidance for Medical Gloves: A Workshop Manual, US Department of Health and Human services, Public Health service, Food and Drug Administration, Meryland, Chapter-1(1996).
2. M.D.Morris and T.D.Pendle. *Rubber World* **208** (3), 19 (1993).
3. A.F.Nutter. *Brit J.Dermatol.* **101**, 597(1979).
4. B.G.Audley and S.J.Dalrymple, Proc. Seminar on Latex Processing Technology: Understanding its Science. Hertford p-6 (1991).
5. S.J.Dalrymple and B.G.Audley. Proc, Seminar on Latex Technology and Processing. Hertford p-63 (1992).
6. S.F.Dillard and M.A.Mac Collum. Proc. International Latex Conference: Sensitivity to Latex in Medical Devices. Baltimore, paper 11 (1992).
7. K.Turjanmaa and T.Reunala. International Latex Conference: Sensitivity to Latex in Medical Devices. Baltimore, paper 17 (1992).
8. K.Turjammaa. Latex Protein Allergy: the latest position. International Conference. Paris p-7, (1995).
9. Is 13422:1992. Indian standard: Disposable Surgical Rubber Gloves-Specification. Bureau of Indian standards, New Delhi (1992).
10. IS 3400 (part 1):1987. Methods of that for vulcanized rubbers: Tensile stress-strain properties (second revision).
11. IS 3400 (part 4):1987. Methods of test for vulcanized rubbers; Accelerated ageing (second revision).
12. F.Yusof and H.Y.Yeang. *J.nat. Rub. Res.* **7**, 206(1992).
13. E.W.Madge. *Rubber Chem. Technol.* **8**,501 (1935).
14. H.F.Smith. *J.Rubber Res. Inst. Malaya,* **11**,44 (1941).
15. A.D.T.Gorton. *J.Rubber Res. Inst. Malaya,* **20**,27 (1967).
16. D.C.Blackley, High polymer latices Vol.2 Chapter IX, Maclarum & Sons Ltd., London (1966).

TABLE 7.1

Formation of latex compounded for preparing examination gloves

Ingredient	*Dry weight*	*Wet weight*
60% Natural latex	100	160.7
10% Potassium hydroxide	0.1	1.0
50% zincdiethyl ditho carbanate	1.0	2.0
50% sulphur	1.75	3.5
50%zinc oxide	0.25	0.5

TABLE 7.2

Physical requirements of examination gloves made out of natural latex, as per IS 13422:1992

Property	*Before ageing*	*After ageing*
Tensile strength (MPG) min.	24	18
Modulus, M 500 (MPG) max.	5.5	Not specified
Elongation at break (%) min.	750	560

TABLE 7.3

Physical properties of examination gloves

Property	*SCL gloves*		*DCL gloves*		*LPL gloves*	
	Before ageing	*After ageing*	*Before ageing*	*After ageing*	*Before ageing*	*After ageing*
Tensile Strength (MPa)	31.45	27.41	27.12	22.34	30.52	25.18
Modulus M 500 (Mpa)	1.95	1.65	1.78	1.4	1.98	1.56
Elongation break	1264	943	1090	761	1276	902
Thickness (mm)	0.116	—	0.106	—	0.108	—

TABLE 7.4

Extractable protein content in the examination gloves

Glove made from	*E P content (mg/kg)*
SCL	560.4
DCL	265.3
LPL	12.4

TABLE 7.5

Effect of storage on EP content in the examination gloves

Glove made from	*EP content (mg/kg)*
SCL	600.8
DCL	298.0
LPL	16.6

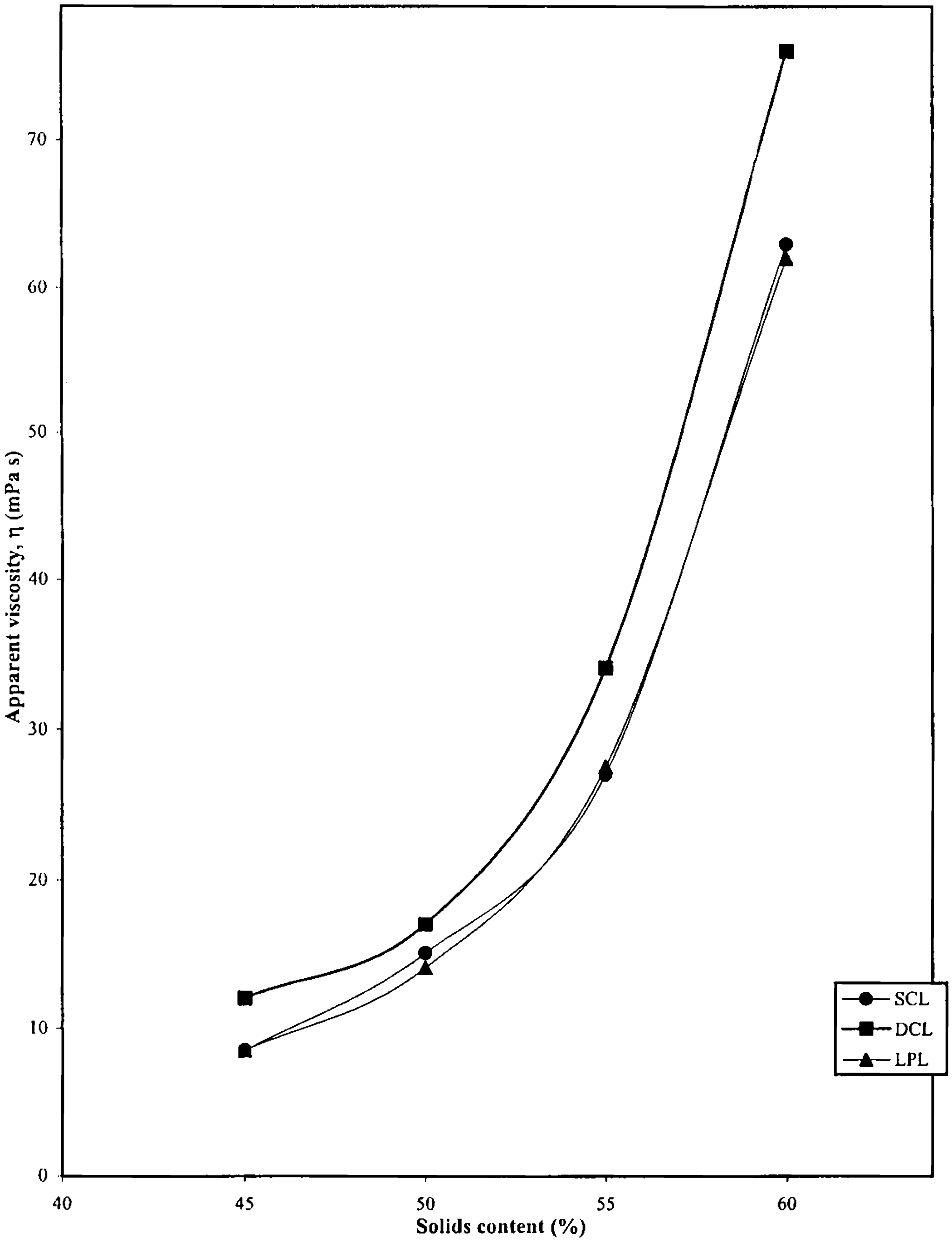


Fig 7.1. Effect of solids content on apparent viscosity of compounted latices at 30°C.

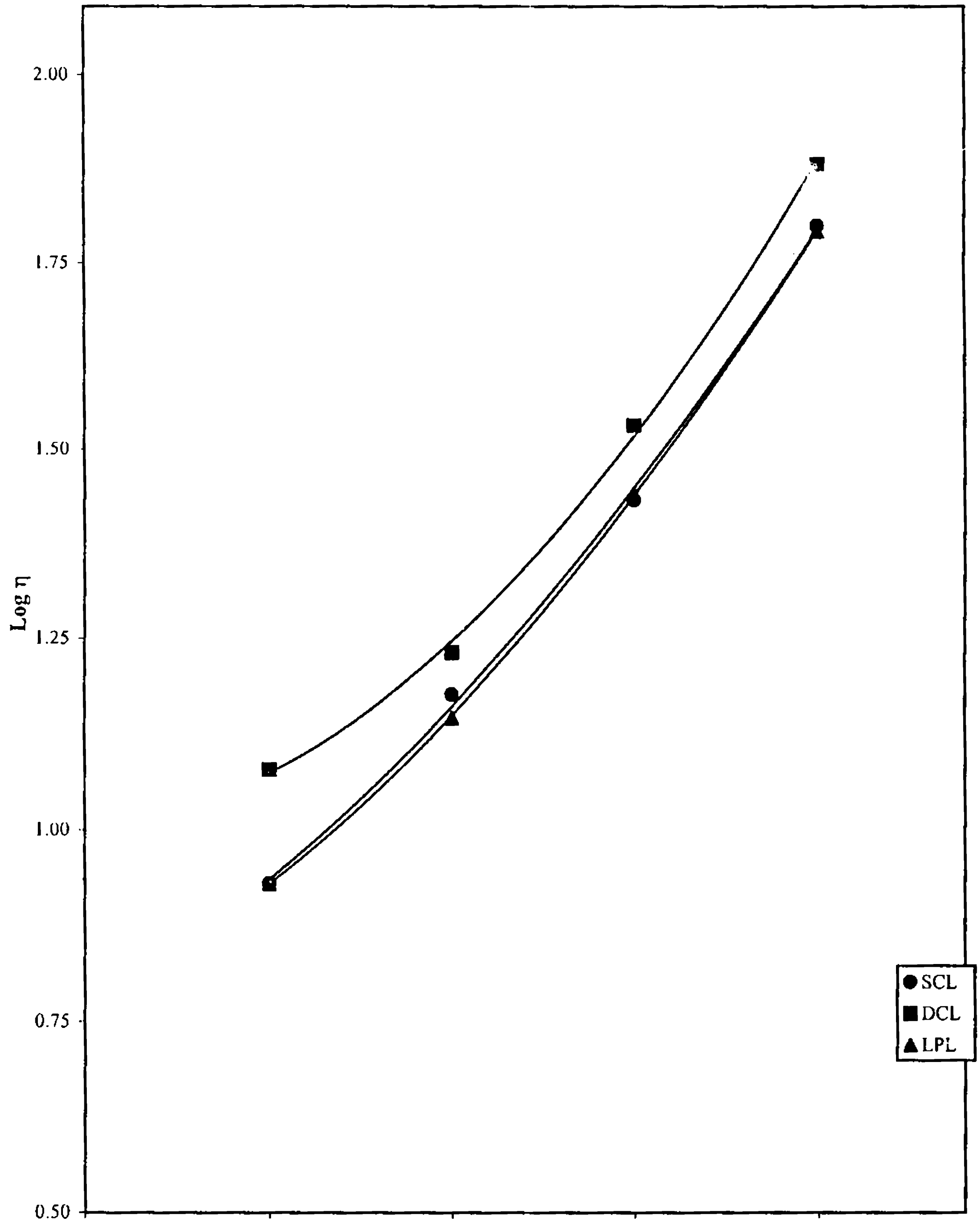


Fig 7.2. Effect of solids content on log (viscosity) of compounted latices at 30°C.

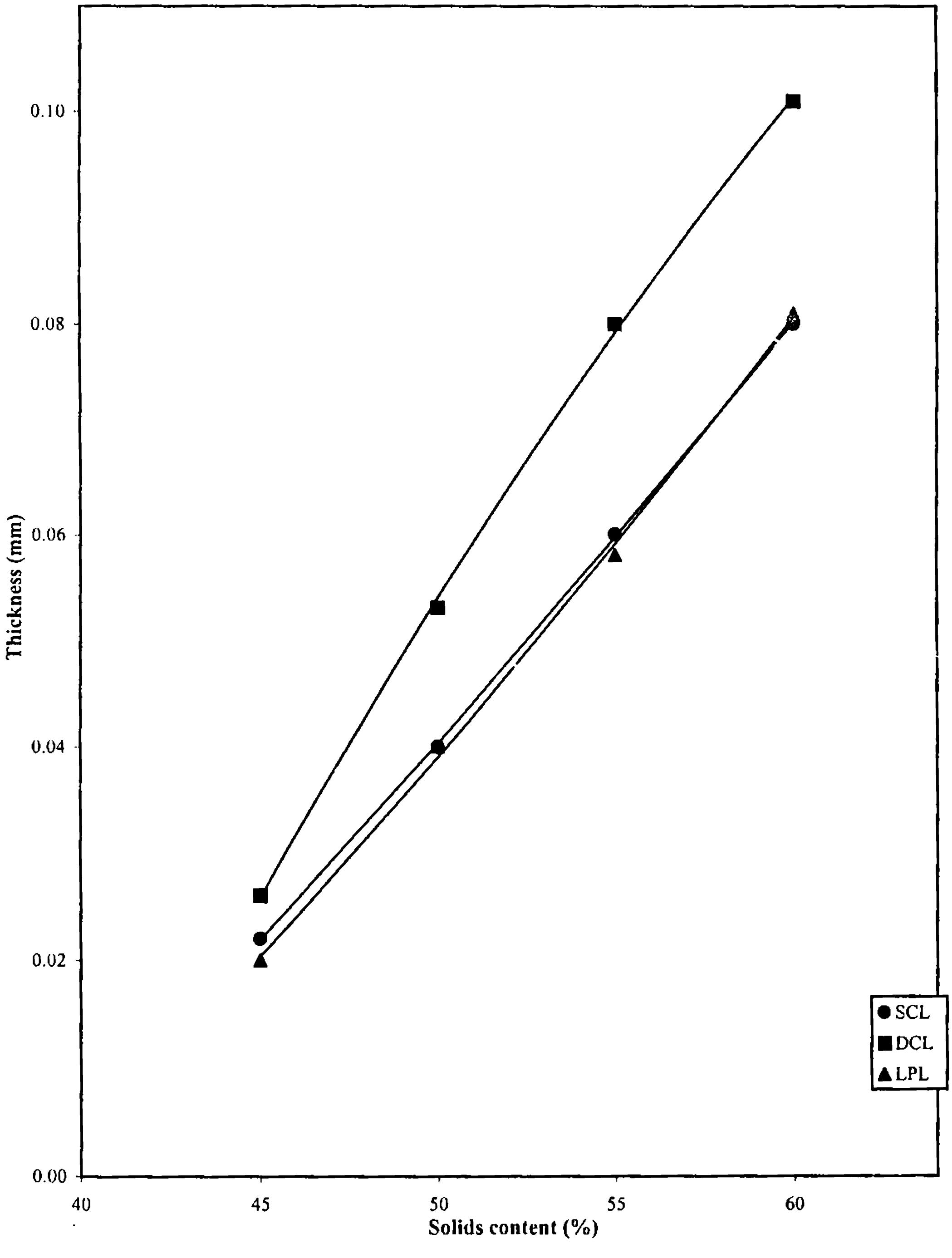


Fig 7.3. Effect of solids content on thickness of deposit in straight dipping of compounted latices.

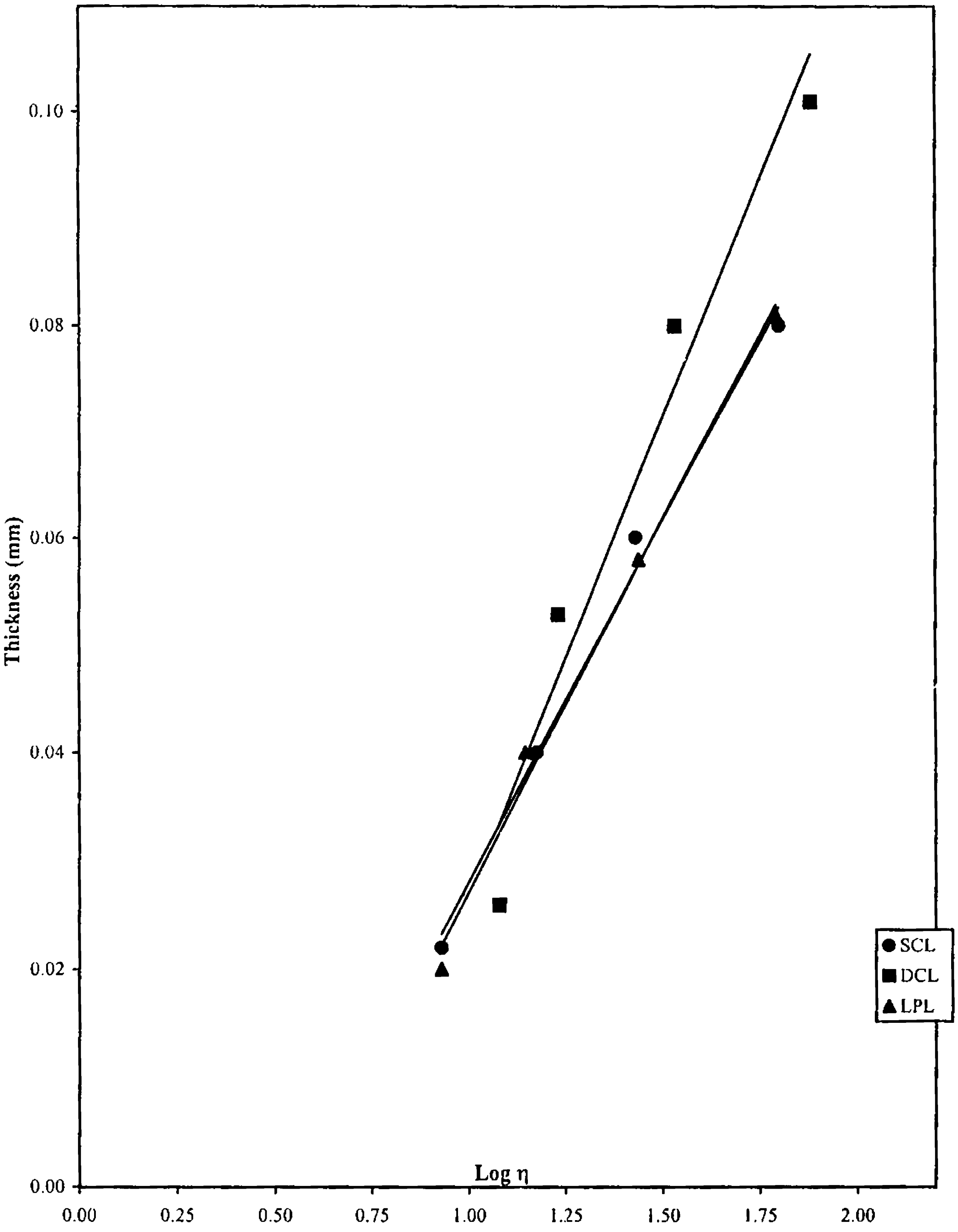


Fig 7.4. Effect of viscosity of latex compound on thickness deposit in straight dipping.

CHAPTER 8

SUMMARY AND CONCLUSIONS

Allergic reactions caused by extractable proteins in latex products, like examination gloves, catheters and condoms, are of great concern now. Conventional methods in overcoming protein allergy problems are long duration leaching, chlorination and use of de-protenized latex. Long on line leaching is not possible in automatic dipping plants for gloves or condoms. Chlorination causes yellowing of products and reduction in tensile properties. Current methods of de-proteinization of latex are mostly based on enzymes. Method of de-proteinization is expensive and cumbersome and physical properties of vulcanized films made out of conventionally de-proteinized latex are poor. The de-proteinizing enzyme itself may cause allergic reactions. Hence systematic studies were undertaken on the production of low protein latex by a non- enzymic method, evaluation of its properties, processability and its application in a limited scale.

Chapter 4 describes a method of production of low protein latex, its properties and behaviour in coagulant dipping. Two anionic and two non-ionic surface active materials were screened for their ability to displace proteins from the rubber- serum interface in latex. Among the four surface active-materials, polypropylene glycol (PPG) of average molecule weight 4000, showed the best performance PPG was added to 60% high ammonia preserved centrifuged latex at various concentrations and the optimum level was found to be 0.2% on the wet weight of latex.

The preparation of low protein latex (LPL) involves the addition of an aqueous solution of PPG to 60% centrifuged latex to the extent of 0.2% and the mixture was allowed to equilibrate for 22h. The latex was diluted to 30% DRC by addition of 1.6% aqueous ammonia and further concentrated by centrifuging. Treatment of concentrated latex with PPG stabilizes the latex further at room temperature, as against certain enzyme processes where latex tends to be destabilized.

IR studies on latex films showed that the intensity of N-H peak (characteristic of proteins) is considerably reduced in LPL. Total protein content in cast films of

LPL is low, compared to SCL and DCL. Extractable protein content in LPL films is only 4 mg/kg, which is very close to the values reported for surface chlorinated examination gloves. These observations confirm the inference that PPG displaces a fraction of proteins from rubber-serum interface in latex.

The raw latex properties of LPL are very good, it shows low VFA number, KOH number and high MST. The viscosity and zinc oxide viscosity of LPL are low. It shows a high ZST value, indicating high chemical stability. These results indicate good processability for LPL. However, its ZHST values are lower than that of ordinary latex, due to the presence of PPG, a heat sensitizing chemical. However, compounded latex is not generally heated in dipping process and hence low ZHST values do not affect its processability.

Latex has to be inevitably stored for a period before it is consumed by the industry. Properties of latex like MST, ZST, viscosity and KOH number undergo changes during storage. During storage, like SCL, MST of LPL increases up to about 60 days and shows slight fall. At all durations of storage MST of LPL is higher than that of SCL and DCL. The chemical stability of latex is an important parameter from the point of view of latex compounding. LPL shows high chemical stability, due to a reduction in the content of anionic stabilizers. Chemical stability is assessed by ZST values. Storage of LPL is accompanied by increase in ZST up to about 60 days, remains more or less constant for the next 30 days and then shows a gradual fall; however, even after 6 months of storage ZST of LPL is observed to be reasonably high, above 200 sec.

Viscosity is an important property of latex from the angle of product manufacture. Like SCL and DCL, storing of LPL is accompanied by increase in viscosity. For any given period of storage, LPL shows lowest viscosity, compared to SCL or DCL. This behaviour of advantage in the production of thin articles like examination gloves and condoms.

KOH number of latex gives an indirect indication of the total onions. High KOH number is generally accompanied by low chemical stability. KOH number of LPL is the least among the three lattices; also the rate of increase is slightly lower in LPL. Thus LPL has good properties on storage.

The tensile properties of LPL films are good, comparable to SCL. The values obtained for LPL films are much better than those reported for enzyme deprotenized natural latex films. LPL films on accelerated heat ageing show good retension of tensile properties, very similar to SCL films.

LPL can be used for coagulant dipping. However, for a given coagulant, thickness of LPL films are lower than SCL films. But this behaviour of LPL can be put to advantage in dipping products like examination gloves. In dry coagulant dipping thickness of the dry LPL film varies linearly with the concentration of coagulant.

Vulcanized LPL films after short leaching contain very low levels of extractable proteins. The value obtained for LPL films are much lower than those of SCL or DCL.

Since LPL contains lesser quantities of proteins than SCL, its response to vulcanization is some what different. Vulcanization characteristics of LPL are described in Chapter 5, Chapter 5A describes conventional sulphur cure, 5B describes EV cure and 5C describes radiation cure.

LPL can be post vulcanized in conventional sulphur cure system. Crosslink density of the film initially increases with cure time, reaches a maximum and then declines. For a given duration of post vulcanization, crosslink density of LPL films are lower than those of SCL films. Thus the rate and state of cure of LPL films are low. Under-cured LPL films are accompanied by increase in crosslink density on accelerated heat ageing, while over cured LPL films show a decrease in crosslink density.

Tensile properties of conventionally sulphur cured LPL films are slightly lower than SCL, but much better than those reported for enzyme deprotenized latex films. Tensile strength and modulus of LPL films are maximum when post-cured for 1h at 100°C. Retention of tensile properties on accelerated heat ageing are good for LPL films. Tensile properties of LPL films before and after ageing are sufficient to meet the specifications common dipped products like examination gloves or condoms.

As reported in the case of ordinary centrifuged latex, replacement of a portion of zinc diethyl dithiocarbamate (ZDC) accelerator by zinc mercapto benzothiazole (ZMBT) cured LPL films in conventional system and modulus of the films are improved. For the under-cured LPL film (vulcanized at 100°C for 0.5h) modulus is maximum for 0.5/0.5phr ZDC/ZMBT combination. However, best combination of physical properties are obtained for 0.75/0.25phr ZDC/ZMBT combination. For this ZDC/ZMBT combination as accelerator, modulus and tensile strength are maximum when LPL films are cured forlh. However, similar to SCL, partial replacement of ZDC by ZMBT is accompanied by a reduction in tensile strength. LPL containing varying proportions of ZMBT, on accelerated heat ageing show maximum modulus when ZMBT content is about 0.25phr. Thus to achieve the best combination of physical properties, both before and after accelerated heat ageing 0.75/0.25phr ZDC/ZMBT combination cured for 1h is recommended for LPL.

Studies were carried out on prevulcanization of LPL in the conventional sulphur cure system. Assessment of the state of cure by solvent swelling method, followed by computation of crosslink density indicated that state of cure was too poor at 50°C and hence was not of any practical use. Reasonably good level of prevulcanization could be achieved at 60°C; however attempts to prevulcanize LPL at 70°C was not successful due to colloidal destabilization due to the presence of PPG, a heat sensitizing agent. The state of cure of LPL films, prevulcanized at 60°C was lower than that of similarly prepared SCL films. This shows that LPL is slow curing than SCL, but slightly better than DCL.

Tensile properties of films prepared from conventionally sulphur pre-vulcanized latices were evaluated. It is observed that tensile properties of LPL films are slightly lower than SCL films, but higher than those of DCL films; the observed tensile properties of LPL films are sufficient enough to meet the specification of common latex products. Duration of prevulcanization, where tensile strength of films are observed to be maximum is generally considered as the optimum duration of prevulcanization. Thus at 60°C in conventional sulphur cure system optimum duration of prevulcanization is about 2.75h for LPL.

Effect of accelerated heat ageing on crosslink density of conventionally sulphur prevulcanized latex films were studied. The reduction in crosslink density on ageing was less in LPL films, compared to SCL films. SCL films initially prevulcanized for 2h. showed maximum crosslink density after heat ageing. For LPL film, it was about 2.25h prevulcanized film. Behaviour of DCL films were inferior to LPL films.

Accelerated heat ageing of conventionally sulphur prevulcanized latex films result in reduction of tensile properties. Aged modulus of LPL films, are somewhat lower than SCL films but above DCL films, but aged tensile strength of LPL films are almost comparable to SCL films. 2h prevulcanized LPL film had highest tensile strength on accelerated ageing, where as with SCL, it was 3h film. The tensile properties of LPL films after ageing, however, meet the specifications for latex products like examination gloves and condoms.

Tensile properties of conventionally prevulcanized LPL films are improved by leaching, the longer the leaching better the film properties. However, based on practical considerations, leaching for 0.5h may be optimum. Leaching of films improves their tensile properties after ageing. It is observed that 0.5h leached LPL films show highest modulus and tensile strength after heat ageing.

Extractable protein (EP) content was estimated in conventionally sulphur prevulcanized latex films prepared from SCL, DCL and LPL. For the three types of latex films, EP content is unleached films increased with duration of prevulcanization. On leaching for 5min. EP content was considerably reduced in the leached film. Both before and after leaching, EP content was least in LPL films. Depending on duration of prevulcanization, EP content in LPL films, after leaching for 5min. was in the range 30-60mg/kg. This EP range compares with chlorinated gloves, and is lower than LOPROL, a commercially available deprotenized latex in Malaysia. Prolonged leaching reduces EP still further.

Chapter 5B describes the behaviour LPL when cured in EV system. Like SCL, LPL films can be post-cured in EV system using low amounts of sulphur and high levels of accelerator. Crosslink density of LPL films increase with duration of post-cure. For a given duration of post cure, crosslink density of LPL films are lower than SCL films but higher than DCL films. Accelerated heat ageing causes increase in crosslink density in LPL films. Crosslink density in aged LPL films are lower than aged SCL film, but higher than aged DCL films.

Modulus and tensile strength of EV cured LPL films increase with duration of post-cure. Accelerated heat ageing of under-cured latex films is accompanied by improvement in physical properties. Extent of improvement decreases with increase in initial duration of post-cure. Tensile properties of LPL films both before and after ageing are slightly lower than corresponding SCL film, but better than DCL films. For achieving the highest physical properties in EV system, LPL films may be post-cured at 100°C for 1.5h.

There is marked difference in prevulcanization characterstics of LPL and SCL in EV cure system. For a given time of prevulcanization, crosslink density of SCL film is the highest. Rate of cure decreases with duration of prevulcanization. For LPL, rate of cure is highest at about 3h heating. Behaviour of DCL is similar to LPL, but the former has lower crosslink density. Modulus and tensile strength of LPL films prevulcanized in EV system are lower than SCL films, but slightly higher than DCL films. Accelerated heat ageing of the LPL films is accompanied by increase in crosslink density and modulus, but the values are lower than aged SCL films; however, tensile strength of aged LPL films are higher than those of SCL films. This behaviour (lower modulus and higher tensile strength) can be of advantage if LPL is used in making surgical gloves.

Chapter 5C describes the behaviour of LPL to crosslinking with the assistance of γ-radiations. With SCL, DCL and LPL crosslink density of radiation prevulcanized films increase with dose of irradiation. With SCL and LPL maximum crosslink density is obtained at a dose of 25kGy. Crosslink densities of SCL and LPL films are comparable and are above those of DCL films.

Modulus of radiation crosslinked SCL and LPL films are comparable, while that of DCL are lower. With the three types of films modulus of films increase with dose of irradiation, where as tensile strength increases with dose, reach a maximum and then decrease. Tensile strength of LPL films is lower than SCL films but higher than DCL films. That dose of irradiation which gives the highest crosslink density for the film is considered as the optimum dose of irradiation, accordingly 15kGy is the optimum dose for the three types of latices. Tensile strength of 28MPa for LPL films prepared by 15kGy irradiated latex is sufficient to meet the specifications for common latex products. Elongation at break of latex films decreases with dose. EB of LPL films decreases with dose of irradiation. EB values of LPL films are slightly lower than SCL films, but above DCL films.

EP content in radiation cured LPL films are much lower than SCL and DCL films. EP content of latex films increases slightly with dose of irradiation. Leaching of radiation crosslinked films reduces EP content. LPL films have EP content less than 10mg/kg, which is a very safe limit.

For a given dose, increase in dose rate slightly increase the crosslink density and modulus of latex films, while tensile strength and EB decreases with increasing dose rate. Dose rate has practically no influence on extractable protein content in the three types of latex films.

It is observed that when LPL is irradiated, crosslink density increases with rubber content in the latex, maximum crosslink density is observed at about 50–52% and then declines. The behaviour is similar to SCL and DCL. At any given rubber content, crosslink density of LPL film is slightly below that of SCL films.

Modulus and tensile strength of irradiated LPL films increase with rubber content in latex during irradiation and maximum tensile properties are observed at 50% DRC. Tensile strength of irradiated LPL film is lower than that of irradiated SCL films. EB of γ-ray crosslinked LPL film decreases with rubber content in latex and minimum is at about 52% for LPL.

Leaching of radiation cured LPL film is accompanied by increase in modulus tensile strength and elongation at break; however, beyond 2h leaching improvement is too small. The result is comparable with SCL.

Leaching of radiation crosslinked latex films show drastic reduction in extractable protein content. Radiation crosslinked LPL film show very low levels of EP content.

Post-heating of radiation crosslinked latex films show small increase in crosslink density when heated for 1h at 80°C and further heating shows a reduction. Rate of drop in crosslink density of LPL films on continued heating is slightly higher than that of SCL. However 2–3h of post-heated latex films show highest modulus and tensile strength. Post-heated radiation cured LPL films post-heated for 3h. Post-heating have modulus and tensile strength above that of similarly treated SCL film. Post curing of latex films is accompanied by a reduction in EB. The extent of reduction in EB of LPL film is lower than that of SCL films.

Modulus of radiation cured latex films is generally low and in the case of LPL, it is slightly lower than SCL films. Addition of small amounts of silica improve modulus of latex films, but tensile strength and elongation at break are reduced.

The viscosity and flow behaviour of lattices are important in product manufacture. The rehological behaviour of LPL are described in Chapter 6. The viscosity of SCL, DCL, and LPL were studied in the solids content range 30–60%. The viscosity of latices increased with solids content in a non-linear manner. Viscosity of LPL is slightly lower than SCL, and DCL has high viscosity. Viscosity of the three latices were studies at varying shear rates and these were found to be pseudoplastic. The zero-shear viscosity of LPL is higher than that SCL; however LPL is slightly more pseudoplastic than SCL.

The apparent viscosity of sulphur prevulcanized LPL was higher than that of sulphur vulcanized SCL and DCL. Sulphur prevulcnized LPL is pseudoplastic and at all shear rates its viscosity is considerably higher than that sulphur prevulcanized SCL and DCL. Also it shows highest zero shear viscosity. Sulphur prevulcanized LPL is more pseudoplastic than sulphur prevulcanized SCL or DCL.

When LPL is radiation vulcanized, its viscosity is higher than radiation vulcanized SCL or DCL. Also its zero shear viscosity is the highest and is more pseudoplastic than the other two latices.

At all shear rates the apparent viscosity of LPL decreases with increase in temperature. Also its zero shear viscosity decreases with rise in temperature; its pseudoplsastic nature is also slightly reduced.

There will be a time interval between production of LPL and its consumption at the manufacturing end. It is observed that during 60 days storage, the viscosity of LPL increases somewhat and becomes slightly less pseudoplastic. The behaviour of compounded latex was evaluated. The viscosity of compounded LPL increases with solids content in a non-linear manner, in a way similar to natural and synthetic latices. The thickness of films obtained by straight dipping of LPL is comparable to SCL, but slightly lower than DCL films. Examination gloves produced from LPL have tensile properties similar to SCL. These LPL gloves meet the Indian Standard IS 13422:1992 specifications for examination gloves. Also its zero shear viscosity increases slightly.

This study is summed up as follow:

- LPL produced by PPG treatment of latex, after film formation shows very low levels of exactable proteins.
- LPL has low non-rubber content compared to other deprotenized latices reported in the literature.
- LPL can be post-or prevulcanized like ordinary concentrated latex.
- LPL can be cured with sulphur and accelerator both in conventional and EV system. It can also be curd by γ-radiation processing.
- The viscosity and flow behaviour of LPL are almost comparable to ordinary centrifuged latex.
- Tensile properties cured LPL films are only slightly lower than ordinary centrifuged latex; however, it is sufficient to meet the properties of almost all latex products, where protein allergy is a serious problem.
- LPL has good storage life.
- The application of LPL in making examination gloves meeting the specifications of IS 13422:1992 is demonstrated.

PUBLICATIONS BASED ON THIS THESIS

1. Preparation and properties of low protein latex.

Proceedings of 18th Rubber Conference. Indian Rubber Manufacturers Research Association, Mumbai (2000).

2. Studies on the radiation vulcanization of low protein natural rubber latex.

Proceedings of International Rubber Conference, Chennai (1998).

3. Sulphur prevulcanization of double centrifuged natural rubber latex.

Rubber India 52 (12), 9(2000).

4. Radiation vulcanization of double centrifuged latex.

Proceedings of National Seminar on Advance in Plastics and Rubbers – Materials and Processing. Anna University, Chennai (2000). Rubber India 53(3), 7,2001.

5. Effect of Vulcanization Systems and Method of cure on Properties of Natural Rubber Latex Films.

Rubber India. 57(5), 9(2005).

6. Sulphur vulcanization of low protein latex in conventional cure system, J. Appl.Polymer Sci. (communicated).

7. Sulphur vulcanization of low protein latex in EV cure system, J. Appl.Polymer Sci. (communicated).

8. Rheological behaviour of low protein latex, Indian J.nat.Rub.Res. (communicated).

9. Applications of low protein latex in production of examination gloves, Rubber India (communicated).