STUDIES ON LATEX RECLAIM AND ITS BLENDS

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CERTIFICATE

This is to certify that this thesis entitled "Studies on Latex Reclaim and its Blends" is a report of the original work carried out by Ms.Mary Joseph under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other Institution.

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DECLARATION

I hereby declare that the thesis entitled "Studies on Latex Reclaim and its Blends" is the original work carried out by me under the supervision of Dr.K.E.George, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 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

POLYMERS

NR	Natural rubber
BR	Poly butadiene rubber
LR(G)	Latex reclaim prepared from gloves
LR(F)	Latex reclaim prepared from foam waste
LR(T)	Latex reclaim prepared from thread waste

ADDITIVES

ZnO	Zinc oxide
MBT	Mercapto benz thiazole
TMTD	Tetramethyl thiuram disulphide
MOR	Benzthiazyl-2-sulphen morpholide
HAF	High abrasion furnace black
S	Sulphur
ZDC	Zinc diethyl dithio carbamates
Vulkanox 4020	N(1,3-dimethyl butyl-N'-phenyl-p-phenylene diamine)
Vulkanox HS	(1,2,dihydro-2,2,4-trimethylquinoline) polymerised

OTHER ABBREVIATIONS

IS	Indian standards
BS	British standards

ASTM	American society for testing and materials
ISNR	Indian standard natural rubber
rpm	Revolutions per minute
phr	Parts per hundred rubber
Po	Initial plasticity
Tg	Glass transition temperature
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.
ΔG	Free energy change of mixing
ΔS	Entropy change of mixing
ΔE	Internal energy change of mixing
SEM	Scanning electron microscope
Nm	Newton meter
VGC	Viscosity gravity constant
Vr	Volume fraction of rubber in the 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
Vs	Molar volume on solvent
ρ_r	Density of rubber
ρ_s	Density of solvent
cc	Cubic centimeter

gm	Gram
h	Hours
mg	Milligram
min	Minute
MPa	Mega pascal
s	second
UTM	Universal testing machine
t_{90}	Optimum cure time
t_{10}	Scorch time
Z	Weight fraction of filler
EV	Efficient vulcanization
IR	Infrared spectroscopy
TGA	Thermogravimetric analysis
CNSL	Cashewnut shell liquid
WTR	Whole tyre reclaim
RHC	Rubber hydrocarbon content

Chapter 1

INTRODUCTION

Rubber industry, due to its spectacular growth, faces a major challenge in this decade to deal with the enormous quantity of waste rubber products. On an average the production of industrial and other elastomer products creates about ten percent of production waste. With an annual increase of 3% in production every year, the disposal of scrap rubber becomes a serious problem year by year.

An easy solution to the problem of disposing scrap rubber is incineration or its use in land fills.[1] But the dumping of waste rubber is prohibited in most countries as it may cause environmental hazards. Burning of scrap rubber as a fuel for thermal power stations and cement plants has been recommended.[2] However, incineration of scrap rubber is not desirable, as it is rich in hydrocarbons and should be ideally returned to the production cycle as useful materials in order to protect the environment and to conserve materials. Hence efforts are being made to recycle scrap rubber. Though various methods of recycling of waste rubber are mentioned in literature, only a few of them are being currently exploited.

Pyrolysis of waste rubber products has been proposed as a means of converting scrap rubber to useful products[3-6]. Off gases and oil formed by pyrolysis are used as fuels and the solid residue which represents the recovered carbon black from the scrap rubber is used as absorbant and filler for the fabrication of various rubber products. However, the pyrolytic black appears to be a poor reinforcing filler and it is more expensive to prepare and burn scrap rubber for fuel than to burn natural gas or coal. Hence pyrolysis of scrap rubber is generally not economically viable.

Another method of recycling scrap is to grind it to fine powder[7-12] either by cryogenic freezing or solvent swelling techniques or by mechanical grinding and work into new rubber as an elastomeric filler. These processes only comminute the vulcanizates and do not devulcanize them. A significant amount of research was being done on the use of finely ground scrap rubber in new rubber compounds.[13-20] The effect of reusing scrap rubber in virgin rubber compounds was evaluated and found that even at low concentrations it adversely affects the physical properties. Burgoyne and co-workers[13] report that mechanically ground scrap rubber having a broad spectrum of particle size acts as a cheap filler having approximately the same effect on properties as soft kaoline clay. According to Bleyie[20] as the particle size decreases, mixing behaviour and mechanical properties of vulcanizates are improved. Acetta and Vergnaud[21,22] have developed a process to upgrade the value of scrap rubber powder without adding virgin rubber and reported that the rubber powder can be converted to plastic or elastomeric material according to the percentage of vulcanizing agent.

For improving the properties and structure of ground rubber – virgin rubber blends attempts have been made to modify the surface of rubber powder by means of chemical methods thereby imparting a wetting effect to the rubber powder or giving it a reactivity towards polymer matrix. Dierkes[23] reports a surface activated crumb 'surcum' as a compounding ingredient with many advantages.

Use of scrap rubber to modify asphalt is another economic solution to the waste disposal problem in the rubber industry.[24-29] Rubber-asphalt membranes are more resilient than surfaces without asphalt rubber. Addition of rubber to asphalt typically increases its softening point and lowers its brittle point. However, its performance largely depends upon the morphology of rubber crumb and its chemical composition.

Although methods described above are promising ones for recycling large amounts of scrap and waste rubber by using them as fuel or compounding ingredient or as asphalt modifier it can hardly be considered satisfactory from the point of view of direct recycling of materials. Therefore recycling of scrap rubber has been practised by the rubber industry for many years using different methods.

In the reclamation process vulcanized rubber is converted into a plasticized vulcanizable material capable of being mixed with natural as well as synthetic rubbers. It is produced by treating scrap vulcanized rubber with devulcanizing agents and plasticizers under pressure and heat and simultaneously or subsequently working the material mechanically. The technical background and various aspects of different reclamation processes are reviewed by Le Beau[30] and more recently Warner[31] also presented another excellent review of the existing literature that is relevant to various methods of devulcanization.

The methods used for the production of reclaimed rubber include oil pan process, the digester process, the reclamater method, the high pressure steam method, Lancastor–Banbury method, Engilnke method etc. All these methods are based on depolymerization by heat treatment and devulcanizing agents for a long period of time at a high temperature.

The net reaction that occurs during any reclaiming process is the result of several competing reactions which include chain scission, depolymerization, chain termination etc. which tend to soften the rubber in contrast to polymerization and crosslinking which tend to harden the rubber.[32] By the alteration of physical and chemical conditions the rates of reactions are altered to favour the first set of reactions and thus produce a devulcanized rubber. To favour the reactions that tend to soften and replasticize rubber, strain is imparted on the rubber either by swelling the particles with solvents or by heating and mechanical working.

Certain definite chemical groups, active in the reclaiming reaction have been recognized. Only some of these will promote the breakdown of the polymer molecules, other will prevent subsequent heat hardening. They do not remove the sulphur from the vulcanizates. They may catalyse the oxidative break down of the polymer chain while at the same time disrupting the sulphur crosslinks thus restoring the polymer to a more or less two dimensional state. Chemicals which have been recognized as active reclaiming agents can be classified into several distinct groups. They include (a) alkyl benzene thiols[32,34]; (b) disulphides[35,36]; (c) mercaptans[36-38] and (d) amino compounds.[39] Ample literature is available about different reclaiming methods and the reclaiming action of different reclaiming agents.[40-51]

Okamoto and co-workers[40] have explained the reclaiming action of thiol compounds such as 2-mercaptobenzothiazole and a salt of this compound with cyclohexylamine and NN'diphenyl p–phenylene diamine and amine compounds. When sulphur crosslinked rubber having a three dimensional network structure is broken on a mill, scission occurs in the molecular chain and sulphur crosslinks resulting in the formation of free radicals. When thiol compounds are used, they act as acceptors for these radicals and are thought to be contributing to plasticization by preventing rebonding.

B.C.Sekhar and co–workers[41] developed a reclaiming mixture marketed under the trade name Delink-R consisting of zinc salt of dimethyl dithiocarbamate and mercapto benzothiazole dispersed in diols with stearic acid, zinc oxide and sulphur. They claim that this mixture when blended with vulcanized crumbs in concentrations of about 6 parts of the reclaiming agent per 100 parts of tire crumb on a mill it effectively delinks the vulcanized network and renders the compound ready for moulding and revulcanization. In the "Delink process" when the proprietary chemicals "Delink-R" are added to the ground vulcanized rubber, the latter gets devulcanized, as the compound is masticated at relatively low temperature (≈ 70 °C). The devulcanized rubber (devulc) alone or in combination with virgin rubber compound is molded and heated to high temperature to complete the vulcanization process. It has been demonstrated that when a natural rubber vulcanizate when treated with "Delink–R", the tensile strength and elongation at break of the 'devulc' compound vulcanizate decrease resulting in an increase in modulus[42].

Yamashita and co–workers[44,45] have successfully reclaimed powdered rubber using iron oxide phenyl hydrazine based catalyst. Nicholas[46] used phase transfer catalysis as means of transporting hydroxide ion from water into swollen rubber particles to cleave polysulphidic crosslinks with little or no main chain scission, so that the scrap rubber is converted into a material nearly resembling the structure of virgin rubber.

Recently a new technique using microwave radiation for devulcanization was developed.[48,51] This is based on the fact that a controlled dose of microwave radiation at a specified frequency level and amount is sufficient to severe all C–S & S–S bonds but insufficient to severe C-C bond. However, this method is applicable only to polar rubbers like IIR and EPDM. Another devulcanization process using ultrasonic waves was also developed recently.[50–53] The principle has been successfully used by Issayev and co–workers. In this process the ground rubber is conveyed by a screw extruder to a thin gap between a stationary die and a vibrating horn. The high frequency of vibration possibly creates cavitation and breaks in crosslinks of the vulcanized rubber. Recent papers on this technique describe ultrasonic devulcanization reactor along with experiments performed on devulcanization of ground tire rubber, SBR, NR and silicon rubber and reported that the process leads to materials with good properties.

Reclaimed rubber unlike virgin rubbers is used in compounds to reduce the compound cost and also to improve the processing characteristics. The three dimensional nature of the rubber fragments and the reduced nerve of the reclaim imparts rate and gauge stability to the calendered and extruded stocks. Reclaim compounds are expected to breakdown in mixing much more quickly than virgin rubbers because of the intense mechanical work and chemical treatment given to the vulcanized rubber in reclaiming process. This may lead to reduction of power consumption during mixing.

But despite the obvious incentives to reduce the compound cost and to conserve energy the reclaim constitutes only a very small percentage of total rubber consumption. This is mainly due to the deterioration of technical properties occurring at the time of reclamation. The material, mixing manpower. energy consumption savings, and alleviation of solid waste disposal are the main benefits associated with the use of reclaim.

The latex industry has expanded largely in recent years to meet the world demand for examination gloves, condoms, latex thread, latex foam etc. Scrap latex products contain rubber hydrocarbon of very high quality, which is only lightly crosslinked.

With the rapid spread of AIDS there is a huge increase in the use of disposable examination gloves to protect the medical staff against diseases transmitted through body fluids. Due to the unstable nature of latex compounds and the strict specifications in the quality of examination gloves the rejection in the latex industry come to as high as 10–15% of the latex consumed.

Latex thread is the main input for the manufacture of elastic tape which is used in all foundation garments. Due to the insufficient maturation and filtration and also due to the unstable nature of latex compound, the rejection in the industry comes to around 12%. In foam industry also due to insufficient gelation and unstability of latex compound and also due to temperature variations of the mould the product waste come to around 5%.

The accumulation of these reject latex products results in serious waste disposal problem for the latex industry. Local authorities prohibit open burning of such waste fearing the environmental pollution. But these rejects represents a source of high quality rubber hydrocarbon for reclamation and reuse, since in all latex product manufacture the basic raw material is high quality latex.

A few processes for extracting rubber hydrocarbon from waste latex products have appeared in literature. Rubber Research Institute of India[54] reported a method for reclaiming latex product waste. In this process waste condoms were powdered and mixed with 10 phr of napthalenic oil and one phr of Renacit-7 in a cold mill and heated to 140°C for 30 minutes. The reclaimed rubber obtained by this processes was found to form a smooth band on the mill. However, it was found that only small amount of such reclaim could be added to raw rubber without affecting the mechanical properties adversely. However, the compound containing this reclaim showed better processing characteristics. Another method for reclaiming latex product waste is reported from Rubber Research Institute of Malaysis.[55,56] However, the details of this process are not available. One another process using solvent swelling technique has also been developed in the department of Polymer Science and Rubber Technology, Cochin University of Science and Technology.[57]

Pearson and Sehweller[58]describe a process to reclaim the 'flash' which is the latex foam oozing out of the mating edges of the mould. The reclaimed rubber is usually referred to as 'desensitized foam'. They also reported that when the desensitized foam is used as an additive it is preferably used in quantities of 5–10% of the rubber ingredient in a solid rubber formulation.

But the latex reclaims produced by the above methods do not possess the properties expected of the high quality rubber hydrocarbon present in the latex products. Obviously reclamation process degrades the rubber hydrocarbon to a great extent.

ELASTOMER BLENDS

A lot of rubber products have been developed by rubber technologists using elastomer blends. The main reasons for utilizing elastomer blends rather than individual elastomers include improved physical properties, increased service life, easier processing and reduced product cost. The importance of elastomer blends has led to extensive literature on this subject[59-86] including a fairly recent reviews by Hess[62] and also by Roland.[63]

The most common technique for producing elastomer blends is mechanical mixing due to its simplicity and low cost. The common industrial methods of mechanical mixing are by the use of a screw extruder or a Banbury mixer or using a two roll mill. These general methods may be further divided into two general categories of 'pre-blending' and 'phase mixing'. In the first case, the compounding ingredients are generally added to the pre-mixed polymers in a manner similar to the mixing of a single elastomer. In a phase mix an attempt is made to control the specific location of filler and/ or extender oil and curing agents. This is generally accomplished by the preparation of separate masterbatches which are then blended mechanically.

The most pertinent polymeric properties pertaining to elastomer blends are homogeneity of mixing (phase morphology) and cure compatibility. When two polymers are blended the necessary condition for miscibility is that the free energy of mixing ΔG_m must be negative, which can be stated as

$$\Delta G_m = \Delta H_m - T\,\Delta S_m$$

where, ΔH_m is the ethalpy of mixing

ΔS_m is the entropy of mixing, and

T is the Absolute temperature

This means that complete mixing of elastomers can be achieved only by exothermic mixing or a large entropy of mixing.[59] Therefore, most of the elastomer blends are immiscible because mixing of elastomers is endothermic and the entropic contribution is small because of the large molecular weights.

But miscibility is not a requirement for most rubber applications. Homogeneity at a fairly fine level is necessary for optimum performance, but some degree of microheterogeneity is usually desirable to preserve the individual properties of the respective polymer components. Studies based on phase contrast optical microscopy[61] and electron micrscopy[64] have shown that almost all bulk mixes of elastomer blends are microhetrogeneous on varying degrees.

Eventhough true miscibility may not be required for good mechanical properties of blends, the adhesion between the polymer phases and the respective interfacial energies are important in enhancing the rubber properties. Sherneve[65] has reviewed the importance and requirements for forming a single network structure including crosslinked macromolecules of both polymers in elastomer blends. To achieve such a covulcanised state, the component polymers should be vulcanized to the same extent with crosslinking across the microdomain interphase. The nature of the polymer like unsaturation, polarity etc. determine the curative reactivity which is also influenced by solubility. Generally vulcanizates with components having similar curative reactivity give better properties.

Roland[63] has summarised the different methods which have been utilized to assess the homogeneity of polymers. These include glass transition behaviour, optical and electron microscopy. When applicable the microscopical methods are the most suitable because they provide information on overall homogeneity and phase morphology.

Phase contrast light microscopy[61,66-69] is applicable to the study of unfilled polymer blends and has been applied extensively to the analysis of binary elastomer combinations. It is based on the differences in the refractive indices of polymers. The microscope optics produce a phase shift between the diffracted and transmitted light which provides interference contrast with only small differences in refractive index. Callan and co-workers[61,70] applied this method extensively for the analysis of a wide range of binary blends.

Transmission electron microscopy (TEM) is an ideal method to the study the morphology of elastomer blends because of its high resolution and applicability to both filled and unfilled systems. However, a major problem associated with TEM analysis of polymer blends pertains to image contrast. For most elastomer combinations there is no contrast between the polymer phases in a TEM. scanning electron microscopy (SEM) involves much simpler methods and the image contrast between the polymer phases can be achieved using staining techniques. It can be applied to study the morphology of fractured surfaces of elastomer blends.[71,72]

Glass transition temperature measurements represents another important method to define overall homogeneity of elastomer blends but do not provide any specific information on blend morphology. Heterogeneous blends clearly exhibits separate Tg peaks for the individual polymer components. A single Tg peak indicate greater homogeneity but does not necessarily mean miscibility.

In general, the properties of elastomer blends are more significantly affected by the filler distribution than they are by morphology. Transfer of carbon black from one elastomer to another is favoured by low unsaturation of the polymer originally containing the black or a low heat history during the preparation of masterbatches. Carbon black distributional variations can cause significant changes in unvulcanized and vulcanized rubber properties. For NR/BR blends reduced hysterises generally occurs with a higher black loading in the NR phase. Tear growth and cut growth tend to be maximized with higher carbon black in the continuous polymer phase.

When a reclaim is blended with natural or synthetic rubbers, the virgin polymer adds strength and the reclaim contributes to improved processing and cooler mixing of the compound. Natural rubber based elastomer blends are extensively used in industries because of its excellent dynamic properties, high resilience, superior building tack, green stock strength etc.

For reducing the compound cost and to conserve raw materials and energy the utilization of reclaim rubber is widely accepted in elastomer blends. Whatever reclaim is used the total cost of the resulting compound including both material and processing costs is lower than that of a compound of equal quality made from new rubber. Reclaim based elastomer blends are widely used in passenger carcass, passenger tyre treads automotive floor mats, mechanical good, semipneumatic tyres, inner tubes etc. Reclaimed rubber in compounds provides higher extrusion rates, reduced die swell and excellent surface finish. Phadake and co–workers[77] observed that the poor physical properties and processing characteristics of reclaim vulcanizates can be improved by blending them with fresh NR. The reclaim in blends increases the hardness and the vulcanizate become progressively stiffer resulting an increase in modulus but a decrease in tensile,tear and flex properties.

Blend of natural rubber (NR) and polybutadiene (BR) are widely used in the manufacture of tyres especially in tyre sidewall compounds. In blends with NR, BR has enabled significantly improved resistance to tread wear and groove cracking without a reduction in resilience. Upto 20% higher tread wear index for 50/50 NR/BR blend was reported[80] over straight NR. In addition to improved tread wear resistance, lower running temperatures and improved cold weather performance for BR compounds were also reported.

However, the improvement in elasticity and abrasion resistance are at the expense of tensile strength and modulus of NR. Also the addition of NR to BR improves the processing of BR. Mill mixing of 50/50 NR/BR blend is much easier than BR alone. Better oil extension and higher black loadings are additional benefits made possible by the development of NR/BR blends, along with less dependence on the availability of NR.[81,82]

The properties of a blend depend on both the polymers themselves and on blend morphology, the location of filler and the crosslinking in each phase. The blend morphology and the filler location in NR/BR blends were well established by Massie and co-workers[83], See Mook Sang[84] and Hess and co-workers[86] using different techniques to optimise the performance of the blend. Brown and coworkers[85] used swollen state NMR technique to study the distribution of crosslinks between NR and BR phase. Hess and co-workers[86] evaluated a series of tread grade commercial carbon blacks in 60/40 NR/BR truck tyre tread formulation and found that a high loading of black in the BR phase caused a low bound rubber development and poor dispersion.

Chlorinated NR

Chlorination of NR has been practised right from the end of the last century.[88,89] Among the possible methods of chlorination only the action of gaseous chlorine in solution has led to a method of production of chlorinated rubber on an industrial scale.

Although numerous investigations[90-94] have been carried out to throw light on the mechanism of chlorination it is still not well understood. The reaction is highly complex and may include addition, substitution, cyclisation etc. Fully chlorinated rubber has a chlorine content of about 65% which corresponds approximately to the empirical formula $(C_{10}H_{11}Cl_7)_n$[95-96] and is believed to have a cyclic structure.

Properties of chlorinated rubber are found to vary in close dependence on the chlorine content. Chlorinated rubbers containing 1 to 17% of chlorine retain to a greater or lesser extent rubber like properties and are capable of hot or cold vulcanization with or without the addition of vulcanizing agents.[97] Chlorinated products with 42 to 52% chlorine are known to possess good film forming properties. But partially chlorinated rubbers differ from fully chlorinated in being unstable to heat and light. They decomposed rapidly at 100°C but more slowly at room temperature.

Fully chlorinated rubber containing 65% of combined chlorine is a cream coloured powder and finds application mainly in paint industry and also in adhesive and ink industries. It gives excellent anticorrosive properties to paints and good protection in industrial and marine environments. Besides incorporating them into solvent adhesives facilitates adhesion to certain substrates.

OBJECTIVES AND SCOPE OF THE PRESENT WORK

From the foregoing discussion it is clear that the reclaiming of latex waste products and its utilization has not achieved its full potential, mainly due to the deterioration of mechanical properties of latex reclaim vulcanizates and also due to the high cost of reclamation process. Obviously the reclamation process done at high temperatures degrade the rubber hydrocarbon to a great extent.

The primary aim of this work has been to develop a cost effective process that can be operated at room temperature for developing latex reclaim with superior mechanical properties. With this objective in mind we propose to study the reclaiming action of four different chemicals on latex products waste. Waste latex products are chosen because it has a higher potential to generate good quality rubber hydrocarbon since all latex products are based on either high quality concentrated latex or creamed latex. Moreover, all latex products are only lightly crosslinked and not masticated and hence not mechanically degraded. We also propose to fully explore the possible application of latex reclaim in various fields.

OBJECTIVES OF THE PRESENT WORK

1. To develop a cost effective process for developing better quality reclaimed rubber from latex products (hereafter referred to as latex reclaim).
2. To study the effect of replacing NR by latex reclaim in NR/BR blends.
3. To evaluate the effect of replacing part of NR by latex reclaim in NR compounds.
4. To produce value added products such as chlorinated rubber directly from latex reclaim by its chlorination and to characterize the product.
5. To produce specific products such as hospital sheeting, cycle tube and rubber gasket from latex reclaim satisfying the relevant IS or ASTM standards.

This thesis is divided into the following chapters.

Chapter 1	INTRODUCTION
Chapter 2	EXPERIMENTAL TECHNIQUES
Chapter 3	PRODUCTION AND EVALUATION OF LATEX RECLAIMS

Part I: Development of latex reclaim from waste examination gloves

Part II: Comparison of mechanical properties of latex reclaim vulcanizates with those of NR

Part III Use of EV system in reclaimed rubber compounds

Part IV Production of latex reclaim from thread waste and foam waste and their characterization

Chapter 4 UTILIZATION OF LATEX RECLAIM IN ELASTOMER BLENDS

Part I: Studies on latex reclaim (gloves)/BR blends and their comparison with NR/BR blends

Part II: Use of foam waste reclaim in NR compounds

Part III: Evaluation of the effect of replacing NR by thread waste reclaim in NR compounds

Chapter 5 PRODUCT APPLICATIONS OF LATEX RECLAIMS

Part I: Typical moulded and extruded goods

Part II: Production of chlorinated rubber from latex waste

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.

ELASTOMERS

1.Natural rubber

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala. The Indian standard specifications for this grade of rubber are given below.

Mooney viscosity [ML (1+4) at 100°C]	82.00
Other parameters	Limit
Dirt content, % by mass, max.	0.05
Volatile matter, % by mass max.	1.00
Nitrogen % by mass max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, min.	30.00
Plasticity retention index, (PRI) min.	60.00

2.Polybutadiene (BR) rubber

Polybutadiene rubber (BR) was obtained from Indian Petrochemicals Corporation Ltd., Baroda. The grade used was Cisamer 1220 having a Mooney viscosity [ML (1+4) at 100°C] of 45.

3.Latex product waste

Waste examination gloves was supplied by Midland Rubber Products Ltd; Kakkanad, Kerala, India.

Waste latex thread was supplied by Rubfila International, Kanjikode, Palakkad, Kerala.

Latex Foam 'flash' was obtained from Galaxy Foam, Industrial Estate Kalamassery, Cochin, Kerala.

RECLAIMING CHEMICALS

1. Mercapto benzothiazole (MBT)

Mercapto benzothiazole having the following specifications was supplied by Bayer India Ltd., Bombay.

Specific gravity	1.45 to 1.52
Melting point	160 to 180°C

2. Renacit–7

Renacit–7 was supplied by Bayer India Ltd., Bombay.

3. Diaryl sulphide

Supplied by Rubber Reclaim Co., of India Pvt. Ltd., New Delhi.

4. Sulphur crosslinked cardanol[1]

Cardanol was separated from CNSL by vacuum distillation at 3–4 mm of Hg and had the following specifications

Colour	Pale yellow
Specific gravity at 29°C	0.9320
Hydroxyl number (mg of KOH/g)	185–200
Iodine value/100 g of resin	237

For preparing sulphur crosslinked cardanol 100 ml of cardanol was introduced into a flat bottomed flask fitted with a reflux condenser and thermometer. Ingredients as shown in Table 2.1 were added as dispersions in carbon tetrachloride. The mixture was heated on a hot plate with magnetic stirring for 8 h at 110°C. Sulphur crosslinked cardanol was obtained in the form of dark viscous liquid.

Table 2.1

Formulation for reacting cardanol with sulphur

Cardanol	100 g
Sulphur	0.5
Zinc oxide	0.5
Stearic acid	0.5
TMTD	0.5
ZDC	0.5
Dispersol F	0.0005

COMPOUNDING INGREDIENTS

1. Zinc oxide

Zinc oxide (ZnO) was supplied by M/s.Meta Zinc Ltd., Bombay. It had the following specifications:

Specific gravity	5.5
Zinc oxide content	98%
Acidity	0.4%
Heat loss max. (2 h at 100°C)	0.5%

2. Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps Pvt. Ltd., Bombay and had the following specifications.

Specific gravity	0.85±0.01
Melting point	50–69°C
Acid number	185–210
Iodine number	9.5 max.
Ash content	0.1% max.

3. Tetramethyl thiuram disulphide (TMTD)

Tetramethyl thiuram disulphide was supplied by Polyolefins Industries Ltd., Bombay. It had a melting point of 136°C and specific gravity of 1.4.

4. Benzthiazyl-2-sulphenmorpholide (MOR)

Benzthiazyl–2–sulphenmorpholide (MOR) was supplied by ICI Ltd., India. It had a specific gravity of 1.34.

5. Sulphur

Sulphur was supplied by Standard Chemical Company (Pvt.) Ltd., Madras, India and had the following specifications.

Specific gravity	2.05
Acidity	0.01% max.
Ash	0.01% max
Solubility in CS_2	98%

6. High abrasion furnace black (HAF, N–330)

High abrasion furnace black 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

7. Precipitated silica

It was obtained from Lunar Chemicals, Kanpur, India. The specific gravity was 1.95.

8. Precipitated calcium carbonate

Supplied by Rubo Chemicals India Pvt. Ltd., Dadar, Bombay.

9.Aromatic oil

Aromatic oil was supplied by Hindustan Petroleum Corporation. It had the following specifications.

Specific gravity	0.95–0.98
Viscosity gravity constant (VGC)	0.907
Aniline point	38°C

10. Vulkanox 4020

Vulkanox 4020 N(1,3-dimethyl butyl-N'-phenyl-p-phenylenediamine) was obtained from Bayer India Ltd. It had a specific gravity of 1.1.

11. Vulkanox SP

Commercial phenolic type antioxidant vulkanox SP (mixture of styrenated phenols) was obtained from Bayer India Ltd. It had a density of 1.08 g/cc.

12. Vulkanox HS

Commercial antioxidant vulkanox HS (1,2-dihydro-2,2,4-trimethyl quinoline, polymerised) was obtained from Bayer India Ltd. It had a specific gravity of 1.1.

13. Dispersol–F

Dispersol–F (sodium salt of a disulphonic acid) used was buff coloured powder supplied by ICI Ltd., India.

14.Zinc diethyl dithiocarbamate (ZDC)

Zinc diethyl dithiocarbamate (ZDC) was supplied by Polyolefines Industries Ltd., Bombay. It had a melting point of 178°C and a specific gravity of 1.50.

OTHER ADDITIVES

Potassium iodide, starch, sodium thiosulphate, potassium dichromate, potassium permanganate, sodium carbonate, sodium sulphite stronsium chloride, cadmium acetate and iodine used were of analytical grade.

SOLVENTS

1. Acetic acid, formaldehyde, toluene and carbon tetrachloride used were of analytical grade. Commercial toluene also was used.

2. Reagents for network structure elucidation

Propane-2-thiol and piperidine were analytical grade reagents supplied by Fluka, Germany.

EXPERIMENTAL METHODS

(a) Mixing and homogenisation using mixing mill

Mixing and homogenisation of elastomers and compounding ingredients were done on a laboratory size (6 x 12)" two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002x100)" Then it was given two 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 the mastication. After the nerve had disappeared the compounding ingredients were added as per ASTM-D 3184 (1980) and ASTM D 3182 (1982) 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 homogenised by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm.

(b) Determination of cure characteristics

The cure characteristics of the elastomers were determined on a Goettfert elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with 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 shown by the mix at the test temperature before the onset of cure.
2. Maximum torque: This is the torque recorded after curing of the mix is completed.
3. Scorch time (t_{10}): This is the time taken 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.

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

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.

(c) Moulding of test specimens

The test specimens were prepared in standard moulds by compression moulding on an electrically heated press having 30x30 cm platens at a pressure of 120 kg/cm^2 on 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 h and were used for subsequent physical tests. For samples having thickness more than 5 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

PHYSICAL TEST METHODS

(a) Tensile stress-strain behaviour

Tensile properties of elastomers were determined according to ASTM D 412 (1980) using dumbbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at room temperature 28±2°C. Samples were punched out from compression moulded sheets using a dumbell die (c–type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by two grips, the upper grip 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 90^0 angled 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 ± 2^0C.

(c) Hardness

The hardness (Shore A) of the moulded samples was measured using Zwick 3115 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on a hardness tester using 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 has been established with the specimen.

(d) Compression set

The samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 h in an air oven at 70^0C. 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

$$\text{Compression set (\%)} = \frac{t_0 - t_1}{t_0 - t_s} \times 100$$

where t_0 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 used was ASTM D 395 (1982) (method B).

(e) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader. Sample having a diameter of 12±0.2 mm and a thickness of 16 to 20 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 was taken. The weight after final run was also noted. The difference in weight is the weight loss of the test piece after its travel through 42 m on a standard abrasive surface. It is expressed as volume loss (cc/h). The abrasion loss was calculated as follows:

$$V = \frac{\Delta M}{\rho}$$

where ΔM – mass loss, ρ – density of the sample and V – abrasion loss.

(f) Rebound resilience

Dunlop tripsometer (BS 903, past 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 30^{0}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 45^0 in all cases.

(g) Ageing studies

Physical properties like tensile strength, elongation at break, modulus and tear strength were measured after ageing according to ASTM D 573 - 88 procedure. The dumbbell samples were punched out from the vulcanized sheet and kept in air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break and modulus were measured before and after ageing. The percentage retention of these properties was evaluated for assessing the effect of ageing.

(h) Initial plasticity

The initial plasticity of the samples were measured according to ASTM D 3194-73 method. A test portion of about 30 gm rubber sample was taken and passed three times between mill rolls at room temperature with the opening adjusted so that the final sheet thickness is approximately 1.7 mm. Immediately the sheet was doubled and the two halves were pressed tightly together to avoid the formation of air bubbles. The test pieces were cut from the doubled sheet with the punch and their thickness were measured until three test pellets were obtained with a thickness of 3.4 mm having a volume of 0.40 cm^3. Then the sample was placed between a bleached unglazed acid free tissue paper and then inserted between the heated platen of the Wallace rapid plastimeter. The medium values of the three results of the test pieces were taken as initial plasticity (P_0).

(i) Density

The densities of the 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 is given by,

$$\text{Density} = \frac{\text{Weight of specimen in air}}{\text{Loss of weight in water}} \times 100$$

(j) Thermogravimetric analysis

The thermogravimetric analysis of the samples were done using a Shimadzu-50 thermogravimetric analyser. About 10 mg of the sample was taken in a platinum crucible and the experiment was done in air atmosphere at a heating rate of 10°C/min. The weight loss of the sample was taken and then plotted against temperature.

(k) Mooney viscosity measurements

The mooney viscosity of the raw rubbers were measured on a 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 1 min. after the platens were closed and the rotation of the die was then started. Reading after 4 minutes was reported as the Mooney viscosity [ML (1+4) at 100°C]. The procedure as given in ASTM D 1646 (1981) was followed.

MORPHOLOGY STUDIES

(a) Using optical microscope

The morphology of rubber compounds was investigated using a Nikon phase contrast optical microscope model Alphaphot-2. For optical microscopy compounds were dissolved in a suitable solvent and the solutions were cast into thin films. They were cut into convenient size and mounted on a microscopic slide. Photographs were taken at a magnification of 450 times.

(b) Using scanning electron microscope

Scanning electron microscopic studies were found to be a very powerful tool in polymer research for studying morphology.[2,3]

Scanning electron microscope model (H–6010A Hitachi) was used to investigate the morphology of fractured surfaces. In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X–rays. These signals are monitored by detectors (photo multipher tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in cathode ray tube (CRT) and photographed using 120 roll black and white film.

The SEM observations reported in the present study were made on the fracture surface of tensile and tear test specimens, and abraded surface of the samples. A thin specimen of the samples was prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an Ion Sputter (Eiko IB–3 ion coater–Hitachi) for gold coating of the sample to make it conducting. Gold coated sample was observed in the SEM.

(c) Using photomicrographs

Dispersion of ingredients in compounded rubber stock was studied using photomicrographic technique. The technique employs an MP4 polaroid land camera with a magnification of 30 times.

In this technique cured rubber samples were carefully microtomed smooth and straight razor blade guillotine which was then sandwitched on a rectangular sample holder so that sample cut surface was even with the top edges of the glass holder. Sample was positioned to shine across the sample parallel to the razor cut.

The angle of incident light was kept nearly 30 degree. Sample was viewed through reflex viewer and scanned for area of lowest dispersion. Sample was focussed by adjusting the microscope until the sample image was sharp. After recommended development time of the polaroid photograph it was compared to the set of 10 dispersion standard micrographs of equal magnification and was assigned numerical rating of 1-10 with 10 being best.

CHEMICAL TEST METHODS

(a) Free sulphur estimation

Free sulphur in the crosslinked product was determined according to ASTM D 297-72A.

The principle of this method is based on the reaction of free sulphur with sodium sulphite to give sodium thiosulphate which is finally titrated against standard iodine solution.

$$S + Na_2SO_3 \longrightarrow Na_2S_2O_3$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

2 gm of the sample was digested gently with 100 ml of aqueous sodium sulphite solution (5 g/litre) for 16 h in presence of 5 ml of sodium stearate suspension in water (1 g/litre) to assist wetting and approximately 1 g of paraffin wax to avoid aerial oxidation. 100 ml of stronsium chloride (5 g/litre) solution was added to precipitate fatty acids and 10 ml of cadmium acetate solution (30 g/litre) to remove accelerators. The precipitate was separated by filtration. It was then washed twice with 75 ml portions of cadmium acetate solution (1.2 g/litre). To the filtrate 10 ml 40% formaldehyde solution was added with vigorous stirring and subsequently it was acidified with glacial acetic acid (10 ml). The solution was cooled below 10°C by adding enough crushed ice and titrated with 0.05 N iodine solution using starch as indicator.

A blank run was taken without sample and the free sulphur content was calculated using the following equation:

$$\text{Free sulphur \%} = \frac{(x-y) \times N \times 0.032 \times 100}{W}$$

where x is the volume of iodine solution required for titration of the sample in cc, y the volume of iodine solution required for the titration of the blank in cc, N, the normality of iodine solution and W the weight of sample taken.

(b) Determination of chlorine content

2 g of the sample covered with 1:1 mixture of Na_2CO_3 K_2CO_3 and was taken in a platinum crucible and heated for 4 hrs at 900°C in a muffle furnace. The crucible with the fused sample was then placed in a beaker containing about 150 ml of water and heated until the fusion mixture dissolves in water. Conc. HNO_3 was added dropwise to neutralise the solution. Approximately 35 ml of standard 0.1 N $AgNO_3$ solution was then added and the precipitated AgCl was filtered off. The filtrate was titrated with 0.1 M sodium thiocyanate using ferric alum as the indicator.

A blank run was taken without sample and the chlorine content was calculated using the following equation:

$$\text{Chlorine content of the sample \%} = \frac{(x-y) \times N \times 35.5 \times 100}{W \times 100}$$

where x is the volume of thiocyanate solution required for the titration of the blank in cc, y the volume of thiocyanate solution required for the titration of the sample in cc, N the normality of thiocyanate solution, and W, weight of the sample taken.

(c) Determination of concentration of crosslinks

The concentration of crosslinks (crosslink density) of the vulcanizates were determined from the equilibrium swelling data as follows:

Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.2 gm weight were punched out from the central portion of the vulcanizate and allowed to swell in toluene containing 0.1% phenyl–β–naphthalene for 36 hours. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again.

The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding[4] from the following equation

$$V_r = \frac{(D-FT)\,\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}}$$

where

T, is the weight of the specimen

D, the deswollen weight of the test specimen

F, the weight fraction of insoluble components

A_0 the weight of the absorbed solvent corrected for the swelling increment

ρ_r the density of rubber, and

ρ_s the density of solvent

For NR $\rho_{r(NR)}$ was taken as 0.92 g/cm^3

and for toluene $\rho_{s\,(toluene)}$ was taken as 0.886 g/cm^3

In the case of carbon black filled vulcanizates the value of V_r was converted into V_{r0} (the value V_r would have had in the absence of black) by means of the following equation which was derived by Porter[5].

$$V_{r0}/V_r = 0.56 \times e^{-z} + 0.44$$

where z is the weight fraction of filler.

The crosslink density $1/2M_c$ was determined from V_{r0} using Flory-Rehner equation[6,7]

$$1/2M_c \qquad \frac{-[\ln(1-V_{r0}) + V_{r0} + \quad V_{r0}^2]}{2\,\rho_r\,V_s\,(V_{r0})^{1/3}}$$

where V_s is the molar volume of solvent (V_s (toluene) = 106.2 cc/mol) and χ is the parameter characteristic of interaction between rubber and solvent. Values of parameter χ taken for NR-toluene[8,9] was 0.42.

(d) Determination of concentration of polysulphidic crosslinks[10-12]

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanizate before and after treatment with propane-2-thiol and piperiydine which cleaves the polysulphidic crosslinks in the network. Vulcanizate sample weighing about 0.2–0.3 gm was allowed to stand in excess of the solvent (toluene/benzene) containing 0.1% PBN for 24 hours at room temperature. Then the solvent was replaced by a solution (100 ml) of 0.4 M propane–2–thiol and piperidine in the solvent containing 0.5% PBN for 2 hours. On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was then kept in excess of the solvent with 0.1% PBN for 24 hours and finally extracted for 2 hours in pure solvent. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (V_r) was then determined as before and the crosslink density was determined.

(e) Acetone extract determination

The procedure adopted was according to BS 1673 part 2, 1967. About 1 gm of the sample of 1.6 mm thickness was weighed to the nearest milligram and wrapped in a filter paper in such a manner that the pieces were separated from each other. The test pieces were kept in the soxhlet type apparatus and sufficient acetone was poured to fill the extraction cup. The apparatus was assembled and the extraction vessel was heated continuously on a thermostatically controlled water bath for not less than 12 hours and not more than 16 hours, the rate of evaporation being controlled to give 5 to 8 extractions per hour. After the extraction period was over the combined acetone from the extraction flask and cup was recovered by distillation. After most of the acetone was recovered, the contents of the flask was dried in an oven at 70°C for about 1 hour to remove the last traces of acetone. The flask was cooled to room temperature in a desiccator and weighed. Heating, cooling and weighing were repeated until concordant values were obtained. Acetone extract was calculated from the equation

$$\text{Acetone extract \%} \quad = \quad \frac{B-C \times 100}{A}$$

where A is the weight of the sample taken in gm

B, the weight of extraction flask and extracted residue in gm

and C, the weight of empty flask in gm

(f) Volatile matter determination

Volatile matter of the sample was determined according to IS specifications for analysis of dry rubber. About 30 gm of the sample was cut and wrapped air tight in a polyethylene bag. Then 10 g was weighed from this and passed through the mill rolls set 0.5 mm apart and a friction ratio 1:14. Then the test pieces were placed on an aluminium tray and kept inside the oven at 100°C for 4 hours. At the end of heating each test pieces were inserted in a polyethylene bag and clipped quickly. The test pieces were allowed to cool for half an hour and then removed from the bag and weighed. The volatile matter was calculated from the relation

$$\text{Volatile matter (\%)} = \frac{A-B \times 100}{A}$$

where A is the weight of test piece in gm, and

B, the eight of test piece after drying in gm.

(g) Ash content determination

Ash content was determined according to ASTM D 1278 68a, 1969. About 5 gm of the sample was weighed, wrapped in an ashless filter paper and placed in a silica crucible which had been previously ignited for 15 minutes and weighed. Then the crucible was introduced into a muffle furnace at 550°C for 4-5 hours heating. When ashing was completed, the crucible was allowed to cool in a desiccator and then weighed. Ash content of the sample was determined from the relation

$$\text{Ash content (\%)} = \frac{A - B \times 100}{C}$$

where A is the weight of crucible plus ash in gm

B, the weight of empty crucible in gm

and C, the weight of sample taken in gm.

(h) Rubber hydrocarbon content determination

The rubber hydrocarbon content was determined by substracting the weight of all other constituents from the relation

Rubber hydrocarbon content (%) = 100 – (Acetone extract + Volatile matter + Ash content). The method is outlined in BS 906: Part B 11, 1960.

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Chapter 3

PRODUCTION AND EVALUATION OF LATEX RECLAIMS

PART I

DEVELOPMENT OF LATEX RECLAIM FROM WASTE EXAMINATION GLOVES

INTRODUCTION

Latex products generally contain superior quality rubber compared to dry rubber products, since they are not masticated or subjected to high temperature during vulcanization. For example, waste examination gloves contain lightly crosslinked rubber hydrocarbon of very high molecular weight without any fillers. Hence the factory rejects of gloves industry represent a source of high quality rubber hydrocarbon for reclamation and reuse.

Rubber Research Institute of India[1] and Malaysia[2,3] have developed techniques for reclaiming waste latex products. Rubber Research Institute of India has reported a process of reclaiming waste condoms by thermo-mechanical method using Renacit–7 as the reclaiming agent. The latex reclaim produced by this method can replace raw rubber up to about 25% of its weight in filled NR compounds without much deterioration in mechanical properties. The details of the process adopted by Rubber Research Institute of Malaysia are not available. Another technique of swelling the waste latex products in organic solvents followed by mechanical breakdown has been developed in our laboratory.[4]

The latex reclaim produced by this method can replace the natural rubber upto about 50% of its weight in filled compounds without reduction in mechanical properties.

From the foregoing discussion, it is clear that the reclaiming of waste latex products and its utilization has not achieved its full potential. The primary aim of our work has been to develop a cost–effective technique for reclaiming waste latex products without the application of heat.

In this study four different chemicals, viz., (1) MBT (Mercapto benzothiazole); (2) Renacit-7 (zinc salt of pentachlorothiaphenol); (3) Diaryl sulphide; (4) Sulphur crosslinked cardanol[5] are proposed to be tried as reclaiming agents.

Mercapto benzothiazole is an organic accelerator used in rubber compounding, and contains a thiol group. Okamoto and co-workers[6] have investigated the reclaiming action of MBT on ground rubber obtained from passenger car tyres and found that thiol compounds act as acceptors of free radicals formed during thermochemical process and contribute to plasticization by preventing recombination. Renacit-7 is used as a peptiser in rubber compounding and can act as a free radical acceptor during polymer chain breakdown or crosslink breaking.

Sulphur crosslinked cardanol contains S–S–linkages.[5] Though compounds containing S–S–linkage do not remove sulphur from the vulcanizate they may catalyze the oxidative breakdown of the polymer chain while at the same time oxidiatively disrupting sulphur crosslinks thereby restoring the vulcanized polymer to a more two dimensional state.[7,8] The sulphur crosslinked cardanol was prepared by adding sulphur, ZDC, TMTD and zinc stearate as dispersions in cardanol and then heating the mixture for 8 hours at 110°C. Diaryl sulphide is a commercial reclaiming agent.

The reclaiming action of these chemicals is proposed to be compared with a commercial reclaiming agent 'Delink-R'.[9,10]

EXPERIMENTAL

The reclaiming of the waste examination gloves was done as follows. The waste product was passed through a laboratory two roll mill at a friction ratio of 1:1.25 with a tight nip at room temperature for 3 minutes to facilitate the mechanical breakdown of the rubber. Then the reclaiming agents were added in different quantities according to the formulation given in Table 3.1. In order to get a seeding effect 10 phr of highly masticated NR was also added. The homogenization of the reclaims was done by milling for another three minutes and then the reclaimed rubber was removed from the mill in the form of a sheet. A control mix (A) and also a reclaim using the commercial reclaiming agent

Table 3.1: Formulation for reclamation

Ingredients (g)	A	B			C			D			E				F
		1	2	3	1	2	3	1	2	3	1	2	3	4	
Waste examination gloves	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Masticated NR	10	10	10	10	10	10	10	10	10	10	10	10	10	10	6
Reclaiming chemicals															
1. MBT		0.5	1	1.5											
2. Renacit-7					0.5	1	1.5								
3. Diaryl sulphide								0.5	1	1.5					
4. Sulphur crosslinked cardanol											0.5	1	1.5	2	
5. Delink-R															6
Process aid															2

'Delink' (F) were also prepared according to the formulation given in the Table 3.1. The formulation for mix (F) was selected as directed by the suppliers of Delink. In order to optimize the amount of chemicals used as reclaiming agents, the Mooney viscosity of the mixes containing varying amounts of these agents were measured.

The other properties of reclaimed rubber like initial plasticity, volatile matter, acetone extract, ash content, free sulphur content and rubber hydrocarbon content were determined for the reclaimed rubber samples having the minimum Mooney viscosity according to the relevant ASTM standards.

RESULTS AND DISCUSSION

Fig.3.1 shows the variation of the Mooney viscosity of mixes with the amount of different chemicals used as reclaiming agents. The Mooney viscosity of the control mix (A) is found to be very high compared to all other mixes. From the figure it is clear that when the reclaiming agent is added to the mix in 0.5 g—1.5 g range there is a sharp decrease in the Mooney viscosity of the mixes. It is also found that for the mix containing MBT and Renacit–7 the minimum Mooney value is obtained at 0.5 phr level of the respective reclaiming agents, for diaryl sulphide at 1 phr and for sulphur crosslinked cardanol at 1.5 phr respectively.

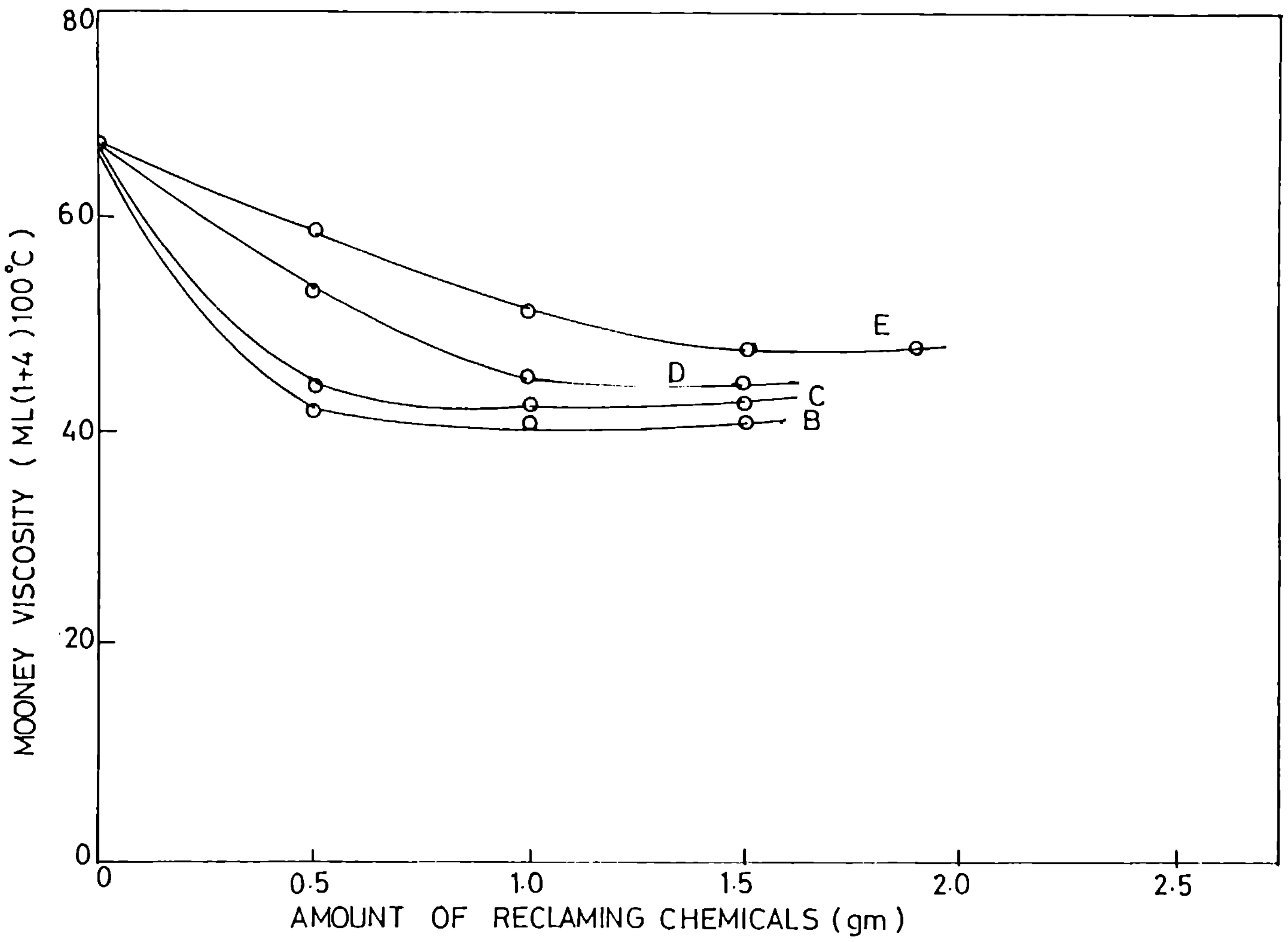

Fig.3.1: Variation of Mooney viscosity of mixes with the amount of reclaiming agents.
(B) - MBT, (C) - Renacit-7, (D)-Diaryl sulphide, (E)- Sulphur cross-linked cardanol.

The initial plasticity and Mooney viscosity of mixes prepared using optimum phr of the four reclaiming agents used and Delink–R as reclaiming agent are shown in Table 3.2. The initial plasticity and Mooney viscosity values are found to be comparable to that of natural rubber and found to be in the processable range so that they can be easily mixed with natural and synthetic rubbers. This shows that MBT, Diaryl sulphide, Renacit–7 and sulphur crosslinked cardanol are effective in reclaiming waste latex products.

The volatile matter and acetone extract values of the reclaims are also comparable to that of NR as shown in Table 3.2. The ash content of latex reclaim is found to be low compared to WTR reclaim, since examination gloves do not contain any filler. The amount of free sulphur in the reclaim shows the presence of unutilized sulphur in the reclaim. It may be observed that free sulphur content in the reclaimed rubber samples are higher than that in the control mix (A). This may be due to the breaking of S–S–crosslinks. The mix (F) contains higher free sulphur content. It may be due to the higher sulphur content of the Delink-R.[9]

CONCLUSIONS

1. This study shows that the method utilized for reclaiming of waste latex products is a promising one for generating good quality reclaim.

2. The chemicals like MBT, Renacit-7, diarylsulphide and sulphur crosslinked cardanol can act as reclaiming agents for waste latex products.

Table 3.2: Characterization of reclaims

Properties	A	B	C	D	E	F
Mooney viscosity [ML(1+4)100°C]	68	44.5	46	47	49	39
Initial plasticity P_0	54	24.9	27	29	26	29.9
Free sulphur, % by mass	0.52	0.7	0.68	0.66	0.7	2.23
Acetone extract, % by mass	5.06	5.10	5.09	5.25	5.25	5.50
Volatile matter, % by mass	0.61	0.608	0.614	0.619	0.605	0.30
Ash content % by mass	2.42	2.46	2.48	2.46	2.44	6.20
Rubber hydrocarbon content (%)	91.39	91.13	91.16	91.08	91.00	85.77

PART II

COMPARISON OF MECHANICAL PROPERTIES OF LATEX RECLAIM VULCANIZATES WITH THOSE OF NR

INTRODUCTION

Acetta and Vergnaud[11,12] have studied vulcanization of reclaimed rubber powder with vulcanizing agents without adding fresh rubber and found that rubber powder can be converted to a plastic or elastomeric material according to the percentage of vulcanizing agents. Phadke and co-workers[13] have studied the vulcanization of reclaimed rubber and found that the physical properties of reclaimed rubber vulcanizates are inferior to those of the NR vulcanizates and the reclaim compounds exhibit comparatively poor processing characteristics.

In contrast to other rubber reclaims latex reclaim contains rubber hydrocarbon of very high quality. In this study the cure characteristics and mechanical properties of natural rubber are proposed to be compared with those of 100% latex reclaims prepared using different reclaiming agents. The carbon black distribution in different vulcanizates are also proposed to be investigated.

EXPERIMENTAL

The reclaimed rubbers were compounded according to the formulation given in Table 3.3. The mix F_1, prepared using Delink-R contains only 40 phr carbon black and aromatic oil as suggested by the Delink suppliers. The mix F_2 was also prepared using Delink-R with 40 phr of carbon black and all other curatives as in the case of other reclaim mixes. To compare the cure characteristics and mechanical properties of reclaim compounds with those of NR, virgin NR was also compounded and vulcanized according to the same formulation (A_1).

The optimum cure time T_{90} and the scorch time T_{10} of the compounds were determined on a Goettfert Elastograph model 67.85. The compounds were then vulcanized up to their optimum cure times in an electrically heated hydraulic press at 150°C.

The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM D 412-80. The tear resistance of the vulcanizates were evaluated as per ASTM D 624-81. The ageing resistance of vulcanizates were determined by keeping the sample at 70°C for 24 and 48 hours in a laboratory air oven and then measuring the retension in properties.

Compression set of the samples was measured as per ASTM D 395-82. The hardness (Shore A) was measured using a Zwick 3115 hardness tester in accordance with ASTM D 2240-81. The abrasion resistance of the samples were measured using a DIN abrader.

Table 3.3: Formulation and cure characteristics of latex reclaim and NR compounds

	A_1	B_1	C_1	D_1	E_1	F_1	F_2
NR	100						
Latex reclaim		110.5	110.5	111	111.5	114	114
ZnO	5	5	5	5	5		5
Stearic acid	2	2	2	2	2		2
Vulkanox 4020	1.5	1.5	1.5	1.5	1.5		1.5
Carbon black (HAF-N330)	40	40	40	40	40	40	40
Aromatic oil	6	6	6	6	6	6	6
MOR	0.8	0.8	0.8	0.8	0.8		0.8
Sulphur	2.5	2.5	2.5	2.5	2.5		2.5
<u>Cure characteristics at 150°C</u>							
T_{10} (Scorch time in min)	2.9	1.32	1.6	1.5	1.00	0.32	0.88
T_{90} (Optimum Cure time in min)	8.1	2.16	2.5	2.3	2.32	5.08	2.36

B_1	Latex reclaim obtained using 0.5 phr MBT as the reclaiming agent.
C_1	Latex reclaim obtained using 0.5 phr Renacit-7 as the reclaiming agent.
D_1	Latex reclaim obtained using 1 phr Diaryl sulphide as the reclaiming agent.
E_1	Latex reclaim obtained using 1.5 phr sulphur crosslinked cardanol as the reclaiming agent.
F_1& F_2	Latex reclaim obtained using Delink-R as the reclaiming agent.

The total crosslink density and the percentage of polysulphidic linkages of the vulcanizates were determined as per the procedures outlined in chapter 2 by equilibrium swelling of the vulcanizates in toluene..

The carbon black dispersion in the vulcanizates were studied using photo micrographic techniques. The technique employs an MP4 Polaroid land camera with 30 times magnification.

RESULTS AND DISCUSSION

Table 3.3 shows the cure characteristics of NR and reclaim compounds. The T_{10} and T_{90} values of reclaim compounds are much lower than those of the NR compound. This is possibly due to the presence of crosslinking precursors and/or unreactive curatives in the latex reclaim.[13-15] Usually ultra accelerators like ZDC are used in the latex products. The scorch time of latex reclaim compounds prepared using Delink-R (F_1 and F_2) are found to be very low. This may be due to the higher accelerator content of Delink-R.[9]

The average crosslink density and the percentage of polysulphidic linkages of the vulcanizates are shown in Table 3.4. It shows that the total crosslink density as well as the percentage of polysulphidic crosslinks of the reclaim vulcanizates are higher than those of the NR vulcanizate. This is obviously due to the presence of crosslinking precursors and/or unreacted curatives in the reclaim.

The hardness of reclaim vulcanizates (Table 3.4) are found to be much higher than that of NR while the compression set values are much lower. This is due to the higher crosslink density in the reclaim vulcanizates.[13]

The abrasion resistance of reclaim vulcanizates was slightly inferior to those of NR (Table 3.4). This may be due to the comparatively lower bonding between the particles in latex reclaim vulcanizates as the particles are already vulcanized.[16]

Fig.3.2 shows the tensile strength of NR and latex reclaim vulcanizates before and after ageing. There is only a marginal difference in tensile strength before ageing. This clearly shows that the reclamation process done at room temperature does not result in any appreciable degradation of the rubber hydrocarbon in the reclaim. The reclaim vulcanizate B_1 shows higher tensile strength compared to other reclaims. This shows that MBT is superior compared to other reclaiming agents. The lower tensile strength is shown by reclaim vulcanizates F_1 and F_2 prepared using Delink–R. This may be due to the lower amount of curatives added in mix F_1 and due to very high crosslink density in F_2.

Table 3.4: Vulcanizate properties of latex reclaims and NR

Properties	A_1	B_1	C_1	D_1	E_1	F_1	F_2
Crosslink density (gm mole/cc) x 10^{-5}	4.16	6.84	7.08	7.11	7.77	2.71	11.2
Polysulphidic linkages (%)	64.4	78.6	81.7	73.9	84	54	85.5
Compression set (%)	34	26	26	28	27.9	32.5	22
Abrasion resistance (volume loss, cc/h)	2.74	3.88	3.68	4.57	4.6	4.93	5.8
Hardness (Shore A)	56	63	63	61	64	54	66

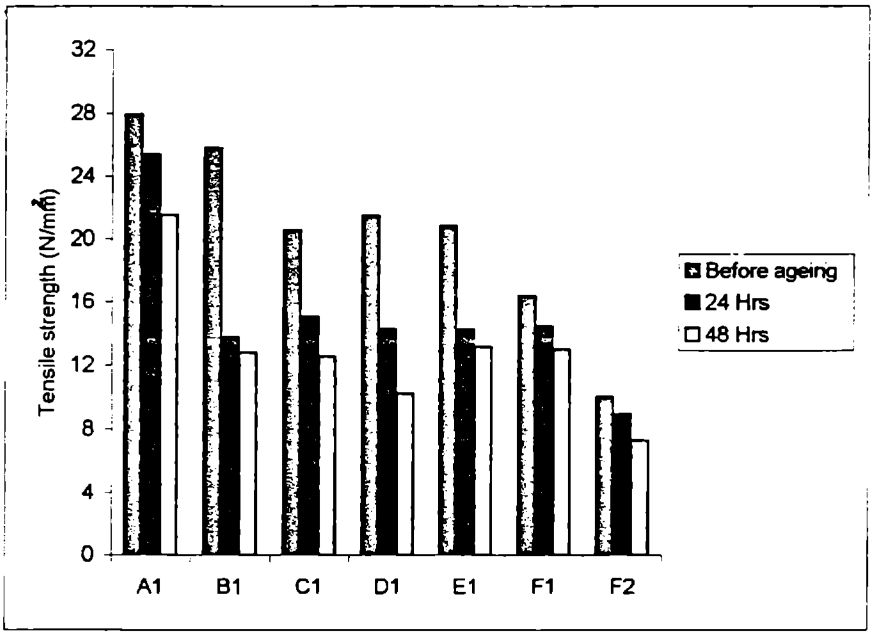

Fig.3.2: Tensile strength of NR (A_1) and latex reclaim vulcanizates (B_1, C_1, D_1, E_1, F_1, F_2).

The ageing resistance of reclaim vulcanizates are found to be lower than those of the NR vulcanizate. This may be due to the presence of higher percentage of polysulphidic crosslinks in the reclaim vulcanizate (Table 3.4).

Fig.3.3 shows the elongation at break of NR and latex reclaim vulcanizates before and after ageing. The elongation at break values of all latex reclaim vulcanizates are found to be much lower than those of the NR vulcanizates. This may be due to the increased crosslink density of the latex reclaim vulcanizates. Reclaim vulcanizate F_1 shows comparatively higher elongation at break compared to other reclaim vulcanizates. This may be due to the lower amount of curatives added to it.

Fig.3.4 shows the tear strength of NR and reclaim vulcanizates before and after ageing. There is only a marginal decrease in tear strength for the reclaim vulcanizates compared to NR vulcanizates. The reclaim vulcanizate prepared using MBT as reclaiming agent gives comparatively superior properties. But the properties of reclaim vulcanizates F_1 and F_2, prepared using the reclaiming agent Delink-R are inferior to those of other reclaim vulcanizates. Here also the ageing resistance of reclaim vulcanizates are lower than those of the NR vulcanizates.

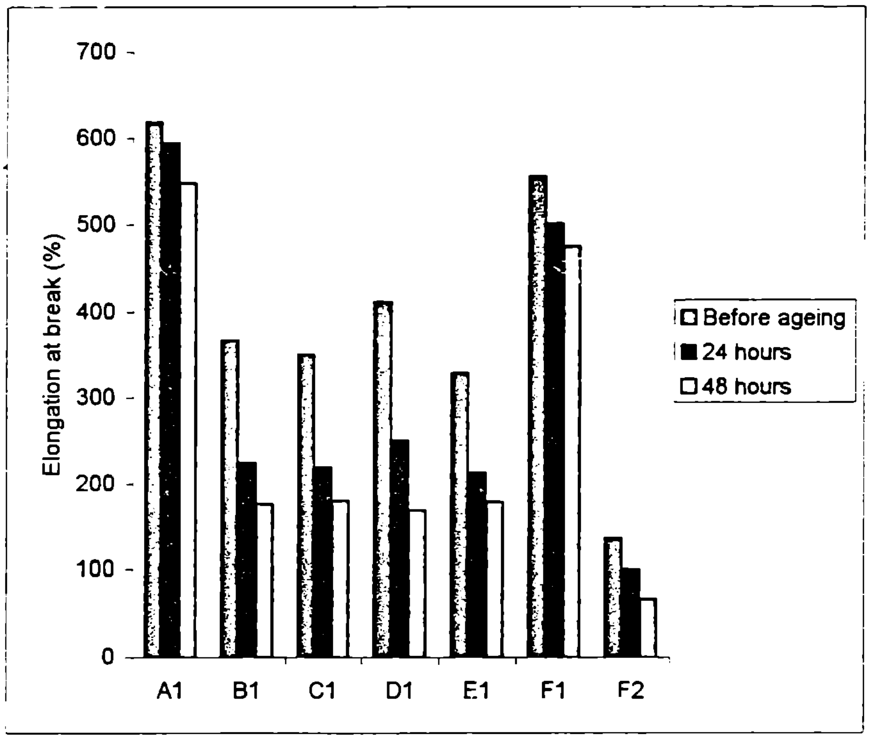

Fig.3.3: Elongation at break of NR (A_1) and latex reclaim vulcanizates (B_1, C_1, D_1, E_1, F_1, F_2)

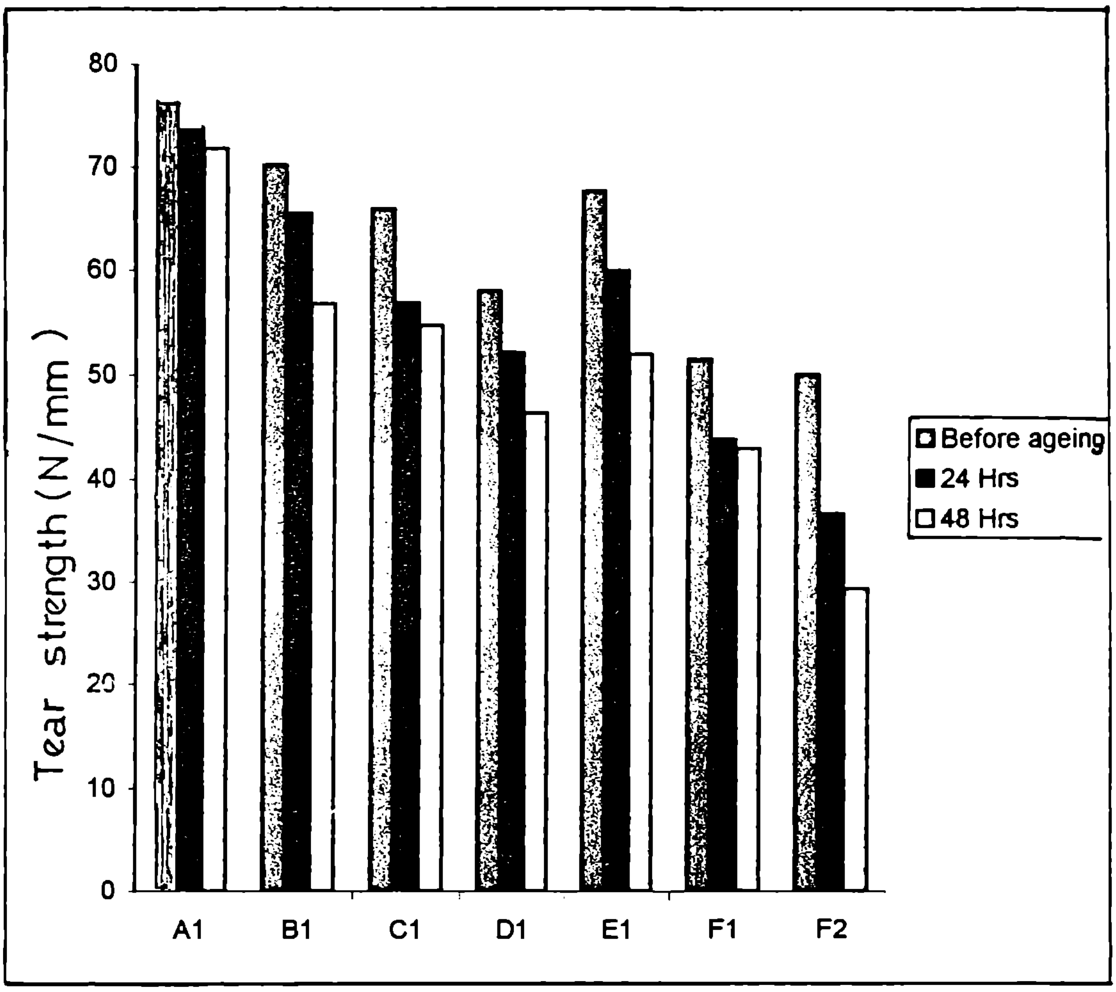

Fig.3.4: Tear strength of NR (A_1) and latex reclaim vulcanizates (B_1, C_1, D_1, E_1, F_1, F_2).

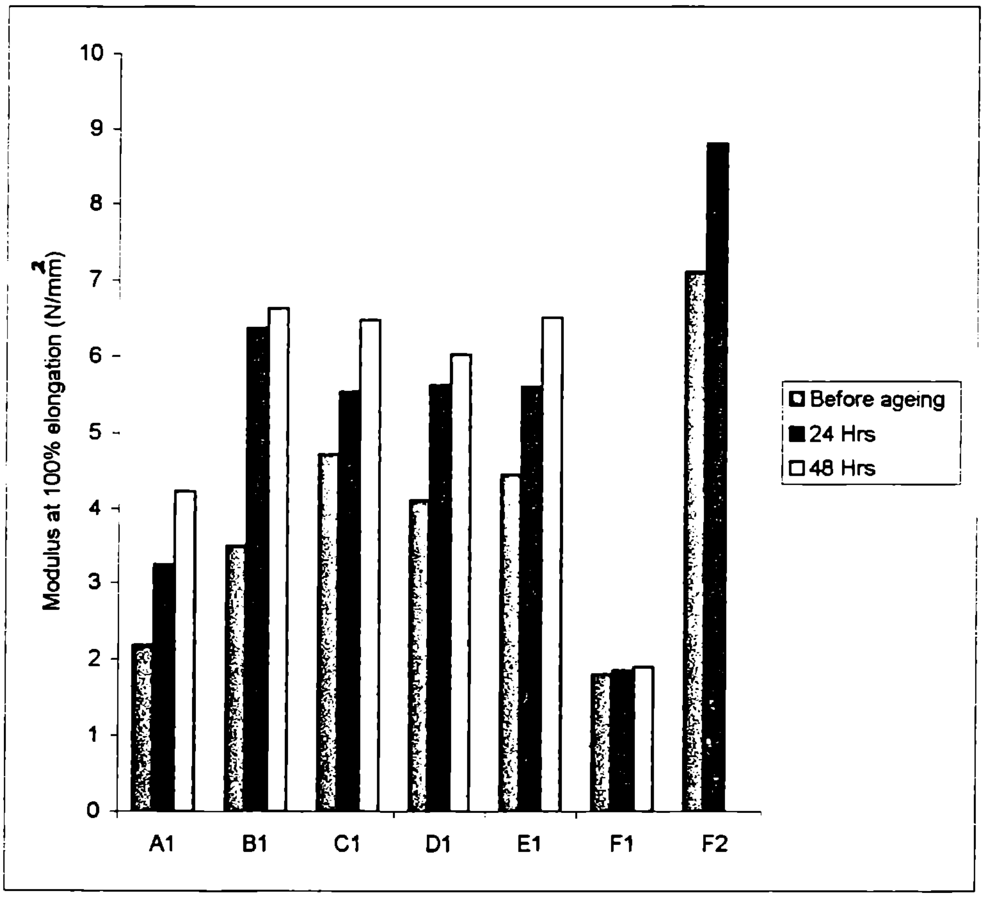

Fig.3.5: Modulus at 100% elongation of NR (A_1) and latex reclaim vulcanizates (B_1, C_1, D_1, E_1, F_1, F_2)

Fig.3.6 NR (A_1)

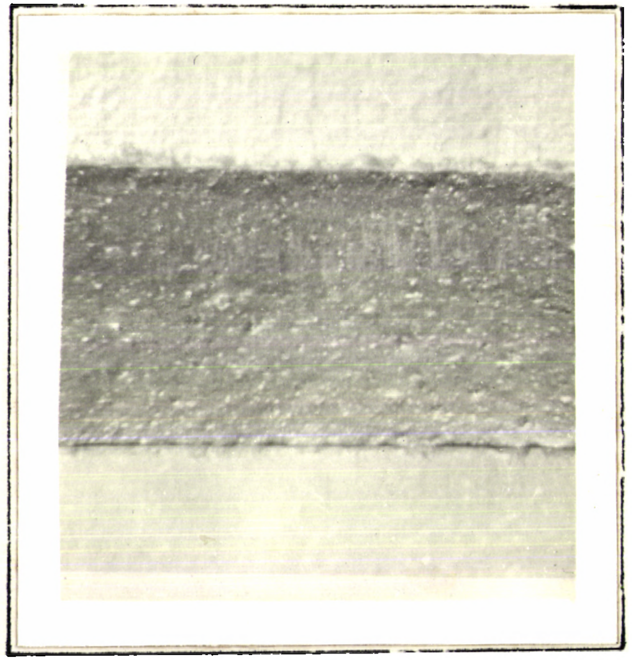

Fig.3.7 Latex reclaim (B_1)

Photomicrographs of the vulcanizates.

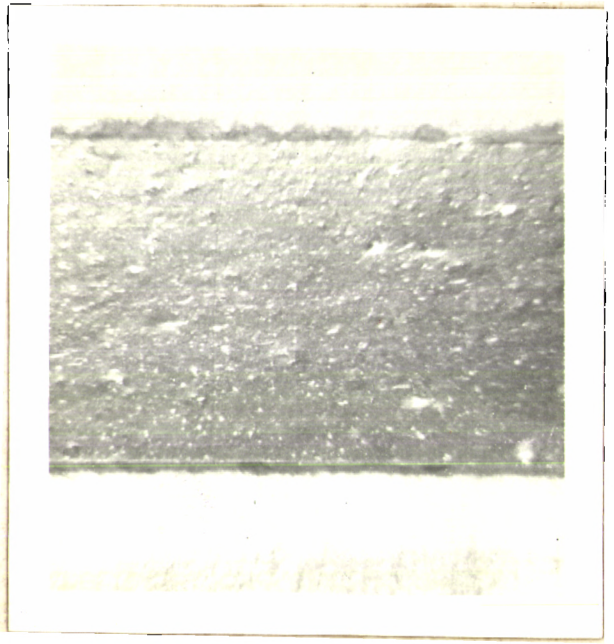

Fig.3.8 Latex reclaim (C_1)

Fig.3.9 Latex reclaim (D_1)

Photomicrographs of the vulcanizates.

Fig.3.10 Latex reclaim (E_1)

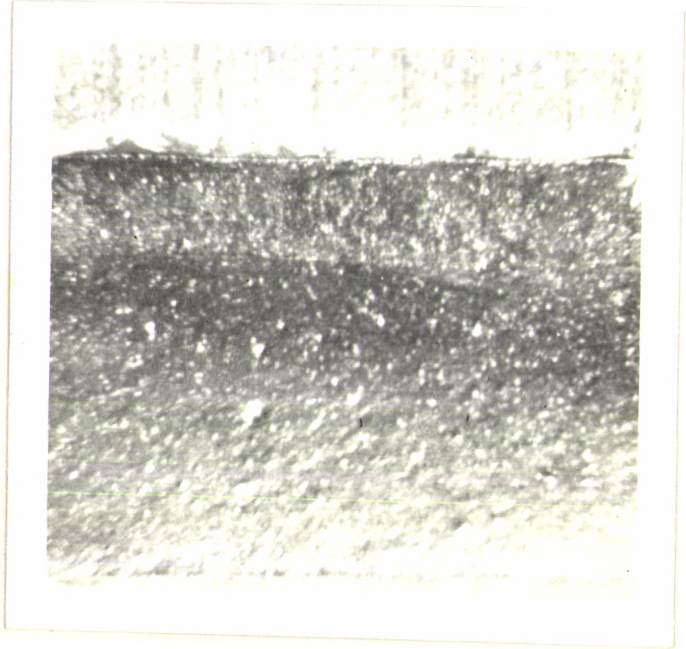

Fig.3.11 Latex reclaim (F_1)

Photomicrographs of the vulcanizates.

Fig.3.12 Latex reclaim (F_2)

Photomicrograph of the vulcanizate

The modulus at 100% elongation of NR and latex reclaim vulcanizates before and after ageing are shown in Fig.3.5. The modulus of all latex reclaim vulcanizates are much higher than those of the NR vulcanizates. This may be attributed to the increased crosslink density in the reclaim vulcanizates. The vulcanizates F_1 prepared using Delink-R shows very low modulus obviously due to the lower crosslink density as shown in Table 3.4.

Figs.3.6 to 3.12 show the photomicrographs of vulcanizates. The dispersion of carbon black in NR vulcanizates is found to be more uniform compared to that of the latex reclaim vulcanizates. The reclaims prepared using MBT, Diaryl sulphide, and sulphur crosslinked cardanol show more uniform distribution of carbon black compared to the vulcanizates prepared using Delink–R and Renacit-7.

CONCLUSIONS

1. The reclaimed rubber prepared using MBT as the reclaiming agent gives higher mechanical properties compared to reclaimed rubbers prepared using other reclaiming agents. MBT also seems to have commercial viability since it is superior to Delink in the vulcanizate properties and processing safety.

2. The tensile strength and tear strength of the reclaim vulcanizates are found to be slightly lower than those of NR vulcanizates but after ageing these properties are found to be inferior for the reclaimed rubber vulcanizates.

PART III

USE OF EV SYSTEM IN RECLAIMED RUBBER COMPOUNDS

Compounding of an elastomer using an EV system increases the ageing resistance of the vulcanizates. In order to improve the ageing resistance of latex reclaim vulcanizate, the latex reclaim is proposed to be compounded employing an EV system and its ageing resistance is proposed to be evaluated.

EXPERIMENTAL

The latex reclaim prepared using MBT was selected for this study. The reclaim was compounded according to the formulation given in Table 3.5. To compare its cure characteristics and mechanical properties, NR was also compounded and vulcanized according to the same formulation.

The scorch time and optimum cure time of the compounds were determined on a Geottfert Elastograph model 67.85 and then they were vulcanized up to their optimum cure times in an electrically heated hydraulic press at 150°C.

The tensile and tear strength were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/min according to relevant ASTM standards. The ageing resistance of the vulcanizate were studied by ageing the sample at 70°C for 24 and 48 hours in a laboratory air oven. Samples for compression set and hardness were moulded and tested as per relevant ASTM standards. The abrasion resistance of the samples were measured using a DIN abrader.

The total crosslink density and the percentage of polysulphidic linkages were determined from the equilibrium swelling data of the vulcanizates in toluene.

SEM studies of the tensile and abraded surfaces of both NR and latex reclaim vulcanizates were taken using a SEM model Hitachi—H-6010 A – scanning system.

RESULTS AND DISCUSSION

Table 3.5 shows the cure characteristics of NR and latex reclaim vulcanizates. It may be observed that in low sulphur vulcanization also the reclaimed rubber compound shows lower scorch time and cure time than virgin NR compounds. This may be due to the presence of unused accelerators present in latex reclaim. Compared to conventional vulcanization system, EV system gives improved scorch safety.

Fig.3.13 shows the tensile strength and tear strength of latex reclaim (B_2) and NR (A_2) vulcanizates before and after ageing. The ageing resistance of vulcanizates are improved considerably. This behaviour is expected since low sulphur vulcanization system leads to a higher percentage of mono and disulphidic crosslinks.

Table 3.5: Formulation and cure characteristics of NR and latex reclaim compounds

	A_2	B_2
NR	100	
Latex reclaim		110.5
ZnO	5	5
Stearic acid	2	2
Vulkanox 4020	1.5	1.5
Carbon black (HAF–N330)	40	40
Aromatic oil	5	5
MOR	3.5	3.5
Sulphur	0.5	0.5
Cure characteristics at 150°C		
T_{10} (Scorch time in min)	4.0	2.04
T_{90} (Optimum Cure time in min)	9.6	6.12

Table 3.6: Vulcanizate properties of NR and latex reclaim

Properties	A_2	B_2
Crosslink density (gm mole/cc) x 10^{-5}	3.53	6.24
Polysulphidic linkage (%)	50.5	60.28
Compression set (%)	31	23
Abrasion resistance (volume loss, cc/h)	2.86	4.93
Hardness (Shore A)	54	60

Fig.3.14 shows the elongation at break and modulus at 100% elongation of both latex reclaim (B_2) and NR (A_2) vulcanizates before and after ageing. The retention in elongation at break, after ageing of reclaim vulcanizate., is very much improved. The modulus at 100% elongation also shows only a marginal increase due to ageing.

Table 3.6 shows other vulcanizate properties of NR and reclaim vulcanizates A_2 and B_2. The hardness of reclaim vulcanizate is found to be much higher while the compression set value is much lower than that of NR vulcanizate. This may be expected since as in the case of conventional system, in EV system also, the total crosslink density of reclaim vulcanizate is much higher than that of NR vulcanizate. But, the percentage of polysulphidic linkages is considerably lower for the latex reclaim vulcanizate when it is compounded in a low sulphur vulcanization system. This explains the comparatively higher ageing resistance of vulcanizate B_2 over B_1.

Figs.3.15 and 3.16 show the SEM photographs of the tensile fracture surface of NR (A_2) vulcanizate before and after ageing. The fracture surface of NR vulcanizate before ageing shows improperly dispersed filler agglomerates which nucleates fracture through cracks.[17] But the aged surface shows more shear lines which may result in a lower tensile strength.

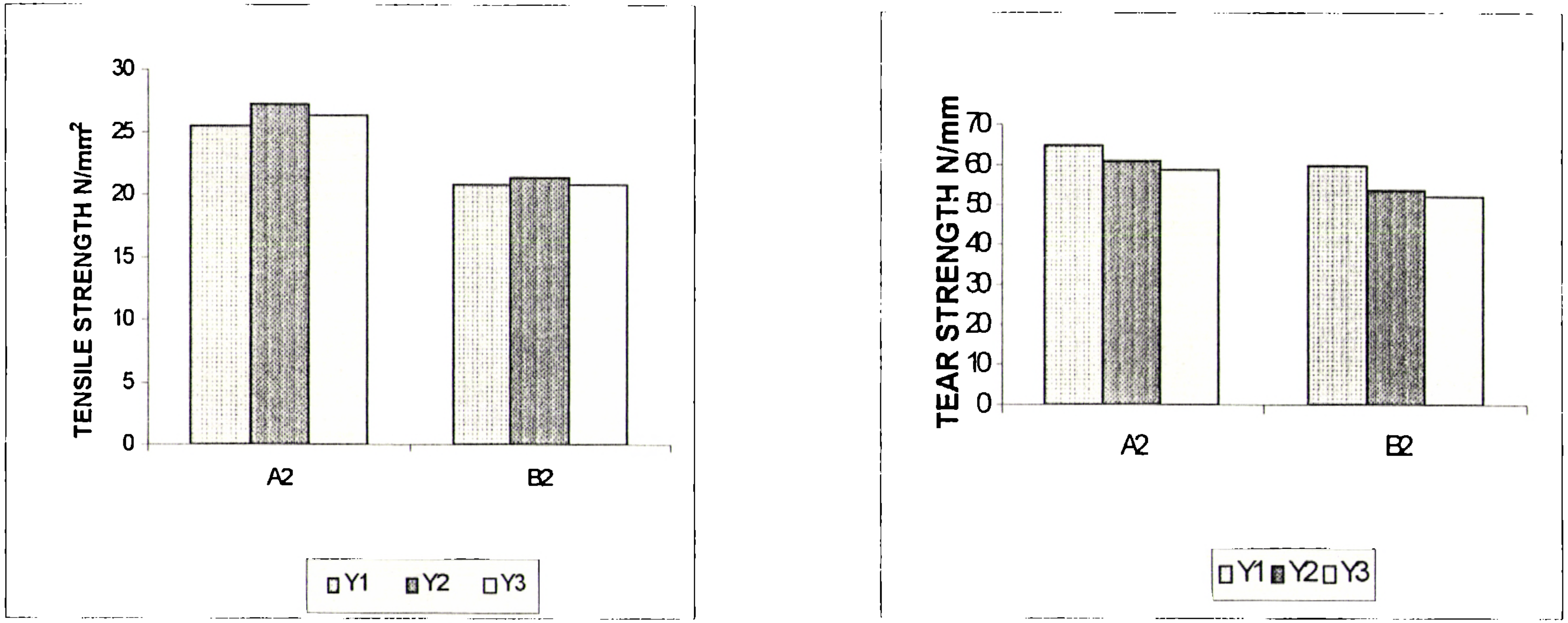

Fig.3.13 Tensile and Tear properties of NR (A_2) and Latex reclaim (B_2) Vulcunizates (EV System)
Y1 before ageing, Y2 ageing 24 hrs., Y3 - ageing 48 hrs.

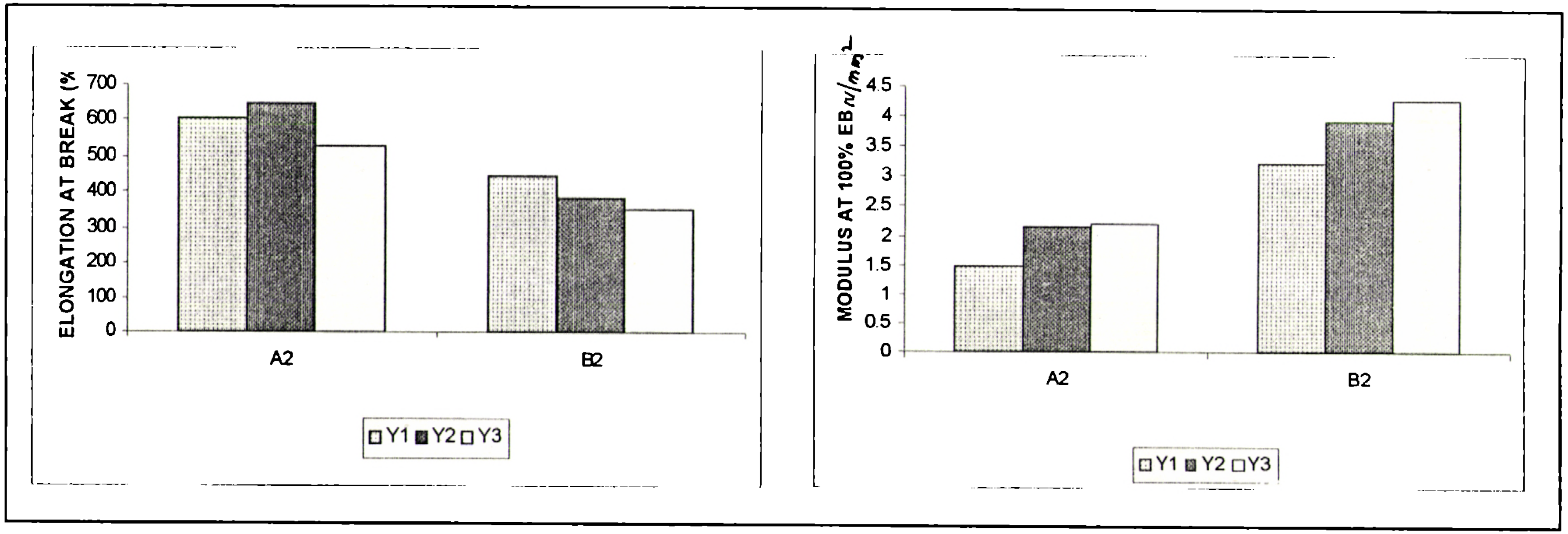

Fig.3.14 Elongation at break and Modulus at 100% Elongation of NR (A_2) and latexreclaim (B_2) Vulcanizates (EV System)
Y1 before ageing, Y2 ageing 24 hrs., Y3 - ageing 48 hrs.

Figs.3.17 and 3.18 show the SEM photographs of tensile fracture surface of latex reclaim vulcanizate before and after ageing. Before ageing, the fracture surface shows a number of tear lines with small pitted areas. The small pits which appear on the surface may be formed due to the removal of loosely bound agglomerates from the matrix during fracture (The cracks on the surface are more visible and broad when compared to NR vulcanizate). This is probably the reason for the lower tensile strength compared to the NR vulcanizates. The aged tensile fracture surface of latex reclaim vulcanizates also shows the curved tear lines but a more crumbled fracture surface.

The SEM photograph of the abraded surface of the filled NR vulcanizate is shown in Fig.3.19. It gives a well defined ridge pattern and close spacing of the ridges. The formation of ridges by microtearing and the subsequent removal of material from the surface influence tensile strength and tear strength of the matrix.[18]

Fig.3.20 shows the SEM photograph of the abraded surface of the latex reclaim vulcanizate. Here the abrasion pattern is not well defined and shows a coarse pattern and the material removal is found to occur in small lumps. This is probably the reason for the lower abrasion resistance compared to the NR vulcanizate.

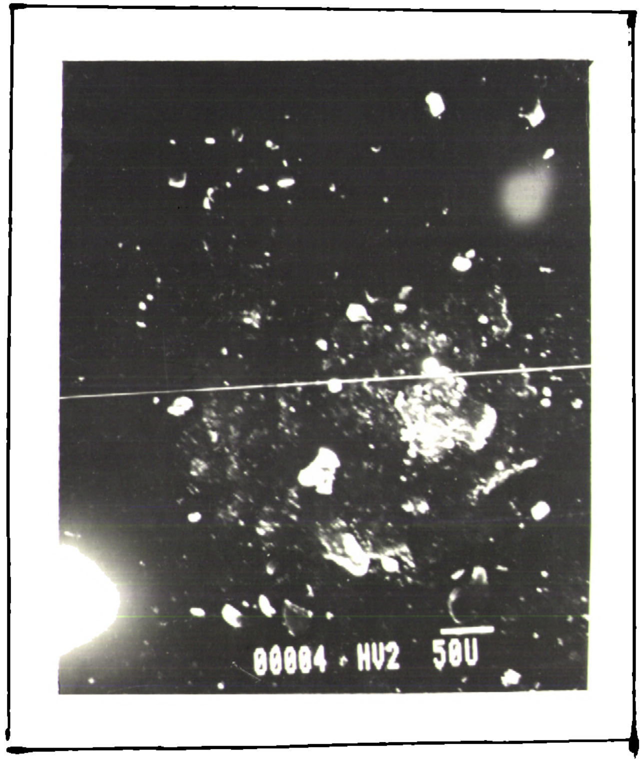

Fig.3.15 Before ageing

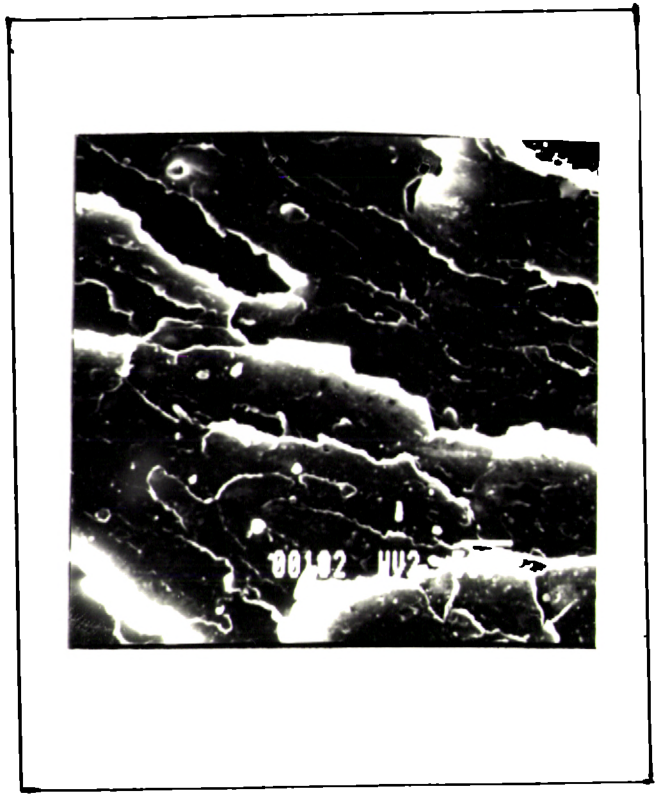

Fig.3.16 After ageing

SEM photographs of tensile fracture surface of NR vulcanizates

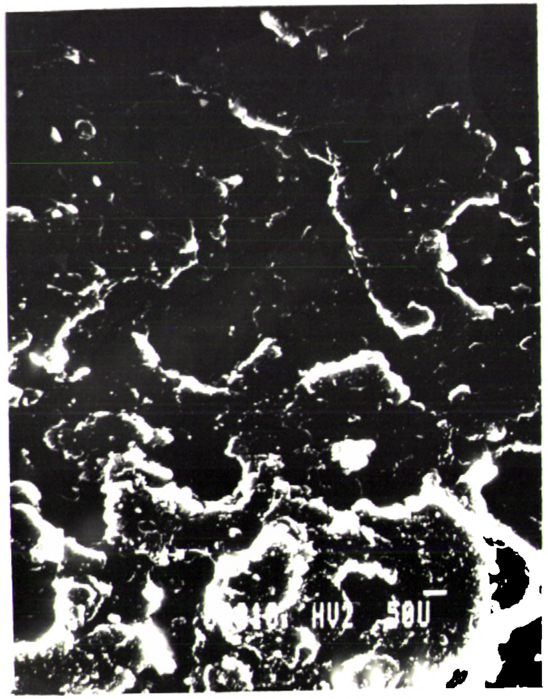

Fig.3.17 Before ageing

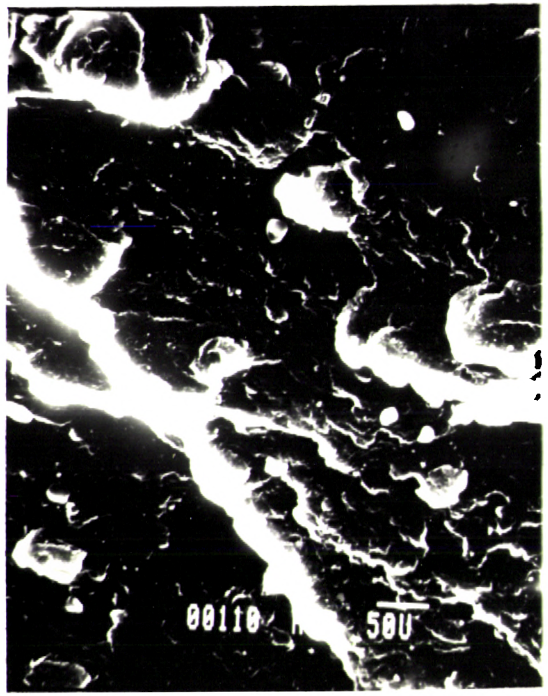

Fig.3.18 After ageing

SEM photographs of tensile fracture surface of latex reclaim vulcanizates

Fig.3.19 NR (A_2)

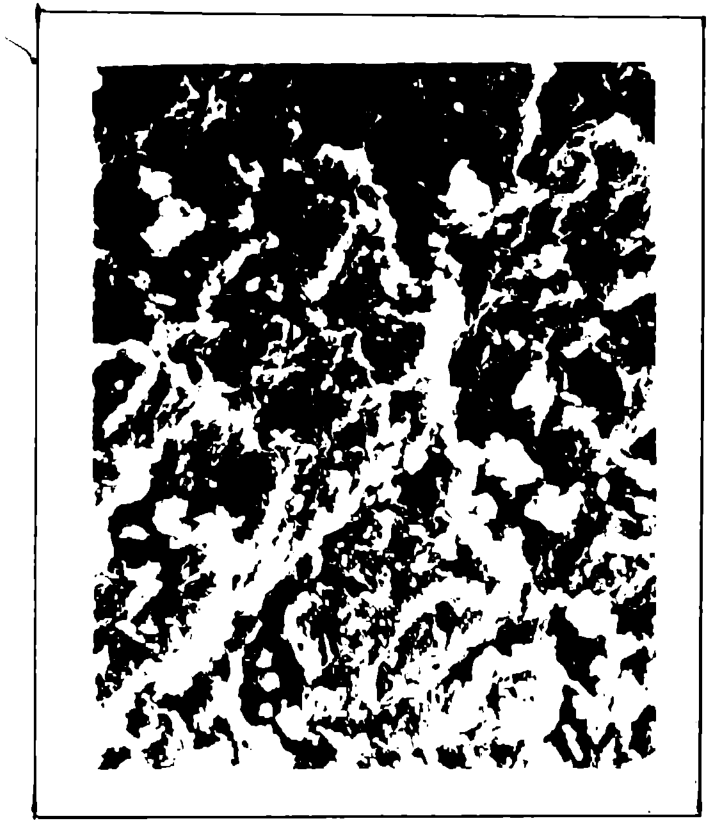

Fig.3.20 Latex reclaim (B_2)

SEM Photographs of the abraded surface of vulcanizates.

CONCLUSION

The study shows that the ageing resistance of the reclaimed rubber vulcanizates can be improved by the use of an efficient vulcanization system.

PART IV

PRODUCTION OF LATEX RECLAIM FROM THREAD WASTE AND FOAM WASTE AND THEIR CHARACTERIZATION

INTRODUCTION

Latex thread and latex foam industry generate a good percentage of latex product waste. In literature some methods are available about the reclaiming of latex foam waste as described below.

Flood and Mulligan[19] describe an apparatus to pick up spilled latex foam squeezed out of the moulds. The spilled foam is then desensitized by the addition of dilute alkali hydroxide or alkali borate solution which prevents gelling of the foam so that this reclaimed foam may be added to fresh latex foam and reused. P.J.Dasber[20] describes another process which converts the waste latex foam rubber to grannular size suitable for acid or alkali reclaiming by the pan or autoclave process. Pearson and Schweller[21] also describe a process to reclaim the 'flash' which is the foam oozing out of the mating edges of the mould. The reclaimed foam is usually referred to as desensitized foam, the accelerators having been eliminated during this reclaiming process.

In this study we report the reclaiming of thread waste and foam waste using MBT (Mercapto benzothiazole) as the reclaiming agent.

EXPERIMENTAL

The waste latex products such as thread waste and uncured foam waste (flash) were passed through a two roll mill at a friction ratio of 1:1.25 with a tight nip at room temperature for 3 minutes so that the material undergoes mechanical breakdown. Then MBT and highly masticated NR were added to the ground latex products according to the formulation given in Table 3.7. The homogenization of the reclaims was done for another 3 min. in a cold mill and then the reclaimed rubber was removed from the mill in the form of a sheet. The properties of reclaimed rubbers like Mooney viscosity, initial plasticity, volatile matter, acetone extract, ash content, free sulphur, and rubber hydrocarbon content were determined according to the relevant ASTM standards.

RESULTS AND DISCUSSION

Table 3.8 shows the properties of the reclaims prepared from thread waste and uncured foam waste. The Mooney viscosity and initial plasticity values of the reclaim are found to be in the processable range and so it can be easily incorporated into natural as well as synthetic rubbers. The Mooney viscosity of these reclaims are found to be higher than that prepared from the examination gloves. This is an indication of the poor quality of the reclaims produced from thread waste and foam waste. The high ash content of the foam waste may be due to the filler incorporated to the latex foam compound. The amount of free sulphur in the reclaims show the presence of unutilized sulphur in the latex thread

Table 3.7: Formulation for reclaiming thread waste and foam waste

Ingredients (g)	H	I
Thread waste	100	
Foam waste		100
Masticated NR	20	20
MBT	0.5	0.5

Table 3.8: Properties of Latex Reclaim

Properties	H	I
Mooney viscosity ML (1+4) 100°C	48	54
Initial plasticity P_0	35	46
Free sulphur (% by mass)	0.95	1.54
Volatile matter (% by mass)	0.58	0.67
Ash content (% by mass)	10.94	48.42
Rubber hydrocarbon content (%)	87.53	49.37

and foam waste. Comparatively higher free sulphur content of foam waste may be due to the uncured nature of the foam waste.

CONCLUSION

The latex reclaim prepared from the foam waste and thread waste contain only a lower amount of rubber hydrocarbon compared to that prepared from examination gloves.

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Chapter 4

UTILIZATION OF LATEX RECLAIM IN ELASTOMER BLENDS

PART I

STUDIES ON LATEX RECLAIM (GLOVES) /BR BLENDS AND THEIR COMPARISON WITH NR/BR BLENDS

The reclaiming of latex products like examination gloves, latex thread, foam waste etc. show that, the one produced from waste examination gloves [here after referred to as LR(G)] give comparatively high quality reclaim and it can be processed like raw NR. In this study, the latex reclaim prepared from examination gloves is used for making blends with BR.

Blends of natural rubber (NR) and polybutadiene (BR) are widely used in the manufacture of tyre especially for tyre tread and sidewall. In blends with natural rubber, polybutadiene improves resistance to tread wear and groove cracking without reduction in resilience. Sarbach and co–workers[1] reported a 20% higher tread wear index for 50/50 NR/BR over NR alone. Better oil extension and higher black loadings are the additional benefits made possible by using BR along with NR.[2,3]

In addition to improved tread wear resistance, improved cold weather performance is also reported for NR/BR blends compared to NR alone. However, the improvements in elasticity and abrasion resistance are at the expense of tensile strength and modulus of NR. Also the addition of NR to BR improves the processing properties of NR. Mill mixing of 50/50 NR/BR blend is much easier than that of BR alone.

There are many references in literature which have addressed the issue of optimising the properties of NR/BR blends.[4-14] But blends of reclaimed NR with BR are not reported so far since usually NR reclaim possess inferior mechanical properties.

The aim of the present study is to evaluate the properties of LR(G)/BR blends and to suggest a suitable blend as retread material. A commercially viable tread compound based on 60/20/20 NR/LR(G)/BR blend was evaluated for its suitability to be used as a retread material.

EXPERIMENTAL

Polybutadiene (BR) was masticated on a laboratory two roll mill and the latex reclaim prepared from examination gloves in the form of a sheet was added at different percentages and the blends were compounded according to the formulation given in Table 4.1. To compare the properties of reclaim/BR blends, NR/BR blends were also prepared at different percentages according to the formulation given in the same table.

The optimum cure time T_{90} and the scorch time T_{10} of the compounds were determined on a Goettfert Elastograph model 67.85.

The compounds were then vulcanized up to their respective optimum cure time in an electrically heated hydraulic press at 150°C.

The tensile properties of the vulcanizates were evaluated using dumbbell shaped samples punched out of the compression moulded sheets on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM D 412-80. The tear resistance of the samples were evaluated as per ASTM D 624-81.

Compression set was evaluated as per ASTM D 395-1982. Rebound resilience of the vulcanizates were evaluated using Dunlop tripsometer as per B.S. 903 Part 22, 1950. The abrasion resistance of the samples was tested using a DIN abrader.

To improve the ageing resistance of the LR(G)/BR blends, the blends were also prepared with a low sulphur-vulcanization system as given in Table 4.2. For comparison NR/BR blends were also prepared with a similar formulation. The compounds were then vulcanized up to their respective optimum cure time. Tensile and tear properties of the vulcanizates were evaluated as per standard procedure.

Retension in tensile properties and tear strength were evaluated after ageing the samples at 70°C for 24 and 48 hrs.

The carbon black dispersion of the blends were investigated by photomicroscopy. Specimens for photomicroscopic studies were prepared by carefully microtoning a thin section of the sample by using a razor blade. The specimen was then sandwiched between two rectangular glass sample holders and observed under the microscope with a magnification of 30 and the photographs were taken using a Polaroid MP4 land camera.

The fracture mechanism of the blends were evaluated by viewing their fracture surfaces through a scanning electron microscope. Thin specimens of the tensile and tear fractured surfaces of the samples were sputter coated with gold and the SEM photographs were taken using a Hitachi model scanning electron microscope.

Two compounds T_1 and T_2 were selected for retread and their formulations are given in Table 4.3. The compound were prepared and vulcanized up to their optimum cure time. Tensile properties, tear resistance, abrasion resistance, hardness and ageing resistance of the vulcanizates were evaluated.

RESULTS AND DISCUSSION

The cure characteristics of LR(G)/BR and those of NR/BR blends are shown in Table 4.1. In both cases there is a gradual increase in the cure time and scorch time as the BR content increases. But the scorch and cure time values of LR(G)/BR blends are much lower than those of the corresponding NR/BR blends. This shows the presence of crosslinking

Table 4.1: Formulation and vulcanizate properties of LR(G)/BR and NR/BR blends

Latex Reclaim (Gloves) (R.H.C.- 91.4%)	110	99	77	55	33	11	0						
NR								100	90	70	50	30	10
BR	0	10	30	50	70	90	100		10	30	50	70	90
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
Vulkanox 4020	1	1	1	1	1	1	1	1	1	1	1	1	1
MOR	1	1	1	1	1	1	1	1	1	1	1	1	1
Carbon Black (HAF-N 330)	45	45	45	45	45	45	45	45	45	45	45	45	45
Aromatic oil	6	6	6	6	6	6	6	6	6	6	6	6	6
Sulphur	2	2	2	2	2	2	2	2	2	2	2	2	2
Cure characteristics													
Scorch time (T_{10})	1.08	1.4	1.48	2.2	3.0	5.4	6.5	2.9	3.2	3.5	3.8	4.48	4.56
Cure time (T_{90})	2.2	2.9	3.16	4.2	5.9	11.8	13.8	8.4	9.2	10.3	11.2	12.3	12.9
Vulcanizate properties													
Abrasion resistance (volume loss, cc/hr)	3.87	3.57	3.37	2.65	1.92	1.07	0.892	2.74	2.54	2.23	2.007	1.67	0.937
Compression set (%)	30.16	29.41	25.42	23	20.12	18.57	17	33.74	30.72	26.40	24.20	22.18	19.04

precursors and/or unreacted curatives in the waste latex gloves.[15] It may also be noted that 100% latex reclaim compound shows the lowest values of scorch time and cure time.

Fig.4.1 shows the the variation in tensile strength of LR(G)/BR and NR/BR blends with BR content. The tensile strength of LR(G)/BR blend are only slightly lower than those of the NR/BR blends especially at higher percentages of BR. This shows that reclamation process done at room temperature does not result in an appreciable degradation of the rubber hydrocarbon present in the latex reclaim. But the ageing resistance of these blends is found to be comparatively low (not shown in the figure). This may be due to the higher percentage of polysulphidic crosslinking in the reclaim.

Fig.4.2 shows the variation in tear strength of LR(G)/BR and NR/BR blends with BR content. The tear strength of LR(G)/BR blends are not much lower than those of the NR/BR blends. This further shows the better quality of rubber hydrocarbon derived from the latex reclaim.

Fig.4.3 shows the variation in elongation at break of LR(G)/BR and NR/BR blends with BR content. The elongation at break of the reclaim blends show a significant reduction compared to those of NR/BR blends. It may be due to the increased crosslink density in the reclaim blends.

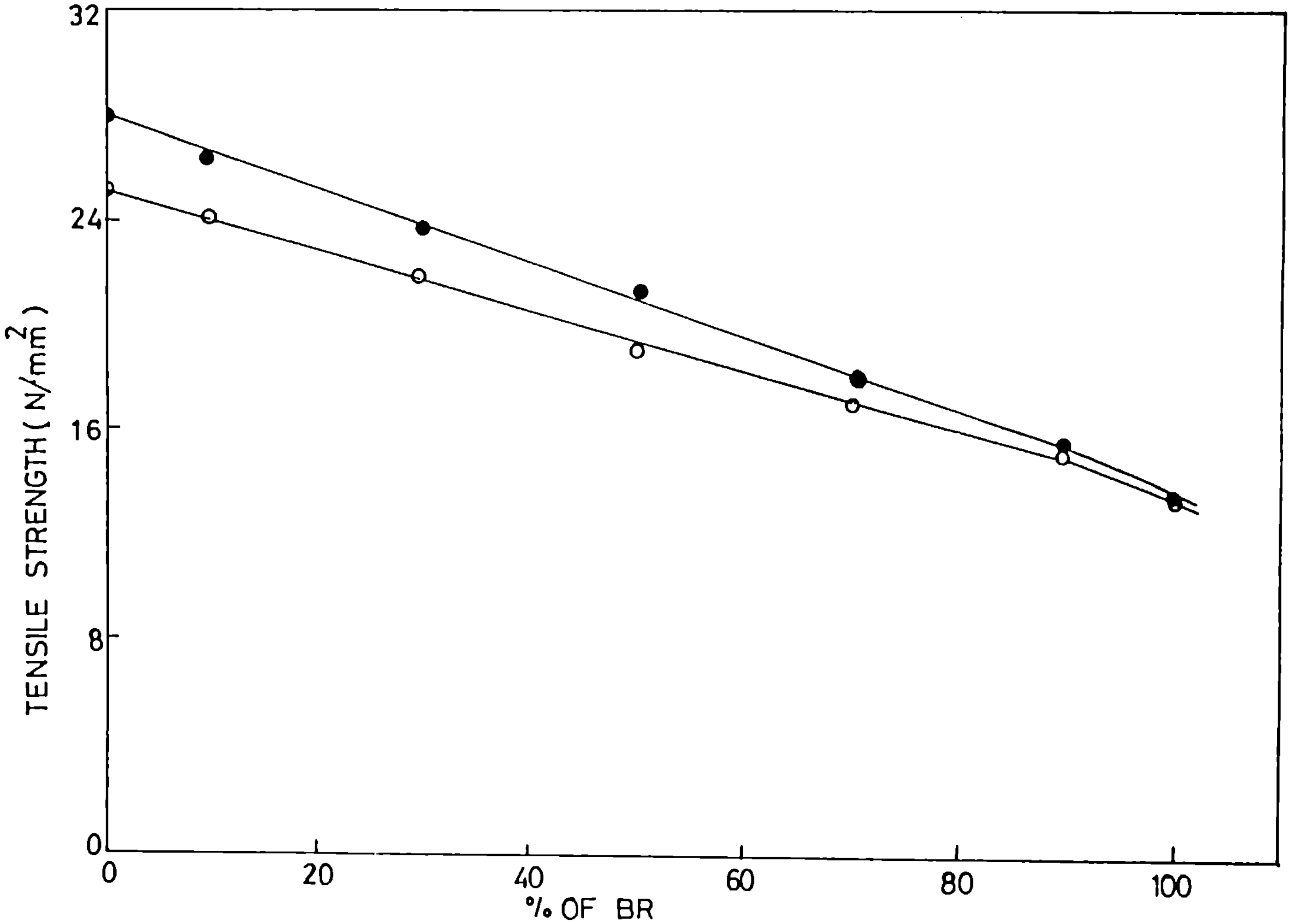

Fig.4.1; Variation in tensile strength of LR(G)/BR and NR/BR blends with BR content. (●) - NR/BR, (○) - LR(G)/BR.

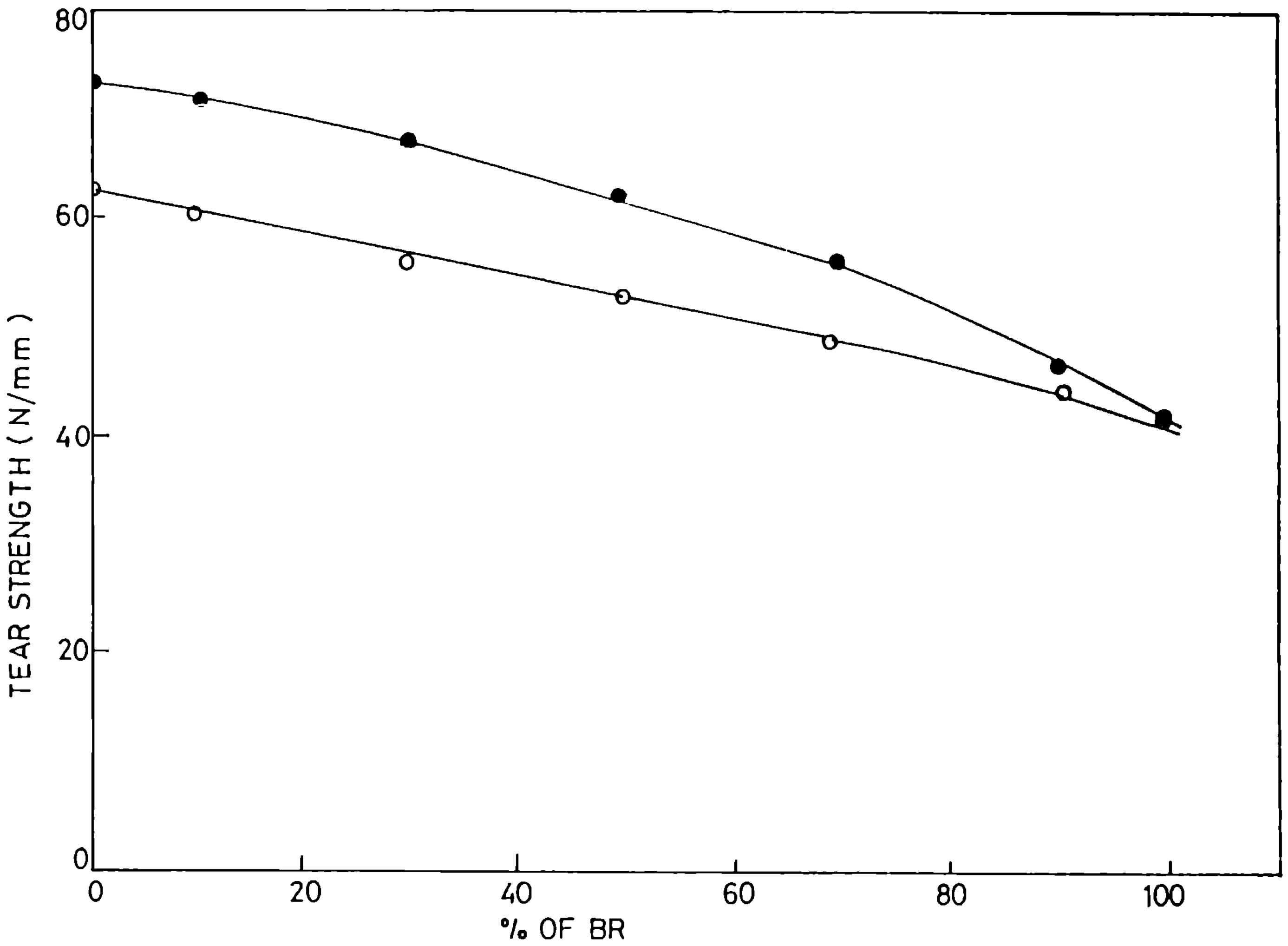

Fig.4.2: Variation in tear strength of LR(G)/BR and NR/BR blends with BR content. (●)- NR/BR, (○)- LR(G)/BR.

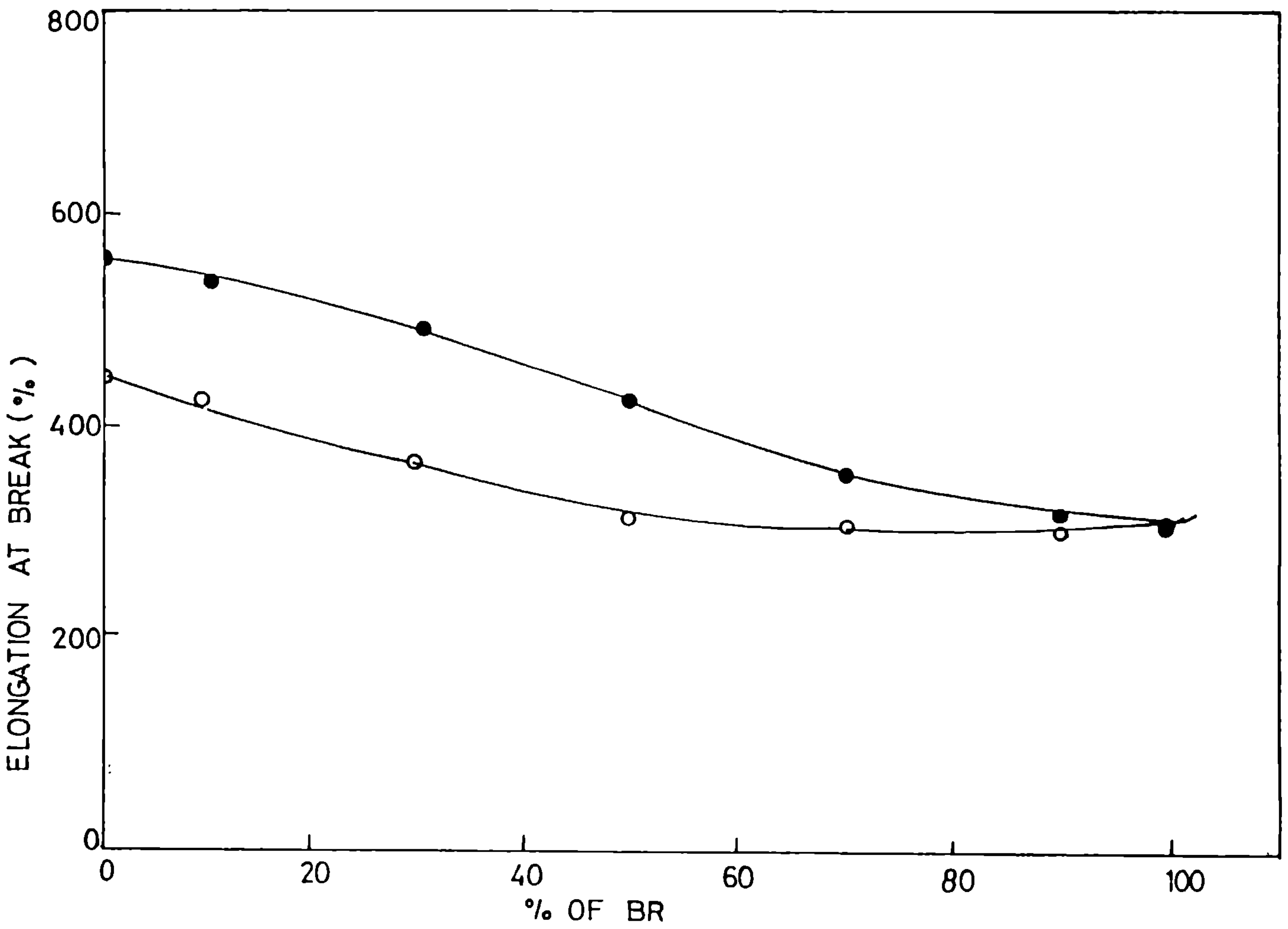

Fig.4.3: Variation of elongation at break of LR(G)/BR and NR/BR blends with BR content. (●) - NR/BR, (○)- LR(G)/BR.

Fig.4.4 shows the variation of 100% modulus of LR(G)/BR and NR/BR blends with BR content. The modulus of LR(G)/BR blends are higher than those of the NR/BR blends at all compositions. This may be attributed to the increased amount of crosslink density in LR(G)/BR blends.

Fig.4.5 shows the rebound resilience of LR(G)/BR and NR/BR blends. The rebound resilience of NR/BR blends are higher than those of reclaim blends at all compositions.

The abrasion resistance of LR(G)/BR blends is inferior to that of NR/BR blends (Table 4.1). This may be due to the lower bonding between the reclaim and BR. The compression set values of LR(G)/BR blends are lower than those of the NR /BR blends at all composition which further confirms the increased crosslink density in the reclaim blends.

Figs.4.6 and 4.7 are the photomicrographs of 70/30 LR(G)/BR and NR/BR blends. In both cases LR(G) and NR phases are the continuous phase and NR/BR surface show a comparatively better dispersion compared to reclaim blend. Figs. 4.8 and 4.9 are the photomicrographs of 30/70 LR(G)/BR and NR/BR blends respectively. Since BR phase is the continuous phase, the carbon black dispersion is more or less similar in both cases.

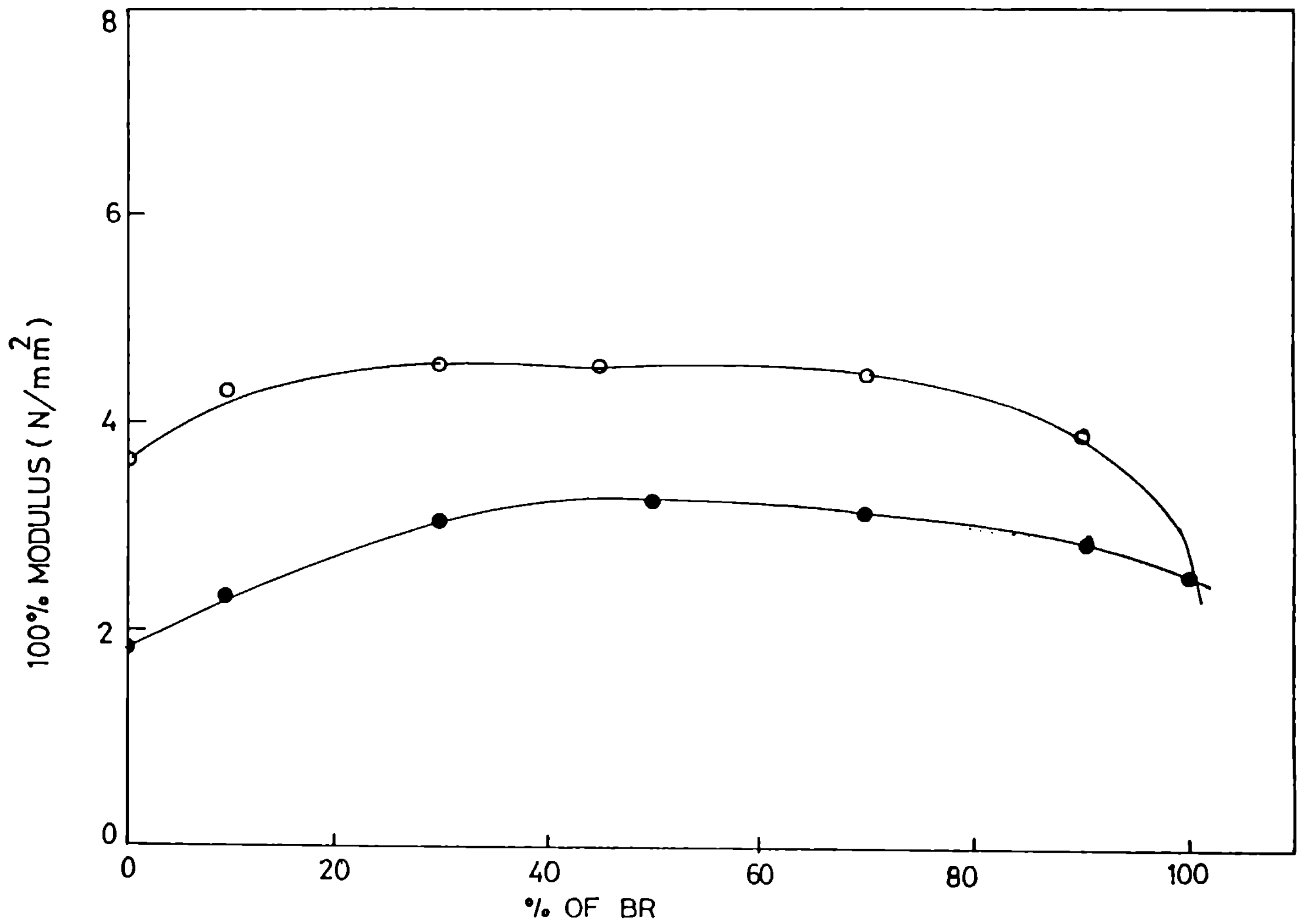

Fig.4.4: Variation of modulus of LR(G)/BR and NR/BR blends with BR content. (●) NR/BR, (○) LR(G)/BR.

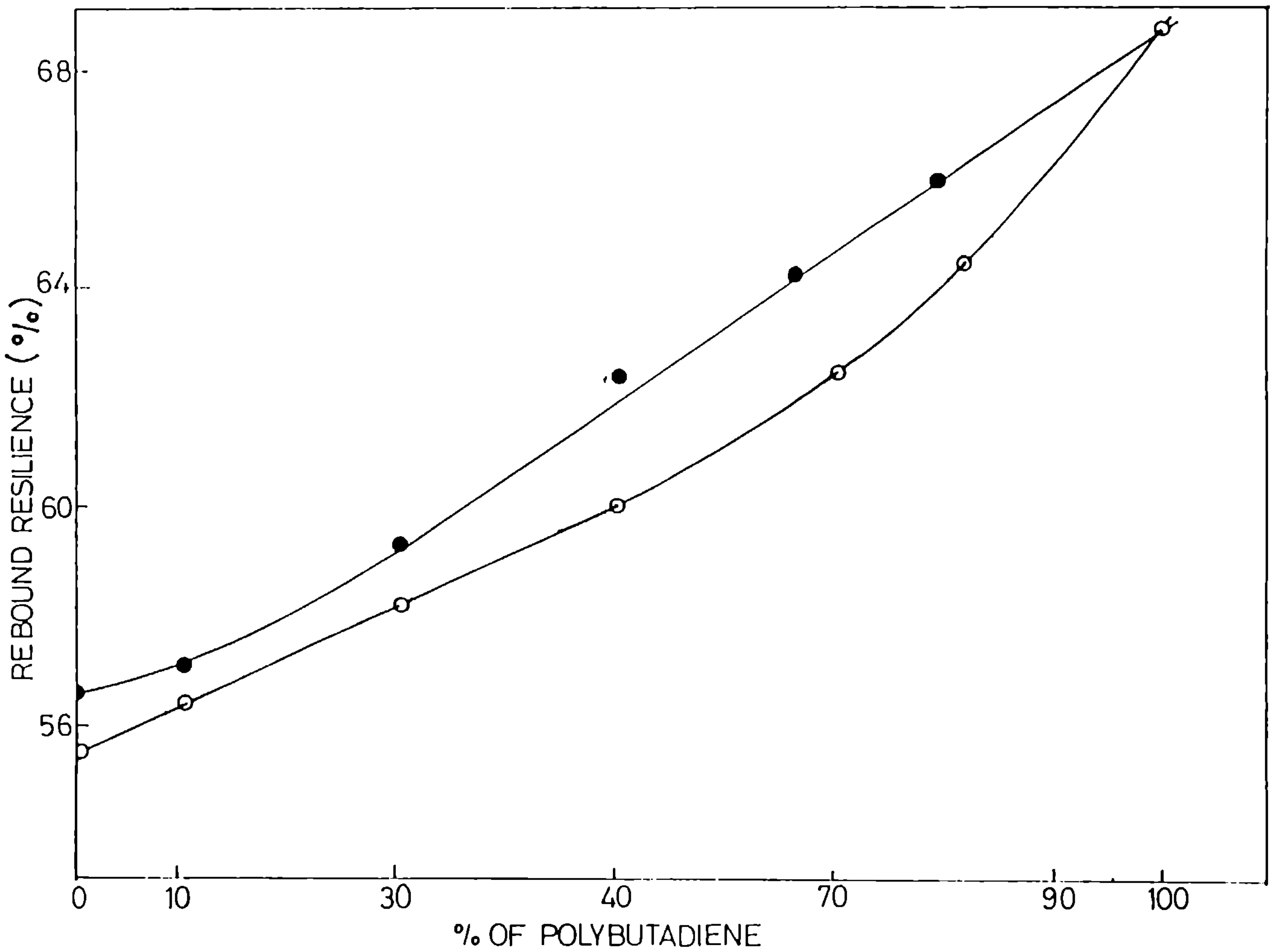

Fig.4.5: Variation of rebound resilience of LR(G)/BR and NR/BR blends with BR content~~s~~. (●) NR/BR, (○) LR(G)/BR

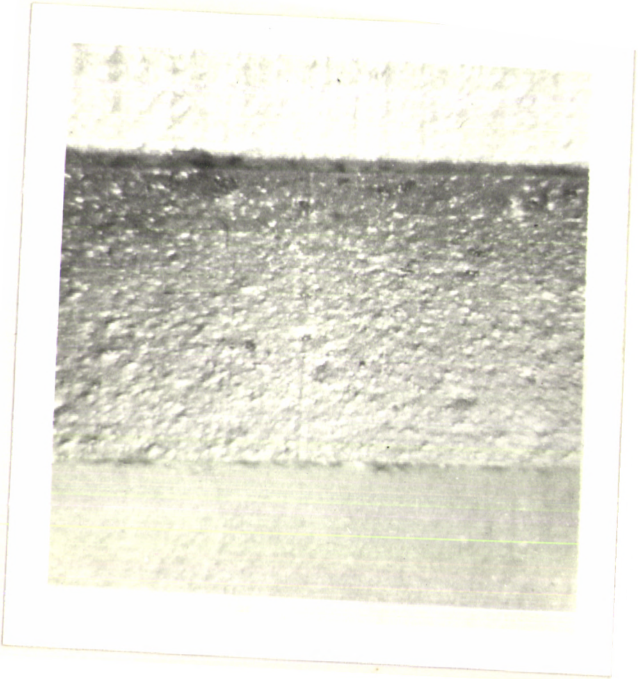

Fig.4.6 LR(G)/BR

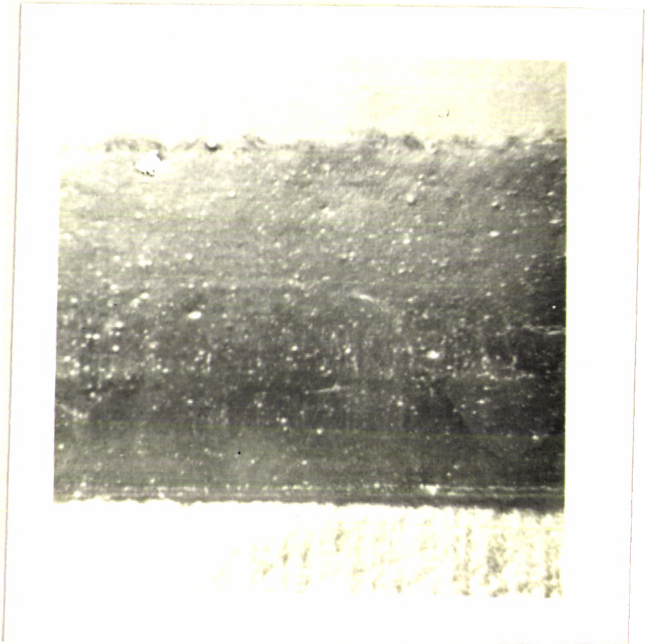

Fig.4.7 NR/BR

Photomicrographs of 70/30 blends

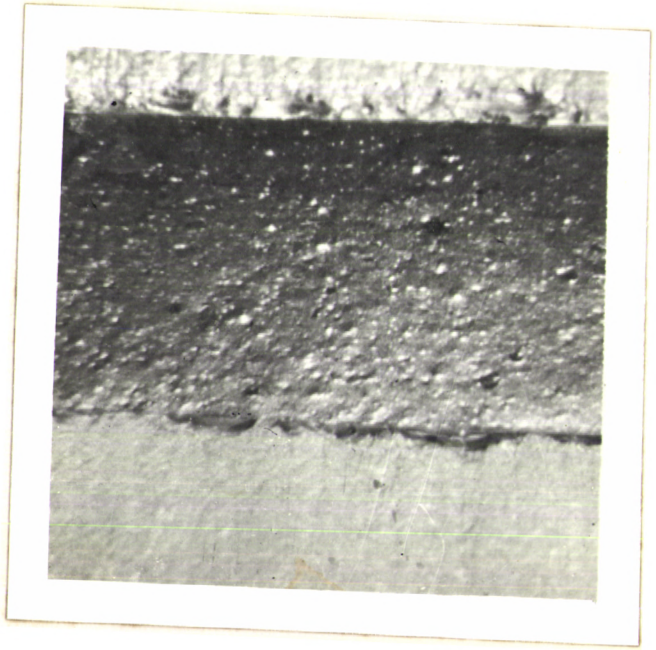

Fig.4.8 LR(G)/BR

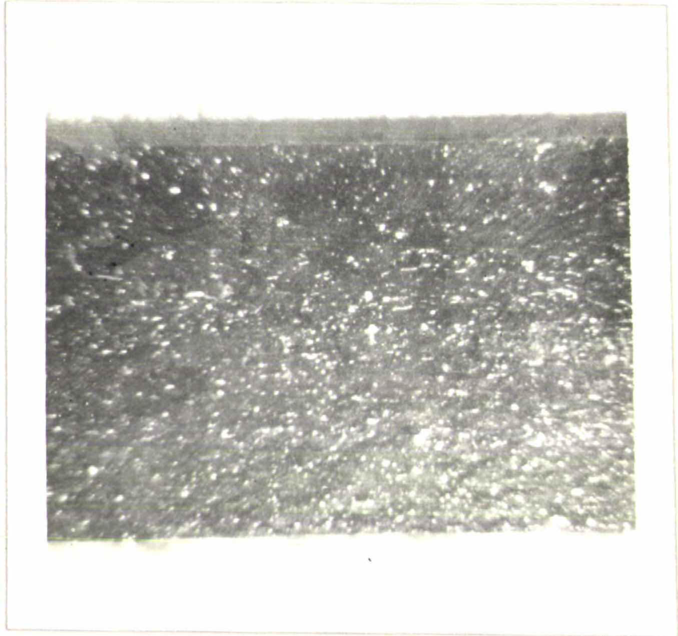

Fig.4.9 NR/BR

Photomicrographs of 30/70 blends

Table 4.2 shows the cure characteristics of LR(G)/BR and NR/BR blends with a low sulphur vulcanization system. Here also in both cases there is a gradual increase in the scorch time and cure time as the BR content increases and the scorch and cure time values of LR(G)/BR blends are lower than those of the corresponding NR/BR blends. The difference in scorch time of LR(G)/BR and NR/BR blends is comparatively low for EV system.

Figs.4.10 and 4.11 show the variation in tensile strength of LR(G)/BR and NR/BR blends (EV system) with BR content, before and after ageing. The tensile strength of LR(G)/BR blends is lower than that of NR/BR blends at higher percentage of NR. But at higher percentages of BR, the tensile properties of both the blends are comparable. The ageing resistance of LR(G)/BR blends are only slightly inferior to those of NR/BR blends at all compositions.

Figs.4.12 and 4.13 show the tear strength of LR(G)/BR and NR/BR blends (EV system) before and after ageing. The tear strength of LR/BR blends are not much lower than those of NR/BR blends. But the ageing resistance of the reclaim blends is greatly improved with a low sulphur vulcanization system. This is due to the low percentage of polysulphidic crosslinks formed with an EV system.

Table 4.2: Formulations and cure characteristics of LR(G)/BR and NR/BR blends (EV system)

Latex reclaim (gloves) (R.H.C.-91.3%)	110	88	66	44	22	0					
NR							100	80	60	40	20
BR	0	20	40	60	80	100	0	20	40	60	80
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Vulkanox 4020	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Carbon Black (HAF-N 330)	40	40	40	40	40	40	40	40	40	40	40
Aromatic oil	5	5	5	5	5	5	5	5	5	5	5
MOR	3.5	3.55	3.6	3.65	3.7	3.75	3.5	3.55	3.6	3.65	3.7
Sulphur	0.5	0.48	0.46	0.44	0.42	0.4	0.5	0.8	0.46	0.44	0.42
Cure characteristics at 150°C											
T_{10}, (Scorch time, min)	2.4	2.56	2.68	4.72	5.44	6.8	4.08	6.24	7.28	8.00	8.88
T_{90}, (Optimum cure time, min)	6.12	7.44	9.28	12.24	16.32	22.0	9.6	15.04	16.24	17.68	20.08

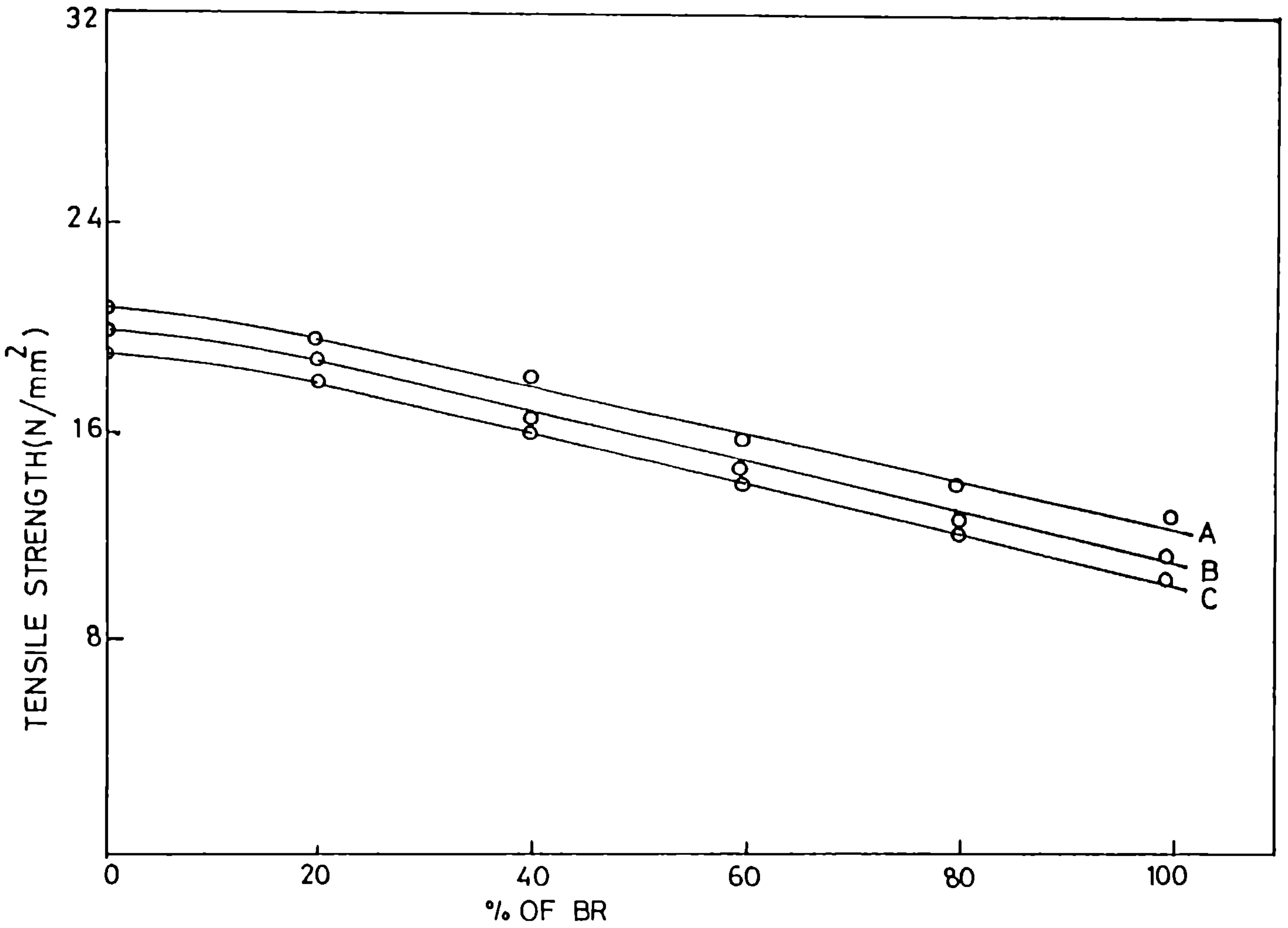

Fig.4.10: Variation in tensile strength of LR(G)/BR blends with BR content (EV System),(A)- Before ageing,(B)- After 24 hrs ageing at 70°C, (C)- After 48 hrs ageing at 70°C.

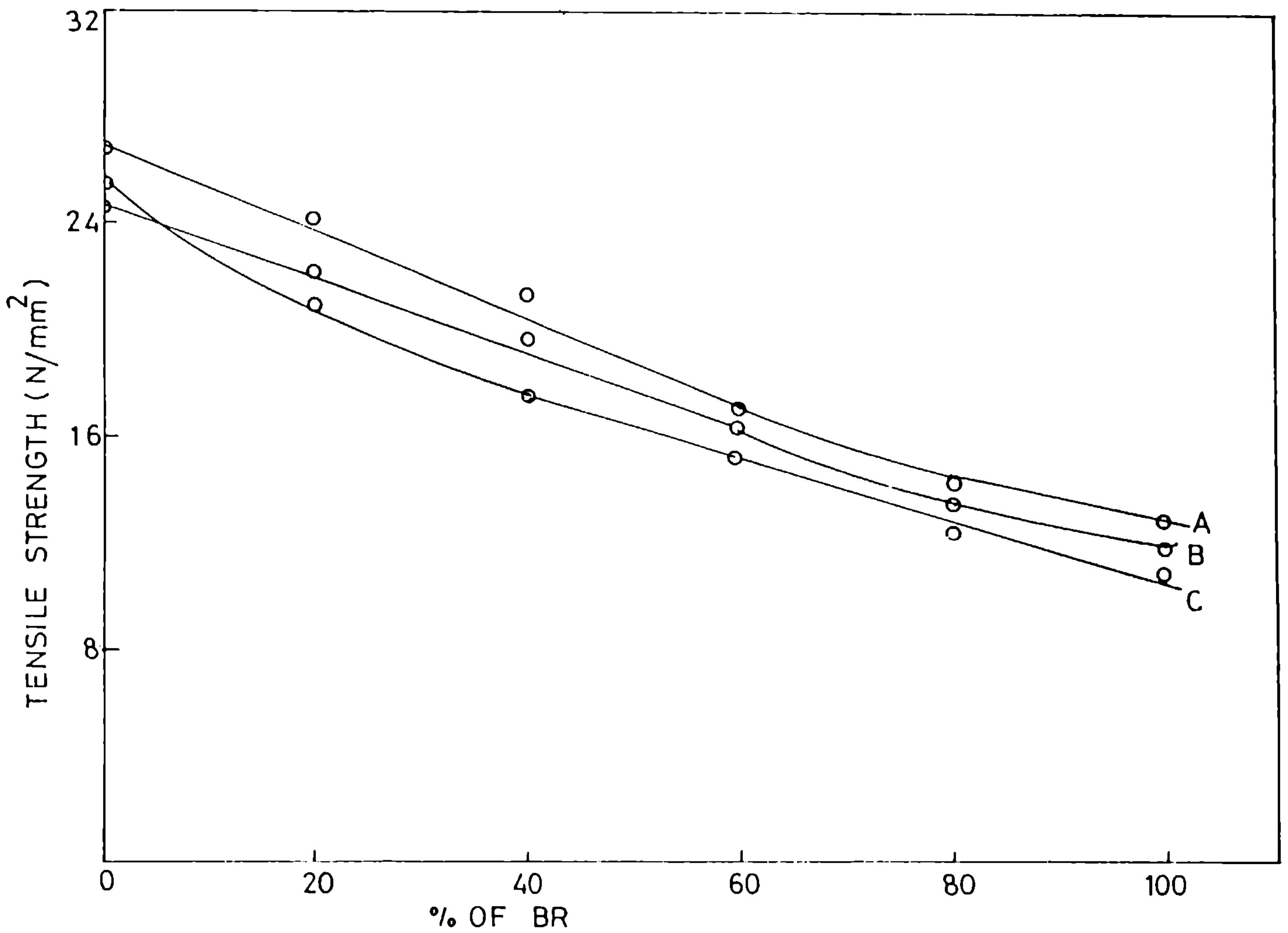

Fig.4.11: Variation in tensile strength of NR/BR blends with BR content. (EV System). (A)- Before ageing, (B)- After 24 hrs ageing at 70°C, (C)- After 48 hrs ageing at 70°C.

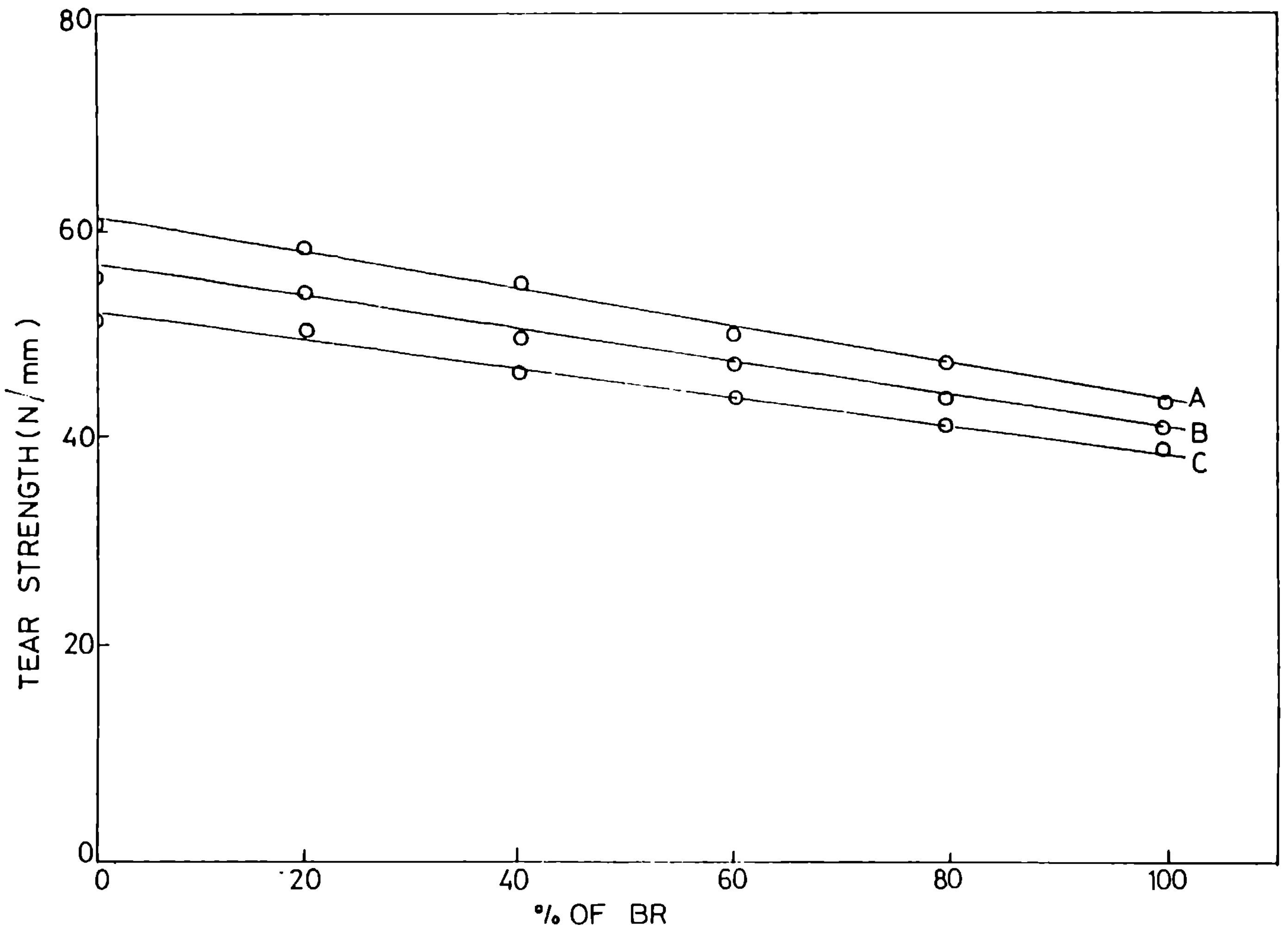

Fig.4.12: Variation in tear strength of LR(G)/BR blends with BR content (EV System). (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

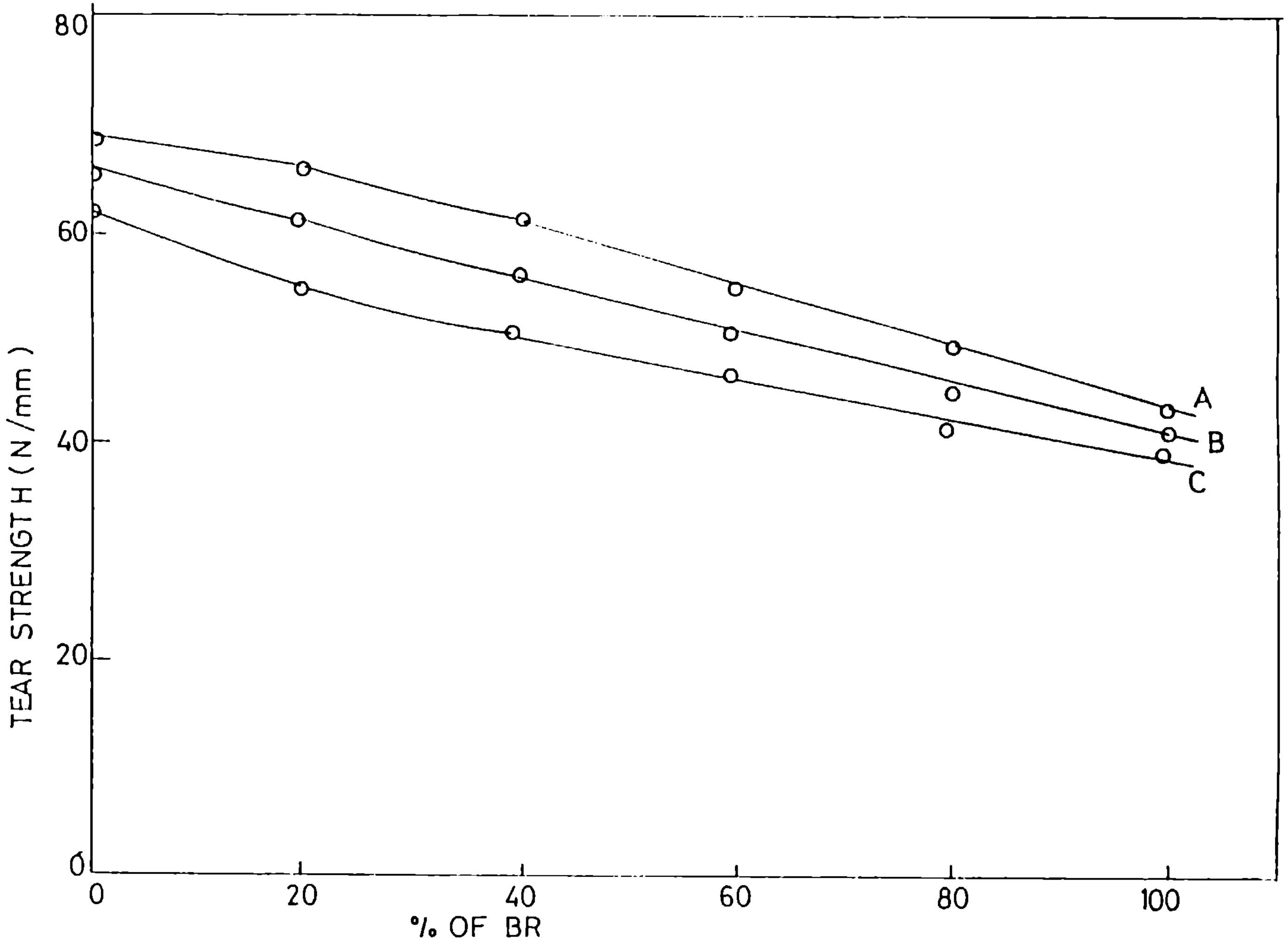

Fig.4.13: Variation in tear strength of NR/BR blends with BR content (EV System). (A)- Before ageing, (B)- After 24 hrs ageing at 70°C, (C)- After 48 hrs ageing at 70°C.

The variation of elongation at break of LR(G)/BR and NR/BR blends with BR content, and their retension after ageing are shown in Figs.4.14 and 4.15. The elongation at break of the reclaim blends is much lower than that of NR/BR blends especially at higher percentages of NR. This may be due to the increased crosslink density in the reclaim phase. Here also the retension in elongation at break of reclaim blends are improved when the blend formulation contains a low amount of sulphur.

Figs.4.16 and 4.17 show the variation of 100% modulus of LR(G)/BR and NR/BR blends with BR content before and after ageing. The 100% modulus of reclaim blends is higher than that of 100% BR vulcanizate before and after ageing, while that of NR/BR blends is lower than that of 100% BR. This may be due to the increased crosslink density in the reclaim blends.

Figs.4.18 and 4.19 are SEM photographs of the tensile fracture surface of 40/60 LR(G)/BR and NR/BR blends respectively. Both of them contain shear lines on the fracture surface. But in the case LR(G)/BR blend, the shear lines are more visible and broad compared to NR blends. This may result in lower tensile strength when compared with NR blends.

Figs.4.20 and 4.21 are the SEM photographs of tear fracture surface of 40/60 LR(G)/BR and NR/BR blend respectively. Both of them contain parabolic tear lines. The NR/BR blend surface is more uniform and contains randomly distributed tear lines which accounts for the

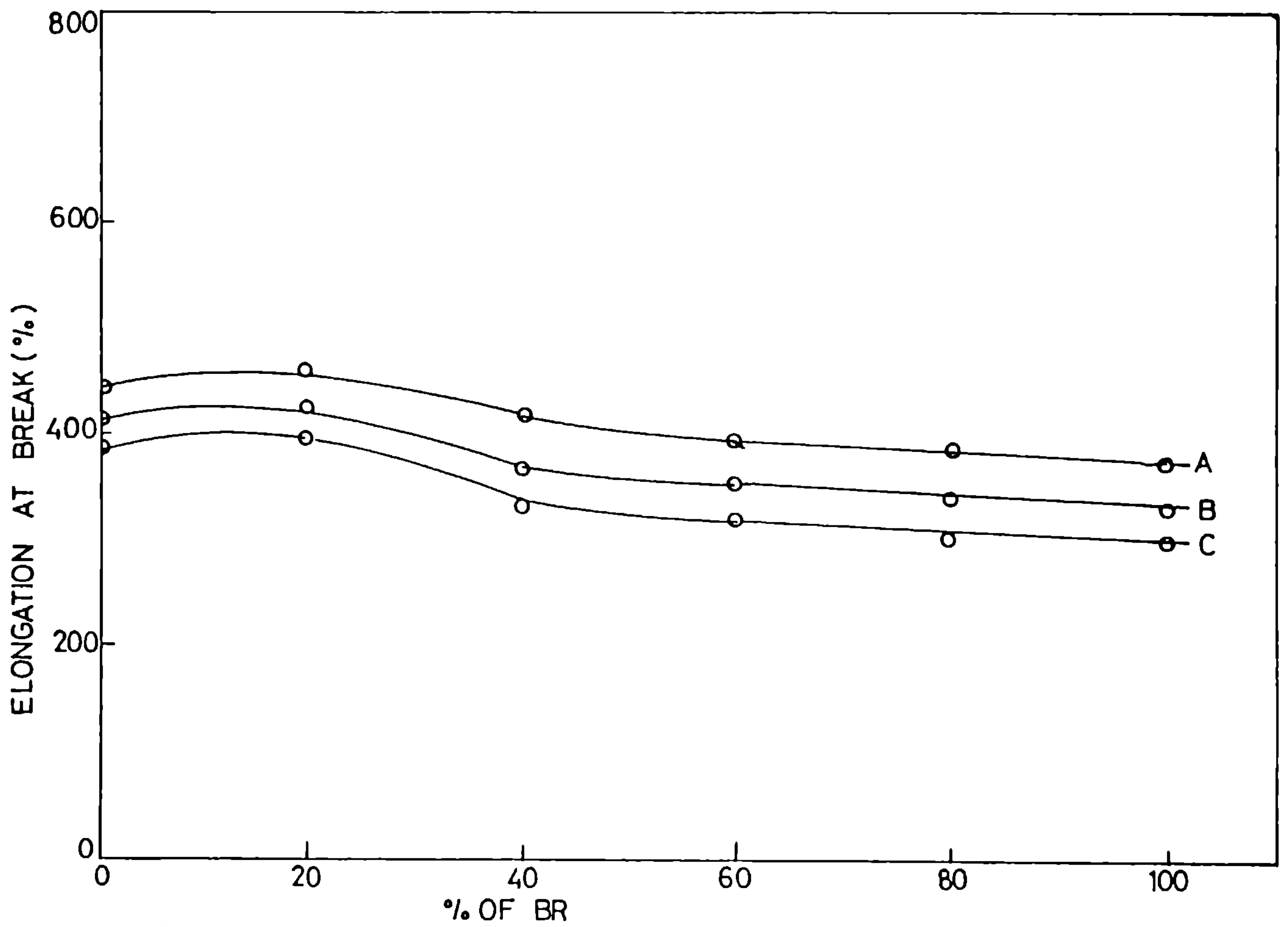

Fig.4.14: Variation of elongation at break of LR(G)/BR blends with BR content (EV System). (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

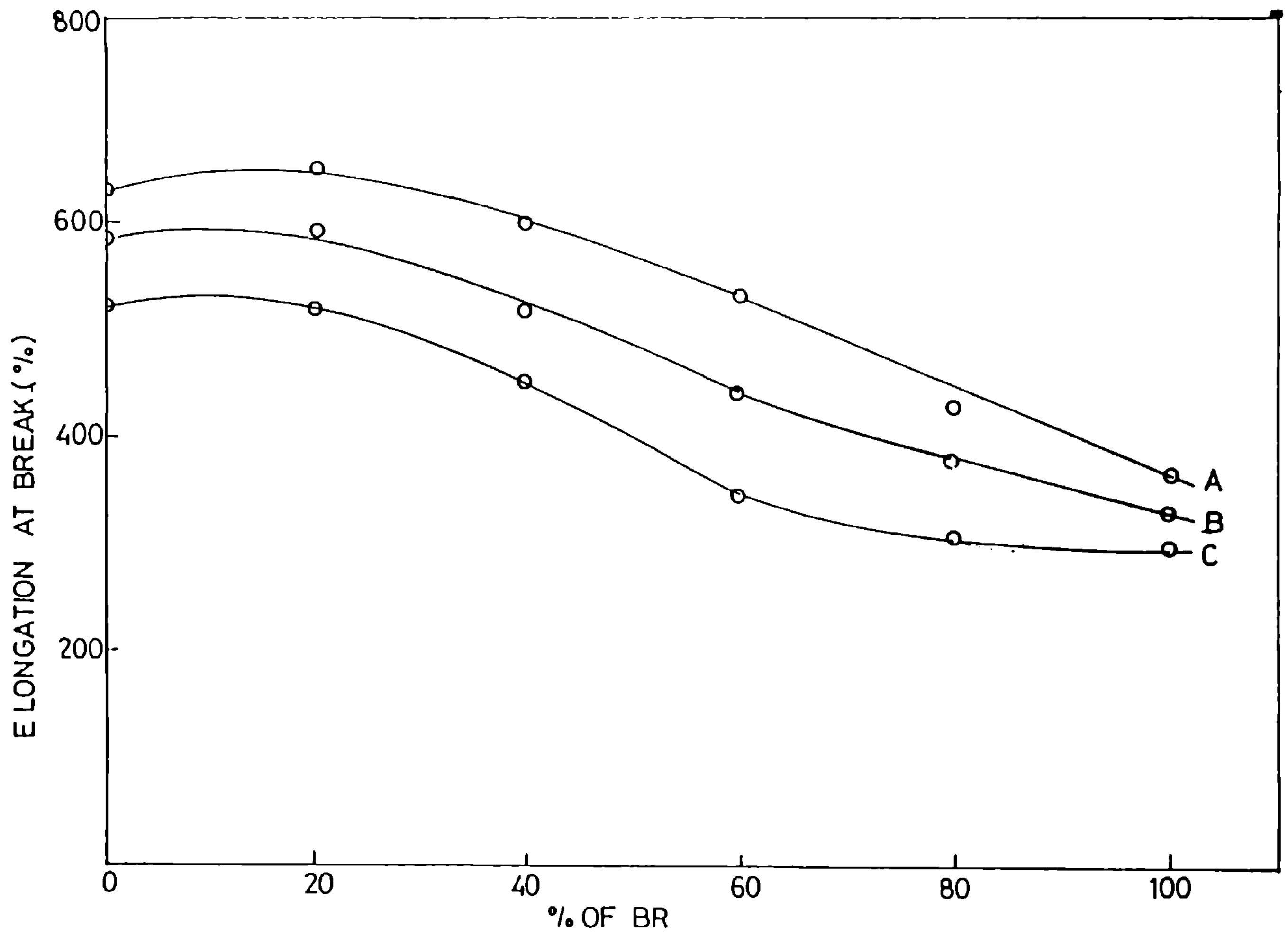

Fig.4.15: Variation of elongation at break of NR/BR blends with BR content (EV System). (A)- Before ageing, (B)- After 24 hrs ageing at 70°C, (C)- After 48 hrs ageing at 70°C.

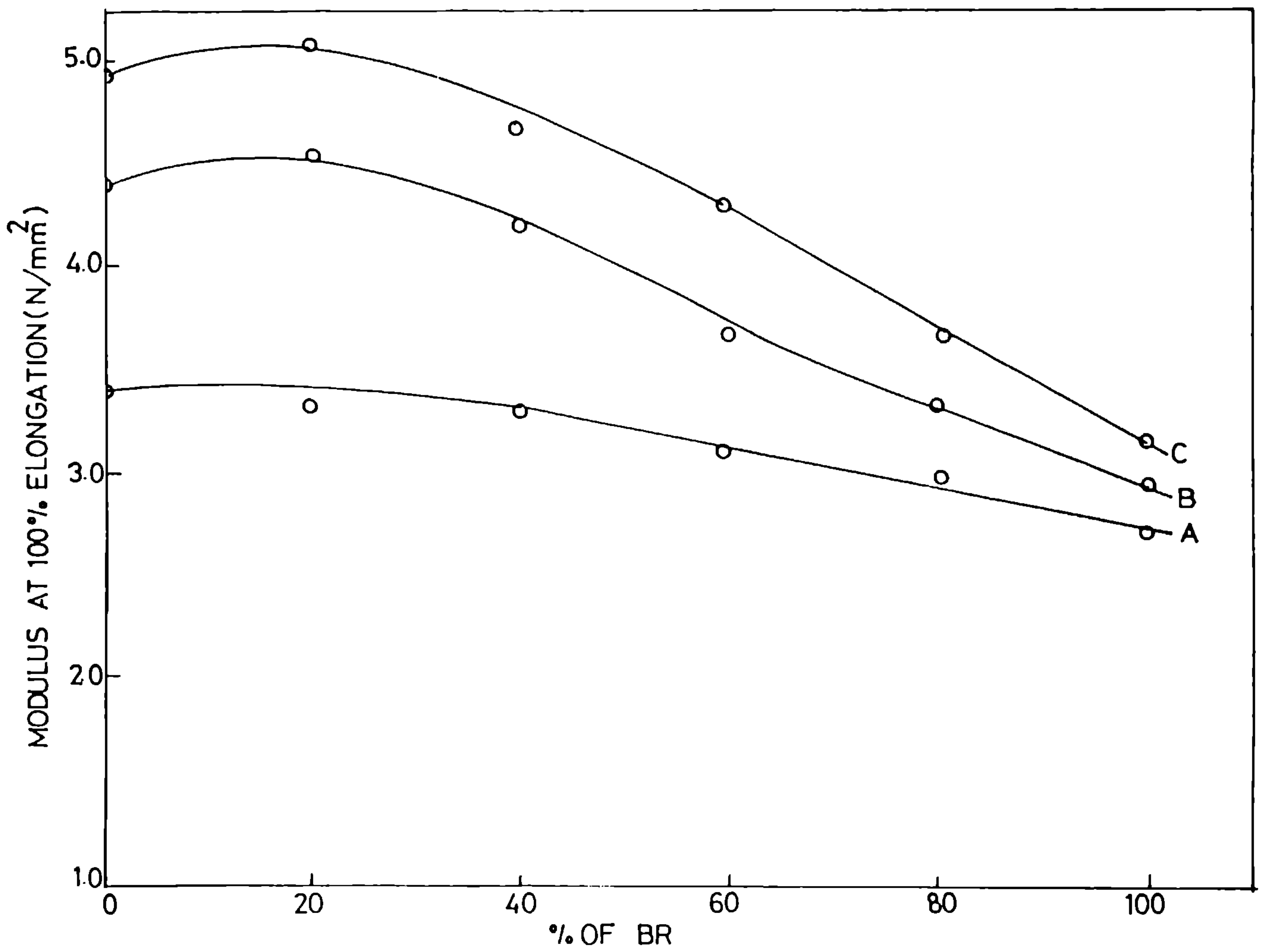

Fig.4.16: Variation of modulus of LR(G)/BR blends with BR content (EV System). (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

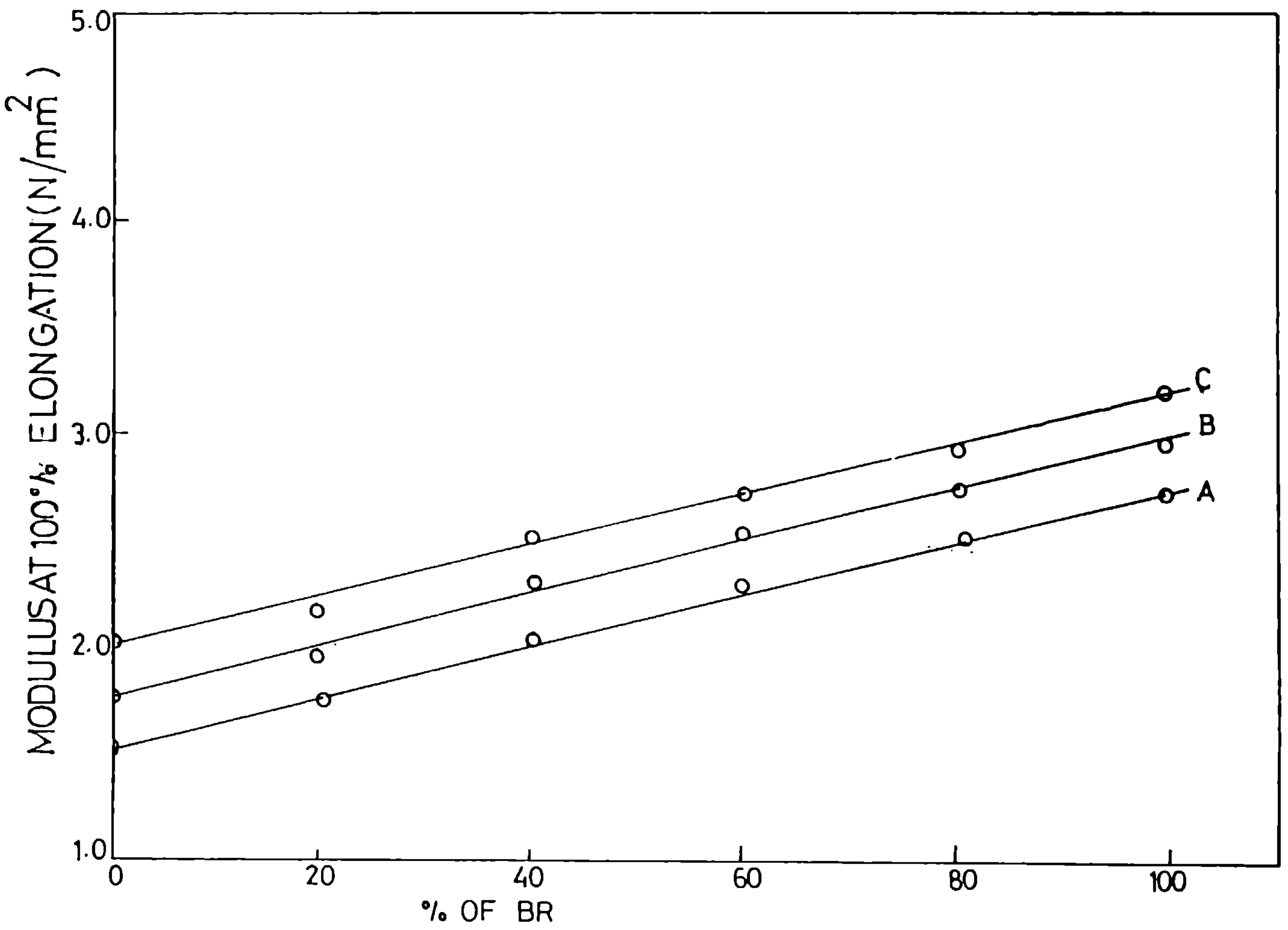

Fig.4.17: Variation in modulus of NR/BR blends with BR content (EV System). (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

Fig.4.18 LR(G)/BR

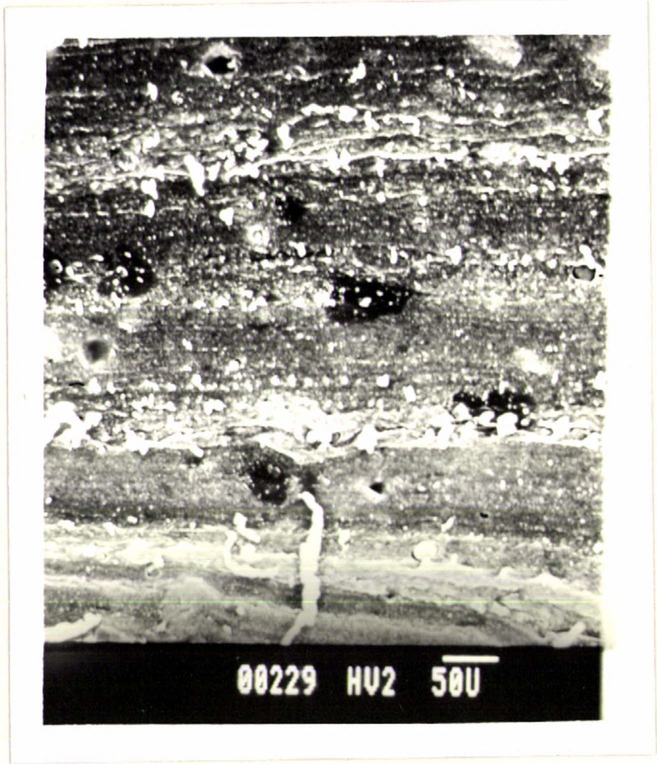

Fig.4.19 NR/BR

SEM Photographs of tensile fracture surface of 40/60 blends

Fig.4.20 LR(G)/BR

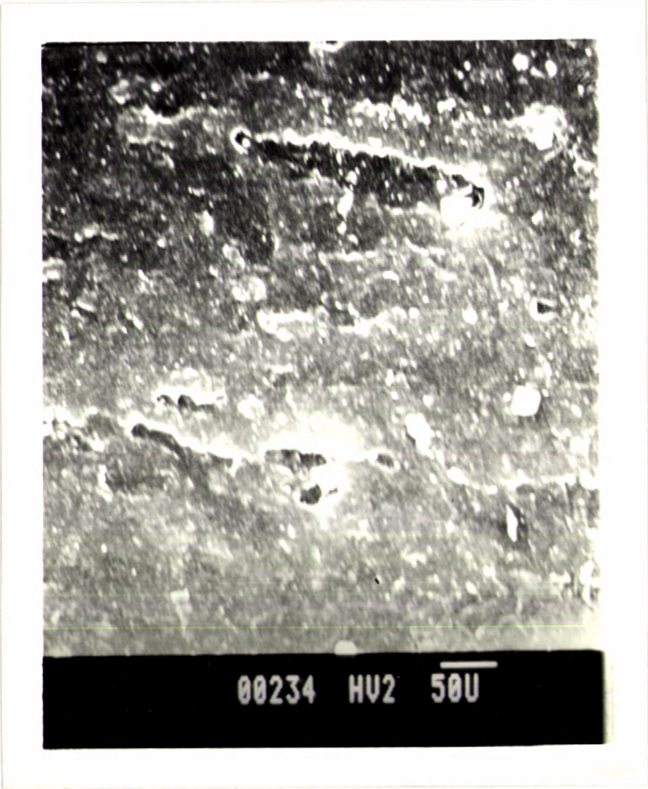

Fig.4.21 NR/BR

SEM Photographs of tear fracture surface of 40/60 blends higher tear resistance of NR/BR blend. But the tear fracture surface of LR(G)/BR blend show comparatively broad parabolic tear lines which give a rough torn surface resulting in lower tear strength compared to NR/BR blends.

Table 4.3 shows the cure characteristcs of the tread compounds T_1 and T_2. The scorch and cure time values of the compound T_1 is lower than those of the T_2 compound. This may be due to the higher percentage of reclaim in T_1. The scorch and cure time T_2 is found to be comparable to that of commercial tread compound.

Table 4.4 shows the mechanical properties of the proposed retread compound vulcanizates before and after ageing. Though vulcanizates T_1 and T_2 show comparable mechanical properties before ageing, the retension of properties is poor for vulcanizate T_1 compared to T_2. This may be due to the fact that T_1 contains a higher percentage of reclaim which may leads to a comparatively low ageing resistance. But vulcanizate T_2 which contains only a small percentage of latex reclaim show a better ageing resistance than T_1. For T_2 there is only a marginal reduction in abrasion resistance when 20 parts of NR being replaced by latex reclaim. The hardness of the vulcanizate T_2 is also within the IS limit of a tread compound. Therefore formulation T_2 is proposed for tread compounds.

Table 4.3: Formulation and cure characteristics of tread compounds

	T_1	T_2
NR	20	60
Latex reclaim (Gloves) (R.H.C.–91.4%)	66	22
Polybutadiene	20	20
ZnO	5	5
Stearic acid	2	2
Carbon black (HAF N–330)	40	40
Vulkanox 40:20	1	1
Aromatic oil	5	5
MOZ	0.8	0.8
Sulphur	2	2
Cure characteristics at 150°C		
T_{10} (Scorch time in min.)	1.3	1.9
T_{90} (Optimum cure time in min.)	2.5	5.9

Table 4.4: Vulcanizate properties of tread compounds

Properties	T_1	T_2
Tensile strength (N/mm^2)	23.17	25.87
Elongation at break (%)	483	556
Tear strength (N/mm)	58.4	65
Aged properties (Aged for 24 h at 100°C)		
Tensile strength (N/mm^2)	9.97	18.69
Elongation at break (%)	192	383
Tear strength (N/mm)	53	57.8
Aged properties (Aged at 48 h at 100°C)		
Tensile strength (N/mm^2)	8.41	13.79
Elongation at break (%)	122	212
Tear strength (N/mm)	42	52
Abrasion resistance (volume loss, cc/hr)	3.67	2.39
Hardness (Shore A)	60	56

CONCLUSIONS

1. The study shows that the latex reclaim is a potential candidate for developing blends with polybutadiene (BR) rubber and the blend can replace its more expensive counterpart Natural rubber/Polybutadiene rubber in most applications. The mechanical properties of the latex reclaim/BR blends are very much comparable to those of Natural rubber/BR blends.

2. A typical formation employing latex reclaim/NR/BR blend is also suggested for tread compound.

PART II

USE OF FOAM WASTE RECLAIM IN NR COMPOUNDS

INTRODUCTION

Foam waste contains lower amount of rubber compared to gloves, since the former contains significant amount of filler. The reclaimed foam is usually referred to a desensitised foam. W.L.Pearson and H.E. Schweller[17] suggest that when the desensitised foam is used as an additive in rubber compounds it is preferably used in quantities of 5–10% of the rubber in a solid rubber formulation.

This study proposes to find the effect of adding latex reclaim (foam) in various percentages in carbon black filled NR compounds.

EXPERIMENTAL

Natural rubber was masticated on two roll mill and the latex reclaim (foam) [hereafter referred to as LR(F)] in the form of a sheet was added at different percentages and the blends were compounded on a mixing mill as per formulations given in Table 4.5.

The scorch time T_{10} and optimum cure time T_{90} of the compounds were determined on a Goettfert Elastograph. The compounds were then vulcanized upto their optimum cure times in an electrically heated hydraulic press at 150°C. The tensile and tear properties were measured on a Zwick universal testing machine according to relevant ASTM standards. Compression set and hardness of the samples were also determined as per relevant standards. The abrasion resistance of the samples were evaluated using a DIN abrader. The ageing resistance of the vulcanizates were evaluated after ageing the samples at 70°C for 24 h and 48 h in a laboratory air oven.

The carbon black dispersion in NR/LR(F) blends was studied using photomicrographs. The SEM photographs of abraded surface of 50/50 NR/LR(F) blends and that of 100% NR were taken to study the abrasion mechanism.

RESULTS AND DISCUSSION

Table 4.5 shows the cure characteristics of NR and NR/LR(F) compounds. The scorch time and cure time of the blend compounds decrease gradually with the amount of latex reclaim. This is possibly due to the presence of crosslink precursors and/or unreacted curatives in the latex reclaim.

Fig.4.22 shows the variation in tensile strength with the addition of latex reclaim. The tensile strength shows only marginal variations upto about 15 per cent of reclaim content and thereafter it decreases sharply. This may be due to the presence of non-reinforcing fillers present in the foam waste. Further, it is observed that when the reclaim content in the blend is more than 50 per cent it becomes difficult to compound the blend on the mill.

Table 4.5: Formulation and vulcanizate properties of NR/LR(F) blends

	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}	F_{11}
NR	100	95	90	85	80	75	70	65	60	55	50
Latex Reclaim (Foam, R.H.C.-49.5%)	0	10.1	20.2	30.3	40.4	50.5	60.6	70.7	80.8	90.9	101
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Vulkanox HS	1	1	1	1	1	1	1	1	1	1	1
MOR	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Carbon black (HAF N-330)	30	30	30	30	30	30	30	30	30	30	30
Aromatic oil	5	5	5	5	5	5	5	5	5	5	5
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Cure characteristics at 150°C											
Scorch time (T_{10}), min.	2.9	2.6	2.4	1.8	1.4	1.2	1.08	1.04	0.84	0.8	0.72
Opt. Cure time (T_{90}), min.	8.1	6.5	5.9	4.2	3.5	3.0	2.64	2.56	2.2	212	2.0
Maximum torque	0.202	0.321	0.323	0.378	0.541	0.495	0.515	0.615	0.648	0.741	0.781
Vulcanizate properties											
Hardness (Shore A)	51	55	58	60	65	67	68	71.5	72	76	78
Abrasion resistance (volume loss, cc/hr)	2.91	2.86	3.13	3.5	4.2	4.13	4.22	4.28	4.84	5.67	6.62
Compression set (%)	28.47	28.77	29.34	32.85	33.55	33.94	34.11	34.97	35.05	36.87	37.71

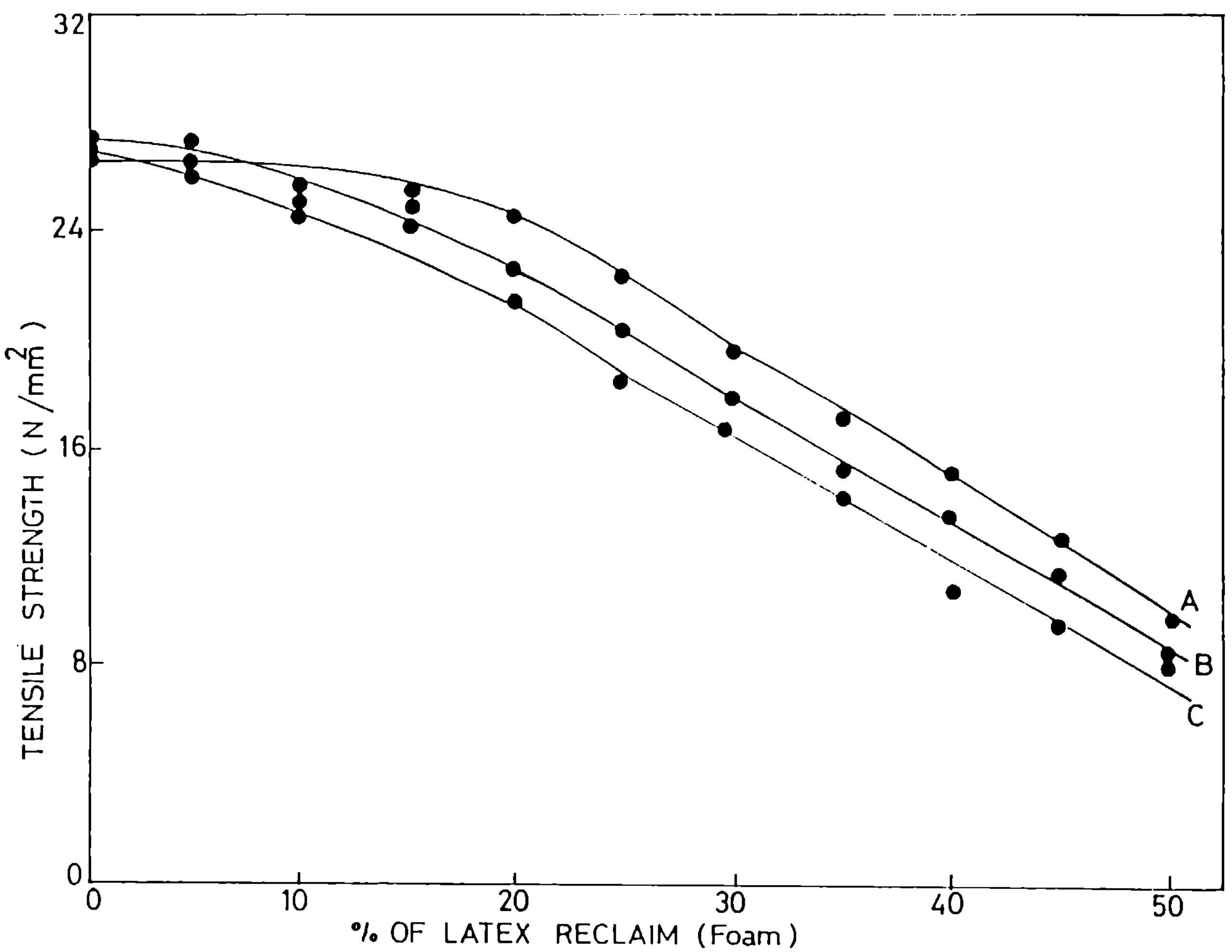

Fig.4.22: Variation of tensile strength of NR/LR(F) blends with reclaim content.
(A) - Before ageing, (B) - 24 hrs ageing at 70°C, (C) - 48 hrs ageing at 70°C.

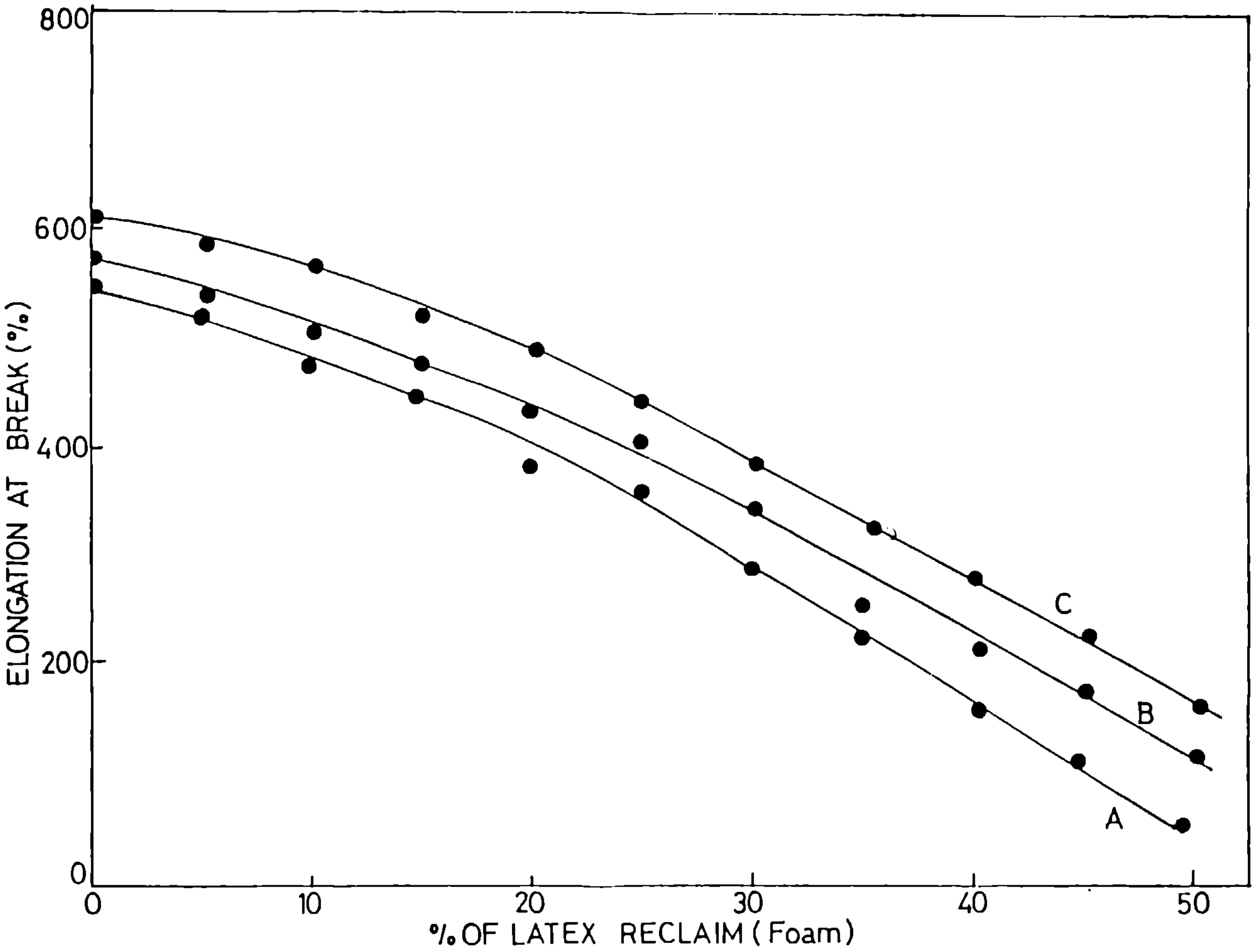

Fig.4.23: Variation of elongation at break of NR/LR(F) blends with reclaim content. (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

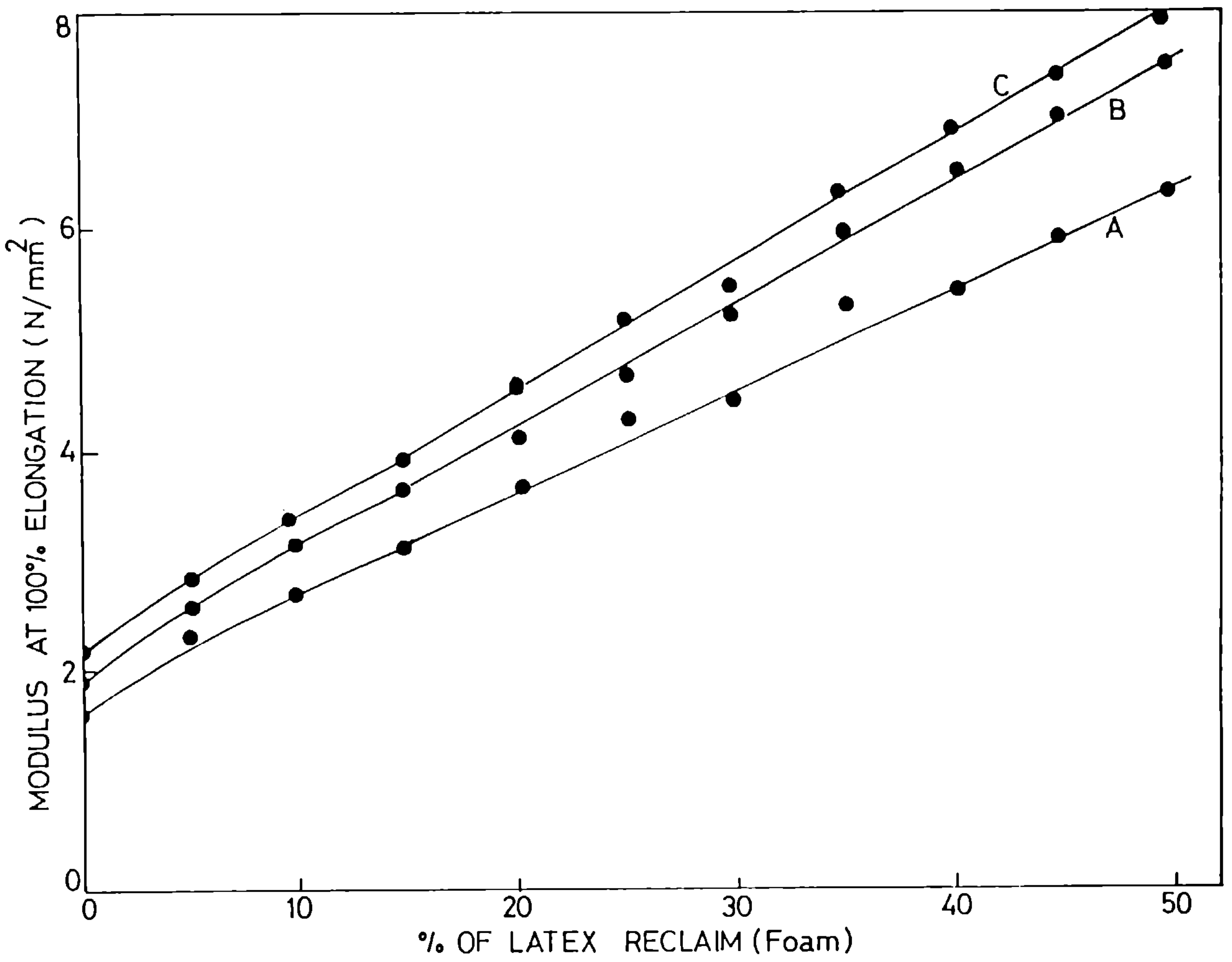

Fig.4.24: Variation in modulus of NR/LR(F) blends with reclaim content. (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

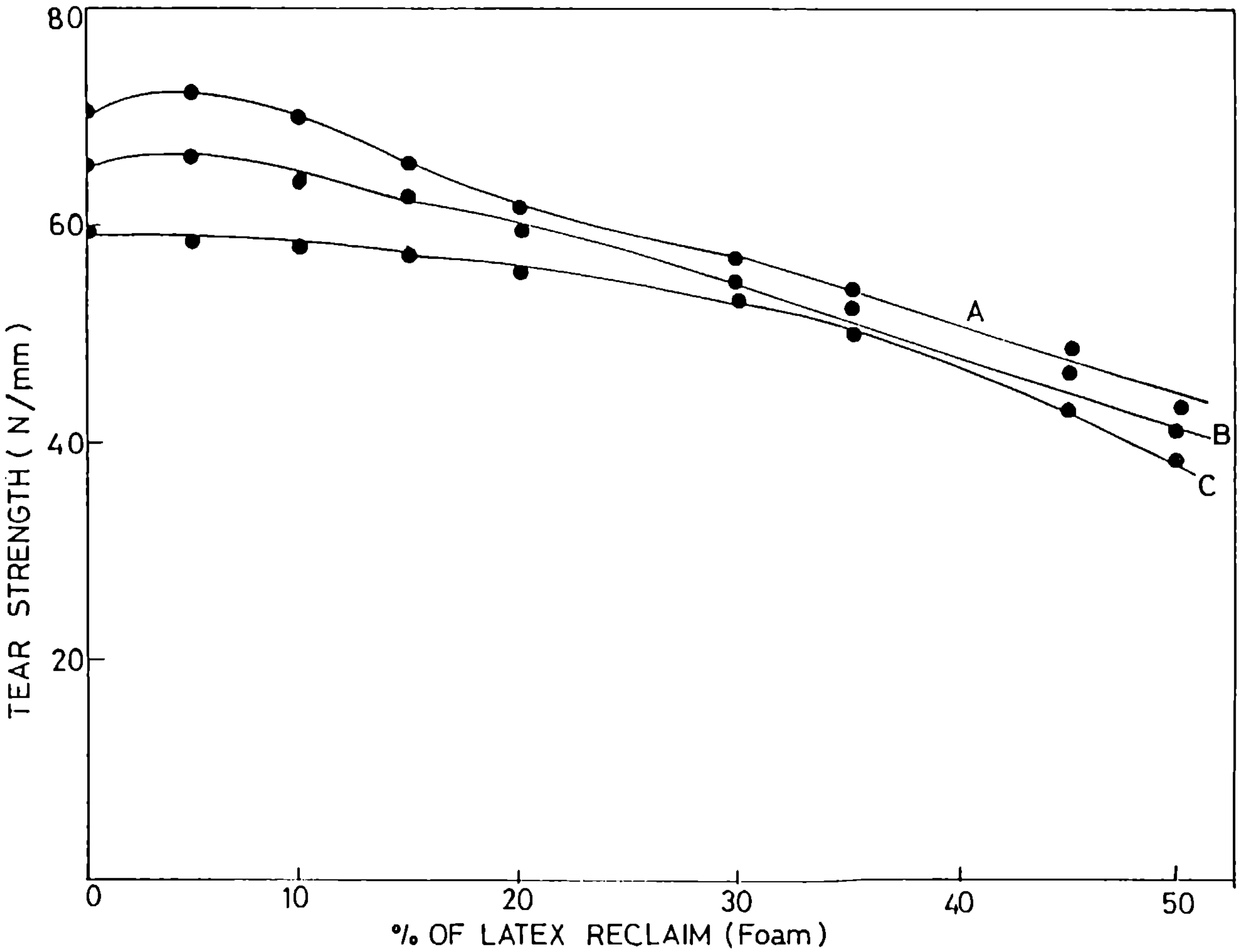

Fig.4.25: Variation of tear strength of NR/LR(F) blends with reclaim content. (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

Fig.4.23 shows the variation in elongation at break with the amount of latex reclaim and its retension after ageing. The significant reduction in elongation at break may be due to the higher crosslink density in the blends and non-reinforcing fillers incorporated in the foam.

The variation in modulus with the amount of latex reclaim and its retension after ageing are shown in Fig.4.24. There is a sharp increase in modulus with the addition of latex reclaim. This further points to higher crosslink density in the blend, presence of filler in the foam waste reclaim, and the reduction in elongation at break of the vulcanizates.

Fig.4.25 shows the variation in tear strength with the amount of latex reclaim. The variation in tear strength is similar to that of the tensile strength. It also shows marginal variations upto 15% and thereafter decreases sharply with the addition of latex reclaim.

The hardness of the blends increase with the increase in the percentage of latex reclaim as expected. The compression set increases with the addition of latex reclaim. This may be due to the presence of nonreinforcing fillers in the reclaim. The abrasion resistance of the blends also decreases with increase in the amount of latex reclaim as expected (Table 4.5).

Fig.4.26 100% NR

Fig.4.27 75/25 NR/LR(F)

Photomicrographs

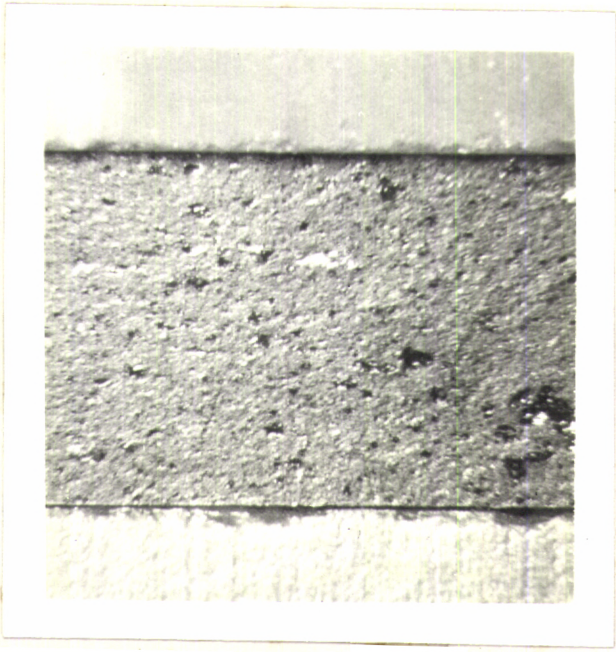

Fig.4.28 Photomicrograph of 50/50 NR(LR(F).

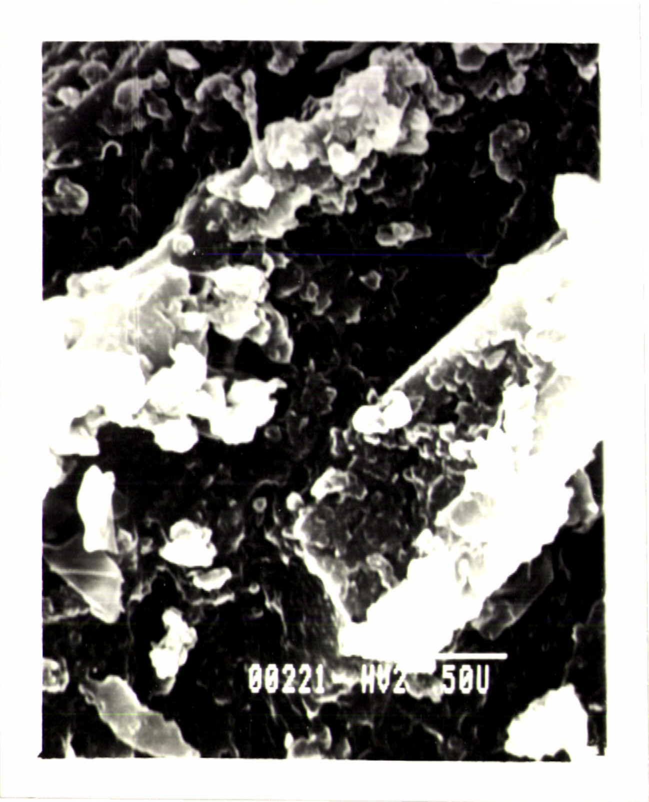

Fig.4.29 100% NR

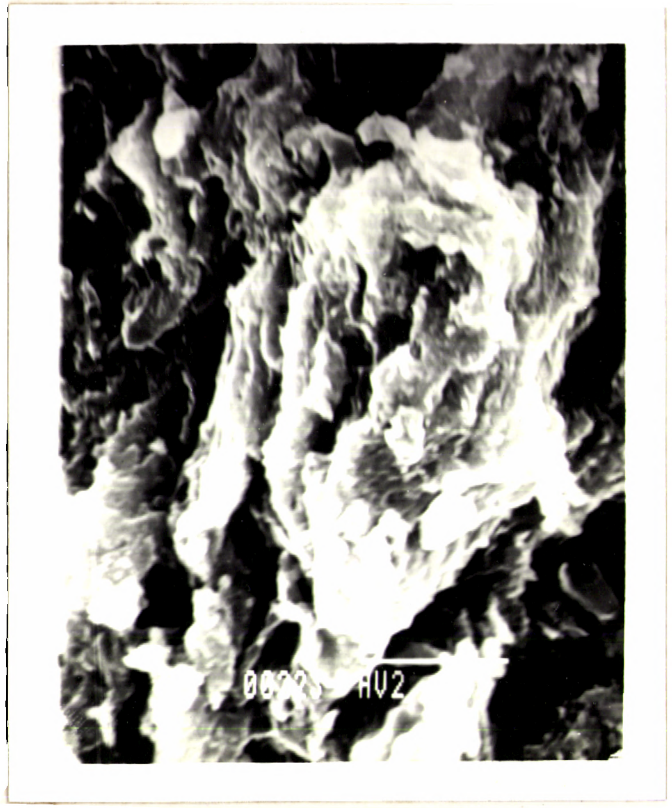

Fig.4.30 50/50 NR/LR(F)

SEM Photographs of abraded surfaces.

Figs.4.26, 4.27 and 4.28 show the photomicrographs of 100% NR and 75/25 and 50/50 NR/LR(F) blends respectively. From the photomicrographs it is clear that as the percentage of reclaim in the blend increases the surface of the blend becomes more uneven which is an indication of poor carbon black dispersion.

Figs.4.29 and 4.30 show the SEM photographs of the abraded surface of 100% NR and 50/50 NR/LR(F) vulcanizates respectively. The abrasion pattern of 100% NR vulcanizate is fairly well defined ridge pattern. The formation of ridges by microtearing and subsequent removal of the material from the surface influence the tensile strength, tear strength and cut growth resistance of the matrix. But the abrasion pattern of 50/50 NR/LR(F) is less well defined with a coarse ridge pattern which may lead to a low abrasion resistance.[16]

CONCLUSION

Latex reclaim prepared from foam waste can replace raw NR upto 15% without much deterioration in mechanical properties.

PART III

EVALUATION OF THE EFFECT OF REPLACING NR BY THREAD WASTE RECLAIM IN NR COMPOUNDS

INTRODUCTION

Due to high structural regularity of natural rubber, NR based elastomer blends are widely used in industrial applications. They have excellent dynamic properties, high resilience, better processing and superior building tack. For reducing compound cost and to conserve raw materials and energy, the utilization of reclaim rubber is widely employed in the industry.

In contrast to latex reclaim prepared from glove waste, latex reclaim prepared from thread waste contains rubber hydrocarbon of inferior quality. This study proposes to find the effect of replacing virgin NR by thread waste latex reclaim in various percentages in NR compounds.

The cure characteristics and mechanical properties of NR, thread waste latex reclaim and their blends were studied and compared along with their morphology.

EXPERIMENTAL

Natural rubber (NR) was masticated on a laboratory two roll mill and the latex reclaim prepared from thread waste [hereafter referred to as LR(T)] in the form of a sheet was added at different percentages and the blends were compounded on a mixing mill as per the formulation given in Table 4.6. Latex reclaim (thread) alone was also compounded with the same formulation.

The optimum cure time of the compounds were determined on a Goettfert elastograph. The compounds were then vulcanised up to their respective optimum cure time in an electrically heated hydraulic press at 150°C. The tensile and tear properties were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/min. according to the relevant ASTM standards. Samples for compression set and hardness were moulded and tested as per relevant ASTM standards. The ageing resistance of the vulcanizates were studied after ageing the sample at 70°C for 24 and 48 hours in a laboratory air oven. The abrasion resistance of the samples were evaluated using a DIN abrader.

The carbon black dispersion in the vulcanizates were studied using photomicrographs and the abrasion resistance of the samples were studied using SEM photographs.

RESULTS AND DISCUSSION

Table 4.6 shows the cure characteristics of the compounds. There is a gradual reduction in the scorch time and cure time with the addition of latex reclaim in the compounds. This is possibly due to the presence of crosslink precursors and/or unreactive curatives in the latex reclaim. The

Table 4.6: Formulation and vulcanizate properties of NR/LR(T) blends

	T_1	T_2	T_3	T_4	T_5	T_6	T_7
NR	100	80	60	50	40	20	0
Latex reclaim (thread. R.H.C.-87.5%)	0	23	45.71	56	67.2	89.6	114
ZnO	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
MOR	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Vulkanox HS	1	1	1	1	1	1	1
Carbon black (HAF N-330)	30	30	30	30	30	30	30
Aromatic oil	5	5	5	5	5	5	5
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Cure characteristics at 150°C							
Scorch time (T_{10} in minutes)	2.9	2.1	1.52	1.2	0.72	0.52	0.56
Cure time (T_{90} in minutes)	8.1	5.6	4.28	4.2	3.8	3.72	2.88
Maximum torque (Nm)	0.202	0.345	0.437	0.509	0.538	0.617	0.867
Vulcanizate properties							
Hardness (Shore A)	51	55	60	62.5	65	69	72
Compression set (%)	31.94	36.30	38.81	41.66	42.33	43.27	44.25
Abrasion resistance (volume loss, cc/hr)	2.91	3.02	3.62	3.95	4.19	5.12	6.37

maximum torque is found to increase with the increase in the percentage of latex reclaim. This may be attributed to the higher crosslink density in the reclaim blends which increases with the amount of reclaim. The 100% latex reclaim (thread) shows the highest value of maximum torque.

Fig.4.31 shows the variation in tensile strength with the addition of latex reclaim. The tensile strength shows a gradual decrease up to 40% reclaim content and thereafter decreases sharply with the addition of latex reclaim (thread). The ageing resistance of the blends also show the same type of variation.

Fig.4.32 shows the variation of tear strength with the amount of latex reclaim. The variation in tear strength is also similar to that of the tensile strength. This may also be due to the fact that in the blend up to 40% of latex reclaim, NR may be the continuous phase.

The variation of modulus with the amount of latex reclaim and the retension in modulus with ageing are shown in Fig.4.33. There is a gradual increase in modulus with the addition of latex reclaim. This may be due to the increased amount of crosslink density in the blends and the reduction in elongation at break of the vulcanizates containing latex reclaim.

Fig.4.34 shows the variation in elongation at break with the amount of latex reclaim and its retension after ageing. The significant

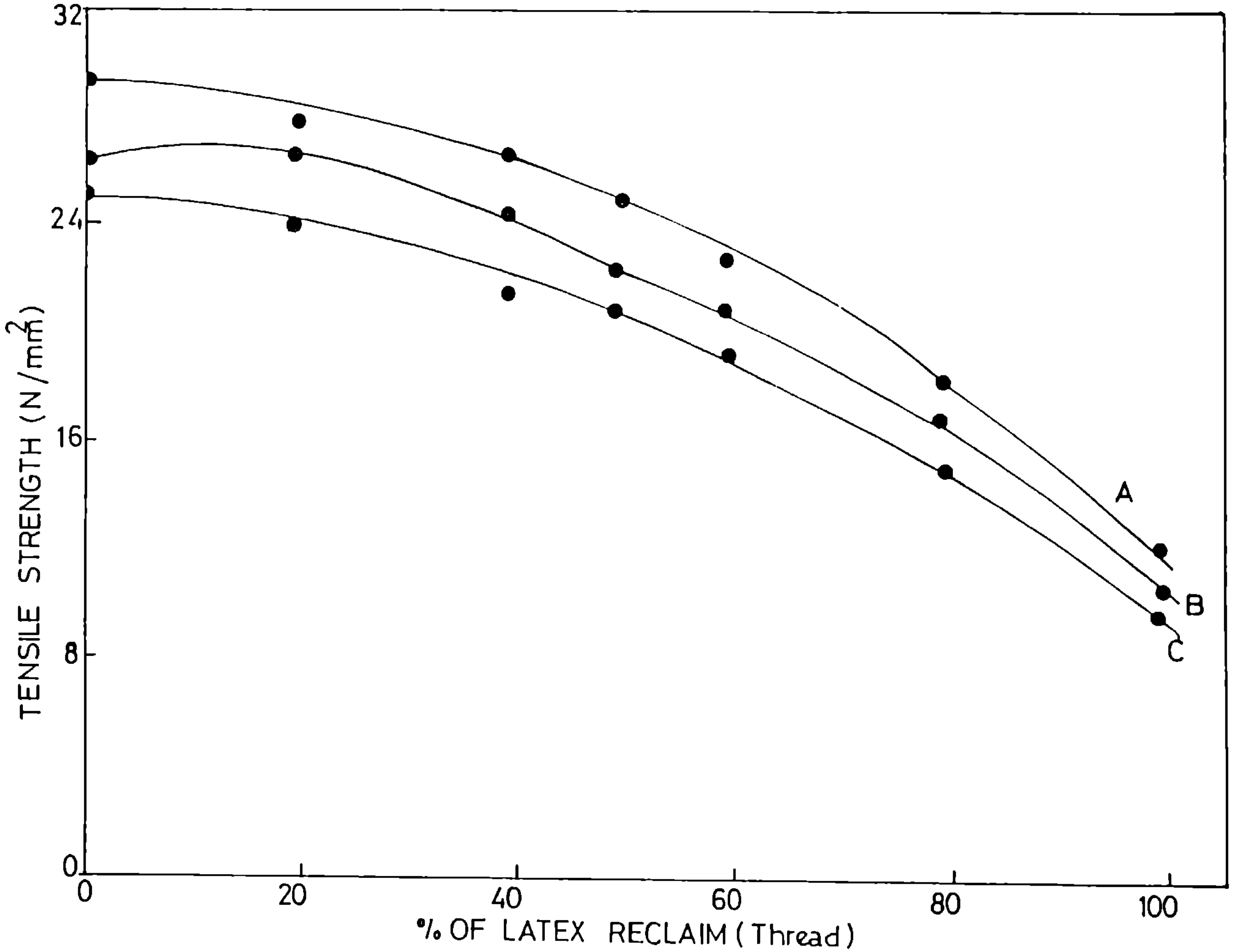

Fig.4.31: Variation in tensile strength of NR/LR(T) blends with latex reclaim. (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

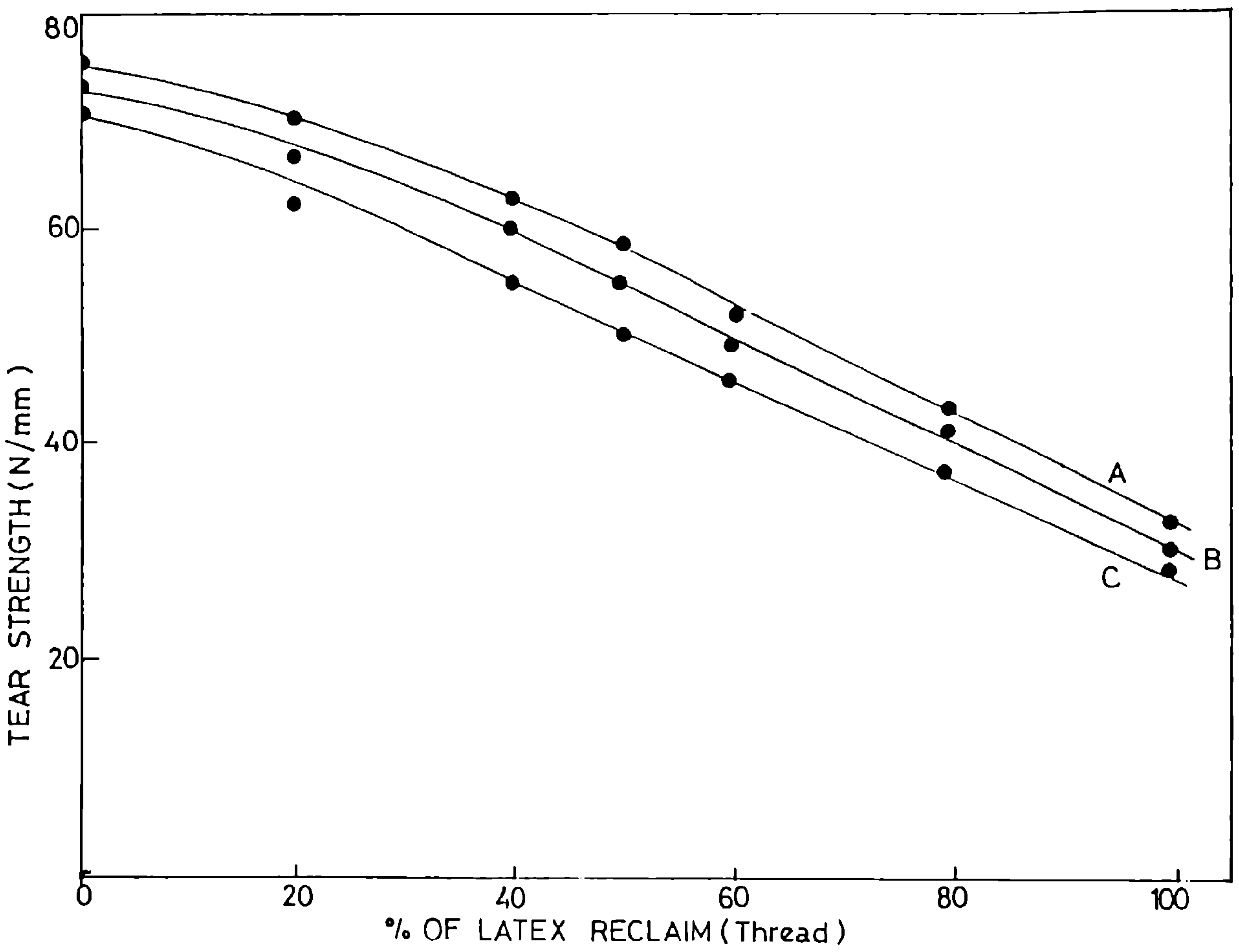

Fig.4.32: Variation in tear strength of NR/LR(T) blends with latex reclaim. (A)- Before ageing, (B)- After 24 hrs ageing at 70°C, (C)- After 48 hrs ageing at 70°C.

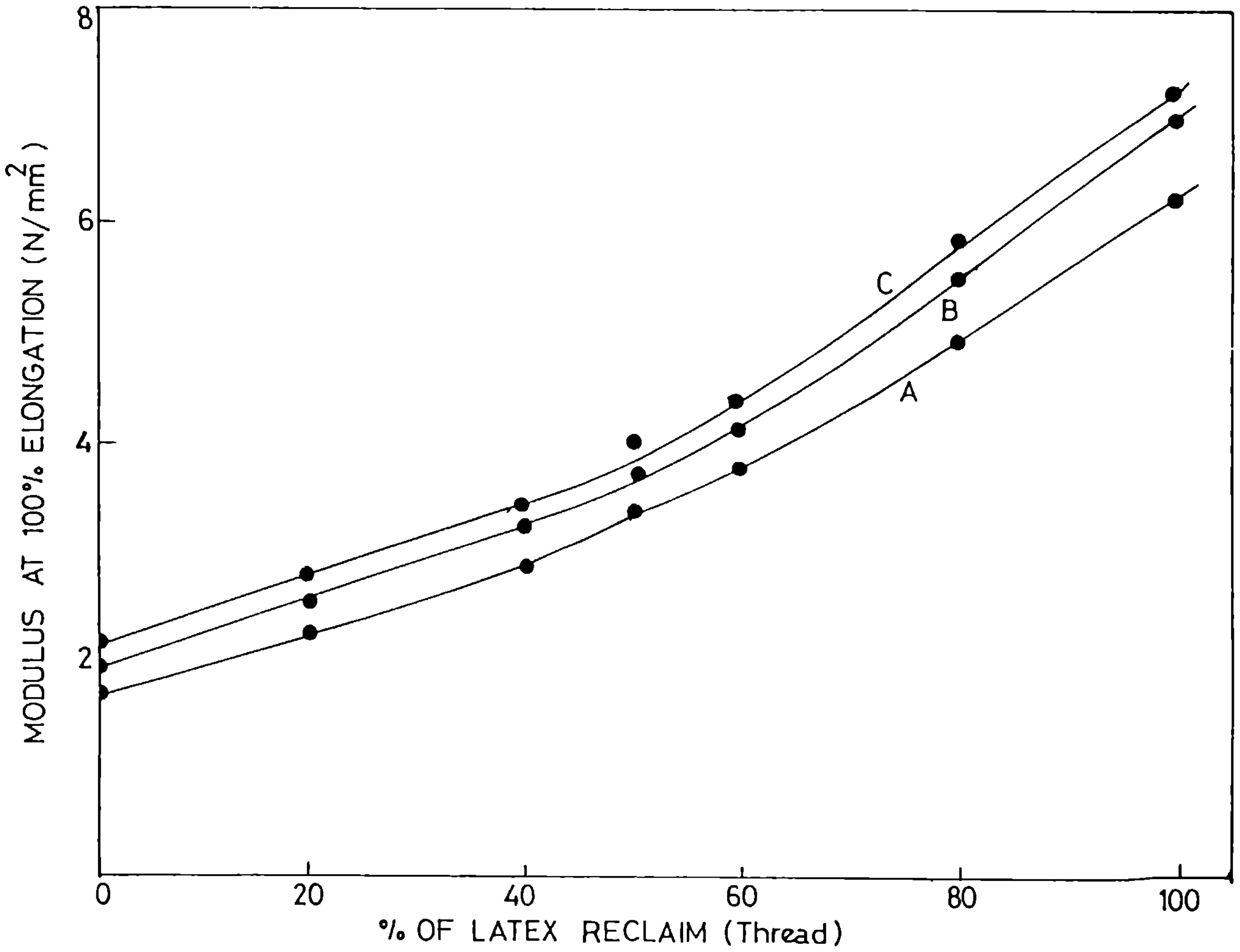

Fig.4.33: Variation of modulus of NR/LR(T) blends with latex reclaim. (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

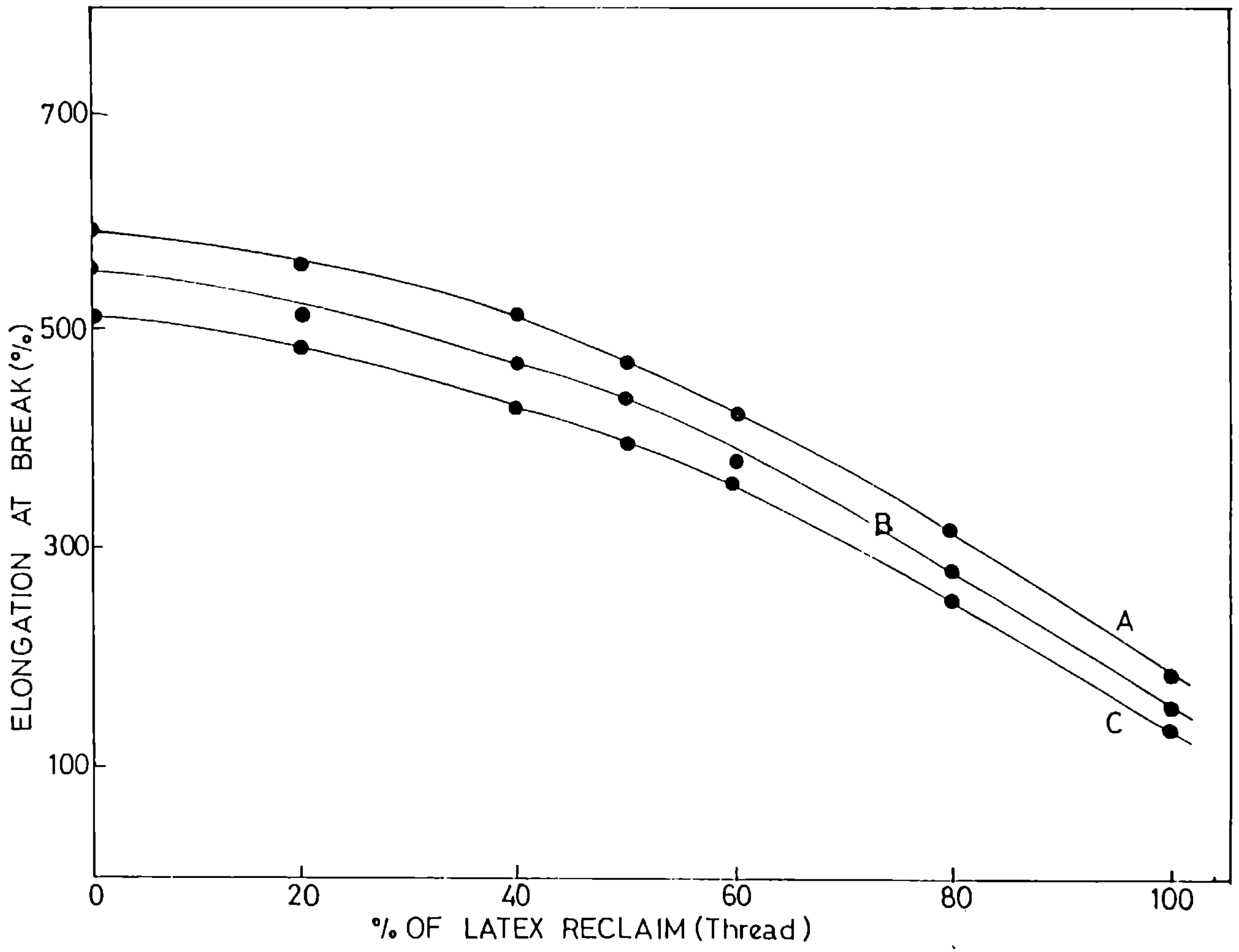

Fig.4.34: Variation of elongation at break of NR/LR(T) blends with latex reclaim. (A) - Before ageing, (B) - After 24 hrs ageing at 70°C, (C) - After 48 hrs ageing at 70°C.

reduction in elongation at break may be due to the increased crosslink density in blends compared to virgin NR vulcanizate and also due to the amount of filler incorporated in the thread waste reclaim.

The hardness of the blends increase with the increase in the amount of latex reclaim as expected (Table 4.6) which further confirms the increased crosslink density in NR/LR(T) blends. There is a marginal increase in compression set when the amount of LR(T) is increased. This may be due to the presence of fillers in the thread waste.

The abrasion resistance of the vulcanizates decreases with the amount of latex reclaim (thread) (Table 4.6). This may be due to the comparatively lower bonding between the NR and reclaim particles and further due to the filler present in the thread waste.

Figs.4.35 and 4.36 show the photomicrographs of 100% LR(T) and 50/50 NR/LR(T) blends. The carbon black dispersion becomes more uniform when the percentage of NR increases. Fig.4.37 shows the SEM photographs of the abraded surface of the 100% LR(T). Comparing it with that of 100% NR (Fig.4.29) it may be observed that the ridges present in the abraded surface of 100% LR(T) are more deformed resulting in higher abrasion resistance.

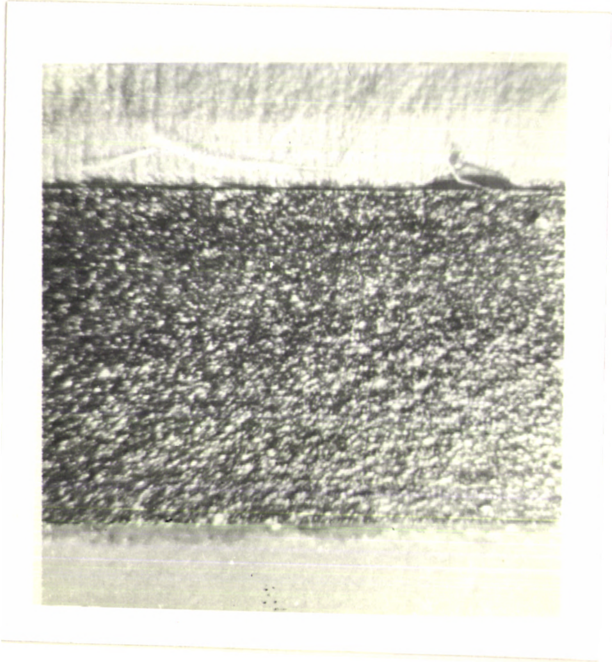

Fig.4.35 100% LR(T)

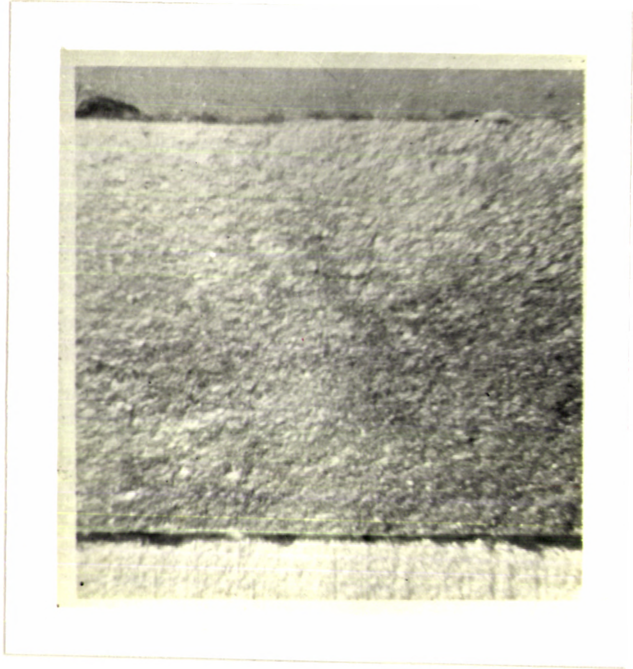

Fig.4.36 50/50 NR/LR(T)

Photomicrographs

Fig.4.37 SEM Photograph of abraded surface of 100% LR(T) vulcanizate

CONCLUSION

The study shows that the reclaim produced from thread waste can replace NR in its compounds upto 40% without much deterioration in properties.

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Chapter 5

PRODUCT APPLICATIONS OF LATEX RECLAIMS

This part of the study have undertaken for developing specific rubber products from latex reclaim.

PART I

TYPICAL MOULDED AND EXTRUDED GOODS

A. HOSPITAL RUBBER SHEETING WITHOUT REINFORCING FABRIC.

Reclaimed rubber is not usually used in hospital sheetings as the tyre reclaims are black in colour. But as the latex reclaim is white in colour it may be used in the manufacture of the hospital sheeting.

EXPERIMENTAL

Based on the properties of the reclaims prepared from examination gloves, thread and foam waste, three different formulations were selected for preparing hospital sheets from NR/latex reclaim blends (Table 5.1). The compounds were prepared and vulcanized upto their optimum cure time. (Compounds HSC-1, HSC-2 and HSC-3).

The tensile properties of the sheets were evaluated on a Zwick universal testing machine model 1445 as per IS 3406 (part I) 1965. The ageing resistance of the sheets were evaluated by testing the tensile properties after the accelerated ageing at 70°C for 168 hours in an air oven as per IS 3400 (part IV) 1965. To study the ageing resistance in live steam the samples were also subjected to ageing in an autoclave. In this autoclave test the dumbbell test pieces were subjected to a steam pressure of 0.1 MN/m^2 for 20 minutes in an autoclave after the removal of air. After this process the samples were taken out from the autoclave and exposed to air at room temperature for 2 hours and then the autoclaving test was repeated. Then the samples were conditioned for 24 hours at 27°C and then subjected to tensile test.

The tension set of the samples were tested at 250% elongation at room temperature and giving 15 minute recovery time, as per IS 3400 (part XIII) 1972.

To check whether any acidic additives was used, the pH of the aqueous extract of the samples were tested by refluxing the samples in water for half an hour and then testing the extract with phenolphthalein and methyl orange.

The resistance of the hospital sheet samples towards detergents and disinfectants were tested by immersing the test samples in phenol at room temperature for 15 min., in ammonia solution for 30 min. at room temperature and in soap solution for 10 min. at boiling temperature and then examining the samples visually.

Table 5.1: Formulation and cure characteristics for hospital sheet compounds

	HSC-1	HSC-2	HSC-3
NR	40	60	70
Latex reclaim			
LR (Gloves, R.H.C.- 91.4%)	66		
LR (Thread, R.H.C.- 87.5%)		47.2	
LR (Foam, R.H.C.- 49.5%))			60.6
ZnO	5	5	5
Stearic acid	2	2	2
Silica	40	20	
Precipitated $CaCO_3$	20	10	
Ethyleneglycol	1	1	
MOR	2	2	2
TMTD	1	1	
Vulkanox SP	1.5	1.5	1
Sulphur	0.5	0.5	0.5
Cure characteristics at 150°C			
T_{10}(Scorch time in min.)	2.6	2.24	1.68
T_{90} (Optimum cure time in min.)	4	4.96	2.16

Table 5.2: Properties of hospital sheets

Properties	HSC-1	HSC-2	HSC-3
Tensile strength (N/mm^2)	18.62	16.97	14.5
Elongation at break (%)	345	340	320
Tension set (%)	6.6	4.4	5
After accelerated ageing			
Change in tensile strength (%)	-16	-14.2	- 14
Change in elongation at break (%)	-10.7	-12.4	-15.7
After autoclaving test			
Change in tensile strength (%)	-16.6	-12.5	-13.8
Change in elongation at break (%)	-12.7	-14.4	-15

RESULTS AND DISCUSSION

Table 5.2 shows the properties of the different vulcanizates of the blends HSC-1, HSC-2 and HSC-3. All of them possess a tensile strength of more than 14 MN/m^2 and an elongation at break of lower than 350%, and a tension set lower than 10% which are within the IS specification.

After the accelerated ageing at 70°C for 168 hours in air oven and autoclave test the tensile properties of the rubber sheeting showed only a marginal variation which was well within the limits suggested in IS.

The aqueous extracts of all the three rubber sheets were found to be neutral and the test pieces did not show any tackiness or other apparent deterioration when tested according to appendix C of IS 8164-1976.

CONCLUSIONS

1. The NR/latex reclaim blends can be used for the manufacture of hospital sheetings.
2. The latex reclaim prepared from gloves can replace upto 60% of NR while the reclaims prepared from thread and foam wastes can replace 40% and 30% respectively in hospital sheet compounds.

B. CYCLE TUBES

Cycle tubes are usually manufactured from natural rubber, synthetic rubber or a blend of NR and synthetic rubber.

In this study a blend of NR and latex reclaim prepared from gloves is tried for making cycle tubes.

EXPERIMENTAL

A 60/40 NR/LR(G) blend was selected as the base material for the cycle tube and was compounded according to the formulation given in Table 5.3 and vulcanized upto its optimum cure time in an electrically heated hydraulic press at 150°C and the mechanical properties of the vulcanizate was evaluated.

The tensile strength and elongation at break of rubber vulcanizate was evaluated on a Zwick universal testing machine model 1445 according to the IS 3400 (Part I) – 1965 employing type I dumbbell test specimen. Tension set of the vulcanizate was evaluated according to the method given in IS: 3400 (Part XIII) 1972 using dumbbell test pieces stretching to 300±30 percent between the reference lines. Ageing resistance of the vulcanizates were evaluated by ageing the tensile test samples in an air oven at 70±1°C for 168 hours in accordance with IS 3400 (Part IV) 1965 and tested according to IS 3400 (part I) 1965.

The suggested compound was also tried in actual production. For this the NR/latex reclaim blend prepared was extruded through a screew extruder using a die for cycle tube on to a mandrel and was vulcanized in an autoclave for 30 minutes at 60 pound pressure. The tube was fitted with a valve and joined together using a room temperature curing system.

Table 5.3: Formulation and cure characteristics of cycle tube compound

Ingredients	
NR	60
Latex reclaim (gloves. R.H.C– 91.4%)	44
ZnO	5
Stearic acid	2
Carbon black (HAF- N-330)	30
Aromatic oil	5
Vulkanox 4020	1.5
MOR	2
TMTD	0.5
Sulphur	0.5
Cure characteristics at 150°C	
T_{10}(Scorch time in min.)	1.6
T_{90} (Optimum cure time in min.)	5.2

Dumbbell test pieces were cut keeping the joint in the middle of the narrow portion of the dumbbell, and tested for the joint adhesion strength on a Zwick universal testing machine model 1445 using a crosshead speed of 200 mm/min.

The tube was then tested for leak by subjecting it to an inflating pressure of not exceeding 3.2 kgf/cm^2 and immersing in water.

RESULTS AND DISCUSSION

Table 5.4 shows the properties of the cycle tube compound prepared from 60/40 NR/LR(G) blend.

The tensile strength as well as the elongation at break of the vulcanizate are found to be within the IS specification. These properties after ageing for 168 hours at 70°C are also found to be within the limits of the IS.

The joint adhesion strength of the extruded tube was also found to be well above the IS limit and does not show any sign of leakage when immersed in water after subjecting the tube with an inflating pressure of 3.2 kgf/cm^2.

C. RUBBER SHEET GASKETS

In this part of the work latex reclaim prepared from thread waste was used to design a compound for rubber sheet gasket satisfying the

Table 5.4: The required properties of the cycle tube

Properties	
Tensile strength (N/mm^2)	22.69
Elongation at break (%)	560
Tension set (%)	9.11
Joint adhesion strength (kg/cm^2)	8.2
After ageing	
Change in tensile strength (%)	−11.34
Change in elongation at break (%)	-12.5

Table 5.5: Formulation and cure characteristics of gasket compound

Ingredients	
NR	20
Latex reclaim (Thread, R.H.C.-87.53%)	91.4
Carbon black (HAF N-330)	60
Aromatic oil	5
ZnO	4
Stearic acid	2
MOR	0.8
Vulkanox 4020	1
Sulphur	1
Cure characteristics at 150°C	
T_{10} (Scorch time in min.)	0.52
T_{90} (Optimum cure time in min.)	3.6

ASTM D 1330-85. This specification covers gaskets cut from sheet rubber which are intended for general gasket applications on water (grade I) air (grade II) and low-pressure steam (grade III).

EXPERIMENTAL

For preparing a compound for general purpose rubber gasket for use in water and air (grade I and II) 80/20 latex reclaim (thread)/NR blend was selected and compounded according to the formulation given in Table 5.5 and vulcanized upto its optimum cure time.

The tensile properties of the vulcanizate were evaluated on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM D 412-80. The ageing resistance of the vulcanizate was determined by keeping the sample at 70°C for 94 hrs in a laboratory air oven and then measuring the tensile properties. Compression set was measured as per ASTM D 395-82. The hardness (shore A) of the sample was measured using a Zwick 3115 hardness testor in accordance with ASTM D 2240-81.

RESULTS AND DISCUSSION

Table 5.6 shows the physical requirements for rubber gasket as per ASTM D 1330-85 for water and air (grade I and II) of the designed compound.

The tensile strength and elongation at break of the vulcanizate are found to be well above the ASTM specification.

Table 5.6: Properties of Rubber sheet gasket compound vulcanizate

Properties	
Hardness (Shore A)	75
Tensile strength (N/mm^2)	14.25
Elongation at break (%)	178
Compression set (%)	39
After ageing 94 hrs at 70°C	
Change in tensile strength (%)	− 6.6
Change in elongation at break (%)	−13.48

The ageing resistance of the vulcanizate also satisfies the prescribed ASTM specification which allows a deterioration of tensile strength and elongation at break of upto 25%.

The hardness samples is found to be 75 (Shore A) which is also well within the range prescribed by ASTM. Compression set is also found to be lower than that of the prescribed maximum value of 40

CONCLUSION

The study shows that the latex reclaim can be used along with virgin natural rubber for the manufacture for several commercial products.

PART II

PRODUCTION OF CHLORINATED RUBBER FROM LATEX WASTE

INTRODUCTION

Chlorination of natural rubber has been practised right from the end of the last century. Among the possible methods of chlorination[1], only the action of gaseous chlorine on rubber in solution had led to a method of production of chlorinated rubber on an industrial scale. By the prolonged action of chlorine rubber is converted into a hard white product which is quite inelastic in nature and is characterized by its stability towards heat and chemical reagents. The properties of this product of rubber thus obtained vary in close dependence on the chlorine content which may be as much as 60–65%.[2]

Although numerous investigations[3-6] have been carried out to throw light on the mechanism of chlorination and structure of chlorinated rubber, the mechanism is still not well understood. The reaction is highly complex and may include addition, substitution and cyclisation. During early stages of chlorination in solution substitution takes place. Further chlorination leads to more substitution and addition reactions as well as cyclisation. Fully chlorinated rubber has a chlorine content of about 65%

which corresponds approximately to the emperical formula $(C_{10}H_{11}C_7)_n$ which is believed to have a cyclic structure.

The chlorinated product of natural rubber has a set of particularly interesting properties and it finds application mainly in the paint industry and also in adhesives and ink manufacture. It gives excellent anticorrosive properties to paints and good protection in industrial and marine environments. Besides, incorporating them into some solvent adhesives, facilitates adhesion to certain substrates.

Since the latex reclaim obtained from the examination gloves contains high quality rubber hydrocarbon without any filler and other extractables, attempts have been made to chlorinate a dispersion of a latex reclaim (from examination gloves) in carbon tetrachloride by gaseous chlorine.

EXPERIMENTAL

The latex reclaim prepared from examination gloves was dispersed in carbon tetrachloride to get approximately a 3.5% dispersion. Chlorine gas was passed through the dispersion at a moderate rate. Uniformity of the reaction was ensured by keeping the dispersion under a constant agitation. Under these conditions the effect of the time of chlorination was followed by withdrawing small portion of the reaction mixture at definite intervals varying from 30 minutes to 180 minutes and estimating the chlorine content in each sample. After 3 hours of chlorination the chlorinated rubbery layer get separated from the solvent. The chlorinated layer was poured into water at 90°C (flash distillation). After the solvent was totally evaporated the chlorinated rubber mass floated at the top of the water which was removed and dried at 70°C for 2–3 hours. It was then powdered, washed with water thoroughly to remove any traces of HCl. The powdered product was again dried in an air oven at 70°C for a period of not less than 24 hours.

The chlorinated product thus obtained was characterized by four different methods.

Chlorine content of the chlorinated reclaim was estimated by volumetric method. Accurately weighed sample was fused with 1:1 Na_2CO_3 K_2CO_3 fusion mixture at 850°C for four hours in a platinum crucible. The fused sample was extracted with distilled water and then neutralised with Conc. HNO_3. To the concentrated solution specified amount of $AgNO_3$ solution was added. The precipitate was filtered and washed with distilled water and the filtrate was treated against standard thiocynate solution using ferric alum as the indicator and the chlorine content was calculated.

In order to determine the various chemical groups present in the product, infrared spectrum of the chlorinated reclaim rubber and a commercial sample were taken using Shimadzu IR spectrophotometer.

The thermal stability of chlorinated rubber prepared was compared with that of a commercial product in a Shimadzu-50 thermogravimetric analyser.

Thin films of the reclaim rubber and that of the chlorinated product were observed using a Nikkon optical phase contrast microscope and photographs were taken giving 450 times magnification.

RESULTS AND DISCUSSION

Variation of chlorine content with the time of chlorination is given in Table 5.7. From the table it is clear that the chlorine content of the samples increases with the time of chlorination and reaches a maximum of 52% after 3 hrs of chlorination.

Table 5.7: Effect of period of chlorination

Sl.No.	Duration of reaction (hrs)	Percentage of chlorine by weight
1	0.5	5.014
2	1	11.3
3	1.5	23.56
4	2	33.43
5	2.5	40.82
6	3	52.8

Table 5.8: IR frequencies (in cm^{-1}) of samples of chlorinated rubber and assignments of peaks

Peaks (cm^{-1})	Assignment of peaks
1430	CH_2 bonding
1445	CH_3 deformation
1300 1270 910	Unidentified frequencies
790-625	C-Cl frequencies

Figs.5.1 and 5.2 show the IR spectra of chlorinated product from latex reclaim and that of a commercial sample. Table 5.8 shows the characteristic absorption frequencies and their corresponding assigned peaks.[9] From the table it is clear that the peak in the region 800–600 cm^{-1} represents C–Cl group whose intensity increases with increase in chlorine content. The IR spectra of both the commercial sample and the chlorinated reclaim rubber show peaks in the region 600–800 cm^{-1} corresponding to C–Cl absorption.

From the thermograms of chlorinated rubber produced (Fig.5.3) and that of the commercial product (Fig.5.4) it is clear that the thermal degradation of both the samples have three distinct regions. The initial phase of degradation occurs between 100-150°C due to the evolution of HCl from the CH_2Cl group.[6] The second region of degradation starts between 250–350°C and this is attributed to the degradation of CHCl and $CHCl_2$ group. The third and final stage of degradation is attributed to the degradation of organic material. In the case of both the samples this degradation takes place at around 600°C. It may be concluded that the chlorinated latex reclaim has more or less the same thermal stability as that of the commercial product.

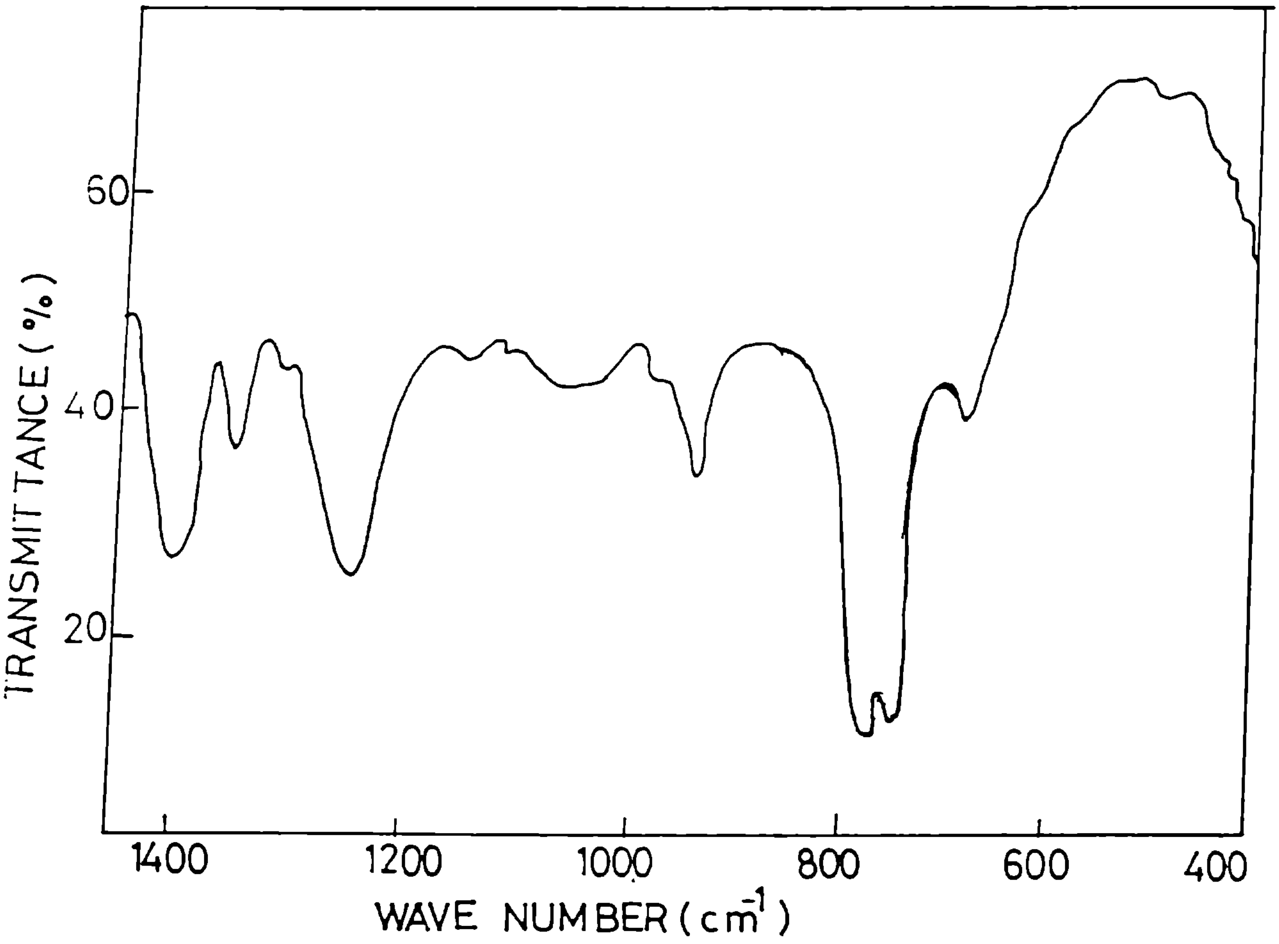

Fig.5.1 Infrared spectrum of chlorinated latex reclaim.

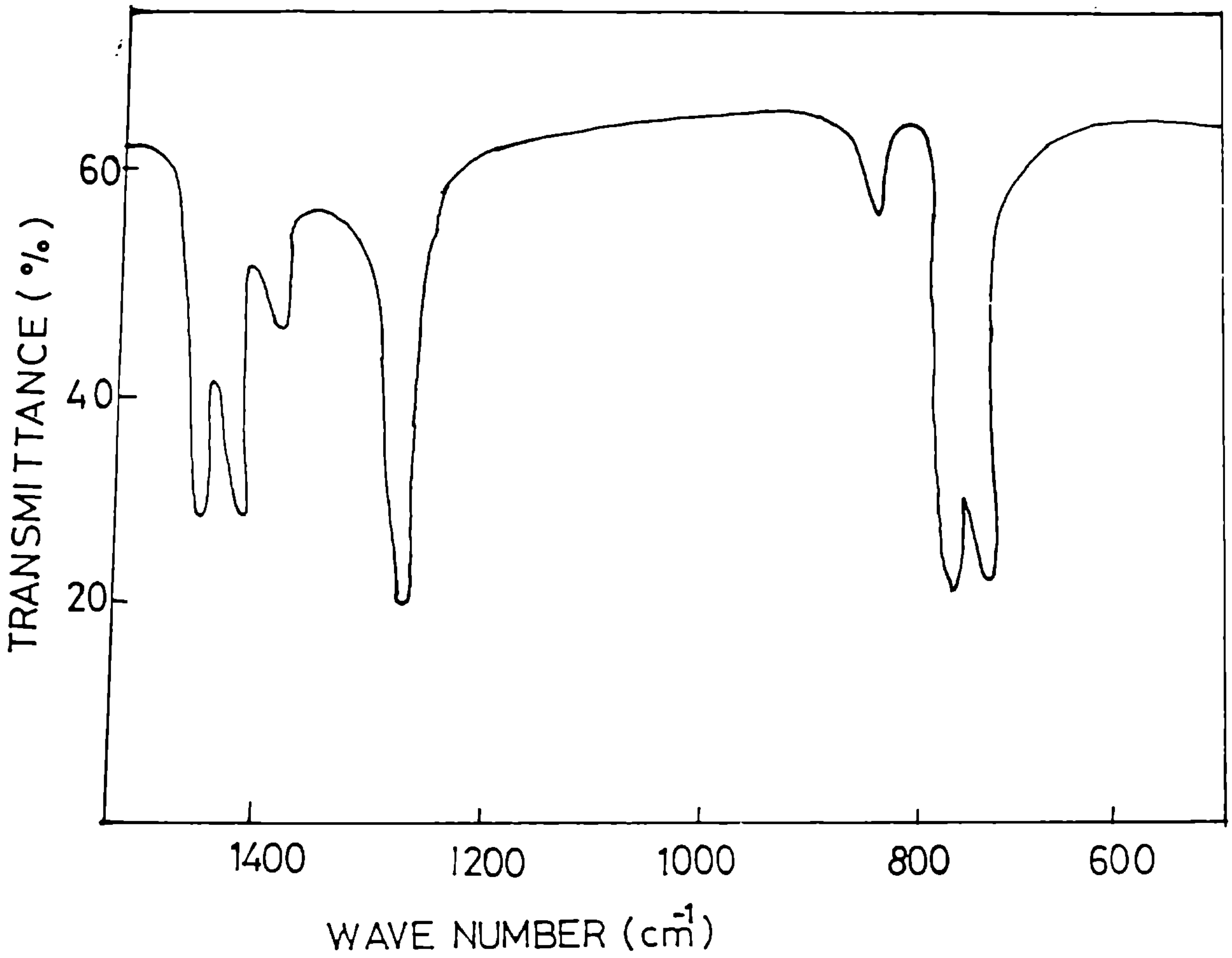

Fig.5.2 Infrared spectrum of chlorinated NR

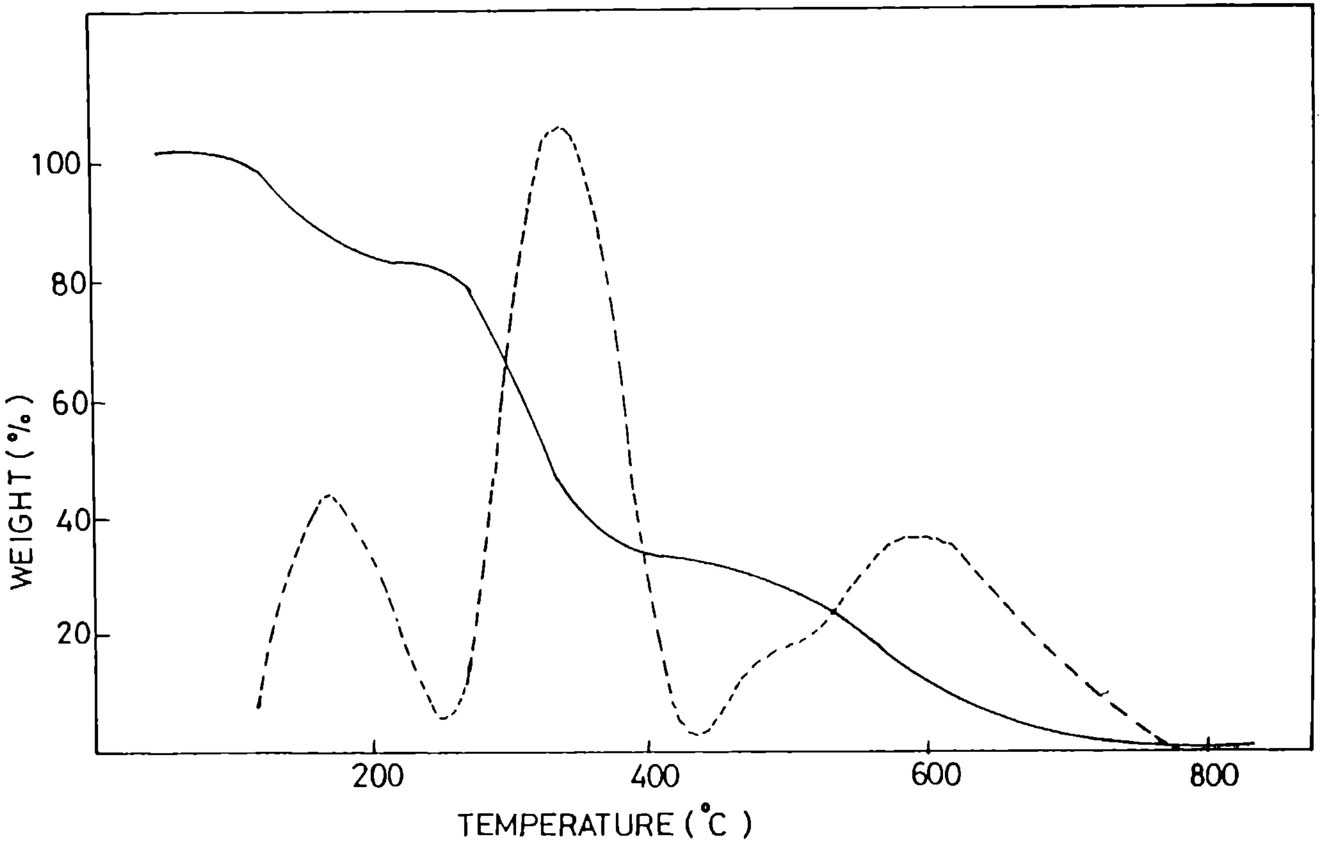

Fig.5.3: Thermogram of chlorinated latex reclaim.

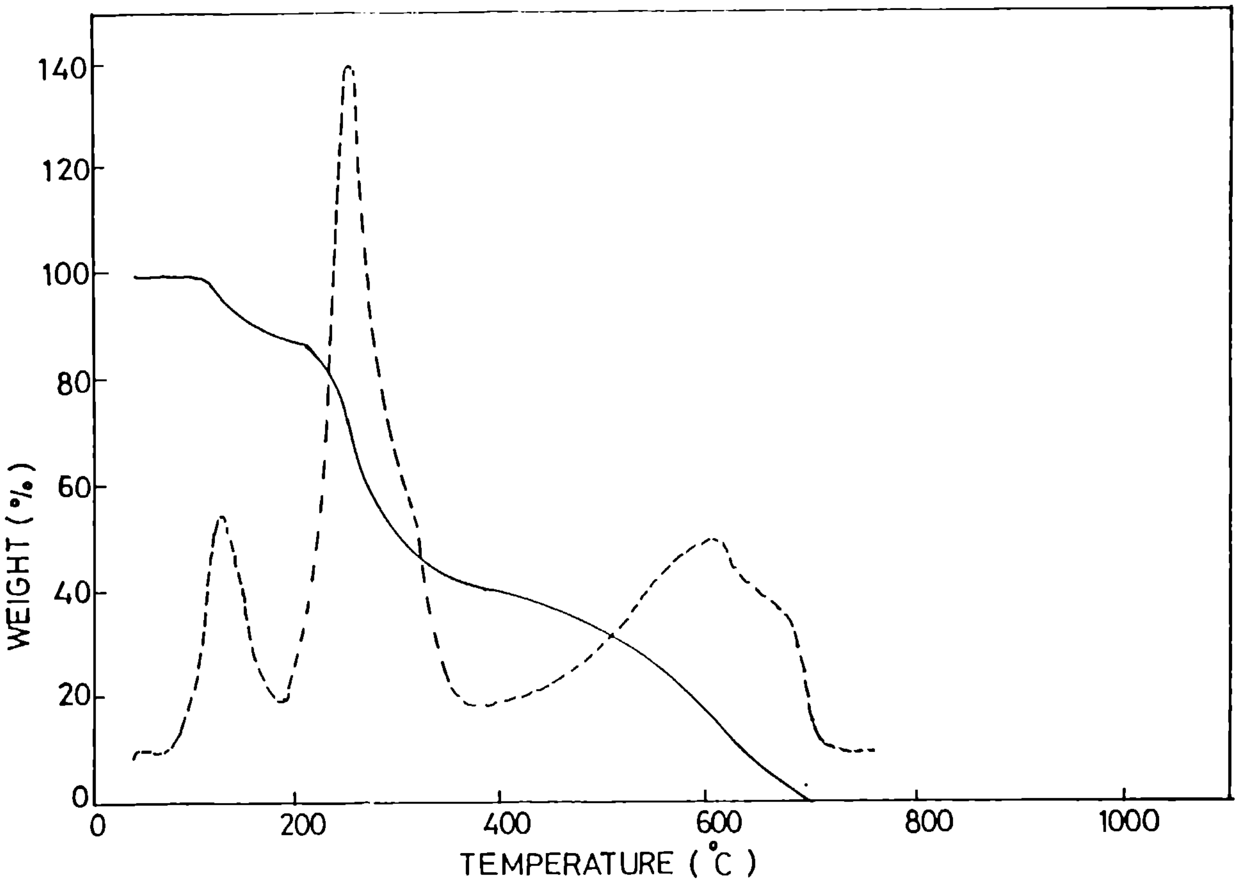

Fig.5.4 Thermogram of chlorinated NR.

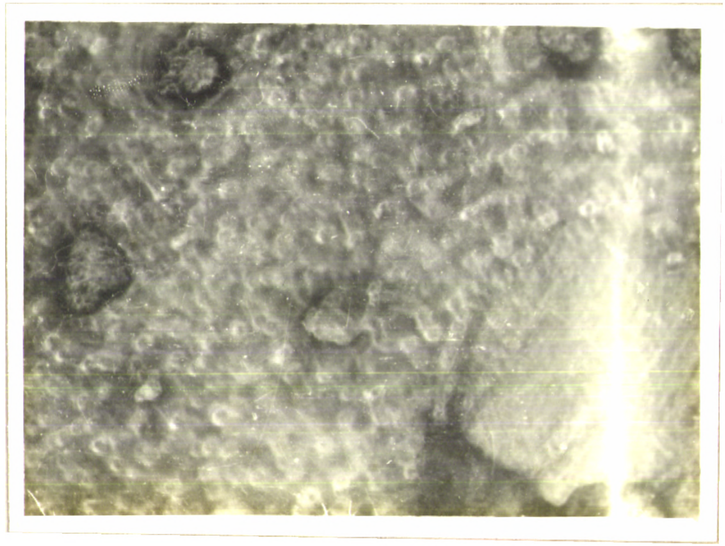

Fig.5.5 Reclaimed rubber

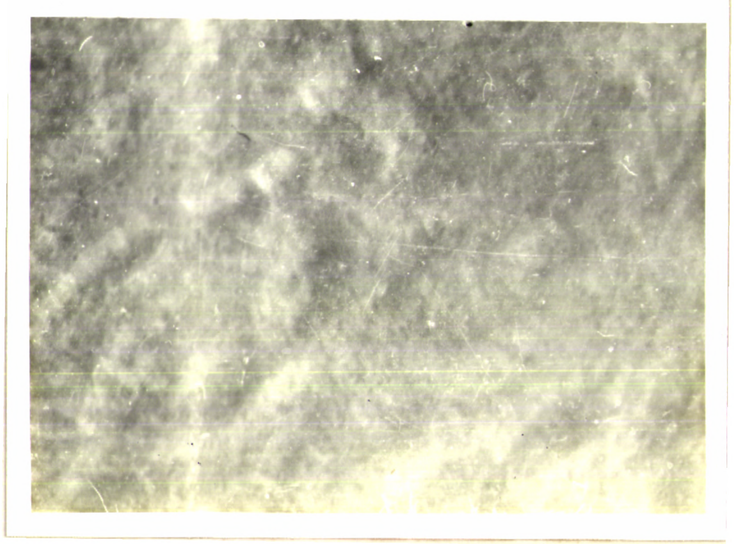

Fig.5.6 Chlorinated reclaim
(After 3 hours)

Optical photographs of thin films

Figs.5.5 and 5.6 are the optical photographs of thin films of reclaimed rubber and that of chlorinated latex reclaim after 3 hours of chlorination. From the photographs it is clear that during chlorination there is an observable particle size reduction.

CONCLUSIONS

The study shows that the process developed for the production of chlorinated rubber from latex reclaim is a very potential method of producing chlorinated rubber economically. The product compares favourably with the commercially available chlorinated rubber, manufactured from virgin rubber.

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Chapter 6

SUMMARY AND CONCLUSIONS

The primary objective of this work has been to develop an economic process for developing good quality latex reclaim from waste latex products such as examination gloves, latex threads and latex foam without using high temperature which degrade the rubber. Waste latex products were chosen because all latex products manufacture is based on either high quality concentrated latex or creamed latex and therefore has a higher potential to generate good quality rubber reclaim. Moreover, all latex products are only lightly crosslinked and not masticated and hence not degraded.

With this objective in mind, we investigated the reclaiming action of four different chemicals viz., MBT (Mercapto benzo thiazole), Renacit-7 (Zinc salt of pentachloro thiophenol), Diaryl sulphide and sulphur crosslinked cardanol, on latex product waste, and found that these chemicals are effective in reclaiming waste latex products and the reclaiming method employed is a promising one for generating good quality reclaim. The reclaims produced by the action of these chemicals were also compared with that of a commercial reclaiming agent Delink-R.

The latex reclaims produced by the method outlined above have properties such as initial plasticity, acetone extract and volatile matter comparable to those of raw NR. The rubber hydrocarbon content is slightly lower while the ash content is slightly higher for the latex reclaim. The amount of free sulphur in the reclaim shows the presence of unutilised sulphur in the reclaim. The details of the reclaiming process using the four reclaiming agents, the characterization of the products and the comparison with the reclaim produced by the commercial reclaiming agent Delink-R are described in part I of chapter 3.

In the next part of the study, the mechanical properties of NR vulcanizate were compared with those of 100% latex reclaim vulcanizate prepared using different reclaiming agents. The properties of the reclaim vulcanizates were also compared with those of the reclaim vulcanizates prepared using the commercial reclaiming agent Delink-R. The study shows that the tensile strength and tear strength of the reclaim vulcanizates are only marginally lower than those of raw NR vulcanizate. But the ageing resistance of the reclaim vulcanizate is found to be inferior to that of NR vulcanizate. The reclaimed rubber prepared using MBT as reclaiming agent shows the highest mechanical properties. Photomicrographic studies of the NR and latex reclaim vulcanizates show that the carbon black dispersion in reclaim prepared using MBT, diaryl sulphide and sulphur crosslinked cardanol is more uniform compared to that in the vulcanizates prepared using Delink-R and Renacit–7. This part of the study is described in part II of chapter 3.

The use of EV system in reclaimed rubber compound for improving the ageing resistance of latex reclaim vulcanizate is described in part III of chapter 3. The study shows that the ageing resistance of the reclaimed rubber vulcanizate can be improved by the use of an efficient vulcanization system. The scanning electron microscopic studies show that the fracture mechanism of the vulcanizates in tension and abrasion are similar to that of raw NR vulcanizate.

The reclaiming process employed to produce latex reclaim from examination gloves was applied to produce reclaim from other waste latex products such as thread waste and foam waste. The latex reclaim developed from these wastes contains only a lower amount of rubber hydrocarbon compared to that prepared from examination gloves. The details of the reclaiming process are outlined in part IV of chapter 3.

Because of the commercial importance of blends of different elastomers, the next part of the study was done on the blends of latex reclaim (from examination gloves) with polybutadiene rubber. Part I of chapter 4 describes the studies on latex reclaim/BR blends and their comparison with NR/BR blends using both a conventional system and an EV system. The study shows that the latex reclaim can be successfully employed for developing blends with polybutadiene rubber (BR) and the blend can replace its more expensive counterpart NR/BR in most applications. The mechanical properties of the latex reclaim/BR blends are found to be comparable to those of NR/BR blends. A commercially viable tread compound based on 60/20/20 NR/LR/BR was also prepared and evaluated.

Part II of chapter 4 describes the utilization of latex reclaim (from foam waste) in filled NR compound. It is found that the latex reclaim prepared can replace raw NR only upto about 15% of NR/LR(F) blends without much deterioration in mechanical properties since foam waste contains a high amount of filler.

The effect of replacing NR by thread waste reclaim in NR compounds is given in part III of chapter 4. The study shows that the thread waste can replace NR in its compounds upto 40% without affecting the properties.

In part I of chapter 5, latex reclaims prepared from different types of latex wastes are evaluated for preparing specific rubber products like hospital sheets, cycle tubes and gaskets satisfying the relevant IS or ASTM standards. In the case of hospital sheets the latex reclaim prepared from gloves could replace upto 60% of NR, while reclaim from thread waste could replace upto 40% of NR and the reclaim from foam waste could replace upto 30% of NR.

In the case of cycle tube, a blend of 60/40 NR/latex reclaim (gloves) is suggested and is found suitable.

For making rubber gaskets 20/80 NR/latex reclaim (thread) blend is suggested. This blend vulcanizate is also found to satisfy the relevant ASTM standards for the gasket.

Since the latex reclaim obtained from examination gloves contains high quality rubber hydrocarbon without any filler, attempts have also been made to produce chlorinated rubber by the chlorination of latex reclaim dispersion in carbon tetrachloride and found that it possesses almost the same characteristics of commercial chlorinated rubber. Details of this study are given in part II of chapter 5.

LIST OF PUBLICATIONS

1. "Production of chlorinated rubber from latex reclaim",

   Mary Joseph, Rani Joseph and K.E.George

   Proceedings of 7th Kerala Science Congress, 27–29 January 1995, pp.60-62.

   (Won the "Young Scientist Award" of the Kerala Science Congress for the year 1995 for this paper).

2. "Production of latex reclaim from latex waste"

   Mary Joseph, Rani Joseph and K.E.George

   Journal of Polymer Recycling (In press).

3. "Studies on Natural rubber/polybutadiene blends Use of latex reclaim"

   Mary Joseph, Rani Joseph and K.E.George

   (Communicated to Kautschuk Gummi Kunststoffe).