STUDIES ON LATEX COMPOUNDING

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By

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JANUARY 1996

CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Smt. LALIAMMA JOSE under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of the work reported in this thesis has been presented for any other degree from any other

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DECLARATION

I hereby declare that the thesis entitled "**Studies on Latex Compounding**" is the original work carried out by me under the supervision of Dr.RANI JOSEPH, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

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CONTENTS

LIST OF ABBREVIATIONS USED IN THIS THESIS

Polymers

NR - Natural rubber
HA Latex - High ammonia latex
SBR - Styrene-butadiene rubber
PVC - Poly(vinyl chloride)

Additives

S - Sulphur
ZnO - Zinc oxide
ZDC - Zinc diethyl dithiocarbamate
TMTD - Tetramethyl thiuram disulphide
CBS - N-cyclohexyl benzothiazole-2-sulfenamide
TMTM - Tetramethyl thiuram monosulphide
HAF black - High abrasion furnace black
MgO - Magnesium oxide
SP - Styrenated phenol
ATNR - Amine terminated liquid natural rubber
$CaCO_3$ - Calcium carbonate
HCl - Hydrochloric acid
NaOH - Sodium hydroxide
NH_3 - Ammonia
DOP - Dioctyl phthalate

Na_2CO_3 - Sodium carbonate

PTA - Phosphotungstic acid

TCA - Trichloro acetic acid

DBP - Dibutyl phthalate

Other Abbreviations

ISNR - Indian standard natural rubber

ASTM - American Society for Testing and Materials

rpm - Revolutions per minute

phr - Parts per hundred rubber

T - Temperature

ML(1+4)at 100°C - Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100°C

R - Gas constant

E - Activation energy

n - Power law index

η - Viscosity

D_e - Diameter of the extrudate

D_c - Diameter of the capillary die

UV - Ultra-violet

Vis - Visible

IR - Infra-red

Nm - Newton meter

V_r - Volume fraction of rubber network

V_{ro} - Value of V_r for filled vulcanizates

M_c - Number average molecular weight of rubber chains between crosslinks

χ - Polymer-solvent interaction parameter

V_s - Molar volume of solvent

ρ_r - Density of rubber

ρ_s - Density of solvent

MPa - Mega Pascal

R_B - Bound rubber content

τ_{wapp} - Apparent shear stress at the wall

$\dot{\gamma}_{wapp}$ - Apparent shear rate at the wall

τ_w - True shear stress at the wall

$\dot{\gamma}_w$ - True shear rate at the wall

L - Length of capillary die

R - Radius of the capillary die

δ - Solubility parameter

Ø - Volume fraction

EP content - Extractable protein content

CHAPTER 1

INTRODUCTION

Latex is defined as a stable dispersion of a polymeric substance in an essentially aqueous medium [1]. Based on the origin, latices are classified as natural, synthetic and artificial according as they occur naturally as the products of metabolism of various plants and trees, as they are produced directly from the corresponding monomers or as they are produced by dispersion of the bulk polymer in an aqueous medium. Of the different natural latices, the principal one - natural rubber latex is obtained from the bark of the tree Hevea brasiliensis, of the family Euphorbiaceae. Natural rubber latex is a white opaque liquid with a specific gravity which varies between 0.974 and 0.986. It is a weak lyophilic colloidal system of spherical or pear shaped rubber globules suspended in an aqueous serum. The rubber globule is surrounded by a protective layer of proteins and phospholipids which imparts the prophyllic colloidal nature to latex and the stability of latex is due to the negative charge present on the protective layer [2]. Also it contains a variety of non-rubber constituents both organic and inorganic, in addition to rubber. The proportion of these constituents may vary, with clones, nutrition, climate etc. But in general the composition of latex is as follows:

Constituent	Percent
Rubber	30-40
Protein	2-2.5
Resin	1-2
Sugar	1-1.5
Water	55-66
Ash	0.7-0.9

Characterization of rubber hydrocarbon by intrinsic viscosity, osmotic pressure, light scattering sedimentation velocity analysis methods has yielded considerable information on the size and shape of rubber molecules in solution and has established that the rubber hydrocarbon of Hevea brasiliensis comprises a series of polymer homologs with average molecular weight in the region of 500,000 to 1,000,000 and with a broad distribution of molecular weight from well over 1,000,000 down to less than 100,000 [3]. Fresh latex, as it comes out from the tree, is slightly alkaline or neutral. It becomes acidic rapidly due to bacterial action [1]. The formation of organic acids neutralises the negative charge on rubber particles and the latex gradually gets coagulated on keeping [4]. Therefore fresh latex cannot be kept for long without adding preservative [5-7]. A preservative is a chemical or mixture of chemicals which when added to latex can prevent bacterial action in it and at the same time stabilize it. Ammonia is the most popular latex preservative. Usually concentrated latex is preserved with 0.7% ammonia. But a variety of other substances also can be used with advantage along with a low level of ammonia (0.2%) for effective latex preservation [8,9,10]. Field latex with 30-40% rubber is concentrated and preserved latex concentrates are generally marketed in two concentrations.

1. Latex between 36 and 50% dry rubber content (drc)
2. Latex between 51 and 60% drc.

Several methods of concentrating the latex are in practice: evaporation, creaming, centrifuging and electrodecantation. Concentration is advantageous since less water is transported and higher solid content is required for most manufacturing operations [11].

Natural rubber is a high molecular weight polymeric substance with viscoelastic properties. Structurally it is 1,4-polyisoprene. Because of this, natural rubber shows all the reactions of an unsaturated compound. It gives addition compounds with halogens, hydrogen chloride and several other reactants that react with olefins. An interesting reaction of natural rubber is its combination with sulphur. This is known as vulcanization. This reaction converts the plastic properties of raw rubber into elastic properties. Thus vulcanized rubber will have very high tensile strength and its hardness and abrasion resistance also will be high. Because of the unique combination of these properties, natural rubber finds application in the manufacture of a variety of products.

Requirements of composition and physico-chemical properties of preserved latex concentrate [12].

		Type HA	Type MA	Type LA
1.	Dry rubber content percent by weight (Min.)	60	60	60
2.	Total solid content per cent by weight (Min.)	61.5	61.5	61.5
3.	Non-rubber solids per cent by weight (Max.)	2	2	2
4.	Coagulam content per cent by weight (Max.)	0.08	0.08	0.08

5.	Sludge content per cent by weight (Max.)	0.10	0.10	0.10
6.	Alkalinity as ammonia per cent on water content	1.6 (min.)	0.8-1.6	0.8 (max.)
7.	KOH Number (Max.)	1.0	1.0	1.0
8.	Mechanical stability, seconds (Min.)	475	475	475
9.	Volatile fatty acid number (Max.)	0.15	0.15	0.15
10.	Copper content ppm on total solids (Max.)	8	8	8
11.	Manganese content ppm on total solids (Max.)	5	5	5

The significance of these properties has been discussed by Blackley [13].

Specifications for centrifuged or creamed, ammonia-preserved NR latices are set out in ISO 2004. Those for evaporated NR latices are the subject of ISO 2027. ISO 2004 deals with three types of centrifuged latex (HA, LA and MA) and two types of creamed latex (HA and LA). ISO 2027 covers three types of evaporated latex [14].

When ammonia is added for preserving latex, the proteins and lipid materials are hydrolysed slowly releasing fatty acids which form soaps [15] and the adsorption of these soaps is thought to account for the spontaneous rise in mechanical stability when ammoniated latex concentrate is stored [16,17].

Currently the dominant area of manufacture using NR latex is the production of dipped goods [18]. Dipped goods include a wide range of products such as gloves, balloons, catheters, teats etc. In these types of products, the latex used must produce continuous films on the former and maintain film integrity during the drying/ vulcanizing stage. Natural rubber latex is outstanding in this respect that it forms strong films which can withstand rapid drying. Also natural rubber latex products are exceptional in terms of tensile strength and elongation coupled with relatively low modulus values, which are ideal characteristics for gloves, balloons and teats. The versatility of natural rubber latex in terms of production processes is quite remarkable. Recently there has been a sharp increase in the use of NR examination gloves by medical personnel as a preventive measure against the spread of blood-borne viral diseases such as AIDS [19]. But the observed changes in latex consumption have not been accompanied by corresponding changes in production technique [18]. Improved formulations, test methods and process control are to be introduced.

The advantages of the direct use of latex are well recognised because of the simplicity and economy of the practical techniques as well as the mechanical properties of the articles obtained. Because the rubber has not been submitted to mastication, it retains its intrinsic qualities unimpaired [20].

In the last few years, there has been widespread concern about the presence of nitrosoamines, which are potential carcinogens, in baby bottle teats and soothers made from latex. Some countries have established standards for maximum nitrosamines and nitrosatable amines in these products [19]. It has been shown that NR latex is free from nitrosamines and contains only relatively low concentrations of nitrosatable amines, well below the maximum limits [21].

Latex Compounding and Vulcanization

A rubber polymer by itself has such poor properties that it has limited commercial value. A variety of materials must be added to rubber to improve its properties and to make it commercially useful. The science of adding these ingredients to rubber in order to produce the best possible product and to assure efficient, trouble-free manufacturing of this product is known as compounding [22]. In all latex processes a stable colloidal system is maintained until, at the desired time, it is made unstable and converted to a solid product [18].

Raw rubber flows on standing and does not retain its shape. Thus for rubber to become truly useful, its chains must be permanently linked together to increase its strength. Accelerators were first discovered in 1906. More efficient accelerators such as dithiocarbamates, thiuram, MBTS etc. were discovered around 1920. Thus vulcanization is the chemical reaction which brings about the formation of crosslinks between the long polymer chains. The three dimensional structure so produced restricts the free mobility of the molecules and gives a product having reduced tendency to crystallise, improved elasticity and substantially constant modulus and hardness characteristics over a wide temperature range [11]. Vulcanization of rubber changes its physical properties. It increases viscosity, hardness, modulus, tensile strength, abrasion resistance and resilience and decreases elongation at break, compression set, hysteresis and solubility in solvents. All of these changes are proportional to the degree of crosslinking except tensile which reaches a maximum at about one crosslink per every 150 monomer units. The length of the sulphur crosslinks also affects the physical properties, longer crosslinks - polysulfide crosslinks - improve tensile strength, tear strength and fatigue properties. On the other hand, shorter crosslinks improve thermal and oxidative stability and give lower compression set. Structural characterisation of sulphur vulcanized rubber networks were done by B.Savilla et al. [23]. Studies of the chemistry of vulcanization today occupy a central position in current efforts to achieve better product performance from available rubbers. The vulcanizate properties are not functions of crosslink density only, but they are affected by the type of crosslink, nature of polymer, type and amount of fillers etc. [24,25].

Compounding Ingredients

The range of compounding ingredients used in latex technology is extremely broad and wider than that for solid polymers. Compounding ingredients for latex may be divided into the following categories [26].

1. Stabilisers including surfactants
2. Vulcanizing agents
3. Accelerators
4. Activators
5. Antioxidants and
6. Fillers.

The water soluble materials are added as solutions, insoluble solids as dispersions and immiscible liquids as emulsions. The particle size of the ingredients should be reduced to that of the rubber particles in latex for getting uniform distribution in the latex compound [27-31]. The most common technique used to produce dispersions for latex compounding is ball milling. In the ball mill, the particle size of the dispersion is reduced to the colloidal range. The method of operating ball mills has been described in various publications [32,33]. Liquid compounding ingredients that are water-immiscible can be emulsified in water with the aid of an emulsifying agent such as potassium oleate.

Compounding of latex should be performed in a vessel that is chemically resistant to the latex and the compounding ingredients. The compounding ingredient is best added to the continually stirred latex in a slow steady stream, with a minimum of splashing. The compounded latex should be stored in a covered, chemically resistant vessel for maturation. Latex formulations are usually calculated on dry rubber content.

Surface-Active Agents

Surface-active agents are substances which bring about marked modifications in the surface properties of aqueous media, eventhough they are present only in very small amounts (of the order of 1% or less) [27]. These surface active agents are of great importance in the technology of polymer latices and it is in this respect that latex technology differs most significantly from that of dry polymers and polymer solutions. The surface active agents can be classified as wetting agents, viscosity modifiers, protective colloids, dispersing agents, dispersion stabilisers, emulsifiers etc. according to their function. The second classification is by chemical nature and divides these into anionic, cationic, amphoteric and non-ionogenic types [27]. Wetting agents are used to reduce the interfacial tension between two surfaces. Proteins, alginates, polyvinyl alcohols and cellulose derivatives are used as protective agents and viscosity modifiers in the processing of latex compound [34,35]. The dispersing agents prevent the dispersed particles from reaggregating and alkyl sulfonates are generally used for this. Emulsifying agents are soaps, usually oleates.

Vulcanizing Agents

Sulphur is the most universal vulcanizing agent for natural rubber latex. Sulphur should be of good quality and should be finely ground. Tetramethyl thiuram disulphide may be used to cure many polymers without the addition of sulphur. But the vulcanization of this system proceeds at a useful rate only at relatively high temperatures (140°C). But thiourea is able to activate vulcanization by tetramethyl thiuram disulphide even at 100°C. The excellent heat and ageing resistance of thiuram vulcanizates are retained when cure is activated by the addition of thiourea [36]. Dunn reported that butyl xanthogen disulphide in conjunction with a zinc dithiocarbamate may be used to vulcanize latex film in the absence of sulphur [37]. It has been claimed that organic peroxides and hydroperoxides may be used to vulcanize natural rubber latex deposits, giving products of a high order of translucency [27].

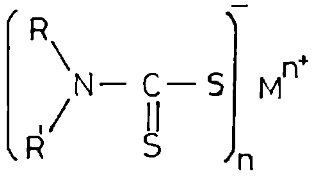
Accelerators

Accelerators play an important role in the vulcanization of rubber and they affect the scorch safety, the rate of cure and the length and number of the crosslinks formed [22]. The structural modification of the main chain which can occur during the accelerated vulcanization process has already been studied in detail [38]. The function of accelerator combination is to increase the crosslinking efficiency and to minimise wastefully combined sulphur by decreasing (1) cyclic monosulfide formation, (2) vicinal crosslinks, and (3) the length of sulphur chain, 'S_x' in crosslinks [39].

The most important classes of accelerators are metal salts of dialkyl dithiocarbamates [27]. The thiazoles and to a lesser extent the thiurams are of importance as secondary accelerators used in conjunction with dithiocarbamates. The metal xanthates also find limited application [27].

(1) Dithiocarbamates

The salts of the dialkyl dithiocarbamic acids have the generic structure as



Although a considerable range of accelerators are available under this, zinc diethyl dithiocarbamate (ZDC) is the most widely used. This is very active in latex mixes even in the absence of ZnO and activates thiazole accelerators [40].

Thiozoles

The most common thiozole in latex compounding is the zinc salt of 2-mercaptobenzthiozole (ZMBT). It is activated by thiurams and dithiocarbamates. Thiozoles are insufficiently active to be used on their own for latex work, but they function as secondary accelerators for the dithiocarbamate giving vulcanizate of high modulus [27].

Thiurams

As a class, the thiurams are insufficiently active to accelerate satisfactorily the sulphur vulcanization of diene rubbers in latex form. They may be used as secondary accelerators in conjunction with the dithiocarbamates [27].

Activators

The accelerators require zinc oxide for activation in all types of rubber [41]. Zinc oxide increases the tensile strength and modulus of the vulcanizates. Zinc oxide used for activation should be low in lead content.

The thickening produced by ZnO in ammonia preserved latex and the subsequent loss in stability of the latex are well known [42]. Jordan showed that the increase in viscosity in the presence of ZnO varied in accordance with the KOH number of the latex [43].

Antioxidants

The common antioxidants used in latex are of two types [27]:

(1) Amine derivatives which are powerful antioxidants but which tend to cause discolouration of the rubber during ageing, and

(2) Phenolic derivatives, which are not such effective antioxidants, but which have the advantage of not causing discolouration.

Fillers

Fillers are added to rubber latex to modify its properties and to reduce cost [44]. Non-black fillers have always been an important part of the rubber industry. A broad spectrum of performance properties from nonreinforcing, but economical, to highly reinforcing - exists in these non-black fillers [45]. Today the principal non-black fillers are clays, calcium carbonate and silicas.

Reinforcement by a filler is the enhancement of one or more properties of an elastomer by the incorporation of that filler, thus making it more suitable for a given application [46,47].

It is generally agreed that strong links exist between rubber chains and reinforcing filler particles [48,49]. Nature of polymer filler attachments in vulcanizates has been investigated in greater detail by Rehner [50]. Many concepts have been given for the filler reinforcement [50-52]. The use of china clay in latex compounding has been studied by Van Rossem [53]. But it is well known that the reinforcing fillers normally employed in the dry rubber technique behave, when they are introduced into the latex,like inert fillers or they even appreciably lower the mechanical properties of the vulcanizates [54]. The principal obstacle to the development of the technology of production of rubber articles from latex has been the absence of a rubber reinforcement effect in latex and the consequent impossibility of obtaining strong rubbers by direct introduction of fillers into latex. For the production of filled latex compounds of high strength it is necessary to ensure

(a) a high degree of dispersion of the fillers and other ingredients added to the latex.

(b) Simultaneous precipitation of the particles from the latex mix.

(c) 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 [55].

In the case of dry rubber, fillers like calcium carbonate and clay are found to reduce the tensile properties but silane coupling agent treated clays are found to show improved tensile properties [56,57]. Earlier workers have studied the reinforcement of silica filler in NR, in the presence of silane coupling agent [58]. So if one of the additives in latex compounding can improve the rubber-filler interaction, the filled latex vulcanizate can show improved mechanical properties. Reinforcing resins were introduced when LeBras and Piccini prepared a resorcinol - formaldehyde condensate - and added the aqueous solution to rubber latex, which also contained dispersed curing agents. In 1947, lignin, a byproduct from paper manufacture, was introduced as a reinforcing filler and added to natural latex in the form of an aqueous solution to observe the reinforcing effects of the final product. Starch derivatives have been reported as having certain reinforcing effects (Buchanan et al. 1968, Van Alphen (1954) and Houwink and Van Alphen (1955) published reports on the use of aminoplasts (aniline-formaldehyde), melamine-formaldehyde and urea-formaldehyde condensation products formed in stabilized acidified latex as reinforcing fillers. More recently Radhakrishnan Nair et al. have studied the role of certain surface modifying agents like diethylene glycol, triethanolamine and bis(triethoxysilyl propyl)tetrasulphide (Si-69) in improving the mechanical properties of the rubber compound [59]. It has been shown that peptising agents, plasticizing agents etc. can be incorporated in NR latex for the purpose of modifying its properties [60,61]. The use of poly glycol HS 35/40 in NR latex has also been studied [62].

Among the commonly used fillers and reinforcing agents, carbon black offers the most potential reinforcement [63]. Carbon black contributes much to increase the desirable properties of vulcanized rubber and it is almost a universal compounding ingredient for quality stocks [46]. Addition of black to elastomers increases the properties of the crosslinked products [64]. The modification of an elastomer by carbon black reinforcement and vulcanization generates a unique three-dimensional viscoelastic network that transforms the soft elastomer into a strong, elastic product [65]. Many studies have been published explaining the reinforcing properties of carbon black in rubber [66,67]. But incorporation of carbon black with dry rubber presents problems like difficulty in maintenance of cleanliness in the factory and huge power consumption [68]. So attempts to mix black with NR in the latex stage were made. A patent applied in 1922 by Peterson [69] contains all the elements of the processes for filler-latex masterbatching. A number of patents were later applied for latex masterbatch preparation [70]. Carbon black must be adequately dispersed in order to obtain the maximum benefits of carbon black reinforcement. The most fundamental and important feature of the reinforcement of rubber by fillers is the size of the filler particles. It is well known that rigid macroscopic particles of fillers weaken the polymer and as the particle size decreases a reinforcement is observed [71]. From the earlier works, it is clear that latex masterbatch process can deliver a premix which can be given a shorter mixing cycle and still result in an extremely well dispersed compound [72]. In spite of these advantages, this process has not been successful so far, mainly due to (a) the difficulty in reducing the viscosity of rubber in NR latex and (b) the low mechanical stability of NR latex.

It is reported that direct addition of black to latex is not practicable because it may result in poor dispersion of black in rubber [73]. Certain attempts made for the preparation of dispersant free masterbatch wherein dry black was added directly to the latex without making it a dispersion are also reported [74]. According to H.A. Braendle while considering SBR-C black compounds, the columbian carbon process makes possible (a) lower mooney viscosity compounds, (b) much better dispersion of black in the rubber and (c) better hysteresis properties of the vulcanizates [70]. The reinforcement of elastomers by carbon black is governed by the morphology of the black and its physical and chemical interactions with the polymer. One of the methods for measuring black-polymer interaction is bound rubber analysis [75]. Attempts were made to correlate bound rubber formation with mechanical properties for rubber-carbon black compounds [76]. Recently more elaborate techniques have been described for estimating bound rubber [77-79]. Bound rubber formation in SBR-carbon black has been explained in detail by G.R.Cotten [80].

Knowledge of the flow behaviour of polymer compounds is of great importance to optimize processing operations [81]. Many excellent works on the rheological behaviour and the extrusion characteristics of polymer compounds have been reported [82-85].

A most convenient method to develop polymer compositions having the required properties involves physical blending of two or more polymers. All important synthetic rubbers are frequently blended with natural rubber. A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compounding with blends of two or more elastomers is an attractive method for attaining properties not available in a single elastomer [86-95]. In general, the rubber used in practical application is frequently a blend of elastomers. There are several methods of forming elastomer blends, such as mixing of melts, mixing of solutions, mixing of latices etc. [96]. In phase mixing, separate masterbatches are employed. Extensive studies on blended masterbatches of NR, BR and SBR were carried out by Hess and coworkers [97-99]. The filler distribution in elastomer blends has some inherent special characteristics [100]. When fillers are mixed into blends such as NR/SBR, the filler is unevenly distributed between the two polymers [86]. The new electron microscope technique permits study of the heterogeneity of elastomer blends and filler distribution therein [101,102]. The homogeneity of these blends is shown to be influenced by mixing procedure and polymer characteristics such as viscosity and various interaction effects [103]. A detailed study of elastomer blends was done by Corish and Powell [89]. The effect of heterogeneous carbon black distribution on the properties of polymer blends was studied [104,105]. The effects of curing temperature and curing systems on the technical properties, polymer-filler interactions and network structures of various blends including NR/SBR blend was also studied [106]. A study of morphology, curing characteristic and physical properties of NR/SBR and NR/BR blends was done by F.Gharavi and A.A.Katbab [92].

Blends of immiscible polymers may result in very interesting properties. By blending a costlier polymer with a cheaper one, two advantages can be obtained at the same time. They are: (1) reduction in cost of the blend and (2) keeping the level of the properties without any major decrease. PVC has assumed a leading position among plastics because of its economic and design advantages. It is a material of choice due to lower cost, greater availability and improved performance. PVC exhibit good mechanical toughness, resistance to weathering and electrical insulating properties. Although they have a high-melt viscosity and require heat stabilizers, they are fairly easily processed by extrusion, calendering, milling or injection-molding techniques. PVC materials have excellent resistance to inorganic acids, alkalis, water and very good resistance to oxygen and ozone degradation. PVC resin is so amenable to widespread property modification that it accounts for the number one position in overall product volume and number of applications [107,108].

Blends of several elastomers with PVC have been developed to achieve a number of purposes. One of the commercially important and miscible polymer blends is that of NBR and PVC. The primary purpose of such blends is to provide elastomer having enhanced ozone resistance. However, PVC also serves to reinforce the rubber. Modulus, hardness and abrasion resistance increase with increasing PVC content [109,110]. Tensile strength also frequently increases with PVC content while elongation decreases. A number of thermoplastic elastomers from elastomers and PVC are reported such as polyesters with PVC, ethylene copolymers with PVC etc. [111,112]. The modulus, flame resistance and oil resistance of natural rubber can be significantly improved by blending with poly(vinyl chloride) [113-115]. However, developing moderate mechanical properties is a problem due to the immiscible nature of the two polymers and the insufficient fusion characteristics of PVC particles. However, certain additives are capable of improving the miscibility of these polymers and the fusion characteristics of PVC particles [116-118]. Plasticizers are chemicals employed to enhance the flexibility of compounds by lowering the T_g of the matrix polymer. Plasticizers, in general, reduce the modulus of a PVC compound, decrease hardness, decrease mechanical strength but increase elongation [119]. The inferior properties displayed by immiscible blends is due to the incompatibility of the constituents on a molecular scale since the mechanical behaviour of the blend is related to phase structure. The incorporation of compatibilisers is found to promote miscibility as they are able to make specific interactions with each of the blend components [120,121]. The compatibilising action of certain solid phase dispersants in PVC/polyethylene and PVC/PS blends has been reported earlier [122-124]. The mechanical, rheological and morphological studies of PVC/epoxidised NR (ENR) have shown that higher levels of epoxidation makes NR to be more compatible with PVC [125,126]. It is apparent that the mechanical properties of a blend will be a function of the processing method used. Mixing of latices is a suitable method of obtaining polymer blends, with more uniform distribution and this method of preparation of polymer blends is economically attractive also.

The surface of NR latex vulcanizates usually exhibits a degree of self-tack and this tackiness causes latex products to stick to each other when handled in bulk [15]. Surface treatments of latex products are done to reduce the surface tack and friction of these products

[127]. Surface modification methods include chemical, photochemical methods and physical techniques [128]. Chemical methods include reactions such as halogenation. The effect of bromination on the surface properties of rubber has been reported already [129,130].

Certain allergic reactions arising from contact from natural rubber latex products have been attributed to latex proteins leached from their surfaces [131]. Recently, there have been reports that natural latex gloves and other surgical aids can cause hypersensitivity reactions [132]. There is evidence suggesting that the water-extractable proteins in latex is the cause of the immediate allergic reactions. One of the very effective approach for reducing soluble proteins is by chlorination [133,134]. It is believed that chlorine renders the proteins insoluble or it forms an impermeable barrier that prevents proteins migrating to the glove surface [133]. However, the simplest method of protein reduction is to leach the gloves on the production line [133,134]. Leaching of latex products is necessary in order to remove residual coacervant and other water soluble residues.

OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Rubber products were being made from natural rubber latex long before the advent of solid rubber processing. With the development of efficient methods for concentration and preservation, large scale production of latex products such as foam rubber, dipped goods etc. started. But the use of fillers in latex products is limited since they affect the mechanical properties adversely. However, it may be possible to incorporate physical modifiers to improve the rubber-filler interaction thereby opening the way for filled latex products.

Organic accelerators used in latex compounds are basically different from those used in dry rubber compounds. In the manufacture of high quality products two or more accelerators are normally used. The protection of a vulcanizate against ageing depends mainly on the nature of accelerators employed and only less on the antioxidants. Hence novel accelerator combinations in latex product may give better ageing resistance in comparison to conventional accelerator systems.

Carbon black is a highly reinforcing filler and latex stage carbon black masterbatching may overcome the disadvantages of dry rubber-carbon black mixing. If the mechanical stability of latex can be improved by adding surface active agents and the mooney viscosity of the latex-black masterbatch can be reduced by mastication in presence of ZnO and stearic acid, latex stage addition of carbon black may be a promising technique.

Polymer blends are widely used these days for optimising properties of individual polymers and cost reduction. Latex stage blending of PVC and NR may yield blends with interesting properties.

One of the most common surface treatments of elastomers is halogenation. Natural rubber is very reactive towards the halogens. By halogenation, the surface tackiness can be reduced, and both ageing resistance and surface smoothness can be improved. Physical agents such as glycerol, silicone oil etc. also reduce the surface tackiness of latex sheets. Leaching can improve the feel of the product as well as its resistance to water absorption and ageing. The efficiency of leaching may be further improved by using different media, temperatures etc.

The main objectives of the present investigations are:

1. To investigate methods of improving the polymer-filler interaction by employing surface active agents so as to improve the mechanical properties and reduce the cost of latex products and to evaluate the processability of such filled compounds.

2. To study the effect of new accelerator combinations such as CBS/TMTM and thiocarbanilide/TMTD in NR latex compound and to compare the properties and ageing resistance of the vulcanizates with that containing the conventional ZDC/TMTD combination.

3. To develop a method for preparing natural rubber/carbon black and natural rubber/silica masterbatch in the latex stage and to evaluate their efficiency in comparison to conventional compounds in respect of filler dispersion, mechanical properties and ageing resistance and the processability.

4. To investigate the suitability of the latex stage black masterbatch of NR for the preparation of NR/SBR blends

and to compare the mechanical properties and processability of these blends with those of conventional NR/SBR blends.

5. To improve the mechanical properties of the NR latex-PVC blends by using ATNR (Amine terminated natural rubber) as a compatibilizer and to compare the mechanical properties and processing behaviour of these latex stage NR/PVC blends with those of the conventional melt mixed NR/PVC blends.

6. To investigate methods of reducing the tackiness of NR latex products by modifying the surface through chemical and physical means.

7. To investigate the efficiency of leaching of latex products with medium of different pH values at different temperatures.

This thesis is divided into the following chapters:

Chapter 1 Introduction

Chapter 2 Experimental Techniques

Chapter 3

Part I Effect of polyethylene glycols and glycerol in filled natural rubber latex vulcanizates

Part II Novel accelerator systems (TMTM/CBS and thiocarbanilide/TMTD) in natural rubber latex

Chapter 4

Part I Latex stage masterbatching of carbon black and silica with natural rubber latex

Part II Mechanical properties of the blends of NR latex/carbon black masterbatch and SBR

Part III Rheological behaviour of NR latex/carbon black masterbatch and NR latex/black masterbatch/SBR blend

Chapter 5

Part I Latex stage blending of NR/PVC

Part II Surface treatments and leaching studies of NR latex vulcanizates

Chapter 6 Summary and Conclusions

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

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

Materials

Polymers

1. Centrifuged NR latex

High ammonia type 60 per cent centrifuged latex conforming to the specifications of the Bureau of Indian Standards (BIS 5430 - 1981) obtained from M/s.Padinjarekara Agencies, Kottayam was used in this study. The properties of the latex used are:

	Parameters	Value
1.	Dry rubber content, % by mass	60.00
2.	Non-rubber solids, % by mass	1.50
3.	Coagulam content, % by mass	0.03
4.	Sludge content, % by mass	0.007
5.	Alkalinity as ammonia, % by mass	0.75

6.	KOH Number	0.65
7.	Mechanical stability time, sec.	1075.00
8.	Volatile fatty acid number	0.04
9.	Copper content, ppm on total solids	3.00
10.	Manganese content, ppm on total solids	2.00

2. Field latex

Field latex which has a dry rubber content of 33% and obtained from M/s.Kattakkayam Latex, Alwaye was used in this study. The properties of the field latex used are as follows:

	Percentage
Total solid content	36
Dry rubber content	33
Proteinous substances	1-1.5
Resinous substances	1-2.5
Ash	upto 1
Sugars	1

3. Natural rubber

Natural rubber (NR) used was solid block rubber ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam. The Mooney viscosity (ML(1+4) at 100°C) of the rubber was 85.3.

4. Styrene butadiene rubber

Styrene butadiene rubber (SBR) Synaprene 1502 had a styrene content of 23.5% and a Mooney viscosity (ML(1+4) at 100°C) of 49.2. The rubber was obtained from Synthetics and Chemicals Ltd., Bareilly.

5. Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) used was emulsion grade with a K value 70, supplied by Chemplast, Madras.

Compounding Additives

Accelerators

A short description of the important accelerators used are given below:

Zinc diethyl dithiocarbamate (ZDC)

This ultra accelerator is a white powder of density 1.47 and melting point 178°C. It ensures rapid low temperature vulcanization in the presence of sulphur and is active in latex mixes even in the absence of zinc oxide.

Tetra methyl thiuram disulphide (TMTD)

Tetra methyl thiuram disulphide used was supplied by Poly Oleifins Industries Ltd., Bombay having the following specifications:

Melting point	136°C
Specific gravity	1.4

N-cyclohexyl benzothiazole-2-sulfenamide (CBS)

N-cyclohexyl benzothiazole-2-sulfenamide (CBS) was supplied by Polyolefins Industries Ltd., Bombay and had the following specifications.

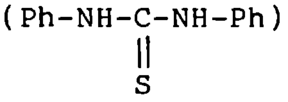
Specific gravity	1.27
Melting point	101°C

Tetramethyl thiuram monosulfide (TMTM)

Tetramethyl thiuram monosulfide used was supplied by AKZO NOBEL Chemical, Netherlands, having the following specifications:

Specific gravity	1.370
Melting point	106.7°C

Thiocarbanilide



$$(\mathrm{Ph{-}NH{-}}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}NH{-}Ph})$$

Thiocarbanilide was prepared in the laboratory by reacting aniline with carbon disulphide in the presence of ethyl alcohol.

Melting point — 136°C

Preparation of thiocarbanilide

In a one litre round bottomed flask fitted with an efficient double surface condenser, 40 g of aniline, 50 g of carbon disulphide and 50 g of absolute ethanol were taken. The contents were heated in an electrically heated waterbath for 8 hours. The residue in the flask was shaken with excess of dilute hydrochloric acid (1:10) to remove unreacted aniline, filtered using a vacuum pump and then washed with water. The product was then dried in a vacuum oven.

Other Chemicals

Sulphur

Sulphur was supplied by Standard Chemical Company Pvt. Ltd., Madras having the following specifications:

Specific gravity	2.05
Solubility in CS_2	98% max.

Zinc oxide

Zinc oxide (ZnO) was supplied by M/s.Meta Zinc Ltd., Bombay having the specifications given below:

Specific gravity	5.5
Zinc oxide content	98%

Magnesium oxide (MgO) used in the study was commercial grade having a specific gravity of 3.6.

Stearic acid

Stearic acid used in the study had the following specifications:

Melting point	50-69°C
Acid number	185-210
Iodine number	9.5
Specific gravity	0.85±0.01

Antioxidants

Styrenated phenol (SP)

It was obtained from M/s.Indian Explosives Ltd., Calcutta.

Vulkanox 4020 NA

Vulkanox 4020 NA was supplied by Bayer Chemicals, Bombay.

Plasticizers

Amine terminated liquid natural rubber (ATNR) was prepared by UV irradiation of NR solution in toluene in the presence of ethylene diamine.

Preparation of amine terminated liquid natural rubber

Natural rubber was masticated for 30 minutes at 50°C. 100 g of masticated rubber was dissolved in 450 ml toluene and the solution was charged into a flat bottomed borosilicate glass flask. 50 ml of ehtylene diamine together with 50 ml of tetra hydro furan was added and thoroughly mixed with the rubber solution. This solution was kept in sunlight for irradiation. After about 60 hours of irradiation, the product was precipitated using methanol and dried in vacuum. The sample was purified by repeated precipitation by methanol from a toluene solution and dried in a vacuum oven.

DOP - Dioctyl Phthalate used was commercial grade.

Surface Active Agents

Dispersol F

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

Potassium oleate

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

Other additives such as polyethylene glycols, glycerol, oleic acid, KOH, ethylene glycol, aniline, carbon disulphide, ethylene diamine, bromine water, sodium hypochlorite solution (approx. 4%) HCl, NaOH, acetic acid, NH_3 solution and toluene used were of analytical grade.

Aromatic oil used was commercial grade supplied by Hindustan Petroleum Corporation. Silicone oil used was supplied by Reliance Silicones (India) Ltd., Bombay.

Fillers

High Abrasion Furnace Black (HAF-N330)

High abrasion furnace black (HAF) was supplied by M/s.Carbon and Chemicals (India) Ltd., Kochi. It had the following specifications:

Iodine adsorption	80 mg/g
DBP absorption	105 cm^3/100 g
Mean particle diameter	32 nm

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

EXPERIMENTAL METHODS

Compounding of Latex

The solid ingredients were added into latex as dispersions. The dispersions were prepared using a ball mill [1]. The materials were made to disperse in water by grinding action and the dispersing agent was used to prevent the dispersed particles from reaggregating. The quantity of dispersing agent to be used depends on the nature of materials to be dispersed. For very fine particle size ingredients like zinc oxide, the quantity of dispersing agent required is about 1 per cent by weight whereas for materials like sulphur 2 to 2.5 per cent is required.

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

Sulphur dispersion (50%)

Sulphur	100
Dispersol F	3
Distilled water	97

Ball milled for 72 hours

ZDC dispersion (50%)

ZDC	100
Dispersol F	2
Distilled water	98

Ball milled for 48 hours

ZnO dispersion (50%)

ZnO	100
Dispersol F	2
Distilled water	98

Ball milled for 48 hours

Precipitated silica (25%)

Precipitated silica	100
Dispersol F	2
Distilled water	98

Ball milled for 24 hours

Precipitated calcium carbonate (50%)

Precipitated calcium carbonate	100
Dispersol F	2
Distilled water	98

Ball milled for 24 hours

China clay (50%)

China clay	100
Dispersol F	2
Distilled water	98

Ball milled for 24 hours.

Dispersions of TMTD and CBS were prepared using the same procedure described above. 20% dispersion of carbon black without dispersol F was also prepared.

Preparation of Emulsions

The liquid additives which are immiscible with water, were added into latex as emulsions. The following receipe was used for preparing emulsions.

Antioxidant - sp (50%)

A	Antioxidant sp	100
	Oleic acid	3
B	Liquor ammonia	3
	Distilled water	94

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

Aromatic oil (50%)

A	Aromatic oil	100
	Oleic acid	3
B	Liquor ammonia	3
	Distilled water	94

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

De-Ammoniation of latex

High Ammonia (HA) type concentrated latex and ammonia preserved field latex were de-ammoniated to 0.2% by stirring in a laboratory type de-ammoniation tank for 3 hours. Otherwise, the high ammonia content in latex will create problems during conversion to solid products or in the stability of the latex compound in the presence of zinc oxide [2]. The concentration of ammonia in latex was estimated as per BIS: 3708-Part I 1966.

Compounding

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

Maturation

The latex compound was matured for 24 hours. This enables the compound to free itself of air entrained during the preparation and allows the stabilisers to distribute themselves uniformly throughout the aqueous and dispersed medium. During this maturation period important changes take place [3]. Absorption of vulcanization ingredients onto, or into, the rubber particle surface commences and becomes a continuing process with time and temperature. Further it allows time for the reaction of ammoniated latex with zinc oxide for getting uniform physico-chemical properties.

Preparation of latex film

Latex films were cast on glass dishes using the latex compound as described by Flint and Naunton[4]. The size of the glass dishes was 6"x6" and about 25 ml of the latex compound was poured and uniformly distributed so that a film of thickness 0.9-1 mm was obtained upon drying. These glass dishes with the latex compound were placed on levelled table and dried overnight.

Vulcanization of latex films

The vulcanization of latex films was carried out in a laboratory air oven at 120°C. The time for optimum cure was determined by vulcanizing the film for different durations of time at 120°C and determining the tensile strength of the vulcanizate in each case. The optimum cure time was taken as the time for attaining maximum tensile strength.

NR-PVC blend preparation and compounding

A Brabender Plasticorder (torque rheometer) model PL 3S was used for blending NR and PVC. It is a device in which the torque can be measured during mixing under pre-selected conditions of shear and temperature. The mixing of the polymers in the mixing chamber is done by two rotors rotating in opposite directions. The speed control of the rotors (range 0-150 rpm) is done by means of a D.C. thyristor controlled drive. The temperature of the mixing chamber is controlled by circulating hot silicone oil. The temperature can be set at any value upto 300°C.

Dry NR and PVC along with other compounding ingredients except accelerators and sulphur were mixed in the Brabender plasticorder at 150°C and 40 rpm for 5 minutes. Later, sulphur and accelerаters were added in a cold two roll laboratory mixing mill.

NR latex and the PVC dispersion were blended properly using a high speed mechanical stirrer (4000 rpm) and then the blend was coagulated using 2% acetic acid. After drying, the blend was mixed with other compounding ingredients except accelerators and sulphur at 150°C and 40 rpm for 5 minutes. Subsequently sulphur and accelerators were added in a cold two roll laboratory mixing mill.

Elastomer blend preparation

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip of (0.002x100)". Then it was given 2 passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 70±5°C during mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 4 3184 (1980) in the order activators, fillers, accelerators and curing agents. Before the addition of accelerators and sulphur, the batch was thoroughly cooled.

After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. For the preparation of compounds of elastomer blends, NR was masticated to the mooney viscosity level of the synthetic rubber, and then the other additives were added as described above unless otherwise specified.

Cure Characteristics

Using Goettfert Elastograph

The cure characteristics of the compounds were determined using a Goettfert Elastograph model 67.85. It is a microprocessor controlled rotorless curemeter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle (±0.2°). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. The following data can be taken from the torque-time curve.

1. Minimum torque: Torque obtained by the mix after homogenizing at the test temperature before the onset of cure.

2. Maximum torque: this is the torque recorded after the curing of the mix is completed.

3. Scorch time (t_{10}): This is the time for attaining 10% of the maximum torque.

4. Optimum cure time (t_{90}): This is the time taken for attaining 90% of the maximum torque.

5. Cure rate: Cure rate was determined from the following equation

$$\text{Cure rate (Nm/min.)} = \frac{L_{max.} - L_{min.}}{t_{90} - t_{10}}$$

where L_{max} and L_{min} are the maximum and minimum torque respectively and t_{90} and t_{10} the times corresponding to the optimum cure time and scorch time respectively.

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

Moulding of Test Specimens

The test specimens for determining the physical properties were moulded in standard moulds by compression moulding in an electrically heated hydraulic press having 30x30 cm platens at a pressure of 120 kg/cm^2 in the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150°C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness of more than 6 mm (compression set, abrasion resistance etc.), additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

Physical Test Methods

At least five specimens of each sample were tested for each property as follows and the mean values are reported.

a) Tensile stress-strain behaviour

Tensile properties of the cured samples were determined according to ASTM D 412 (1980) using dumbell specimens on a Zwick Universal testing machine model 1445. All the tests were carried out at 28±2°C. Sample were punched out from compression moulded sheets using a dumbell die (C-type) in the mill grain direction. The thickness of the narrow portion was measured by a thickness gauge. In the universal testing machine the sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. for elastomeric specimens. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

b) Tear resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on a Zwick Universal testing machine. The speed of extension was 500 mm/min. and the test temperature 28±2°C.

c) Hardness

The hardness (Shore A) of the moulded samples was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens.

d) Compression set

The samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100$$

where t_o and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used. The procedure given in ASTM D 395 (1982) (method B) was followed.

e) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN Abrader. Sample having a diameter of 6±0.2 mm and a thickness of 6 to 10 mm, was kept on a rotating sample holder and 10 N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight was calculated. The abrasion loss is expressed as the volume of the test piece getting abraded away by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows:

$$V = \Delta m / \rho$$

where Δm = mass loss, ρ = density of the sample and v = abrasion loss. The abrasion loss of a standard sample was also calculated in a similar manner.

The abrasion resistance index was calculated as follows:

$$\text{Abrasion resistance index} = \frac{\text{Abrasion loss of standard sample}}{\text{Abrasion loss of test sample}} \times 100$$

f) Density

The densities of the polymer samples were estimated by the method of displacement of liquid (ASTM D 792). In this method, the weight of the specimen in air was first noted and then the specimen was immersed in a liquid and its loss of weight in liquid was determined. The density was calculated as

$$\text{Density} = \frac{\text{Weight of specimen in air x density of the liquid}}{\text{Weight loss of specimen in liquid}}$$

g) Rebound resilience

Dunlop tripsometer (BS 903, Part 22, 1950) was used to measure rebound resilience. The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as follows

$$\text{Rebound resilience (\%)} = \frac{1-\cos\theta_2}{1-\cos\theta_1} \times 100$$

where θ_1 and θ_2 are the initial and final rebound angles respectively. θ_1 was kept 45° in all cases.

h) Ageing studies

Dumbell samples for evaluation of physical properties were prepared and kept in an air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, tear strength, elongation at break etc. were measured after ageing. The percentage retention of these properties was evaluated for assessing the effect of ageing. The procedure given in ASTM D 573 was followed.

i) Heat build up

The Goodrich flexometer conforming to ASTM D 623-67 method A was used for measuring heat build up. The test was carried out with cylindrical samples of 2.5 cm in height and 1.9 cm in diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.9 kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat developed was sensed by thermocouple and relayed to a digital temperature indicator. The temperature rise (ΔT)°C at the end of 20 minutes was taken as heat build up.

j) Flex resistance

The test is intended to compare the resistance of rubbers to the formation and growth of cracks and is recommended when flexing is encountered in service as in the case of a side wall. The apparatus used was a Wallance Demathia flexing machine as per ASTM D 430-57 T. Moulded test specimens with a circular groove, conditioned for 24 hours were tested in duplicate. The number of flexing cycles for crack initiation and for complete failure were noted on the counter. The test was conducted at ambient temperature.

MORPHOLOGY STUDIES

Using optical microscope

The morphology of the compounds and vulcanizates was investigated by taking photomicrographs on Leica Wild M8 Zoom stereo microscope and Wild mps 46/52 photoautomat using NOVA FP_4 films. Test samples (slides) were prepared by dipping glass plates in compounded latex, so that a thin coating of the latex compound was formed on the glass plate. After drying and curing, photographs of these samples were taken at different magnifications.

For taking polaroides, MP_4 Land camera was used. For this the vulcanized test piece was cut to a convenient size and mounted on a microscope slide. Photographs were taken at a magnification of 30.

Mooney viscosity measurement

The mooney viscosities of the rubber samples were measured on the mooney viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc rotating (2 rev/min.) in a cylindrical cavity set at 100°C and filled with rubber under test. In running a viscosity test, the sample was allowed to warm up for one minute after the platens were closed and the motor was then started. Reading after 4 minutes was reported as the mooney viscosity of rubber [ML(1+4) at 100°C]. The procedure according to ASTM D 1646 (1981) was followed.

RHEOLOGICAL STUDIES

Rheological studies of latex compounds were done using a Brookfield viscometer. It is a technical viscometer and is used for determining the viscosity of latex compounds. It consists of a rotating member which is usually a cylinder driven by a synchronous motor through a torque spring. The viscous drag on the cylinder causes an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disc is rotating. The torque and therefore the viscosity is indicated by means of the pointer and scale. A range of speed of the discs and cylinders are available so that a wide range of viscosity may be covered. Using this viscometer, viscosities of filled NR latex compounds at different rpm were calculated.

Rheological evaluation using a Capillary Rheometer

Melt rheological measurements were made using a capillary rheometer attached to a Zwick Universal testing machine, model 1474. The extrusion assembly consisted of a hardened steel barrel underneath the moving crosshead of the machine. A hardened steel plunger which was accurately ground to fit inside the barrel was held to the load cell by a latch assembly. The barrel was thermally insulated from the rest of the machine. The capillary used was made of tungsten carbide steel. It had a length to diameter ratio of 40, with an angle of entry of 180°C. The barrel was electrically heated and accurately controlled. The crosshead speed could be varied in the range 0.5-500 mm/min.

The test sample in small pieces, was put into the barrel of the capillary rheometer and forced down to the capillary by the plunger attached to the moving crosshead. After a warm up period of 3 min. the sample was extruded through the capillary at 10 speeds. Forces corresponding to specific plunger speeds were measured by the pressure transducer attached to the plunger and were recorded using a strip chart recorder assembly.

The force and crosshead speed were converted into apparent shear stress τ_w and shear rate $\dot{\gamma}_w$ at the wall, respectively, using the following equations involving the geometry of the capillary and the plunger

$$\tau_w = \frac{F}{4AP[(l_c/d_c)]}$$

$$\dot{\gamma}_w = \frac{(3n' + 1}{4n'} \times \frac{32Q}{\pi d_c^3}$$

where F is the force applied at a particular shear rate, A the cross-sectional area of the plunger, l_c the length of the capillary, d_c the diameter of the capillary, Q the volume flow rate and n' the flow behaviour index, defined as

$$n' = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_w)}$$

and determined by regression analysis of the values of τ_w and $\dot{\gamma}_w$ obtained from the experimental data. The shear viscosity, η was calculated as

$$\eta = \frac{\tau_w}{\dot{\gamma}_w}$$

Rheological evaluation using Gottfert Viscotester 1500

Rheological measurements were also made using the capillary rheometer-Gottfert viscotester 1500. The measurement and calculations are similar to those described.

Extrudate swelling

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 24 hrs. using a binoculor steromicroscope. The extrudate swelling was calculated as the ratio of the diameter of extrudate to that of the capillary (d_e/d_c)

CHEMICAL TEST METHODS

Determination of volume fraction of rubber

Samples of approximately 0.3 g weight were punched from the vulcanized latex film and allowed to swell in distilled toluene for 48 hrs. Swollen samples were blotted with filter paper and weighed quickly in a stoppered weighing bottle. Samples were dried in an oven for 24 hrs. at 70°C and then in vacuum and finally weighed after allowing them to cool in a desiccator. Duplicate readings were taken for each sample. The volume fraction of rubber was calculated by the method reported by Ellis and Welding [5] which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

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

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

For NR, specific gravity of 0.92 was chosen and for toluene a value of 0.886. From the above data, V_r, the volume fraction of rubber in the vulcanizate was determined and from V_r the crosslink density [½MC] was calculated as follows

$$\frac{1}{2}\,MC = \frac{-[\ln(1-V_{ro}) + V_{ro} + \chi V_{ro}^{2}]}{2\,\rho_r V_s (V_{ro})^{1/3}}$$

where V_s = molar volume of solvent, V_s(toluene) = 106.2 cc/mol, χ = parameter characteristic of interaction between rubber and solvent, χ for NR-toluene = 0.42 [6].

Determination of rubber filler interaction

The 'V_r' values of the filled (V_{rf}) and the gum (V_{ro}) vulcanizates were determined. The extent of rubber filler interaction was then studied using the equation given by Cunneen and Russel [7]

$$\frac{V_{ro}}{V_{rf}} = ae^{-z} + b$$

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

Ammonia-modified swelling

The samples of the vulcanized latex films containing different filler contents were swollen for 48 hrs. in flat dishes containing toluene in ammonia atmosphere [8]. For this the samples were put in a desiccator the bottom of which contained liquor ammonia. After swelling in ammonia atmosphere the samples were thoroughly washed with toluene and dried in a vacuum desiccator at room temperature and V_r value was calculated. The difference in V_r values of the vulcanizate swollen in toluene and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond. In this the ammonia permeates the toluene solvent and preferentially cleaves the rubber filler attachment.

Iodine adsorption number of HAF

Iodine adsorption number of HAF was determined as per ASTM D 1510 [9].

DBP absorption test was conducted as per ASTM D 2414.65 [10].

Bound rubber content determination

The solvent used for the bound rubber determination was toluene. Approximately 0.2 g of the compound was cut into small pieces and placed into a stainless steel wire mesh cage of known weight. The cage was then immersed in 25 ml of solvent for seven days at room temperature and the solvent was renewed after three days. After extraction, the rubber and the cage were dried for one day in air at room temperature and then for 24 hrs. in an oven at 105°C. The bound rubber of the polymer (R_B) was then calculated as described by S.Wolff et al. [11] according to the following equation.

$$R_B = \frac{W_{fg} - W[m_f/(m_f + m_p)] \times 100}{W[m_p/(m_f + m_p)]}$$

where W_{fg} is the weight of the carbon black and gel, m_f the weight of the filler in the compound, m_p the weight of the polymer in the compound and w the weight of the specimen.

Estimation of chlorine

Accurately weighed samples of the sheets were taken in platinum crucibles and covered with a mixture of sodium carbonate and potassium carbonate (1:1). These were kept in a muffle furnace for 4 hours, at 900°C. The fusion mixture was dissolved in water and after neutralising with conc. HNO_3, about 35 ml of $AgNO_3$ (0.1N) was added and filtered. The filtrate was titrated with 0.1N sodium thiocyanate. $AgNO_3$ was standardised with $K_2Cr_2O_7$. A blank test was also conducted. The chlorine content x was determined using the equation

$$x = \frac{(\text{Blank - Sample volume})}{\text{W x 100}} \text{ x N x 35.5 x 100}$$

where w is the weight of sample and N is the normality of thiocyanate.

Transmittance study

Spectroscopic investigations were done using Hitachi UV vis NIR Spectrophotometer model 330. The percentage transmittance of the samples was measured at 2000 nm. The percentage transmittance is a measure of the transparency of the sheets.

Estimation of extractable protein (EP) content

Extraction of total soluble proteins

Samples of two pieces measuring 7x7 cm and weighing about 1.5 to 2.0 g each were cut from the latex gloves/films. Each piece was again cut into 16 pieces of equal size. The pieces were weighed accurately and extracted with 50 ml distilled water in a 10 cm diameter glass container at room temperature for 24 hrs. with occasional agitation. The extract was then centrifuged in a REMI Laboratory centrifuge R 8C at 3,500 rpm for 30 minutes to remove any insoluble matter.

Protein purification and concentration from the extract

Proteins in the extract were purified and concentrated by precipitation with Trichloro acetic acid (TCA) and phosphotungstic acid (PTA).

To 6 ml of the protein extract, 1 ml of 35% (W/V) TCA was added and mixed. Then 1 ml of 40% (W/V) PTA was added, mixed well and allowed to stand for 20 minutes. The precipitated protein was then recovered by centrifuging the mixture in a REMI Laboratory centrifuge R 8C at 3,500 rpm for 30 minutes and decanting away all the supernatent. The very thin film of the precipitate was then redissolved in 2.6 ml of 0.1 M sodium hydroxide for at least 20 minutes.

Protein estimation

Protein samples were assayed by the Modified Micro Lowery Assay method [12]. The reagents were prepared as follows:

Reagent A - 6% sodium carbonate in 0.2M sodium hydroxide.
Reagent B - 1.5% copper sulphate in 3.0% sodium citrate

Reagent C - (Working reagent prepared on the day of estimation) 50 ml of reagent A mixed with 1 ml of Reagent B.

Reagent D - Folins - Ciocaults Reagent. Diluted 3 parts of reagent with 1 part water.

The test reaction was carried out directly in the centrifuge tube. 0.3 ml of Reagent C was added to 2.6 ml of the test sample already present in the centrifuge tube. The contents were mixed well and allowed to stand for 10 minutes.

0.1 ml of Reagent D was then added and mixed well in a cyclo mixer. The mixer was then allowed to stand for 30 minutes and the absorbance was read on the spectrophotometer, Shimadzu UV 240 at 750 nm. The concentration of proteins was read against the standard protein used for calibration (Bovine serum albumine, 0-120 mg/ml).

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CHAPTER 3

PART I: USE OF NOVEL ADDITIVES FOR IMPROVING THE RUBBER-FILLER INTERACTION IN LATEX VULCANIZATES

The major advantages of adding filler to rubber compound are the reduction in cost of the products and the reinforcement of rubber. Many studies have been published explaining the reinforcing properties of carbon black in rubber [1,2]. But the use of fillers, both reinforcing fillers like carbon black, silica etc. and nonreinforcing fillers like clay, calcium carbonate etc., in latex products is limited since they affect the mechanical properties adversely [3]. The reduction in vulcanizate properties may be due to the lack of proper distribution of filler in the latex, time gap between the deposition of the filler and rubber particles and the presence of protective surface coating both on the rubber particles and the filler [4]. In order to improve rubber-filler interaction, coupling agents are used in dry rubber compounding particularly in the case of nonreinforcing fillers [5,6]. But in latex compounding such coupling agents are not common as it will affect the stability of the latex. However, it may be possible to incorporate modifiers to improve the rubber-filler interaction and hence develop filled latex products. Earlier workers have studied the reinforcement of silica filler in NR, in the presence of silane coupling agent [7]. More recently N.Radhakrishnan Nair et al have studied the role of certain surface modifying agents like diethylene glycol, tri-ethanolamine and bis(triethoxysilyl propyl)-tetra sulphide (Si-69) in improving the mechanical properties of the rubber compound [8]. It has been shown that peptising agents, plasticizing agents etc. can be incorporated in NR latex for the purpose of modifying its properties [9,10]. The use of poly glycol H.S. 35/40 in NR latex has also been studied [11]. In this study, polyethylene glycols and glycerol have been tried as potential modifiers for improving the mechanical properties of filled NR latex vulcanizates. The ageing resistance of the vulcanizates in the presence of these modifiers is also proposed to be studied. The processability and the filler distribution of the modified vulcanizates are also proposed to be investigated.

EXPERIMENTAL

Polyethylene glycols of mol. wt. 300, 600, 1000, 2000, 4000 and 6000, referred to as PEG 300, PEG 600, PEG 1000, PEG 2000, PEG 4000 and PEG 6000, were used in this study.

Compounding and preparation of sheets

Polyethylene glycols and glycerol were prepared as 50% solutions in water. The dispersions of the vulcanizing agents and the fillers (silica, calcium carbonate and clay) were prepared in water using the dispersing agent - Dispersol F. Carbon black (HAF N-330) dispersion was prepared without dispersol F. A base latex compound was prepared as per the formulation given in Table 3.1.

Effect of concentration of polyethylene glycol

To a portion of the base latex compound 20 phr of clay was added as a 40% dispersion in water. The latex-filler system was treated with polyethylene glycol (PEG 6000) at different dosage of 0, 0.5, 1.0, 1.5 and 2.0 phr. Latex films were prepared by casting the compounds in glass dishes. After drying the films at room temperature for 24 hrs, they were vulcanized at 120°C for 40 minutes in an air oven. Dumbell shaped tensile test specimens were punched out of these cast sheets. The tensile properties were measured using a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min. as per ASTM D 412-80.

Optimum cure time of the latex sheets

In order to study the effect of PEG and glycerol on optimum cure time, the base latex compound was mixed

Table 3.1

Formulation of the base latex compound

Ingredients	Parts by weight (wet) gm.
60% Centrifuged latex	167.00
10% KOH	1.00
10% Potassium oleate	1.00
50% ZnO	0.75
50% ZDC	3.00
50% S	3.00

with 10 phr of silica/$CaCO_3$/clay as a 40% dispersion in water and 1.0 phr (the optimum concentration) of PEG 300 as 50% solution in water. Latex films were prepared by casting the compounds in glass dishes. After drying the films at room temperature for 24 hrs they were vulcanized for times varying from 28-40 minutes at 120°C. The tensile properties of these sheets were measured. The same study was done with latex compounds containing 1 phr of glycerol instead of PEG and also with base latex compound containing 10 phr of silica/$CaCO_3$/clay without PEG/glycerol.

Mechanical properties of filled latex vulcanizates

A portion of the base latex compound was mixed with 10, 20 and 30 phr each of silica and was mixed with 1 phr of PEG (mol. wt. 300, 600, 1000, 2000, 4000 and 6000) and glycerol. Cast latex films of the compounds containing PEG/glycerol were prepared and vulcanized at 120°C for optimum cure time. The compounds were also prepared without PEG/glycerol and cast latex films were cured upto the optimum cure time. The tensile properties of the films were determined.

The same experiment was repeated with dispersions of $CaCO_3$, clay and carbon black. In the case of $CaCO_3$ and clay, the filler concentration could be further increased to 40 and 50 phr. But with silica and carbon black the maximum filler loading was about 30 phr above which the compound got destabilised.

Ageing studies

Test specimens from these sheets were aged at 70°C for 48 hrs and the retention in tensile properties was determined.

Determination of rubber-filler interaction

The vulcanized latex films were subjected to swelling for 48 hrs. in toluene. The extent of rubber-filler interaction was studied using the equation given by Cunneen and Russel [12]. According to this,

$$V_{ro}/V_{rf} = a.e^{-z} + b$$

where V_{ro} and V_{rf} are the volume fractions of rubber in the gum and filled vulcanizate respectively. Z is the weight fraction of the filler in the vulcanizate and a and b are constants. By plotting V_{ro}/V_{rf} against e^{-z}, value of 'a' (slope) and 'b' (intercept) were determined.

Ammonia-modified swelling

The extent of rubber-filler attachment was further studied by conducting the swelling of vulcanized samples for 48 hrs in toluene in ammonia atmosphere [13].

Optical studies

The morphology of the filled compounds with and without PEG/glycerol was studied. The compounds were matured for 24 hrs and were cast into thin films. It was then cut into a convenient size and mounted on a microscope slide. Photomicrographs were taken on Leica wild M_8 Zoom stereo microscope and wild MPs 46/52 photoautomat using NOVA FP_4 films.

Rheological behaviour of the filled compounds was investigated using a Brookfield viscometer.

RESULTS AND DISCUSSION

Fig.3.1 shows the effect of different dosage of PEG 6000 on the tensile strength of the clay filled (20 phr) vulcanizate. The tensile strength of the vulcanizates increases as the amount of polyethylene glycol increases and reaches a maximum at 1 phr and above 1 phr there is not much change. The variation in modulus also shows that the optimum dosage of PEG is about 1 phr (Fig.3.1.).

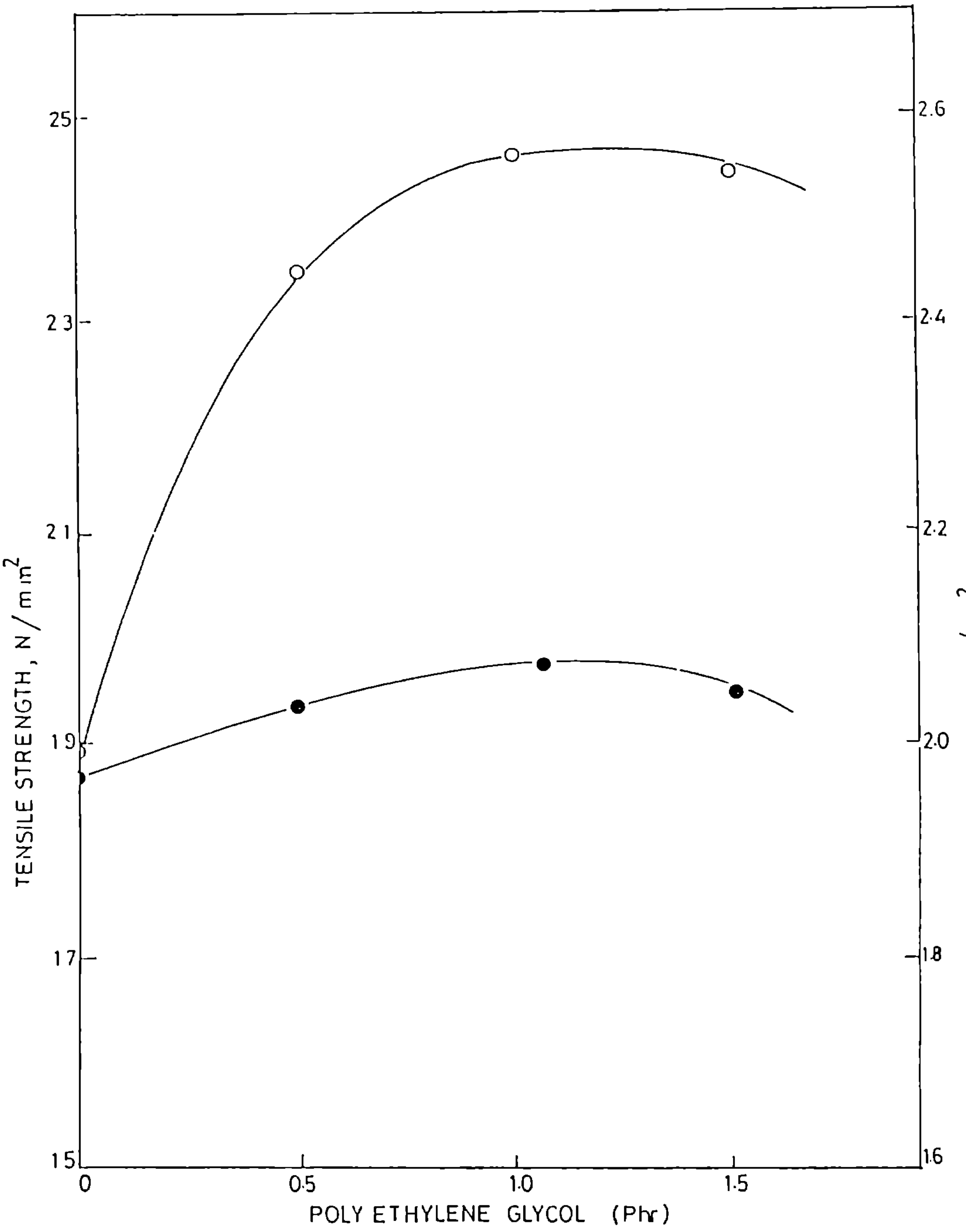


Fig.3.1 Variation of tensile strength 'O' and modulus '●' of clay filled (20 phr) latex vulcanizate with amount of PEG 6000.

Figs.3.2 to 3.4 show the variation of tensile strength with cure time. For compounds containing PEG, the tensile strength increases, as the cure time increases and reaches a maximum at 30 minutes, thereafter decreases. The attainment of maximum tensile strength occurs at 32 minutes for the compounds containing glycerol and at 34 minutes for compounds without PEG/glycerol. It shows that the addition of PEG/glycerol can reduce the optimum cure time. This may be attributed to the reduced accelerator adsorption on the filler surface in the presence of PEG and glycerol. All the three fillers studied follow the same trend. Figs.3.5 and 3.6 show the variation of tensile strength of the silica filled natural rubber latex vulcanizate before and after ageing respectively. The addition of optimum amount of PEG of different mol. wt. in the compounds improve the tensile properties before and after ageing. This may be attributed to the improved filler-rubber interaction and the more homogeneous distribution of filler in the latex compounds in the presence of PEG or glycerol. Low molecular weight glycols are found to be more effective in improving the tensile properties. Figs.3.7 and 3.8 show the variation of tensile strength of the calcium carbonate filled NR latex vulcanizates, with the amount of filler before and after ageing. The filled compounds containing

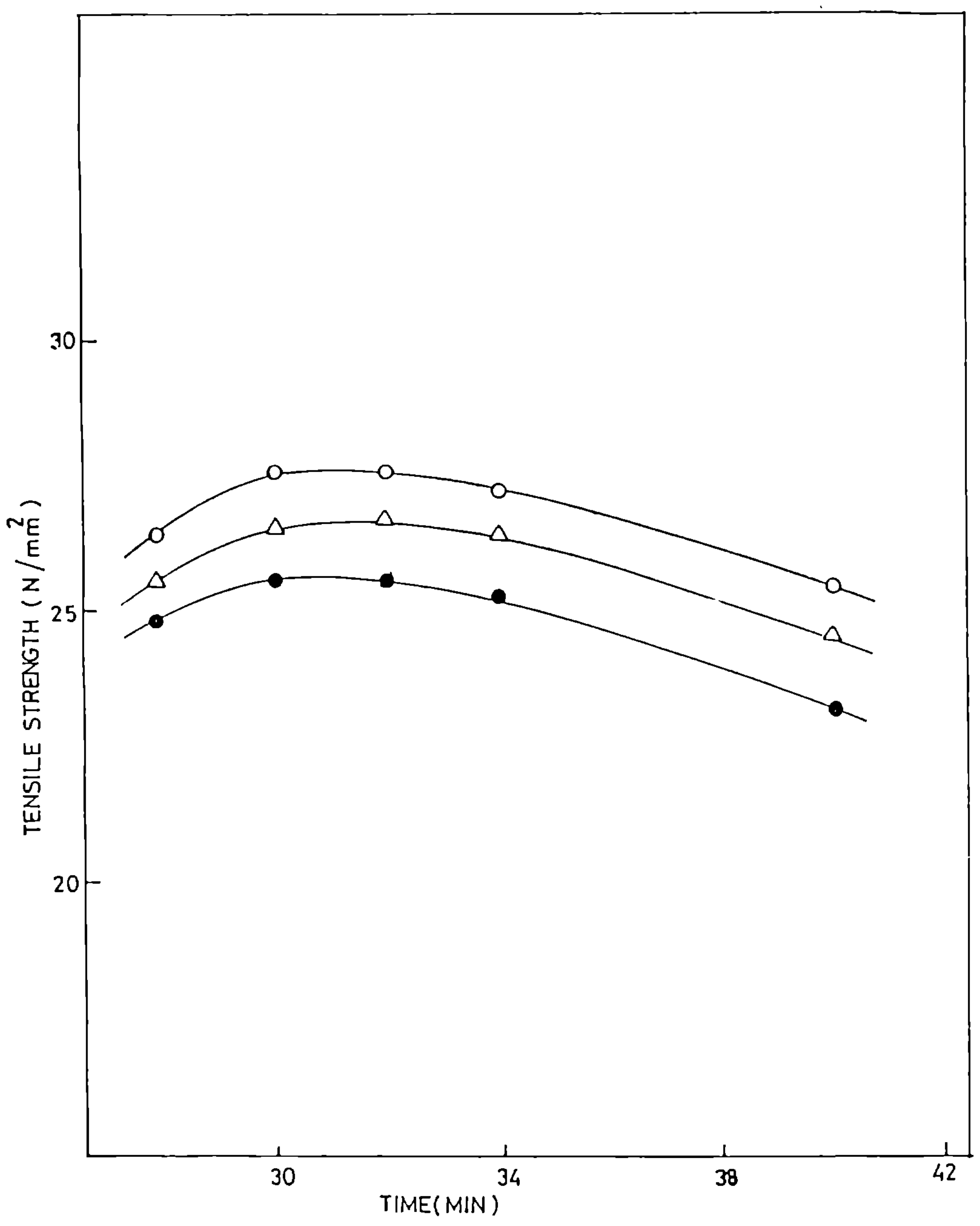


Fig.3.2 Variation of tensile strength with cure time of the filled (10 phr) NR latex vulcanizate containing PEG 300. 'Δ' silica, 'O' $CaCO_3$ and '●' clay.

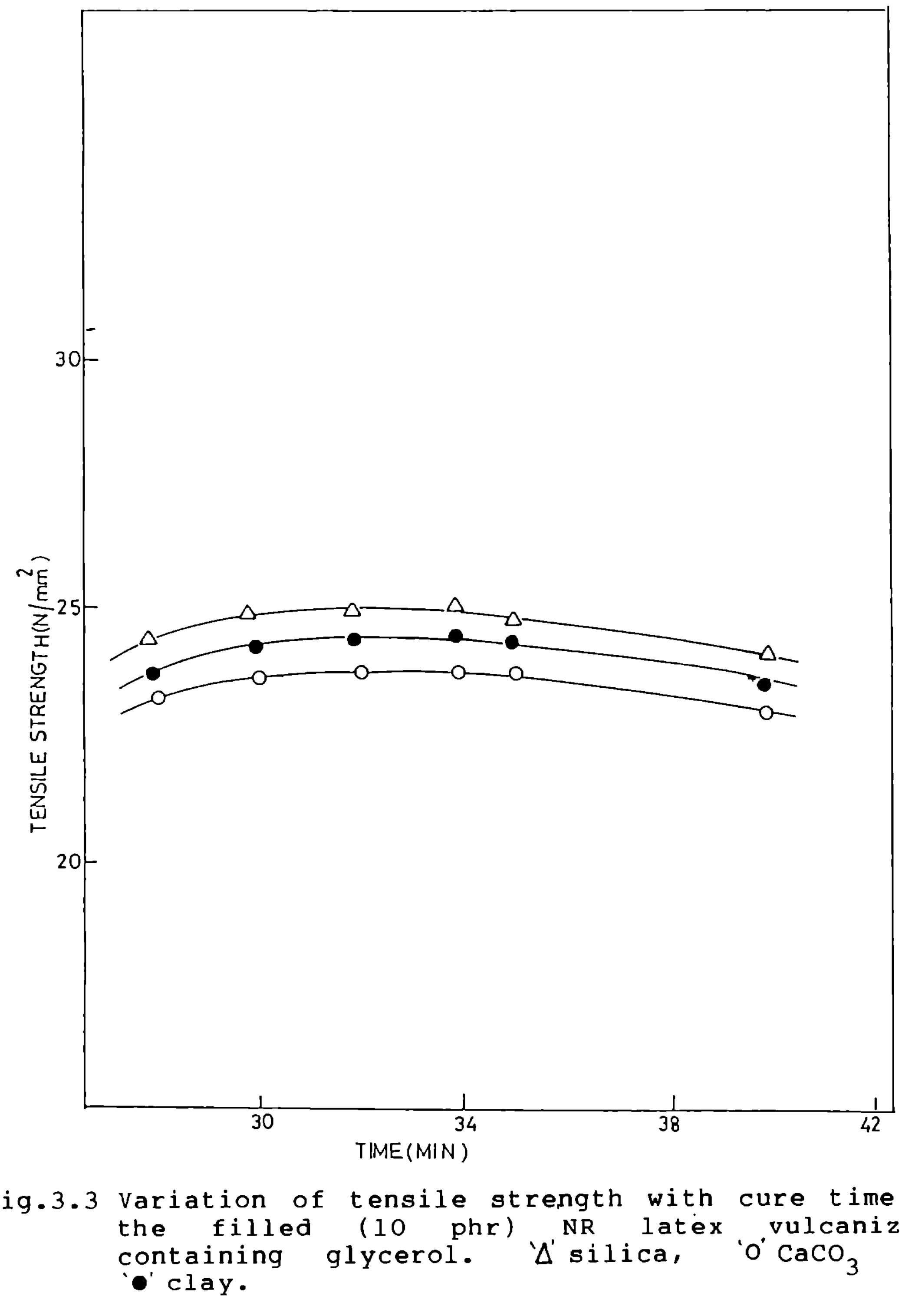


Fig.3.3 Variation of tensile strength with cure time of the filled (10 phr) NR latex vulcanizate containing glycerol. 'Δ' silica, 'O' $CaCO_3$ and '●' clay.

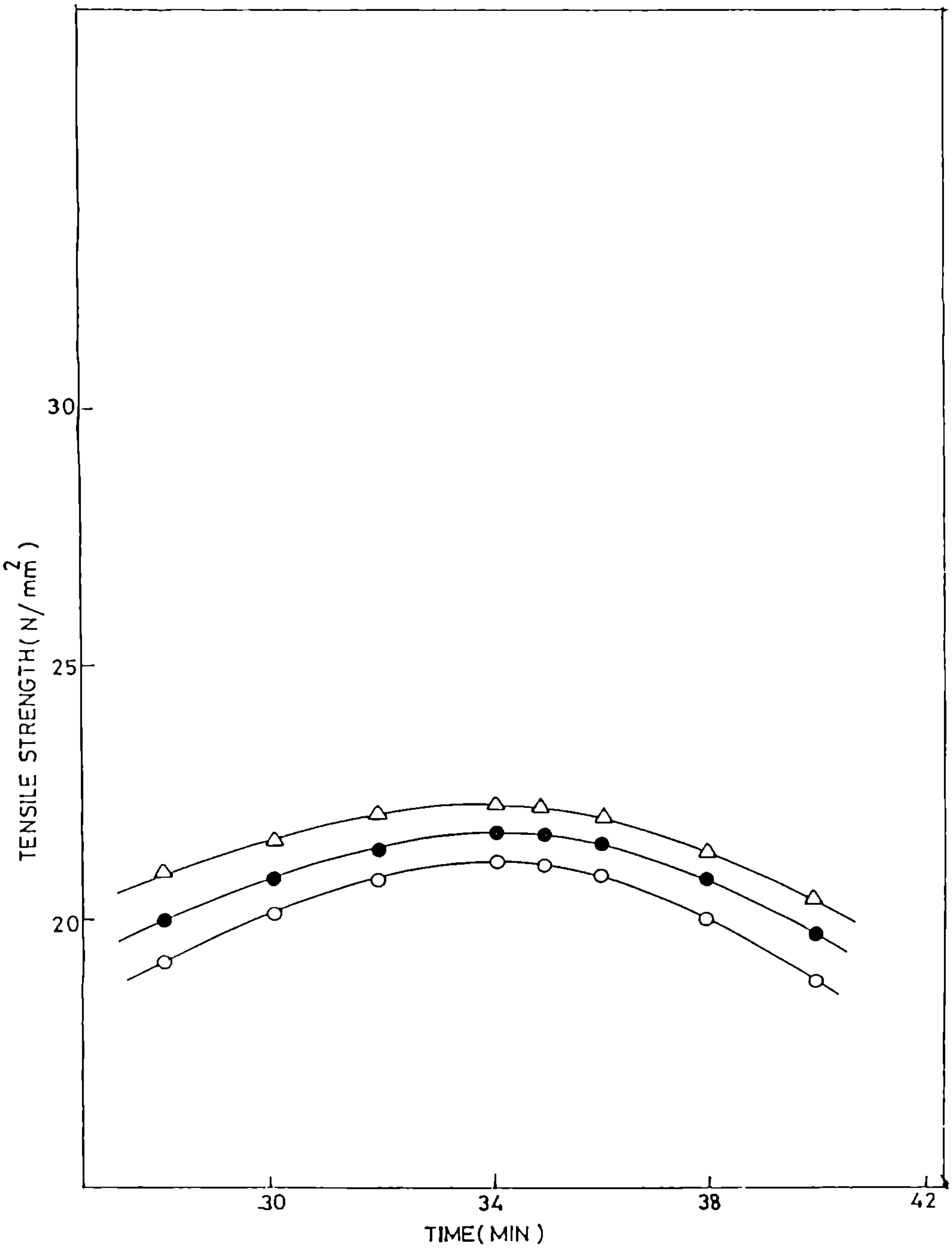


Fig.3.4 Variation of tensile strength with cure time of the filled (10 phr) NR latex vulcanizate. 'Δ' silica, 'O' $CaCO_3$ and '●' clay.

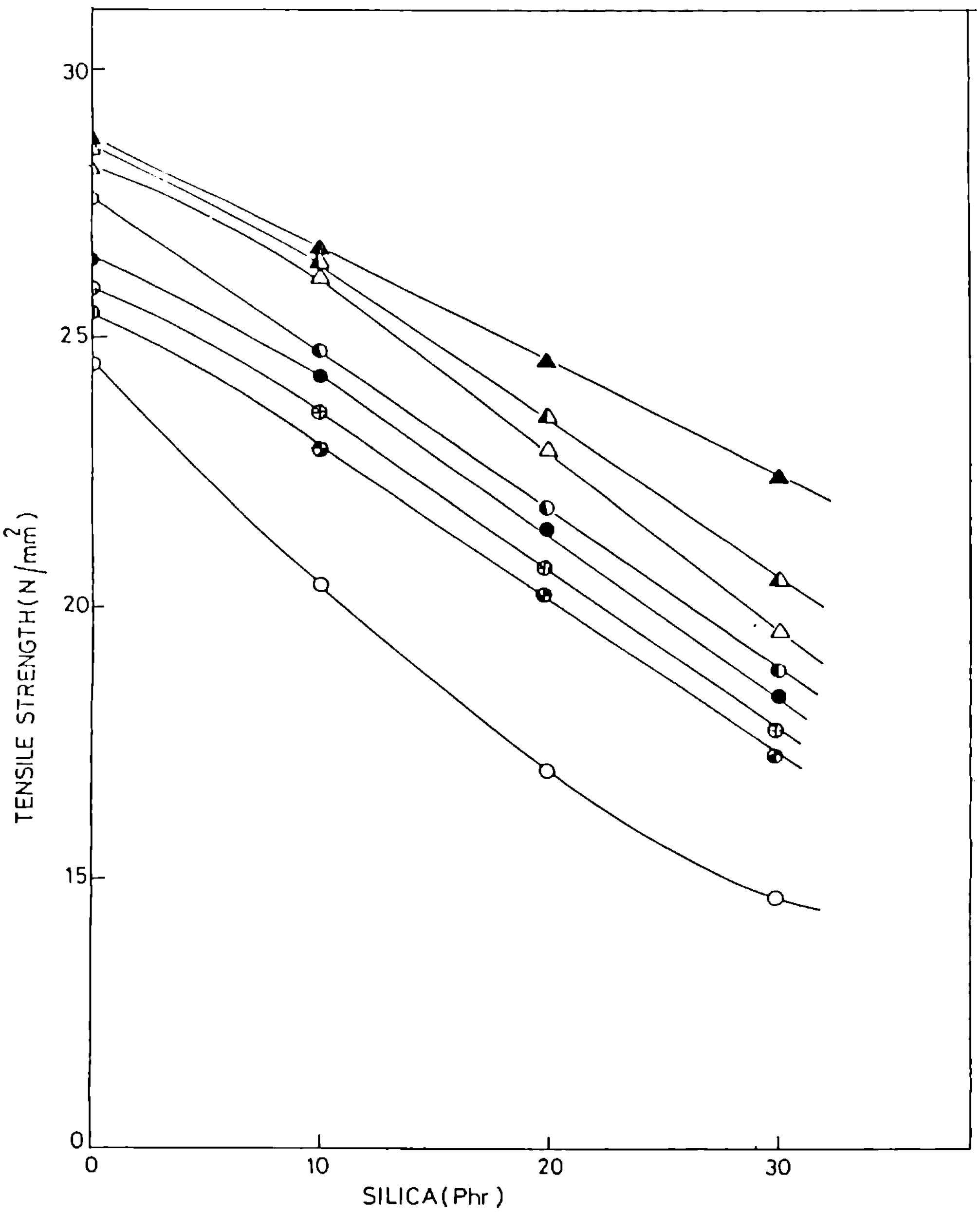


Fig.3.5 Variation of tensile strength with amount of silica before ageing. `▲' PEG 300, `◭' PEG 600, `△' PEG 1000, `●' PEG 2000, `⊕' PEG 4000, ◍ PEG 6000, `◐' glycerol and `○' without PEG/glycerol.

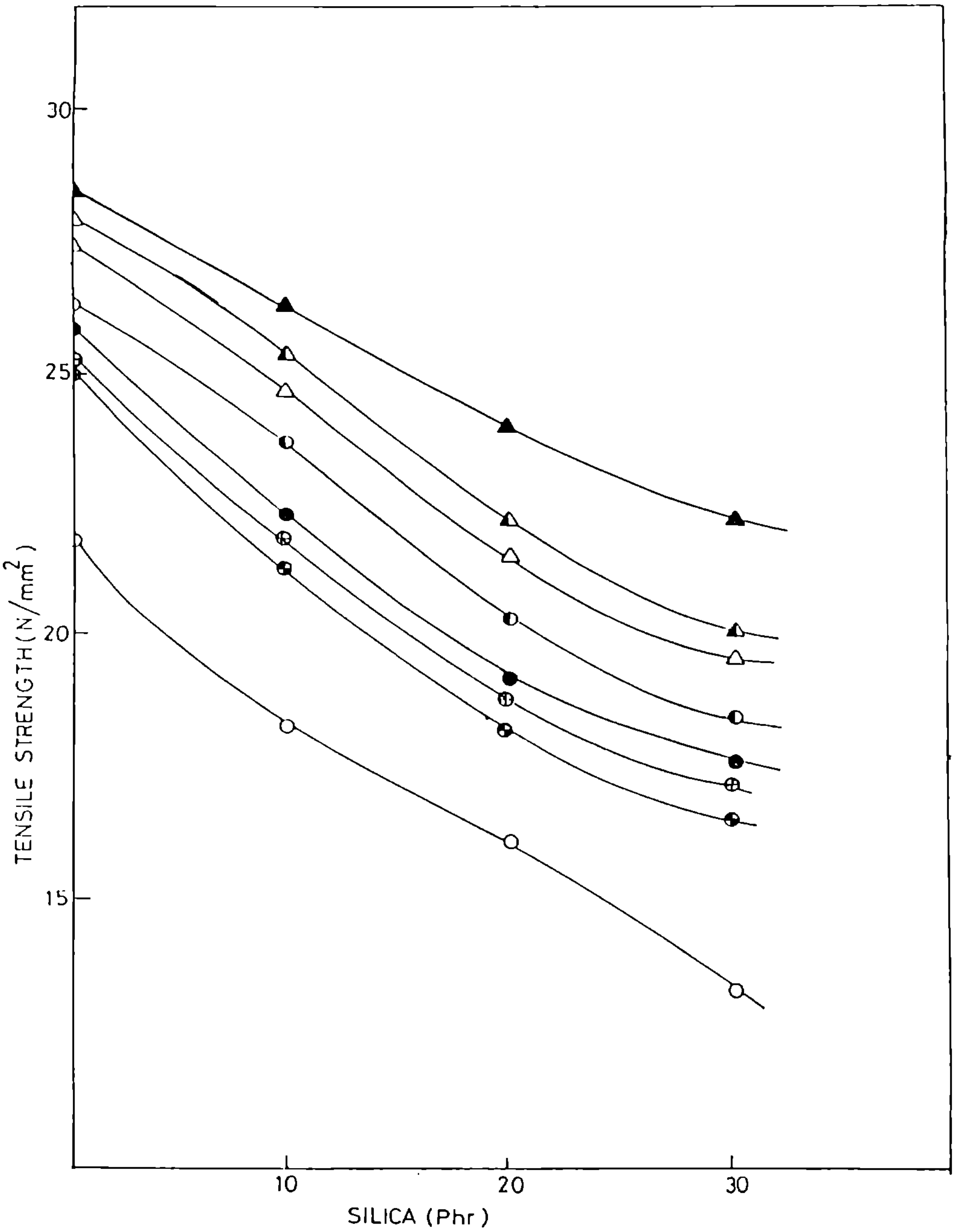


Fig.3.6 Variation of tensile strength with amount of silica after ageing. '▲' PEG 300, '▲' PEG 600, '△' PEG 1000, '●' PEG 2000, '⊕' PEG 4000, '⊕' PEG 6000, '◐' glycerol and 'O' without PEG/glycerol.

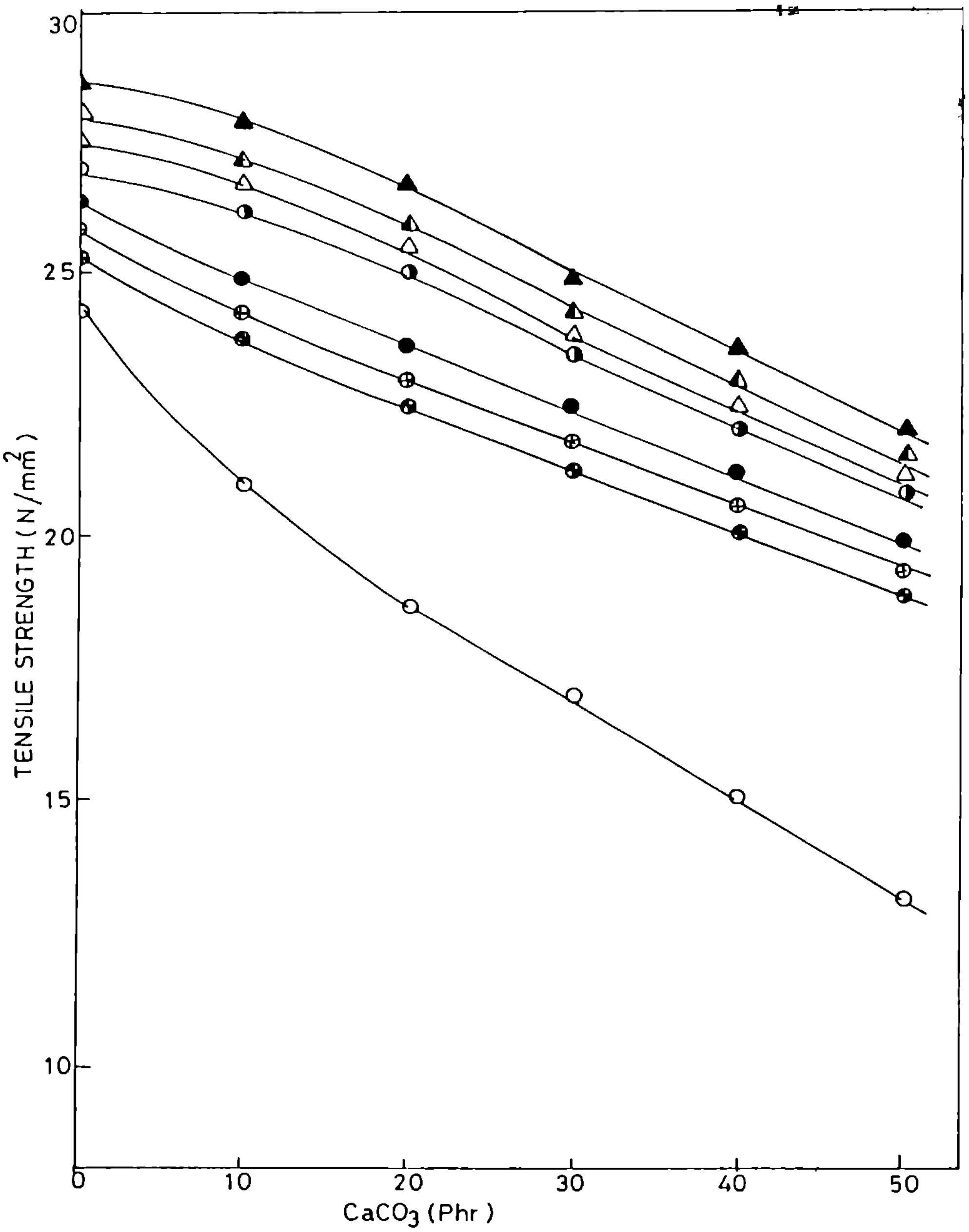


Fig. 3.7 Variation of tensile strength with amount of CaCO$_3$ before ageing. '▲' PEG 300, '◭' PEG 600, 'Δ' PEG 1000, '●' PEG 2000, ⊕ PEG 4000, '⊛' PEG 6000, '◐' glycerol and 'O' without PEG/glycerol.

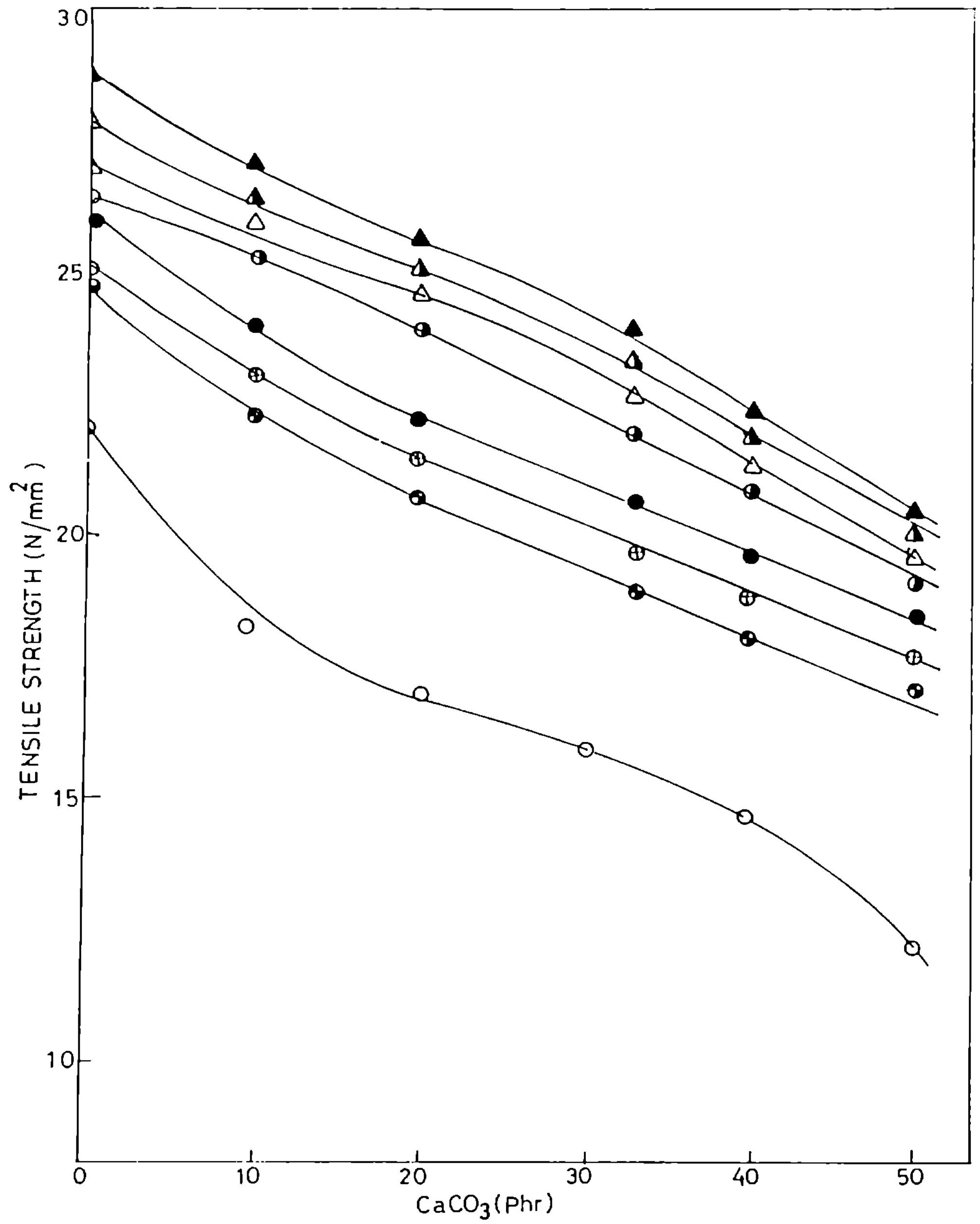


Fig.3.8 Variation of tensile strength with amount of $CaCO_3$, after ageing. '▲' PEG 300, '▲' PEG 600, '△' PEG 1000, '●' PEG 2000, '◐' PEG 4000, '◐' PEG 6000, '◐' glycerol and 'o' without PEG/glycerol.

PEG or glycerol are found to show improved tensile strength similar to the silica filled compounds. Figs.3.9 and 3.10 showing the variation of tensile strength of clay filled NR latex vulcanizates before and after ageing also follow a similar pattern. The improvement in tensile strength is found to be more in the case of calcium carbonate and clay compared to silica. Glycerol is found to be less effective compared to PEG of mol. wt. upto 1000 and more effective compared to PEG of mol. wt. above 2000.

Fig.3.11 gives the variation of tensile strength of the carbon black filled NR latex vulcanizates, with the amount of black before and after ageing. Here also, the filled compounds containing PEG are found to show enhanced tensile strength similar to the silica filled vulcanizates.

Fig.3.12 describes the variation of modulus of the filled NR latex vulcanizates with filler concentration in the presence of PEG 600. Fig.3.13 shows variation of modulus of filled NR latex vulcanizate with amount of filler in the absence of PEG. The modulus is found to be higher for compounds containing PEG. This increased modulus shown by vulcanizates containing PEG may be attributed to the higher polymer-filler interaction in presence of PEG and also due to the more uniform filler

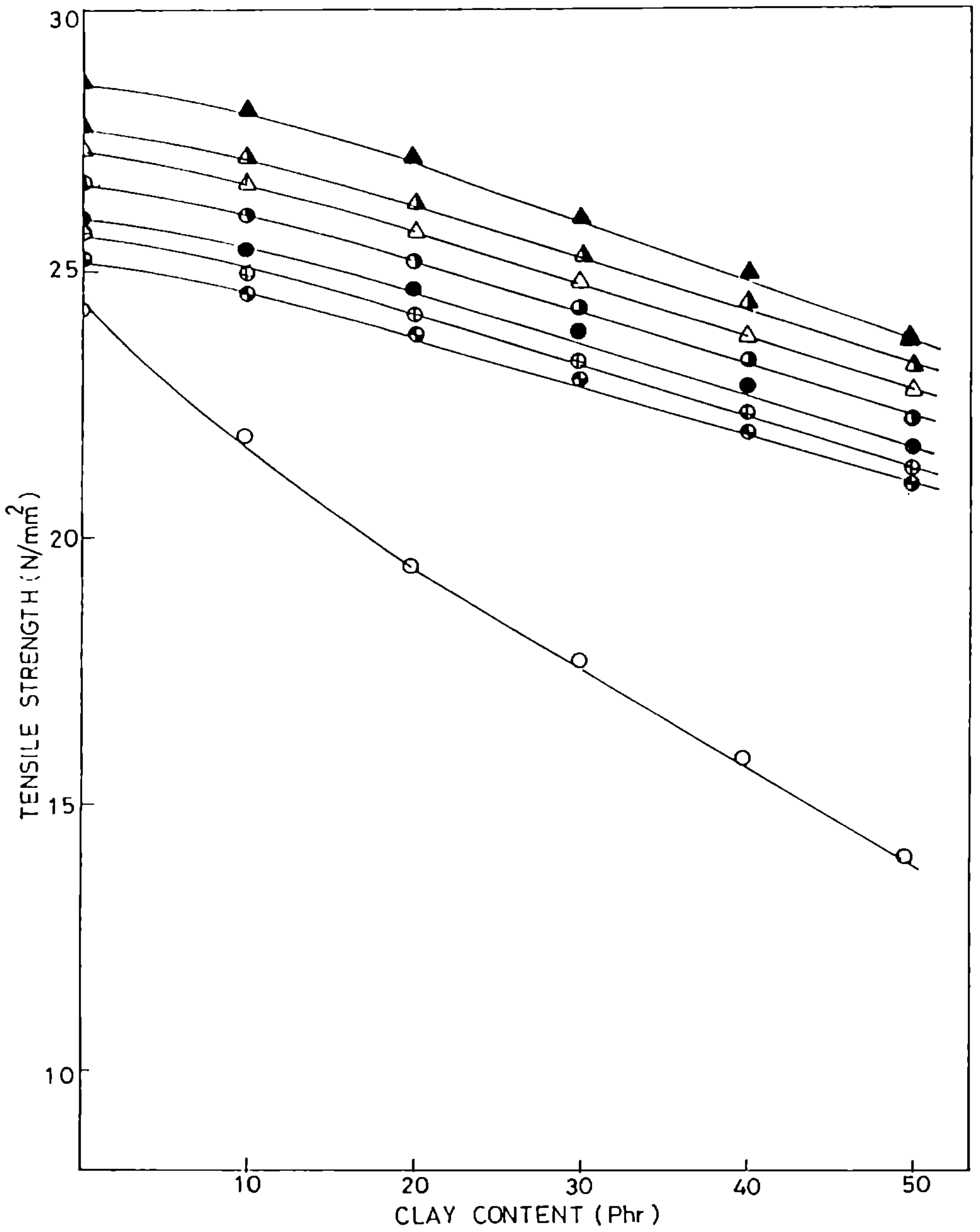


Fig.3.9 Variation of tensile strength with amount of clay before ageing. '▲' PEG 300, '◭' PEG 600, '△' PEG 1000, '●' PEG 2000, '⊕' PEG 4000, '◉' PEG 6000, '◑' glycerol and 'O' without PEG/glycerol.

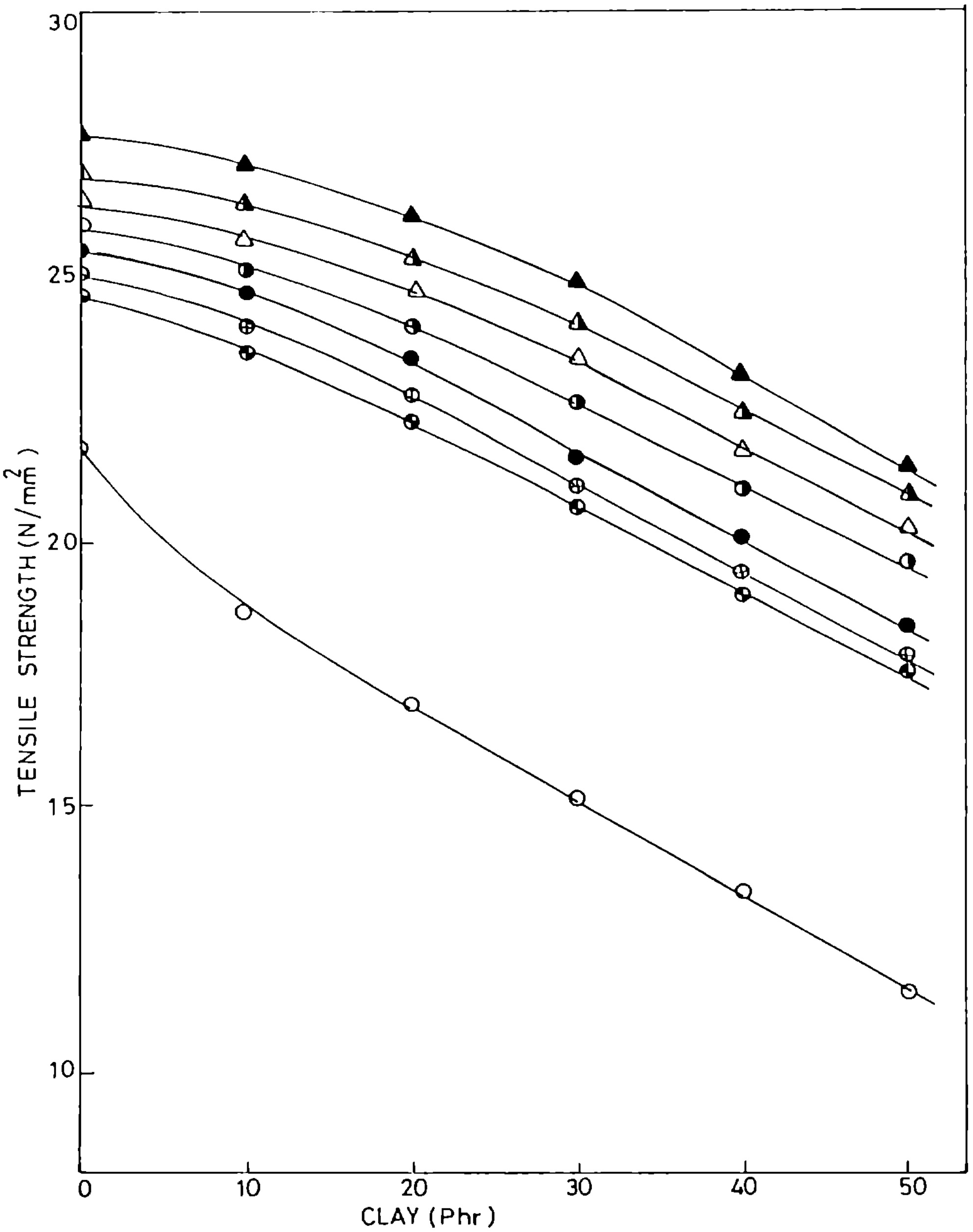


Fig.3.10 Variation of tensile strength with amount of clay after ageing. '▲' PEG 300, '◭' PEG 600, '△' PEG 1000, '●' PEG 2000, '⊕' PEG 4000, '◕' PEG 6000, '◑' glycerol and 'O' without PEG/glycerol.

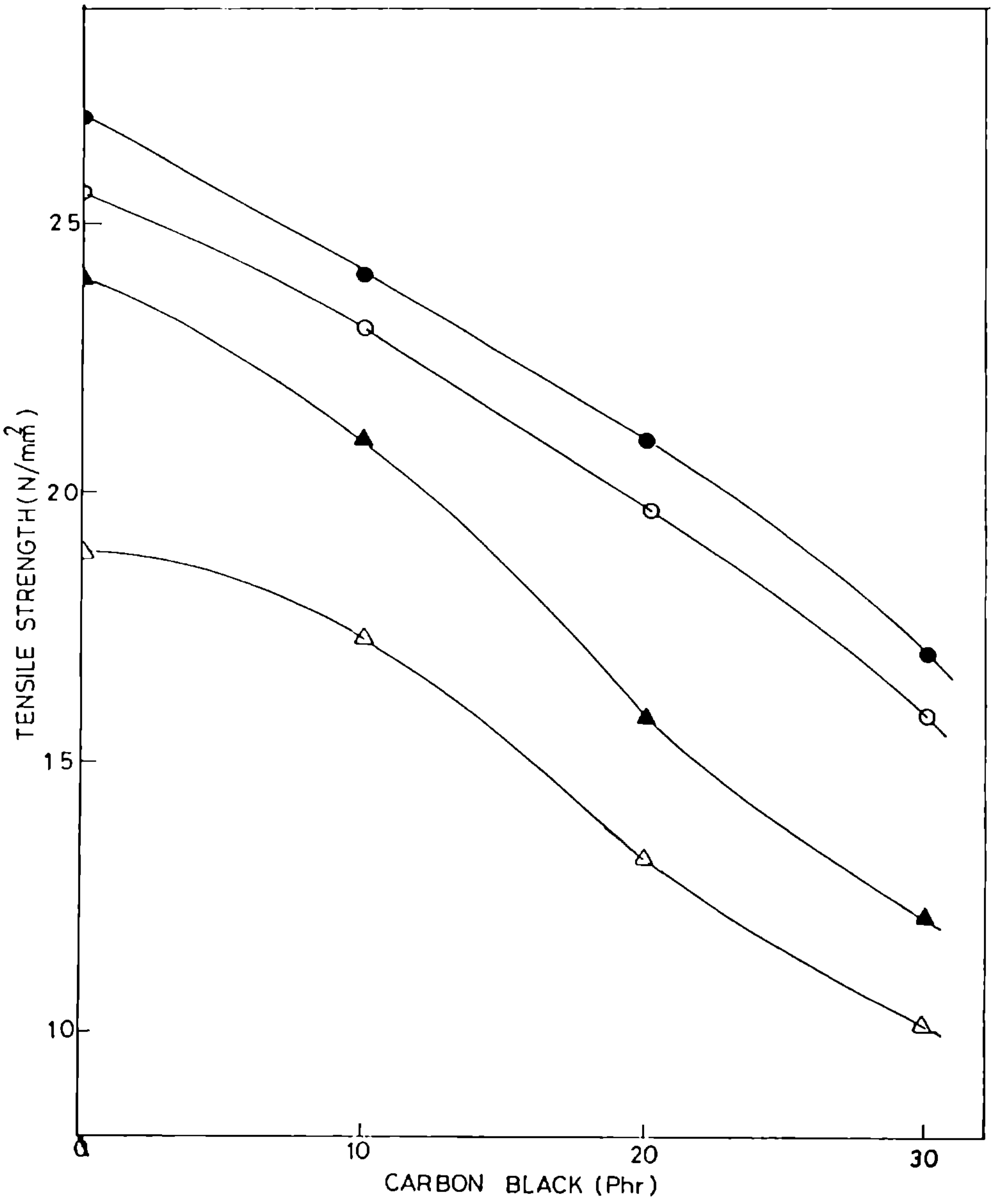


Fig. 3.11 Variation of tensile strength with amount of carbon black, before and after ageing.
'●' Unaged with PEG '▲' Unaged without PEG.
'○' Aged at 100°C - 24 hrs with PEG. △ Aged at 100°C - 24 hrs without PEG.

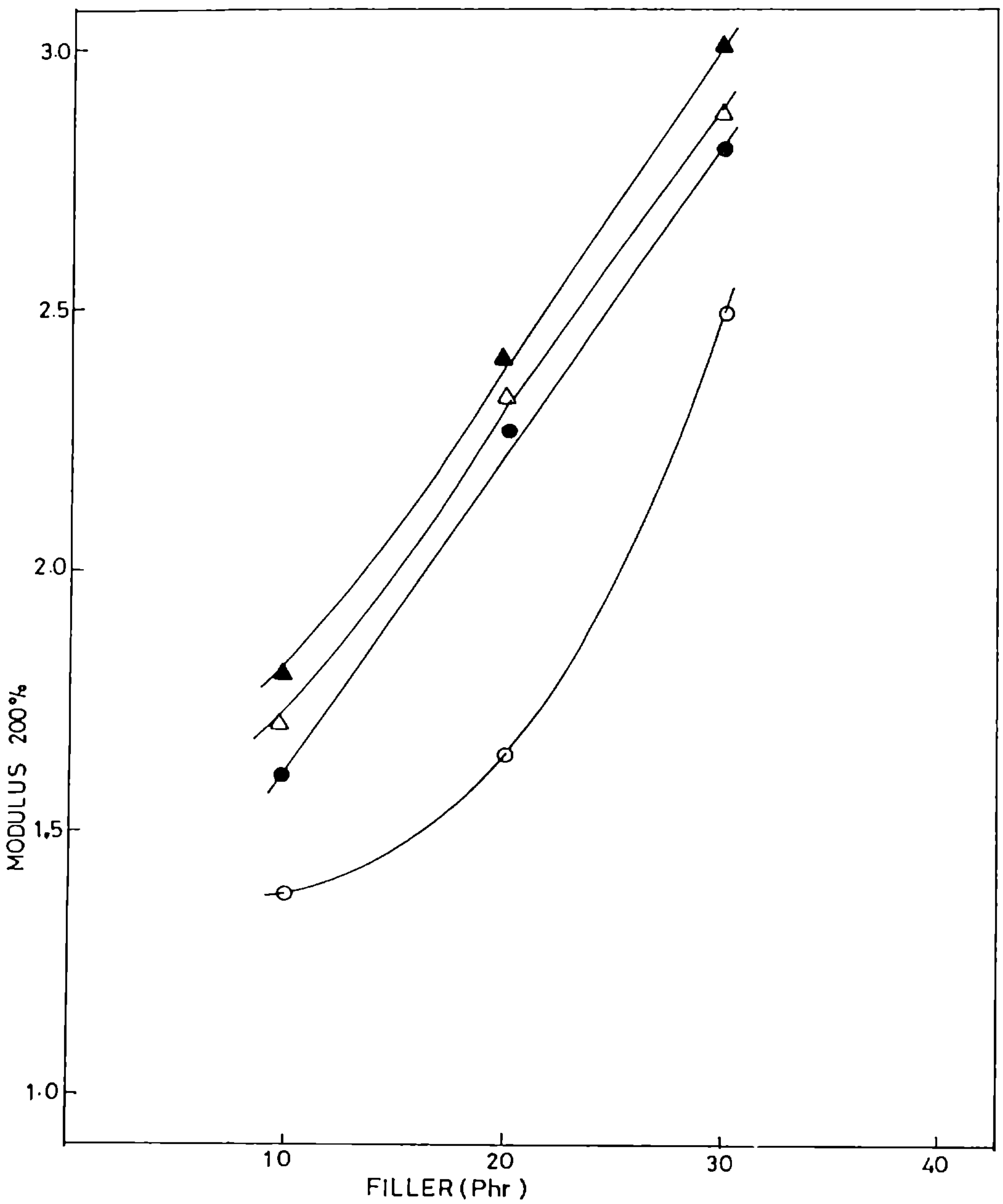


Fig.3.12 Variation of modulus with amount of filler in presence of PEG 600. ▲ carbon black, △ silica, ● clay and ○ $CaCO_3$

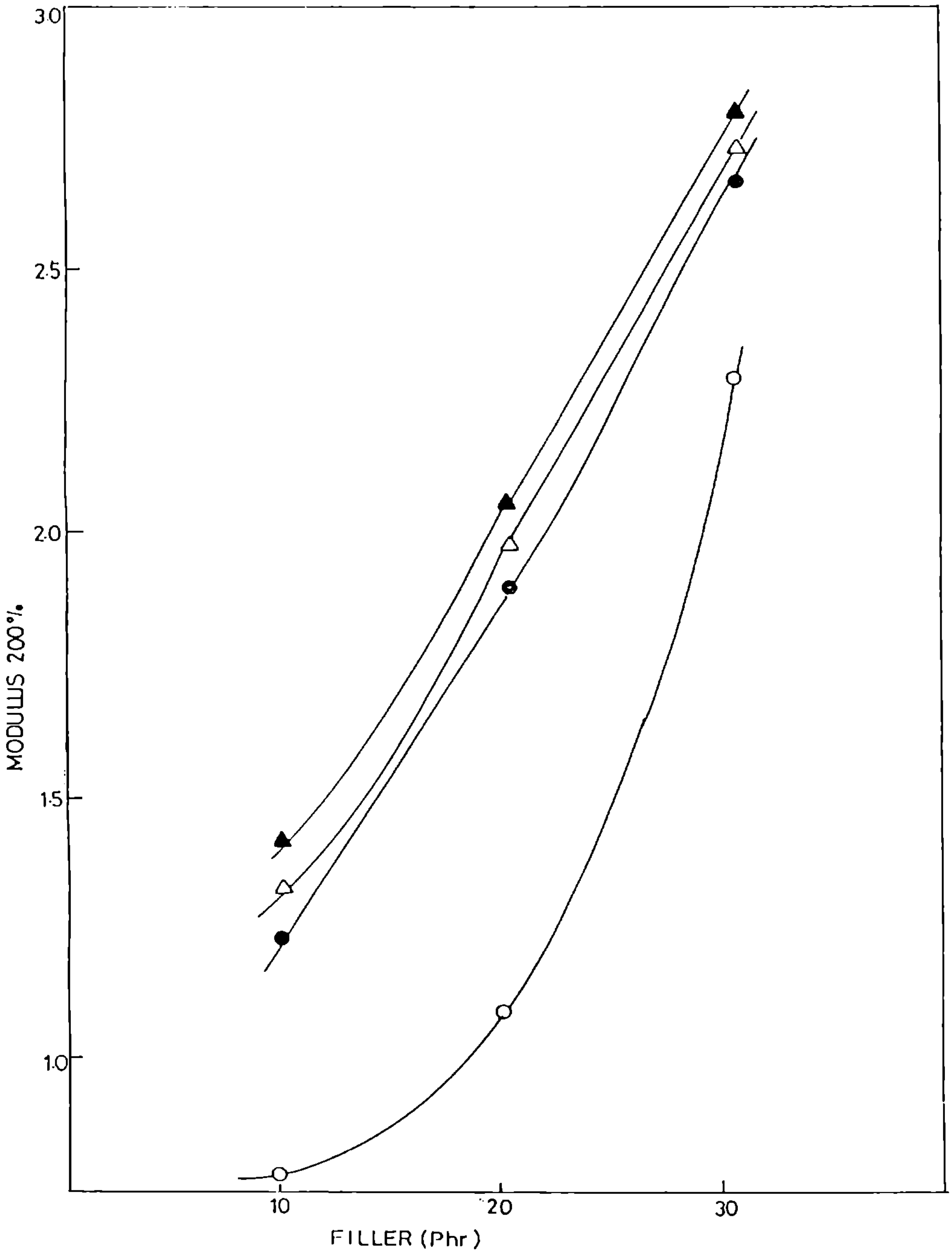


Fig.3.13 Variation of modulus with amount of filler in the absence of PEG 600. ▲ carbon black, △ silica, ● clay and ○ $CaCO_3$

distribution. Figs.3.14 and 3.15 show the variation of elongation at break of the filled vulcanizates in the presence of PEG 600 and the variation of elongation at break of the filled NR latex vulcanizate with the amount of filler in the absence of PEG respectively. The elongation at break is found to be lower for compounds containing PEG. This may be attributed to the increased polymer-filler interaction.

Fig.3.16 shows the variation of V_{ro}/V_{rf} with e^{-z}. The latex compounds containing PEG or glycerol exhibit higher slope than the compounds without PEG/glycerol. This shows that addition of PEG/glycerol restricts swelling due to more polymer-filler attachment. Table 3.2 shows the V_r values of compounds containing 10 phr silica, 10 phr $CaCO_3$ and 10 phr clay in the presence of PEG/glycerol, before and after ammonia modified swelling. The values show that there is good bonding between the filler and rubber. The interaction is found to be more pronounced in the compounds containing clay and silica. For latex compounds with higher filler loading (20 and 30 phr) the V_r values before and after ammonia modified swelling show the same trend (Table 3.3).

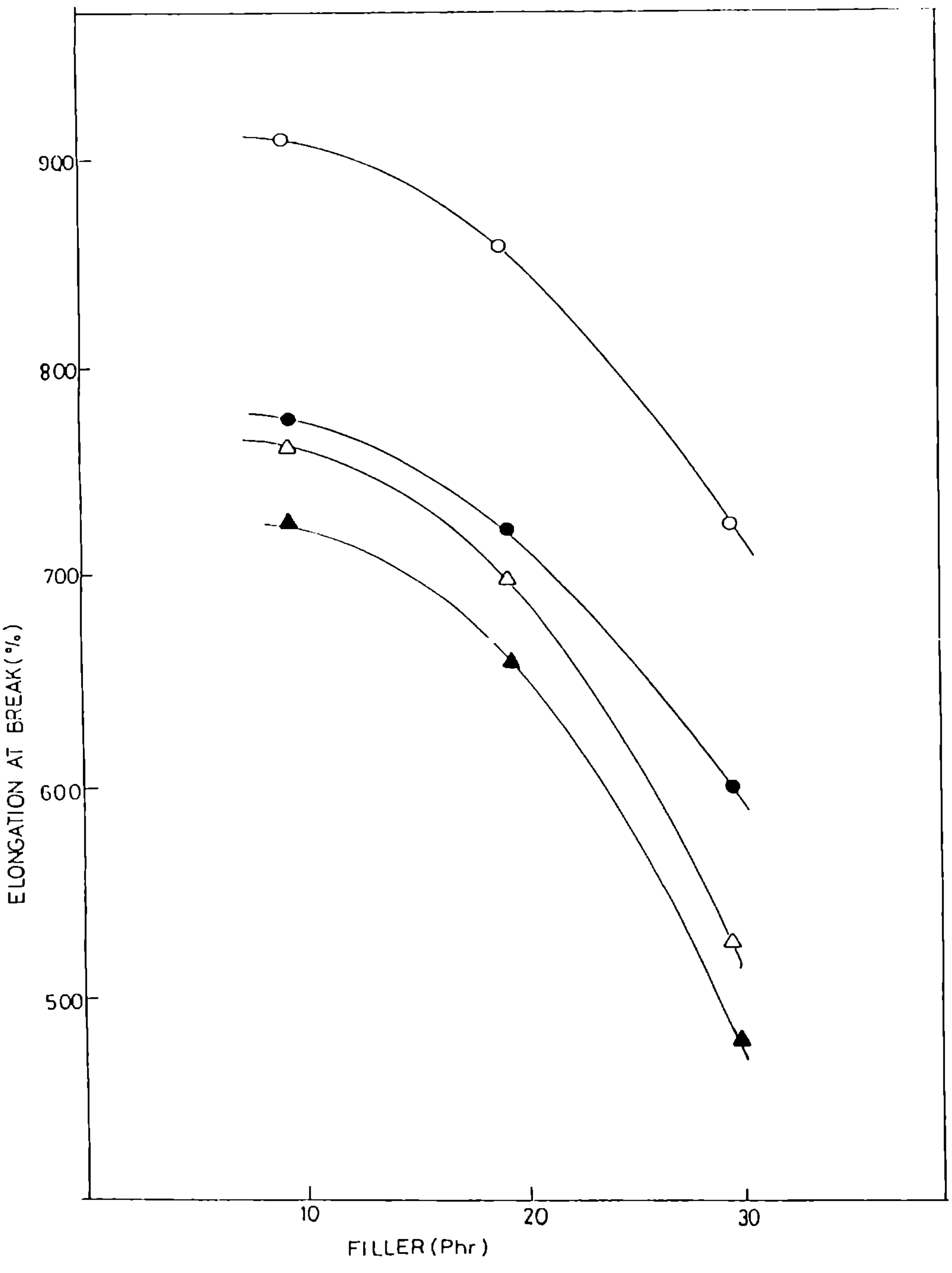


Fig.3.14 Variation of elongation at break with amount of filler in the presence of PEG 600 ▲ carbon black, △ silica, ● clay and ○ $CaCO_3$

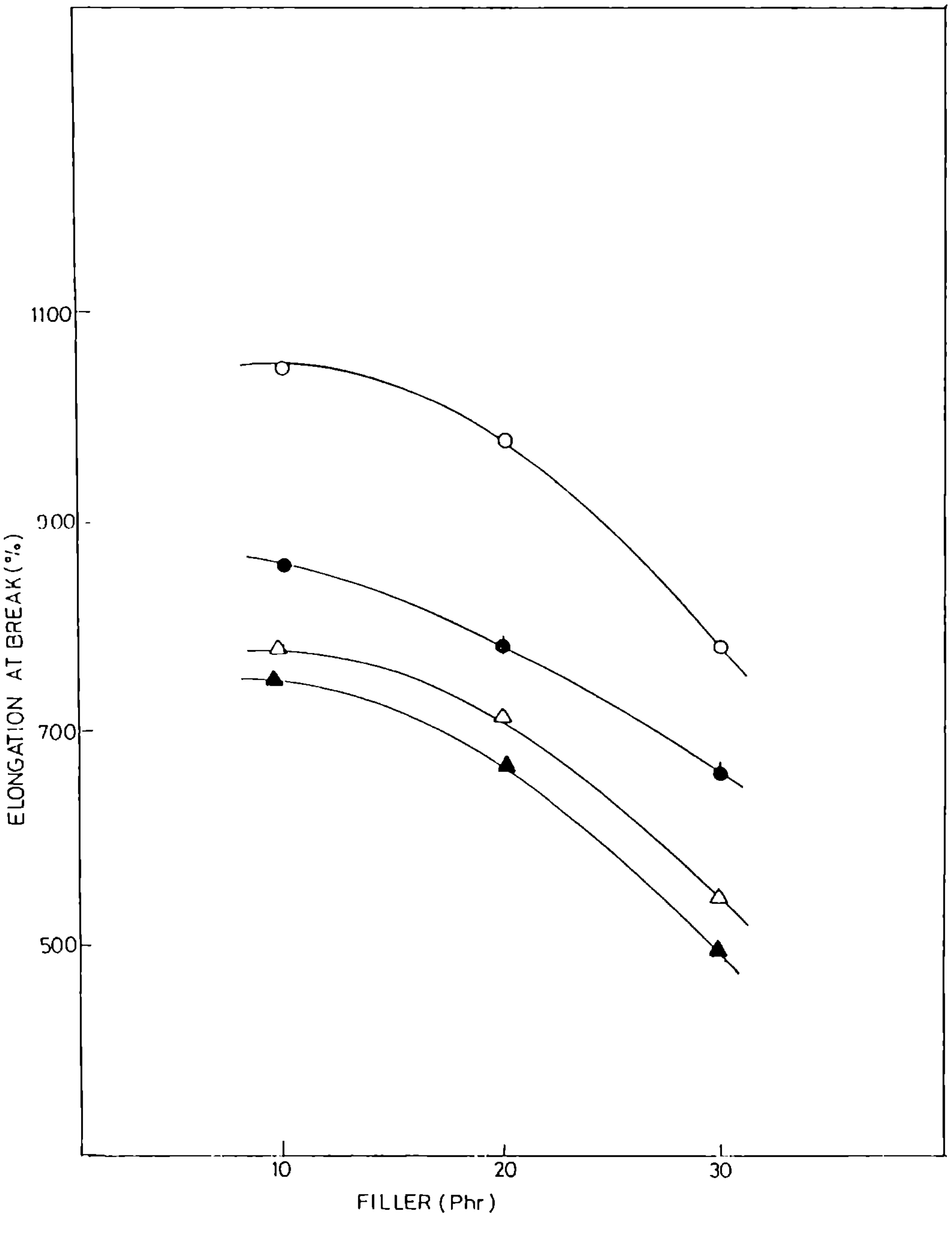


Fig.3.15 Variation of elongation at break with amount of filler in the absence of PEG. '▲' carbon black, '△' silica, '●' clay and 'o' $CaCO_3$

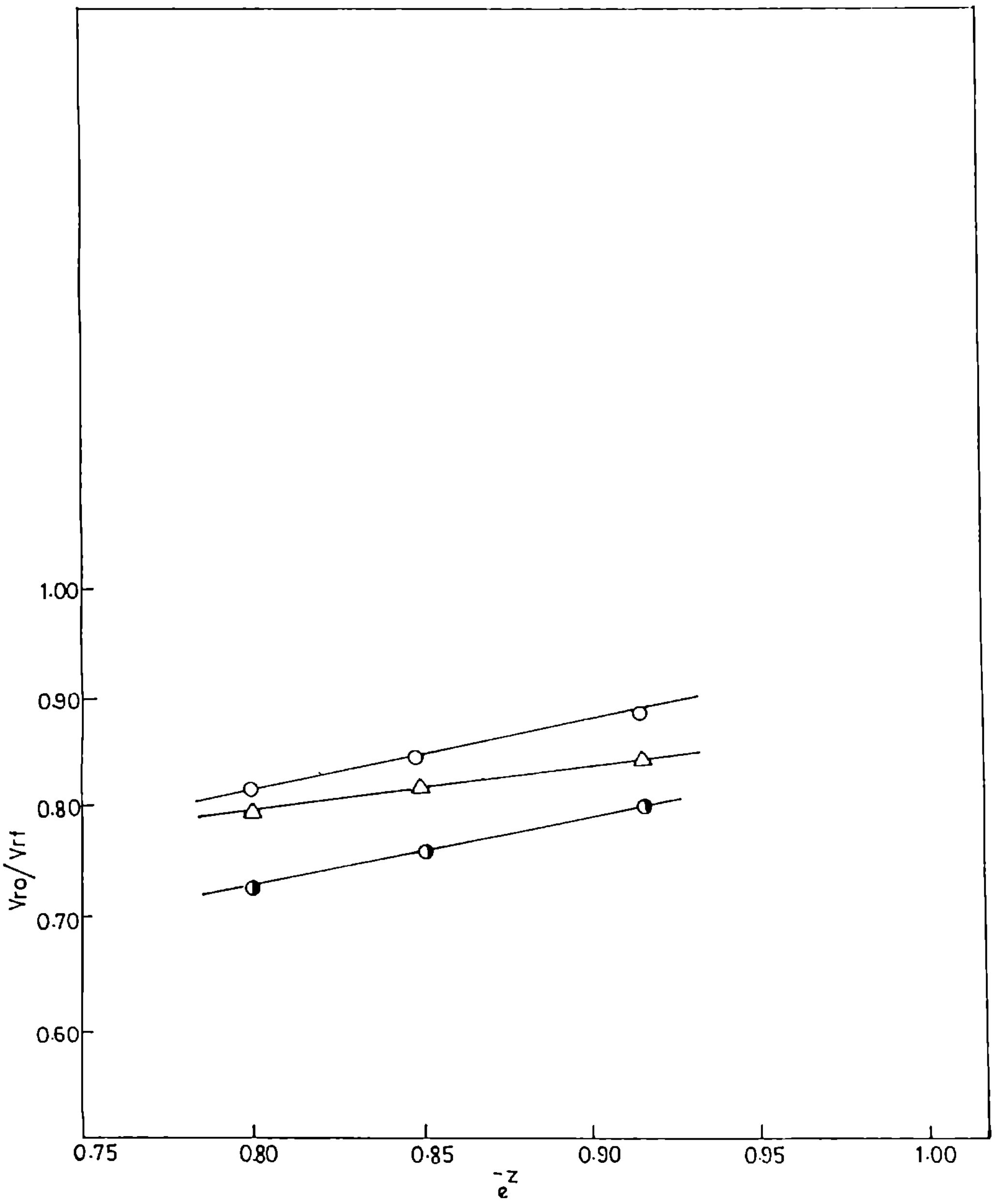


Fig.3.16 Variation of V_{ro}/V_{rf} with e^{-z}. Δ silica alone, '◐' silica with PEG 300 and 'O' silica with glycerol.

Table 3.2

V_r values before and after ammonia modified swelling

Filler (phr)	PEG (mol.wt.)	V_r Original	V_r after NH_3 modified swelling
Silica (10)	300	0.1820	0.1583
	600	0.1743	0.1582
	1000	0.1847	0.1721
	2000	0.1775	0.1689
	4000	0.1725	0.1680
	6000	0.1889	0.1769
	Glycerol	0.1647	0.1542
$CaCO_3$ (10)	300	0.1769	0.1719
	600	0.1689	0.1660
	1000	0.1682	0.1646
	2000	0.1740	0.1730
	4000	0.1521	0.1492
	6000	0.1562	0.1547
	Glycerol	0.1666	0.1641
Clay (10)	300	0.1705	0.1520
	600	0.1582	0.1507
	1000	0.1812	0.1749
	2000	0.1708	0.1660
	4000	0.1676	0.1640
	6000	0.1495	0.1453
	Glycerol	0.1801	0.1744

Table 3.3

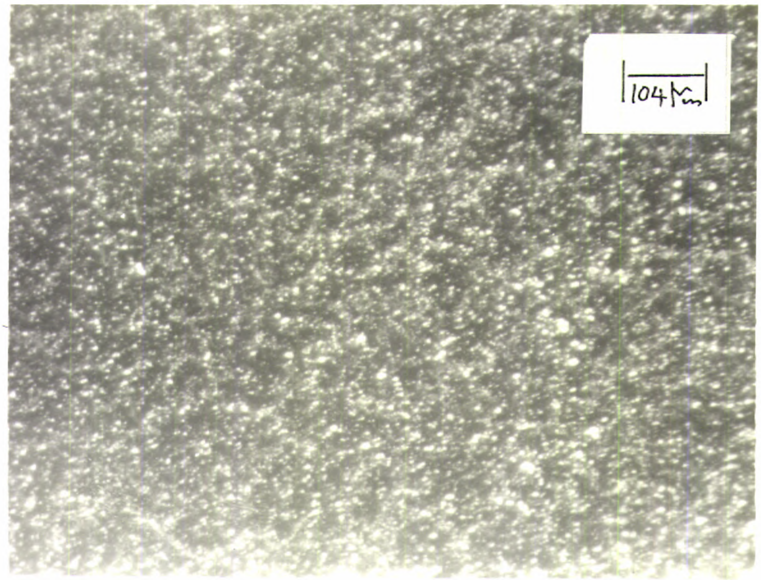
V_r values before and after ammonia modified swelling

Filler	phr	PEG 6000	V_r Original	V_r after NH_3 modified swelling
Silica	20	0	0.1624	0.1568
		1.0	0.1662	0.1527
	30	0	0.1538	0.1509
		1.0	0.1520	0.1439
$CaCO_3$	20	0	0.1562	0.1547
		1.0	0.1418	0.1270
	30	0	0.1422	0.1403
		1.0	0.1521	0.1323
Clay	20	0	0.1676	0.1645
		1.0	0.1746	0.1689
	30	0	0.1564	0.1535
		1.0	0.1710	0.1531

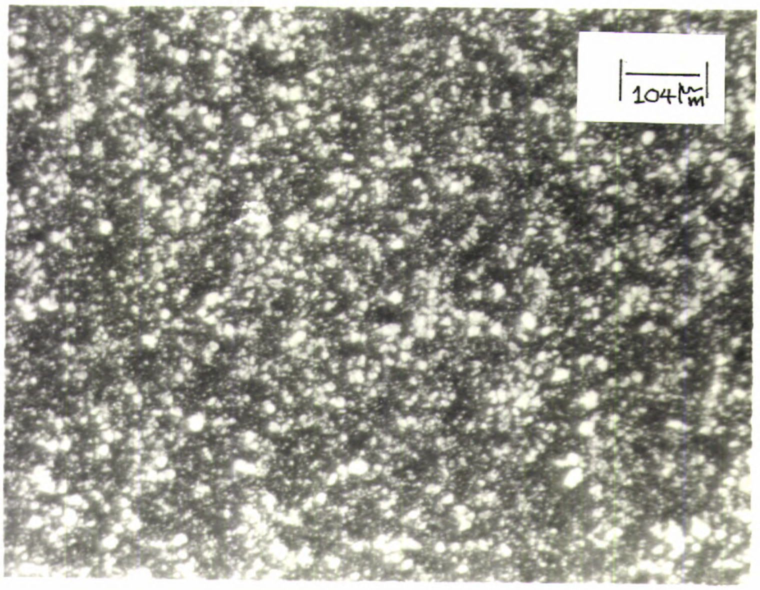
Fig.3.17 shows the photographs of latex compounds containing 20 phr silica alone, silica with PEG 300 (1 phr) and silica with glycerol (1 phr). Fig.3.18 shows photographs of latex compounds containing 20 phr $CaCO_3$ alone, $CaCO_3$ with PEG 300 (1 phr) and $CaCO_3$ with glycerol (1 phr). Fig.3.19 shows the photographs of latex compounds with 20 phr clay alone, clay with PEG 300 (1 phr) and clay with glycerol (1 phr). It is observed that there is more uniform distribution of the filler in the matrix when PEG or glycerol is present.

Figs.3.20 to 3.25 show the rheological behaviour of the latex compounds. Figs.3.20 to 3.22 show the variation of viscosity with rpm of 20 phr each of clay, silica and calcium carbonate respectively. In all these cases, the compounds show pseudoplastic behaviour as evidenced from the decrease in viscosity with rpm for a constant filler content, as expected. Addition of PEG increases the viscosity probably due to surface interactions.

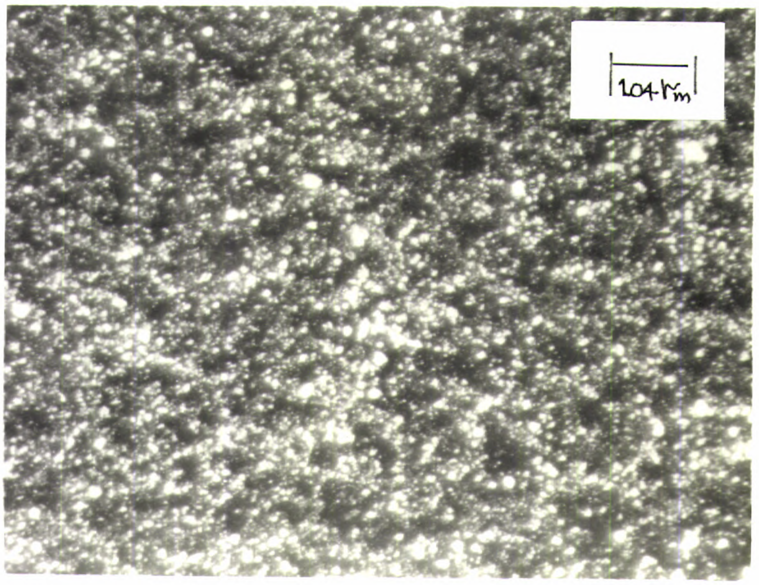
Figs.3.23 to 3.25 show the variation of viscosity with filler content (clay, silica and clacium carbonate respectively). With increase in filler content, the viscosity increases at a fixed rpm as expected.



Silica
alone

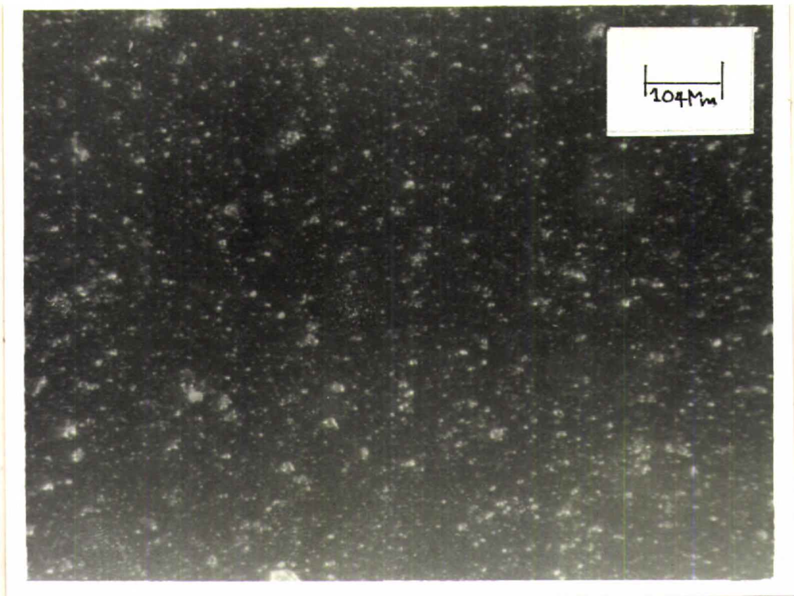


Silica
with PEG

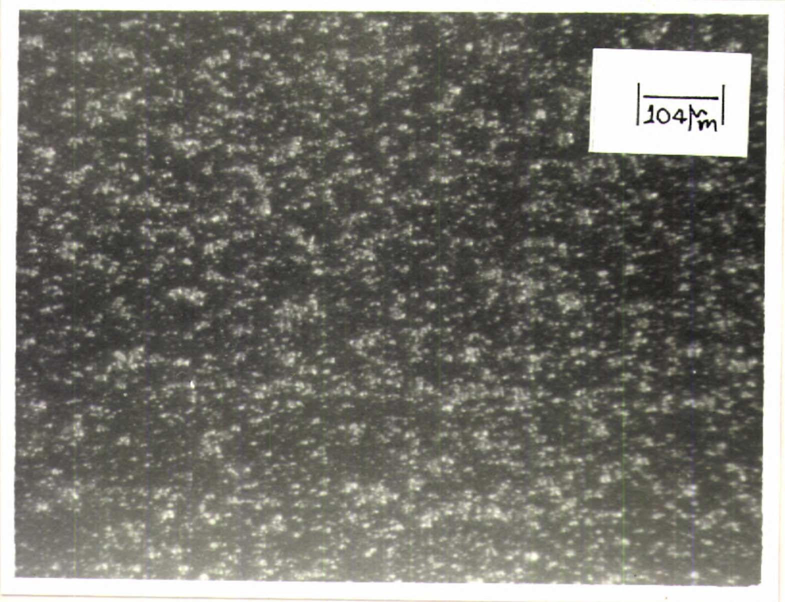


Silica
with glycerol

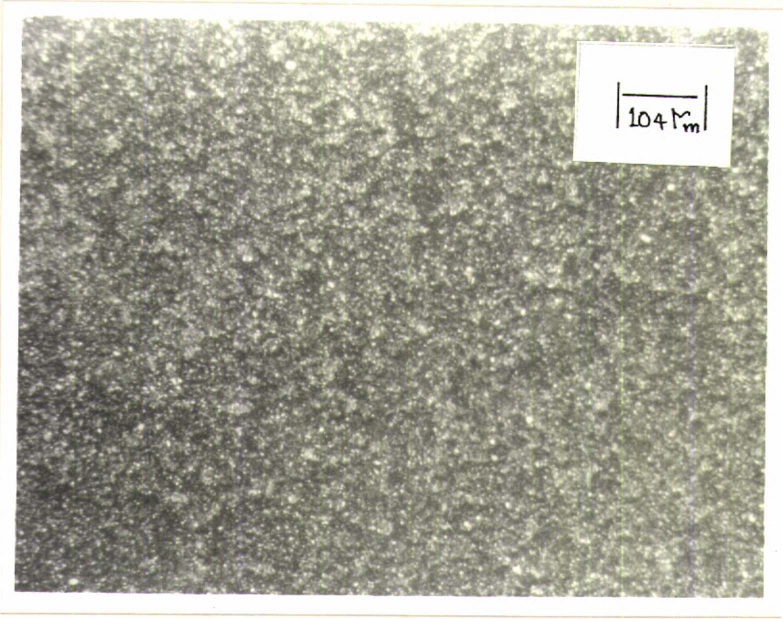
Fig.3.17 Optical microscope photographs of silica filled (20 phr) NR latex compounds.



Calcium carbonate alone

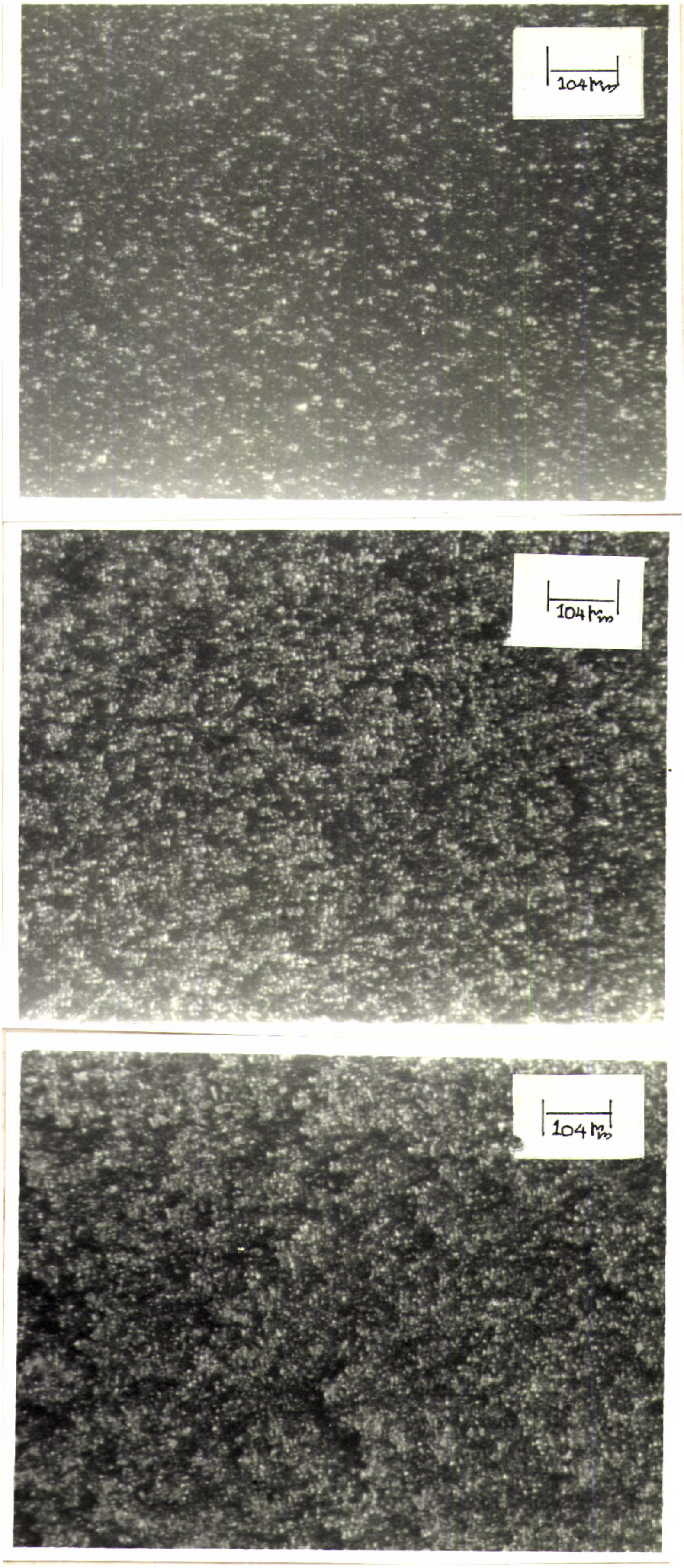


Calcium carbonate with PEG



Calcium carbonate with glycerol

Fig.3.18 Optical microscope photograph of calcium carbonate filled (20 phr) NR latex compounds.



Clay alone

Clay with PEG

Clay with glycerol

Fig.3.19 Optical microscope photographs of clay filled (20 phr) NR latex compounds.

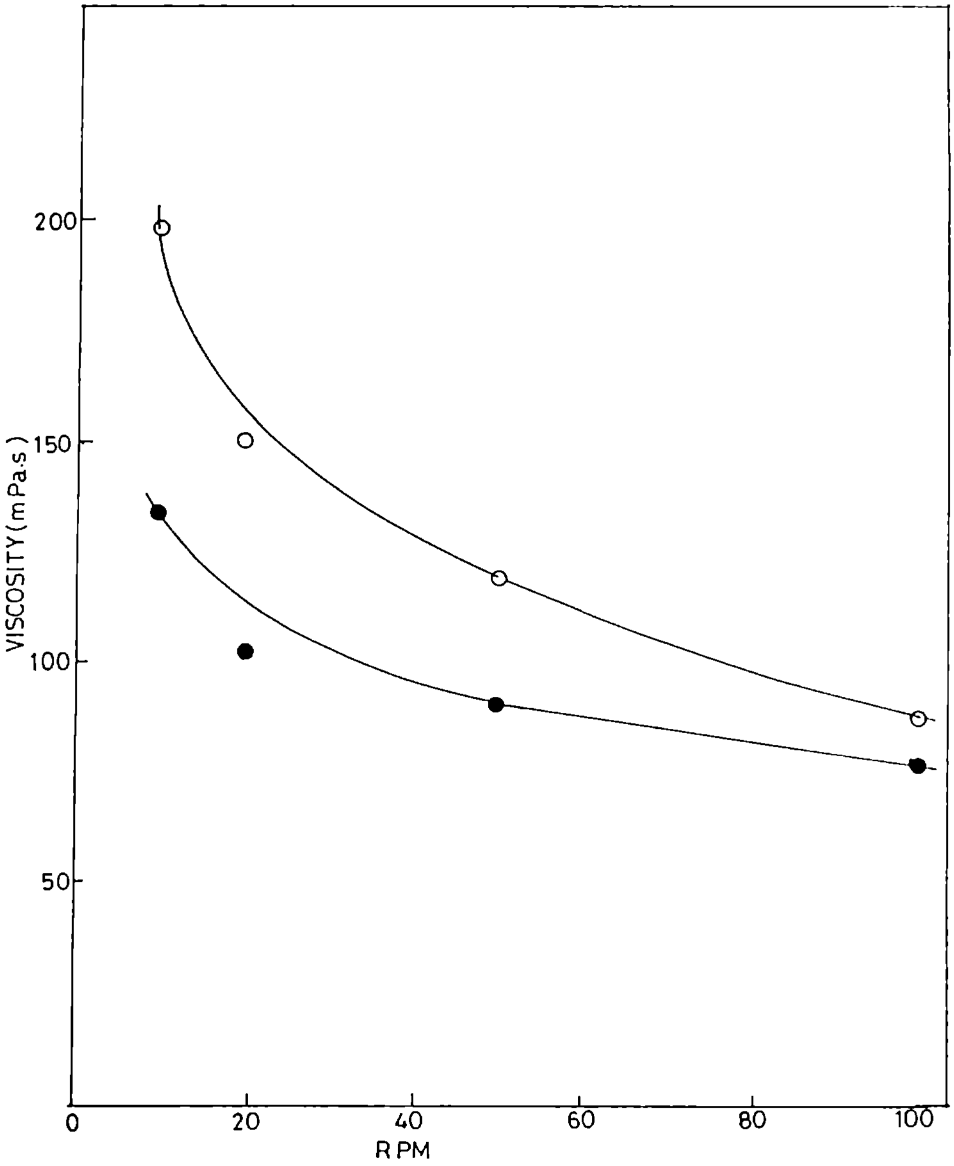


Fig.3.20 Variation of viscosity of clay (20 phr) filled NR latex vulcanizate with rpm. 'O' with PEG, '●' without PEG.

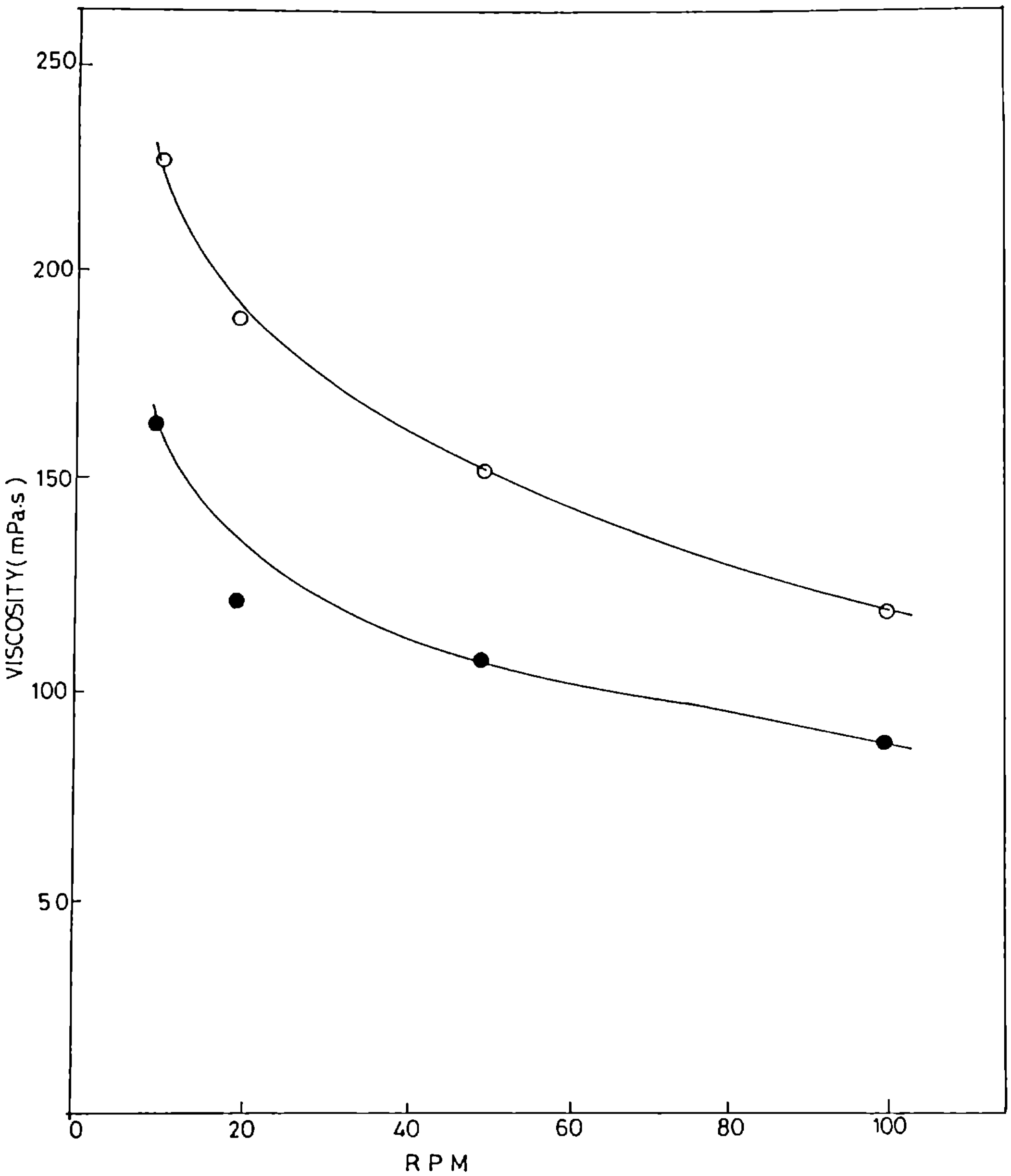


Fig.3.21 Variation of viscosity of silica (30 phr) filled NR latex vulcanizate with rpm. 'O' with PEG, '●' without PEG.

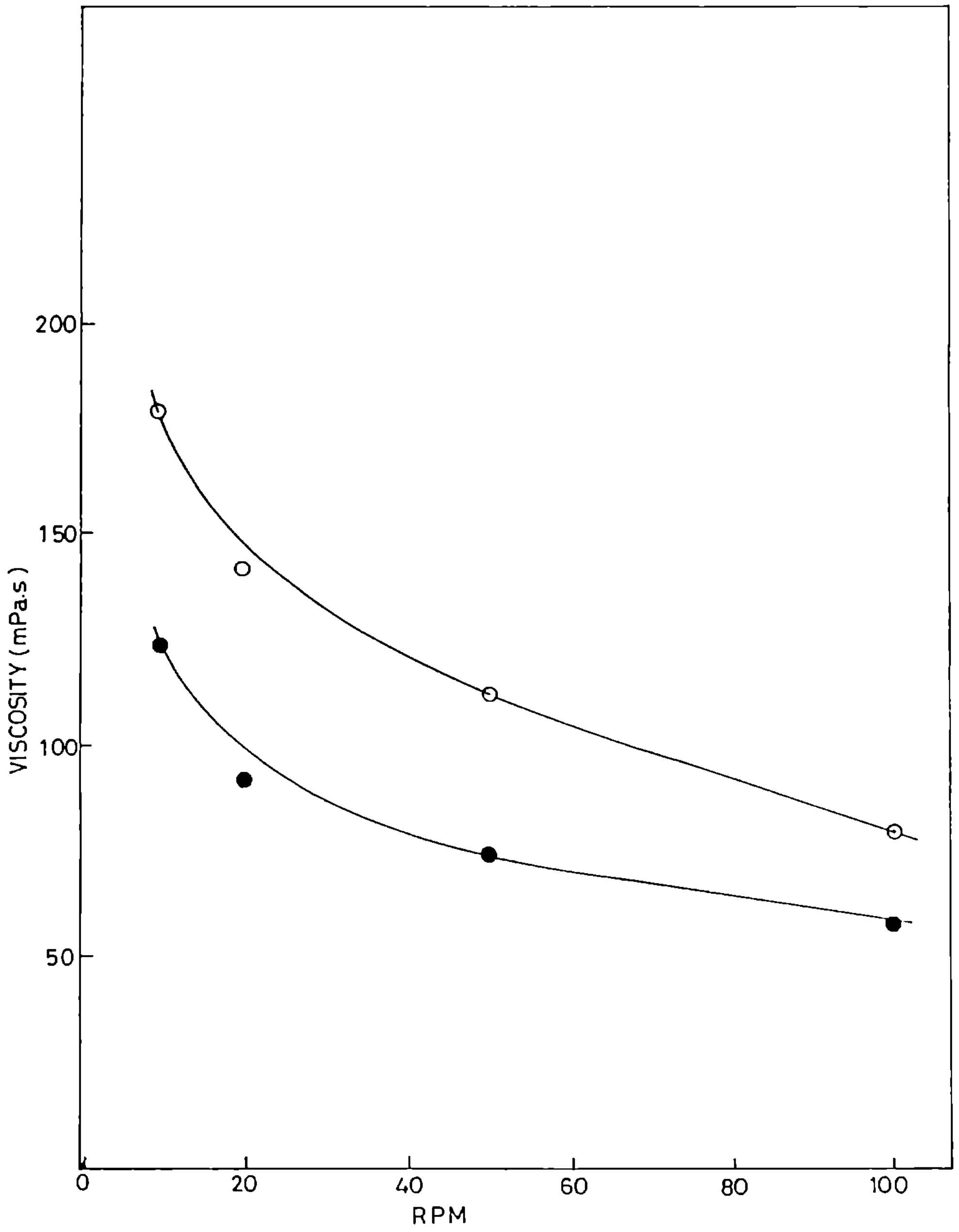


Fig.3.22 Variation of viscosity of $CaCO_3$ (10 phr) filled NR latex vulcanizate with rpm. 'O' with PEG, '●' without PEG.

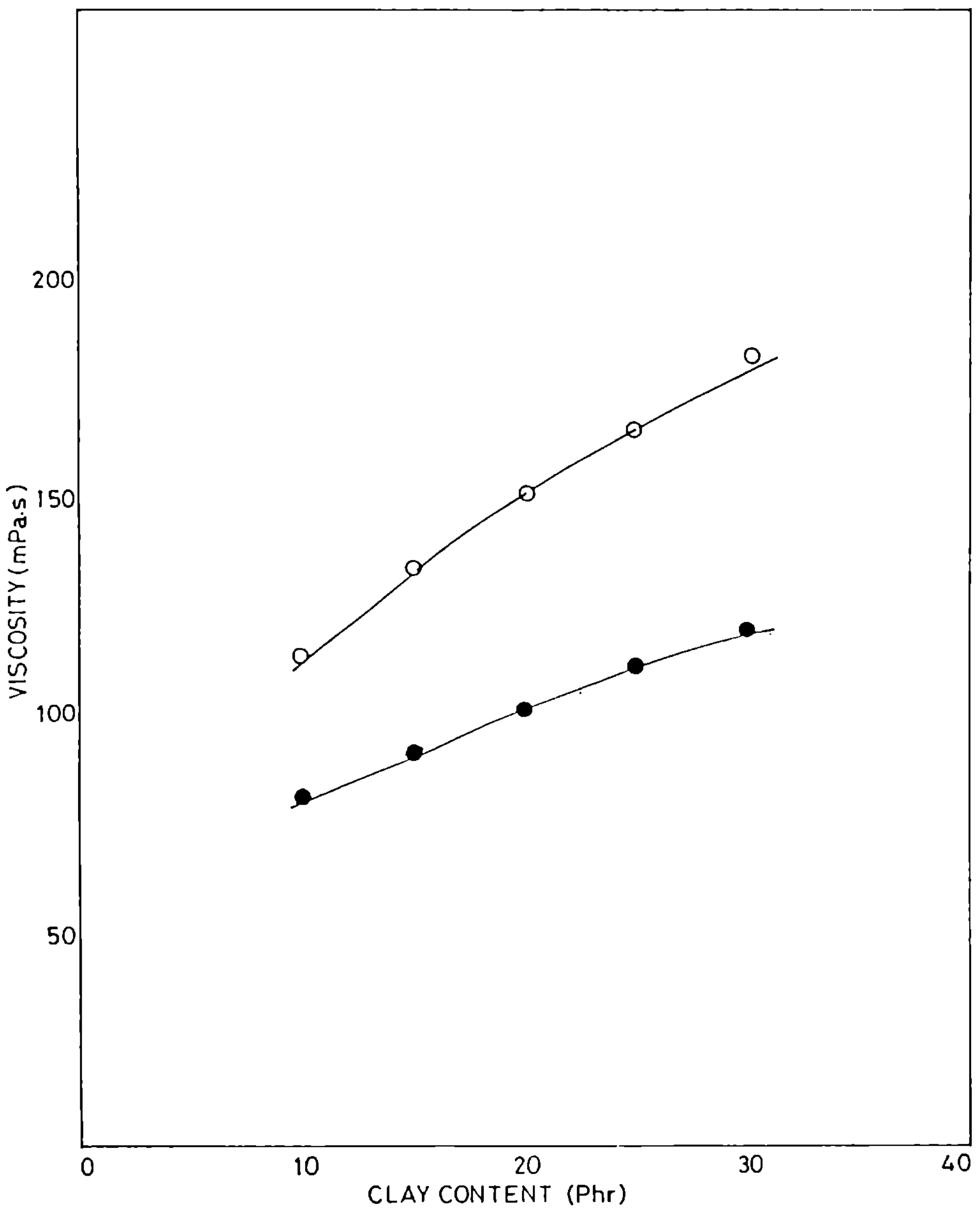


Fig.3.23 Variation of viscosity of clay filled latex vulcanizate with the amount of clay at 20 rpm. 'O' with PEG, '●' without PEG.

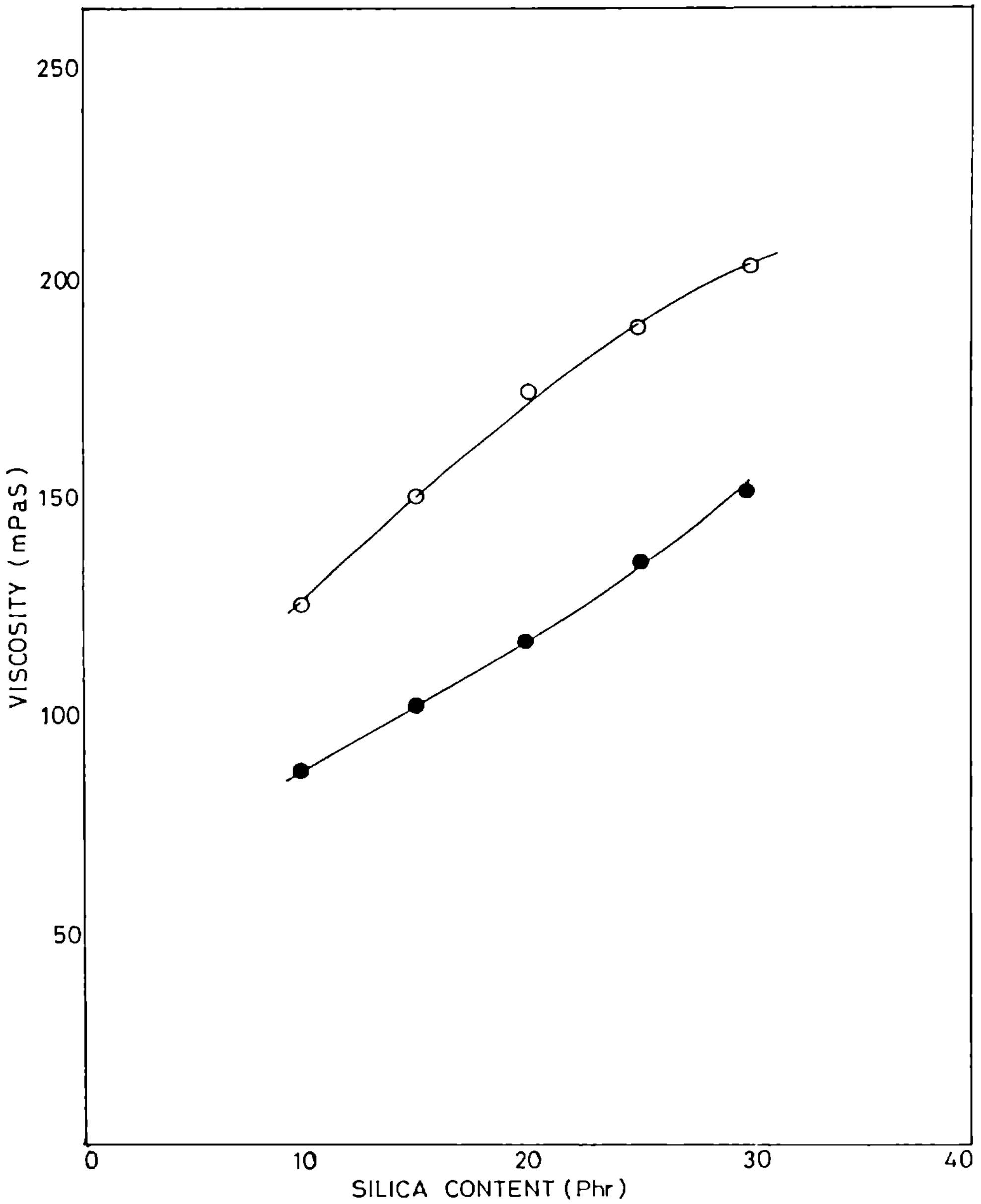


Fig.3.24 Variation of viscosity of silica filled latex vulcanizate with the amount of silica at 20 rpm. 'o' with PEG, '●' without PEG.

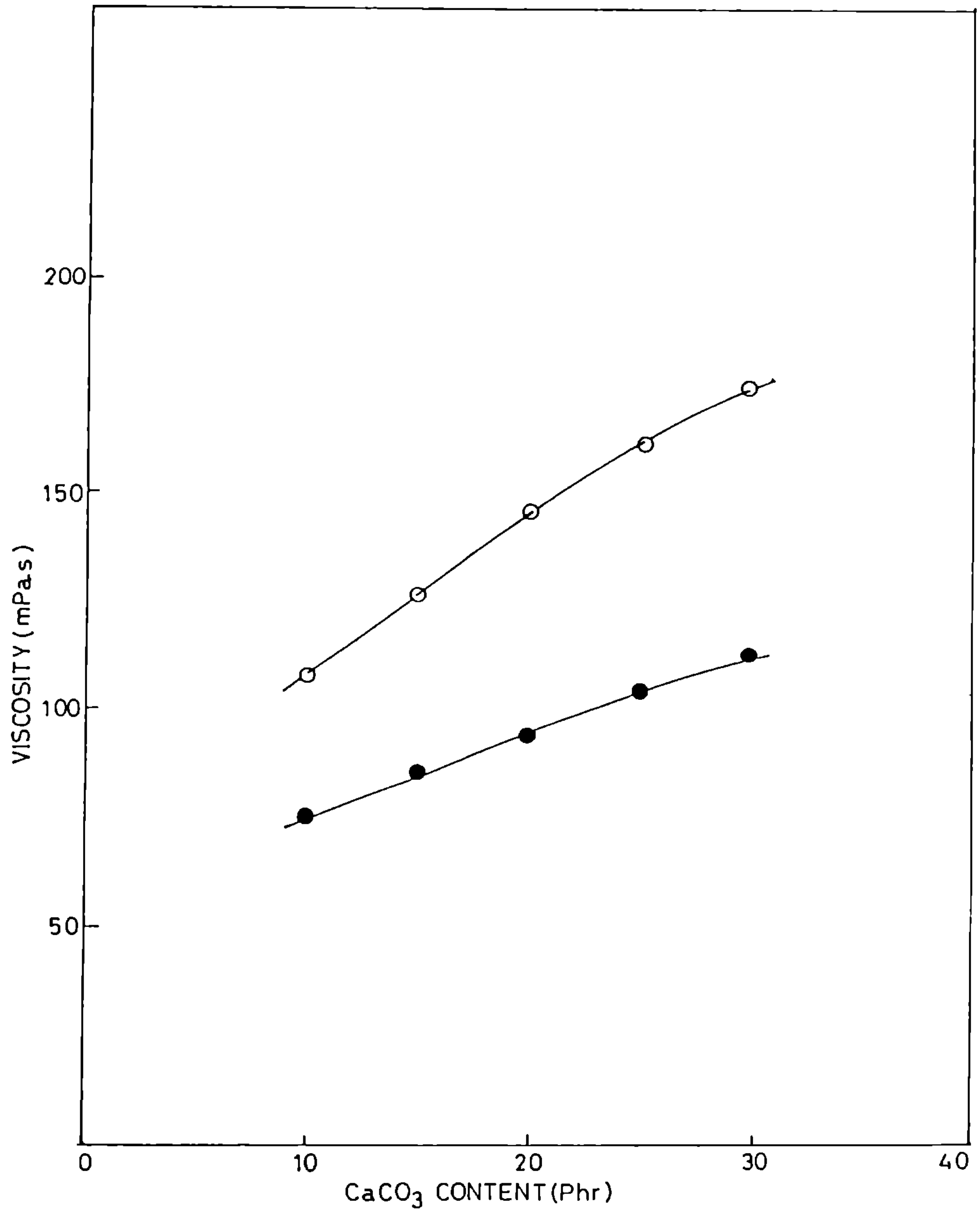


Fig.3.25 Variation of viscosity of CaCO$_3$ filled latex vulcanizate with the amount of CaCO$_3$ at 20 rpm. 'O' with PEG, '●' without PEG.

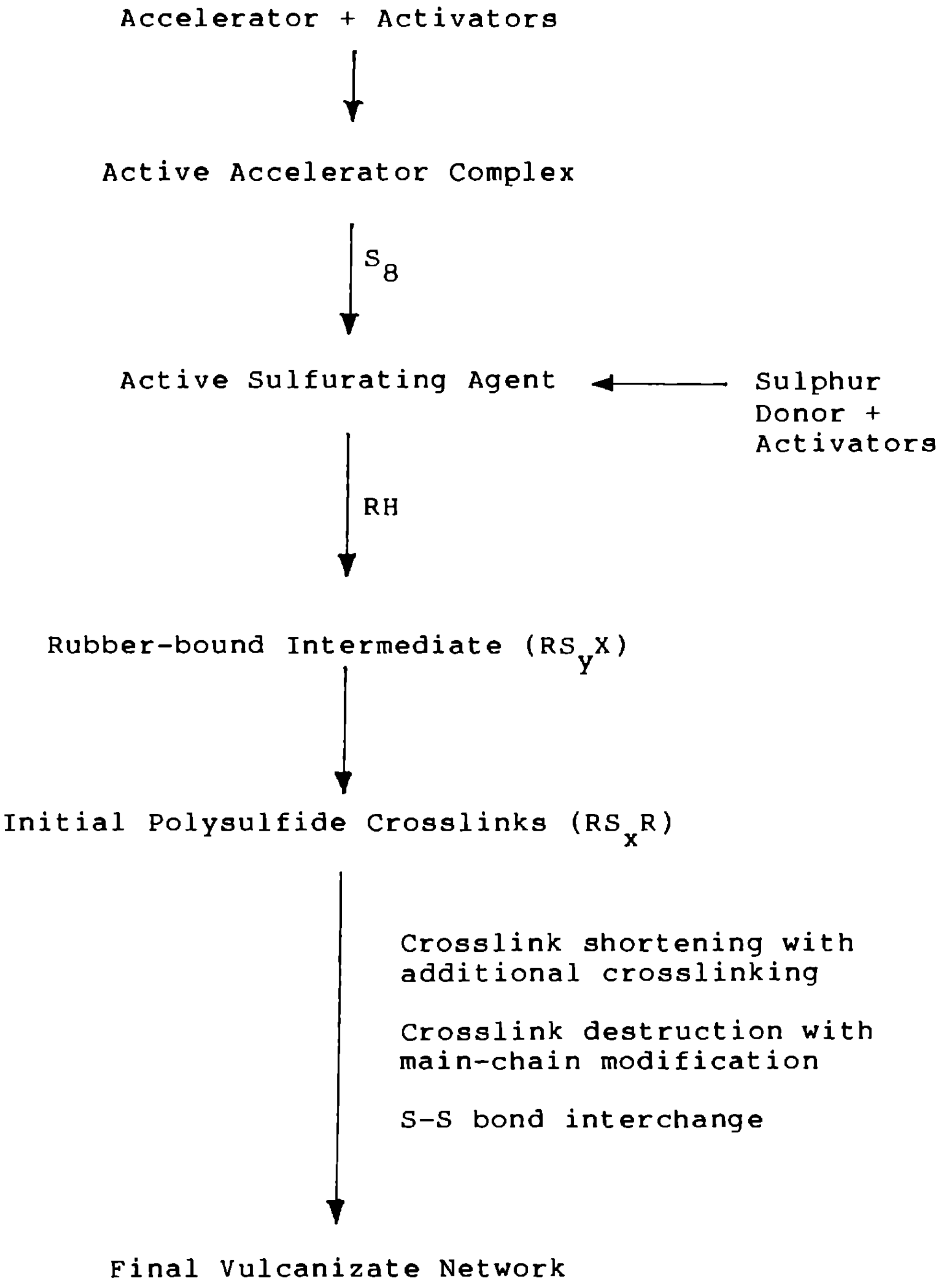
CONCLUSION

Polyethylene glycols and glycerol act as surface active agent in latex compounds and improve filler polymer interaction. They improve the filler dispersion in the rubber matrix.

PART II: NOVEL ACCELERATOR SYSTEMS (TMTM/CBS) AND (TMTD/THIOCARBANILIDE) IN NR LATEX

Organic accelerators not only increase the rate of vulcanization but also give vulcanizates having greatly improved physical properties [14]. The accelerators enable vulcanization time to be reduced. The proportion of sulphur required for optimum physical properties can also be reduced, thus improving the resistance of rubber goods to ageing and preventing blooming of sulphur [15]. Accelerators have a great effect on the cure characteristics and the physical, mechanical and chemical properties of the product [16]. The heat resistance of the vulcanizate is also determined by the accelerator used and the vulcanization system as a whole [16]. Accelerators include the thiurams, sulfenamides, thiocarbamates, mercaptobenzothiazoles etc. A few specialized compounds such as thiocarbanilide are employed as accelerators for chloroprene rubber [17]. The variety of accelerators accounts for the wide applicability of elastomers in a variety of applications.

An overall scheme of vulcanization defined by Morrison and Porter [18] is shown below.



GENERAL MECHANISM OF VULCANIZATION
R = rubber chain, H = allylic proton and
X = accelerator residue

This scheme summarizes the key steps of the accelerated sulphur vulcanization reactions.

The structural modifications of the main chain which can occur during the accelerated vulcanization process have already been studied in detail [19]. The function of accelerator combination is to increase the crosslinking efficiency and to minimise unused sulphur by decreasing (a) cyclic monosulfide formation; (b) vicinal crosslinks and (c) the length of sulphur chain 'S_x' in crosslinks [20]. In the manufacture of high quality products accelerator systems which utilize two or more accelerators in a synergistic manner is of interest [21]. Vulcanizates obtained by using binary accelerator systems are found to have superior physical and chemical properties [21,22]. Mixed in the proper proportions, binary systems can lead to significant improvement in curing behaviour and mechanical properties [23]. The impetus for the increasing use of binary systems is a result of several factors including a desire to optimize the end use properties and better control of processing safety.

Organic accelerators used in latex compounds are basically different from those used in dry rubber compounds

[24]. Ultra accelerators are used in latex compounding and the accelerators should be dispersed uniformly in the latex mixture without causing it to coagulate or to thicken. In order to achieve uniform dispersion in the latex the accelerators must be readily dispersible in water. As the vulcanization temperature for a latex compound is substantially lower than that for the dry rubber compound, the choice of accelerators and their proportion is different from that of a dry rubber compound and has to be made carefully. Hence novel accelerator combinations were tried to get better ageing resistance and faster curing rate in comparison to conventional accelerator systems.

In this study, two new binary accelerator systems CBS/TMTM and TMTD/thiocarbanilide were tried in NR latex compound. The mechanical properties of vulcanized films were compared with those containing ZDC/TMTD accelerator combination.

EXPERIMENTAL

Centrifuged latex containing 60% DRC was used for the study. All water insoluble compounding ingredients were prepared as 50% dispersions, using a ball mill. The stabilizers used, potassium hydroxide and potassium oleate were prepared as 10% solutions in water.

Formulations of the latex compounds are given in Table 3.4. The centrifuged latex was first deammoniated to 0.2 per cent ammonia content and was stabilized by adding potassium hydroxide and potassium oleate solutions. Thiocarbanilide was prepared in the laboratory as per the procedure described in chapter 2. The vulcanizing agent sulphur, TMTD, TMTM, CBS, ZDC, thiocarbanilide and ZnO were added as dispersions.

Optimum cure time of the latex sheets

All compounding ingredients were added to the latex in the order as shown in the table 3.4. The compounded latex was kept for maturation for 24 hrs. Latex films were prepared by casting the compounds in glass dishes. After drying the films at room temperature for 24 hrs, they were vulcanized at 120°C, varying the time from 25 to 40 minutes in an air oven. Dumbell shaped tensile pieces were punched out of these cast sheets and tensile properties were measured using a Zwick universal testing machine. The cure time of the sample for which the maximum tensile strength was obtained, was taken as the optimum cure time. Mechanical properties such as tear strength, elongation at break and modulus of latex sheets containing optimum quantities of accelerators, cured at optimum cure time, were also determined.

Table 3.4

Formulations of the latex compounds

Ingredients	Parts by weight (wet) gm.		
60% Centrifuged latex	167	167	167
10% KOH	5.0	5.0	2.5
10% Potassium oleate	5.0	5.0	2.0
50% ZnO	1.5	1.5	1.0
50% ZDC	2.0	0	0
50% TMTD	2.0	0	1.5
50% CBS	0	2.0	0
50% TMTM	0	2.0	0
50% Thiocarbanilide	0	0	3.0
50% S	1.0	1.0	3.0

Ageing studies

Test specimens from these sheets were aged at 70°C for 3 to 6 days and the retention in tensile properties were determined.

Determination of volume fraction (V_r) and crosslink density of the latex sheets

The vulcanized latex films were subjected to swelling for 48 hrs in toluene. From the initial weight, swollen weight and deswollen weight, volume fraction of rubber (V_r) and the crosslink density were calculated.

Spectroscopic technique for determining the transparency

Visual examination of vulcanized films containing thiocarbanilide/TMTD system showed superior transparency. UV-VIS NIR spectrophotometer was used to measure the percentage of transmittance of light by each latex film. Very thin films of different accelerator combinations were taken and the percentage transmittance was noted at wavelength 2000 nm. In order to study the effect of sulphur concentration on transparency, the concentration of sulphur in the latex compound was varied from 0.5 phr to 4 phr (wet weight) and the transmittance value at a particular wavelength (2000 nm) was determined. ZnO concentration was varied from 0.2 phr to 1.2 phr and the percentage transmittance at 2000 nm wavelength was studied.

The amount of clay was varied from 0.5 phr to 5.0 phr and the variation in percentage transmittance was also measured.

The effect of thickness of the vulcanizate on the percentage transmittance was studied by preparing latex films of thickness varying from 0.025 mm to 0.30 mm.

The effect of coagulant on the transmittance of latex films was studied using a wet coagulant (10% acetic acid), and also dry coagulant (mixture of calcium nitrate and calcium chloride).

RESULTS AND DISCUSSION

Fig.3.26 shows the variation of tensile strength of NR latex vulcanizates having ZDC/TMTD, CBS/TMTM and TMTD/thiocarbanilide accelerator systems at different cure times. It shows that for ZDC/TMTD and CBS/TMTM systems, as the cure time is increased from 25 to 40 minutes, the tensile strength increases, reaches a maximum at 30 minutes and then decreases. But the attainment of maximum tensile strength occurs at 27 minutes for the TMTD/thiocarbanilide

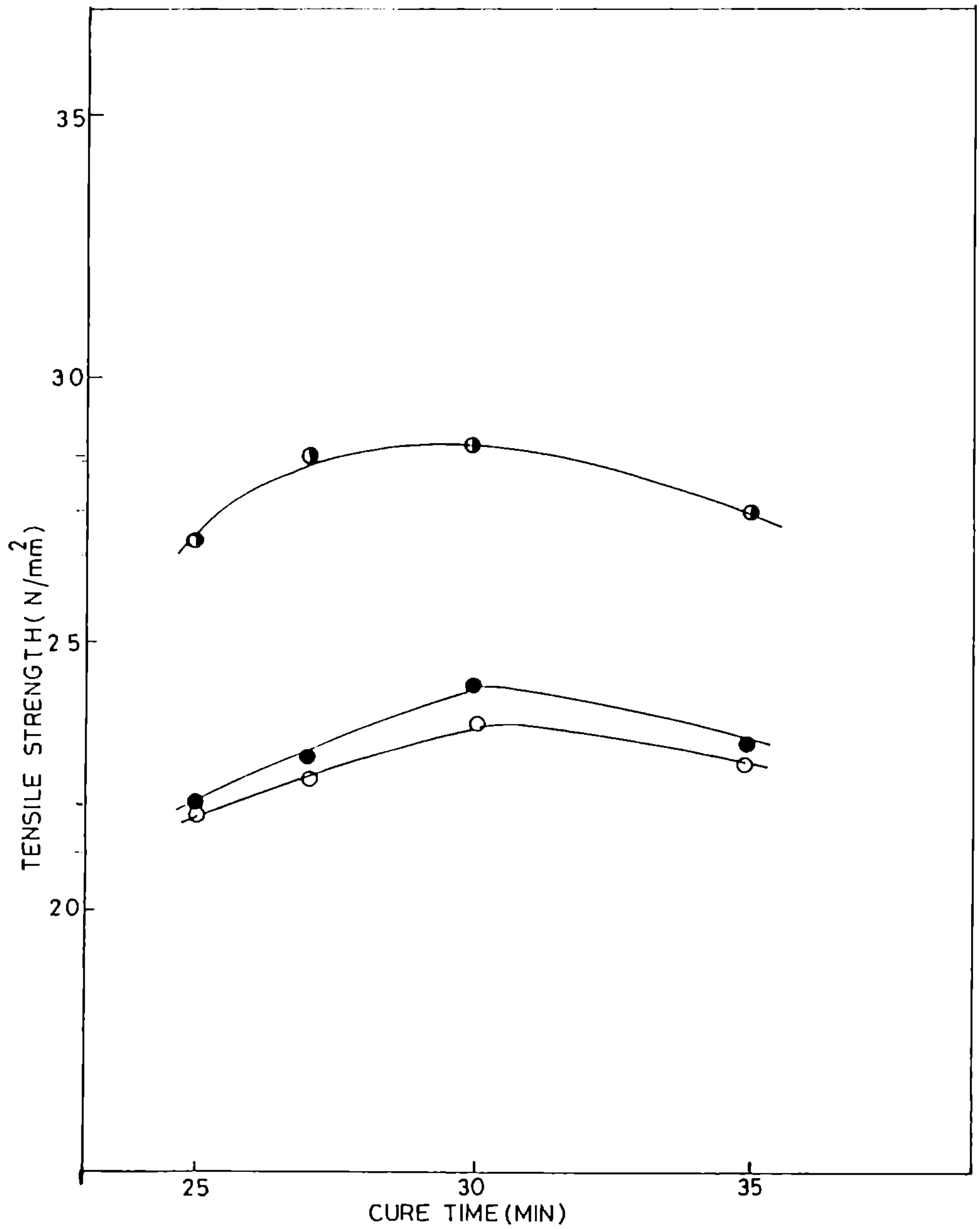


Fig.3.26 Variation of tensile strength with cure time of NR latex vulcanizate with different accelerator systems. 'O' with ZDC/TMTD system, '●' with CBS/TMTM system and '◑' with thiocarbanilide/TMTD system.

compound. This shows that TMTD/thiocarbanilide combination is a faster accelerator system compared to CBS/TMTM and ZDC/TMTD. Tensile strength of latex sheets with CBS/TMTM system and ZDC/TMTD system are found to be comparable. But the tensile strength of sheets with TMTD/thiocarbanilide system is superior. This may be due to the more homogeneous distribution of water soluble thiocarbanilide in latex.

Table 3.5 gives the variation in tensile strength of the latex vulcanizates after ageing. Here also for CBS/TMTM and ZDC/TMTD systems, the tensile strength retention is comparable whereas the ageing resistance is

Table 3.5

Variation of tensile strength of latex vulcanizates after ageing

	Original	Aged at 70°C	
	Tensile strength (N/mm^2)	Tensile strength after 3 days (N/mm^2)	Tensile strength after 6 days (N/mm^2)
Thiocarbanilide/ TMTD	29	27.0	25.2
CBS/TMTM	24	21.5	18.9
ZDC/TMTD	23.5	21.0	18.5

also found to be superior for TMTD/thiocarbanilide system. The enhancement in tensile properties and ageing resistance may be attributed to improved dispersion of the thiocarbanilide in NR latex as thiocarbanilide is soluble in water in alkaline pH.

Table 3.6 shows the percentage transmittance of ZDC/TMTD, CBS/TMTM and TMTD/thiocarbanilide systems at the wavelength 2000 nm. From the figures it is clear that almost 80% of the light is transmitted by latex sheets of TMTD/thiocarbanilide combination whereas for latex sheets

Table 3.6

Percentage transmittance of latex vulcanizates

Accelerator system	Percentage transmittance at λ = 2000 nm
TCA/TMTD	80.0
CBS/TMTM	68.4
ZDC/TMTD	69.5

with ZDC/TMTD and CBS/TMTM systems, the percentage transmittance is much lower. This proves that films of TMTD/thiocarbanilide are more transparent. This superior transparency also may be due to the homogeneous dispersion of thiocarbanilide in NR latex since thiocarbanilide is soluble in ammonia water. NR latex is preserved with ammonia and even at the time of compounding, latex contains approximately 0.2% ammonia in it, which facilitates the dissolution of thiocarbanilide in NR latex.

Table 3.7 shows the variation of elongation at break, modulus and tear strength of latex sheets with ZDC/TMTD, CBS/TMTM and TMTD/thiocarbanilide systems. The 100% modulus of the vulcanizate containing CBS/TMTD is found to be higher than the other two which is in accordance with the higher crosslink density. For ZDC/TMTD system the elongation at break is slightly higher which may be due to the lower crosslink density. But TMTD/thiocarbanilide system has a higher tear strength. The improved tear strength may be due to the more uniform distribution of the accelerator systems.

Table 3.8 shows the V_r values and crosslink densities of latex vulcanizates with ZDC/TMTD, CBS/TMTM and

Table 3.7

Variation of elongation at break, modulus and tear strength of latex vulcanizates

Accelerator system	Elongation at break (%)	Modulus (100%) (N/mm^2)	Tear strength (N/mm)
TCA/TMTD	665	0.83	56
CBS/TMTM	666	0.89	46
ZDC/TMTD	840	0.78	44

Table 3.8

V_r values and crosslink densities of latex vulcanizates

Accelerator system	V_r value	Crosslink density (gm mol/cc)
TCA/TMTD	0.182	4.5×10^{-5}
CBS/TMTM	0.210	6.2×10^{-5}
ZDC/TMTD	0.172	3.99×10^{-5}

TMTD/thiocarbanilide systems. The V_r values and the crosslink densities are comparable.

Fig.3.27 shows that as the concentration of sulphur increases in the latex compound, the percentage transmittance decreases. When the sulphur concentration is high it may result in the formation of crystals of free sulphur in the matrix and eventually sulphur blooming may reduce the transmittance.

Fig.3.28 shows that as the amount of ZnO in the latex compound increases, the film becomes less and less transparent. The high tinting power of zinc oxide may be the reason for significant reduction in transparency.

Fig.3.29 shows the effect of a filler (clay) on the transparency of the latex film. As the amount of clay increases in the compound, the transparency decreases. This reduction in transparency may be caused by the scattering of light by the rubber particles. When there is large difference between the refractive index of rubber particle and filler, this effect is usually observed.

Fig.3.30 shows the relationship between thickness of the latex film and its transparent nature. It is shown

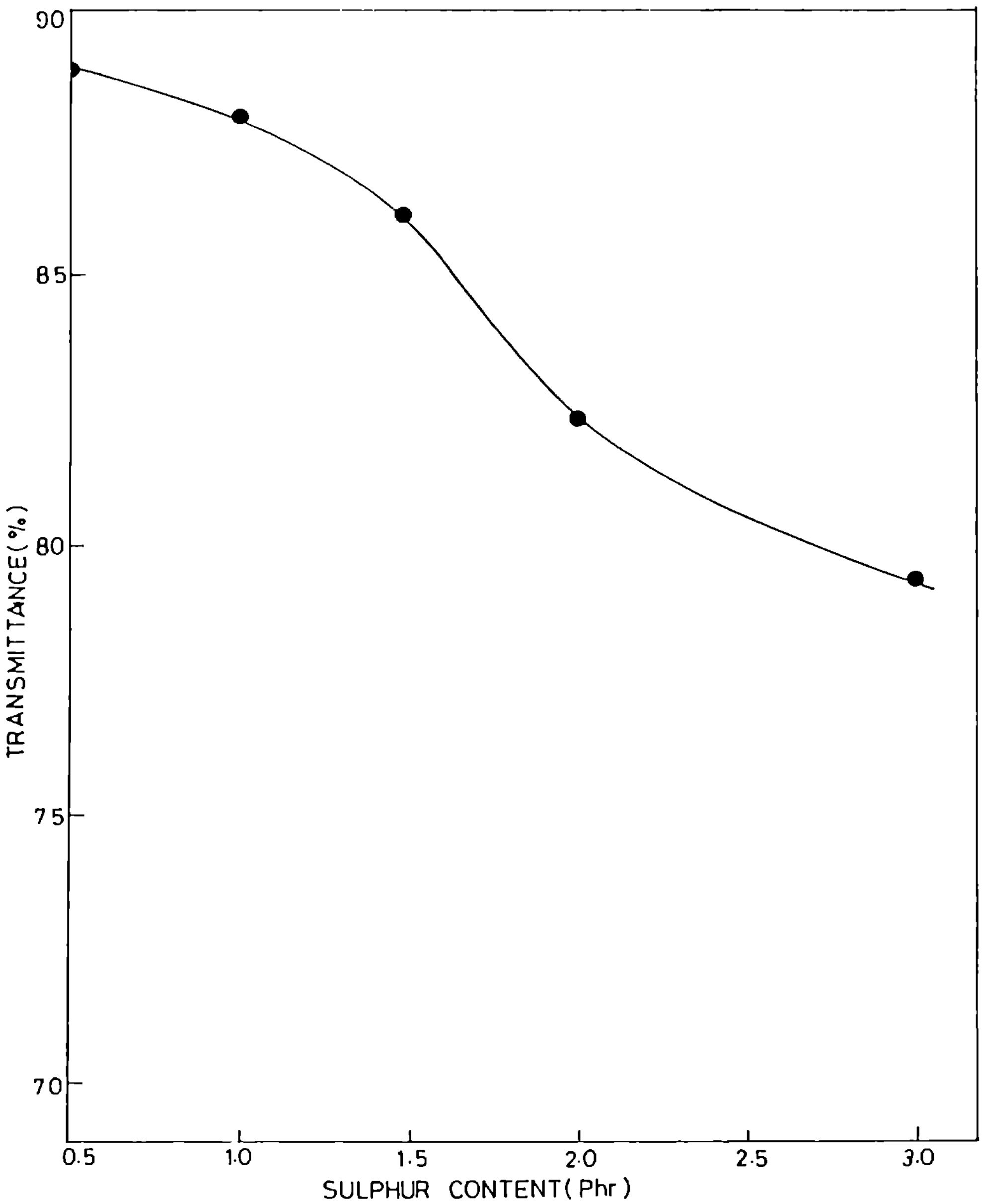


Fig.3.27 Variation of percentage transmittance of NR latex film with sulphur content.

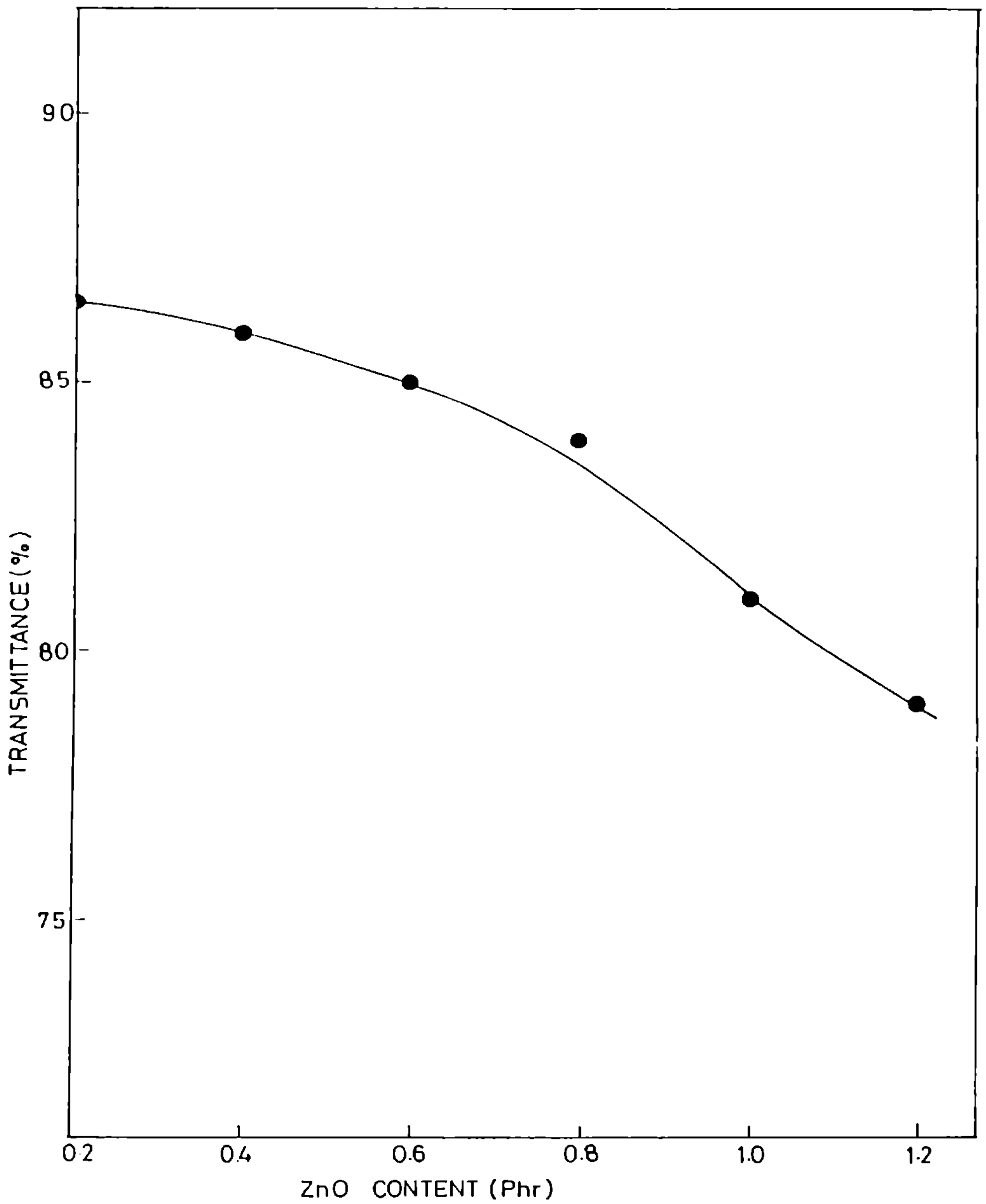


Fig.3.28 Variation of percentage transmittance of NR latex film with ZnO content.

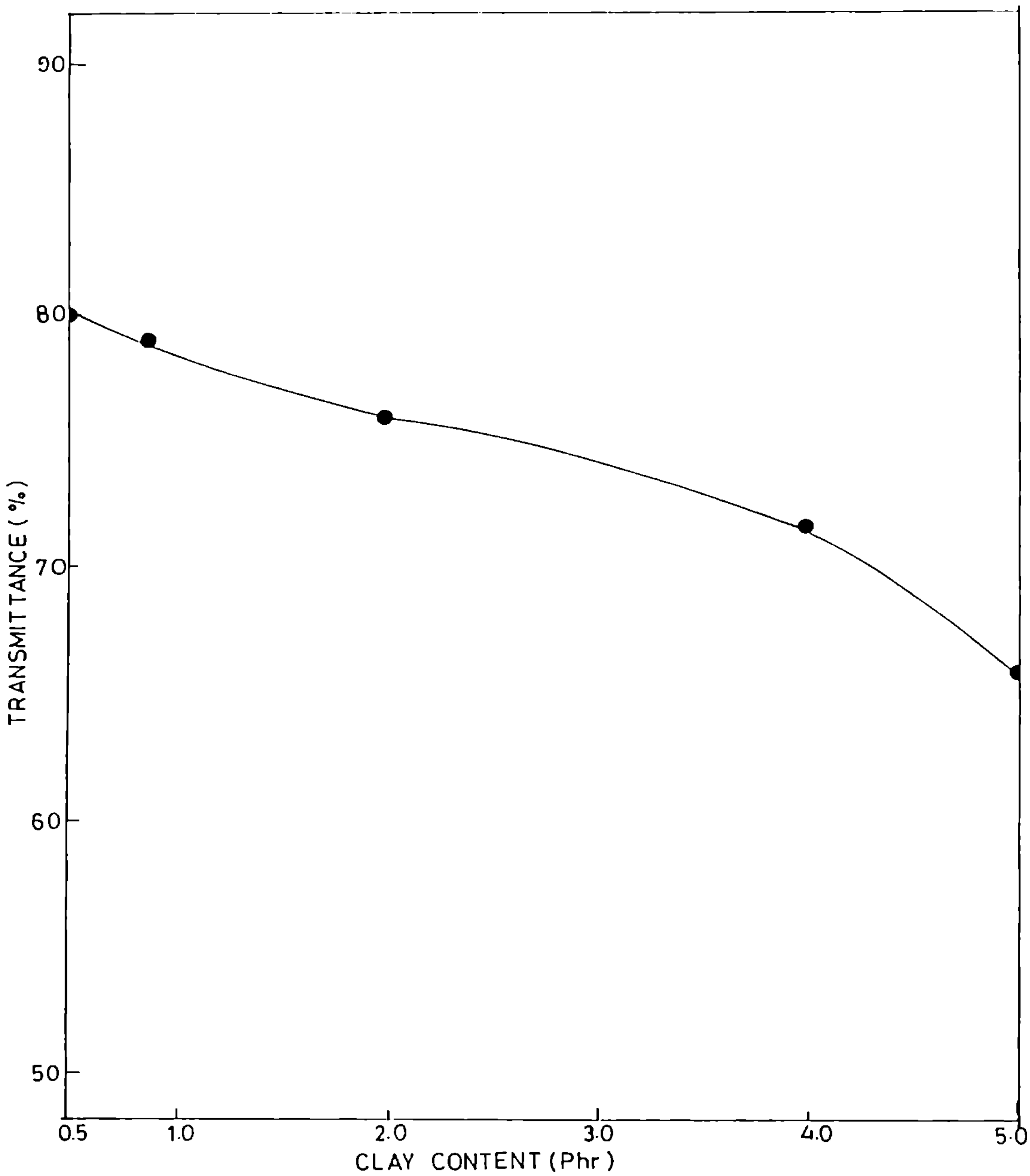


Fig.3.29 Variation of percentage transmittance of NR latex film with clay content.

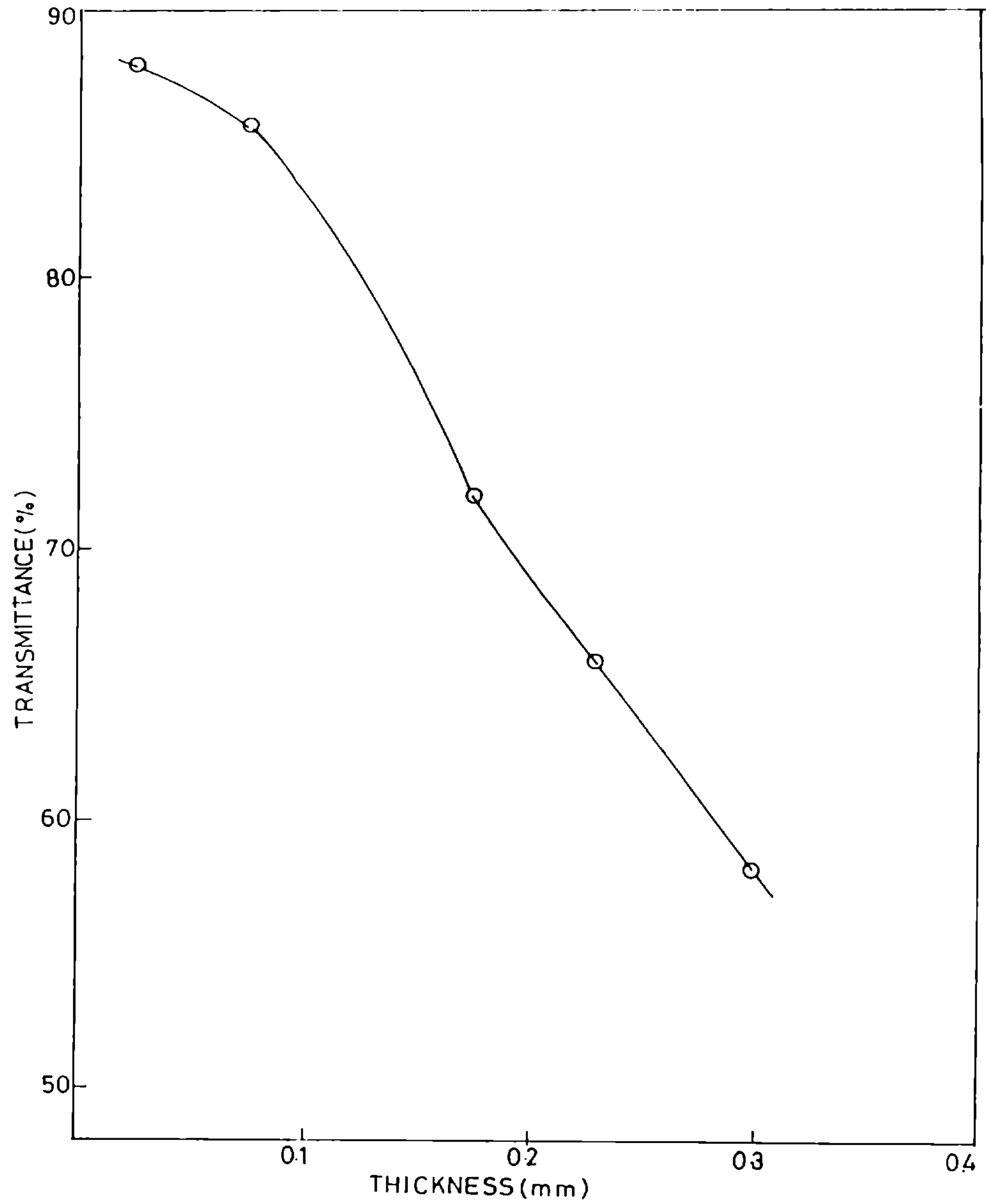


Fig.3.30 Variation of percentage transmittance with thickness of latex films.

that transparency is inversely proportional to thickness of the film as expected.

CONCLUSION

The properties of CBS/TMTM sheets are comparable to those of ZDC/TMTD sheets. Ageing resistance of vulcanized films containing CBS/TMTM is also not adversely affected. So this new accelerator system seems to be promising one.

TMTD/thiocarbanilide system is found to be a fast curing accelerator system. This system gives latex sheets of enhanced tensile strength and ageing resistance. Also their transparency is superior to those of films prepared with other accelerator systems. Therefore this new accelerator system has good potential in natural rubber latex systems, particularly for making transparent products.

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CHAPTER 4

PART I: LATEX STAGE MASTERBATCHING OF CARBON BLACK AND SILICA WITH NATURAL RUBBER LATEX

Fillers have always been an important part of the rubber industry. The principal reinforcing fillers are silicas and carbon blacks. Recently, the rubber industry has been concentrating more attention on reinforcing silica fillers due to the low cost [1,2,3]. Reinforcement by silicas and silicates has been reviewed in detail [4]. Silicas are added to NR to improve tack, increase hardness, improve durability and reduce cost [5]. Carbon black is considered as universal compounding ingredient due to its high efficiency to increase the mechanical properties of vulcanized rubber [6]. Many studies have been published explaining the reinforcing properties of carbon black in rubber [7,8]. But incorporation of black in dry rubber requires huge power consumption and makes the maintenance of cleanliness in the factory difficult [9]. So attempts have been made to mix black with NR in the latex stage. It has been already established that latex masterbatch process can give an extremely well dispersed compound with a shorter mixing cycle [10].

The size of the filler particles plays an important role in the reinforcement of rubber and as the size of filler particle decreases, the reinforcing effect increases [11]. Direct addition of fillers to latex is not possible as it may result in poor dispersion of filler in rubber [12]. Two major disadvantages of latex masterbatch process are the difficulty in reducing the initial viscosity of rubber and the low mechanical stability of NR latex. Objectives of this study have been to find ways of circumventing these problems, viz., to improve the stability of latex by adding surface active agents like polyethylene glycol so that filler dispersion can be mixed with NR latex with proper mechanical stirring, and to reduce the mooney viscosity of the latex-filler mix by mastication of the master batch with ZnO and stearic acid. By using these two techniques NR latex-filler masterbatches (hereafter referred to as modified mixes) are proposed to be prepared by varying the amount of filler from 10 to 50 phr. The mechanical properties of these modified mixes will be then compared with corresponding filled dry rubber compounds (hereafter referred to as conventional mixes). The ageing characteristics of these compounds and the distribution of filler in both of the vulcanizates are also proposed to be investigated.

EXPERIMENTAL

NR latex used was field latex containing 30% DRC. Carbon black was HAF N 330.

Preparation of NR-carbon black compounds

NR was masticated and compounded in a laboratory mixing mill according to ASTM D 3182 (1982) as per the formulation given in Table 4.1. The optimum cure times of the compounds were determined on a Goettfert Elastograph at 150°C. These rubber compounds were moulded in a laboratory hydraulic press at 150°C upto their optimum cure time. The tensile properties of the vulcanizates were evaluated as per ASTM D 412 (1980). The ageing resistance of the vulcanizates was studied after ageing the samples at 100°C for 24 and 48 hrs. Samples for hardness, compression set, rebouhd resilience and heat build up were moulded and tested as per relevant ASTM standards.

Preparation of latex-carbon black masterbatches

A 20% dispersion of HAF was prepared using a ball mill (20 hrs) without any dispersing agent. Field latex was mixed with 1 phr PEG (surface active agent) [13] and 10, 20, 30, 40 and 50 phr each of carbon black dispersion using a high speed mechanical stirrer for 2 minutes. For the

Table 4.1

Formulations of conventional and modified mixes

Ingredients (dry wt.) gm.	Conventional mixes					Ingredients (dry wt.) gm.	Modified mixes				
NR	100	100	100	100	100	Latex-black masterbatch	110	120	130	140	150
ZnO	5	5	5	5	5	ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2	Stearic acid	2	2	2	2	2
NA 4020	1	1	1	1	1	NA 4020	1	1	1	1	1
HAF	10	20	30	40	50	HAF	--	--	--	--	--
Aromatic oil	--	--	--	5	6	Aromatic oil	--	--	--	--	--
CBS	0.6	0.6	0.6	0.6	0.6	CBS	0.6	0.6	0.6	0.6	0.6
TMTD	0.2	0.2	0.2	0.2	0.2	TMTD	0.2	0.2	0.2	0.2	0.2
S	2.5	2.5	2.5	2.5	2.5	S	2.5	2.5	2.5	2.5	2.5

modified mix with 50 phr carbon black, a sample with 6 phr aromatic oil was also prepared. The masterbatches were prepared by coagulating the mixes with 2% acetic acid. These were compounded in a two roll mill as per formulation given in Table 4.1, after reducing the viscosity by masticating with ZnO and stearic acid alone in the mill for 1-4 minutes. Mooney viscosities of all samples were measured initially and after mastication. The optimum cure times of these compounds were determined on a Goettfert Elastograph at 150°C. The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 150°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties, ageing resistance, hardness, compression set, resilience and heat build up of the vulcanizates were evaluated as before. Bound rubber content of all these samples were determined as per the procedure given in chapter 2.

In order to study the effect of ball milling on particle size, the iodine adsorption number of HAF was determined before and after milling as per ASTM D 1510. To understand the structure of carbon black in the dispersion, DBP absorption test was conducted as per ASTM D 2414-65 on milled HAF sample.

Optical studies of both modified and conventional mixes were done using a polariod MP_4 Land Camera. The compression moulded sheets of modified and conventional mixes were cut into thin slices, mounted by means of two tight clips and photos were taken at a magnification of 30.

Swelling measurements of both mixes were done by swelling 0.3 g of each sample in toluene for 48 hrs. The swollen sample was weighed, the solvent removed in vacuum and weighed again. Values of V_r, the volume fraction of rubber in the swollen gel were determined [14].

Preparation of NR-silica compound

NR was masticated and compounded in the laboratory mixing mill as per the formulation given in Table 4.2. The optimum cure time at 150°C was determined as described earlier. This rubber compound was moulded in a hydraulic press at 150°C upto the optimum cure time. The tensile properties, ageing resistance, compression set, abrasion resistance, resilience, heat build up and flex resistance were evaluated.

Preparation of latex-silica masterbatch

Experiments were conducted to study the effect of latex stage silica masterbatching of NR latex. A 25% dispersion of silica was prepared using a ball mill as per the formulation given in chapter 2. Field latex was mixed with 1 phr PEG and 30 phr silica dispersion using a high speed stirrer (4000 rpm) for 2 minutes. The masterbatch was prepared by coagulating this with 2% acetic acid. The mooney viscosity of this masterbatch was reduced by masticating with ZnO and stearic acid in the mill for 1 minute and then compounded in the two roll mill as per the formulation given in Table 4.2. It was moulded in a hydraulic press at 150°C upto the optimum cure time. The tensile properties, ageing resistance, compression set, abrasion resistance, resilience, heat build up and flex resistance were evaluated as per the procedure described in Chapter 2.

Swelling measurements of both modified and conventional silica mixes were done by swelling 0.3 g of each sample in toluene for 48 hrs and V_r values were calculated.

RESULTS AND DISCUSSION

There is a slight reduction in scorch time and cure time as shown in Table 4.3 when the amount of carbon

Table 4.2

Formulations of conventional and modified silica mixes

	Conventional mix (gm)	Modified mix Wet weight (gm)	
NR	100	Latex-silica masterbatch	130
Silica	30	Silica	--
ZnO	5	ZnO	5
Stearic acid	2	Stearic acid	2
DEG	2	DEG	2
NA 4020	1	NA 4020	1
CBS	0.8	CBS	0.8
TMTD	0.2	TMTD	0.2
S	2.5	S	2.5

black is increased from 10 to 50 phr in both mixes. The modified mixes show lower scorch time and cure time compared to the conventional mixes. This may be due to the lower accelerator adsorption on the carbon black surface in the modified mixes. The compression set, resilience, heat build up and hardness are found to be comparable for both mixes.

Fig.4.1 shows the variation of tensile strength with the amount of carbon black before and after ageing. The modified mixes have superior tensile strength compared to conventional mixes. The ageing resistance is also found to be superior. This may be attributed to the uniform distribution of carbon black and also to the higher molecular weight of rubber in the modified mixes. Fig.4.2 shows the variation in the elongation at break with amount of carbon black before and after ageing. The modified mixes show lower elongation at break compared to the conventional mixes. This may be due to the higher crosslink density and the higher filler polymer interaction. The reduction in elongation at break after ageing is less for the modified mixes compared to the conventional mixes. This may be due to its resistance to main chain rupture.

Table 4.3

Cure characteristics and vulcanizate properties of black compounds

	Black loading (Phr)	Scorch time (min.)	Cure time (min.)	Hardness (Shore A)	Compression set (%)	Resilience (%)	Heat build up (°C)
Conventional mix	10	2.52	4.86	43	24	79	7
	20	2.20	4.56	43	25	76	10
	30	2.28	3.76	47	28	74	13
	40	1.88	3.48	49	30	69	22
	50	1.84	3.44	50	31	62	29
Modified mix	10	1.32	4.36	43.5	25	76	7
	20	1.12	3.80	47	27.5	73	10
	30	0.84	3.56	49	31	73	14
	40	0.80	2.96	52	34	69	21
	50	0.80	2.76	53	36	62	30

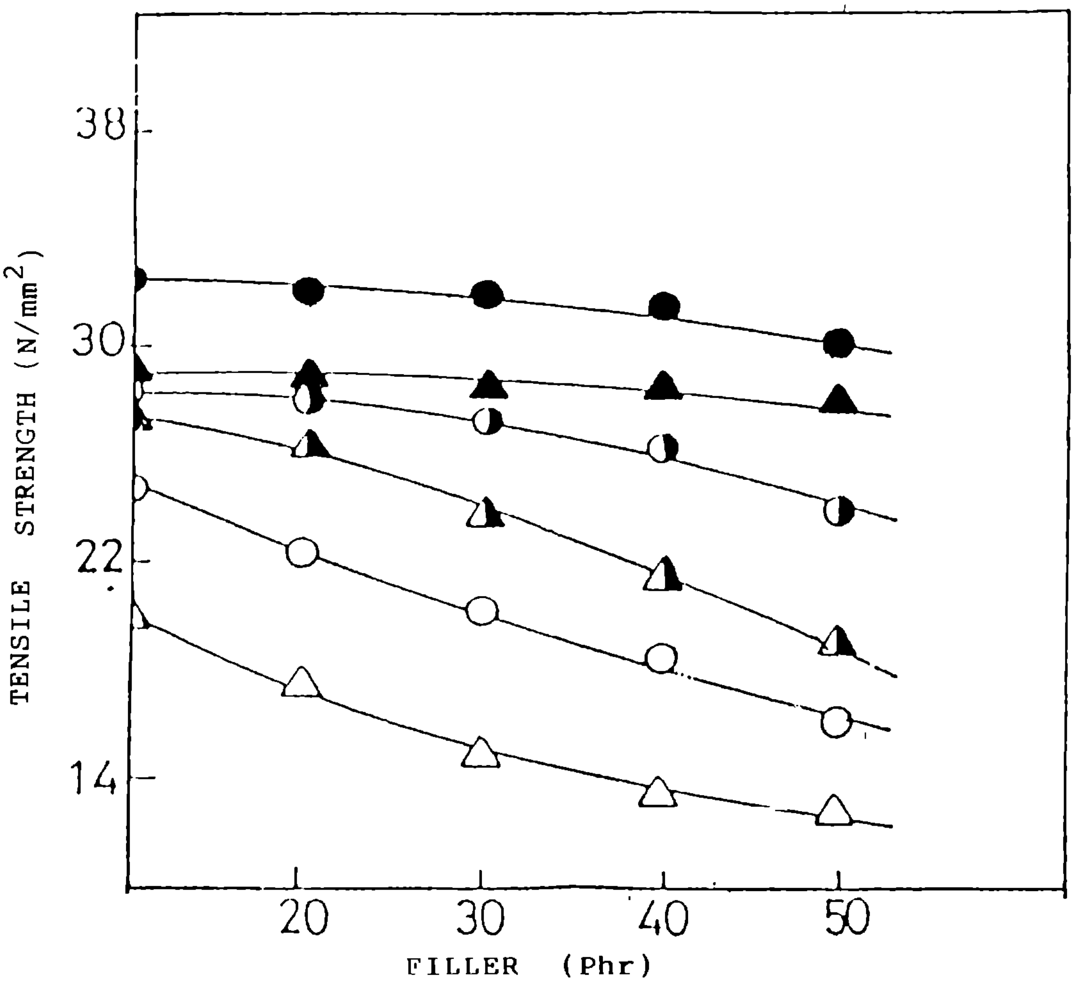


Fig.4.1 Variation of tensile strength with carbon black content
(●)modified (◑) aged at 100°C for 24 hours
(○) aged for 48 hours (▲)conventional
(◭)aged for 24 hours (△)aged for 48 hours

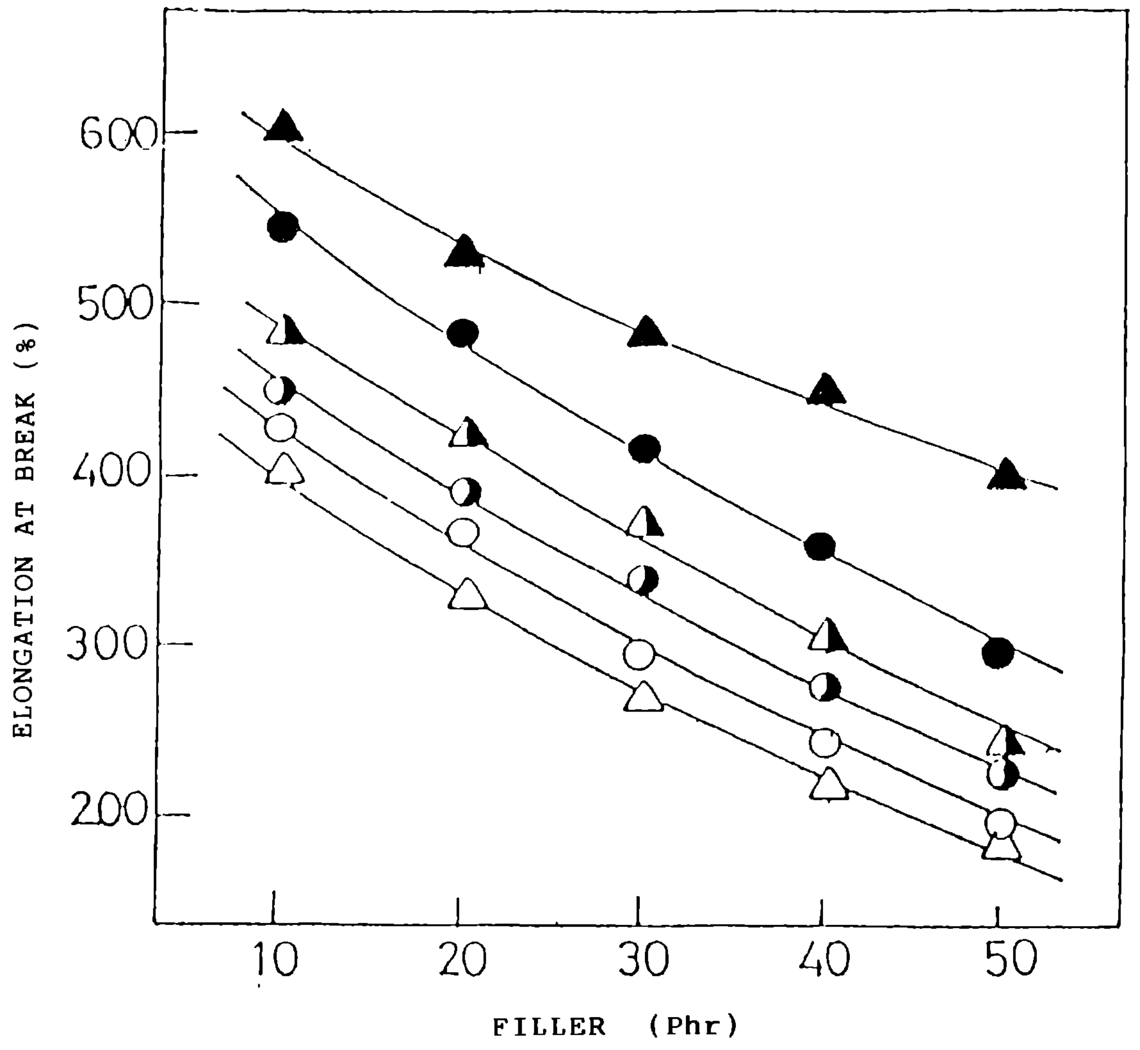


Fig.4.2 Variation of elongation at break with carbon black
(●)modified (◑) aged at 100 C for 24 hours
(○)aged for 48 hrs (▲) conventional
(◭)aged for 24 hrs(△)aged for 48 hours

Figs.4.3 and 4.4 show the variation of modulus (at 100% elongation) with the amount of black before and after ageing. Modulus is higher for the modified mixes. This may be due to higher crosslink density and the higher polymer filler interaction. The modulus after ageing was found to be higher for the modified mixes compared to conventional vulcanizate. This shows its higher resistance to main chain breakdown during ageing.

The bound rubber content is found to be higher for the modified mixes (Table 4.4). This proves that there is more rubber-filler interaction in the modified mixes. Table 4.4 also shows that the V_r value, which is a measure of the total crosslink density, is higher for the modified mixes.

The modified mixes containing 30, 40 and 50 phr carbon black show high mooney viscosity but it can be reduced considerably by masticating the mixes with ZnO and stearic acid for 1, 2 and 4 minutes respectively (shown in Table 4.5).

The iodine adsorption number of carbon black is found to be the same before and after ball milling as shown

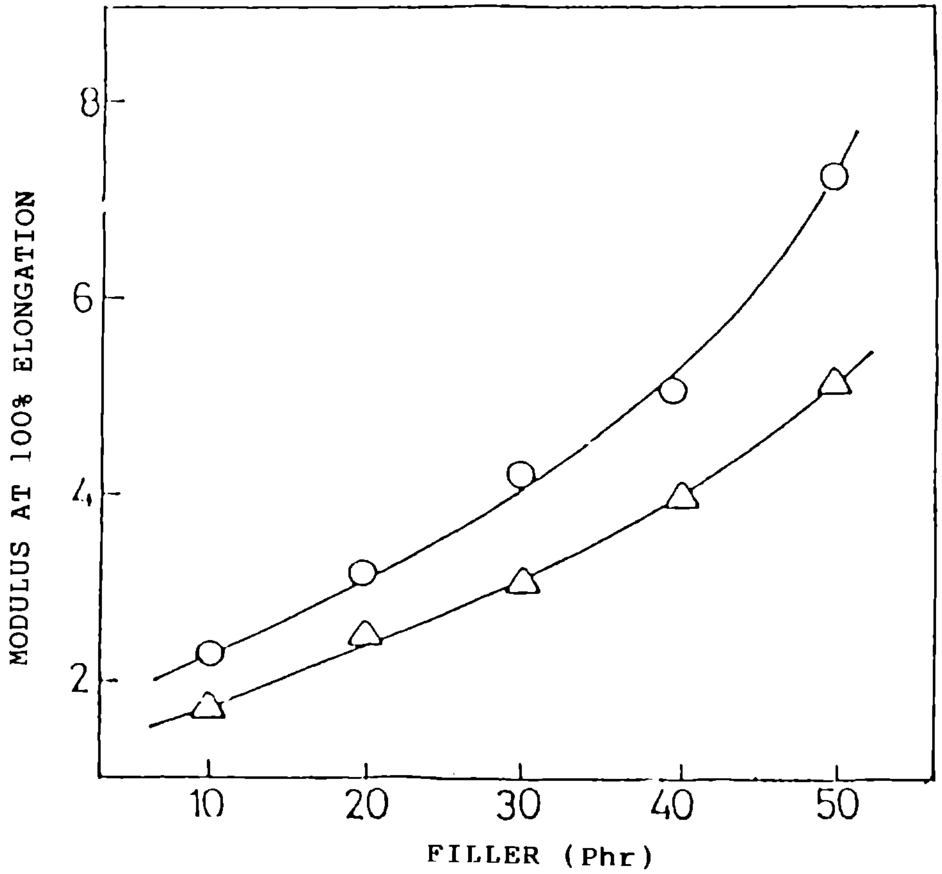


Fig.4.3 Variation of modulus with carbon black content

○ modified △ conventional

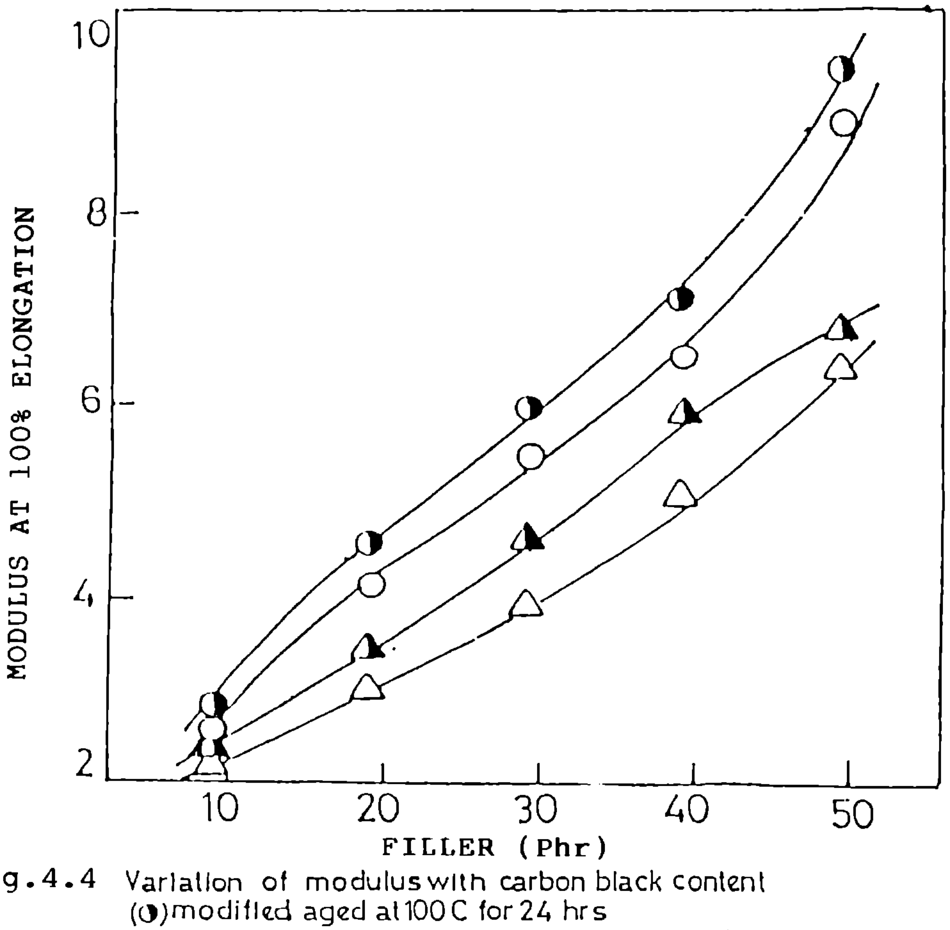


Fig.4.4 Variation of modulus with carbon black content
(◑)modified aged at 100 C for 24 hrs
(○)aged for 48 hrs (▲)conventional aged for 24 hrs
(△)aged for 48 hrs

Table 4.4

Bound rubber and V_r values of NR-carbon black mixes

	Black loading (Phr)	Bound rubber (%)	V_r values
Conventional mix	10	17	0.2369
	20	22.5	0.2410
	30	39	0.2461
	40	41	0.2388
	50	50	0.2478
Modified mix	10	37.5	0.2486
	20	53	0.2632
	30	57	0.2811
	40	60	0.2879
	50	66	0.2940

Table 4.5

Mooney viscosity of masterbatch at 135°C

Black loading (Phr)	Mooney viscosity ML(1+1.5)		Time of of mastication (min)	Mooney viscosity after mastication
	With PEG	Without PEG		
10	52	60	--	--
20	54	65	--	--
30	68	80	1	52
40	86	99	2	54
50	110	120	4	56

in Table 4.6. This shows that ball milling does not change the particle size of the carbon black. The DBP absorption study shows that the structure of carbon black is not changed during ball milling as shown in Table 4.6.

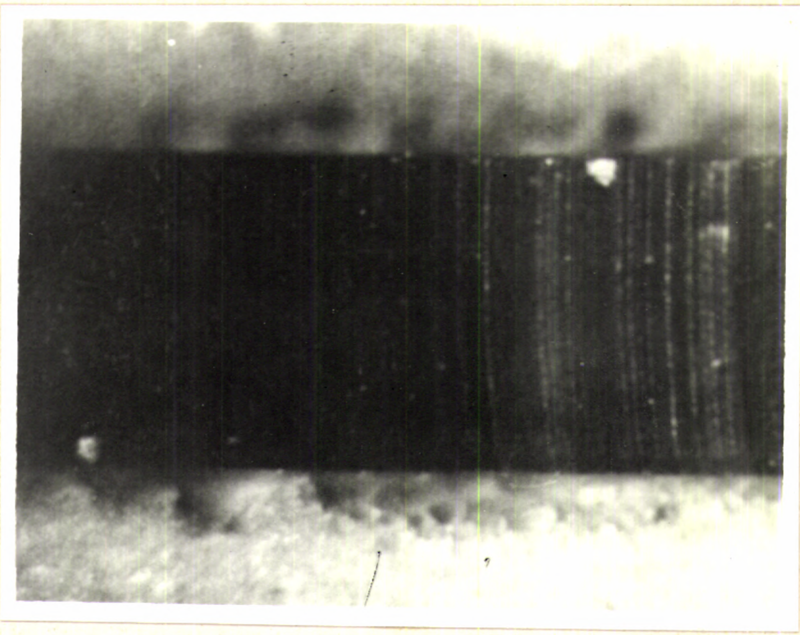
Fig.4.5 shows the photographs of the modified mix and conventional mix with 50 phr carbon black. The carbon black distribution is found to be more uniform in the modified mixes.

Table 4.7 shows the vulcanizate properties of silica filled compounds (both conventional and modified). Here the modified mix with 30 phr silica shows a slightly improved tensile strength. The ageing resistance is also higher for the modified mix. Elongation at break, modulus, heat build up are comparable for both mixes. Compression set value is lower for modified mix. Abrasion resistance, resilience and flex resistance are higher for the vulcanizates of the modified mixes compared to conventional mixes. This superior mechanical properties of the modified vulcanizates may be attributed to the uniform filler distribution, during latex stage masterbatching.

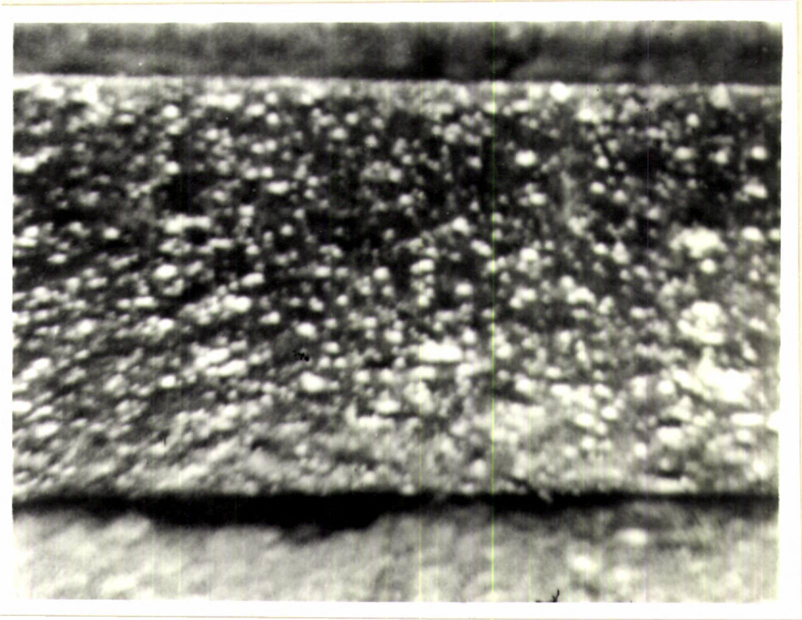
Table 4.6

Iodine number and DBP absorption values of carbon black

Carbon black	Iodine Number	DBP absorption (m/100 g)
Original	87	102
In dispersion	87	102



Modified mix



Conventional mix

Fig.4.5 Photographs of the modified and conventional mixes with 50 phr carbon black.

Table 4.7

Vulcanizate properties of silica filled compounds

	Silica loading (Phr)	Tensile strength (N/mm^2)			E_B (%)	Modulus 100% MPa	Compression set (%)	Abrasion resistance index (%)	Resilience (%)	Heat build up (°C)	Flex resistance cycles
		Unaged	Aged at 70°C 24 hrs.	Aged at 70°C 48 hrs.							
Conventional	30	22	20.6	17.5	570	2.60	35	126	76.8	8	23002-221310
Modified	30	23	21.3	19	575	2.62	31	150	86.9	8	78260-140573

CONCLUSION

Latex stage masterbatching is a very promising technique for improving the mechanical properties of rubber vulcanizates. The improvement in mechanical properties results from the more uniform distribution of the filler compared to the conventional vulcanizates. The better dispersion of filler results in better ageing resistance.

PART II: STUDY ON THE MECHANICAL PROPERTIES OF THE BLEND OF NR LATEX/CARBON BLACK MASTERBATCH AND SBR

Polymer blends are widely used these days for optimising properties of individual polymers and for cost reduction [15]. By blending two rubbers, the right compromise in properties can be obtained. All important synthetic rubbers are frequently blended with natural rubber. In general, the rubber used in practical application is usually a blend of elastomers. The importance of carbon black distribution on physical properties in elastomer blends was already indicated [16]. The filler distribution in elastomer blends has some special characteristics [17]. When fillers are added into blends such as NR/SBR, the filler is unevenly distributed between the two polymers [18]. The effect of heterogeneous carbon black distribution on the properties of polymer blends was studied [19,20]. The effect of curing temperature and curing systems on the technical properties, polymer-filler interactions and network structures of various blends was also studied [21]. A study of morphology, curing characteristics and physical properties of NR/SBR and NR/BR blends was done by F.Gharavi and

A.A.Katbab [22]. A comprehensive study of black distribution between 50/50 blends of several elastomers was also done [23].

In this study, latex stage carbon black masterbatching of NR is proposed to be done and this latex-carbon black is proposed to be blended with SBR at different ratios. The mechanical properties of the black masterbatched NR/SBR blend will be compared with those of conventional NR/SBR blends. The ageing characteristics of these blends and the distribution of carbon black in both blends are also proposed to be investigated.

EXPERIMENTAL

Preparation of NR latex-carbon black masterbatch/SBR blends

Field latex was mixed with 1 phr polyethylene glycol and 10, 20, 30, 40 and 50 phr each of carbon black dispersion using a high speed mechanical stirrer for 2 minutes. The masterbatches were prepared by coagulating this mixture with 2% acetic acid. Hereafter this mix is referred to as N-LCM (NR-Latex carbon black masterbatch).

The N-LCM/SBR compounds were prepared using a two roll mill, varying the N-LCM/SBR ratio as 80/20, 60/40, 40/60 and 20/80. N-LCM was first masticated in the mill for 2 minutes and then SBR was added and compounded according to ASTM D 3182 (1982). The formulations are given in Table 4.8.

Preparation of filled NR-SBR blends

NR was first masticated in a two roll mill for one minute and then SBR was added. These NR/SBR blends were compounded according to ASTM D 3182 (1982) as per the formulation given in Table 4.8. The optimum cure time of these compounds were determined on a Goettfert model 67.85 at 150°C.

Both these N-LCM/SBR blends and NR/SBR blends were moulded in a laboratory hydraulic press at 150°C upto their optimum cure time. The tensile properties of the vulcanizates were evaluated as per ASTM D-412 (1980). The samples were aged at 100°C for 24 and 48 hrs. and ageing resistance was studied. Samples for hardness, compression set, abrasion resistance, rebound resilience, heat build up and flex resistance were moulded and tested as per relevant ASTM standards.

Optical studies of both N-LCM/SBR and black filled NR/SBR blends were done using a polaroid MP_4 Land camera.

Table 4.8

Formulations of NR/SBR and N-LCM/SBR blends

Ingredients (dry wt.) gm.	Conventional mix (NR/SBR)				Ingredients (dry wt.) gm.	Modified mixes (N-LCM/SBR)			
NR	80	60	40	20	Latex black masterbatch [N-LCM]	120	90	60	30
SBR	20	40	60	80	SBR	20	40	60	80
ZnO	5	5	5	5	ZnO	5	5	5	5
Stearic acid	2	2	2	2	Stearic acid	2	2	2	2
HAF 330	50	50	50	50	HAF 330	10	20	30	40
Aromatic oil	6	6	6	6	Aromatic oil	1.2	2.4	3.6	4.8
NA 4020	1	1	1	1	NA 4020	1	1	1	1
CBS	0.8	0.8	0.8	0.8	CBS	0.8	0.8	0.8	0.8
TMTD	0.24	0.28	0.32	0.36	TMTD	0.24	0.28	0.32	0.36
S	2.4	2.3	2.2	2.1	S	2.4	2.3	2.2	2.1

The compression moulded sheets of both blends (N-LCM/SBR 80/20) and (NR/SBR 80/20) were cut into thin slices and mounted by means of two tight clips and photos were taken at a magnification of 30.

RESULTS AND DISCUSSION

Fig.4.6 shows the tensile strength of both N-LCM/SBR and NR/SBR blends before and after ageing. The tensile strength of N-LCM/SBR blends are better than those of NR/SBR blends, before and after ageing. This is probably due to the uniform distribution of carbon black in latex masterbatches.

Addition of polyethylene glycol to latex improves its stability so that carbon black dispersion can be mixed with NR latex with proper mechanical stirring [24]. In the absence of polyethylene glycol, uniform distribution of carbon black dispersion in the latex is difficult as the latex gets coagulated during mechanical agitation.

Fig.4.7 shows the photographs of N-LCM/SBR (80/20) and NR/SBR (80/20) blends with 50 phr carbon black. The carbon black distribution is found to be more uniform for N-LCM/SBR blend.

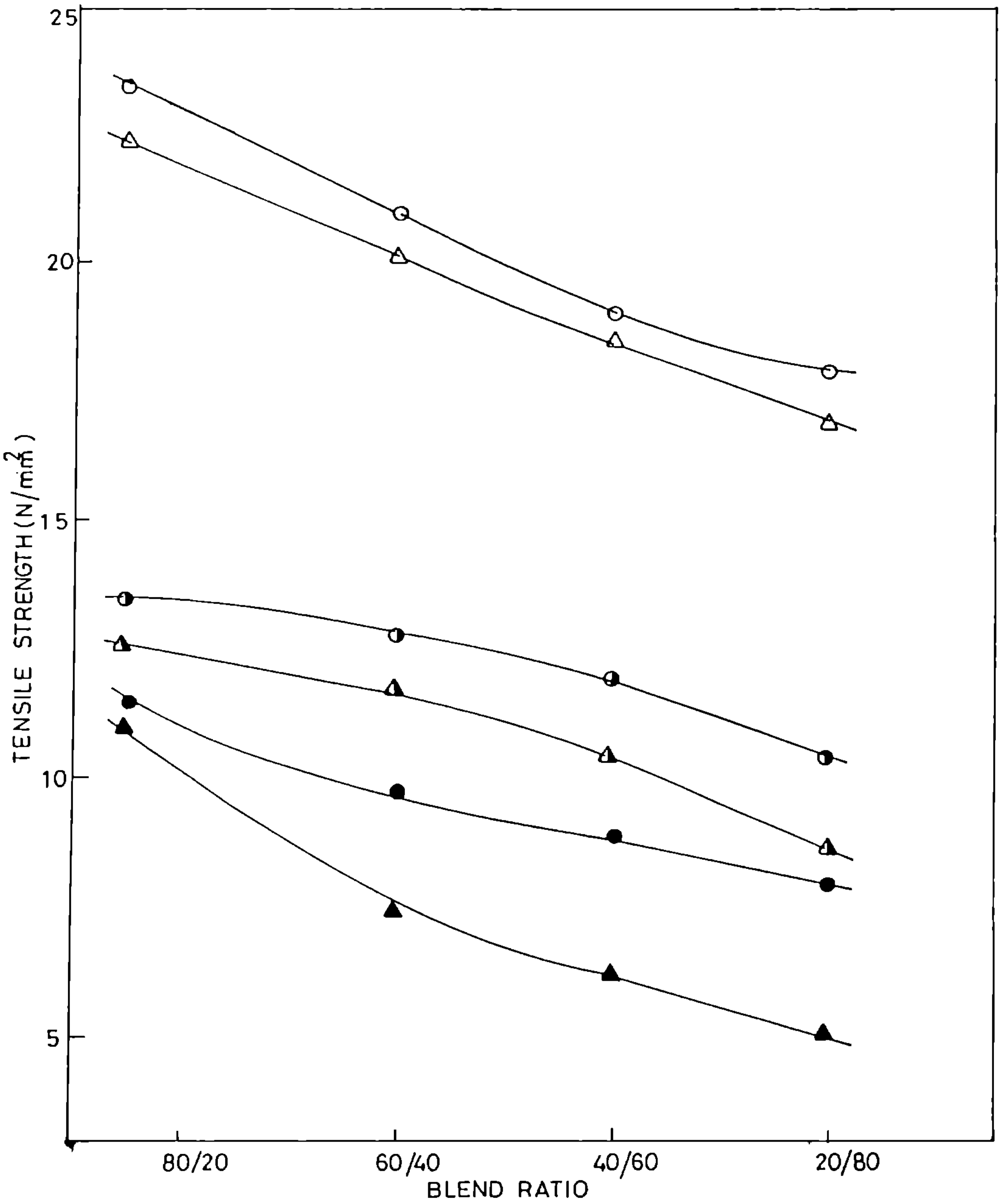
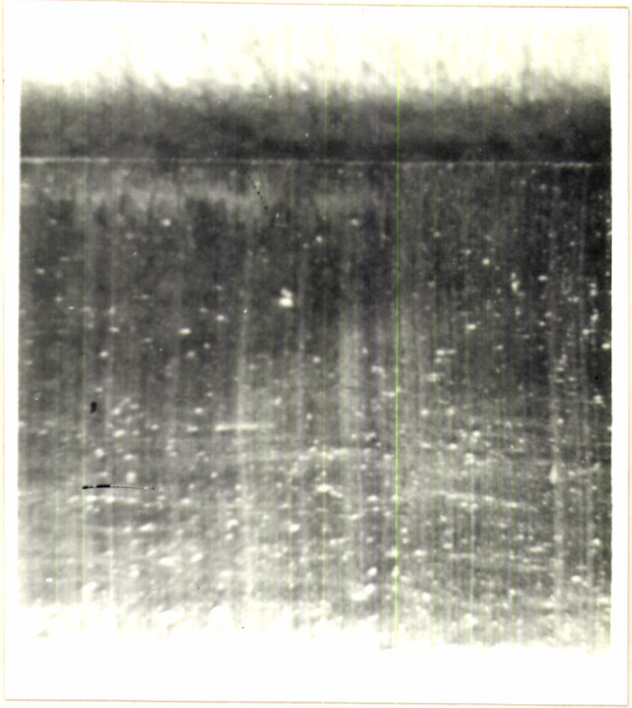
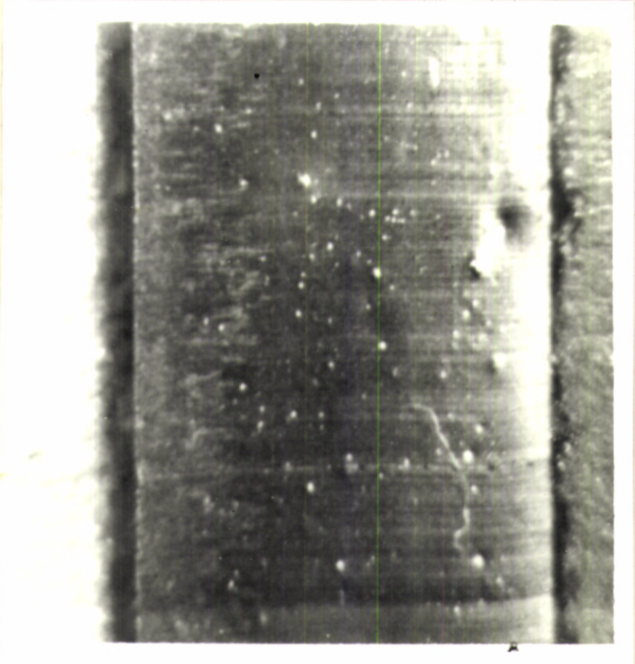


Fig.4.6 Variation of tensile strength of N-LCM/SBR and NR/SBR blends with blend ratio. 'O' N-LCM/SBR, '◑' aged at 100°C for 24 hrs, '●' aged at 100°C for 48 hrs, 'Δ' NR/SBR, '◭' aged at 100°C for 24 hrs, '▲' aged at 100°C for 48 hrs.



N-LCM/SBR (80/20) blend



NR/SBR (80/20) blend

Fig.4.7 Photographs of N-LCM/SBR and NR/SBR blends with 50 phr carbon black.

Table 4.9 shows the cure characteristics of N-LCM/SBR blends and NR/SBR blends. N-LCM/SBR blends are found to cure at a similar rate compared to NR/SBR blends. As shown in Table 4.10, N-LCM/SBR blends have higher modulus but lower elongation at break compared to the conventional NR/SBR blends. This may be due to the higher polymer-filler interaction in the case of N-LCM/SBR blends. The resilience, flex resistance and hardness are superior for N-LCM/SBR compounds (shown in Table 4.10). The compression set and abrasion resistance are comparable for both types of blends. The heat build up is lower for N-LCM/SBR blends. All these confirm the higher polymer filler interaction and the uniform filler distribution in the modified blends.

CONCLUSION

Latex stage blending can improve the dispersion of carbon black in NR. The NR latex carbon black masterbatch/SBR blend vulcanizates show superior mechanical properties before and after ageing in comparison to black filled dry NR/SBR vulcanizates.

Table 4.9

Cure characteristics of NR/SBR and N-LCM/SBR blends

Blend	Blend ratio	Scorch time (min.)	Cure time (min.)
NR/SBR blends	80/20	1.76	3.72
	60/40	1.76	3.76
	40/60	2.36	3.72
	20/80	2.15	3.20
N-LCM/SBR blends	80/20	1.64	3.56
	60/40	1.70	3.64
	40/60	2.12	3.66
	20/80	2.04	3.04

Table 4.10

Mechanical properties of NR/SBR and N-LCM/SBR blends

	Blend ratio	E_B (%)	Modulus (100%) MPa	Hardness (Shore A)	Compression set (%)	Abrasion resistance Index	Resilience (%)	Heat build up °C	Flex resistance cycles
NR/SBR blends	80/20	423	3.57	57	32	120	52	36	40624-66851
	60/40	385	4.11	58	28	119	55	34	16792-32342
	40/60	381	3.2	62	26	119	55	35	11154-22913
	20/80	379	3.04	64	24	121	55	35	25432-50676
N-LCM/SBR blends	80/20	392	5.13	57	27	121	72	30	146927-182543
	60/40	370	4.20	60	24	120.6	69	35	137927-165930
	40/60	368	3.60	64	22	121	65	35	134233-150533
	20/80	340	3.13	67	20.5	121	62	35	135281-157892

PART III: RHEOLOGICAL STUDY OF NR LATEX/CARBON BLACK MASTERBATCH AND NR LATEX-BLACK MASTERBATCH/SBR BLEND

Melt flow behaviour of polymers is of great importance to optimize processing operations. According to the ASTM standards processability is the relative ease with which a raw rubber or mix is shaped in the processing equipment [25]. A large number of indepth studies have been reported on the melt flow behaviour of elastomers and their blends [26-32].

The rubber industry operates with devices imparting shear stresses and shear rates over a wide range. Therefore the viscosity of a polymer as a function of shear rate and temperature is very important. Viscosity data and melt elasticity behaviour at various temperatures are useful in selecting the processing conditions and in designing the processing instrument. Brydson [33] indicated the need for rheological studies and their importance in selecting a polymer and its processing conditions.

The objective of this study is the evaluation of the processing behaviour of NR latex/carbon black masterbatch and NR latex/carbon black masterbatch/SBR blends in comparison to conventional counterparts (NR/carbon black mix and carbon filled dry NR/SBR blend) using a capillary rheometer. The effects of shear stress, filler concentration, blend ratio and temperature on melt viscosity, and elasticity have been investigated. Further, the morphology of extrudate has also been examined.

EXPERIMENTAL

Preparation of NR latex/carbon black masterbatch compound (modified) and NR/carbon black compound (conventional)

NR latex/carbon black masterbatch was prepared as per the procedure given in Chapter 4, Part I. The modified compound and conventional compound were prepared in a laboratory model two-roll mill as per the formulation given in Table 4.1. The final sheeting was done by passing the compound through a tight nip. Care was taken to ensure that the NR was masticated to the same extent in all the systems.

Rheological studies were carried out using a capillary rheometer, attached to a Zwick Universal testing machine, model 1474. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) and the shear viscosity η was calculated as

$$\eta = \frac{\tau_w}{\dot{\gamma}_w}$$

Extrudate swelling

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 24 hrs. of extrusion and the extrudate swelling was calculated as the ratio of the diameter of extrudate to that of the capillary (d_e/d_c). Photographs of these extrudates at different shear rates were also taken.

Preparation of NR latex/carbon black masterbatch/SBR (modified blend, N-LCM/SBR) and conventional carbon black filled NR/SBR blend

Formulations of N-LCM/SBR blend and NR/SBR blend are given in Table 4.8. All these blends were prepared on a two roll mixing mill. Rheological measurements of these blends were made using the capillary rheometer-Goettfert viscotester 1500. The extrudates were collected and the extrudate swelling was calculated. Photographs of these extrudates at different shear rates were also taken.

RESULTS AND DISCUSSION

Fig.4.8 shows the variation of shear viscosity with shear rate at 95°C for the modified and conventional mixes with 40 and 50 phr carbon black. As the shear rate increases, shear viscosity decreases, showing that the compounds are pseudoplastic in nature, as expected. The shear viscosities of the modified mixes are found to be comparable to that of the conventional mixes.

In Fig.4.9, variation of shear viscosity with filler loading at two shear rates is shown. It is found that on increasing the filler loading, the shear viscosity increases at both the shear rates. The increase in shear viscosity when the amount of filler is increased from 40 to 50 phr is more in modified compounds. When 6 phr of oil is incorporated in the modified compound containing 50 phr black, the viscosity variation is found to be almost similar to that of the conventional compounds.

The dependence of melt viscosity on temperature is shown in Fig.4.10, in semilogarithmic Arrhenius plots of $\log\eta$ vs. 1/T. In this figure, the logarithm of viscosity is plotted as a function of reciprocal temperature. The activation energies of flow can be calculated from the

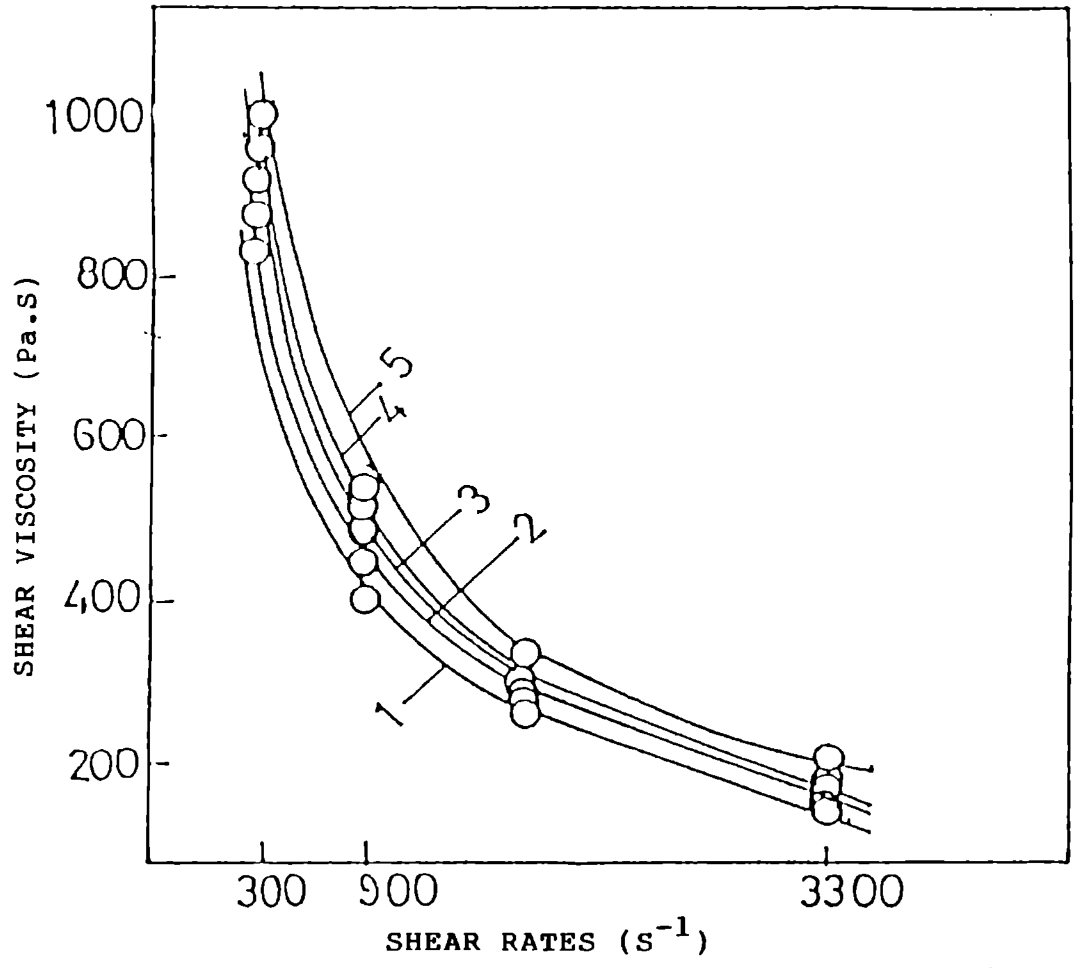


Fig.4.8 Variation of shear viscosity with shear rate at 95°C
(1) modified mix with 40 phr carbon black
(2) Conventional with 40 phr carbon black
(3) modified with oil with 50 phr carbon black
(4) modified without oil 50 phr carbon black
(5) conventional with 50 phr carbon black

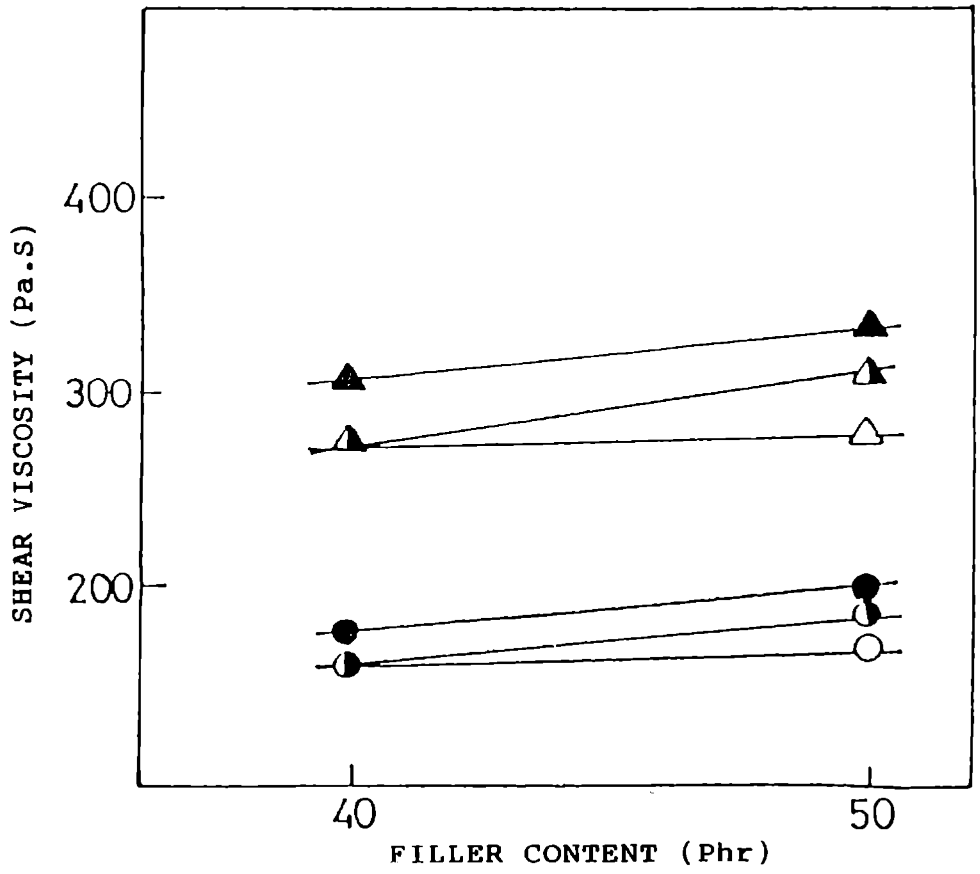


Fig.4.9 Variation of shear viscosity with carbon black at 95°C

(◭)modified
(△)modified with oil
(▲)conventional
} shear rate 1666 S^{-1}

(◑)modified
(○)modified with oil
(●)conventional
} shear rate 3333 S^{-1}

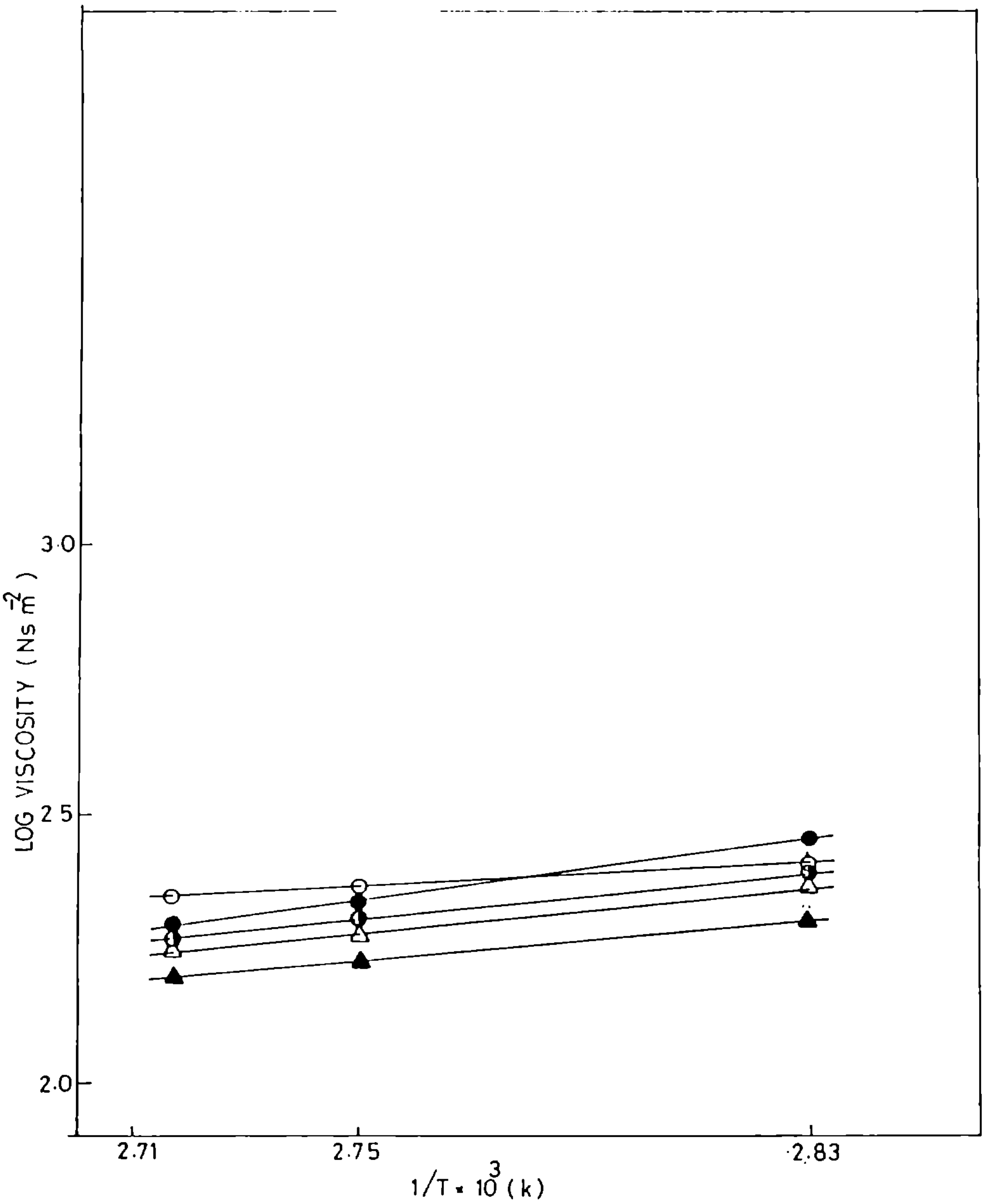


Fig.4.10 Variation of viscosity with temperature.

- ▲ modified mix with 40 phr black
- △ conventional mix with 40 phr black
- ◑ modified with oil with 50 phr black
- ● modified without oil with 50 phr black
- ○ conventional with 50 phr carbon black.

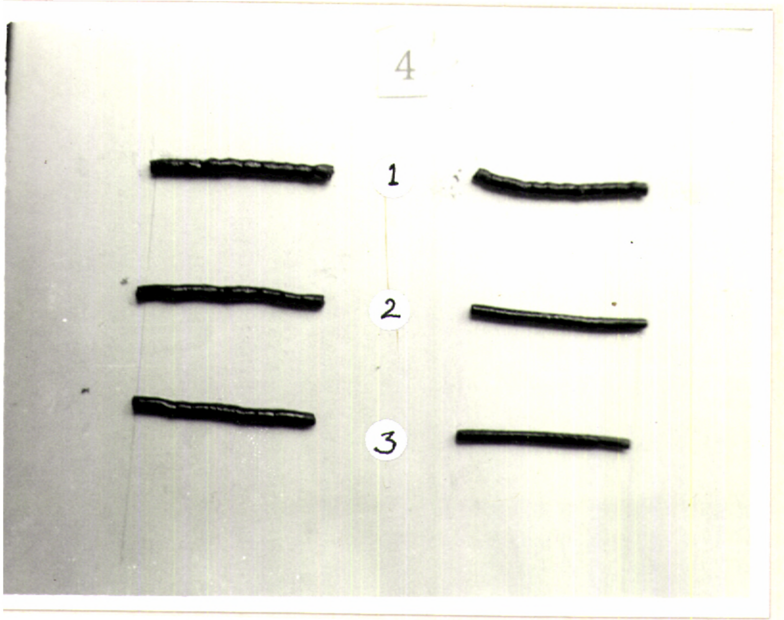
slopes of these lines. In the Arrhenius equation, η is related to absolute temperature T by the following equation

$$\eta = A.e^{E/RT}$$

where A is a constant characteristic of the polymer, ΔE is the activation energy and R is the universal gas constant.

For both modified and conventional mixes containing 40 phr carbon black, the activation energies are almost same. But for compounds with 50 phr carbon black, the conventional mix has slightly less activation energy than the modified mixes with and without oil. The activation energy provides valuable information on the sensitivity of the material towards the change in temperature. The higher the activation energy, the more temperature sensitive the material will be.

Figs.4.11 and 4.12 show the photographs of the extrudates of all compounds at 90°C and 95°C at different shear rates (833 s^{-1}, 1666 s^{-1}, 3333s^{-1}). The surface smoothness of the extrudate improves when the temperature of extrusion is changed from 90 to 95°C and also when the shear rate is increased from 833 to 3333s^{-1}. The extrudate

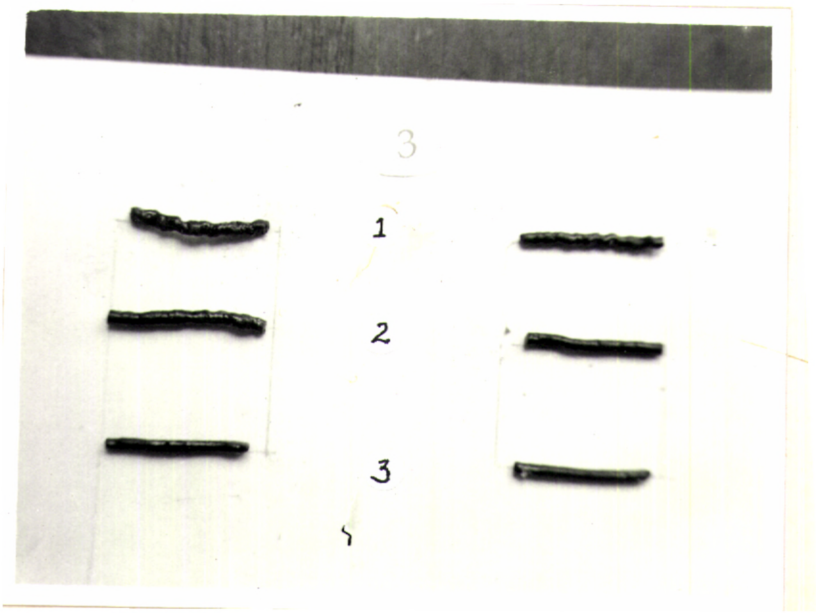


Shear rates (s^{-1})

1 - 833
2 - 1666
3 - 3333

90°C 95°C

Fig.4.11 Photograph of the extrudates of the modified mix with 50 phr carbon black at different shear rates



Shear rates (s^{-1})

1 - 833
2 - 1666
3 - 3333

90°C 95°C

Fig.4.12 Photograph of the extrudates of the conventional mix with 50 phr carbon black at different shear rates.

behaviour of both modified and conventional mixes is found to be almost similar at 40 phr carbon black loading. But at 50 phr carbon black loading, the conventional mix gives a smooth extrudate at 95°C at shear rates 1666 and 3333 s^{-1} but the modified compounds give rough extrudates. But when 6 phr oil is incorporated into the modified compound a smooth extrudate is obtained, at all shear rates.

Die swell of modified mixes and conventional mixes are shown in Table 4.11. Die swell of both mixes are comparable. It may be inferred that the elastic nature of the latex stage and conventional mixes are comparable.

Figs.4.13 and 4.14 show the variation of shear viscosity with shear rate of N-LCM/SBR blends and NR/SBR blends respectively at 150°C. As the shear rate increases, shear viscosity decreases. This confirms the pseudoplastic behaviour of these compounds. The change in viscosity with shear rate is comparable in both cases. This shows that latex masterbatch blending with SBR does not affect the processability.

Fig.4.15 shows the variation of shear viscosity with blend ratio. As SBR content increases, shear

Table 4.11

Die swell values at shear rate 333 s^{-1}

	Carbon black loading (phr)	Temperature	
		90°C	95°C
Modified	40	1.19	1.15
	50	1.17	1.16
	50 with oil	1.08	1.2
Conventional	40	1.20	1.16
	50	1.16	1.16

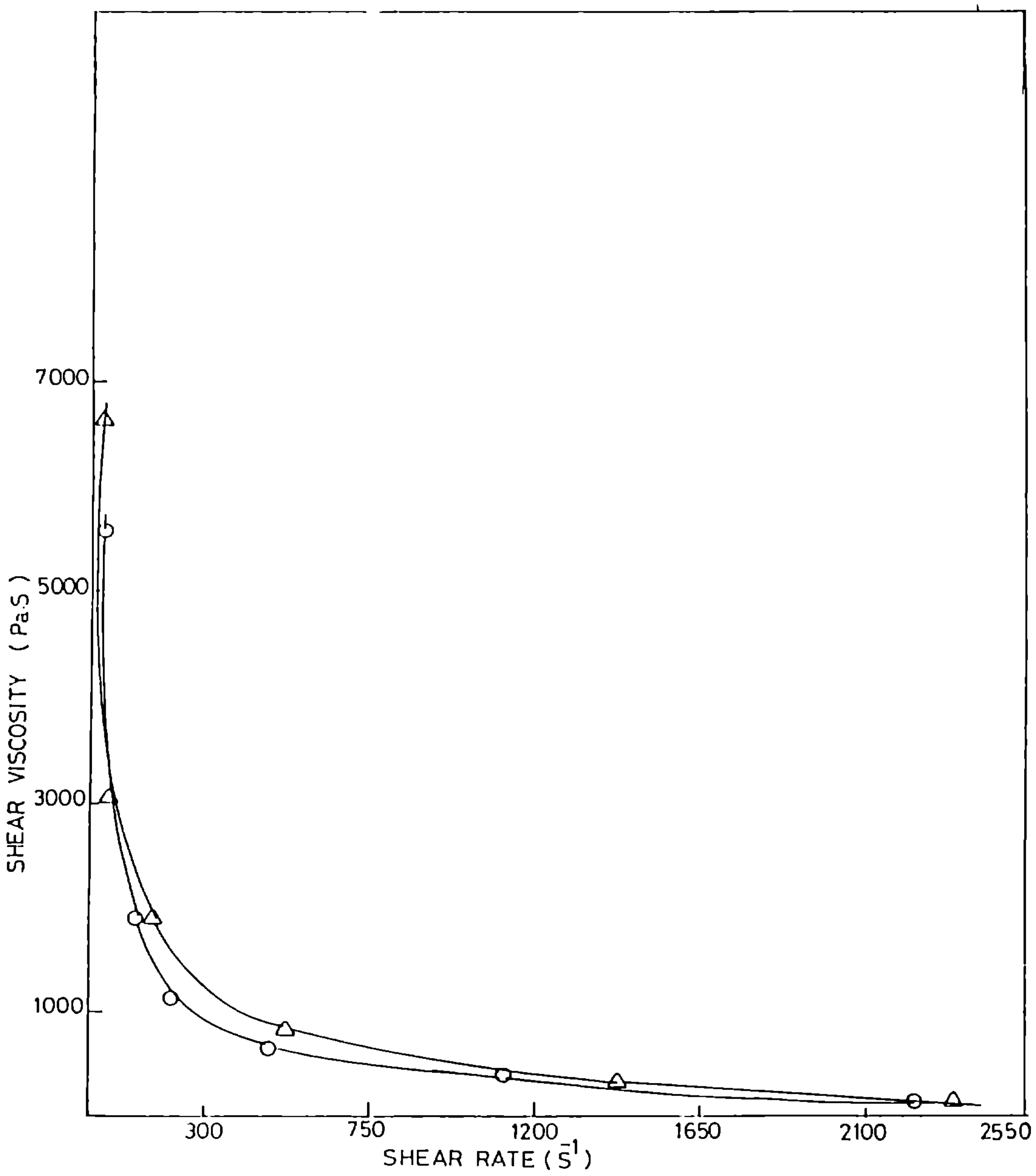


Fig.4.13 Variation of shear viscosity with shear rate of N-LCM/SBR, at 150°C
○ 80/20 N-LCM/SBR △ 20/80 N-LCM/SBR.

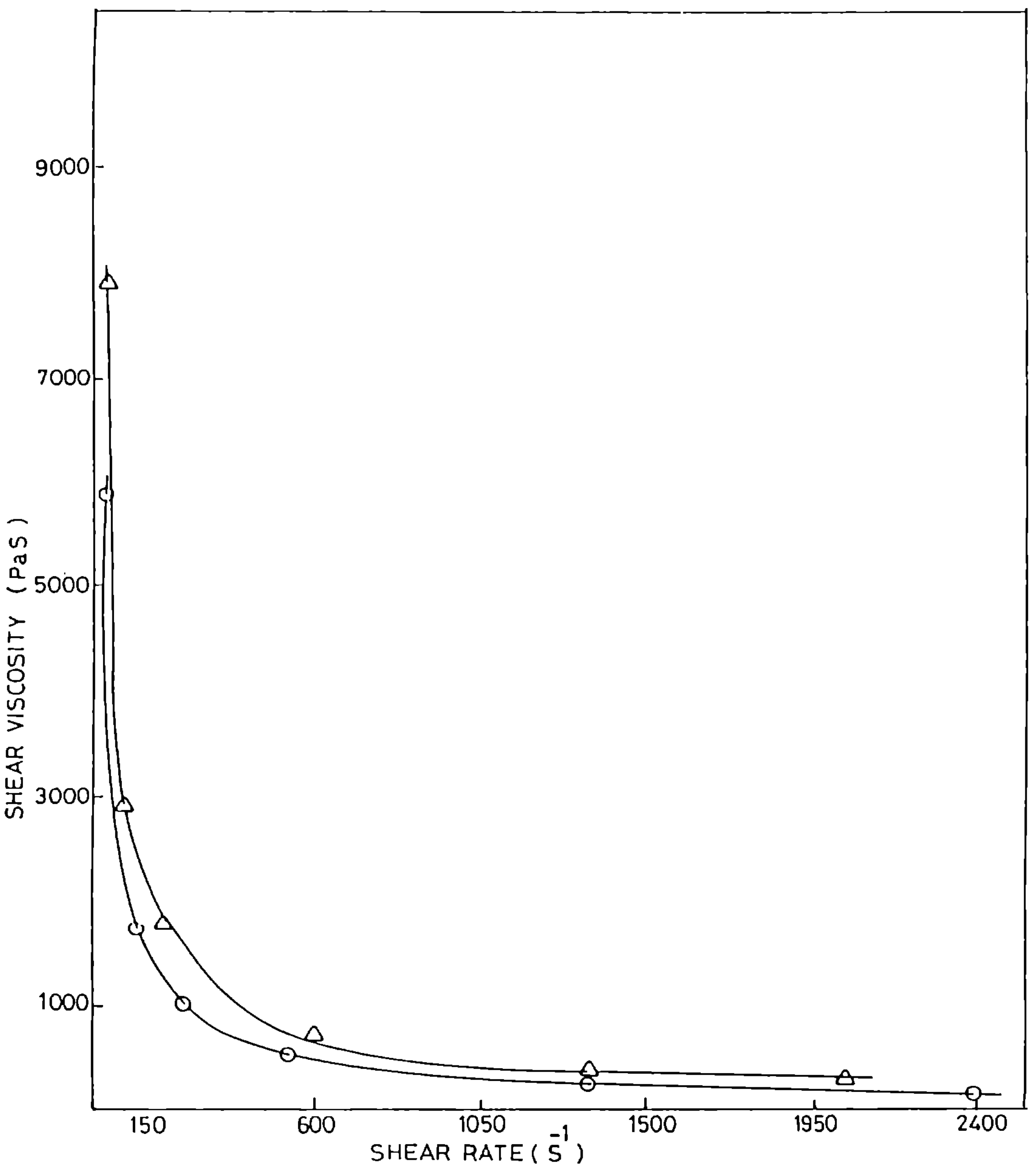


Fig.4.14 Variation of shear viscosity with shear rate of NR/SBR at 150°C
○ 80/20 NR/SBR, △ 20/80 NR/SBR.

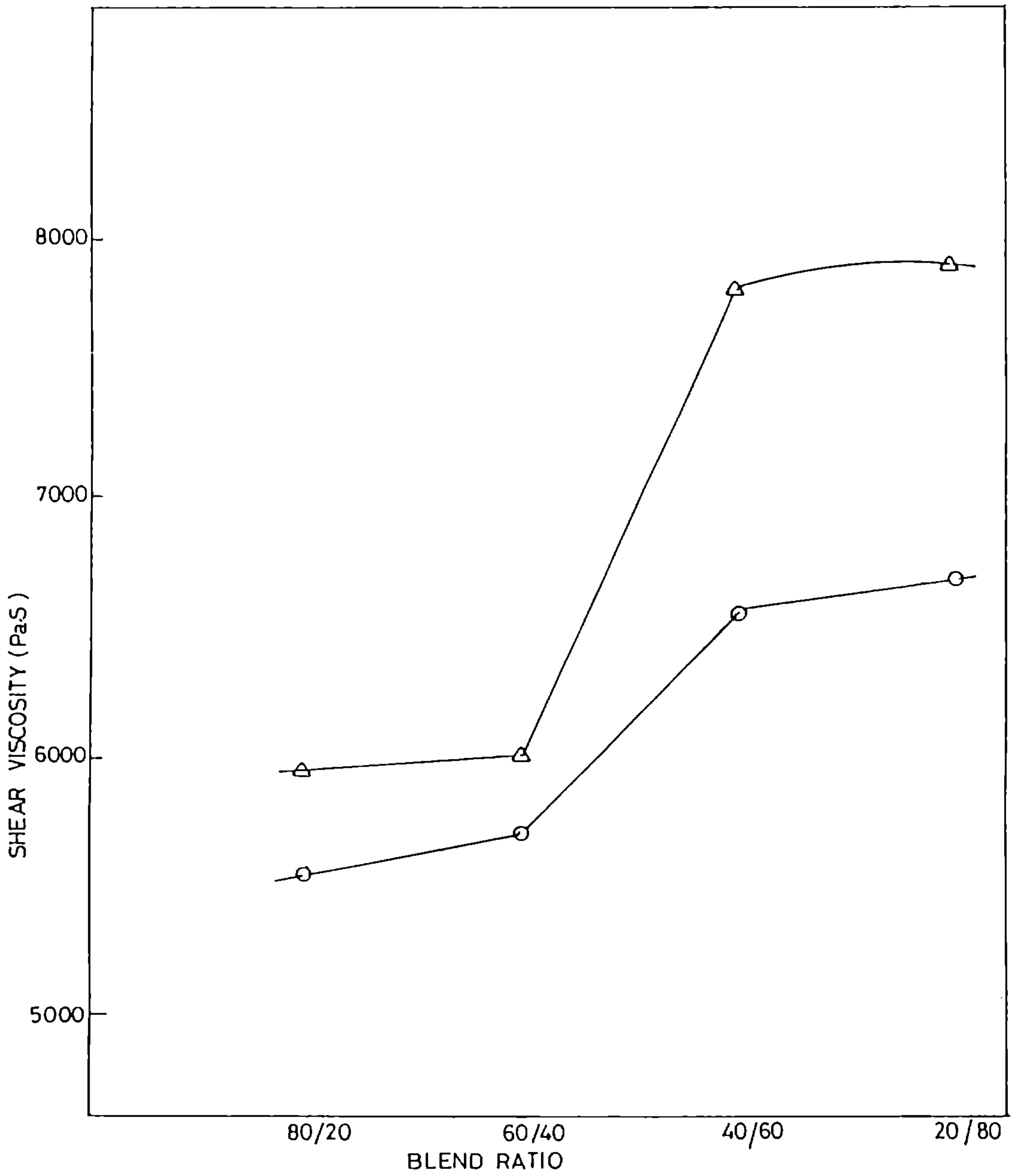


Fig.4.15 Variation of shear viscosity with blend ratio at shear rate 29 S^{-1}
○ N-LCM/SBR, △ NR/SBR.

viscosity increases in both cases. But the increase in viscosity is less for N-LCM/SBR, compared to NR/SBR. Therefore the processability of N-LCM/SBR will be easier than NR/SBR blends.

Die swell of N-LCM/SBR blends and NR/SBR blends at different shear rates are given in Table 4.12. In all cases, the die swell of N-LCM/SBR blends is lower than that of NR/SBR blends. Since die swell of the compounds is related to their elastic nature these results indicate that the processing of the latex stage blends will be comparatively easier.

Figs.4.16 and 4.17 show the photographs of the extrudates of N-LCM/SBR and NR/SBR blends at different shear rates. In all cases, N-LCM/SBR extrudates are having improved surface smoothness compared to NR/SBR extrudates which further confirms the better processability of N-LCM/SBR blends.

CONCLUSION

The pseudoplastic nature of both modified and conventional mixes and N-LCM/SBR and NR/SBR blends are confirmed. This study further shows that latex stage

Table 4.12

Die swell of the extrudates at different shear rates

	Blend ratio	Die swell at shear rates (s^{-1})				
		29	110	230	520	1200
N-LCM/SBR blend	80/20	2.564	2.45	2.49	2.48	2.47
	60/40	2.47	2.40	2.44	2.47	2.51
	40/60	2.47	2.40	2.46	2.53	2.57
	20/80	2.30	2.27	2.25	2.37	2.72
NR/SBR blend	80/20	2.70	2.52	2.56	2.62	2.58
	60/40	2.50	2.426	2.54	2.48	2.64
	40/60	2.64	2.50	2.567	2.689	2.63
	20/80	2.575	2.487	2.404	2.565	2.78

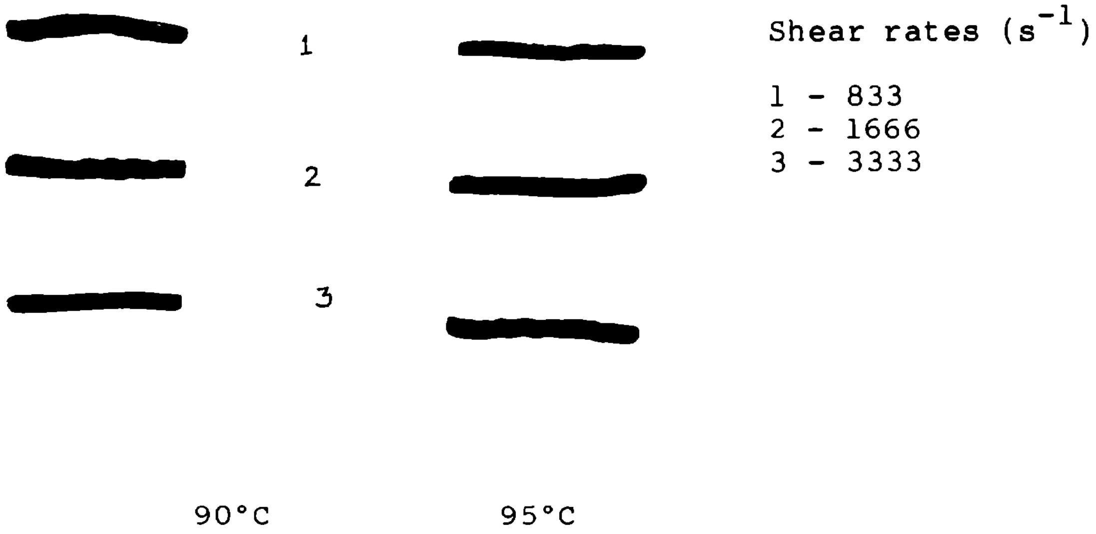


Fig.4.16 Photograph of the extrudates of N-LCM/SBR blend different shear rates

Fig.4.17 Photograph of the extrudates of NR/SBR blend at different shear rates

masterbatching of carbon black will not affect the processability adversely. The processability of N-LCM/SBR blend is found to be better than that of NR/SBR blend.

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CHAPTER 5

PART I: LATEX STAGE BLENDING OF NATURAL RUBBER AND POLY(VINYL CHLORIDE)

Poly(vinyl chloride) (PVC) is the most widely used polymer and the factors responsible for PVC's number one position are low cost and ability to be compounded into various flexible and rigid forms with good physical, chemical and weathering properties. Blends of several elastomers with PVC have been developed to achieve a number of purposes. Modifying elastomers with PVC is one of the promising methods of improving the oil, petrol, ozone and fire resistance of the vulcanizates based on them [1,2]. But modification of an elastomer which is immiscible with PVC usually leads to insufficient fusion characteristics of PVC particles and hence it may not be possible to achieve a marked improvement in the physico-mechanical properties of the vulcanizates. However certain additives are capable of improving the miscibility of these polymers and the fusion characteristics of PVC particles [3-5]. The incorporation of plasticizers in the blend is found to promote miscibility as they are able to make specific interactions with each of the blend components [6,7].

The mechanical properties of an immiscible blend will be strongly dependent upon the blending method used. There are several methods of forming polymer blends such as melt mixing, solution mixing, mixing of latices etc[8].Of these methods, mixing of latices is advantageous in many respects because it does not use any solvent and does not require much energy. The energy saving resulting from mixing the components as latices is usually substantial so that this method of preparation of polymer blends is economically attractive, and hence it is a common industrial method. The objective of the present study is to develop NR/PVC blends by blending of the latices.

EXPERIMENTAL

Centrifuged latex with 60% DRC was used for this study. A 50% dispersion of PVC was prepared using a ball mill, as per the formulation given in Table 5.1.

Latex stage blending and compounding of NR and PVC

The required quantity of centrifuged latex was taken, deammoniated and a base latex compound was prepared as per the formulation given in Table 5.2. All compounding ingredients were added as dispersions. The compounded latex was kept for maturation for 24 hrs. Latex films were prepared by casting the compounds in glass dishes. After

Table 5.1

Formulation of 50% PVC dispersion

Ingredients	Dry weight (gm.)
PVC	100
MgO	4.0
ZnO	4.0
Stearic acid	2.0
Dispersol F	2.0
Water	100

Table 5.2

Formulation of base latex compound

Ingredients	Wet weight (gm.)
60% Latex	167
10% KOH	1.0
10% Potassium oleate	1.0
50% ZDC	3.0
50% ZnO	1.0
50% SP	2.0
50% S	3.5

drying the films at room temperature for 24 hrs, they were vulcanized at 120°C, for 30 minutes.

Deammoniated latex was mixed with 10, 20, 30 and 40 phr each of 50% PVC dispersion, and compounded as per the formulation in Table 5.2. Cast latex films of the compounds were prepared and after drying, vulcanized at 120°C for 30 minutes.

Dumbell shaped tensile pieces were punched out of these cast sheets and tensile properties were measured using a Zwick universal testing machine.

Ageing studies

Test specimens from these sheets were aged at 100°C for 24 hrs. and the retention in tensile properties was determined.

Optical study

The morphology of the latex/PVC compounds was studied. Photographs were taken on Leica wild M_8 Zoom stereo microscope and wild MPs 46/52 photoautomat using NOVA FP_4 films.

RESULTS AND DISCUSSION

Fig.5.1 shows the variation of tensile strength with PVC content, both unaged and aged. Tensile strength is maximum with 10 phr PVC content. After that there is a reduction in tensile strength as the PVC content increases. Properties of the aged samples also show the same trend. From the graph it is clear that PVC modified blends have comparatively better ageing resistance than the NR latex vulcanizate. Table 5.3 shows the variation of elongation at break and modulus both before and after ageing.

As the PVC content increases, there is a slight reduction in elongation at break but the modulus increases with PVC content as expected. Ageing of these samples at 100°C for 24 hrs. further reduces the elongation at break and hence the modulus is marginally increases on ageing.

Figs.5.2 to 5.4 show the photographs of NR latex compound and NR-latex/PVC (with 10 and 20 phr PVC) compound respectively. These photographs show that the particle of PVC get uniformly distributed in natural rubber latex during the latex stage mixing. This homogeneous distribution may be the reason for the higher tensile properties of vulcanizates containing 10 and 20 phr of PVC and their better ageing resistance.

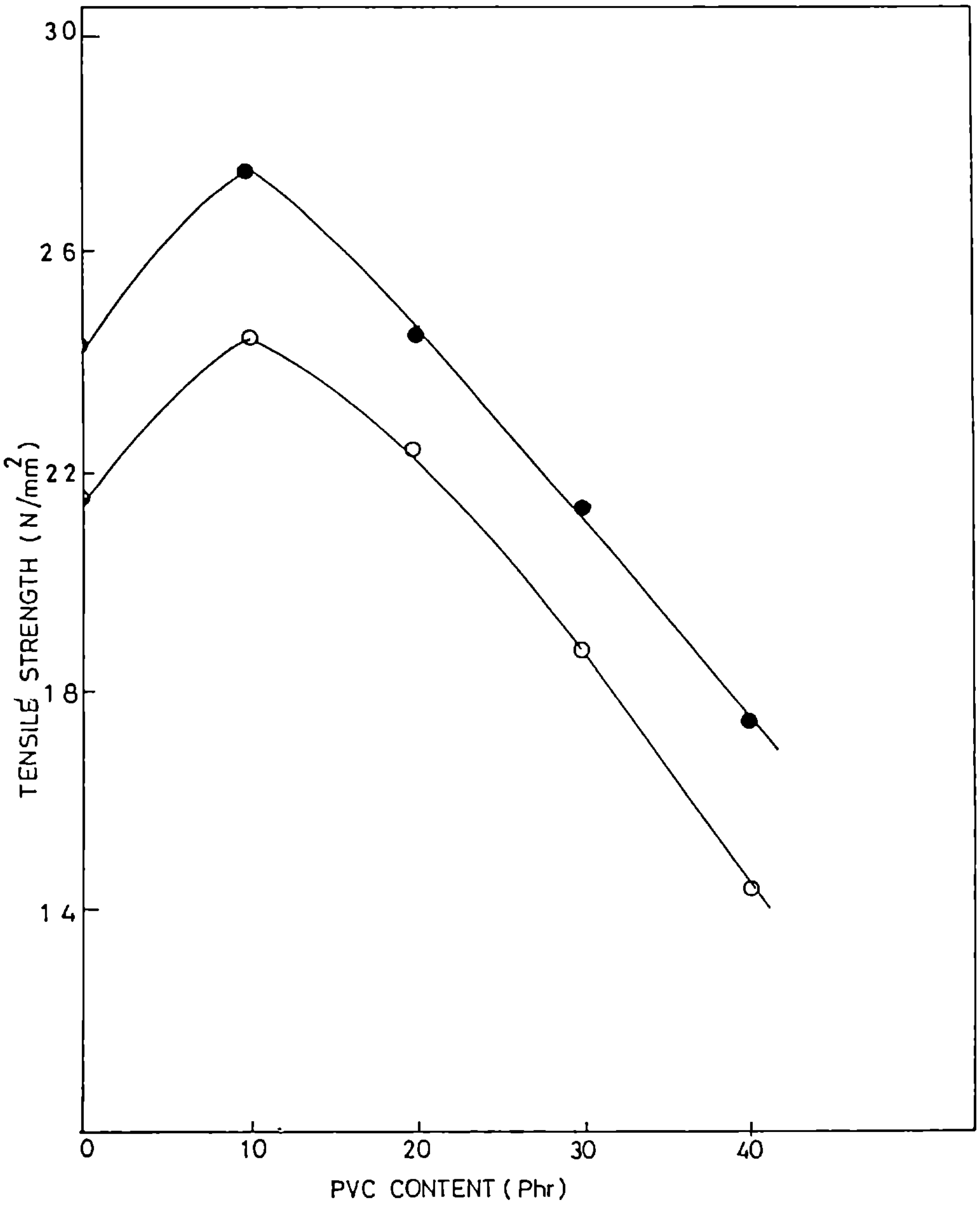


Fig.5.1 Variation of tensile strength with PVC content
● Unaged, ○ Aged at 100°C for 24 hrs.

Table 5.3

Variation of elongation at break and modulus of Latex/PVC sheets

PVC content (phr)	Elongation at break (%)		Modulus (200%) (N/mm²)	
	Unaged	Aged at 100°C 24 hrs	Unaged	Aged at 100°C 24 hrs.
0	1076	910	1.04	1.15
10	968	850	1.27	1.32
20	901	825	1.45	1.53
30	802	785	1.55	1.63
40	750	701	1.70	1.76

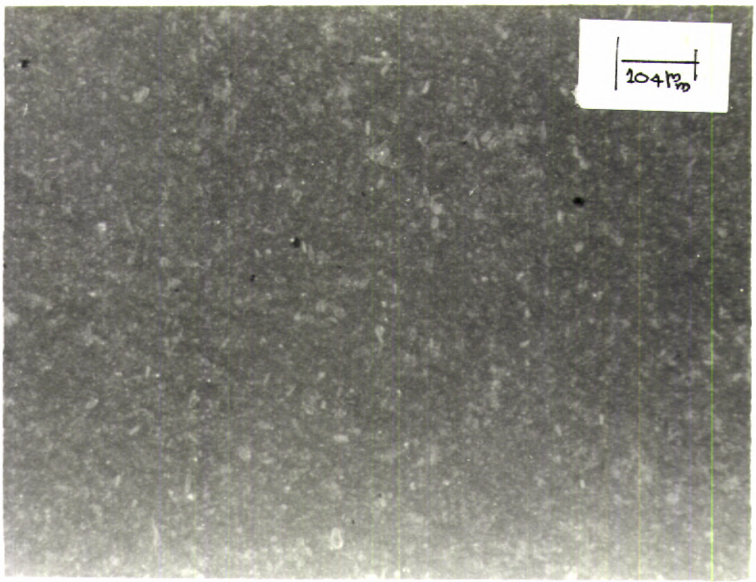


Fig.5.2

Photograph of NR latex compound alone

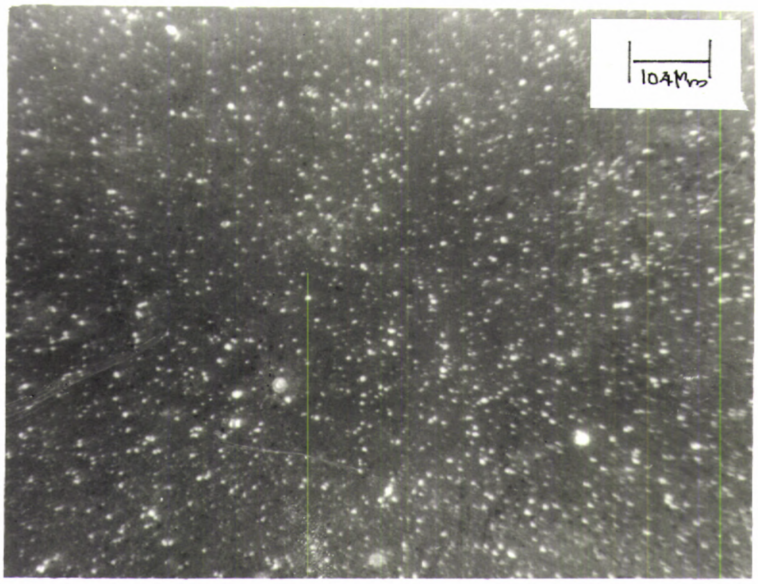


Fig.5.3

Photograph of NR latex/PVC compound (10 phr PVC)

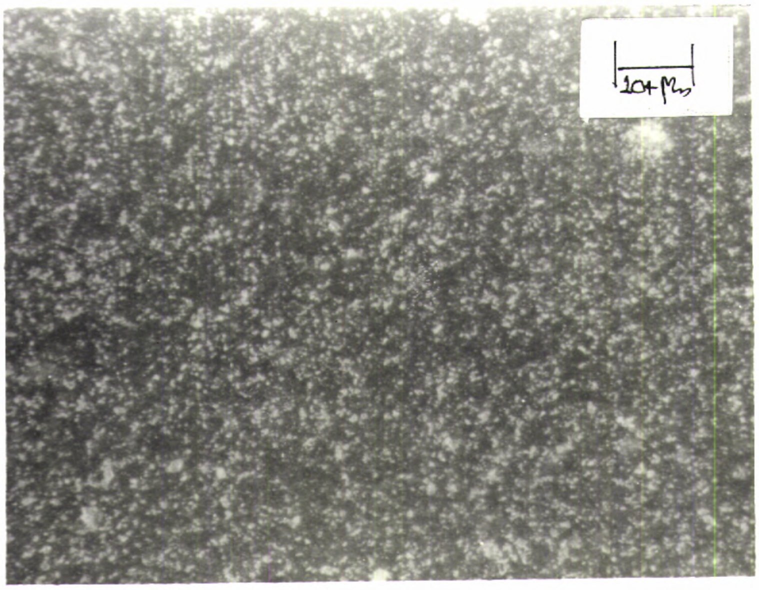


Fig.5.4

Photograph of NR latex/PVC compound (20 phr PVC)

Latex stage masterbatching of NR and PVC

In this study, amine terminated natural rubber (ATNR) was tried as a potential additive in NR/PVC. ATNR was prepared by UV irradiation of NR solution in toluene in presence of ethylene diamine. The details of the preparation are given in Chapter 2.

NR latex and the PVC dispersion were blended properly in the ratio 80/20, 70/30, 60/40 and 50/50 using a high speed mechanical stirrer (4000 rpm) and the blend was coagulated using 2% acetic acid. After drying, the blend was mixed with other compounding ingredients except accelerators and sulphur at 150°C and 40 rpm in a Brabender plasticorder model PL 3S for 5 minutes. Later sulphur and accelerators were added in a cold two roll laboratory mixing mill. Formulation of the compounds are given in Tables 5.4 and 5.5. Dry NR and PVC were mixed in the ratio 80/20, 70/30, 60/40 and 50/50 and compounded in a similar fashion. The optimum cure time for both compounds were determined on a Goettfert elastograph. The compounds were then compression moulded upto their optimum cure time in a laboratory hydraulic press. The tensile properties of the vulcanizates were measured on a Zwick universal testing machine.

Table 5.4

Formulations of NR/PVC compounds with DOP

Ingredients	(Dry wt.) gm				Ingredients	(Dry wt.) gm			
NR latex	80	70	60	50	NR	80	70	60	50
PVC	20	30	40	50	PVC	20	30	40	50
ZnO	4	3.5	3	2.5	ZnO	4.8	4.7	4.6	4.5
MgO	--	--	--	--	MgO	0.8	1.2	1.6	2.0
Stearic acid	1.6	1.4	1.2	1.0	Stearic acid	2	2	2	2
DOP	8	12	16	20	DOP	8	12	16	20
NA 4020	0.8	0.7	0.6	0.5	NA 4020	0.8	0.7	0.6	0.5
CBS	0.8	0.7	0.6	0.5	CBS	0.8	0.7	0.6	0.5
TMTD	0.32	0.28	0.24	0.20	TMTD	0.32	0.28	0.24	0.20
S	2.4	2.1	1.8	1.50	S	2.4	2.1	1.8	1.5

Table 5.5

Formulations of NR/PVC compounds with ATNR

Ingredients (Dry wt.) gm					Ingredients (Dry wt.) gm				
NR latex	80	70	60	50	NR	80	70	60	50
PVC	20	30	40	50	PVC	20	30	40	50
ZnO	4	3.5	3	2.5	ZnO	4.8	4.7	4.6	4.5
MgO	--	--	--	--	MgO	0.8	1.2	1.6	2.0
Stearic acid	1.6	1.4	1.2	1.0	Stearic acid	2	2	2	2
ATNR	10	15	20	25	ATNR	10	15	20	25
NA 4020	0.8	0.7	0.6	0.5	NA 4020	0.8	0.7	0.6	0.5
CBS	0.8	0.7	0.6	0.5	CBS	0.8	0.7	0.6	0.5
TMTD	0.32	0.28	0.24	0.20	TMTD	0.32	0.28	0.24	0.20
S	2.4	2.1	1.8	1.50	S	2.4	2.1	1.8	1.5

Ageing studies.

The ageing resistance of the vulcanizates was assessed by measuring the retention in tensile properties at 70°C for 24 and 48 hrs.

Rheological studies

The rheological behaviour of both these blends was evaluated using a capillary rheometer attached to a Zwick universal testing machine at different crosshead speeds (0.2-20 mm/min) at 150°C. Forces corresponding to specific speeds were measured. The force and crosshead speed were converted to apparent shear stress and shear rate and the shear viscosity was calculated. The extrudates were collected and the extrudate swelling was calculated. Photographs of these extrudates at different shear rates were also taken.

Determination of oil resistance

The oil resistance of the latex blend of NR/PVC and dry blend of NR/PVC vulcanizates was determined by keeping the 50/50 samples in different oils at ambient temperature for one week. The percentage increase in weight of both samples was calculated.

RESULTS AND DISCUSSION

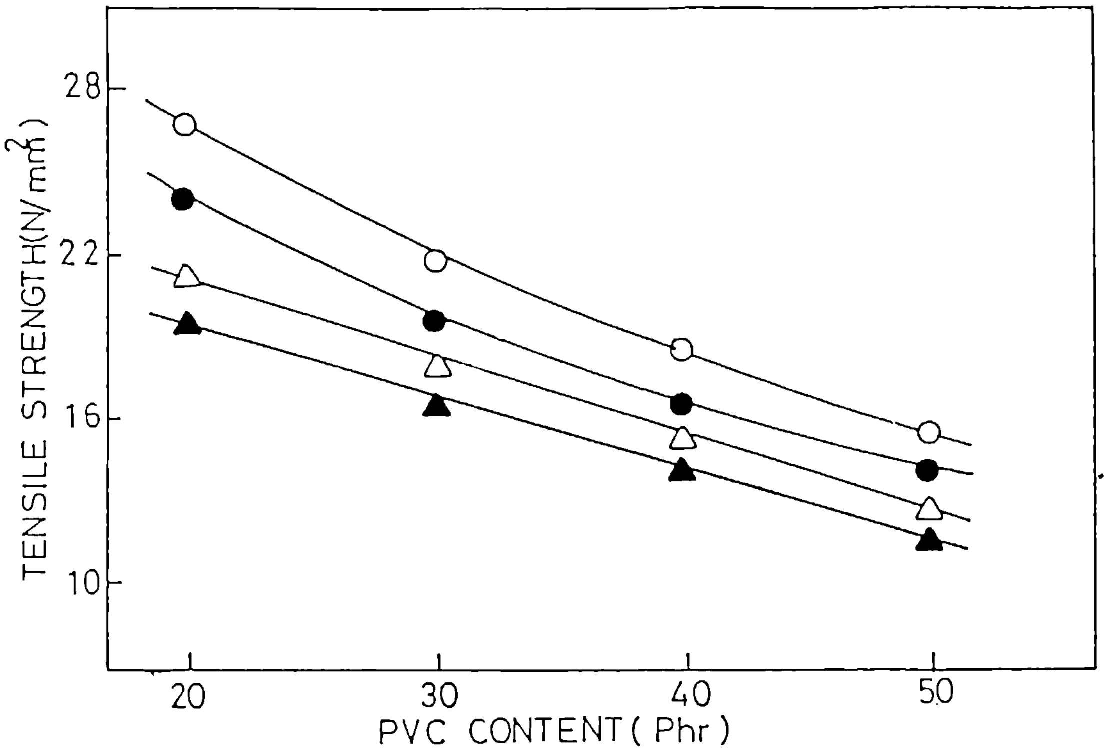
Table 5.6 shows the tensile properties of NR/PVC blends (both latex stage blend and dry blend) containing DOP. The tensile strength and elongation at break are found to be decreasing with increase in PVC content. This may be due to the incompatible nature and inhomogeneous distribution of the two polymers. The variation of tensile strength of NR/PVC blends (containing ATNR) with PVC content (both unaged and aged) is shown in Fig.5.5. It shows that blending the polymers in the latex stage results in much improved tensile strength compared to solid stage blending. This is obviously due to better homogenity and dispersion resulting from the latex stage mixing. The ageing resistance of the blends prepared by latex stage mixing is also higher than that of the conventional blends, which further shows the superiority of the latex stage mixing.

Fig.5.6 shows the variation of elongation at break of the blends with PVC content. As the PVC content increases, there is a gradual reduction in elongation. The blends prepared by latex stage blending show better elongation at break compared to dry stage blending both before and after ageing. This may be due to better particle distribution which is possible in latex stage blending.

Table 5.6

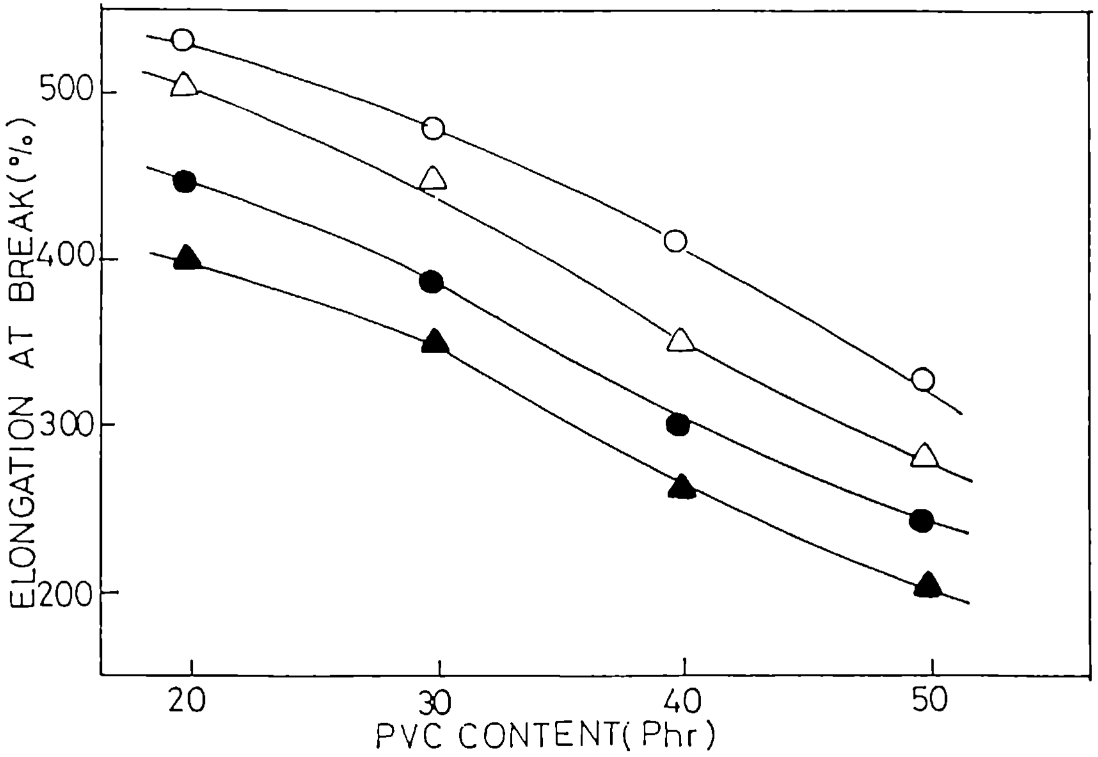
Tensile properties of NR/PVC blends containing DOP

	Blend ratio	Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (100%) (N/mm^2)
Latex/ PVC	80/20	18	485	3.20
	70/30	17	390	3.78
	60/40	13	300	4.20
	50/50	11	189	4.75
NR/PVC	80/20	12	460	2.20
	70/30	10	370	3.10
	60/40	7	215	3.90
	50/50	5	142	4.25



Variation of tensile strength with PVC content. '○' Latex stage blend, '●' aged at 70°C for 48 hrs, '△' Dry blend, '▲' aged at 70°C for 48 hrs.

FIG.5.5



Variation of elongation at break with PVC content
'○' Latex stage blend, '●' Aged at 70°C for 48 hrs,
△ Dry blend, '▲' Aged at 70°C for 48 hrs.

FIG 5.6

Fig.5.7 shows the variation of modulus of the blends with PVC content (Both unaged and aged). Modulus increases as the PVC content increases. Latex stage blends show higher modulus compared to dry blends both before and after ageing. This again proves the better particle distribution during latex stage blending.

The NR/PVC blends containing ATNR are found to show superior tensile strength and elongation at break compared to NR/PVC containing DOP as shown in Table 5.6 and Figs.5.5 and 5.6. This proves that ATNR can act as an effective combatibiliser in NR/PVC blend. Figs.5.8 and 5.9 compare the flow curves of the NR/PVC blends at temperatures 90°C and 150°C respectively. The blends prepared by latex stage mixing show lower viscosity than the corresponding dry blends at the same shear rate. This shows that the processing of latex blends will be comparatively easier than the dry blends. As the shear rate increases, shear viscosity decreases. This confirms the pseudoplastic behaviour of the material. At lower temperature (90°C) PVC does not melt and that may be the reason for the increase in viscosity with PVC content. Fig.5.10 shows the variation of shear viscosity with PVC content at 90°C at two shear rates (33 S^{-1} and 333 S^{-1}).

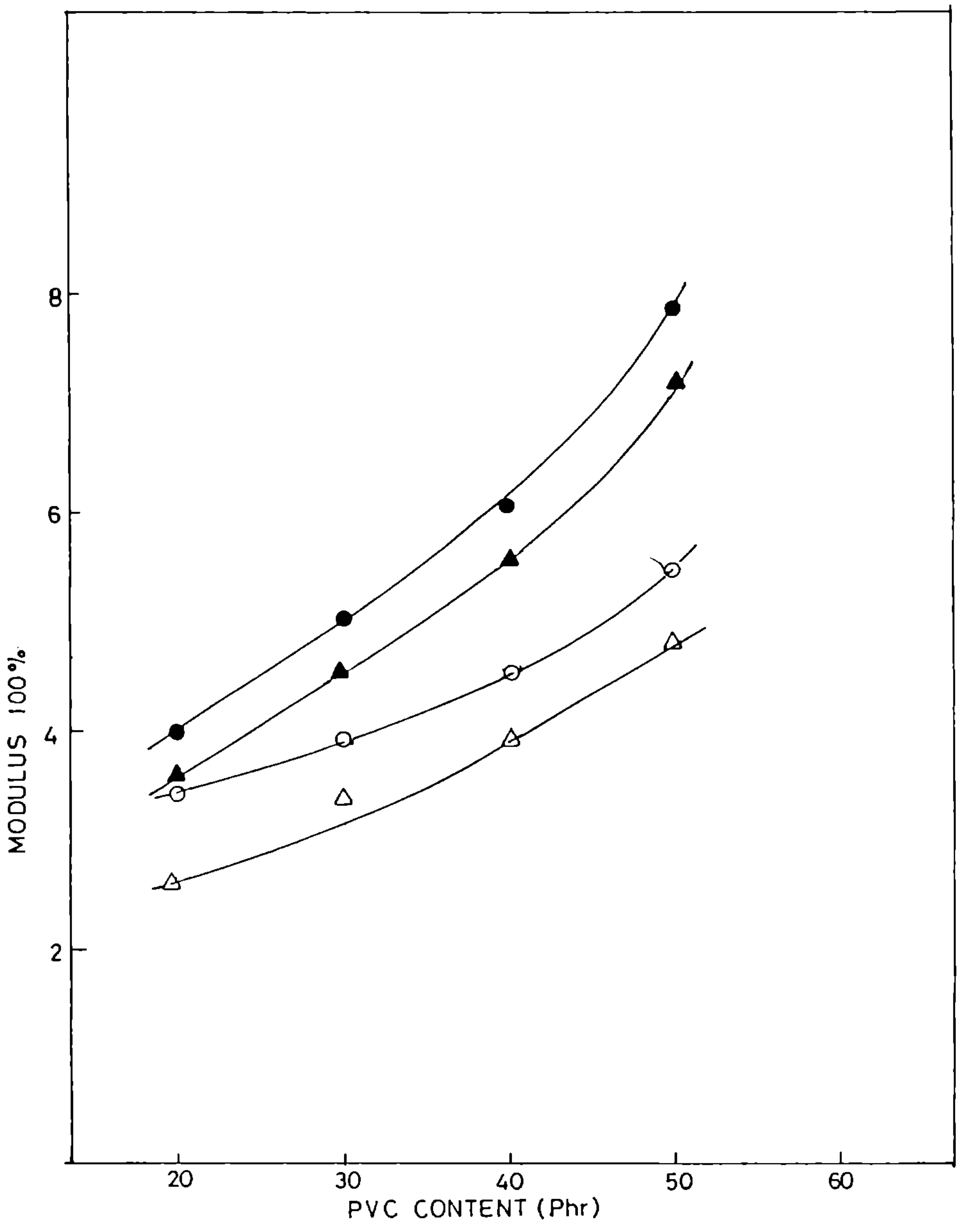


Fig.5.7 Variation of modulus with PVC content. ○ Latex stage blend, ● Aged at 70°C for 48 hrs, △ dry blend, ▲ aged at 70°C for 48 hrs.

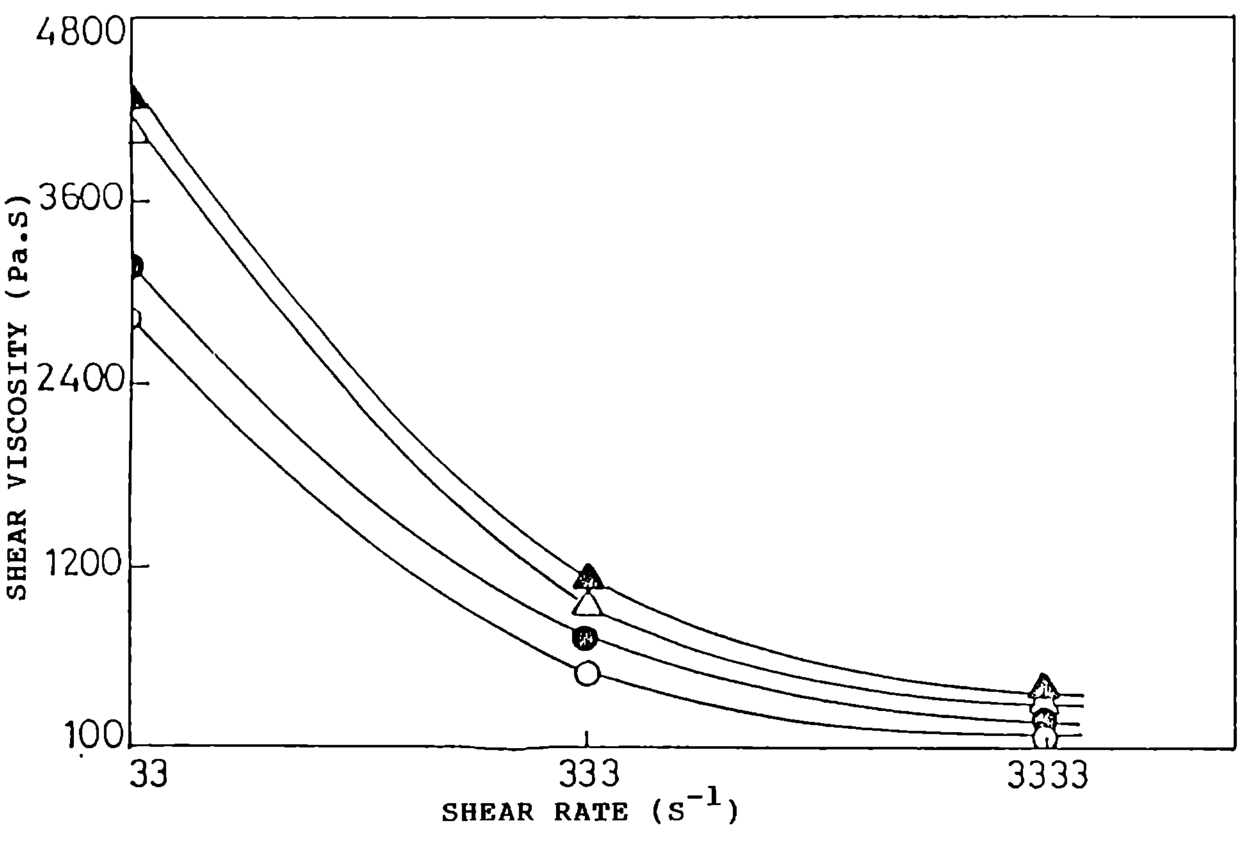


Fig.5.8 Variation of shear viscosity with shear rate at 90°C
'○' Latex stage blend with 30 phr PVC
'● Latex stage blend with 40 phr PVC
'△ Dry blend with 30 phr PVC
'▲ Dry blend with 40 phr PVC.

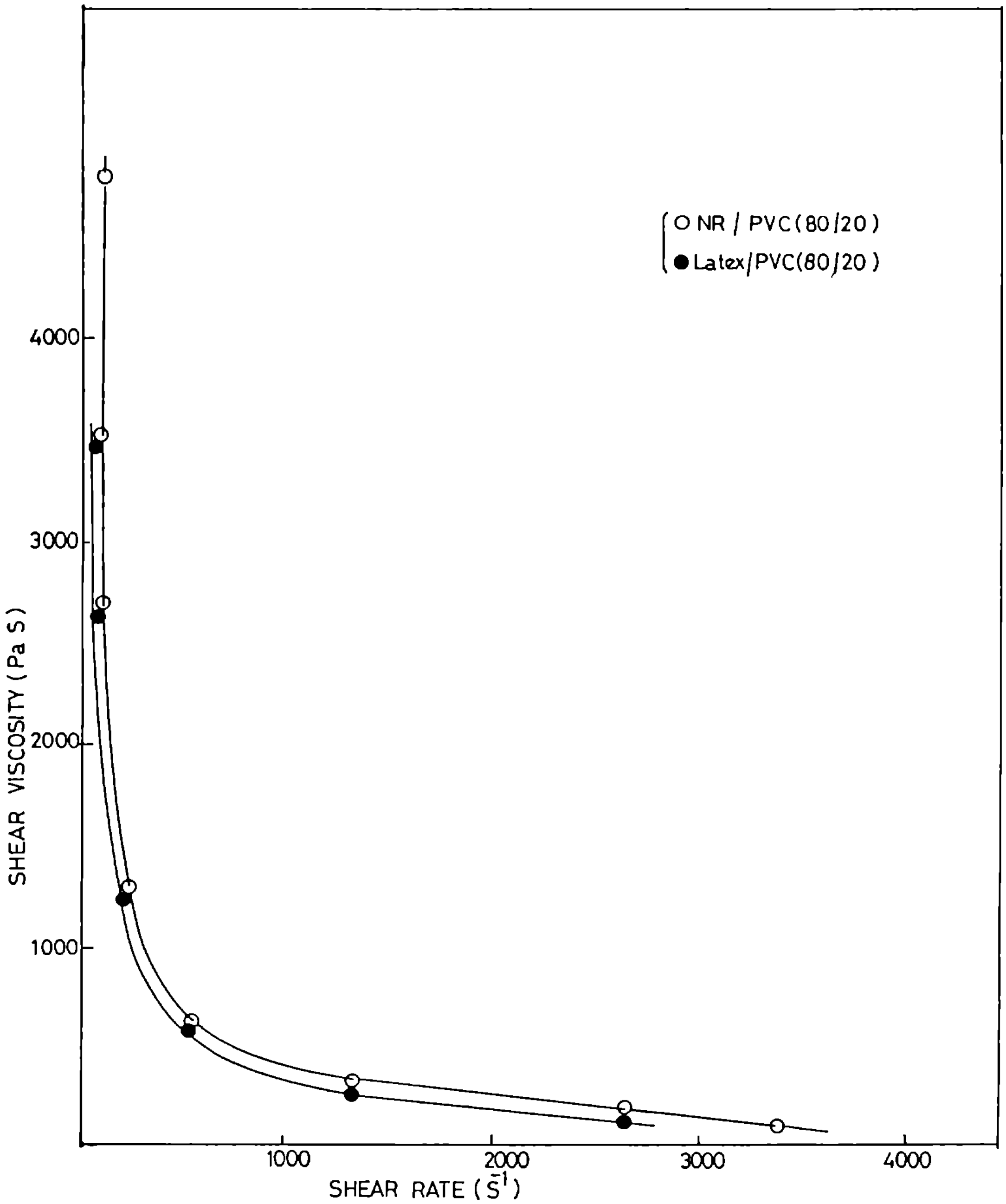


Fig.5.9 Variation of shear viscosity with shear rate at 150°C.
● Latex stage blend with 20 phr PVC, O dry blend with 20 phr PVC.

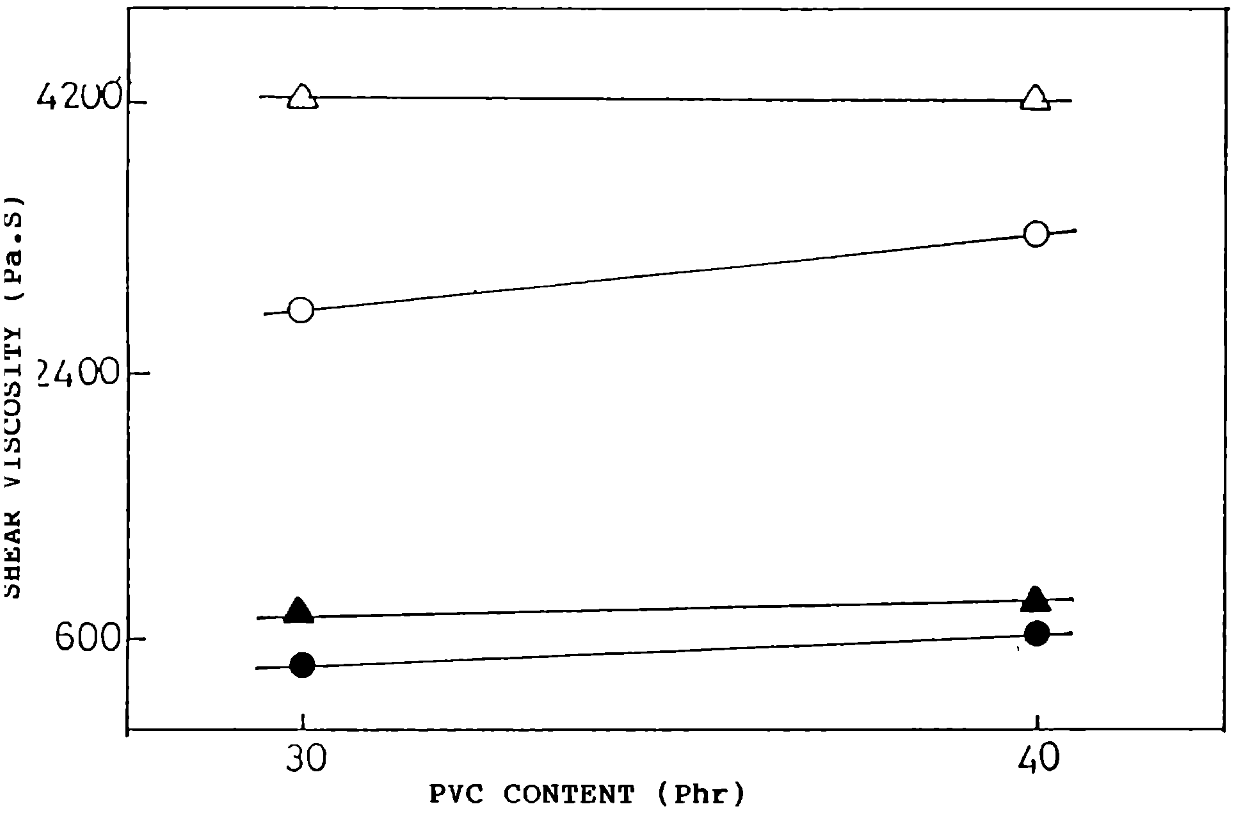


Fig.5.10 Variation of shear viscosity with PVC content at 90°C.
'○' Latex stage blend, and '△' Dry blend at shear rate 33 s^{-1}
'●' Latex stage blend and '▲' Dry blend at shear rate 333 s^{-1}

Fig.5.11 shows the variation of shear viscosity with PVC content at 150°C at a constant shear rate.

According to Fig.5.10 as the PVC content increases, the shear viscosity increases. At lower temperature (90°C) homogenization may not be complete and that may be the reason for the increase in viscosity with PVC content.

Fig.5.11 shows that as the PVC content increases, the shear viscosity decreases. In this case the blending was done at 150°C and hence PVC may be melted, as the result of which viscosity decreases with PVC content. For all blend ratios (80/20, 70/30 and 60/40) latex stage mixed blends show lower viscosity than the corresponding dry blends. This again confirms the superior processability of latex stage blends.

Figs.5.12 to 5.15 show the photographs of the extrudates of 70/30 latex/PVC, 60/40 latex/PVC, 70/30 NR/PVC and 60/40 NR/PVC blends respectively at different temperatures and at different shear rates. In all cases, the latex/PVC extrudates have more improved surface smoothness compared to dry NR/PVC extrudates.

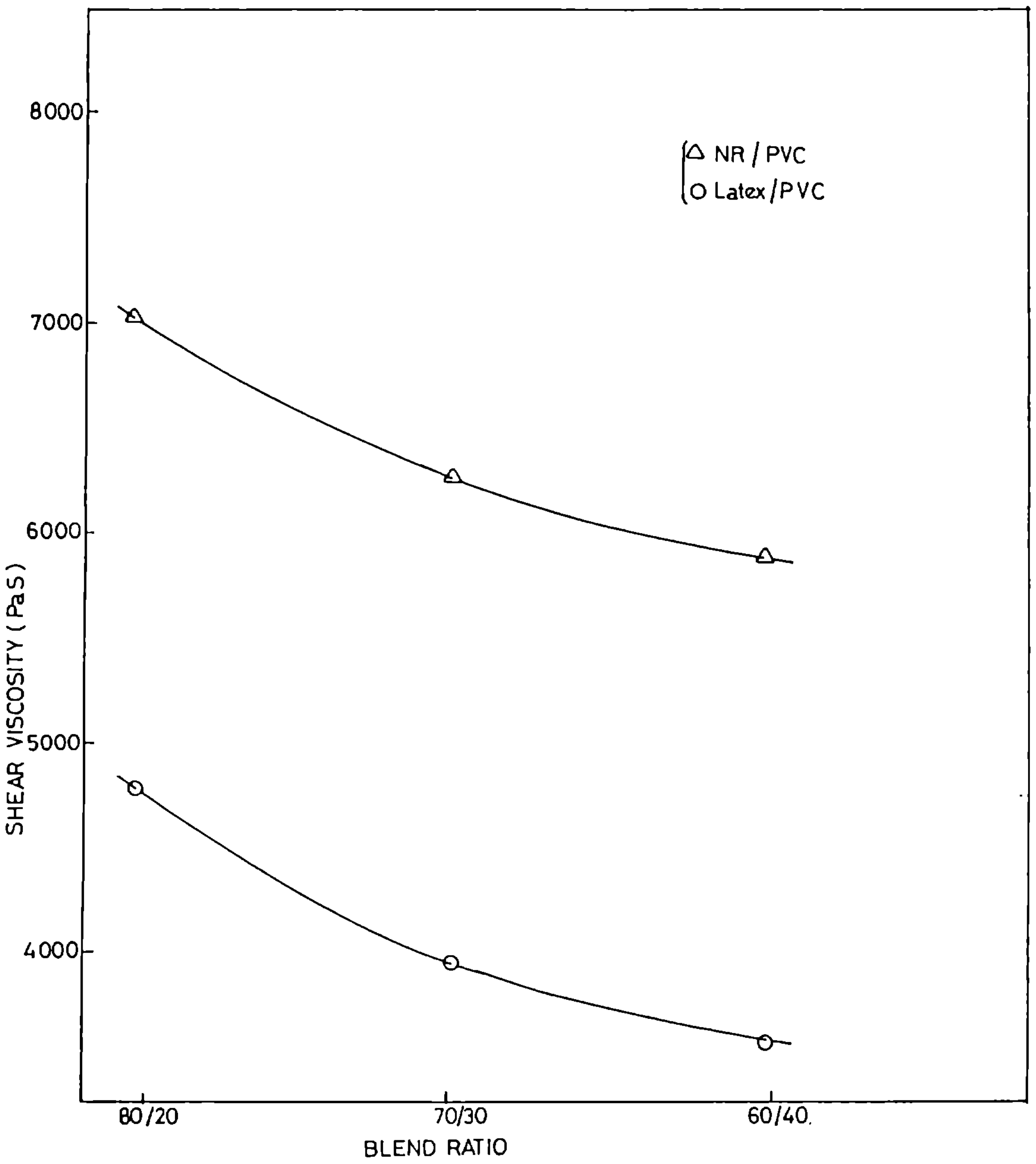
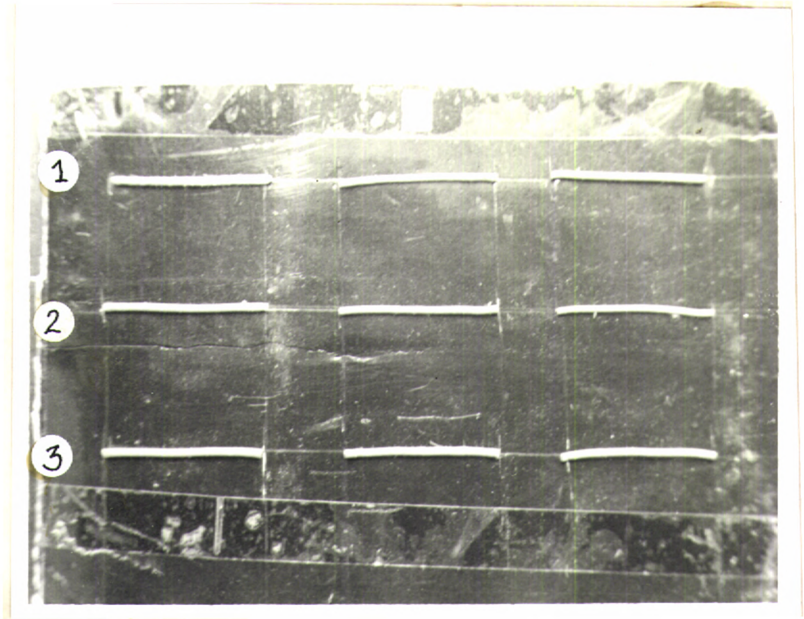


Fig.5.11 Variation of shear viscosity with PVC content at 150°C
○ Latex stage blend, △ dry blend.

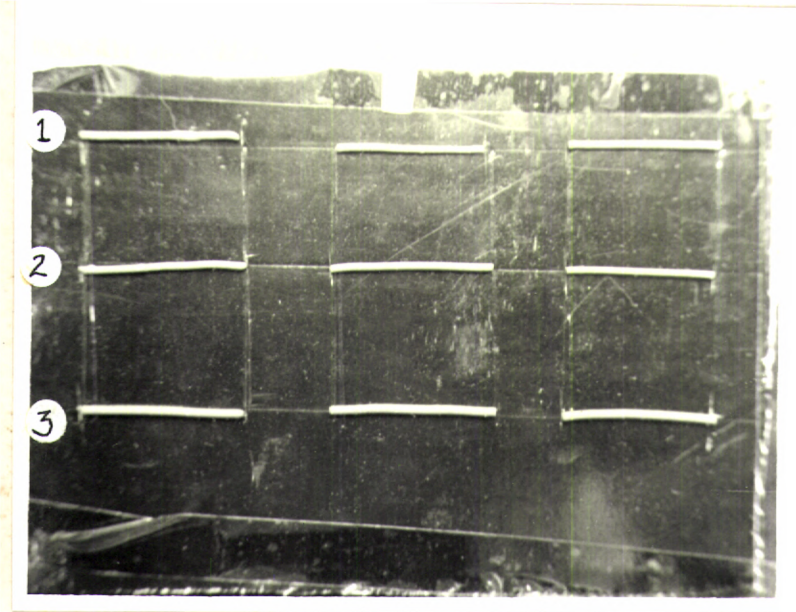


Shear rates (s^{-1})

1 - 33.3
2 - 333
3 - 3333

90°C 100°C 110°C

Fig.5.12 Photograph of the extrudates of NR latex/PVC (70/30) blend

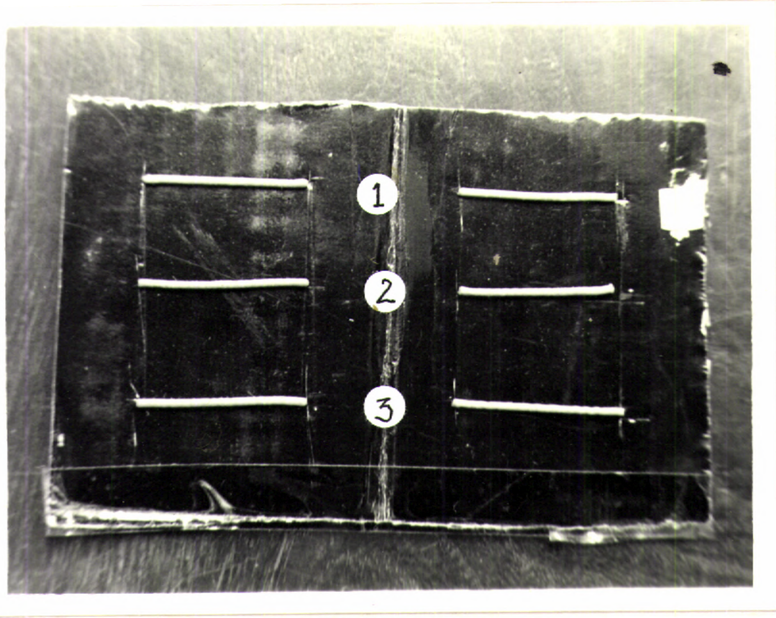


Shear rates (s^{-1})

1 - 33.3
2 - 333
3 - 3333

90°C 100°C 110°C

Fig.5.13 Photograph of the extrudates of NR latex/PVC (60/40) blend.

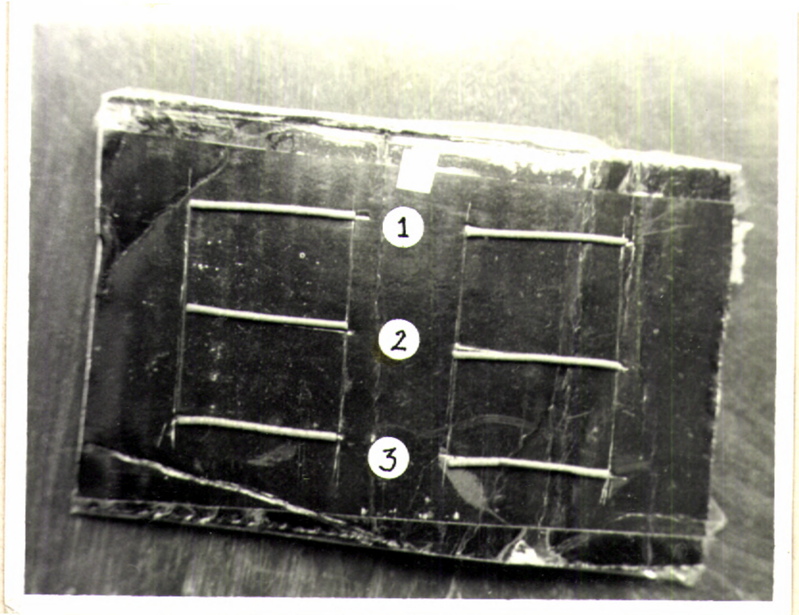


Shear rates (s^{-1})

1 - 33.3
2 - 333
3 - 3333

90°C 100°C

Fig.5.14 Photograph of the extrudates of NR/PVC (70/30) blend



Shear rates (s^{-1})

1 - 33.3
2 - 333
3 - 3333

90°C 100°C

Fig.5.15 Photograph of the extrudates of NR/PVC (60/40) blend

Table 5.7

Die swell of the extrudates at different shear rates at 100°C

	Blend ratio	Die swell at shear rates (s^{-1})		
		33	333	3333
NR latex/PVC	70/30	4.2	4.3	5.0
	60/40	4.1	4.4	4.9
Dry NR/PVC	70/30	4.9	5.0	5.2
	60/40	4.5	4.5	5.1

Table 5.8

Oil resistance of NR/PVC blends (50/50)

Blend	Percentage increase in weight		
	Napthanic oil	Engine oil	Transformer oil
Latex stage blend NR/PVC	51	9.5	43
Dry NR/PVC blend	61	12.5	50.5

Table 5.7 shows the die swell values of both latex/PVC and NR/PVC blends at different shear rates. The die swell of latex/PVC blends are lower than those of NR/PVC blends. All these results indicate that the processing behaviour of the latex stage blends will be superior to that of the solid blends. Table 5.8 shows the oil resistance of both latex/PVC blends and NR/PVC blends. Latex stage blends show higher oil resistance than dry blends. This improved oil resistance may be due to the improved dispersion and interaction of NR and PVC due to the latex stage blending.

CONCLUSION

Blending natural rubber and PVC in the latex stage is a promising method for improving the mechanical properties of the blends. Amine terminated natural rubber is an efficient compatibiliser for the system. The thermal ageing resistance, oil resistance and the processing behaviour of the latex stage blends are also superior to those blends prepared by direct mixing of the solid polymers.

PART II: SURFACE TREATMENTS AND LEACHING STUDIES OF NR LATEX PRODUCTS

In normal NR latex with 30-40% total solid content, the non-rubber content is 3-4% of which 0.95% is proteins [9]. It has been established that the main cause of the allergic reactions in human beings by latex products is due to presence of water extractable proteins in latex [10]. This has resulted in various studies relating to the presence of proteins in latex [11] and these studies are of much relevance today. Standard dermatological tests is the main evidence for the above findings [12,13]. Extractable proteins from latex gloves has been the subject of several studies and numerous research papers have been published based on these studies [14-18]. Recently it is established that leaching of the latex sheets is the simplest method of protein reduction [19-20]. Chlorination may be another method for reducing soluble proteins. It is believed that chlorine may render the proteins insoluble or it may form an impermeable barrier that prevents proteins migrating to the surface. It is in this context that surface treatment and leaching of latex products assume importance.

Surface of NR latex vulcanizates exhibit a self tack and this tackiness causes latex products to stick to each other when handled in bulk [21]. The purpose of surface treatments of latex products is usually the reduction of surface tack of these products [22]. Chemical methods and physical techniques were used for surface modification [23]. Chemical methods include reactions such as halogenation which is one of the most common methods of surface treatments of elastomers. Natural rubber is very reactive towards the halogens. Differential halogenation on the inner and outer surfaces of surgical gloves to balance gripping requirements and ease of release has also been reported. Another important use of surface halogenation of elastomers is the improvement of adhesion of the elastomer to a subsequent coating. The chemistry of aqueous chlorination on NR surfaces has been discussed extensively [24].

Leaching is the process by which hydrophylic materials from latex dipped products is removed by washing them in water [25]. Besides improving the feel of the product, leaching can improve its resistance to water absorption and ageing. Leaching considerably increases the tensile strength of the latex film. The efficiency of leaching may have a significant effect on the product characteristics such as clarity, blooming and discolouration [26]. Leaching of latex film reduces the extractable protein content. But the extent of reduction is dependent on the condition of leaching.

In this study, NR latex vulcanizates are subjected to surface treatments like chlorination, bromination and treatment with polyethylene glycol, glycerol and silicone oil. Leaching of latex vulcanizates is done under alkaline, acidic and neutral medium. The extractable protein content of all sheets are also determined.

EXPERIMENTAL

Preparation of NR latex vulcanizates

Centrifuged latex with 60% DRC was deammoniated and the base latex compound was prepared as per the formulation given in Table 5.2.

The compounded latex was kept for 24 hrs. for maturation and then made into thin sheets of 0.2 mm thickness by pouring into glass plates. After drying these sheets for 24 hrs. at room temperature, these were cured in an air oven at 120°C for 30 minutes. Dumbell shaped tensile pieces were punched out of these casted sheets and tensile properties were measured. Ageing of these sheets at 100°C was done and the retention in tensile properties were determined.

Surface halogenation of latex sheets

Chlorination

The cured latex films were subjected to chlorination by dipping the samples in sodium hypochlorite solution which was acidified with conc. HCl. The quantity of HCl was varied from 0.5 to 2 ml to study its effect on chlorination. The dipping time was also varied from 5 to 20 seconds. As excessive chlorination may cause discolouration of the product, care was taken to give only a mild chlorination by reducing the time of dipping to a few seconds.

Bromination

The cured latex films were immersed in bromine water for 5, 10, 15, 20 and 25 seconds respectively.

All these halogenated sheets were washed first in 2% ammonia water and finally in distilled water. After drying, tensile strength of these sheets was determined and compared with the tensile strength before halogenation.

These halogenated sheets were aged at 100°C for 24 hrs. and the retention in tensile strength was determined.

Physical treatments

The cured latex films were dipped in silicone oil, polyethylene glycol of mol. wt. 600 and glycerol, varying the time of dipping. These sheets were then dried and the tensile properties were determined before and after ageing at 100°C for 24 hrs.

Optical study

Visual examination of the surface treated sheets showed no discolouration even after ageing. In order to study the surface texture of the chlorinated sheets and sheets treated with silicone oil, PEG and glycerol, photographs of these sheets were taken using Leica wild M_8 Zoom Stereo microscope and wild MPs 46/52 photoautomat using Nova FP4 films.

Leaching of latex sheets

Leaching of the cured latex sheets were done (1) under alkaline conditions using ammonia and sodium hydroxide solutions, (2) under neutral condition using water, and (3) under acidic condition using acetic acid and hydrochloric acid.

Leaching with 0.05N NH_3 solution (pH 12)

A dilute solution of ammonia (0.05 N) was taken and the effect of varying temperature of leaching on the retention of tensile strength was measured. The solution was stirred continuously during the leaching process. The samples were dipped in the solution for 4 minutes. The temperature selected were 30°C, 40°C and 50°C. After leaching, the samples were dried and aged for 3 days at 70°C. Tensile strength of the sheets before and after ageing was determined.

Leaching with NaOH solution

Similarly a dilute solution of sodium hydroxide (0.125 N with pH 13.1) was taken and the leaching of the latex sheets was done at temperatures 30, 40 and 50°C. The leaching time was 4 minutes. The ageing resistance of the sheets were determined after ageing at 70°C for 3 days.

Leaching with neutral medium and acidic solutions

The same experiment was repeated with different leaching media as pure water (pH = 7), 0.05 N hydrochloric acid (pH = 1.25) and silute solution of acetic acid (0.08 N with pH = 1.08). In all cases, the leaching time was 4 minutes and the temperature was 30, 40 and 50°C. After ageing at 70°C for 3 days, tensile strength was determined.

Estimation of Extractable Protein content

In order to understand the effect of halogenation, leaching and treatment of sheets with silicone oil, PEG and glycerol, on the reduction of protein content, estimation of extractable protein of these sheets was done, as described in Chapter 2.

RESULTS AND DISCUSSIONS

Table 5.9 shows the effect of time and amount of hydrochloric acid on the chlorine content of latex sheets. Initially, the percentage of chlorine increases both with chlorination time and the amount of hydrochloric acid added. But there is an optimum time (15") after which the amount of acid has no effect on surface chlorination, the chlorine content seems to be constant.

Table 5.10 shows the physical properties of chlorinated sheets. Tensile strength, elongation at break and modulus of the chlorinated and untreated sheets are comparable. This shows that chlorination under the above condition does not affect the properties of latex vulcanizates adversely.

The ageing resistance of the chlorinated sheets is slightly higher than that of the untreated sheets. This is

Table 5.9

Estimation of chlorine

Time of chlorination (sec.)	Volume of HCl added (ml.)	Percentage of chlorine added
5	0.5	0.15
5	1	0.378
5	2	0.852
10	0.5	0.35
10	1	0.78
10	2	1.07
15	0.5	1.06
15	1	1.26
15	2	1.26

Table 5.10

Physical properties of chlorinated sheets

Vol. of HCl added (ml.)	Time of chlori-nation (sec.)	Unaged			Aged at 100°C - 24 hrs.		
		Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (100%) (N/mm^2)	Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (100%) (N/mm^2)
0	0	23	890	0.88	16.5	828	0.92
0.5	5	28.6	888	0.85	21	861	0.93
1	5	26	852	0.94	23	838	0.97
2	5	25.8	877	0.83	22.5	859	0.96
0.5	10	23.5	880	0.83	20	852	0.91
1	10	25	849	0.75	22.4	822	0.84
2	10	24.5	793	0.57	20	731	0.64
0.5	15	25.4	794	0.72	18.6	737	0.84
1	15	27	752	0.84	21.3	710	0.98
2	15	25.5	827	0.84	22.2	811	0.92

in accordance with the earlier observation that chlorination can slow down surface ageing [27].

On ageing, there is a slight reduction in the elongation at break and an increase in the modulus of the latex sheets. This may be due to additional crosslinking during ageing. Table 5.11 shows the physical properties of brominated sheets. Bromination does not reduce the physical properties of the latex sheets before ageing. The ageing resistance of the brominated sheets are slightly improved as in the case of chlorinated sheets. On ageing, elongation at break decreases and modulus slightly increases.

Table 5.12 shows the properties of latex sheets treated with silicone oil, PEG and glycerol. Tensile strength, elongation at break and modulus of the treated and untreated sheets are comparable. The properties after ageing are also comparable. It is observed that the time of dipping has no effect on the properties. The reason may be the absence of any chemical reaction taking place during these treatments. When latex sheet is treated with silicone oil, PEG or glycerol, only physical change may be taking place.

Table 5.11

Properties of brominated sheets

Time of bromination (sec.)	Tensile strength (N/mm²)	Elongation at break (%)	Modulus (100%) (N/mm²)	Aged at 100°C - 24 hrs		
				Tensile strength (N/mm²)	Elongation at break (%)	Modulus (100%) (N/mm²)
5	26.7	835	0.70	20	824	0.74
10	27	831	0.83	18	823	0.85
15	23.5	783	0.88	16.8	716	0.96
20	26.7	795	0.81	18.27	723	0.93

Table 5.12

Properties of sheets dipped in silicone oil, PEG and glycerol

	Time of dipping (sec.)	Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (200%) (N/mm^2)	Aged - 100°C - 24 hrs.		
					Tensile strength (N/mm^2)	Elongation at break (%)	Modulus (200%) (N/mm^2)
SILICONE OIL	5	21	836	1.4	18.24	812	1.46
	10	22.1	823	1.54	17.11	800	1.57
	15	20	835	1.11	18	813	1.15
	20	17.3	840	1.35	16.44	823	1.42
PEG	5	20.5	850	1.27	18.3	817	1.32
	10	22	827	1.42	19.3	803	1.50
	15	22.5	836	1.24	20.4	805	1.33
	20	19.7	843	1.19	17.8	816	1.24
GLYCEROL	5	21.7	843	1.43	19.2	817	1.52
	10	22.3	826	1.29	19.9	801	1.33
	15	21.3	845	1.44	18.7	826	1.47
	20	22.4	839	1.23	19.5	819	1.31

Fig.5.16 Photograph of original NR latex sheet

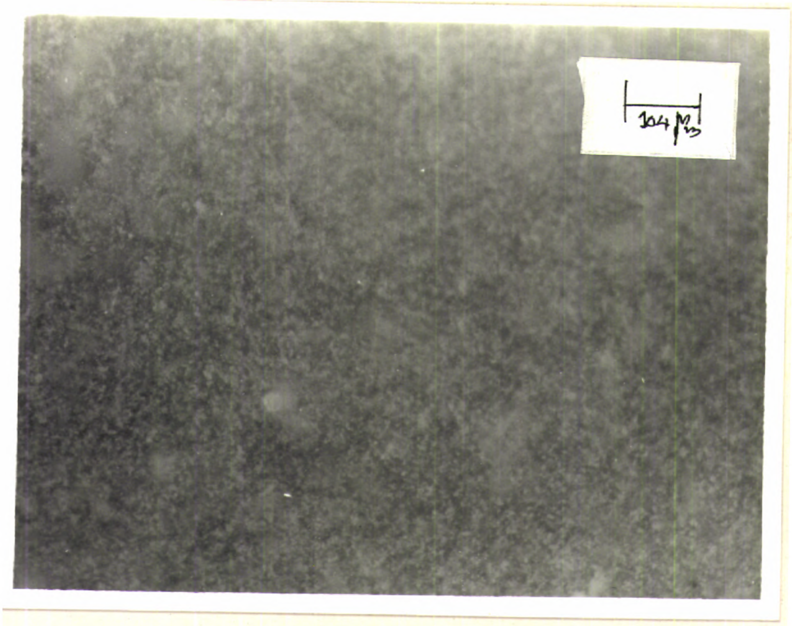


Fig.5.17

Photograph of chlorinated latex sheet (Chlorination time 5 seconds)

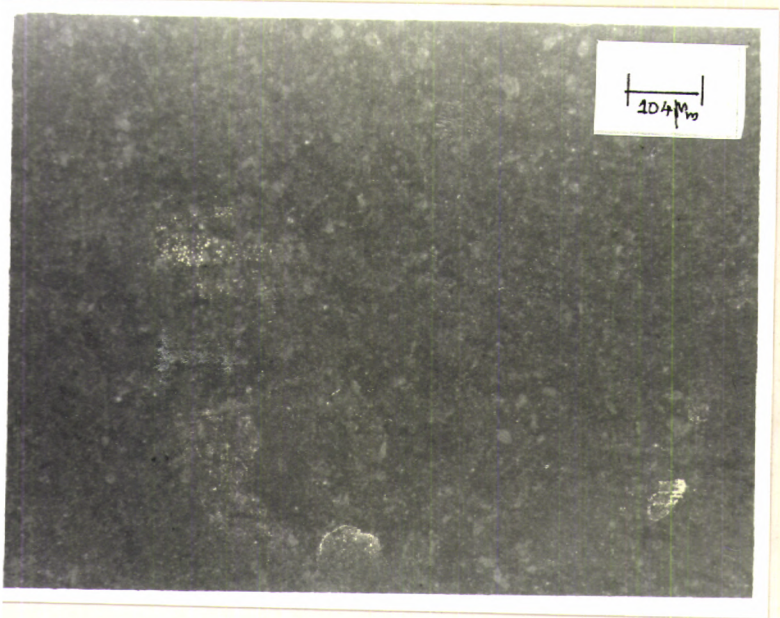


Fig.5.18

Photograph of chlorinated latex sheet (Chlorination time 10 seconds)

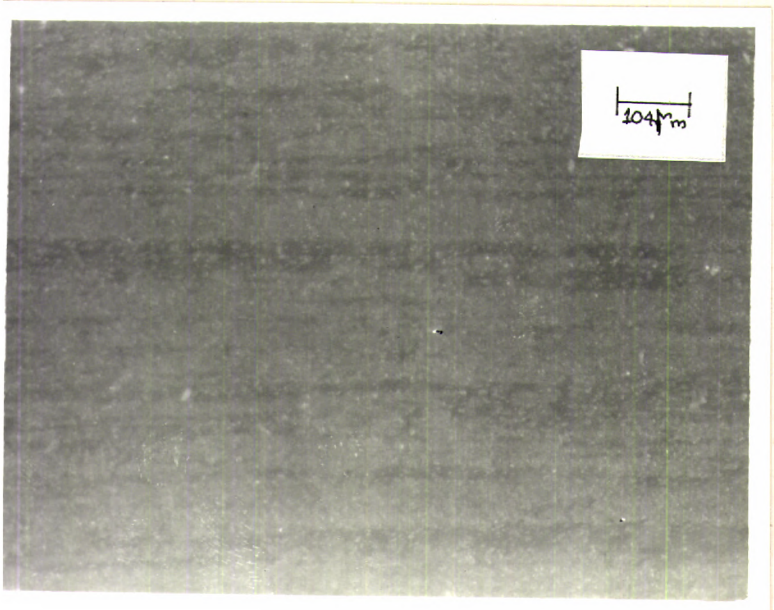


Fig.5.19

Photograph of chlorinated latex sheet (Chlorination time 15 seconds)

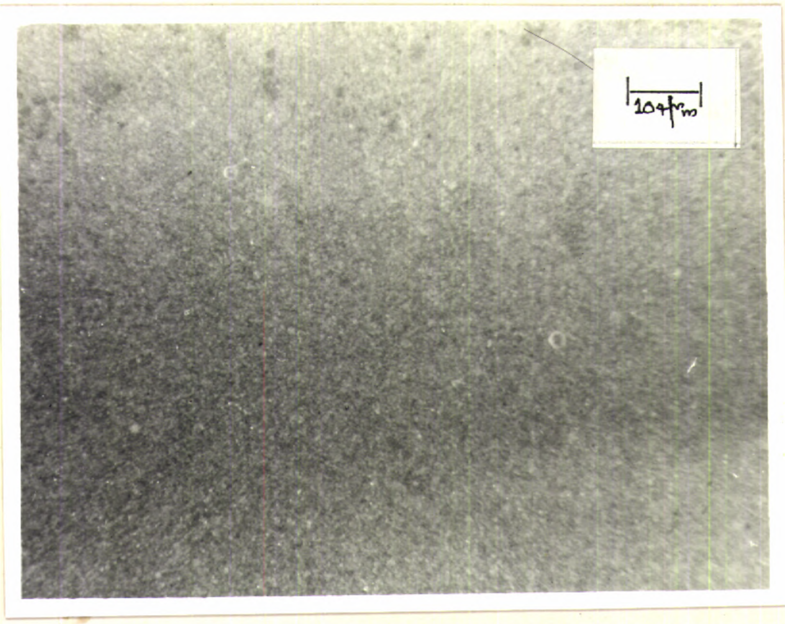


Fig.5.20

Photograph of NR latex sheet treated with silicone oil

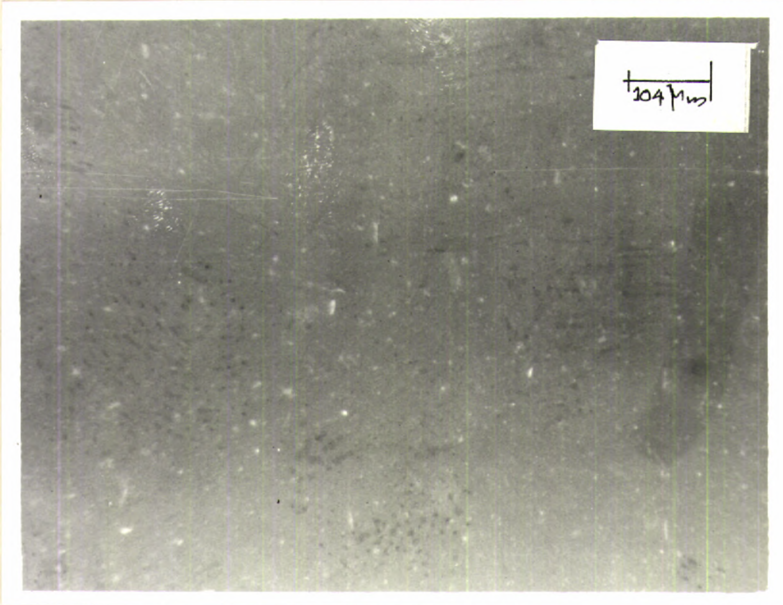


Fig.5.21

Photograph of NR latex sheet treated with PEG

Fig.5.22

Photograph of NR latex sheet treated with glycerol

Figs.5.16 to 5.22 show the photographs of latex sheets - original, chlorinated and sheets treated with silicone oil, PEG and glycerol. The chlorinated sheets (Figs.5.17-5.19) are having smoother surfaces compared to unchlorinated sheets, as halogenation involves the addition of the halogen molecule across the double bonds of the rubber molecules on the surface reducing the tackiness due to the presence of a very thin film of less elastic substance [28]. Figs.5.20 to 5.22 indicate that sheets treated with silicone oil, PEG and glycerol are having smoother surfaces compared to untreated sheets. This may be, as in the case of chlorination, due to the reduction in tackiness due to surface modification. The latex film do not show any discolouration after chlorination. This may be due to the mild chlorination as the chlorination time was strictly restricted to a few seconds.

The effect of leaching at different temperature and at different pH media on tensile properties is given in Table 5.13. For all the three media, as the temperature of leaching increases from 30 to 40°C, there is an increase in the percentage retention of tensile strength. But above 40°C, there is not much increase in the thermal resistance and it shows a tendency of levelling off after 40°C. The reason may be that the materials causing degradation may be extracted at about 40°C. The thermal resistance of all the leached samples under all pH media (neutral, acidic and alkaline) are found to be comparable. This shows that the medium of leaching has not much effect on the properties.

Tables 5.14 to 5.16 show the effect of halogenation, treatment with silicone oil, PEG and glycerol and leaching of latex sheets on the extractable protein content. Halogenation considerably reduces the protein content. For chlorination, the extraction of soluble protein is rapid initially, but the rate of extraction levels off after 15 seconds, at the above rate of chlorination. For bromination, the EP content reduces upto 20 seconds and after that the rate of extraction levels off.

The EP content of latex sheets after treatment with silicone oil, PEG and glycerol, is found to be low compared to the original value. But the time of treatment does not have any effect on reducing the EP content. This shows that on these treatments, only a physical layer may be formed on the rubber surface which prevents the extraction of protein.

Table 5.13

Leaching study - leached, aged at 70°C for 3 days

PH of the medium	Temperature (°C)	Percentage retention of Tensile strength
pH = 1.25 0.05N HCl	30	91
	40	92.3
	50	92
pH = 1.079 0.083 N Acetic acid	30	88.5
	40	93.9
	50	92.1
pH = 7 Water	30	89
	40	91.6
	50	91.2
pH = 12.5 0.07 N Ammonia	30	89
	40	90
	50	90
pH = 13.1 0.125 N NaOH solution	30	88
	40	89
	50	89

Unleached latex sheet - aged at 70°C for 3 days.
Percentage retention = 84.

Table 5.14

Effect of halogenation on EP content

Chlorination		
Time of chlorination (seconds)	Vol. of HCl added (ml)	EP content remaining after treatment (mg/kg)
0	0	950
5	0.5	650
	1	470
	2	390
10	0.5	660
	1	450
	2	385
15	0.5	400
	1	380
	2	370
20	0.5	385
	1	380
	2	381

Bromination

Time of bromination (seconds)	EP content (mg/kg)
5	650
10	570
15	501
20	460
25	459

Table 5.15

Effect of physical treatment of latex sheets on EP content

Dipping agent	Dipping time (seconds)	EP content (mg/kg)
Silicone oil	5	510
	10	511
	15	505
PEG_{600}	5	495
	10	501
	15	498
Glycerol	5	506
	10	503
	15	497

Table 5.16

Effect of leaching on EP content

pH of the medium	Temp. (°C)	EP content (mg/kg)
Acidic	30 40 50	480 430 431
Neutral	30 40 50	485 440 439
Alkaline	30 40 50	487 432 431

It is seen that the EP content can be greatly reduced by leaching under all the three media. The media do not show much effect on the protein extraction. But at 40°C, the extraction is found to be faster compared to 30°C, and above that the rate of extraction levels off.

CONCLUSION

The study shows that mild halogenation can improve the surface smoothness of latex films, without any discolouration. Also, by treatment of latex sheets with silicone oil, PEG and glycerol, surface smoothness can be increased without much change in physical properties. The extractable protein content of the latex sheets can be considerably reduced by halogenation, leaching and by treatment with silicone oil, PEG and glycerol.

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CHAPTER 6

SUMMARY AND CONCLUSIONS

The main objective of the present study was to explore ways of making latex products more cost effective and versatile. Polyethylene glycol was identified as a surface active agent in latex compounds which improves the filler-polymer interaction and also distributes the filler more uniformly. The use of such surface active agents can develop filled latex products with improved mechanical properties at a lower cost.

The most widely used accelerator combination in latex products is ZDC/TMTD. Since vulcanization of latex products is usually done at 100-120°C, even with such ultra-accelerators, the curing time may be as high as 20-30 minutes. A novel faster curing combination viz., TMTD/thiocarbanilide was identified. In addition to giving faster curing this accelerator system also produces transparent vulcanizates with improved ageing resistance. This part of the study is described in Chapter 3.

Latex stage mixing of fillers such as carbon black and silica is being attempted so as to overcome the drawbacks of adding them to dry rubber. Addition of these filler dispersions destabilise the latex restricting the use of fillers in any appreciable level. In this study dispersions of carbon black and silica were successfully added to NR latex under high speed stirring without destabilizing latex. This has been made possible by incorporating surface active agents like PEG into the latex. After coagulation, the latex stage mixed vulcanizates displayed improved mechanical properties and ageing resistance compared to their dry rubber counterparts. The rheological evaluation of the latex stage mixed compounds revealed similar processing behaviour to those of the dry rubber compounds. The suitability of these latex stage carbon black masterbatches to form blends with other elastomers like SBR was also found to be superior to that of the dry rubber masterbatches. These studies are described in Chapter 4.

Since polymer blends are widely used these days, the next part of the study was to develop blends of natural rubber and polyvinyl chloride in the latex stage. Since the majority of polymer blends are basically incompatible, the method of blending is a critical factor in deciding the properties of the blend. Latex stage mixed blends displayed superior mechanical properties than the blends prepared from blending solid polymers.

A common problem with the booming latex products like examination gloves is the objectionable protein level. The next part of the study was to investigate methods of reducing the extractable protein content. Leaching under different conditions, chlorination, bromination and siliconisation reduced protein content appreciably and improved the ageing resistance of the latex products. These studies are reported in Chapter 5.

LIST OF PUBLICATIONS FROM THE WORK

1. Study of the effect of polyethylene glycol in filled natural rubber latex vulcanizates
   L.Jose and R.Joseph
   Kautschuk Gummi Kunststoffe (Germany), 46(3), 220 (1993).

2. Study of the effect of polyethylene glycols and glycerol in filled natural latex vulcanizates
   L.Jose and R.Joseph
   International Journal of Polymeric Materials (USA), 27(3-4), 189 (1995).

3. Effect of latex stage mixing on the technical properties of NR-PVC blends
   L.Jose, R.Joseph and D.Joseph Francis
   Paper presented in the International Symposium on Macromolecules, January 11-13, 1995 at VSSC, Trivandrum (Proceedings, pp.766-771), Allied Publishers Ltd.

4. Latex stage carbon black masterbatching for improved dispersion and improved mechanical properties
   L.Jose, R.Joseph and K.E.George
   Paper presented in the Seventh Kerala Science Congress held at Palakkad, January 27-29, 1995 (Won Young Scientist Award). Proceedings of Seventh Kerala Science Congress, 1995, pp.238-243.