STUDIES ON VULCANISATION KINETICS, THERMAL CONDUCTIVITY AND TECHNOLOGICAL PROPERTIES OF ALUMINIUM POWDER-FILLED NATURAL RUBBER COMPOUNDS

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... to the Loving Memory of my Father

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CERTIFICATE

This is to certify that the thesis entitled " Studies on vulcanisation kinetics, Thermal Conductivity and Technological properties of Aluminium Powder Filled Natural Rubber Compounds ", which is being submitted by Mrs.Sara Chandy in partial fulfillment of the requirements for awarding the degree of Doctor of Philosophy in Polymer Chemistry, under the Faculty of Science of the Mahatma Gandhi University , Kottayam, is a record of bonafide research work carried out by her under my direct supervision and guidance. No part of the results embodied in the thesis has been submitted for the award of any other degree or diploma earlier. It is also certified that Mrs.Sara Chandy has fulfilled the course requirements and passed the qualifying examination for the Ph.D. Degree.

Dr.Baby Kuriakose

Declaration

I hereby declare that this thesis entitled ***Studies on Vulcanisation Kinetics, Thermal Conductivity and Technological Properties of Aluminium Powder-Filled Natural Rubber Compounds*** *is a record of the research work carried out by me under the supervision and guidance of Dr. Baby Kuriakose, Deputy Director, Rubber Chemistry, Physics and Technology Division, Rubber Research Institute of India. No part of this thesis has been presented for any other degree or diploma earlier.*

Sara Chandy

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GLOSSARY OF TERMS

A_p	Cross-sectional area of the plunger
BR	cis-1,4-Polybutadiene rubber
d_c	Diameter of capillary
d_e	Diameter of extrudate
F	Force on plunger
K	Specific reaction rate constant
K & H	Constants of the probe
l_c	Length of capillary
M rad	Mega rad
M_H	Maximum torque
M_L	Minimum torque
MPa	Mega Pascal
n'	Flow behaviour index
NR	Natural rubber
OCT	Optimum cure time
phr	Parts per hundred of rubber
Q	Volumetric flow rate
rpm	Revolutions per minute
R_s	Surface resistance in ohms
V_r	Volume fraction of rubber in swollen vulcanisate
%	Per cent
ρ	Density
τ	Shear stress at wall
λ	Thermal conductivity
η	Shear viscosity
ΛE	Activation energy
$\dot{\gamma}_w$	Shear rate at wall
$\dot{\gamma}_{wa}$	Apparent shear rate at wall

Preface

Most of the work on use of filler in rubber compounds were concentrated on studying the factors affecting processing characteristics, reinforcement, polymer-filler interaction, vulcanisate properties, etc. Filler examined in rubber compounds were mostly carbon blacks and silica. However, use of metal powders as filler in rubber compounds was examined only to a very limited extent. The main objective of the present study is to examine the possibility of using aluminium powder as a filler in natural rubber compounds, with a view to improving the thermal conductivity. Hence in this work, cure characteristics, vulcanisation kinetics, melt flow behaviour, vulcanisate properties, thermal conductivity and ageing characteristics of compounds with different loadings of aluminium powder have been examined in detail. In all the cases, high abrasion furnace black and acetylene black which are known to provide good reinforcement and thermal conductivity respectively were also included for comparison. The subject matter of the thesis has been divided into eight chapters.

The first chapter consists of a brief review of the earlier work in elastomer reinforcement by fillers and scope of the present work. The second chapter deals with the materials used and the experimental procedures adopted in the investigation.

Chapter three describes the effect of aluminium powder on scorch time, cure characteristics and kinetic parameters of vulcanisation of NR compounds. Chapter four deals with the melt rheological behaviour of aluminium powder-filled vulcanisates. Chapter five deals with the physical properties of aluminium powder-filled vulcanisates. In chapter six, the thermal conductivity, electrical resistivity and extent of crosslinking as measured by the V_r values of aluminium powder-filled vulcanisates are described.

Chapter seven contains the ageing characteristics of aluminium powder-filled vulcanisates.

Chapter eight describes the properties of retread compounds containing aluminium powder.

CHAPTER I

INTRODUCTION

I INTRODUCTION

The importance of fillers in the rubber compounds is well known. Fillers are widely used to enhance the performance of rubbers and other polymeric materials. Filler characteristics such as size and shape of particles and aggregates, chemical nature and porosity of surface, dispersibility and tendency to agglomerate and form secondary filler networks determine its effect on rubber compounds.

Fillers can be classified into black and non-black. Soon after carbon black was discovered to be an active filler in rubber, at the beginning of this century, it became one of the most important components in the manufacture of rubber products, with a consumption second only to rubber itself.

The total Indian consumption of black and non-black fillers by the rubber industry during 1995-96 is estimated at about 3,30,000 metric tonnes corresponding to an average loading of 50 phr. The consumption of carbon black was more than that of non-black fillers and amounts to about 2 lakhs metric tonnes during 1995-96.

The results of many studies have been published describing one aspect or another of the behaviour of fillers and these are still appearing. Some excellent review papers and books, survey and analyse the available information such as those by Studebaker [1], Kraus [2,3], Donnet and Voet [4], and Medalia [5]. However, publications on the use of metallic powders as filler and its effect on mechanical and electrical properties of elastomers are only few in number [6,7]. In the following pages, a detailed account of the work done to study the effect of fillers on rubber compounds and vulcanisates is presented.

I.1 Types of Carbon Blacks

Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black, etc. based on their method of manufacture. Among these, the furnace type blacks account for a lions share of the total black consumed by the rubber industry.

The main reason for the predominant use of furnace type carbon blacks, in elastomers, is the reinforcement they impart to the vulcanisates [1,2,8]. Incorporation of carbon blacks into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall performance. A simple classification of rubber grade furnace type carbon black is based on surface area and aggregate morphology measured by dibutyl phthalate absorption (Table I.1).

Table I.1 **Properties of furnace blacks**

Black		Name	Surface area (m^2/g)	Average particle size (nm)	DBP absorption (c^3/g)
ASTM	Type				
N110	SAF	Super abrasion furnace	140	20-25	1.13
N220	ISAF	Intermediate super abrasion furnace	120	24-33	1.14
N330	HAF	High abrasion furnace	80	28-36	1.02
N550	FEF	Fast extrusion furnace	45	39-55	1.21
N660	GPF	General purpose furnace	37	50-60	0.91
N774	SRF	Semi-reinforcing furnace	28	70-96	0.70

I.2 Types of Non-black Fillers

Non-black fillers are classified as

a) Fillers used mainly to reduce cost

b) Semi-reinforcing fillers

c) Reinforcing fillers used to achieve high performance in non-black products.

Non-black fillers such as ground limestone, barytes, clay, kaolin, etc. were used in order to extend and cheapen the compound since it was found that in natural rubber quite a bit of these fillers could be added without detracting too much from the final vulcanisate properties. These inorganic fillers are in the non to low reinforcing range and have high specific gravities compared to the carbon blacks or synthetic silicas and silicates. Recently, new technical developments show promise of closing the wide performance gap between the carbon blacks and inorganic fillers. These included the use of silane coupling agents [9-11], pretreatment of filler surface with silanes and the surface grafting of reactive polymers.

Zinc oxide was the standard reinforcing filler for many years until it was replaced by carbon black during the period of 1917-1929. Today there are hundreds of commercial inorganic fillers providing a performance range from non-reinforcing to highly reinforcing, giving the rubber compounder a wide choice of cost benefit options. Table I.2 gives a simple classification of non-black fillers.

Table I.2 Classification and properties of non-black fillers

Product types and grades	Average particle size (nm)	Surface area (m^2/g)	Specific gravity	Volume specific surface area (m^2/cm^3)	pH	Oil absorption (g/100 g)
Silica precipitated, hydrated	16-100	40-170	1.93-2.05	77-332	5.7-9.5	160-240
Silica anhydrous, fumed	8-15	200-380	2.10	420-798	3.9-4.0	150-200
Aluminium silicate precipitated, hydrated	25	130	2.10	273	10.0	140
Clays	300-1500	8-22	2.60-2.68	21-58	4.1-7.0	29-52
Talcs	100-15000	1.3-17	2.80-2.90	3.8-48	9.8-10	80
Calcium carbonate precipitated	50-700	8-74	2.42-2.71	22-179	9.4	28.60

I.3 Reinforcement of Elastomers by Fillers

A reinforcing filler improves the modulus and failure properties of the final vulcanisate. A practical definition of reinforcement is the improvement in service life of a rubber article. The reinforcement of elastomers by particulate fillers, to a large extent depends on polymer properties, filler characteristics and processing methods. The primary filler factors influencing elastomer reinforcement are:

a) The particle size or surface area which together with filler loading, determines the effective contact area between the filler and the polymer matrix.

b) The structure or the degree of irregularity of the filler unit which plays an essential role in the restrictive motion of elastomer chains under strain.

c) The surface activity which is the predominant factor with regard to filler-filler and filler-polymer interaction.

I.3.1 Effect of Particle Size of the Filler on Reinforcement

The most important parameter influencing reinforcement is primary particle size [2]. Coarse blacks consist of aggregates of simple particles.

The more reinforcing blacks have much smaller primary particles, fused together to form primary aggregates. The size of the primary particles determines the surface area of aggregates since the area used up by fusion of particles is relatively low. These primary aggregates are the units, determining most of the properties the black will impart to the rubber compound.

The total surface area of a particulate solid is directly related to its particle size. If all particles are spheres of the same size, the surface area 'A_s' per gram of the filler is given by the Equation I.1.

$$A_s = \frac{6}{d\rho} \qquad \text{. . . . (I.1)}$$

where d is the diameter and ρ is the density. In reality there is always a distribution of sizes that can be averaged in various ways [12] and particles are usually far from round [13].

Particle size or surface area is a factor of greater importance in reinforcement because it vary over a wide range. Coarse inorganic fillers have surface areas of about 1 m^2/g, fine silicas upto 400 m^2/g, and in the case of rubber grade carbon blacks, there is a variation from 6 m^2/g for medium thermal blacks (N991) to 250 m^2/g for conductive blacks. So there is a factor of 40 between the highest and lowest surface area. No other factor in reinforcement varies over such a wide range.

The use of the same particle size description for silicas and carbon blacks does not imply the same reinforcement. This difference essentially disappears when coupling agents are used with the silicas. Then the silica and carbon black of similar size provide equivalent reinforcement, as measured by modulus, tensile strength and tire-tread wear. So given equivalent surface activity, particle size does relate to reinforcement in the same way for the two types of fillers. Among various types of silicas and silicates, majority are confined to the smaller size classes (<50 nm) and minority in the size classes larger than 50 nm.

Carbon black particles with pores and cracks have surface area greater than blacks of similar size without such features. This leads to an increased number of particles per unit weight. Thus porous black gives decreased resilience and increased electrical conductivity when compared with equal weight loadings of non-porous blacks.

I.3.2 Effect of Structure of the Filler on Reinforcement

Structure of carbon black aggregates is important in understanding the role of carbon blacks in reinforcement and its influence on properties such as modulus, viscosity and die swell which are known to be shape dependent. Aggregate shape or 'structure' increases with greater aggregate complexity and larger number of particles per aggregate. Highly structured aggregates typically have branches that form voids between them, where polymer can be occluded, which results in higher effective loading of the carbon black in an elastomeric compound. Skeletonisation method has been used for the first quantitative and direct measurement of branching in carbon black aggregates [14].

Carbon black aggregates are classified into four different shape categories that included (a) spheroidal, (b) ellipsoidal, (c) linear, and (d) branched [15]. Non-spherical particles have a volume packing which is less dense than that of spheres, leaving a greater volume of voids between the particles.

Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loadings leading to chain-like filler structures or clusters. These are generally termed secondary structure or filler network, even though they are not comparable to the continuous polymer network. Such a structure has a significant effect on the properties of filled rubber. Filler networking is determined by the attractive potential 'S_f' between aggregates in rubber as well as by their distance. Wang *et al.* [16] studied the role of the distance between filler aggregates in the dynamic properties of filled vulcanisates, using fillers with different attractive potential values. This study demonstrated that, at the same interaggregate distance, lower S_f of the filler leads to weaker filler network which is readily broken down and reconstituted.

The most common method of determining the 'structure' of carbon black is based on the measurement of the combined intra and interaggregate void volume by oil absorption (DBPA, ASTM D-2414). The internal void volume may also be measured by the compressibility of the carbon black at high pressures [17]. High structured carbon blacks have high oil absorption and lower compressibility for a given weight of carbon black. Work has been done extensively for carbon black morphological characterisation [18,19]. Tables I.3 and I.4 show in detail the effects of decreasing particle size and increasing structure on the vulcanisate properties and rheological behaviour of unvulcanised compounds respectively [20].

Table I.3 **Effect of particle size and structure on vulcanisate properties**

Vulcanisate properties	Decreasing particle size	Increasing structure
Rate of cure	Decreases	Little
Tensile strength	Increases	Decreases
Modulus	Increases to maximum and then decreases	Increases
Hardness	Increases	"

Elongation	Decreases to minimum and then increases	Decreases
Abrasion resistance	Increases	Increases
Tear resistance	"	Little
Cut growth resistance	"	Decreases
Flex resistance	"	"
Resilience	Decreases	Little
Heat build up	Increases	Increases slightly
Compression set	Little	Little
Electrical conductivity	Increases	Little

Table I.4 **Effect of particle size and structure on processing characteristics**

Processing properties	Decreasing particle size	Increasing structure
Loading capacity	Decreases	Decreases
Incorporation time	Increases	Increases
Oil extension potential	Little	Increases
Dispersability	Decreases	Increases
Mill bagging	Increases	"
Viscosity	"	"
Scorch time	Decreases	Decreases
Extrusion shrinkage	"	"
Extrusion smoothness	Increases	Increases
Extrusion rate	Decreases	Little

I.3.3 Effect of Polymer-Filler Interaction on Reinforcement

When carbon black is mixed into the rubber in conventional equipment, the first step is penetration of rubber into the void space replacing the trapped air and eliminating loose black. This occurs before the black is randomly dispersed. If at this stage considerable rubber-black interaction occurs, subsequent dispersion is rendered more difficult as bound rubber cements many primary aggregates together. For this reason, low structure, higher surface area blacks are difficult to disperse; their small void space and dense packing lead to high local black concentration and their large surfaces provide ample opportunity for early interaction with polymer. At the same time such blacks are quite rapidly incorporated. High structured blacks are more slowly incorporated but more easily attain a satisfactory degree of dispersion.

Continued mixing decreases the number of interaggregate contacts and increases the average distance of separation of the aggregate from each other. Electron microscopic studies have shown the breakdown of aggregates to two-third of their original size, with the extent of breakdown increasing with increased structure and increased polymer-filler interaction [21]. Even in good dispersions, there exist many interaggregate physical contacts.

Mechanical processing of carbon blacks by a novel pressure milling technique [22] provides a controlled breakdown of primary carbon black aggregates. In rubber vulcanisates, the pressure milled carbon blacks give about the same vulcanisate properties as normal carbon blacks with the same void volume or DBP absortion value.

The surface interaction between fillers and rubber molecules or network segments involves a range of bond energies from relatively weak Van der Waals force to very strong chemical bonds [23]. The number of each kind of interaction is unknown [24]. In all cases, physical adsorption undoubtedly occurs to varying degrees depending on the particular surface and molecular segments. Evidence for chemical bonding at the interface is also conclusive for some systems [25]. The relative contributions of physical and chemical interactions to reinforcement, differ both with the nature of the filler and the elastomer. When physical interaction is high, such as that for carbon black in hydrocarbon rubbers, there is little added contribution to reinforcement from the chemical bonding, although this may contribute to other desirable properties. Chemical interaction improves interfacial wetting and adhesion, improves dispersion and prevents reflocculation of dispersed particles. Another effect of chemical interaction is actual bridging of the particle surface to the elastomeric network [26,27].

The adsorption of polymer segments on the filler surface leads to some loss of mobility of the chains. Studies of proton magnetic resonance in carbon black-reinforced rubbers have shown that there is a loss in segmental mobility, but severe restriction of motion is confined to a layer of 5 Å thick at the surface, i.e., a distance of few carbon lengths along the polymer chain [28]. On the other hand, the chains of bound rubber extend far into the polymer matrix where they freely intermix with unadsorbed rubber molecules. On vulcanisation, they become part of the network, undistinguishable from free rubber.

I.3.4 Surface Activity

The surface activity is related to different chemical groups on the surface, such as carboxyl, quinone, phenol and lactone. Unlike white fillers whose chemical groups (hydroxyl and/or metal oxide groups) play an important role in their reinforcing ability for elastomers, the surface chemistry of carbon black has a significant effect on the vulcanisation of compounds. Surface energy of blacks is of much greater importance than their chemical nature with regard to the mechanical properties of the filled elastomers, particularly when general purpose hydrocarbon rubbers are concerned. Surface energies of a series of carbon blacks and the interaction between carbon blacks and elastomers were estimated by Wang and Wolff [29]. Inverse Gas Chromatography (IGC) is one of the most sensitive methods for the investigation of filler surface energies [30-32].

I.3.5 Effect of Bound Rubber on Reinforcement

Bound rubber [33-35] has been used to characterise filler-rubber interaction. Without the formation of bound rubber, carbon black acts as an inert filler, lowering modulus and tensile strength [36]. The bound rubber in a compound generally depends upon the surface area, with a weaker dependence on the structure, as was found for a series of compounds [33]. Wolff *et al.* [37] conducted a study on bound rubber content in SBR compounds with 17 carbon blacks covering a whole range of rubber grades and tested for bound-rubber content. It was found that the bound rubber content of a polymer at high loadings is higher for large surface area carbon blacks. In compounds using silica as the filler, the bound rubber can be greatly altered by chemically modifying the surface using the active hydroxyl sites on the surface to graft blocking agents or coupling agents.

In a series of compounds using fumed and precipitated silicas, Donnet [38] used a short chain alcohol, methanol, and a long chain alcohol, hexadecanol to modify the silica surface. The surface modification effectively prevented the formation of bound rubber with either SBR or NR. The reinforcement of the compound decreased substantially with surface modification.

I.3.6 Role of Coupling Agents

Owing to the hydrophilic character, silicas as such are incompatiable with the rubber matrix and thus lack in full rubber reinforcing ability. In the presence of a coupling agent, which chemically binds silica with rubber, marked increase in reinforcement is observed in silica-filled rubber vulcanisates. In this respect, silanes with appropriate functionality (alkoxy silyl groups) have been successfully employed as coupling agents [9-11,39]. It has been reported [40] that bis(diisopropyl) thiophosphoryl disulfide, an entirely new class of compound can also react with both silica and rubber during vulcanisation.

Wang and Wolff [41] showed that silane modified silica increase its compatibility with hydrocarbon elastomers, hence improves filler dispersion, compound processability and certain vulcanisate properties.

Titanate coupling agents are used for fillers, extenders and reinforcing agents in thermosetting and thermoplastic polymer systems [42].

The influence of fumed silica on the reinforcement properties of silicone rubber was studied by Cochrane and Lin [43]. The network in the vulcanisate is held together by silica-silica interactions and silica-polymer-silica bridge bonds between the silica aggregates. Increasing the silica loading, surface area and structure level increase the number of interactions and hence the network strength. Wang *et al.* [44] conducted a study to characterise the reinforcement of *in situ* precipitated silica in polydimethyl siloxane (PDMS) elastomers in shear and in biaxial extension and the results indicated that PDMS networks filled by the *in situ* precipitated silica have good mechanical properties, not only in uniaxial elongation but in shear and biaxial extension as well. The performance of silicas in polar elastomers is studied [45] using a series of silica and carbon black loaded acrylonitrile butadiene (NBR) compounds with different acrylonitrile contents. The study shows that the changes in viscoelastic properties of the silica-filled compounds can be attributed to improved polymer filler interactions relative to the interaction involved in carbon black-filled compounds.

I.4 Effect of Filler on Viscosity of the Rubber Compound

The flow of filled rubber compounds in the unvulcanised state is of obvious technological importance. The melt viscosity of rubber mixes increases with decreasing particle size and with increasing structure. The melt viscosity of the unfilled polymers is strongly dependent on their molecular weight distribution and the presence or absence of long chain branching [46]. The reason why carbon black imparts so much greater viscosity to the rubber are (a) occlusion of rubber within and between the carbon aggregates [47], (b) immobilisation of a layer of elastomer at the filler surface [48]. Changes in viscosity of filled rubbers is attributed to an entanglement/bound rubber model/for a series of SBR and NR compounds [49,50]. Physical properties of silica were reported to affect the viscosity of reinforced rubbers. Hewitt [51] reported that compound viscosity is directly related to silica surface area. It is also observed that highly developed filler networks of silicas give rise to high viscosities of the filled compounds [52].

Silicas and silicates generally produce higher Mooney viscosity in rubber mixes than other fillers of comparable particle size. This difference between types of filler became less pronounced as the average filler particle size increased [53]. At small size ($\sim$20 nm) HS-200 silica produced a significantly higher viscosity than carbon blacks of comparable size [54]. At large particle size (~ 40 nm) the silica and black produced similar viscosities [53]. In view of the greater increase in viscosity with small particle size, the primary emphasis on improving viscosity was on the more reinforcing silicas. One such study [55] was conducted using similar silicas with average ultimate particle size in the 18-22 nm range. The use of silane coupling agents was also an effective means of reducing viscosity in some elastomers, when silica was the filler [56].

With rare exception, the viscosity of high molecular weight rubbers is shear rate dependent. The presence of filler always increases the shear dependence; i.e., the increase in viscosity caused by the filler is the greatest at low shear rates. The viscosity at vanishing low shear rates becomes effectively infinite. The phenomenon is the result of secondary filler agglomeration, leading to the establishment of a weak filler network held together by Van der Waals forces. This network is progressively disrupted by increasing shearing stresses.

It has been shown that higher shear rates reduced the difference between types of fillers [57-59], so that silicas and carbon blacks have similar viscosities in high shear rate processes, such as extrusion and injection moulding.

I.5 Effect of Filler on Crosslinking Process and Cure Characteristics

Since a large proportion of natural rubber consumed in manufactured goods is compounded with carbon black as a reinforcing filler, it is important to understand the influence of individual carbon blacks upon the reactions taking place during sulphur vulcanisation. The possible influence of carbon black fillers on the total concentration of chemical crosslinks and on the proportions of mono-, di- and polysulphidic crosslinks is regarded as of particular relevance in view of the importance of these factors in determining vulcanisate properties [60,61].

The change in concentration of the effective chains of a rubber network caused by the presence of the filler in vulcanised rubbers has been investigated upto the present by means of the equilibrium swelling method [62-65] with use of Flory equation [66,67] as well as by determination of the equilibrium modulus [68]. Kraus [63] determined the crosslink density of a large series of vulcanisates, filled with carbon black and unfilled. From the increase in crosslink density in the filled vulcanisates, he deduced the number of polymer-filler bonds formed during mixing and vulcanisation as well as the number of those that are formed by the catalytic effect of the filler in course of the crosslinking reaction. Kraus [63] proved further that the filler in a vulcanised rubber, crosslinked with sulphur has no influence on the content of bound sulphur, but influences the number and character of the bonds formed in the system.

Janacek [69] has studied the influence of fillers on the degree of crosslinking of natural rubber and found that the crosslink density increased proportionally with the concentration of the carbon black by volume. Work by Cotton [70] has shown that the chemistry of carbon black surface plays an important part in the initial steps preceeding the actual crosslinking reaction as well as the crosslinking rate itself. Oscillating disc rheometer [71-73] can be used to study the effect of fillers on rate of cure and crosslinking. The rheometer curve (Fig. II.2) taken at curing temperature indicates the induction period, the course of the crosslinking reaction, the occurrence of a plateau or reversal and the time at which optimum cure is reached. The time required to achieve 90% of the maximum increase in torque (M_H) over the minimum (M_L) has been set as the time for optimum cure. M_H will also indicate the characteristic effects of the filler.

Bhowmick and De [74] have studied the effect of addition of HAF black on the kinetics of vulcanisation and the changes in the network structure of natural rubber mixes with a DTDM based accelerator system at 150°C and 180°C. Results showed that addition of HAF black enhanced the polysulphidic crosslinks as well as total crosslinks. They have observed that in the gum vulcanisate the polysulphidic crosslinks decrease continuously with cure time. Loo [75] and Mukhopadhyay and De [76] also made similar observations. In the filled system, however, the polysulphidic crosslinking passes through a maximum which shows that HAF black takes part in the actual sulphuration processes.

Previously, Porter [77] reported that HAF black influences the chemistry of sulphuration of the conventional system and has little effect on the EV system of NR. However, Bhowmick and De [74] showed that HAF black has a pronounced effect on the EV system as well. Previously [78] the increased crosslink density in the filled system has been attributed to the increased polymer-filler attachment which gives rise to restricted swelling in solvents. The recent observations [74] point out that the filler surface may catalyse the sulphuration processes and the observed increase in crosslink density may be due to increase in covalent crosslinks and not merely due to polymer-filler attachment.

Duchacek [79] has studied the effect of HAF carbon black on the course of the tetramethylthiuram disulphide accelerated sulphur vulcanisation of natural rubber at temperatures from 100°C to 140°C. Results show that HAF black does not alter the mechanism of the thiuram accelerated sulphur cure. The rate constants of vulcanisation rise considerably when HAF black is used and is dependent on the HAF black content of the rubber compound. The activation energies of vulcanisation are same as in carbon black-free mixture.

The effect of zinc oxide concentration on the course of tetramethylthiuram disulphide accelerated sulphur vulcanisation of natural rubber has been investigated by Duchacek [80] and found that the concentration of zinc oxide has practically no influence on the rate of thiuram accelerated sulphur cure. The values of the ultimate extents of crosslinking increase with increasing zinc oxide content in the rubber compound upto a certain limit corresponding to the theoretical amount of zinc oxide, which is necessary for the formation of zinc dimethyldithiocarbamate from tetramethylthiuram disulphide and zinc oxide during the vulcanisation reaction.

Effect of aerosil [81] on the course of thiuram accelerated sulphur vulcanisation of natural rubber from 100°C to 145°C shows that aerosil speeds up the course of the vulcanisation upto the value corresponding to the rate of zinc dimethyldithiocarbamate accelerated sulphur cure.

Hema Acharya [82] conducted a systematic study by selecting two carbon blacks namely, HAF and ISAF and changing their dosage to see their effect on the reaction kinetics for NR and polybutadiene rubber. She reported that the vulcanisation reaction seems to be of first order where k value depends on temperature and not on dosage of carbon black.

I.6 Effect of Filler on Vulcanisate Properties

The effect of fillers on the mechanical properties of elastomers is primarily of great interest because fillers can be used very effectively to enhance the ultimate properties. At the same time, however, fillers also affect the viscoelastic properties at small and intermediate strains.

I.6.1 Effect on Modulus

Carbon black raises the modulus of rubber by geometrical constraints which perturb the force field [83], these constraints are magnified by the convoluted shape of carbon black aggregates, within which the occluded rubber is partially shielded from stresses in the matrix [84]. The modulus of filled elastomers rises according to Payne [85] from several contributing factors which can be classified as follows:

a) A pure gum contribution which does not depend much on the kind of elastomer but on the crosslink density.

b) The hydrodynamic effect or strain amplification effect which is based on the concept that the local strain in between the filler particles is amplified over the externally applied macroscopic strain because the particles can be considered rigid compared to the soft rubbery matrix material and thus do not participate in deformation.

c) Elastomer-carbon black bonds are believed to increase the number of crosslinks per unit volume and thus increase the modulus [1].

d) The carbon structure is believed to be responsible for increase in the dynamic [86] as well as static modulus [87] at strains below 1%. Payne's classification of contributions to filler reinforcement does not include possible effects on the formation of structure entanglements. This effect could be playing a role, since entanglements have been shown to influence the modulus of elastomers markedly [88-90].

Compared to the carbon blacks, inorganic fillers have low levels of polymer-filler bonding and larger particle size varieties consists of individual, non-aggregated particles which cannot immobilise or occlude significant amounts of rubber phase. The smaller particle size hydrated silicas are aggregated and form transient structures, but their low level of surface activity for polymer bonding results in small amounts of effectively immobilised rubber. Because of these factors, mineral-filled vulcanisates have considerably lower modulus values compared to carbon black-filled vulcanisates at equivalent hardness.

I.6.2 Effect on Tensile Strength

Tensile strength may be regarded as catastrophic tearing at the tip of a chance flaw [91]. For an elastomeric material with a flaw corresponding to a cut of depth 'C', the stress at break (tensile strength) is given by

$$\sigma_b = (T_c E/\pi C)^{\frac{1}{2}} \qquad \text{. . . . (I.2) 1.2)}$$

and the elongation at break, by

$$e_b = (T_c/\pi C E)^{\frac{1}{2}} \qquad \text{. . . . (I.3)}$$

where T_c is the fracture energy and E is the Young's modulus [91]. Once the cut starts to grow, the stress required for further growth decreases progressively in accordance with Equation I.2, accounting for the catastrophic nature of the rupture.

Since modulus enters in the numerator of Equation I.2, a filler such as carbon black which increases the modulus will also tend to increase the tensile strength. This increase may be counteracted to some extent by a tendency toward larger flaw size in the presence of carbon black and this will depend considerably on the quality of dispersion attained during mixing. Larger flaw size leads to reduced elongation at break as well as reduced tensile strength.

Vulcanisates containing coarser black at high elongation give lower tensile strength [92] than that containing finer particle size blacks. This difference in tensile strength between blacks of widely different particle size is not tremendous. N110 and N765 blacks at 50 phr in SBR-1500 give tensile strengths of 32.3 and 22.7 MPa, respectively [93] i.e., a ratio of 1.42 whereas the blacks differ by a ratio of 4.83 in particle size.

The effects of structure and loading have been studied by Kraus [94] using blacks of approximately the same surface area (100 m^2/g). Results confirmed that with reinforcing blacks, the net effect of loading on tensile strength is that of carbon black plus the occluded rubber.

In accordance with Kraus' results, it is known that [93] at a fixed loading (50 phr), a low structure black gives higher tensile strength and higher elongation than a high structure black of the same surface area, since at this loading, low structure blacks are near the maximum of both properties while high structure blacks are to the right of the maximum. The loading at which the tensile strength is a maximum increases somewhat with increasing particle size [95], perhaps due to lower effectiveness of the occluded rubber with the coarser blacks at high elongations.

The increase in ultimate properties with increased effective loading upto the maximum is presumably due to the increased tear deviation [96]. Carbon blacks lead to tear deviation by creating barriers in the path of the tear. In non-crystallising rubber, it appears that the barriers can be formed by alignment of carbon black aggregates and their linkage, into chains or strands [97]. Evidence for the formation of these strands comes most directly from a large increase in electrical conductivity in the direction of stretching [98]. The positive dependence of tensile strength on the surface area of carbon black may be ascribed to the increased number of strands with blacks of higher surface area. In order to be effective, this tear deviation must act during the initial stages of growth of the random flaws, delaying the onset of catastrophic tearing.

The decrease in tensile strength beyond the maximum loading contrary to the increase which would be expected from an increase in modulus, according to Mullins [99], is due to "serious physical interference between neighbouring particles as the concentration gets sufficiently high." Developing this concept higher, at high loadings the carbon black aggregates may be unable to rearrange into strands during the time of stretching.

Silicas and silicates give tensile strength of similar magnitude as that expected from carbon black of comparable size. Colloidal silica is a good reinforcing agent, imparting high tensile strength and excellent resistance to tearing.

I.6.3 Effect on Abrasion and Wear

The most important effect observed upon introduction of carbon black into rubber was the vast improvement in abrasion resistance. Carbon black contributes strength and abrasion resistance to non-crystallising rubbers, while maintaining to a large extent their desirable elastic properties.

The mechanism of abrasion has been studied, amongst others, by Shallamach [100] who had shown that it is a complicated process of repeated straining of small volumes at the surface resulting finally in tear and their separation from the bulk of the rubber. Hence after a number of cycles of prestress, abrasion loss is the result of a high speed tensile process (Ecker) [101]. Kraus [3] has analysed the effect of the addition of carbon black on abrasion and wear in his excellent review. The abraded volume falls with carbon black loading.

Westlinning [102] compared the abrasion resistance at the same modulus of two series of compounds, one in which the modulus was obtained by the use of sulphur and curatives, the other by the addition of carbon black to a simple base compound. He found that while the abrasion resistance of the latter increased upto a certain maximum, the resistance of the former fell continuously and rapidly. Also abrasion resistance is known to fall rapidly with increased modulus as a result of the use of non-reinforcing fillers.

It is now well established that wear of rubber is not a purely mechanical process in that it contains a contribution due to thermal-oxidative breakdown of the polymer [103-105]. Still under severe conditions, which apply to all accelerated laboratory tests as well as to many situations encountered in tire wear, abrasion is dominated by tearing process.

The strain rates and temperatures prevailing in abrasion are very different from those used in routine laboratory testing of tensile or tear strength. Because of friction, local temperatures may far exceed those of the test track or of the bulk of the rubber [106,107]. Even at small sliding velocities the effective strain rate is very large, as small volume elements of rubber are deformed repeatedly at high strains by the many surface asperities of the track. Grosch and Schallamach [108] estimate strain rate $\epsilon = 100\ \text{sec}^{-1}$ for rubber sliding with a velocity of 1 cm/sec over silicon carbide paper. Ecker [101] has shown that laboratory abrasion loss data may be related to tensile strength measured at 100°C and $\dot{\epsilon} = 150\ \text{sec}^{-1}$.

Irrespective of the shortcomings of laboratory abrasion tests, Equation I.4.

$$A/\mu \approx C/U_b \qquad \text{. . . . (I.4)}$$

where,

A - volume abraded
μ - coefficient of sliding friction
C - proportionality constant
U_b - the work input at break

accounts for some important aspects of the dependence of roadwear on carbon black properties under severe conditions.

The coefficient of friction μ is not particularly sensitive to carbon black addition at normal loadings [101,108] and is essentially independent of particle size and structure for carbon blacks used in tire treads. Thus abrasion loss should be inversely related to U_b; the work input at break. The highest values of U_b are generally realised with small particle blacks. Also structure in carbon black leads to increased tensile strength and U_b at elevated temperatures.

The response of roadwear to carbon black particle size is generally decreased wear with smaller particle size [109-111]. But the predicted beneficial effect of structure is revealed clearly only at severe conditions, where the mechanism of abrasion is tearing [112]. Normal usage of tire always involves some service under severe conditions of wear, so that the use of medium to high structure, blacks is favoured. Detailed quantitative correlations of wear with carbon black particle size and structure are not easily established because of the fundamental difficulty in characterising the morphology of carbon black in quantitative terms. Surface oxidation of carbon blacks generally leads to increased rates of wear with highly unsaturated hydrocarbon rubbers [113,114], but the opposite is observed with butyl rubber. This behaviour has been ascribed to differences in interfacial adhesion.

During abrasion, small particles of rubber of about 1 to 5 μm in size are removed from the surface, leaving pits behind [115]. Eventually, as a result of continued erosion of the rubber surface, large pieces of rubber, of the order of 100 μm in size, are torn away. Most of the loss in weight is due to these larger pieces; they comprise as much as 95% of the total [115,116]. And yet it is detachment of the smaller particles that constitutes the basic abrasion process. If they are not removed, then cumulative erosion of the surface, followed by detachment of larger particles, will not occur.

A new theoretical treatment has been shown to account for observed rates of wear in terms of the resistance of compounds to crack growth under repeatedly-applied tensile stresses [117,118]. A hypothetical mechanism for detachment of small particles of rubber under the action of frictional force is put forward by Gent [119].

I.7 Specific Properties Imparted by Fillers

I.7.1 Effect on flame resistance

Fillers are used satisfactorily in many applications requiring certain specific properties. Elastomers with inherent flame resistance, such as polychloroprene rubber (CR), chlorinated polyethylene rubber (CPE), chlorosulphonated polyethylene rubber (CSPE), fluoroelastomers and silicones are readily selectable for flame resistant applications, but other elastomers which are not inherently flame resistant have been treated successfully by various methods to increase their fire retardancy. One approach to flame-retard rubbers is dilution of the polymer with filler having strongly endothermic transitions. The prominent examples of energy absorbing fillers are hydrates in particular alumina trihydrate (ATH). Alumina trihydrate has exhibited both smoke suppressant and flame retardant effect in a wide variety of elastomers when used at relatively high loadings [120]. At high loadings (>20 wt%) mass dilution and/or endothermal dehydration are thought to slow the build up of heat, favouring char forming processes and reducing the flammability and smoke generation in polydienes [121]. The effect is predominantly physical, but evidence has been found for catalytic activity as well Chalabi, Cullis and Hirschler [122-124] have also reported that, at less than 20 phr, pyrogenic silica is superior to $Al(OH)_3$ for smoke suppression in polystyrene.

Calcium carbonate, a very frequently used filler in all types of polymers, tend to lower the oxygen index (OI) of cured polychloroprene gum compound slightly [125]. The effect is more pronounced with carbonate of small particle size and is probably due to partial absorption of hydrogen chloride by filler. A similar effect was found with zinc oxide [126]. Inert fillers such as clay raise the oxygen index (OI) by dilution of combustiable matter in the rubber compound [125-127]. The effect of a variety of commonly used fillers and flame retardant additives was examined by Bolibar [128]. Among inorganic fillers alumina and kaolin were found to make the largest contribution to flame retardance.

The flammability of black-filled compounds, and unfilled compounds with equivalent formulations were evaluated by Trexler [129]. The flammability ratings of the black and unfilled compounds were the same, except for two polymers, neoprene and hypalon, which were rated as self-extinguishable in the black-filled compounds and combustable in the unfilled compounds.

Mosesman and Ingham [130] investigated two hydrated fillers, alumina trihydrate and magnesium hydroxide together with calcium carbonate and soft clay in an EPDM rubber. It was shown that hydrated fillers delayed smoke emission compared with other fillers; which was attributed to endothermic dehydration. In the flame mode, magnesium hydroxide was the most efffective smoke suppressant. Application of magnesium hydroxide as a flame retardant and smoke suppressant in two EVA copolymers was studied by Holloway [131].

I.7.2 Effect on Electrical Insulation/Conductance

Elastomers are insulators to which conductivity is imparted by addition of conductive fillers. The electrical conductivity of carbon black rubber compounds is augmented by promotion of interaggregate contacts and this is achieved by employing high concentrations of high structure filler and by using porous conductive blacks [132,133]. Carbon blacks of small particle size or a high degree of permanent particle structure generally gives lower values of resistivity [134-136]. The good mechanical properties combined with either low or high electrical resistivity has enabled their use in electrical devices such as high quality communications cables, low loss conventional power apparatus, optical fibers, cable jackets, etc. Enhanced electrical conductivity has also been realised in rubber blends by means of a nonuniform distribution of the carbon black [137,138].

With regard to the physical processes involved in the conduction of electricity, various authors have proposed different mechanisms [139,140]. It is known that deformation, while initially reducing the electrical conductivity of carbon black reinforced rubber, induces at higher strains, an enormous increase in the conductivity of many filled elastomers [141-143]. Higher conductivity can eventually be realised in the double network rubber [144].

Recently, flakes and fibers of aluminiun, exfoliated graphite, nickel flakes, graphite and carbon fibers and aluminium-coated glass fiber are being employed in making conductive polymer composites [145-149]. The use of a combination of carbon fiber and particulate carbon black has also been reported [150,151]. Ferrites have been used to improve magnetic and electrical conductivity of polymers [152,153]. Mica-thermoset resin composites are well known electrical insulators. Epoxy-mica composite has been shown to have enhanced voltage endurance characteristics. Mica, silane and silane-treated mica increases the ambient dielectric properties of vulcanised styrene-butadiene rubber [154].

I.7.3 Effect of Filler on Heat Resistance of Elastomers

The presence of high level of unsaturation in a natural rubber molecule makes it highly susceptible to attack by oxygen. Heat accelerates the oxidation process. During service, a number of rubber products are subjected to varying levels of heat, generated as result of either cyclic mechanical strain as in the case of a running tyre or high ambient temperature. Prolonged exposure to heat causes thermo-oxidative degradation of rubber and results in the deterioration of its desirable properties, eventually leading to premature failure. Thermo-oxidative ageing of rubber is believed to occur in two ways either via main chain scission or crosslink scission. It is reported that carbon black accelerates main chain scission and crosslink scission by surface catalysis [155].

Heat resistant compounds used in seals, gaskets often contain magnesium oxide. Natural mica, washed and ground to pass 200-300 mesh, provides a filler of linear type, imparting resistance to heat and lower permeability of gases.

I.7.4 Effect of Filler on Chemical Resistance of Elastomers

Elastomers find applications in many chemical industries as a protective lining to various metallic vessels, which carry chemicals at different temperatures [156]. Oxygen, ozone, heat, solvents and chemicals are the most common agents which cause degradation of elastomers. In this event, elastomers having a relatively inert backbone structure should be chosen. Fillers also contribute to impart resistance to various chemicals under the service conditions e.g., precipitated barium sulphate is useful under acid immersion conditions.

It has also been reported [157] that a pronounced decrease in matrix swelling due to liquid penetration occurs with increased filler loading and the decrease is a linear function of loading when it is done with carbon black. For loading with inorganic fillers the presence of water soluble constituents in the filler may act as water pools and as a consequence the above pattern of swelling may get altered [158].

I.8 Effect of Filler on Thermal Conductivity of Rubber Compounds

Heat is the most important processing agent both in the manufacture of raw elastomers and processing them to finished products. The rate at which heat can get into and out of rubber i.e., its thermal conductivity controls many applications, affects the design of processing machinery and controls the speed of mixing, extruding and moulding operations.

The basic Fourier equation for the unsteady state conduction of heat in one dimension is

$$\frac{\partial t}{\partial \theta} = \frac{k\partial^2 t}{c\rho\partial x^2} \qquad \ldots\ldots (I.5)$$

where

t - temperature

θ - time

k - thermal conductivity

c - specific heat

ρ - density

x - distance from one surface.

The expression $k/c\rho$ is called 'α' the thermal diffusivity which is a measure of the rate of temperature movement through a body. k, the thermal conductivity can be taken as a measure of the rate of flow of heat through a body. In comparison with other substances, rubber has a very low thermal diffusivity. In the extensive list of Ingersoll *et al.* [159] rubber has the lowest value of 'α' of all substances quoted which include metals, insulating materials, soils, woods, liquids and gases. This low value of 'α' means that a given article made of any of the other materials mentioned can be heated faster than the one made of rubber.

Studies on thermal conductivity of rubber compounds with various fillers are scanty. A large dependence of conductivity on the type of carbon black was reported by Kainradl [160]. His observations can be summarised as follows:

a) Furnace blacks give higher thermal conductivity than channel blacks.

b) Thermal conductivity increased almost linearly with black content in the range 10-50 phr black.

c) Acetylene black imparted the highest thermal conductivity; at 50 phr, conductivity was about twice that with a channel black. Conductivity ranking for various types of black was acetylene black > RF > FEF > HAF > HMF > SRF > HPC > MPC.

d) Mineral fillers gave conductivities intermediate between the highest and lowest values secured with carbon blacks, zinc oxide giving the highest conductivity on a volume basis.

Hands and Horsfall [161] observed high thermal conductivity for N990 than for N110, N220 or N550. They showed that both the diffusivity and conductivity of black loaded natural rubber compounds decrease with increasing temperature. The decrease over the temperature range from room temperature to 200°C, can be as much as 45%. They observed that the thermal conductivity of black loaded NR samples cut from different parts of the same compression moulded vulcanised sheet could differ by upto 25% at room temperature. The difference could be caused by variation in carbon black dispersion across the sheets. Particle size and structure of carbon black seem to affect values erratically, although the trend is towards higher values with larger particle size and higher structure [162]. A linear relationship of thermal conductivity Vs volume concentration of carbon blacks and other fillers is observed except at a very high concentration.

Schilling [163] carried out thermal conductivity determination for NR, butyl rubber, NBR and SBR with a series of loadings of HAF black and silica gel. Oikov [7] investigated the thermophysical properties of NR vulcanisates filled with aluminium. He studied the dependence of coefficient of thermal conductivity and thermal diffusivity of NR vulcanisates on the content of aluminium. Various methods for measuring thermal conductivity are well documented in the literature [162,164-166] including the widely accepted ASTM procedures [167].

I.9 Heat Transfer and Vulcanisation of Thick Articles

During the mixing and moulding stage, the thermoplastic nature of rubber is such that viscosity and other physical characteristics are temperature sensitive. In the vulcanisation of a rubber article in contact with an efficient heating medium, the period during which the temperature within the rubber is rising, is the period of unsteady state heat conduction. If the article is thin this period is short and for most of the cure, the temperature is steady. If the article is thick, the temperature in the interier may never reach the temperature of the heating medium and unsteady state conduction occurs during the whole cure. In the former case calculation of the degree of cure at the coolest point in the article is not so simple. The terms thick and thin as employed here are relative to time. If the total cure is say three minutes, anything over 5 mm may well be called thick. Bearing in mind that the economies of production tend to force the cure time down to the minimum, unsteady state conduction applies through the curing cycle of most articles of thickness greater than 6 to 8 mm.

Rubber is a bad conductor of heat, so cure time is controlled by the length of time required to heat the centre of the article on the one hand and on the other by the amount of overcure which can be accepted on the surface while obtaining full cure in the centre of the product. Some increase in the conductivity is possible by the incorporation of suitable filling materials having inherent high conductivity.

In the case of thick articles, if the surface is close to its optimum cure state, the centre may well be badly undercured causing the article to be too prone to heat build up under rapid cyclic deformation and readily get destroyed. If the centre is adequately cured the surface may be badly overcured resulting in reduced ageing resistance. At the same time the thicker the article, the slower will its inside cool after the article has been removed from the curing environment. Almost exact equivalence of cure of the outside and base of treads has been reported for tyres when they are removed from the mould with the tread base cured only about half as much as the outer surface [168].

In order to make a balance between the uneven state of cure of the surface of a thick article and its core and to ensure adequate processing safety, cure retarders [169] are used in rubber compounds. Retarders prolong the induction period before the onset of vulcanisation. An efficient retarder should influence the induction period, without affecting the actual curing time or the extent of vulcanisation.

Vulcanisation with a high ratio of accelerator to sulphur (an EV system) reduces the reversion of the exterior of a large article during the long period required to cure the interior. EV system gives a network which is thermally more stable than that obtained from a conventional high sulphur formulation [170]. The greater stability is attributed to the formation of high proportion of relatively unreactive monosulphidic [171] crosslinks.

According to Cuthbert [172] the problem of vulcanisation of thick articles can be solved by the application of unsteady state heat conduction theory, in addition to a certain amount of practical experience of minimum and maximum cure the compound can withstand without deterioration in physical properties or ageing resistance.

In simple cures of modertately thick articles, the rough practice of adding 'lag time' to the cure has evidently served for many practical purposes to achieve adequate cure at the centre [173,174]. Conant *et al.* [173] published a nomogram for estimating the additional curing time for various sizes of slabs, blocks, bars, cylinders, cubes and spheres. The additional time was assumed to be independent of the impressed temperature and the error on this account was estimated not to exceed 5% for a resonable range of curing temperatures. Mackae and Zapp [175] made a study of the thermal diffusivity of butyl rubber compounds and time temperature relations at the midplane of rubber slab in connection with their vulcanisation.

Another interesting observation made by Edmondson [176] on thick articles is that if a small amount of surface is ground away, volumes of maximum over cure can be readily removed.

One way of improving the heat transfer is to increase the thermal conductivity of the compound by adding suitable thermally conductive fillers.

I.10 Scope of the Work

A close examination of the detailed literature survey presented in the foregoing pages reveals that most of the work on use of filler in rubber compounds were concentrated on studying the factors affecting processing characteristics, reinforcement, polymer-filler interaction, vulcanisate properties, etc. Fillers examined in rubber compounding were mostly carbon blacks and silica, even though other particulate fillers such as calcium carbonate, clay, mica powder [177], rice husk ash [178], etc. and short fibres such as nylon, aramid, sisal, jute, silk, etc. were also studied in different elastomers [179-183]. Role of fillers in imparting special requirements such as electrical resistance/conductance [132], chemical resistance [157], flame resistance [129], heat resistance [155], etc. were also examined by several research groups. However, use of metal powders as filler in rubber compounds was examined only to a very limited extent. For example, use of brass powder [184] in rubber compounds has been reported to give better bonding of the compound with metals. High loadings of lead powder was found to be useful to impart X-ray resistance.

India is the fourth largest producer of natural rubber in the world, with an annual production of 5,06,910 metric tonnes [185]. We also produce 5,80,000 metric tonnes of aluminium per annum [186,187]. Even though other metals such as copper, iron, manganese, etc. are known to be pro-oxidants for NR, aluminium is comparatively neutral in its action towards natural rubber and hence aluminium vessels are widely used for processing NR latex by the plantation industry. NR is having excellent technological properties but its resistance to oxidation and thermal ageing is very poor. Since NR is a poor conductor of heat, it requires a very long time for vulcanising thick articles such as retread compounds, roll covers, rice polishers, dock fenders, solid tyres, etc. This leads to overcuring at the surface and thermal degradation of the polymer when it is used for such applications. Aluminium is available in powder form, having particle size ranging from 127 to 200 nm. Its thermal and electrical conductance is also very good. At the same time it is not a pro-oxidant for NR. Its specific gravity is 2.69 which is in the range that for fillers such as china clay (2.6), whiting (2.7), calcium carbonate (2.65), talc (2.8), etc. and is much lower than that for zinc oxide (5.60), titanium dioxide (3.9), magnesium oxide (3.6), barytes (4.45), etc. Hence it is worth to take up a detailed study on the use of aluminium powder as a filler in natural rubber compounds.

I.11 Objectives of the Work

Incorporation of filler in rubber compounds brings about a lot of changes in processing characteristics, flow behaviour and vulcanisation kinetics, besides the vulcanisate properties. The main objective of the present study is to examine the possibility of using aluminium powder as a filler in natural rubber compounds, with a view to improving the thermal conductivity. Hence in this work, the changes in the following properties of compounds with different loadings of aluminium powder have been examined in detail. In all the cases, high abrasion furnace black (HAF) and acetylene black which are known to provide good reinforcement and thermal conductivity respectively were also included for comparison.

a) Cure Characteristics, vulcanisation kinetics and extent of crosslinking of aluminium powder-filled NR compounds

Ideally, fillers should *not* affect the cure characteristics, vulcanisation kinetics and extent of crosslinking of rubber compounds. But acidic fillers and those which can adsorb the accelerators are known to retard the cure, resulting in extension of the vulcanisation time. Very fine particle size furnace blacks are difficult to get incorporated in the rubber compound and generate high temperature during mixing, leading to scorching problems. Increase in vulcanisation time affects productivity and scorching makes the compound difficult to process further. If the filler affects the extent of crosslinking, the vulcanisate properties will be affected adversely. Thus a detailed study of all these parameters is essential to assess the suitability of aluminium powder as a filler for rubber compounds.

b) Melt flow characteristics of aluminium powder-filled NR compounds

For making a product the rubber compound is to be subjected to any of the processes such as moulding, extrusion or calendering. All such processes involve flow of the compound under high pressure and temperature. Most of the rubber compounds have pseudoplastic flow characteristics so that their viscosity decreases with increase in rate of shear. But incorporation of fillers normally increases the viscosity. Hence to standardise the processing conditions of rubber compounds containing aluminium powder, knowledge on its viscosity at different temperatures and rates of shear is essential.

c) Vulcanisate properties of aluminium powder-filled NR compounds

Fillers are incorporated in rubber compounds either to enhance the vulcanisate properties or to reduce the cost. Reinforcing fillers when used in rubber compounds at appropriate loadings, enhance properties such as tensile and tear strengths, abrasion resistance, flex resistance, hardness, etc. whereas, the non-reinforcing ones help to reduce the cost of the compound. Aluminium powder which costs about Rs. 150 per kg cannot be considered as a cheap filler. Hence a detailed study on its effect in different vulcanisate properties is necessary to optimise the quantity of filler for achieving the desired level of improvement in a particular property.

d) Thermal conductivity of aluminium powder-filled NR compounds

Natural rubber is a poor conductor of heat and electricity. Fillers such as carbon blacks help to improve these to a certain extent only. Hence it takes a very long time to vulcanise thick articles. One of the important properties of aluminium is its good thermal and electrical conductance. Incorporation of aluminium powder is expected to increase the thermal conductivity of NR compounds. To assess the extent of enhancement in thermal conductivity achieved by adding a definite volume of aluminium powder and to study the effect of temperature on thermal conductivity of aluminium powder-filled NR compounds, a detailed experiment was carried out.

e) *Ageing characteristics of aluminium powder-filled NR compounds*

Rubber vulcanisates are being subjected to the attack of various degrading agents such as oxygen, ozone, light heat, radiation, etc. during service. Depending on the basic structure of the polymer, its resistance to these *degrading agents varies. Natural rubber is having very* active double bonds in its main chain and hence is highly susceptible to the attack of these agents. Many metals such as copper, iron, manganese, etc. are pro-oxidants for natural rubber. Even though aluminium is neutral under normal conditions, it is necessary to study its effect on the resistance of NR compounds under the influence of the above degrading agents, so as to get an idea about the long term performance of the aluminium powder-filled NR vulcanisates.

f) *Properties of retread compounds containing aluminium powder*

There are several rubber products such as retreads, rice polishers, rubber rolls, solid tyres, dock fenders, etc. which take a very long time for vulcanisation. Due to their thick cross-section, extra time is needed for the heat reach the centre portion. This leads to uneven cure and a very badly overcured outer surface for the product which adversely affects its performance. Long cure time affects productivity also. Among such products, retread compound is the one which is produced in large quantities in this country. In this era of energy shortage, it will be a welcome step if the vulcanisation time can be reduced by increasing its thermal conductivity. Hence in the present work an attempt is made in this line also.

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CHAPTER II

EXPERIMENTAL TECHNIQUES

II EXPERIMENTAL TECHNIQUES

II.1 Materials Used

II.1.1 Natural Rubber

The natural rubber (NR) used for the study was technically specified form of rubber, obtained from the pilot crumb rubber factory of the Rubber Research Institute of India, Kottayam. The rubber satisfied the Bureau of Indian Standards specifications of ISNR-5 grade natural rubber. The specification parameters and their limits for the ISNR-5 grade NR are given in Table II.1. The rubber from the same lot has been used in a particular experiment, since the basic properties such as molecular weight, molecular weight distribution and the contents of non-rubber constituents of NR are affected by clonal variation, season, use of yield stimulants and methods of preparation.

II.1.2 cis-1,4-Polybutadiene (Cisamer-1220)

cis-1,4-Polybutadiene (BR) supplied by M/s Indian Petrochemicals Corporation Limited, Baroda was used for the study. It has more than 96% cis content, Mooney viscosity 40 at 100°C, ash content 0.2% and volatile matter 0.3%.

Table II.1 **Characteristics of ISNR-5 grade natural rubber**

Parameters	Limiting value for ISNR-5	Actual value of sample used
Dirt content, % by mass, max	0.05	0.03
Volatile matter, % by mass, max	0.80	0.50
Nitrogen, % by mass, max	0.60	0.30
Ash, % by mass, max	0.50	0.40
Initial plasticity, P_O, min	30	42
Plasticity retention index, min	60	78

II.1.3 Fillers

II.1.3.1 Aluminium powder

Aluminium powder used for the study was supplied by Khosla Metal Powders Pvt Ltd., Pune. The technical details of aluminium powder are given below.

1. Particle size - 127-200 nm (maximum band at 140 nm)
2. Bulk density - 0.36 g/c.c
3. Specific gravity - 2.69
4. pH - 7.00

II.1.3.2 Intermediate Super Abrasion Furnace Black (ISAF)

ISAF black was supplied by Philips Carbon Black Limited, Durgapur. The characteristics of ISAF black are given below:

1. Particle size - 22-26 nm
   (maximum band at 24 nm)
2. Bulk density - 0.35 g/c.c.
3. Specific gravity - 1.81
4. Ash content (%) - 0.5
5. pH - 6.3
6. DBP absorption value - 1.15 c.c/g

22-26 nm

1.15 c.c/g

II.1.3.3 High Abrasion Furnace Black (HAF)

HAF black was supplied by Philips Carbon Black Limited, Durgapur. The characteristics of HAF black are given below:

1. Particle size - 29-38 nm
   (maximum band at 31 nm)
2. Bulk density - 0.39 g/c.c.
3. Specific gravity - 1.81
4. Ash content (%) - 0.4
5. pH - 7.1
6. DBP absorption number - 1.01 c.c/g

II.1.3.4 Acetylene black

Acetylene black was supplied by Tecil Chemicals And Hydro Power Limited, Kottayam. The characteristics of acetylene black are given below.

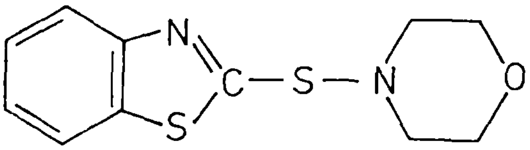
1. Particle size - 40-50 nm (maximum band at 47 nm)
2. Bulk density - 0.06 g/c.c.
3. Specific gravity - 1.81
4. Ash content (%) - 0.20
5. pH - 6.5
6. DBP absorption value - 2.5 c.c/g

II.1.4 Rubber Chemicals

The rubber chemicals used for the study was supplied by ICI India Limited and were chemically pure grade.

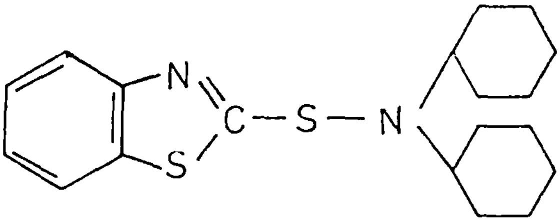
II.1.4.1 Accelerators

II.1.4.1.1 2-(morpholinothio) benzothiazole (MOR)



MOR having melting point 82°C, specific gravity (at 25°C) 1.36 and soluble in toluene was used.

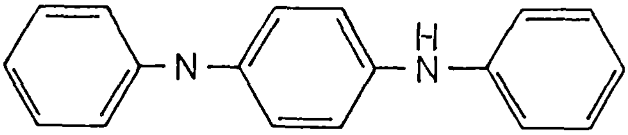
II.1.4.1.2 N,N′-Dicyclohexyl-2-benzothiazyl sulphenamide (DCBS)



DCBS having melting point 90°C, specific gravity (at 25°C) 1.2 and soluble in toluene and carbon tetrachloride was used.

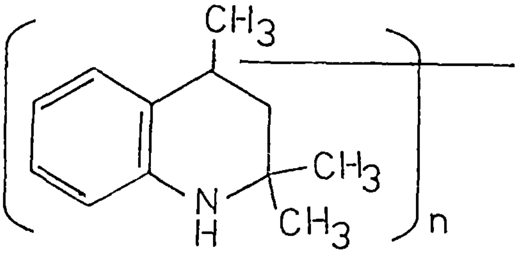
II.1.4.2 Antioxidants

II.1.4.2.1 N,N′-Diphenyl-para-phenylene diamine (DPPD)



DPPD having melting point 136°C, specific gravity (at 25°C) 1.22 and soluble in acetone and ethanol was used.

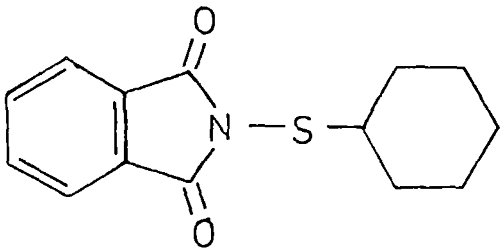
II.1.4.2.2 Polymerised 1,2-dihydro-2,2,4 trimethyl quinoline (TDQ)



TDQ having softening point 75°C, specific gravity (at 25°C) 1.06 and soluble in acetone, benzene, ethanol and chloroform was used.

II.1.4.3 Retarder

II.1.4.3.1 N-(cyclohexylthio)-phthalimide (CTP)



CTP having melting point 90°C, specific gravity (at 25°C) 1.3 and soluble in alcohol, acetone, and toluene was used.

II.1.5 Other Chemicals

II.1.5.1 Zinc oxide (ZnO)

ZnO having specific gravity 5.6 and a purity of 99.4% was used.

II.1.5.2 Stearic acid

Stearic acid having melting point 70°C, iodine value 9.5 and specific gravity 6.84 was used.

II.1.5.3 Sulphur

Rubber grade sulphur was used for the study. It had a melting point 114°C and specific gravity (at 25°C) 2.07. The material was completely soluble in CS_2.

II.1.5.4 Insoluble sulphur

15% oil treated sulphur, insoluble in carbon disulphide was used in retread formulations.

II.1.6 Plasticizer

II.1.6.1 Naphthenic oil

Naphthenic oil used for the study had a specific gravity 0.9, aniline point 77.8°C, flash point 180°C and pour point 6°C.

II.1.7 Solvent

II.1.7.1 Toluene

Toluene used had a boiling point of 110-111°C, specific gravity 0.863 and a purity of 99.5%. The toluene was redistilled before use.

II.2 Preparation of Compounds

II.2.1 Base Formulation (I)

Base formulation (I) used for preparing the compounds is given in Table II.2. Since this work is intended for improving thermal conductivity and vulcanisation characteristics of thick rubber articles, a general formulation suitable for vulcanising such products was selected. Use of sulphenamide accelerators is recommended by the industry in such cases. The formulation also contained necessary protective agents such as TDQ and DPPD either alone or in combination. The fillers were evaluated at equal volume loadings since there is a wide difference in specific gravity of carbon black and aluminium powder. Properties such as thermal conductivity and electrical properties depend on the filling of voids in the network by the filler.

II.2.1.1 Designation of compounds

The compounds are designated as given below:

Gum - compound without any filler

AL05, AL10, AL15, AL20 - compounds containing 5, 10, 15 and 20 volume per cent respectively of aluminium powder in the base formulation.

HF05, HF10, HF15, HF20 - compounds containing 5, 10, 15 and 20 volume per cent respectively of HAF black in the base formulation.

AC05, AC10, AC15, AC20 - compounds containing 5, 10, 15 and 20 volume per cent respectively of acetylene black in the base formulation.

*II.2.2 **Base Formulations (II) and (III)***

For evaluating the effect of aluminium powder in a retread compound, the formulations given in Tables II.3

and II.4 were selected. For getting better mileage a blend of NR and polybutadiene rubber containing ISAF black as filler is used by the industry. Hence in this study, I have taken the above base formulations and aluminium powder was added as an additional ingredient. In these formulations, the quantity of aluminium power added was in parts per hundred rubber by weight and not on volume basis.

The quantity of naphthenic oil added varied in order to keep the hardness of the compounds almost same (in the range of 60 ± 1 shore A). Compounds of the series TR, TRAL5, TRAL10, TRAL15 and TRAL20 were prepared in the normal way by adding ISAF black followed by aluminium powder. Compounds of the series BRAL5, BRAL10 and BRAL15 were prepared by adding the respective quantity of aluminium powder first in polybutadiene rubber, then blending it with NR and then completing the compounding by adding ISAF black, oil, etc. NRAL10 compound was prepared by adding 10 phr of aluminium powder first in NR and then blending it with polybutadiene rubber. Further compounding with ISAF black and other ingredients were done in the usual way.

Table II.2 **Base formulation (I)**

Ingredients	Quantity (phr)
Natural rubber	- 100.0
Zinc oxide	- 5.0
Stearic acid	- 1.0
N-(cyclohexylthio) phthalimide	- 0.3
Polymerised 1,2-dihydro-2,2,4-trimethyl quinoline	- 1.00
2-(morpholinothio)benzothiazole	- 0.75
Naphthenic oil*	- Variable
Filler**	- 0, 5, 10, 15, 20 volume loading
Sulphur	- 2.5

*Naphthenic oil : 10% by wt of the filler added.

**Fillers used : Aluminium powder, high abrasion furnace black and acetylene black were added on volume basis.

Table II.3 **Base formulation (II)**

Ingredients	TR	TRAL5	TRAL10	TRAL15	TRAL20
Natural rubber	60.00	60.00	60.00	60.00	60.00
cis-1,4-Polybutadiene	40.00	40.00	40.00	40.00	40.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00
Stearic acid	2.00	2.00	2.00	2.00	2.00
N,N’-Dicyclohexyl-2-Benzothiazyl sulphenamide	1.00	1.00	1.00	1.00	1.00
N,N’-Diphenyl-para-phenylene diamine	1.00	1.00	1.00	1.00	1.00
Polymerised 1,2-dihydro-2,2,4-trimethyl quinoline	1.00	1.00	1.00	1.00	1.00
Naphthenic oil	5.00	6.50	9.00	10.00	11.00
Intermediate super abrasion furnace black	45.00	45.00	45.00	45.00	45.0
Aluminium power	0.00	5.00	10.00	15.00	20.00
Insoluble sulphur	2.50	2.50	2.50	2.50	2.50

Table II.4 **Base formulation (III)**

Ingredients	BRAL5	BRAL10	NRAL10	BRAL15
Natural rubber	60.00	60.00	60.00	60.00
cis-1,4-Polybutadiene	40.00	40.00	40.00	40.00
Zinc oxide	5.00	5.00	5.00	5.00
Stearic acid	2.00	2.00	2.00	2.00
N,N'-Dicyclohexyl-2-Benzothiazyl sulphenamide	1.00	1.00	1.00	1.00
N,N'-Diphenyl-para-phenylene diamine	1.00	1.00	1.00	1.00
Polymerised 1,2-dihydro-2,2,4-trimethyl quinoline	1.00	1.00	1.00	1.00
Naphthenic oil	6.50	8.00	8.00	9.50
Intermediate super abrasion furnace black	45.00	45.00	45.00	45.0
Aluminium power	5.00	10.00	10.00	15.00
Insoluble sulphur	2.50	2.50	2.50	2.50

II.2.3 Mixing Mill

The compounds were prepared in a two-roll laboratory model open mixing mill of 150 x 300 mm size, having roll temperature set at 60°C, nip gap 1.3 mm and friction ratio 1:1.25. Nip gap, mill roll speed ratio, time of mixing and temperature of the rolls were kept constant during the preparation of all the compounds.

II.2.3.1 Mixing operation

Compound was prepared according to ASTM D-3182-89 method. The elastomer was first passed through the tight nip of the rolls, twice. A blanket of the rubber obtained was then passed through the rolls set at 1.3 mm nip gap and allowed to form a band around the front slow roll. This started with many holes and after continued passing, the band became smooth. The elastomer was then cut back and forth twice to ensure proper blending and to allow the elastomer in the bank to go through the nip. It is important for efficient mixing to maintain a rolling bank on the mill during the incorporation of ingredients. All dry ingredients except the fillers and the cure system were then added to the nip. Carefully collected the materials falling through the nip, from the tray and returned to the mix. The compound was then cut back and forth twice to assure good dispersion of these dry ingredients throughout the batch.

The mill was then slightly opened to increase the nip to 3.0 mm and the fillers along with the liquid plasticizer were added slowly, evenly and alternately to the batch. To prevent excessive loading of fillers at the centre of the mill, strips of compound were cut from the ends of roll several times during this operation and thrown back into the bank. When most of the fillers were incorporated into the compound, the remaining fillers and liquid plasticizer were added to the batch. When no loose filler was visible, the batch was cut back and forth twice more to assure good dispersion. The nip gap was increased to 4.0 mm when higher quantity of filler was added. Sulphur was then added to the batch. When it was well dispersed, the entire batch was cut back and forth at least 4 times to assure thorough cross blending. The mixing cycle was concluded by passing the rolled batch endwise through the mill six times with an opening of 0.8 mm to improve the dispersion. Finally the compound was sheeted out to get 3 mm thickness.

II.3 Testing of Compounds

II.3.1 Scorch Time

Scorch time is the induction period before a noticeable modulus develops. An appreciable level of scorch time ensures processing safety of the compounds. Mooney Viscometer gives a curve (Fig. II.1) on which 'scorch time' is the time 't_5' for the reading to rise by 5 units above the minimum Mooney viscosity (ASTM D-1646-94).

II.3.1.1 Scott Mooney Viscometer

The instrument consist of a motor-driven rotating disk within a cylindrical cavity formed by two dies, maintained at specified conditions of temperature and die closure force. The Mooney Viscometer measures the effect of temperature and time on the viscosity of rubbers.

II.3.1.2 Principle

The viscosity of the rubber compound is recorded during heating at a specified temperature. The minimum viscosity and time for the viscosity to increase by specified amounts are used as a measure of the start and rate of vulcanisation.

II.3.1.3 Measurement procedure

A rotor of 38.10 ± 0.03 mm in diameter was used. The speed of the rotor was 2 rpm. The temperature of the closed dies with rotor in place was kept at 120°C. The rotor was removed from the cavity and quickly inserted the stem through the centre of one of the test pieces and replaced in the cavity. The second test piece was kept on the top of the rotor. The dies were closed immediately and started the timer. After 1 minute, started the motor which drives the rotor. Viscosity was recorded continuously. The time 't_5' required for an increase of 5 units above the minimum viscosity was noted. 't_5' gave the Mooney scorch time at 120°C.

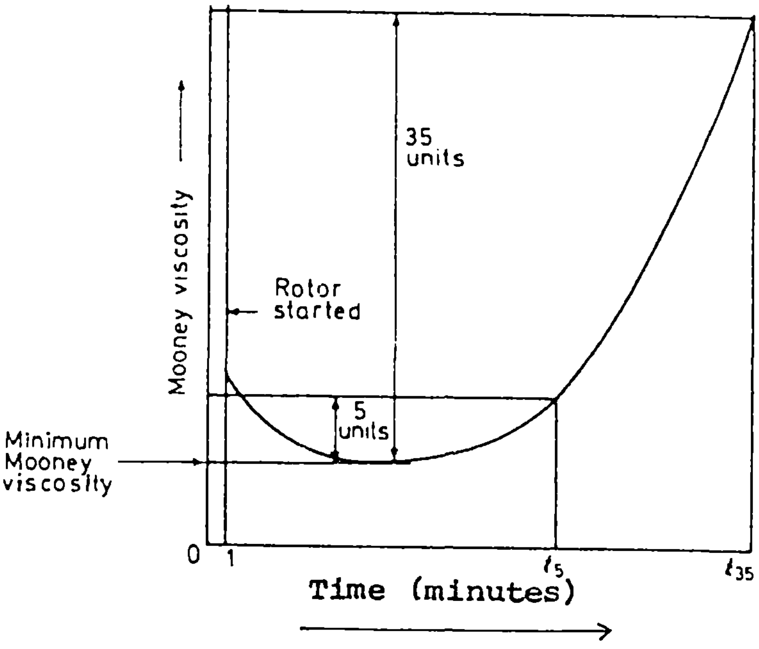


Figure II.1. A typical cure graph by Moony Viscometer.

II.3.2 Optimum cure time

The optimum cure time (t_{90}) corresponds to the time to achieve 90 per cent of the cure calculated from the formula,

$$\text{Optimum cure} = [0.9(M_H-M_L) + M_L] \qquad \ldots . \; (II.1)$$

In the case where the rheograph show maximum in torque readings, M_H and M_L are the maximum and minimum torque respectively.

Optimum cure time was measured using Oscillating Disk Rheometer 100 supplied by Monsanto, according to ASTM D-2084-93 test method. A typical cure curve to a maximum torque with reversion is given in Figure II.2.

II.3.2.1 Measurement procedure

A test specimen of vulcanisable rubber compound was inserted into the cure meter test cavity and after a closure action, was contained in a sealed cavity under positive pressure. The cavity was maintained at some elevated temperature (140, 150, 160°C, etc.). The rubber totally surrounds a biconical disk after the dies were closed. The disk was oscillated at 100 cycles per minutes through a rotational amplitude of 3° and this action exerted a shear strain on the test specimen. The force required to oscillate the disk to the set amplitude was continuously recorded as a function of time, with the force being proportional to the shear modulus (stiffness) of the test specimen at the test temperature. This stiffness first decreased as it warms up, then it increased due to vulcanisation. The test was completed when the recorded torque rose to a maximum value. The time required to obtain a cure curve is a function of the characteristics of the rubber compound and of the test temperature.

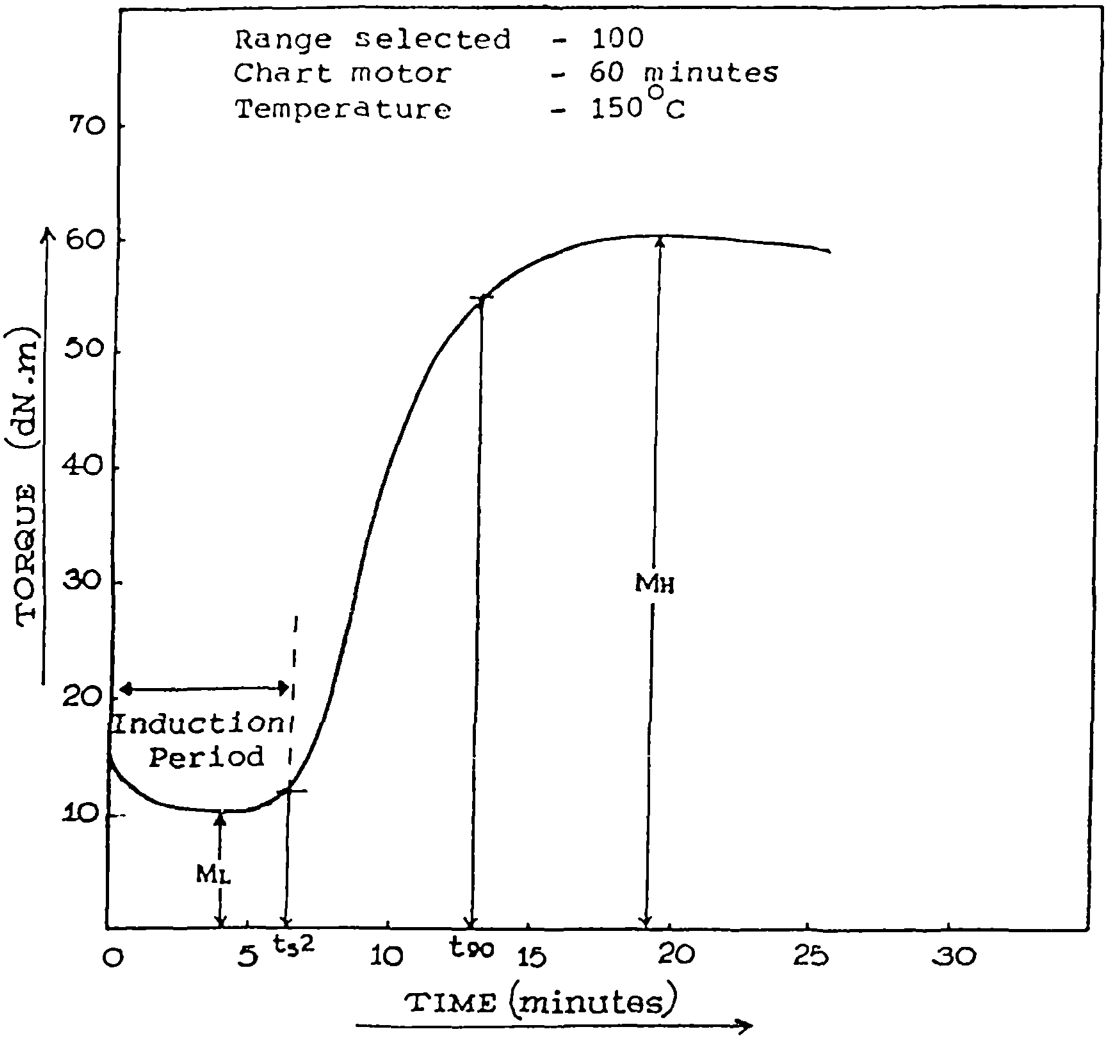


Figure II.2 A typical rheograph by Rheometer 100

II.3.2.3 Scorch time from rheograph

Scorch time (t_s2) is equal to the total time from the start to get 2 units rise in torque from minimum torque.

II.3.2.4 Cure rate index

Cure rate index was calculated as follows

$$\text{Cure rate index} = \frac{100}{(\text{cure time-scorch time})} \quad \ldots . \text{(II.2)}$$

II.4 Moulding of Test Samples

Test samples were compression moulded at 150°C by placing 5% excess of the uncured stock in the cavity of a suitable mould and cured in a hydraulic press having electrically heated platens, to their respective cure times as obtained from Monsanto Rheometer.

II.5 Testing for Vulcanisate Properties

II.5.1 Modulus, Tensile Strength and Elongation at Break

These three parameters were determined according to ASTM D-412-80 test method, using dumb-bell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die, along the mill grain direction of the vulcanised sheets. The thickness of the narrow portion of the specimen was measured using a dial gauge.

The specimens were tested in a Zwick Universal Testing Machine (UTM) Model 1474, at 25 ± 2°C and at a cross-head speed of 500 mm per minute. The elongation at break, modulus and tensile strength were recorded on a strip chart recorder. The machine has a sensitivity of 0.05 per cent of full scale load. The modulus and tensile strength are reported in MPa and the elongation at break in percentage of original length. Five test pieces per sample were used for this test.

II.5.2 Tear Strength

This property was tested as per ASTM D624-81 test method, using unnicked 90° angle test specimens which were punched out from the moulded sheets, along the mill grain direction. Five test pieces per sample were used for this test. This test was also carried out in a Zwick UTM, at a cross-head speed of 500 mm per minute and at 25 ± 2°C. The tear strength values are reported in N/mm.

II.5.3 Hardness

The hardness of the samples was measured as per ASTM D-2240-81 test method using a Shore A-type durometer, which employs a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indenter and the sample, the reading was taken immediately after the establishment of firm contact.

II.5.4 Heat Build up

Heat build up of the samples was measured as per ASTM D-623-93 test method. The test specimen used was cylindrical in shape with a diameter of 17.8 ± 0.1 mm and a height of 25 ± 0.15 mm. It was subjected to rapidly oscillating compressive stresses in Goodrich Flexometer at 1800 cycles per minute. Test was conducted at 50°C. A constant initial compressive load was applied to the specimen through a lever having high inertia and imposing on the specimen an additional high frequency cyclic compression of definite amplitude. The stroke given was 4.45 mm. The increase in temperature at the base of the test specimen was measured with a thermocouple which provided indication of the heat generated in flexing the specimen.

Dynamic set was calculated by measuring the sample height before and after the heat build up test. It was expressed as percentage of the initial sample height.

II.5.5 Abrasion Resistance

The abrasion resistance of the samples was tested using a DIN abrader as per DIN 53516 specification. It consisted of a drum on to which a standard abrasive cloth was fixed. The drum was rotated at a speed of 40 ± 1 rpm and the total abrasion length was 42 meters. Sample having a diameter of 16 ± 0.2 mm and a thickness of 7 mm, was kept on a rotating sample holder. 10 N load was applied. Initially a pre-run was given for the sample and then its weight taken. The weight after the final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece getting abraded away by its travel through 42 m on a standard abrasive surface. The abrasive loss was calculated as follows:

$$V = \frac{\Delta m}{\rho} \qquad \ldots . (II.3)$$

Where Δm = mass loss

ρ = density

V = abrasion loss in mm^3

To check the consistent uniformity of the abrasive surface of the equipment, standard test pieces were prepared and tested in the abrader. The loss of the standard sample was ensured to be in the range of 170-220 mg, as prescribed for the test.

II.5.6 Rebound Resilience

The rebound resilience of the vulcanisate was measured using Dunlop Tripsometer (BS 903, Part 22, 1950). The sample was held in position by applying vacuum. It was conditioned by striking it with the indenter six times. A freely falling hammer was dropped from a given height against the specimen at a known angle. The pendulum rebounded and the rebound angle was noted. The temperature of the specimen holder and the sample was kept constant at 30°C. Rebound resilience was calculated as,

$$\text{Rebound resilience } (\%) = \frac{1-\text{Cos } \theta_2}{1-\text{Cos } \theta_1} \times 100 \qquad \ldots . \text{(II.4)}$$

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

II.5.7 Flexing Resistance

A moulded test specimen of thickness 6.3 mm, length 25.4 cm and breadth 15.24 cm was repeatedly flexed on a Wallace De Mattia flexing machine with a frequency of 300 cycles per minute (ASTM D-430-73). Samples were observed at regular intervals to check crack initiation. Number of cycles for crack initiation and failure were noted.

II.5.8 Compression Set

The initial thickness of the moulded test samples (12.5 mm thickness and 29 mm diameter) was accurately measured and then compressed to give 25 per cent deflection between two parallel plates provided with spacers and was kept in an air oven at 70°C for 22 hours (ASTM D-395-71, Method B). After the heating period, the deflection was released; the samples were cooled to room temperature for half an hour and final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set } (\%) = \frac{t_0 - t_1}{t_0 - t_s} \times 100 \qquad \ldots. \text{(II.5)}$$

where t_0 and t_1 are the initial and final thickness of the specimen and t_s in the thickness of the spacer bar used.

II.6 Volume Fraction of Rubber in Swollen Vulcanisate (V_r)

Crosslink density of the vulcanisate can be determined by the swelling method using Flory-Rehner equation (1) which is given below.

$$V = \frac{1}{V_s \rho} \left[\frac{\ln(1-V_r)+V_r+\chi V_r^2}{V_r^{1/3} - \frac{1}{2}V_r} \right] \qquad \ldots. \text{(II.6)}$$

where V is the crosslink density, V_s is the molecular volume of the solvent, V_r is the volume fraction of rubber in swollen vulcanisate and χ is the interaction constant. Thus V_r, the volume fraction of rubber in the solvent swollen vulcanisate can be considered as a measure of the extent of crosslinking in the vulcanisate.

The solvent used was toluene. Test pieces weighing about 0.2 g and 2 mm thickness were cut from the centre and outer surface of a vulcanised cube of size 5x5x5 cm^3. The test pieces were allowed to swell in toluene at 25°C in squadishes. Initial trials showed that the samples attained equilibrium swelling by about 48 hours. Hence after immersion in toluene for 48 hours, the test pieces were taken out, loose liquid was rapidly removed by blotting with filter paper and the swollen weight immediately measured in stoppered weighing bottles. Swollen samples were then dried in an oven set at 70°C for 24 hours and then in vacuum. The dried samples were weighed accurately after cooling in a desiccator. Three test pieces were taken for each sample to ensure reproducibility. The V_r values were calculated using the method reported by Ellis and Welding [2]. The equation used for calculating the Vr values are given below.

$$V_r = \frac{(D-FT)\,\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}} \quad \ldots\ldots (II.7)$$

where,

T - Initial weight of the test piece

D - Deswollen weight of the test piece

F - The weight fraction of the insoluble component

A_0 - Weight of the absorbed solvent, corrected for swelling increment.

ρ_r - Density of rubber

ρ_s - Density of solvent

From the experimental data, the value of A_0 can easily be calculated as described below:

The weight fraction of the solvent absorbed at any time 't' is given by

$$W_t = \frac{S_t - T}{T} \qquad \ldots . \text{(II.8)}$$

where S_t is the swollen weight of the test piece at any time 't'. If the equilibrium time is taken as 'X' hours, the percentage increment 'dx' after 'x' hours is calculated from the equation:

$$d_x = \frac{100\,(W_x - W_o)}{W_o} \qquad \ldots . \text{(II.9)}$$

where W_o is the weight of the solvent absorbed per gram of the test piece without swelling. W_o is obtained from a plot of W_t against 't', by extrapolating the straight line to zero time. The value of A_o is then given by

$$A_o = A_x \left(1 - \frac{d_x}{100}\right) \qquad \ldots . (II.10)$$

where A_x is the weight of the solvent absorbed after 'X' hours immersion and is equal to $(S_x - D)$. S_x is the swollen weight of the test piece after 'X' hours.

II.7 Measurement of Resistance to Degradation

II.7.1 Hot Air Ageing

Dumb-bell shaped tensile test samples (2 ± 0.2 mm thick) were aged at 70°C and 100°C for 7 days and 3 days respectively in an air circulated oven. The tensile strength was measured before and after ageing. The percentage retention of tensile strength after ageing was calculated as

Tensile strength retention (%)

$$= \frac{\text{Tensile strength after ageing}}{\text{Tensile strength before ageing}} \times 100 \qquad \ldots . (II.11)$$

II.7.2 Exposure to γ-Radiation

Dumb-bell shaped tensile test samples (2 ± 0.2 mm thick) were irradiated with γ-rays from a ^{60}Co source in a Gamma Chamber 900 (Fig. II.3). The samples were irradiated for different radiation doses at a dose rate of 0.321 M rad/h in air at room temperature. The tensile strength was measured before and after irradiation. The percentage retention of tensile strength after irradiation was calculated as in the case of hot air ageing.

II.7.3 Exposure to Ozonised Air

The ozone test chamber manufactured by MAST Development Company, USA, was used to study ozone cracking (Fig. II.4). The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration used was 50 pphm which is generated by an UV quartz lamp. The test was carried out as per ASTM D-1149-81 specification. The test was conducted at 38.5°C.

Rectangular strips of length 95 mm, breadth 25 mm and thickness 2 mm were folded and tied at 25 mm length from the edges to get the required strain (>20%). These were then conditioned for 24 hours. The conditioned samples were exposed to the ozonised air in the Chamber. Periodic observations of the surface of the samples were made for crack initiation.

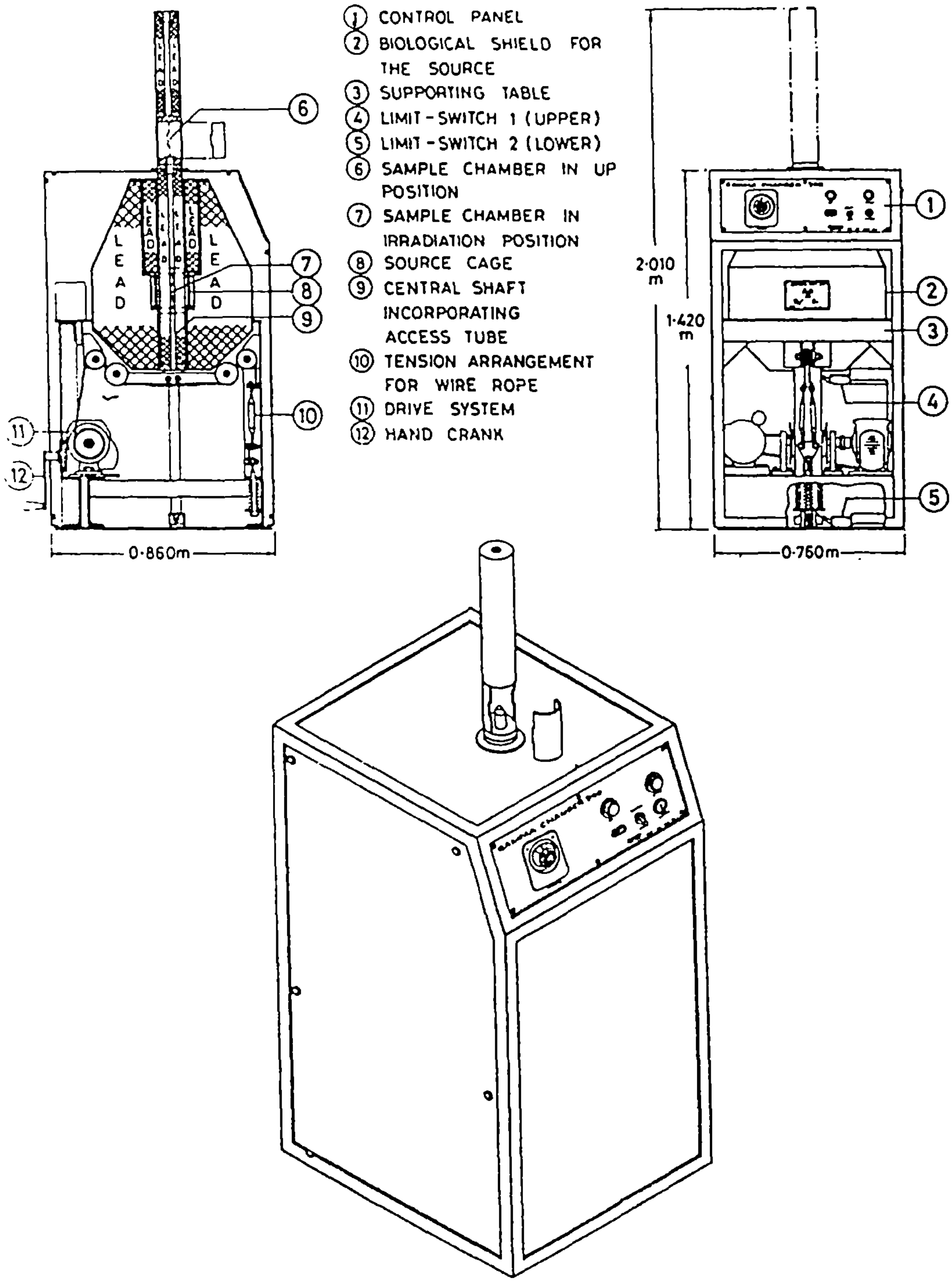


Figure II.3 Gamma Chamber 900

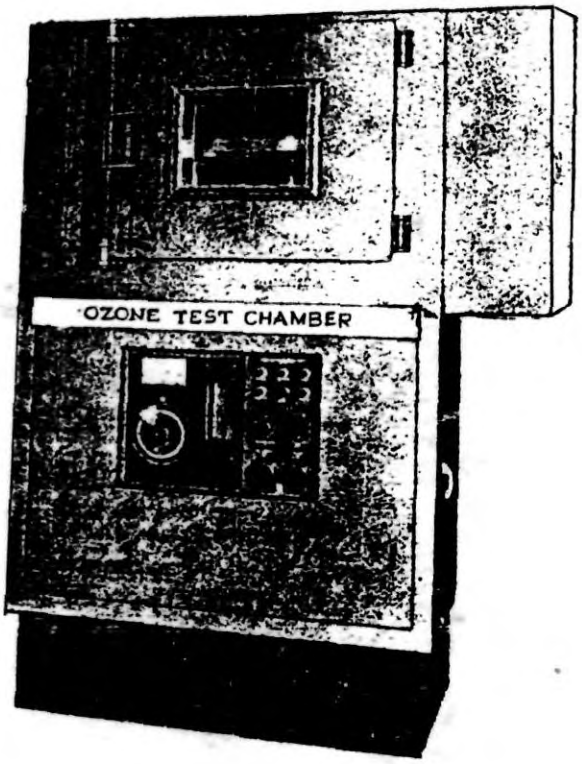


Figure II.4. Ozone Test Chamber.

II.8 Measurement of Rheological Properties

II.8.1 Equipment Details

A capillary rheometer attached to Zwick UTM model 1474 was used to carry out the melt flow studies. The extrusion assembly consisted of a barrel made of hardened steel, mounted on a special support, underneath the moving cross-head of the Zwick UTM. A hardened steel plunger, which is accurately ground to fit inside the barrel is held to the load cell extension. An insulating ring thermally isolates the barrel from the rest of the machine and prevents heat losses due to conduction. The capillary is inserted at the bottom of the barrel and is locked using a clamping device. The capillary is made of tungsten carbide. The barrel was heated using a three zone temperature control system. The difference between the successive temperature zones in the barrel was kept at 5°C and the temperature of the lower zone, where the capillary is located, is taken as the test temperature.

The moving cross-head of the Zwick UTM runs the barrel at a constant speed irrespective of the load on the melt, maintaining constant volumetric flow rate through the capillary. The cross-head speed can be varied from 0.5 mm/min to 500 mm/min giving shear rates ranging from 3 S^{-1} to 3000 S^{-1} for a capillary of l/d = 40. Forces corresponding to specific plunger speeds were recorded on a strip chart recorder. These values were converted into shear stresses.

II.8.2 Test Procedure

The sample to be tested was placed inside the barrel which was maintained at the test temperature. The sample was forced down to the capillary using the plunger attached to the cross-head. After a warming up period of three minutes, the melt was extruded through the capillary at pre-selected speeds of the cross-head. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give ten different plunger speeds. Each plunger speed was continued until the recorded force was stabilized, before changing to the next speed. Forces corresponding to specific plunger speeds were recorded. The force and cross-head speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall by using the following equations.

$$\tau_w = \frac{F}{4\ A_p(l_c/d_c)} \qquad \text{. . . . (II.12)}$$

$$\dot{\gamma}_w = \frac{(3n' + 1)}{4n'} \quad \frac{32\ Q}{\pi d_c{}^3} \qquad \text{. . . . (II.13)}$$

where

F - Force applied at a particular shear rate

A_p - Cross sectional area of the plunger

l_c - Length of the capillary

d_c - Diameter of the capillary

Q - Volume flow rate

n' - Flow behaviour index, defined by

$$\frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})} \qquad \text{. . . . (II.14)}$$

$\dot{\gamma}_{wa}$ - Apparent wall shear rate

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

n' is determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. The shear viscosity was calculated as

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \qquad \text{. . . . (II.15)}$$

The shear stress at the wall requires correction as suggested by Bagley [3]. But the correction factor diminishes as the length to diameter ratio of the capillary increases. For a capillary having l/d ratio 40, it is assumed that the correction factor is negligible. For the analysis of the data, the following assumptions were also made:

1. There is no slip at the capillary wall.
2. The material is incompressible.
3. The fluid is time independent.
4. The flow pattern is constant along the capillary.
5. The flow is isothermal.
6. The flow properties are independent of hydrostatic pressure.

II.8.3 Extrudate Swell

It is expressed as the percentage of increase in diameter of the extrudate to that of the capillary used. The extrudate emerging from the capillary was collected with minimum possible deformation. The diameter of the extrudate was measured after 24 h rest period, using a WILD Stereomicroscope Model M650 at several points on the extrudate. The average value of 10 readings was taken as diameter (d_e) of the extrudate and die swell was calculated as

$$\text{die swell} = \frac{d_e - d_c}{d_c} \times 100 \qquad \text{. . . . (II.16)}$$

where, d_c is the diameter of the capillary. For each sample the extrudate swell at three different shear rates was determined.

II.8.4 Extrudate Deformation: Optical Photographs

Extrudates were collected and allowed to relax for 24 hours. Representative samples were cut from the extrudates and photographs taken.

II.9 Measurement of Thermal Conductivity

II.9.1 Definition

Thermal conductivity, λ , of a solid material is defined as the time rate of steady heat flow, watts, through a unit area, m^2, per unit temperature gradient in the direction perpendicular to an isothermal surface, °C/m: λ is expressed as W/m.k.

II.9.2 Equipment

Quick Thermal Conductivity Meter "Kemtherm QTM-D3" (Figs. II.5 and II.6) supplied by Kyoto Electronics, Japan was used for measuring the thermal conductivity of the vulcanised samples. Kemtherm QTM-D3 makes measurements using a probe based on the transient hot-wire method. The instrument makes the measurement, does automatic data processing and gives digital displays of the thermal conductivity and measuring temperature of samples, simply by keeping a probe on any reasonably flat sample face for only 60 seconds.

II.9.3 Principle of Analysis

The probe method of Kemtherm QTM-D3 needs to have only one sample for the measurement of thermal conductivity, while a conventional hot-wire method requires to have two sample pieces to hold the hot-wire in between.

A thermal conductivity of a certain sample by the probe method will be given by the equation,

$$\lambda = \frac{k.\ I^2 \ln(t_2/t_1)}{(V_2-V_1)} \quad \ldots. \quad (II.17)$$

where K and H are the constants of the probe and they include a resistance of the heating wire, thermoelectric power of thermocouple and a thermal conductivity of the known heat-insulated material. V_1 and V_2 are electromotive forces (mV) at times t_1 and t_2. I is heating current (A).

The probe method requires to have the heater current applied only for 60 seconds and the temperature rise during that period of time is about 20°C. The sample is heated only in the vicinity of the heating wire because of the short heating period. It means that a value obtained in the measurement corresponds to the thermal conductivity in a part of the sample close to its surface where the probe is attached. Heat generated at the heating wire is in the range of 3-30 Kcal/min for a sample of which thermal conductivity is 0.02-10 w/mk.

The temperature of the heating wire goes up exponentially as Figure II.7 shows when a constant power (heat flux) is continuously applied to the thin heating wire which is stretched straight through the centre of a probe.

The probe of QTM-D3 consists of an elastic base of which thermal conductivity is already known and a hot-wire and a thermocouple embedded on the surface of the base as Figure II.8 depicts. They will maintain a good and stable contact with a sample surface by means of a spring loading system. The design of the probe makes it possible to measure the thermal conductivity of a sample with a surface as big as, or even slightly smaller than the bottom of probe (50 x 100 mm). Any special treatments of sample such as cutting, surface polishing, etc. are not required.

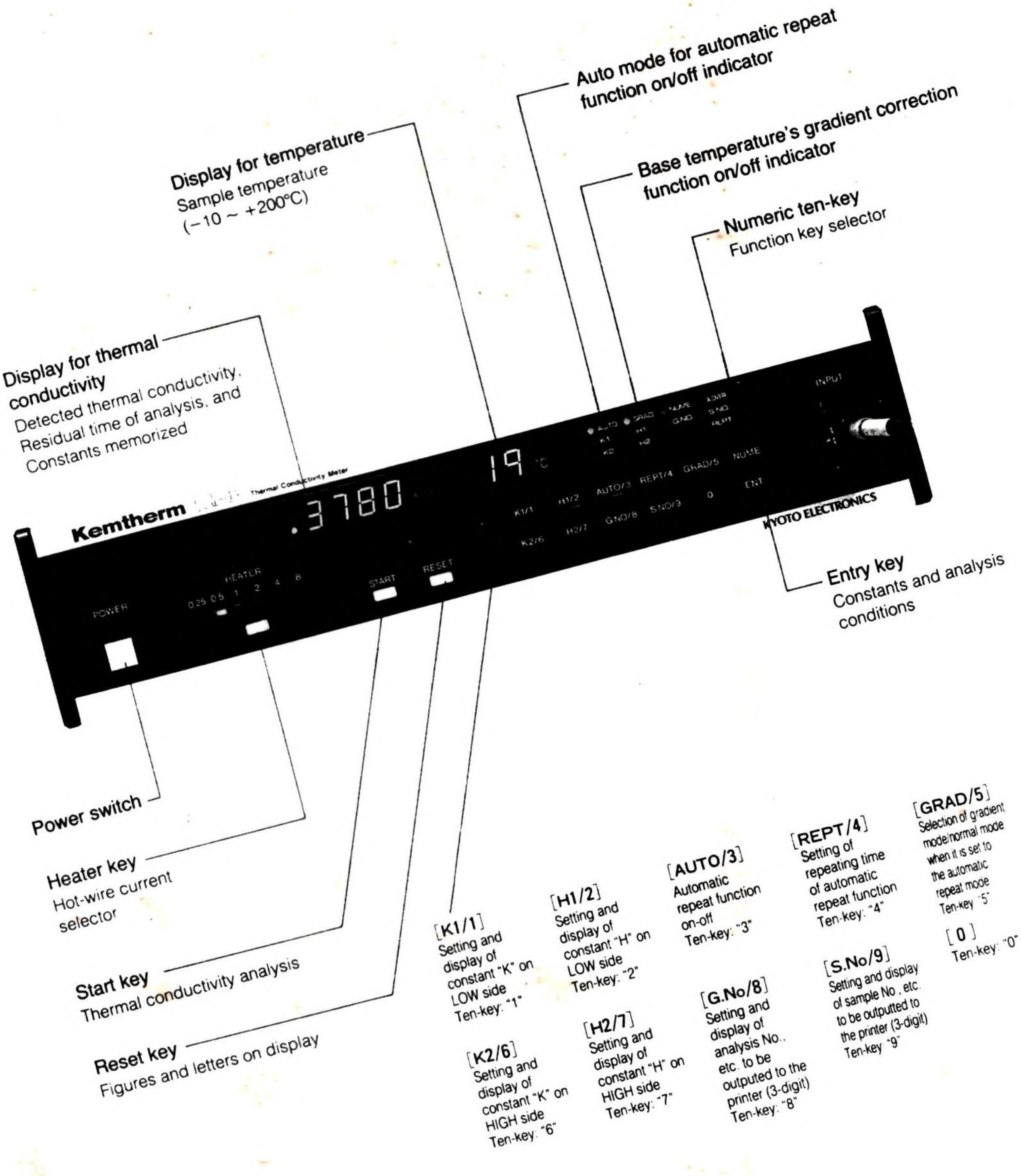
II.9.4 Test Procedure

The equipment was calibrated using a reference plate (0.239 w/mk) having thermal conductivity in the desired range (0.1-0.3 w/m.k). A heater current was selected according to the above range. The probe constants (K and H values) corresponding to the probe used, QTM-PD_1 were entered.

The equipment was given a stabilisation time of half-an-hour. The samples were kept at the test temperature. The probe was kept on the flat face of the sample and waited for 5 minutes to attain the test temperature. Heater was started and thermal conductivity was measured, automatically after 60 seconds.

High temperature measurement was conducted by keeping the samples in a thermostatically controlled hot air chamber of size 20 x 20 x 5 cm^3 for 30 minutes to attain the test temperature. The probe was immediately placed over the hot test sample, the chamber closed and measurements taken, keeping the samples in the chamber itself.

Figure II.5 Quick Thermal Conductivity Meter QTM-D3



Auto mode for automatic repeat function on/off indicator

Base temperature's gradient correction function on/off indicator

Numeric ten-key
Function key selector

Display for temperature
Sample temperature
(−10 ~ +200°C)

Display for thermal conductivity
Detected thermal conductivity,
Residual time of analysis, and
Constants memorized

Entry key
Constants and analysis conditions

Power switch

Heater key
Hot-wire current selector

Start key
Thermal conductivity analysis

Reset key
Figures and letters on display

[K1/1]
Setting and display of constant "K" on LOW side
Ten-key: "1"

[H1/2]
Setting and display of constant "H" on LOW side
Ten-key: "2"

[AUTO/3]
Automatic repeat function on-off
Ten-key: "3"

[REPT/4]
Setting of repeating time of automatic repeat function
Ten-key: "4"

[GRAD/5]
Selection of gradient mode/normal mode when it is set to the automatic repeat mode
Ten-key "5"

[K2/6]
Setting and display of constant "K" on HIGH side
Ten-key: "6"

[H2/7]
Setting and display of constant "H" on HIGH side
Ten-key: "7"

[G.No/8]
Setting and display of analysis No., etc. to be outputed to the printer (3-digit)
Ten-key: "8"

[S.No/9]
Setting and display of sample No., etc. to be outputted to the printer (3-digit)
Ten-key "9"

[0]
Ten-key: "0"

Figure II.6 Quick Thermal Conductivity Meter

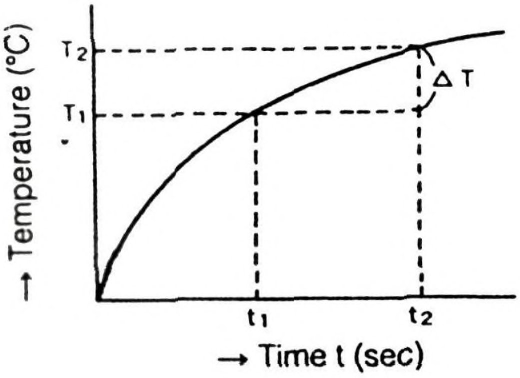


Figure II.7 Relationship between Time and Temperature

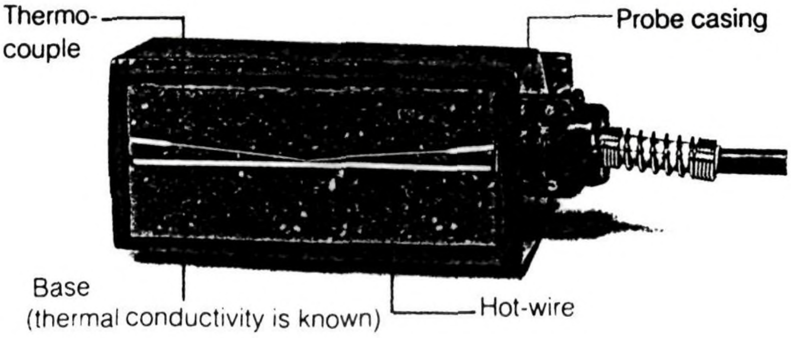


Figure II.8 Construction of probe

II.10 Measurement of Electrical Properties

Electrical properties were measured using Davenport Surface and Volume Resistivity Apparatus as per BS 2782, 230 A and 231 A (1982) test methods. Circular specimens of diameter 95 mm and uniform thickness of 3 mm were moulded between sheets of moisture-sensitive cellophane to avoid surface contamination and minimise distortion of specimen prior to test. The portions of the test sample where the electrodes were coming in contact were coated with calomal graphite to ensure zero contact resistance. Surface resistivity was calculated using equation,

Surface resistivity ($\log_{10}$ ohms)

$$= \log_{10}\left[\frac{2\pi R_S}{\log_e(D/d)}\right] \qquad \ldots\ldots (II.18)$$

where

R_S - Surface resistance in ohms

D - Inner diameter of upper outer electrode (mm) and

d - Diameter of upper inner electrode (mm)

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CHAPTER III

EFFECT OF ALUMINIUM POWDER ON CURE CHARACTERISTICS AND VULCANISATION KINETICS OF NATURAL RUBBER COMPOUNDS

III EFFECT OF ALUMINIUM POWDER ON CURE CHARACTERISTICS AND VULCANISATION KINETICS OF NATURAL RUBBER COMPOUNDS

Fillers constitute a major share of the ingredients in any rubber compound. Ideally, fillers should not affect the cure characteristics of the rubber compound. However, many fillers such as channel blacks, silica, china clay, etc. are known to adversely affect the cure. Fillers which are acidic (e.g., channel black and china clay) retard the vulcanisation process and prolong the vulcanisation time. Very fine particle sized silica, which has polar groups (e.g., -OH) attached to it, adsorbs the accelerators, thereby blocking its effective participation in the vulcanisation process [1]. The net result is an increase in vulcanisation time as well as reduction in the level of technological properties attained. Increase in vulcanisation time affects production and productivity, while a decrease in technological properties affects the quality of the product. Since fillers are used in rubber compounds in large quantities (of the order of 50 to 100 phr or more) either to improve technological properties or to reduce cost, studies on the effect of fillers on the vulcanisation characteristics of the compounds assume importance. Hence in this chapter of the thesis, the results of the studies on the effect of aluminium powder on scorch time, cure characteristics and kinetic parameters of vulcanisation of the NR compounds are presented.

Earlier attempts to study kinetics of vulcanisation by estimating free sulphur, combined sulphur, etc. did not yield satisfactory results because of the complexity of the reactions involved in the vulcanisation of rubber [2]. Sulphur may react with rubber either to form crosslinks or to form pendant cyclic groups which are elastically ineffective. Sulphur can also react with other ingredients such as zinc oxide to form zinc sulphide. Attempts were also made to study vulcanisation kinetics by measuring physical parameters such as modulus, since it is believed that modulus is related to physical degree of crosslinking via the statistical theory of elasticity [3]. But later work indicated that equilibrium modulus and chemical degree of crosslinking were not related linearly at low degree of crosslinking [4]. In rubber vulcanisation, modulus developed is the net result of crosslink formation and degradation. If we assume that M_α is the maximum modulus which would have been attained had reversion been absent, then plots of $(M_\alpha-M)$ against time of cure would be linear (M is the modulus developed at curing time 't') indicating first order rate coefficient. In the work reported by Russell *et al.* [5] and that by *Redding and Smith [6], modulus values corrected for* degradation were used and they obtained first order rate coefficients for the sulphur vulcanisation of elastomers.

In cure meters such as Rheometer R-100, the cure curve obtained is a continuous plot of the modulus developed during vulcanisation against time of cure. In sulphenamide accelerated sulphur vulcanisation of natural rubber, the rate of crosslink formation after the induction period is so fast that the contribution from degradation in the net modulus developed at any time is insignificant upto the period of attaining the maximum modulus. Hence several authors have used Rheometric torque values to study the kinetic parameters of vulcanisation [7-12]. A typical rheograph given in Figure III.1 shows the modulus developed with time of cure for sulphenamide accelerated sulphur vulcanisation of natural rubber.

A general equation for the kinetics of a first order chemical reaction can be written as

$$\ln(a-x) = -kt + \ln a \qquad \ldots. \text{(III.1)}$$

where,

a - initial reactant concentration

x - reacted quantity at time 't'

k - first order reaction rate constant

For the vulcanisation reaction of rubber, the rate of crosslink formation is usually monitored by measuring the torque developed during its course by using a curometer and the torque values thus obtained are proportional to the modulus of the vulcanisate. Referring to Figure III.1, it can be seen that

$$(a-x) = (M_H - M_t) \quad \dots\dots \text{(III.2)}$$

$$a = (M_H - M_L) \quad \dots\dots \text{(III.3)}$$

$$x = (M_t - M_L) \quad \dots\dots \text{(III.4)}$$

where,

M_H - the maximum torque developed

M_t - the torque at time 't'

M_L - the minimum torque

If the reaction is of first order, then a plot of $\ln(M_H - M_t)$ against time (t) should give a straight line whose slope will be the specific reaction rate constant, k. Similarly, the activation energy of the vulcanisation reaction is found out from a modified Arrhenius equation

$$t_{90} = A\, e^{\Delta E/RT} \quad \dots\dots \text{(III.5)}$$

$$\log t_{90} = \log A + \frac{\Delta E}{2.303RT} \quad \dots\dots \text{(III.6)}$$

where,

ΔE - activation energy

t_{90} - time in minutes to attain 90% of the maximum torque

T - Absolute temperature, °K

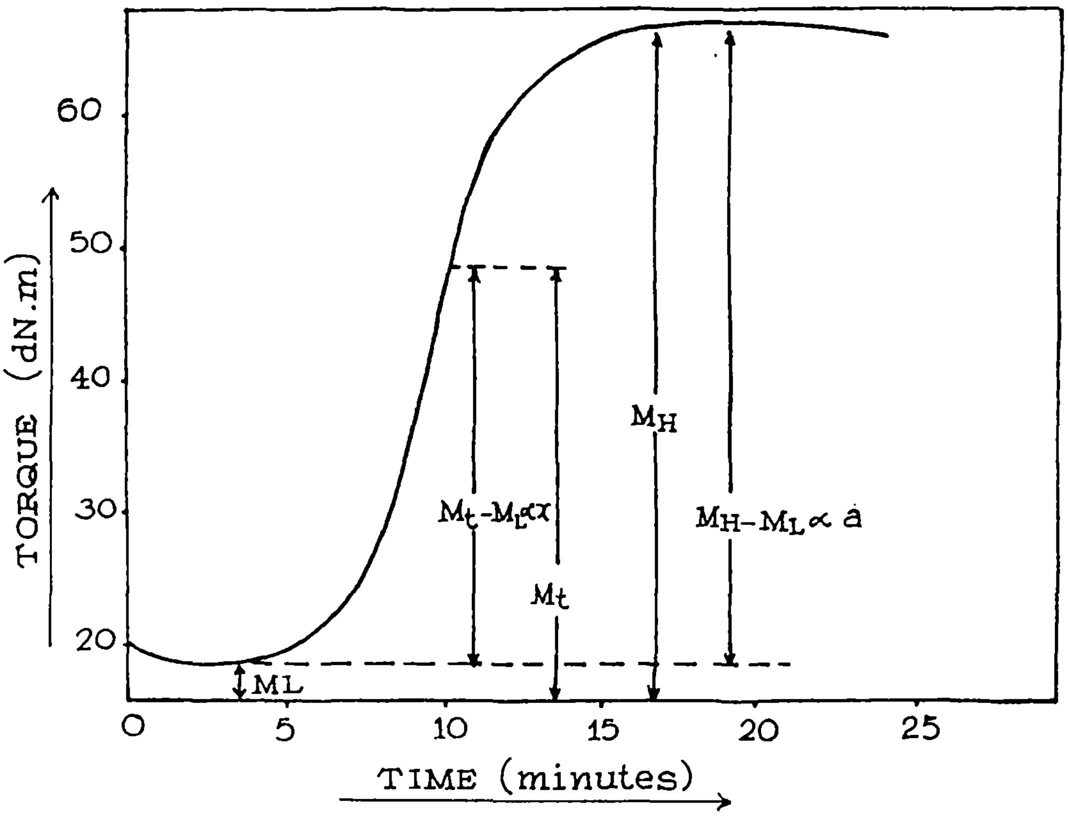

Figure III.1 Guideline to find 'k' value

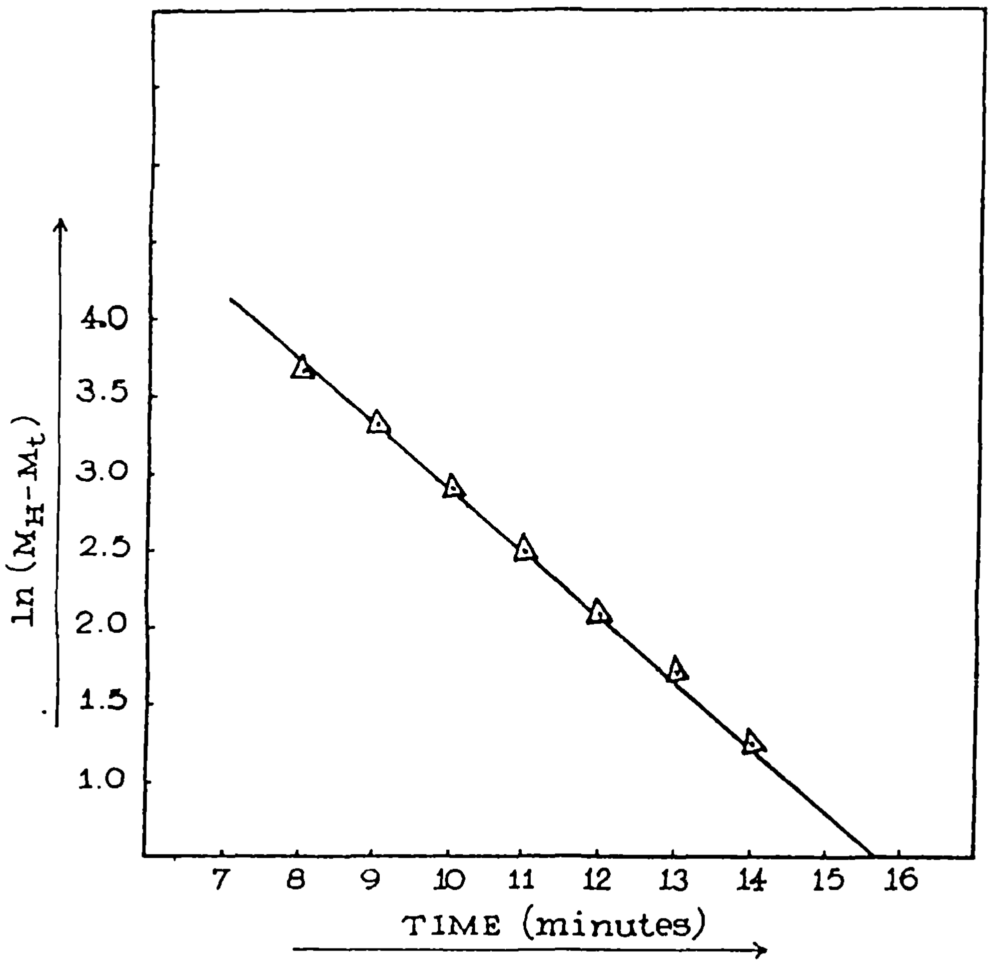

Figure III.2 Plot of $\ln(M_H - M_t)$ Vs time for different extents of cure at 150°C of compound AL15

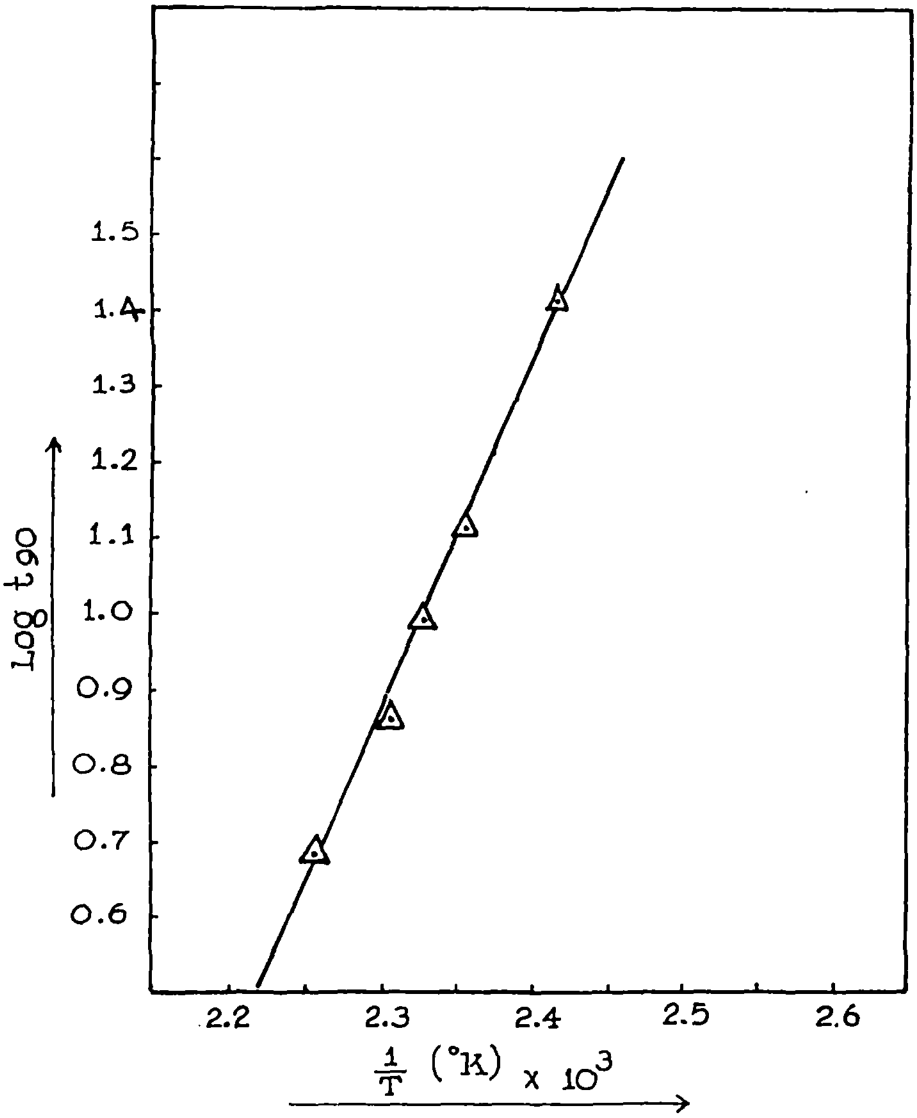

Figure III.3 Typical Arrhenius plot for compound AL15

A plot of log t_{90} Vs 1/T gives a straight line, from the slope of which ΔE is calculated. Typical plots of ln(M_H-M_t) against t at 150°C and log t_{90} against 1/T for the compound containing 15 volume per cent of aluminium powder (AL15) are given in Figures III.2 and III.3 respectively. Tables III.1 and III.2 give the scorch time, curc time and cure rate index at 150°C of the compounds and the kinetic parameters of vulcanisation respectively.

III.1 Effect of Fillers on Scorch Time

Scorch time indicates the period for which a compound can be stored safely before vulcanisation. It also shows whether the compound is processable at higher temperatures. A higher scorch time is desirable in many applications, especially for the vulcanisation of thick articles. The data given in Table III.1 indicate that addition of filler in rubber compounds reduces the scorch time. Among the three fillers, aluminium powder and HAF black incorporated compounds showed slightly lower scorch time compared with those containing acetylene black. However, the difference in scorch times of the filled compounds is only marginal and the value indicate that there is adequate scorch safety for the compounds so that these can be stored or processed without any difficulty.

III.2 Effect of Fillers on Cure Time and Cure Rate Index

As in the case of scorch time, the cure time of the compounds containing aluminium powder and HAF black were lower than that for the compounds containing acetylene black. Compounds containing acetylene black showed higher cure time and lower cure rate index especially at higher loadings. This is due to lower pH (acidic range, 5.5) of acetylene blacks as indicated in Section II.1.3.4. In general compounds containing aluminium powder showed lower cure time. This is associated with a higher cure rate index of the compounds containing aluminium powder. The higher cure rate index and the corresponding decrease in cure time has resulted from the extended time taken to incorporate the filler in the rubber compound. As the specific gravity of aluminium powder is much higher (2.69) than that of carbon blacks (1.81), the quantity of aluminium powder to be incorporated to get equal volume loading as given in base formulation I (Table II.2) is much higher than the carbon blacks. This necessitated, working of the compound in the mill for longer periods, generating higher temperature. The ease with which a filler can be incorporated and dispersed in rubber matrix also depends on its affinity to the polymer, its particle size and structure. Finer particles are difficult to disperse and generate more heat during mixing. Since large quantity (weight basis) of aluminium powder had to be incorporated, it took more time to prepare the compounds which led to generate more heat during mixing. This may be one of the reasons for higher values of cure rate index and reduced cure time for the compounds containing aluminium powder. Another possibility is that aluminium powder assists in the vulcanisation reaction. But this possibility can be ruled out since the compounds containing aluminium powder has almost the same specific reaction rate constant at 150°C compared with HAF black and acetylene black loaded compounds and require similar activation energy as that of the HAF-filled compounds (Table III.2).

M_H-M_L values (Table III.1) indicate modulus increase due to extent of crosslinking and reinforcement by fillers. At equal volume loadings, compounds containing aluminium powder showed lower M_H-M_L values compared with those containing HAF and acetylene blacks, especially at higher loadings. This indicated lower level of reinforcement by aluminium powder. However the V_r values (volume fraction of rubber in solvent swollen vulcanisate) of the aluminium powder-filled samples, vulcanized at 150°C were higher than those of the other samples. This is expected to be due to better thermal conductivity of the compounds containing aluminium powder. This is discussed further in Chapter VI.

Table III.1 **Cure characteristics of compounds**

Sample number	Scorch time at 150°C (min.)	Cure time at 150°C (min.)	Cure rate index at 150°C	M_H-M_L dN.m	V_r at optimum cure tim at 150°C
Gum	11.00	18.0	14.3	45.0	0.149
AL05	7.25	14.0	14.8	48.0	0.189
AL10	7.25	13.5	16.0	49.0	0.197
AL15	6.50	13.0	15.4	50.5	0.201
AL20	7.00	14.0	14.3	53.5	0.221
HF05	9.00	16.0	14.3	48.0	0.157
HF10	8.00	15.0	14.3	50.5	0.163
HF15	7.00	14.0	14.3	52.5	0.168
HF20	6.50	13.5	14.3	55.0	0.170
AC05	8.25	15.5	13.8	49.0	0.153
AC10	9.00	16.5	13.3	53.0	0.165
AC15	9.00	16.5	13.3	55.0	0.170
AC20	8.00	16.0	12.5	59.5	0.173

III.3 Effect of Fillers on Activation Energy

Activation energy (ΔE) values given in Table III.2 indicate that addition of the three fillers to rubber compounds reduced the activation energy for vulcanisation. The gum compound showed higher ΔE value compared with the filled compounds. Among the filled compounds, those containing aluminium powder and HAF black showed almost similar ΔE values whereas for compounds containing acetylene black, the activation energy was lower. The effect of loading of filler on activation energy was less prominent beyond 10 volume per cent.

III.4 Effect of Filler on Rate Constant k

Values of specific reaction rate constant at different temperatures given in Table III.2 indicate that the reaction rate constant depend much on temperature rather than type of filler. The temperature coefficient of vulcanisation was 1.9 to 2.0 in the temperature ranges of 140-150°C and 160-170°C. This showed that the curing time has to be reduced to half when the vulcanisation temperature is increased from 140 to 150°C and from 160 to 170°C. However in the temperature range 150-160°C, the temperature coefficient of vulcanisation was slightly lower, in the range of 1.6 to 1.75.

Table III.2 Kinetic parameters of vulcanisation

Sample number	Specific reaction rate constant (k)				Activation energy ΔE (K.cal/mole)
	140°C	150°C	160°C	170°C	
Gum	0.221	0.423	0.655	1.251	23.48
AL05	0.195	0.402	0.645	1.498	22.10
AL10	0.205	0.387	0.687	1.371	22.18
AL15	0.195	0.390	0.678	1.206	21.74
AL20	0.172	0.358	0.644	1.283	21.12
HF05	0.184	0.384	0.641	1.283	21.97
HF10	0.213	0.400	0.691	1.424	21.51
HF15	0.193	0.389	0.640	1.263	21.87
HF20	0.191	0.392	0.685	1.337	22.01
AC05	0.174	0.360	0.633	1.320	22.30
AC10	0.215	0.410	0.689	1.473	20.91
AC15	0.218	0.381	0.773	1.504	20.02
AC20	0.224	0.363	0.745	1.475	20.59

III.5 Conclusions

Evaluation of the cure characteristics and kinetics of vulcanisation of natural rubber compounds containing aluminium powder, HAF black and acetylene black as fillers showed that compounds containing aluminium powder have lower scorch time, cure time and higher cure rate index compared with compounds containing acetylene black, even though the activation energy for vulcanisation reaction of the former set of compounds are higher than those of the latter. HAF and aluminium powder-filled compounds have almost similar vulcanisation characteristics. The activation energy values are in the range of 20-22 K.cal/mole for the filled compounds and has a temperature coefficient of vulcanisation of 1.9 to 2.0 in the temperature range of 140 to 150°C and 160 to 170°C.

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CHAPTER IV

STUDIES ON RHEOLOGICAL BEHAVIOUR OF NATURAL RUBBER COMPOUNDS CONTAINING ALUMINIUM POWDER

IV STUDIES ON RHEOLOGICAL BEHAVIOUR OF NATURAL RUBBER COMPOUNDS CONTAINING ALUMINIUM POWDER

Rubber compounds are processed by different techniques such as extrusion, calendering, compression, transfer and injection moulding, etc. The rates of shear occurring in these processes range from $10^1 S^{-1}$ to $10^4 S^{-1}$ [1]. Knowledge of viscosity of compounds over a wide range of shear rates is essential to standardise the conditions for each process mentioned above. Rubber compounds exhibit non-Newtonian flow behaviour and most of them are essentially pseudoplastic in nature. The viscosity of such compounds decreases with increase in rate of shear [2]. Thus, viscosity measurement at a particular shear rate and temperature, as done in Mooney viscosity measurement, is not of much practical use. Viscosity changes with temperature also. Studies on viscosity of polymers and their compounds as a function of shear rate/shear stress and temperature assume importance due to its direct dependence on processing methods followed in industry. A lot of rheological work on polymer blends [3-5], rubber compounds [6,7] thermoplastic elastomers [8-12] and composites [13-15] have been done to explain the behaviour of polymer compounds during processing. Hence in this chapter of the thesis, the results of the investigations of the rheological behaviour of natural rubber compounds containing aluminium powder, HAF black and acetylene black are presented. Changes in viscosity of the compounds with rates of shear, temperature and quantity of filler are described in detail. Other parameters such as flow behaviour index, die swell and deformation of extrudates were also studied. The melt flow measurements were made using a capillary rheometer attached to a Zwick UTM (Model 1479). A detailed account of the experimental procedure is given in Section II.8.

IV.1 Effect of Shear Stress on Viscosity

The effects of shear stress on viscosity at 100°C of the NR compounds containing aluminium powder, HAF black and acetylene black are shown in Figure IV.1. It can be seen that as the shear stress increases, the viscosity of all the compounds decreased, indicating pseudoplastic nature of the compounds. The viscosity of the compounds increased with increase in quantity of HAF black and acetylene black in the compound, whereas for the aluminium powder-filled compounds the increase in viscosity was insignificant. There are two other peculiar observations that are evident from this figure. One is that the slope of the curves changes abruptly in the shear stress range of 30×10^4–40×10^4 Pa. This change is prominent in the case of HAF black and acetylene black-filled compounds and at their higher loadings. Below the above range of shear stress, the viscosity of the compounds increased sharply. Such increase in viscosity has been noted in filled systems earlier also. Munstedt [16] has explained that this increase in viscosity is due to formation of a network type structure by the filler, inside the polymer matrix and a minimum stress, called the yield stress, is to be applied to break the structure, before the compound can flow. Both HAF and acetylene blacks are known to have an appreciable level of structure as indicated by the DBP absorption values. Hence the compounds containing these fillers showed higher increase in viscosity at lower shear stress than those containing aluminium powder.

Another point evident from Figure IV.1 is that the compounds containing aluminium powder showed lower viscosity than the gum compound at higher shear stresses, even at 15 volume per cent loading. Such decrease in viscosity with the addition of crosslinked particles [17,18], cryoground rubber [19] and glass powder [20] has been reported earlier also. In the case of cryoground rubber-filled NR compounds, it was explained that during flow through a capillary under high shear stress, NR can undergo stress induced crystallisation, resulting in an increase in viscosity of the unfilled compound.

Cryoground particles, if interacted with the NR, may reduce the stress induced crystallisation during flow, thereby causing a reduction in viscosity. In the case of styrene butadiene rubber which is a non-crystallising rubber, it was explained that addition of glass powder caused wall slip to occur during flow, resulting in decrease of viscosity. However, both the above explanations have not been proved with experimental support. Recently the same phenomenon was observed in the melt flow studies of polypropylene modified with vulcanised crumbs obtained from latex products such as condoms and examination gloves [21]. Even though a proper mechanism for the observed decrease in viscosity could not be established, in the case of aluminium powder-filled compounds, the effect of reduction in viscosity was very prominent as indicated by almost the same viscosity values for the 20 volume per cent loaded compound (AL20) and the gum compound at 100°C.

IV.2 Effect of Shear Rate on Viscosity

Figure IV.2 shows the change in viscosity at 100°C of natural rubber compounds containing 15 volume per cent of aluminium powder, HAF black and acetylene black. In all the cases, the viscosity decreased with increase in shear rate, indicating pseudoplastic nature of the compounds. As in the case of viscosity versus shear stress plots, the viscosity of the aluminium powder-filled compound was lower than that of the gum compound at shear rate greater than $10^3 s^{-1}$. The effects of loading of the three fillers on the viscosity at 100°C of the NR compounds at three different selected shear rates are shown in Figure IV.3. Except for the compounds containing aluminium powder, there was an increase in viscosity with increase in filler content at low and high shear rates. At higher shear rates, the compounds containing acetylene black showed higher viscosity than the HAF black-filled compounds. This is expected to be due to higher structure of the acetylene black compared with HAF black.

IV.3 Effect of Temperature and Shear Rate on Viscosity

The effects of temperature and shear rate on the viscosity of the NR compounds containing 15 volume loading of the three fillers under study are shown in Figure IV.4. As the temperature increased, the viscosity decreased and the drop in viscosity due to increase in temperature was more at higher shear rates. Another important observation from this figure is the change in viscosity values of the gum compound and those containing aluminium powder at temperatures beyond 100°C. The gum compound which showed higher viscosity at temperatures 100°C and below, at all shear rates, showed lower values compared with the aluminium powder-filled compounds at temperatures beyond 100°C. The effect was prominent at higher shear rates.

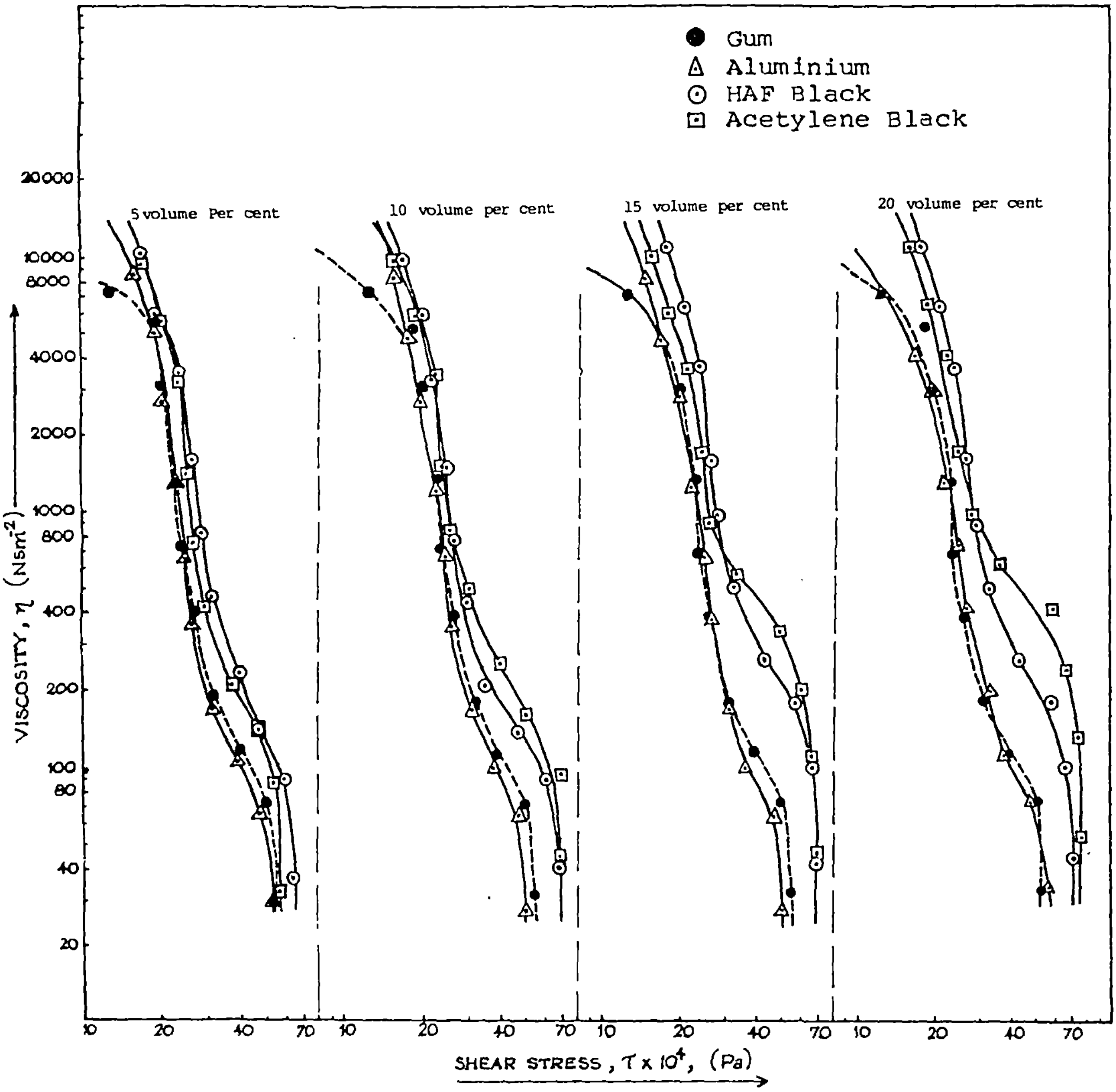

Figure IV.1 Plot of viscosity Vs shear stress at 100°C

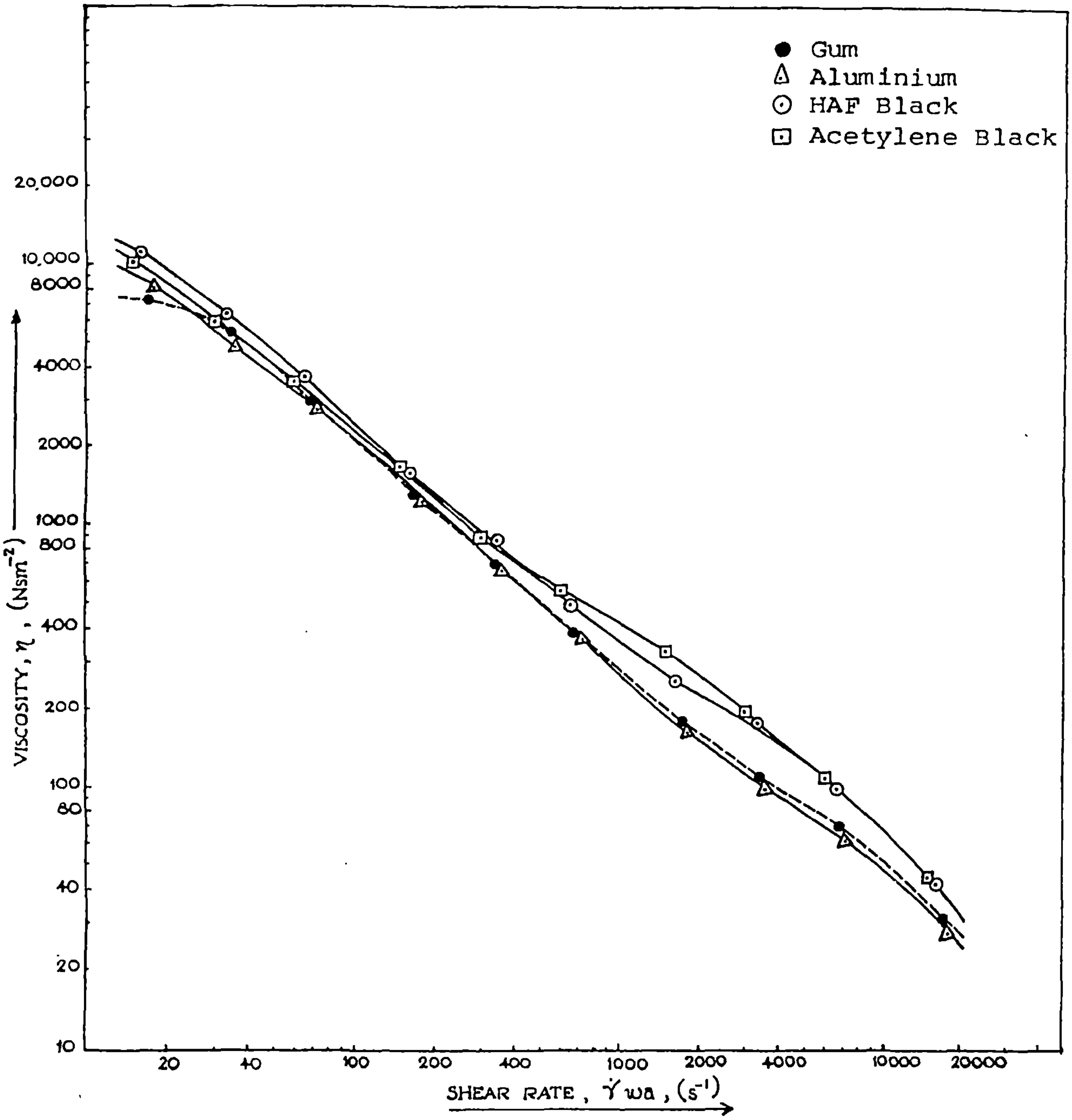

Figure IV.2 Plot of viscosity Vs shear rate ($\dot{\gamma}_{wa}$) of 15 volume per cent loaded samples at 100°C

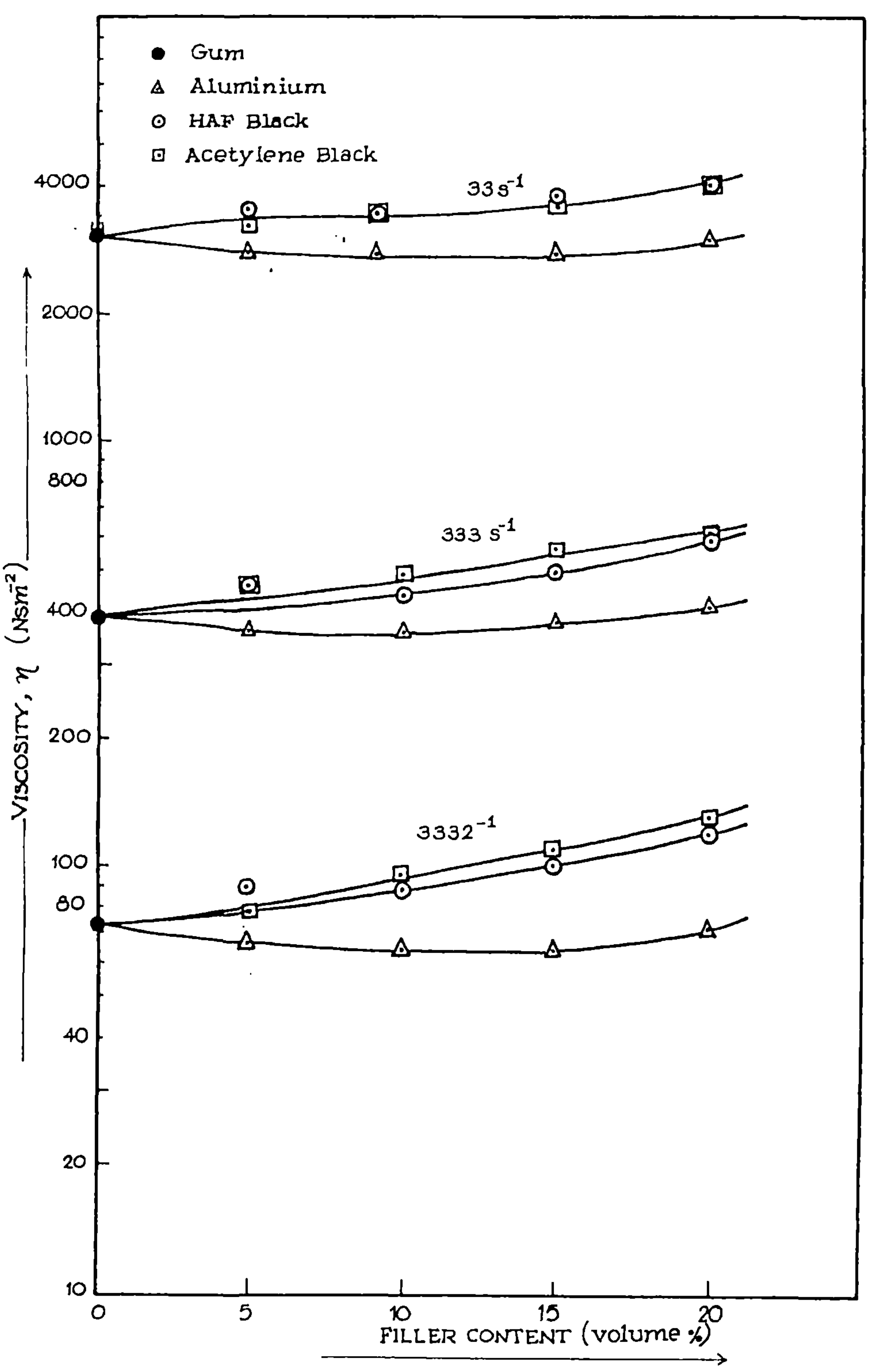

Figure IV.3 Plot of viscosity Vs filler loading at different shear rates at 100°C

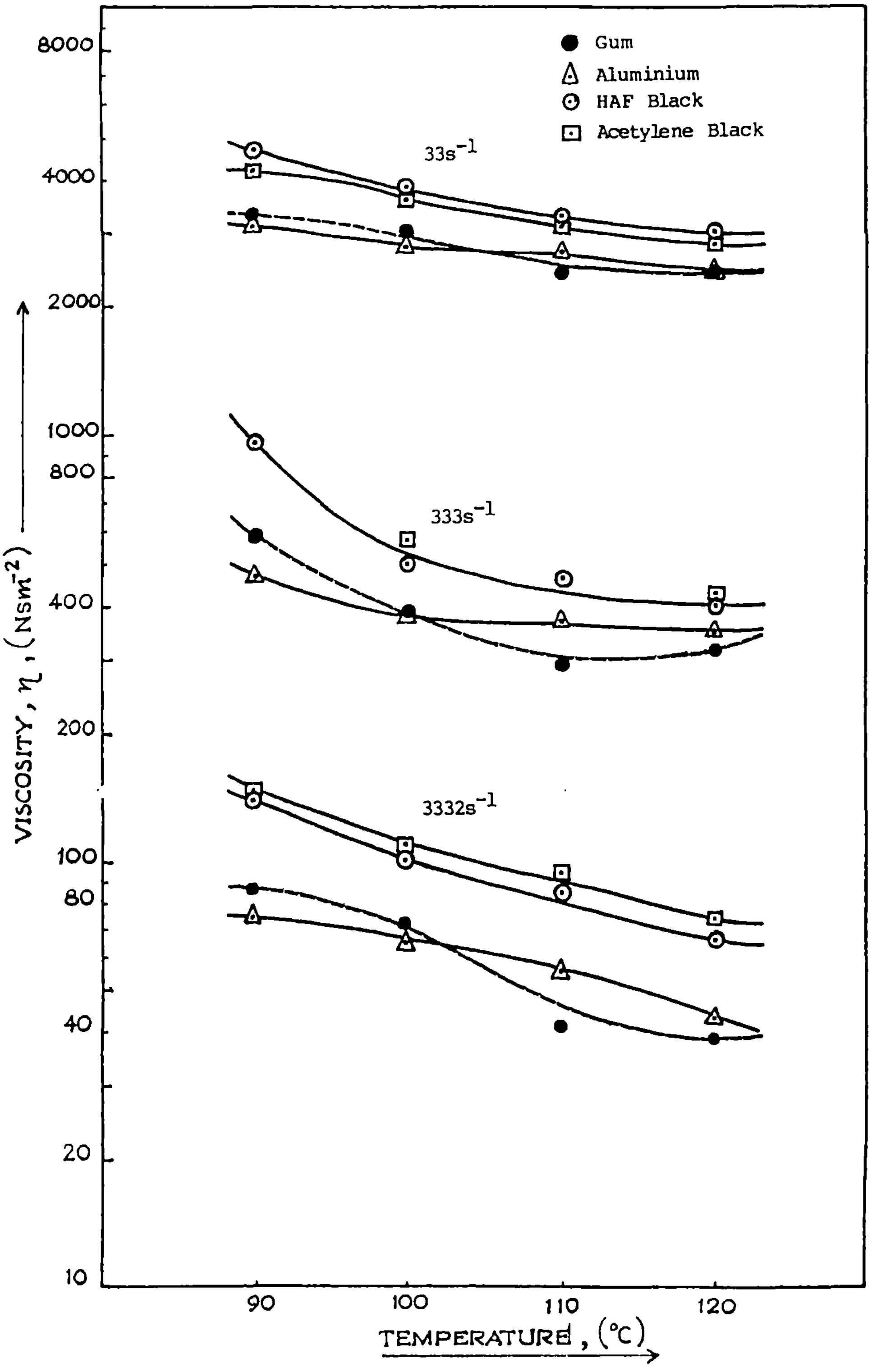

Figure IV.4 Plot of viscosity Vs temperature of 15 volume per cent loaded samples at different shear rates

This observation supports the explanation that aluminium powder may be affecting the stress induced crystallisation of the NR which caused to reduce the viscosity of the aluminium powder-filled compounds. At higher temperatures, the tendency of the gum compound to crystallise while flowing through the capillary under high shear rates will be reduced, resulting in lower viscosity at temperatures beyond 100°C.

IV.4 Effect of Temperature and Quantity of Filler on Flow Behaviour Index (n′)

Value of n′ gives an indication of the flow behaviour of the material. For Newtonian fluids n′ is equal to one and for pseudoplastic materials n′ values will be less than one. The n′ values given in Table IV.1 show that all the compounds under study exhibited pseudoplastic behaviour. In the case of HAF and acetylene black-filled compounds, pseudoplasticity decreased with increase in filler content and increased with increase in temperature, as indicated by steady increase in n′ value in the former case and a steady decrease in the latter case. However, in the case of aluminium powder-filled compounds, at 100°C and below that, the n′ values were lower than that of the gum compound, indicating higher pseudoplasticity. Even though there was marginal increase in n′ values with filler loading, the effect was not significant as in the case of HAF and acetylene black-filled compounds. Another point noted is the increase in n′ value of the gum compound and the aluminium powder-filled compounds at 120°C. No such increase was noticed for HAF and acetylene black-filled compounds at 120°C.

Table IV.1 **Flow behaviour index value (n′)**

Sample	n′ at			
	90°C	100°C	110°C	120°C
Gum	0.202	0.193	0.125	0.161
AL05	0.181	0.175	0.148	0.156
AL10	0.186	0.172	0.145	0.168
AL15	0.185	0.177	0.181	0.179
AL20	0.191	0.199	0.185	0.187
HF05	0.198	0.196	0.185	0.161
HF10	0.216	0.198	0.176	0.175
HF15	0.229	0.208	0.221	0.189
HF20	0.261	0.224	0.234	0.212
AC05	0.202	0.182	0.176	0.164
AC10	0.236	0.218	0.205	0.207
AC15	0.257	0.238	0.233	0.214
AC20	0.365	0.254	0.255	0.218

IV.5 Effect of Aluminium Powder on Die Swell

Die swell occurs due to recoiling of the polymer chains as they emerge from the die after undergoing high rate of shear at the die entry. Several factors such as molecular weight, molecular weight distribution, chain branching, rate of shear, etc. are reported to affect die swell. Filled systems normally show lower die swell since die swell is mostly a polymer dependent phenomenon. As the filler content is increased, the die swell decreased (Figure IV.5) as the percentage of polymer in filled compounds becomes less. Among the three fillers evaluated, aluminium powder-filled samples showed higher die swell at 5 volume per cent loadings but at higher loadings of 20 volume per cent, aluminium powder-filled sample had the least die swell. All compounds containing HAF black showed higher die swell than acetylene black-filled compounds.

IV.6 Deformation of Extrudates

Optical photographs of the extrudates collected at three different shear rates during extrusion at 100°C are shown in Figure IV.6.

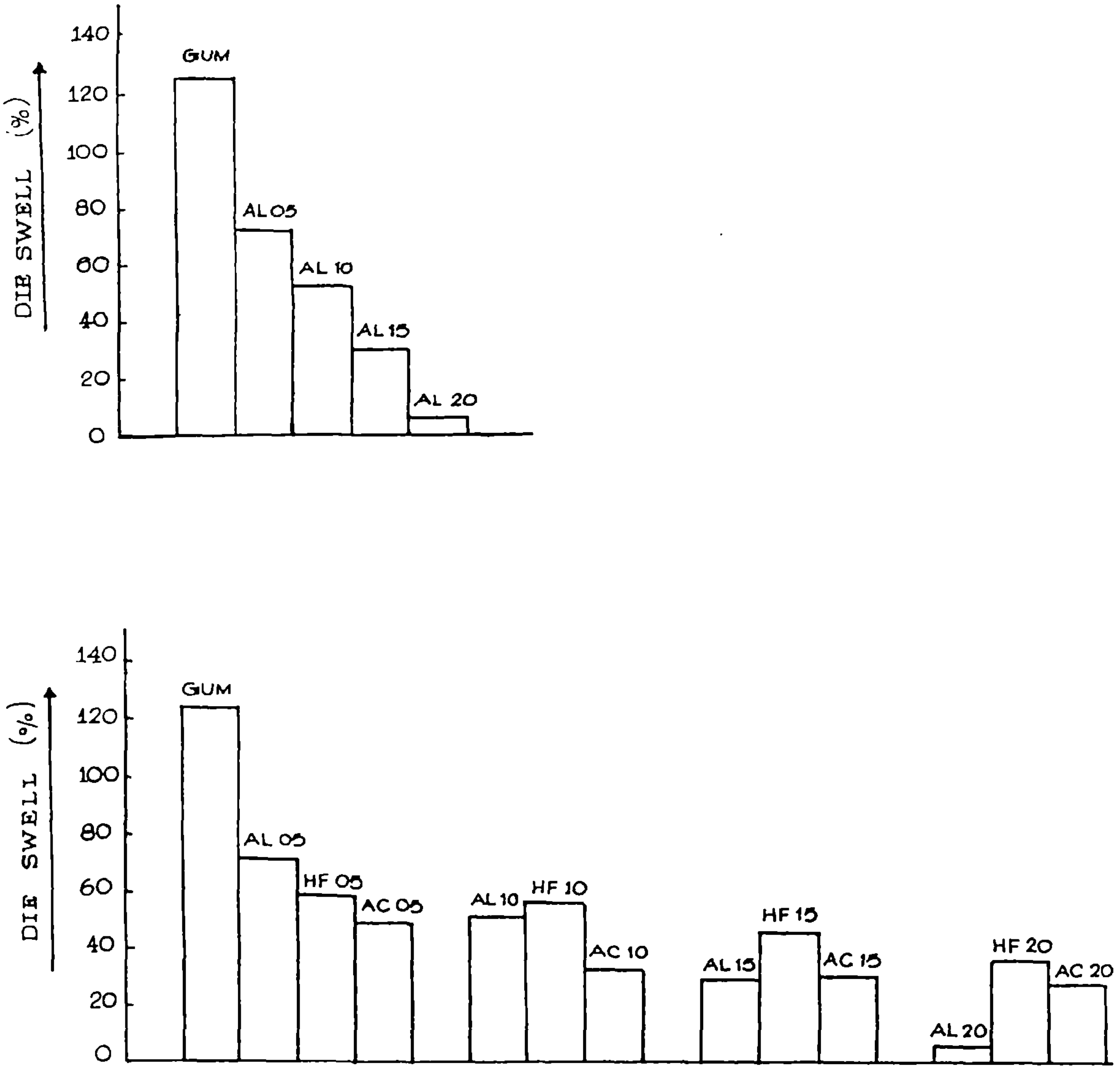

Figure IV.5 Die swell at 100°C and 333 S^{-1} shear rate Vs filler loading

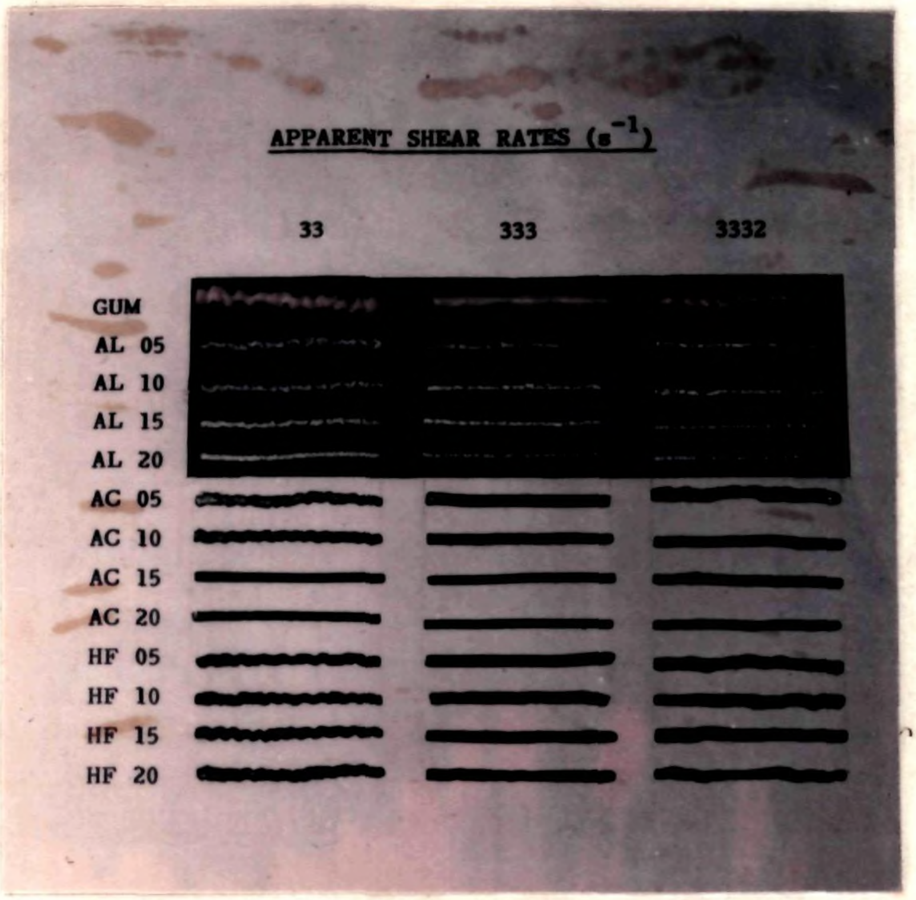

Figure IV.6 Photograph of the extrudates at three shear rates at 100°C

It can be observed that the deformation of the extrudate decreased with loading of filler at all the three shear rates. At a shear rate of 33 S^{-1} compounds containing 20 volume per cent of aluminium powder and 15 and 20 volume per cent of acetylene black gave smooth extrudates. HAF black-filled and the gum compound had the maximum deformation. At 333 S^{-1} all the extrudates were much smoother than those extruded at a higher shear rate of 3332 S^{-1}. The acetylene black-filled extrudates were having smooth surface even at a higher shear rate of 3333 S^{-1}. There are several explanations given for the deformation of the extrudates occurring during extrusion. According to one such explanation, as a result of slow relaxation time relative to the rate of deformation, the stress exceeds the strength of the melt and a fracture results, which propagates circumferentially round the die inlet. According to another explanation deformation of extrudates results from the slip-stick flow at the capillary wall. Whatever the mechanism operating, the deformation occurs only at certain shear rates/shear stresses. In the case of the compounds under study, it was observed that a shear rate of 333 S^{-1} was better for getting smoother extrudates.

IV.7 Conclusions

The study revealed that aluminium powder-filled natural rubber compounds have lower viscosity than HAF and acetylene black-filled compounds. The increase in viscosity with quantity of aluminium powder addition was only marginal. Smooth extrudates of aluminium powder-filled compounds could be obtained in the shear rate range of 333 S^{-1} at 100°C.

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CHAPTER V

TECHNOLOGICAL PROPERTIES OF ALUMINIUM POWDER-FILLED VULCANISATES

V TECHNOLOGICAL PROPERTIES OF ALUMINIUM POWDER-FILLED NR VULCANISATES

Fillers are considered as an unavoidable ingredient in most of the rubber compounds. They are added in rubber compounds either to reduce the cost or to enhance the vulcanisate properties. Properties imparted to the rubber vulcanisates by fillers depend on the type of filler and the quantity added. While reinforcing fillers enhance the strength properties, they reduce processability of compounds and adversely affect heat build up and set in compression or tension. With increase in quantity of any filler in rubber compounds, properties such as modulus, hardness, set and heat build up proportionately increase whereas, resilience and elongation at break decrease [1]. Properties such as tensile strength, tear strength and abrasion resistance pass through a maximum with increase in filler content [2]. The quantity of filler required to impart the maximum property to the vulcanisate varies with type of filler; the reinforcing ones attain the maximum property with lower quantity [3]. The vulcanisate properties also depend on extent of crosslinking and types of crosslinks formed during vulcanisation [4,5]. In this chapter of the thesis the effects of aluminium powder on properties of NR vulcanisates are presented in comparison with those of HAF and acetylene black-filled vulcanisates. Since the same base formulation (I) was used for making all the compounds (except type of filler), it is expected that the observed difference in properties of the vulcanisates is basically due to the effect of fillers. The vulcanisate properties of the compounds under study are given in Table V.1.

V.1 Tensile Strength, Modulus and Elongation at Break

Even though rubber products are seldom elongated to their breaking point during service, tensile strength of rubber vulcanisates is considered to be a quality parameter since any reduction in quality will be reflected in tensile strength also. Tensile strength of aluminium powder-filled vulcanisates was higher than that of the gum vulcanisate (Table V.1) upto 15 volume per cent loading, indicating a semi reinforcing character of this filler. However, at 20 volume loading (53.8 phr), the strength decreased. This could be due to a dilution effect beyond 50 phr, as the polymer content is reduced[6]. At equal volume loadings, HAF and acetylene black imparted higher tensile strength than aluminium powder due to lower particle size of HAF and acetylene blacks compared with aluminium powder. Modulus 300% of aluminium powder-filled vulcanisates increased with increase in quantity of filler. However, as in the case of tensile strength, at equal volume loadings, the increase in modulus was lower compared with that for HAF and acetylene black-filled vulcanisates, which further indicates its low reinforcing character compared with HAF and acetylene blacks. Elongation at break decreased with increase in quantity of filler and the decrease was less for the aluminium powder-filled vulcanisates compared with the HAF and acetylene black-filled ones.

V.2 Tear Strength

Tear strength indicates the capacity of the vulcanisate to resist cutting, chipping and tearing actions during service. More reinforcing fillers impart high tear strength to the vulcanisate. Even though tear strength increased with increase in quantity of aluminium powder in the vulcanisate, the extent of increase was much lower compared with HAF and acetylene black-filled vulcanisates. This again indicates that the reinforcing activity of aluminium powder is lower compared with that of HAF and acetylene black.

V.3 Hardness

The hardness of the vulcanisates increased with increase in quantity of filler added in the case of all the three fillers. However, the extent of increase in hardness was not uniform with filler content. At lower loadings of 5-10 volume per cent, aluminium powder and acetylene black-filled vulcanisates gave higher hardness than HAF black-filled vulcanisates. But at higher loadings of 20 volume per cent, HAF and acetylene black-filled vulcanisates gave much higher hardness values than the aluminium powder-filled one. This observation could be explained as follows.

At all levels of filler loading, the vulcanisates containing aluminium powder have higher V_r values than those containing HAF and acetylene black (Table V.1). But aluminium powder is not having much reinforcing action. Thus at lower loadings, the contribution towards increase in hardness is mainly from higher extents of crosslinking. As the quantity of filler is increased, the contribution due to reinforcement increases and at loading of 15-20 volume per cent of filler, the vulcanisates containing the more reinforcing HAF and acetylene blacks showed higher hardness. This explanation is further supported by the nature of change in rebound resilience, compression set and abrasion resistance of these vulcanisates also.

V.4 Rebound Resilience

Normally with any filler, as the quantity of filler in the vulcanisate is increased, the rebound resilience decreases. This trend is observed in the case of HAF and acetylene black-filled vulcanisates. However, in the case of aluminium powder-filled samples, increase in resilience was noticed at lower loadings. As pointed out earlier, this could be due to higher extent of crosslinking achieved by the vulcanisates containing aluminium powder.

V.5 Compression Set

Compression set results from rearrangement of network structure, degradation of polymer chains, debonding of polymer-filler attachments, etc. It is dependent on type of polymer, nature of crosslinks, type of filler and its quantity [7,8]. In the case of HAF and acetylene black-filled vulcanisates, compression set increased with increase in filler content and the latter showed higher values of set due to high structure of acetylene black used. In the case of aluminium powder-filled vulcanisates, compression set decreased upto 15 volume per cent loading. This is expected to be due to higher extent of crosslinking as indicated by higher V_r values of the vulcanisates. At loadings of 20 volume per cent (53.8 phr) as the quantity exceeded 50 phr, the set value increased. However, it was still less than that of the gum compound. This could be due to more uniform network structure of the 12.5 mm thick test samples at the surface and centre, achieved through improved thermal conductivity of the aluminium powder-filled vulcanisates as explained in Chapter VI.

V.6 DIN Abrasion Loss

Even though there is no direct correlation between laboratory abrasion and field performance where abrasive loss is involved, laboratory results give an indication of the performance of the compounds under identical conditions. In the case of reinforcing blacks like HAF, the abrasion loss decreased with increase in filler quantity. Acetylene black-filled samples also showed the same trend. However, the DIN abrasion loss values of aluminium powder-filled vulcanisates were substantially lower than that of the above two cases, upto 15 volume per cent loading. The abrasion loss of the 20 volume per cent loaded sample was almost double that of the sample containing 15 volume per cent. Since the reinforcement activity of aluminium powder was lower as indicated by the strength properties of aluminium powder-filled vulcanisates, the reason for the improved resistance to abrasion could be the higher extent of crosslinking (higher V_r values) of the samples containing aluminium powder. The increase in abrasion loss beyond 15 volume per cent loading is due to decrease in total polymer content of that sample.

Table V.1 Physical properties of aluminium, high abrasion furnace black and acetylene black-filled vulcanisates

Properties	Gum	AL05	AL10	AL15	AL20	HF05	HF10	HF15	HF20	AC05	AC10	AC15	AC20
Optimum cure time at 150°C (minutes)	18.0	14.0	13.5	13.0	14.0	16.0	15.0	14.0	13.5	15.5	16.5	16.5	16.0
Scorch time at 150°C (minutes)	11.0	7.25	7.25	6.5	7.0	9.0	7.50	7.0	6.5	8.25	9.0	9.0	8.0
Modulus 300% (MPa)	2.3	3.1	3.9	5.0	5.6	4.3	6.2	8.7	14.4	4.6	7.1	9.8	14.4
Elongation at break (%)	678	668	633	593	548	628	613	590	520	617	570	562	534
Tensile strength (MPa)	20.7	22.4	22.5	21.2	18.2	24.5	26.7	29.2	30.8	24.8	25.5	26.4	27.5
Tear strength (N/mm)	31.8	34.1	35.8	39.2	41.6	45.0	52.5	75.0	101.0	43.3	48.0	52.3	60.4
Hardness (Shore A)	37	44	47	50	55	40	45	52	57	44	46	50	58
Rebound resilience (%)	78.3	83.4	80.6	76.1	72.4	74.6	71.3	65.9	57.4	71.3	68.0	62.4	57.4
Compression set (%) 22 h, 70°C	37.7	30.4	29.1	25.1	34.6	40.0	41.7	44.4	48.9	42.0	46.3	49.4	53.0
Abrasion loss (mm^3)	112.0	95.0	77	53	100	103.2	94.1	85.3	66.1	115.4	108.6	89.1	69.3
V_r at optimum cure time at 150°C	0.149	0.189	0.197	0.201	0.221	0.157	0.163	0.168	0.170	0.153	0.165	0.170	0.173

V.7 Conclusions

Evaluation of the technological properties of the vulcanisates containing aluminium powder, HAF and acetylene blacks leads to the following conclusions.

1. The reinforcing activity of aluminium powder is lower than that of HAF and acetylene blacks.
2. The strength properties of NR vulcanisates are not adversely affected by adding aluminium powder upto 15 volume per cent.
3. Aluminium powder-filled vulcanisates have higher resilience, lower set and better abrasion resistance (upto 15 volume per cent loading) than HAF and acetylene black-filled samples.

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CHAPTER VI

THERMAL CONDUCTIVITY OF ALUMINIUM POWDER-FILLED NATURAL RUBBER VULCANISATES

VI THERMAL CONDUCTIVITY OF ALUMINIUM POWDER-FILLED NATURAL RUBBER VULCANISATES

Natural rubber is considered as a poor conductor of heat and electricity. With the exception of a few items, all rubber products have to undergo the process of vulcanisation during manufacture. Vulcanisation is effected by heating the rubber compound at higher temperature. Due to its poor heat conductivity, a thick article takes a very long time to get its centre portion vulcanised, during which the surface gets degraded. Several methods have been adopted to get an even cure of thick articles. These included microwave heating [1], use of heat resistant efficient vulcanisation systems [2], use of delayed action accelerators [3] use of retarders [4], two stage heating, etc. It is known that use of fillers such as carbon blacks and zinc oxide improves the thermal conductivity of rubber compounds to a certain extent [5]. However, even rubber compounds containing a good amount of carbon black are to be heated for very long periods to vulcanise thick articles such as rubber covered rolls, tyre retreads, etc. (2 to 6 hours depending on thickness). Rubber products generate heat due to high frequency flexing during service. Unless the heat generated is dissipated away from inside, it gets accumulated, causing severe thermal degradation of the polymer. Thus the study of improving thermal conductivity of rubber vulcanisates assumes importance.

Even though a lot of work has been reported on heat transfer and vulcanisation of rubber products [6], studies on thermal conductivity of rubber vulcanisates are very few. The influence of degree of vulcanisation on thermal conductivity has already been reported [7,8]. Studies conducted by Neskoromnyi *et al.* [9] showed that as the extent of vulcanisation increases, the thermal conductivity decreases. Orientation of polymer chains and dispersion of fillers were also found to have significant effect on thermal conductivity of rubber vulcanisates [5,10]. Several methods have been described to measure thermal conductivity of rubber vulcanisates [11,12]. In this chapter of the thesis, the results of the thermal conductivity measurements of natural rubber vulcanisates containing alumininum powder are presented in comparison with those of HAF and acetylene black-filled vulcanisates. The details of the equipment used for the measurement of thermal conductivity are given in Section II.9.

VI.1 Effect of Fillers on Thermal Conductivity

The effects of quantity of aluminium powder, HAF black and acetylene black on thermal conductivity at 30°C are shown in Figure VI.1. Among the three fillers aluminium powder showed the highest increase in thermal conductivity at equal volume loading. The straight line graphs obtained indicates almost linear increase in thermal conductivity with loading of aluminium powder. From the slope of the straight lines, the following equations were found good to calculate the thermal conductivity in the range of loading of fillers studied.

$y = 0.0185\,x + 0.167$ for aluminium powder . . . (VI.1)

$y = 0.008\,x + 0.167$ for acetylene black . . . (VI.2)

$y = 0.004\,x + 0.167$ for HAF black . . . (VI.3)

where

y = Thermal conductivity λ at 30°C in w/m.k.

x = Quantity of filler added in volume per cent.

The slightly higher values at the third decimal range, obtained by using the above equations (Table VI.1) may be due other variables such as extent of crosslinking and extent of filler dispersion in the vulcanisate. As pointed out earlier, these two factors also affect the thermal conductivity of the rubber vulcanisates and hence the experimental values are slightly less than the calculated values.

Table VI.1 Effect of fillers on thermal conductivity at 30°C (W/m.k)

Quantity volume per cent	Aluminium powder		Acetylene black		HAF black	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
5	0.255	0.259	0.205	0.207	0.184	0.187
10	0.350	0.352	0.245	0.247	0.200	0.207
15	0.443	0.445	0.284	0.287	0.220	0.227
20	0.531	0.537	0.319	0.327	0.246	0.24

Thermal conductivity of gum vulcanisate is 0.167 W/m.k.

VI.2 Effect of Temperature on Thermal Conductivity

The thermal conductivity of the samples containing different loadings of aluminium powder, HAF black and acetylene black decreased with increase in temperature (Figures VI.2 to VI.4). The decrease was pronounced with increase in filler loading. The change in thermal conductivity of the gum compound was much less compared with the filled samples. Even at a higher temperature of 70°C, the thermal conductivity of the vulcanisates followed the order, aluminium powder > acetylene black > HAF black > gum, at all loadings. The thermal conductivity of the aluminium powder-filled vulcanisates was almost 40 to 50% higher than that of the acetylene black-filled samples at higher loadings of the fillers.

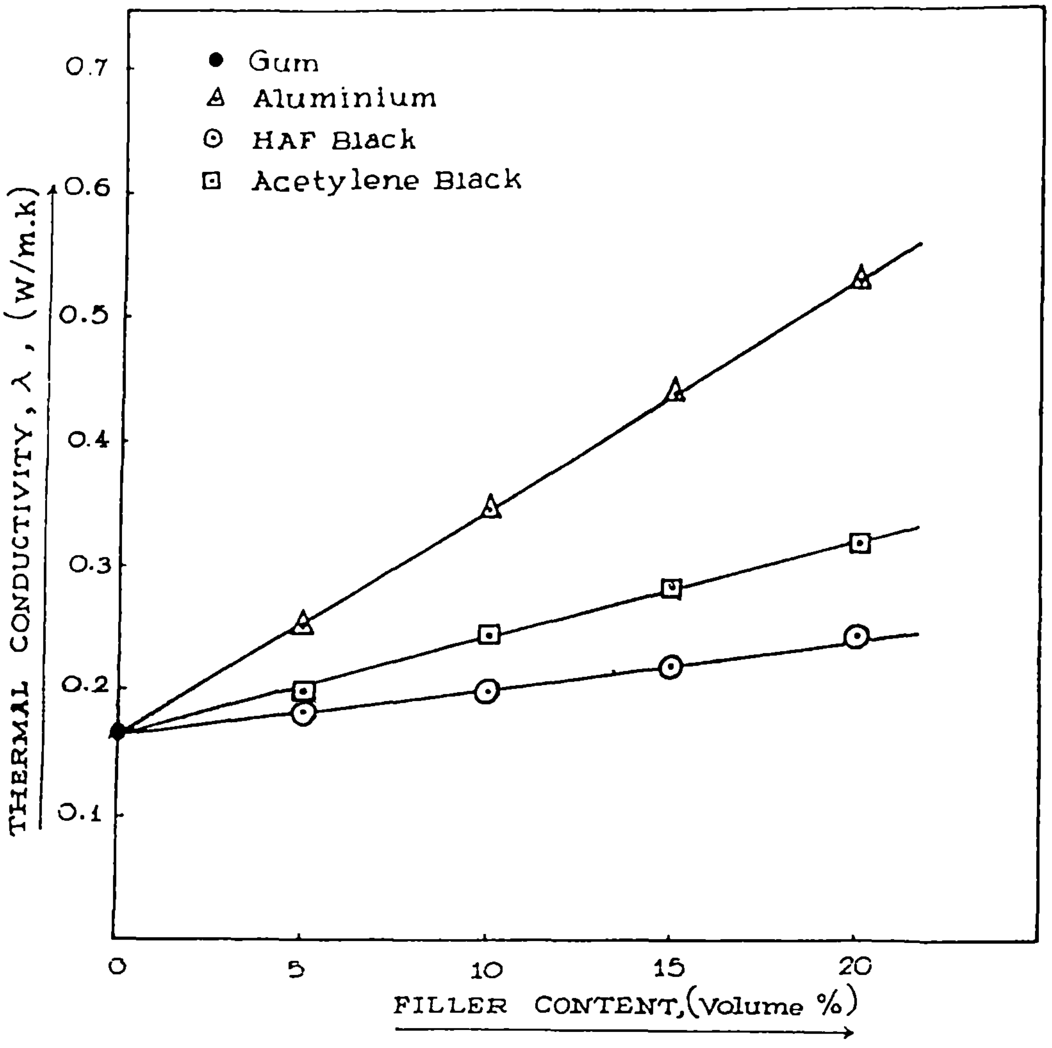

Figure VI.1 Plot of thermal conductivity at 30°C Vs filler loading

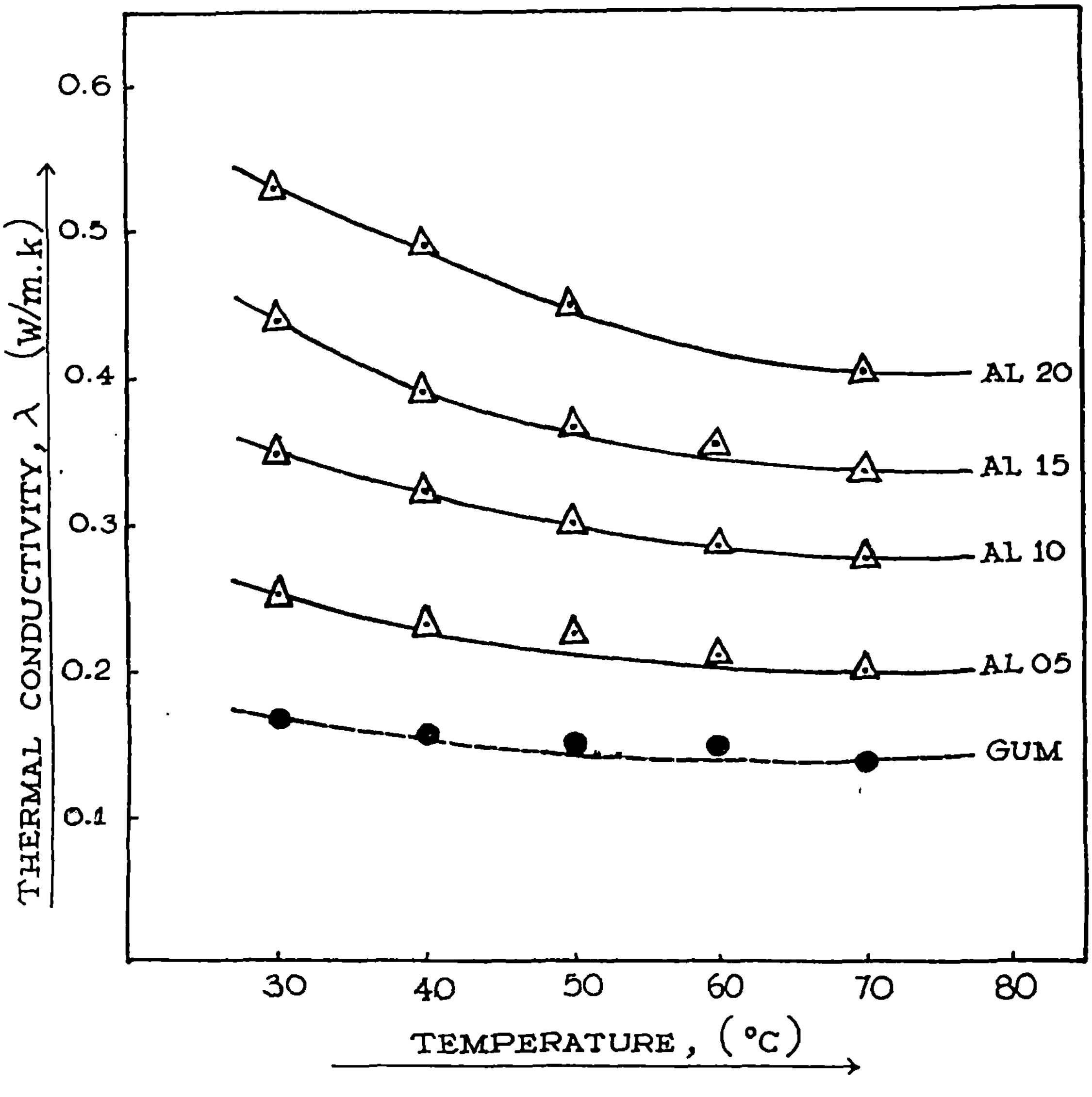

Figure VI.2 Plot of thermal conductivity Vs temperature

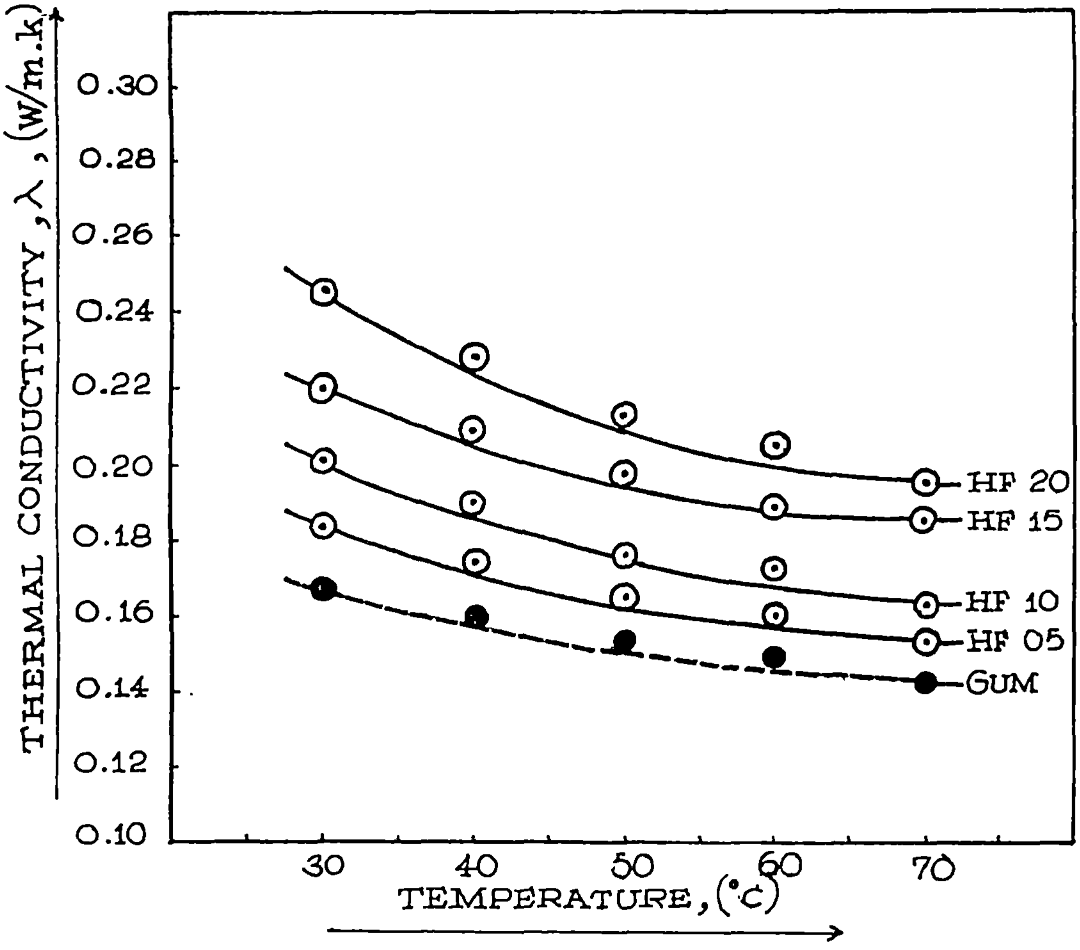

Figure VI.3 Plot of thermal conductivity Vs temperature

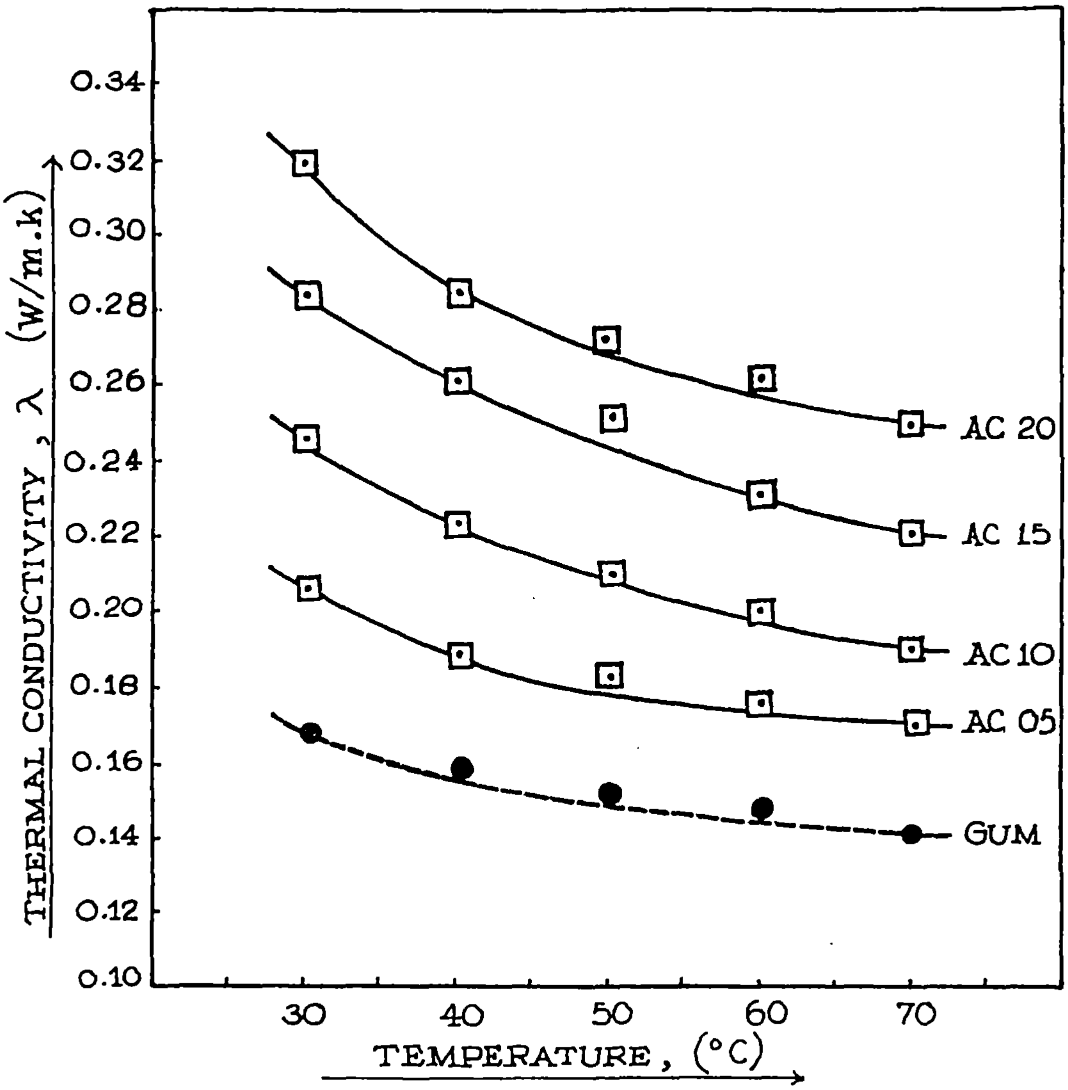

Figure VI.4 Plot of thermal conductivity Vs temperat

VI.3 Effect of Thermal Conductivity on Extent of Crosslinking

The significance of thermal conductivity of rubber compounds is more relevant with the vulcanisation of thick articles. Hence the V_r values of the test pieces taken from the surface and centre of a cube of 5 x 5 x 5 cm^3, vulcanised at different intervals of time, were determined for the vulcanisates containing different loadings of these three fillers. These results are presented in Tables VI.2 and VI.3 respectively.

Examination of the data in Table VI.2 indicates that for the gum compound, it takes t_{90}+12 minutes (where t_{90} is the optimum cure time taken from the rheograph) to reach the maximum V_r values for the sample taken from the surface. It is reduced to t_{90}+10 minutes in the case of sample AL05 and t_{90}+5 minutes for the samples containing 10, 15 and 20 volume per cent loadings of aluminium powder. In the case of HAF black-filled vulcanisates, sample HF05 took t_{90}+12 minutes and all other samples required only t_{90}+10 minutes. In the case of acetylene black-filled samples, it took t_{90}+12 minutes for AC05, t_{90}+10 minutes for AC10 and, t_{90}+8 minutes for AC15 and AC20 samples to attain the maximum V_r values.

Table VI.2 V_r values of sample taken from the outer surface of the cube

Cure time at 150°C	Gum	AL05	AL10	AL15	AL20	HF05	HF10	HF15	HF20	AC05	AC10	AC15	AC20
t_{90}	0.149	0.189	0.197	0.201	0.221	0.157	0.163	0.168	0.170	0.153	0.165	0.170	0.173
$t_{90}+3$	0.180	0.190	0.203	0.208	0.228	0.171	0.172	0.173	0.173	0.166	0.170	0.177	0.180
$t_{90}+5$	0.181	0.192	0.207	0.216	0.234	0.177	0.178	0.179	0.180	0.170	0.173	0.180	0.189
$t_{90}+8$	0.184	0.193	0.206	0.216	0.234	0.180	0.184	0.184	0.186	0.176	0.175	0.183	0.196
$t_{90}+10$	0.186	0.195	0.204	0.216	0.229	0.182	0.188	0.189	0.193	0.177	0.178	0.184	0.196
$t_{90}+12$	0.187	0.195	0.202	0.215	0.226	0.184	0.189	0.190	0.193	0.181	0.179	0.183	0.199
$t_{90}+15$	0.187	0.194	0.201	0.209	0.220	0.185	0.199	0.191	0.197	0.179	0.178	0.183	0.198

Table VI.3 V_r values of sample taken from inside centre of the cube

Cure time at 150°C	Gum	AL05	AL10	AL15	AL20	HF05	HF10	HF15	HF20	AC05	AC10	AC15	AC20
t_{90}	0.080	0.178	0.194	0.197	0.215	0.111	0.128	0.120	0.144	0.132	0.158	0.164	0.170
$t_{90}+3$	0.149	0.189	0.202	0.208	0.227	0.152	0.163	0.151	0.169	0.159	0.167	0.174	0.180
$t_{90}+5$	0.169	0.191	0.202	0.209	0.230	0.169	0.174	0.166	0.180	0.166	0.171	0.180	0.183
$t_{90}+8$	0.182	0.192	0.205	0.214	0.230	0.179	0.180	0.176	0.185	0.173	0.174	0.181	0.192
$t_{90}+10$	0.186	0.193	0.205	0.214	0.226	0.181	0.184	0.187	0.188	0.174	0.179	0.185	0.197
$t_{90}+12$	0.189	0.194	0.204	0.214	0.225	0.183	0.186	0.188	0.190	0.176	0.179	0.183	0.197
$t_{90}+15$	0.190	0.197	0.204	0.215	0.222	0.185	0.192	0.191	0.191	0.178	0.179	0.183	0.198

The effect of thermal conductivity is more evident from the V_r values of the samples taken from inside centre of the cube of 5 x 5 x 5 cm^3. To get maximum or almost stable V_r values, it took more than t_{90}+15 minutes for the gum, AL05, HF05, HF10, HF15 and AC05 compounds. While compounds containing 10, 15 and 20 volume loadings of acetylene blacks (AC10, AC15 and AC20) took t_{90}+10 minutes, only t_{90}+8 minutes and t_{90}+5 minutes were required for compounds containing 10, 15 and 20 volume per cent loadings of aluminium powder. It is worth mentioning here that as pointed out in Chapter III, t_{90} values of the aluminium powder-filled compounds were lower than that of the other compounds. This observation clearly indicates that use of aluminium powder reduce the vulcanisation time of thick articles through improvement in thermal conductivity imparted by this filler.

VI.4 Effect of Aluminium Powder on Electrical Resistivity

Usually there exists a correlation between electrical conductivity and thermal conductivity [5]. In order to examine this, vulcanisates containing 10 volume per cent of HAF black, acetylene black and aluminium powder (HF10, AC10 and AL10) were tested for volume resistivity under the application of 500 V DC supply. The volume resistivity values (ohm. cm) obtained were 57 x 10^4, 16 x 10^4 and 6 x 10^4 respectively for HF10, AC10 and AL10 samples. This indicated that electrical conductivity also showed the same trend as that of thermal conductivity with the addition of aluminium powder. The above values are in the range for antistatic application.

VI.5 Conclusions

The following conclusions could be drawn from the results contained in this chapter.

1. Thermal conductivity of rubber is increased by the addition of HAF black, acetylene black and aluminium powder. At equal volume per cent, aluminium powder gives the highest conductivity.
2. Thermal conductivity decreases with increase in temperature.
3. The time required for attaining the maximum extent of crosslinking (as measured by V_r) for a thick rubber article will be the least when appropriate quantity of aluminium powder is incorporated in the compound.

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CHAPTER VII

AGEING CHARACTERISTICS OF ALUMINIUM POWDER-FILLED NATURAL RUBBER VULCANISATES

VII AGEING CHARACTERISTICS OF ALUMINIUM POWDER-FILLED NATURAL RUBBER VULCANISATES

Rubber products are being exposed to various conditions during service. These include heating, weathering, contact with solvents and oils, exposure to ozonised air, radiation, light, etc. Natural rubber being highly unsaturated, is easily subjected to attack by oxygen, ozone and chemicals, leading to degradation of the polymer chains, causing deterioration of properties. Several methods such as use of waxes [1], antioxidants and antiozonants [2], flexible coatings [3], blending with less unsaturated rubbers [4-6], etc. have been adopted to protect the polymer against these degrading agents. In order to assess the long term serviceability of the vulcanisates, it is essential that the effects of fillers and other chemicals used in rubber compounds on the ageing characteristics of the vulcanisates are studied in detail. Since rubber is mostly exposed to atmospheric conditions during service, attack by oxygen and ozone is the most important factor which causes degradation of the polymer. Nowadays polymeric materials are finding many applications in nuclear field as packings, shock absorbers, coatings, constructional elements, etc. [7]. Hence in this chapter of the thesis, the effects of heat ageing, exposure to ozonized air and γ-radiation on the vulcanisates containing aluminium powder are presented. The experimental details are given in Section II.7 and the original physical properties of the vulcanisates are discussed in Chapter V.

VII.1 Effect of Heat Ageing on Tensile Strength

The action of oxygen on natural rubber is very slow at room temperature. But it is activated by heat. Hence for assessing the long term serviceability of the vulcanisates, it is recommended that the samples may be aged at 70°C for 7 days or at 100°C for 3 days and find out the retention of tensile strength. In this study, the samples were aged at both the above temperatures and the retention of tensile strength evaluated. The results obtained are presented in Table VII.1. In all the cases it is observed that addition of filler improves the ageing resistance at 70°C and 100°C as evidenced by the lower per cent retention of the gum sample. At 70°C, better retention of tensile strength was noticed at 10-15 volume per cent loading of aluminium powder. Among the three fillers, aluminium powder retained the tensile strength after ageing at 70°C at a higher level compared with the other two fillers at 20 volume per cent loading. The higher tensile strength retention (>100%) after ageing at 70°C of the vulcanisates could be due to slow, continued crosslinking of the elastomer. At this temperature, the extent of main chain scission is less and effect of crosslinking predominates. But at a higher temperature of 100°C, the reverse situation occurs and the extent of polymer degradation is very severe, resulting in very low retention of tensile strength.

Table VII.1 **Retention of tensile strength after ageing**

Sample number	Retention of tensile strength (%)	
	Aged at 70°C	Aged at 100°C
Gum	85.0	5.2
AL05	97.3	6.3
AL10	107.1	8.5
AL15	108.0	10.8
AL20	101.9	12.8
HF05	107.8	7.1
HF10	108.1	7.5
HF15	102.6	8.2
HF20	93.8	10.0
AC05	102.9	8.8
AC10	100.0	10.0
AC15	96.9	12.2
AC20	95.3	13.5

One important observation of the results of 100°C ageing is that the retention of tensile strength increased with filler loading and that the aluminium powder-filled and acetylene black-filled vulcanisates showed better retention of tensile strength than HAF black-filled ones at higher loadings. As the thermal conductivity of the former samples are much higher than that of the latter one, more uniform thermal ageing through the cross-section of the samples may be the reason for better retention of tensile strength of the aluminium powder and acetylene black-filled samples.

VII.2 Effect of γ-Radiation on Tensile Strength

The tensile strength of the samples after exposing the test pieces to different dosages of γ-radiation is given in Table VII.2. As in the case of heat ageing, the tensile strength of the gum sample decreased on exposure to γ-radiation. The tensile strength of the gum sample was reduced to half of its original value after exposure to 20 mega rads. Among the filled vulcanisates, those containing aluminium powder showed lower values compared with HAF and acetylene black-filled samples after exposure to γ-radiation. Slight increase in tensile values observed in some samples after exposure to one mega rad of γ-radiation could be due to continued crosslinking that has taken place in those samples.

Table VII.2 Tensile strength before and after γ-irradiation

	Gum	AL05	AL10	AL15	AL20	HF05	HF10	HF15	HF20	AC05	AC10	AC15	AC20
Tensile strength (MPa) before ageing	20.7	22.4	22.5	21.2	18.2	24.5	27.1	29.2	30.8	24.8	25.5	26.4	27.5
Tensile strength after ageing 1 M rad	18.7	22.3	23.2	21.4	16.8	23.6	28.5	29.8	30.5	24.1	25.7	26.7	27.3
Tensile strength after ageing 5 M rads	17.8	23.2	21.9	18.4	16.2	24.7	28.3	29.5	31.9	22.6	25.9	27.2	28.8
Tensile strength after ageing 10 M rads	15.2	21.2	21.3	17.8	16.4	25.1	26.1	26.4	27.4	22.2	23.5	24.7	25.3
Tensile strength after ageing 15 M rads	12.3	18.3	18.8	17.3	15.1	23.2	23.7	24.5	26.1	20.5	22.8	23.4	23.0
Tensile strength after ageing 20 M rads	10.7	18.3	17.6	16.3	13.2	22.2	23.5	23.1	24.4	20.3	22.2	23.7	22.0

But at higher dosages, there was a decrease in tensile strength of all the samples as polymer chain degradation predominated. In the case of aluminium powder-filled vulcanisates even though the final tensile values after exposure to γ-radiation was lower than those of the HAF and acetylene black-filled samples, the extent of decrease from the original value was comparable to that for the other vulcanisates.

VII.3 Ozone Resistance of the Vulcanisates

For assessing the ozone resistance of the vulcanisates, the samples were exposed to ozonised air of 50 pphm ozone concentration. The samples were observed after 2 hours and 20 hours of exposure. Photographs of the samples were taken giving the same magnification in all cases. These photographs are presented in Figures VII.1 and VII.2. Examination of Figure VII.1 indicates that in all the samples cracks due to ozone attack started even at two hours of exposure. However, the nature of cracks observed in different samples were different. In the case of aluminium powder-filled vulcanisates, a large number of small cracks were observed whereas in the other samples much larger cracks, small in number were found.

This was more evident as the quantity of filler is increased. If the filler arrests the growth of the cracks, large cracks may not develop, at the same time it can lead to large number of small cracks as the critical strain required for ozone attack to take place may not be released. Examination of the photographs after 20 hours of exposure, Figure VII.2, gives more evidence to this view point. In the gum sample as well as in the HAF and acetylene black-filled samples large cracks extending from one end to the other end of the test piece can be seen. However, the cracks in the aluminium powder-filled vulcanisates are not continuous and deep like that in other vulcanisates. As the loading of aluminium powder is increased, the length of the cracks is further reduced and there is a clear difference in length of the cracks observed on samples AL05 and AL20. Thus incorporation of aluminium powder was found be better than HAF and acetylene blacks as far as ozone resistance of the vulcanisates is concerned.

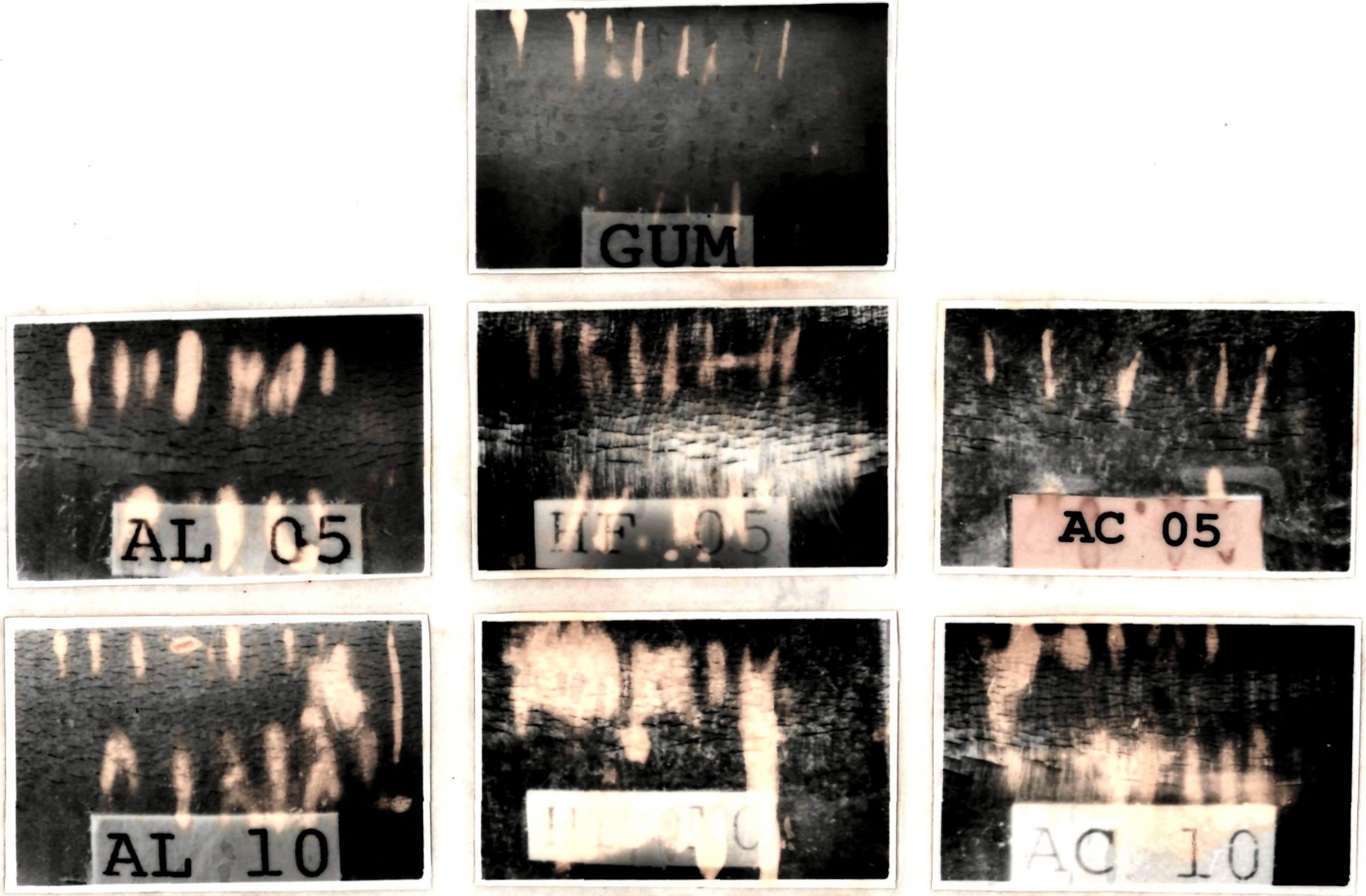

Figure VII.1   Optical photographs of ozone exposed samples (2 hours)
(Contd...)

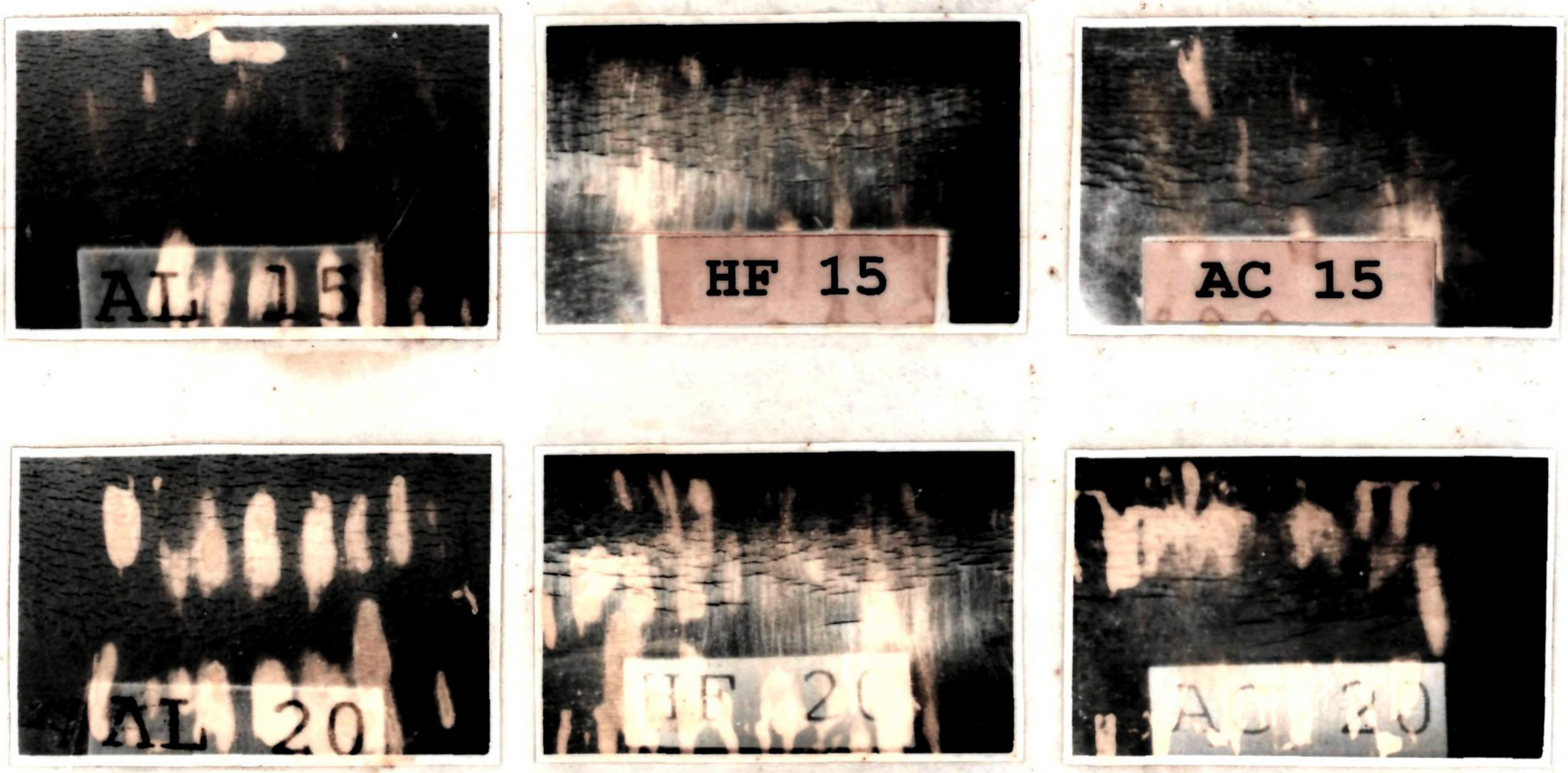

Figure VII.1 Optical photographs of ozone exposed samples (2 hours)

Figure VII.2 Optical photographs of ozone exposed samples (20 hours)

(Contd...)

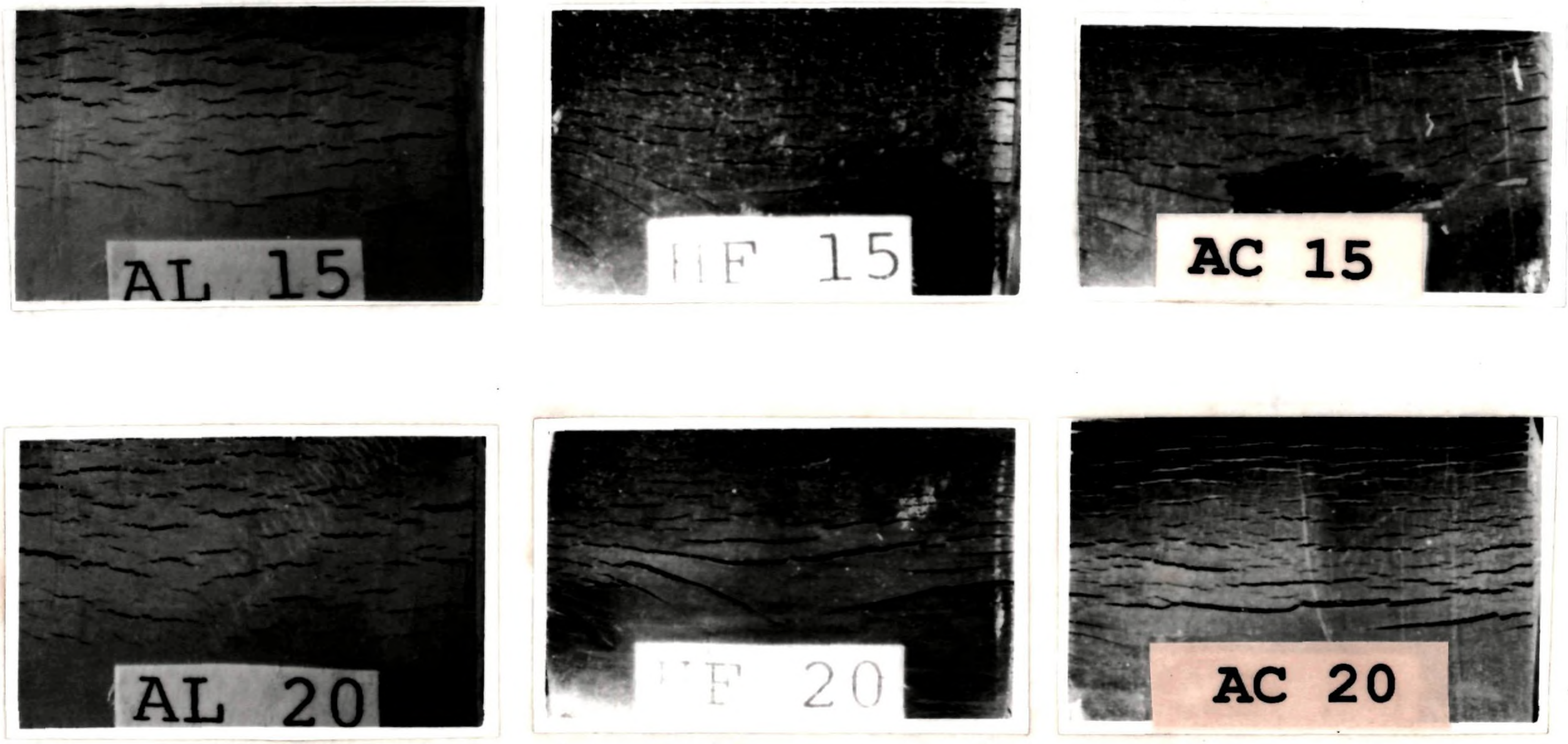

Figure VII.2 Optical photographs of ozone exposed samples (20 hours)

VII.4 Conclusions

The data presented in this chapter indicated that incorporation of aluminium powder in natural rubber compounds does not adversely affect the ageing behaviour of the vulcanisates. It was found to be better than HAF and acetylene black against ozone attack in NR vulcanisates.

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CHAPTER VIII

EVALUATION OF ALUMINIUM POWDER IN TRUCK TYRE RETREAD COMPOUND

VIII EVALUATION OF ALUMINIUM POWDER IN TRUCK TYRE RETREAD COMPOUND

Unlike in many other countries, retreading industry in India is all the more important due to various reasons such as higher price of new tyres, lower retreading charges and fast wearing of the tread portion of the tyre. Both conventional and precured processes are used to retread tyres of common sizes. Performance of retreads depends on many factors such as average load on tyres, speed of the vehicle, road and vehicle condition, besides environmental factors and driving habits. Research work in the field of conventional retreads were mostly aimed at developing compounds having better shelf life, tackiness and improved mileage [1]. With the advent of precured retreading process, factors such as tackiness and shelf life of the compound and heat build up of the vulcanisate assumed less importance due to the specific nature of the process. In this case, other parameters such as mileage, wet skid resistance and fuel economy became prominent aspects for compound design [2]. Whichever be the method adopted for the process, the retread compound undergoes a very long heating cycle during the process of retreading, either to cure the bonding gum (for precured process) or the tread and cushion gum (conventional process). Vulcanised tread undergoes further exposure to temperature due to heat developed during service. Earlier work showed that network structure of the tread undergoes changes during service of the tyre [3,4]. It has been shown that improved performance of the tread compounds could be achieved through network structure modification brought about by the use of a higher dosage of stearic acid [5-7]. Attempts to decrease the overall effect of heating cycle by reducing the vulcanisation time have also been reported [8,9].

However use of fast curing accelerators to reduce the vulcanisation time adversely affects the processing safety and storage quality of the retread compounds. Hence, I have attempted to develop truck tyre retread compound having improved thermal conductivity by adding aluminium powder with a view to reducing the overall vulcanisation time of the normal retread compound. The results of the studies conducted are presented in this chapter of the thesis. The formulations selected was that of a conventional truck tyre retread compound which are given in Tables II.3 and II.4. The difference between these two formulations is that, in the first set, a blend of NR and BR was prepared, to which the reinforcing filler ISAF black was added followed by aluminium powder (compounds marked TR, TRAL5, TRAL10, TRAL15 and TRAL20). The compounding was completed in the usual manner. But in the second set of compounds, aluminium powder was first dispersed in the BR phase which was further blended with

NR and then completed the compounding by adding ISAF black and other ingredients (compounds BRAL5, BRAL10 and BRAL15). In one case (NRAL10) aluminium powder was first dispersed in NR phase which was then blended with BR and then prepared the compound by adding ISAF black and other ingredients. To check the effect of long period of curing on abrasion loss, samples cured at different times [(t_{90}+5), 45, 60 and 120 minutes) were tested for abrasion loss. The results obtained are presented in Tables VIII.1 to VIII.4.

VIII.1 Properties of TR, TRAL5, TRAL10, TRAL15 and TRAL20 Compounds

VIII.1.1 Cure Characteristics

The cure time and scorch time of the compounds given in Table VIII.1 indicate that these are reduced by the addition of aluminium powder in the retread compound. The reduction in cure time and scorch time is due to the effect of aluminium powder to enhance the cure rate index of the compounds as already discussed in Chapter III. However, the scorch safety of all the compounds was more than 20 minutes at 120°C which indicated that these compounds are processable and the retread compounds can be stored for about three to four months as practiced in retreading units.

VIII.1.2 Tensile Strength, Modulus, Elongation at Break and Tear Strength

The modulus 300% and tensile strength given in Table VIII.1 indicate that those properties are not affected by the addition of upto 20 phr of aluminium powder to the normal retread compound. The reduction in elongation at break is due to increase in total filler content. Even though the oil content was increased to keep the hardness to the same level as that of the control (TR) compound, the elongation at break decreased with the addition of aluminium powder, but the tensile strength was not affected. The results of the samples after ageing at 70°C for 7 days also show almost the same trend as that of the control sample. However, there was a reduction in tear strength with the addition of aluminium powder.

VIII.1.3 Resilience, Heat build up and Compression set

Normally addition of filler adversely affects these properties. But in the case of aluminium powder filled vulcanisates this effect was not noticed (Chapter V). In the case of retread compounds also, addition of aluminium powder did not affect the resilience, compression set and dynamic set adversely. This could be due to higher extent of vulcanisation achieved due to the addition of aluminium powder as explained earlier in Chapter V. But there was an increase in heat build up with the addition aluminium powder, which was prominent beyond 15 phr loading. This could be due to a very high increase in total filler content (65 phr) in the compound.

VIII.1.4 De Mattia Flexing

During De Mattia flexing it was noticed that the time for crack initiation increased upto 10 phr loading of the aluminium powder and then slowly decreased. Even for the sample containing 20 phr aluminium powder, flex cycles for crack initiation was higher than that of the normal retread compound. Another peculiar observation is that the flex cycles for complete failure of the sample containing 15 phr aluminium powder was very much higher (>400 K cys). In the case of all the samples containing aluminium powder, it was noticed that the after the initiation of the cracks, there was layer type tearing in which the propagation of tear was in layers. The sample containing 20 phr of aluminium powder (TRAL20) showed lower flex life compared with the control compound (TR).

VIII.1.5 Thermal Conductivity

As expected, the thermal conductivity of the vulcanisates increased with the addition of aluminium powder. There was almost 70% and 80% increase in thermal conductivity at 30°C with the addition of 15 and 20 phr respectively of aluminium powder in the compound. Even though thermal conductivity decreases with increase in temperature (Chapter VI), the increase in thermal conductivity with the addition of aluminium powder will be helpful to reduce the vulcanisation time of retread compounds.

Table VIII.1 **Properties of retread compounds**

Properties	TR	TRAL5	TRAL10	TRAL15	TRAL20
OCT 90% 150°C (minutes)	18	16.5	16	16	16
Scorch time 120°C (minutes)	37	34	28	26	24
Hardness (Shore A)	60	60	60	61	61
Resilience (%)	55.1	55.1	55.1	55.1	54.43
Heat build up (ΔT°C)	37	39	41	44	57
Dynamic set (%)	4.15	4.33	4.33	4.33	4.33
Compression set (%)	33.84	29.57	30.72	31.41	34.09
300% modulus (MPa)					
(BA)	8.35	8.8	8.9	8.65	8.3
(AA)	10.7	10.85	11.1	10.4	10.65
Tensile strength (MPa)					
(BA)	22.5	21.8	22.6	20.4	21.7
(AA)	21.6	19.2	22.4	19.9	20.5
Elongation at break (%)					
(BA)	680	663	655	580	570
(AA)	520	545	549	552	537
Tear strength (N/mm)	59.0	53.2	51.7	46.6	48.3
De Mattia Flexing					
Crack initiation (kcys)	41.5	41.5	57.15	53.25	45.0
Failure (kcys)	257.5	257.5	257.50	>400	213.4
Thermal conductivity (W/m.k.)	0.256	0.341	0.386	0.470	0.495

BA - Before ageing
AA - After ageing at 70°C for 7 days

VIII.1.6 Abrasion Loss

Abrasion resistance is an important property as far as retread compounds are concerned. In retreading the compounds are vulcanised at 60 to 120 minutes or more depending on the thickness of the tread. Hence the abrasion loss of compounds vulcanised at different periods were determined (Table VIII.2). It is noticed that addition of aluminium powder adversely affects the abrasion resistance of the retread compounds. However increased curing time also has a detremental effect on abrasion resistance. Hence if the abrasion loss due to increased vulcanisation time of the control compound could be reduced by giving less vulcanisation time through improved thermal conductivity, the total time for vulcanisation can be saved.

During abrasion loss test, it was noticed that the vulcanisate powder abraded out from the sample was of higher size than that of the control sample. This was suspected to be due to non-uniform distribution of the filler in the two phases of the blend. Hence in the next trial aluminium powder was dispersed in BR phase before blending the polymers initially. The results of tests conducted are presented in Tables VIII.3 and VIII.4.

Table VIII.2 **Effect of time of cure and aluminium powder content on abrasion loss**

Sample No.	Cure time at 150°C (minutes)			
	t_{90}+5	60	90	120
TR	49.0	50.0	56.8	71.3
TRAL5	55.2	70.9	79.3	86.4
TRAL10	82.6	94.5	99.8	100.6
TRAL15	109.5	133.3	147.2	153.9
TRAL20	116.5	147.9	150.6	157.3

VIII.2 Properties of Vulcanisates Containing Aluminium Powder in Polybutadiene Phase

VIII.2.1 Cure Time and Scorch Time

Compared with compounds of the TRAL series, cure time at 150°C of the BRAL series compounds was not different. However there was reduction in scorch time. But all the BRAL series compounds had sufficient scorch safety (>20 minutes) so that these can be processed by extrusion or can be stored for three to four months.

VIII.2.2 Tensile Strength, Modulus, Elongation at Break and Tear Strength

The tensile strength before and after ageing of the vulcanisates was comparable to that of the TRAL series except for the after ageing value of the BRAL15 compound which was lower. In general the BRAL series of vulcanisates had lower modulus and elongation at break. However there was good improvement in tear strength of the BRAL series compounds compared with TRAL series compounds. This is expected to be due to more uniform distribution of the fillers in the two phases of the vulcanisate.

VIII.2.3 Resilience, Heat Build up and Compression Set

There was improvement in rebound resilience and compression set resistance for the BRAL series vulcanisates, but the heat build up and dynamic set of this series of vulcanisates was almost the same as that of the TRAL series compounds.

VIII.2.4 De Mattia Flexing

There was an increase in crack initiation flex cycles for the BRAL series vulcanisates, but the flex cycles for complete failure was marginally lower. In this case also the vulcanisate containing 15 phr loading of aluminium powder showed an unusually high value.

VIII.2.5 Thermal Conductivity

Thermal conductivity increased with aluminium powder loading. However, the values were lower than that of the TRAL series compounds, especially for higher loadings beyond 10 phr.

VIII.2.6 Abrasion Resistance

The abrasion loss of the compounds increased with increase in loading of aluminium powder as well as increase of curing time. However, the increase was much lower compared with that of the vulcanisates of the TRAL series. Examination of the results in Table VIII.4 indicates that a conventional retread compound (TR) cured for 120 minutes has almost the same abrasion loss value (71.3 mm^3) as that of the compound containing additional 10 phr aluminium powder (BRAL10) and cured for 90 minutes. Since the thermal conductivity at 30°C of the BRAL10 compound is much higher (0.378 W/m.k.) than that of the TR compound (0.276 W/m.k.), it is expected that the vulcanisation time of the retread compound BRAL10 could be reduced by about 30 minutes to get almost the same mileage performance.

W / m . k .),

VIII.3 Properties of Compound Containing Aluminium Powder Dispersed in NR Phase

For comparison, all properties of the compound containing 10 phr of aluminium powder dispersed in NR phase first and then blended (NRAL10) were also determined. In general the properties of this compound were marginally better than the TRAL series compounds but were less than that of the BRAL10 compound, especially with respect to abrasion resistance and tear strength.

Table VIII.3 **Properties of retread compounds in which aluminium powder was added in BR**

Properties	BRAL5	BRAL10	BRAL15	NRAL10
OCT 90% 150°C (minutes)	15	16	15	16
Scorch time 120°C (minutes)	23	24	23	28
Hardness (Shore A)	60-61	60-61	60-61	60-61
Resilience (%)	56.40	56.40	56.40	55.10
Heat build up (ΔT°C)	40	42	44	37
Dynamic set (%)	3.94	4.33	4.33	3.54
Compression set (%)	28.79	29.71	39.38	29.08
300% modulus (MPa)				
(BA)	6.69	6.37	7.50	6.36
(AA)	9.33	9.47	9.44	9.55
Tensile strength (MPa)				
(BA)	22.94	20.40	20.03	22.25
(AA)	18.87	19.60	16.31	18.25
Elongation at break (%)				
(BA)	550	500	500	600
(AA)	400	410	325	350
Tear strength (N/mm)	57.55	76.96	53.17	66.51
De Mattia Flexing				
Crack initiation (kcys)	55.60	55.60	55.60	55.60
Failure (kcys)	228	228	>400	228
Thermal conductivity (W/m.k.)	0.340	0.378	0.391	0.383

BA - Before ageing
AA - After ageing at 70°C for 7 days

Table VIII.4 **Effect of curing time on abrasion loss of compounds (aluminium powder in BR phase)**

Sample No.	Cure time at 150°C (minutes)			
	$t_{90}+5$	60	90	120
TR	49.0	50.0	56.8	71.3
BRAL05	53.3	56.2	67.4	77.7
BRAL10	57.4	61.4	72.9	90.5
BRAL15	62.3	66.8	75.9	96.3
NRAL10	73.4	80.0	97.2	125.4

VIII.4 Conclusions

The results presented in this chapter of the thesis leads to the following conclusions.

1. Addition of aluminium powder improves the thermal conductivity of retread compounds.
2. In general the properties except abrasion resistance are not adversely affected by adding upto 10-15 phr of aluminium powder into a conventional retread compound containing 45 phr ISAF black. The effect of increase in abrasion loss is reduced if aluminium powder is first dispersed in BR phase of a NR/BR blend.

3. Increased time of heating adversely affects the abrasion resistance of retread compounds. Hence retread compounds with reduced vulcanisation time could be prepared without affecting the service performance if appropriate quantity (5-10 phr) of aluminium powder is added to the conventional retread compound.

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SUMMARY AND CONCLUSIONS

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This work was aimed at finding out the possibility of using aluminium powder as a filler in natural rubber compounds. Since filler is likely to have effect on vulcanisation characteristics, processing behaviour, technological properties, ageing behaviour, etc. these properties were evaluated in detail. Aluminium is a good conductor of heat and electricity. Hence a detailed study on the thermal conductivity of aluminium powder-filled vulcanisates was also conducted. Heat conduction is a very important aspect, which determines the time of vulcanisation of thick articles. Since aluminium powder-filled vulcanisates were found to have much higher thermal conductivity, the effect of this filler was evaluated in a truck tyre retread compound to examine whether the vulcanisation time could be reduced without adversely affecting the technological properties. For comparison, compounds containing high abrasion furnace black and acetylene black which are known for their reinforcement action and conductivity in rubber compounds respectively were also evaluated.

Evaluation of the cure characteristics of the compounds indicated that aluminium powder-filled compounds are faster curing than the HAF and acetylene black-filled compounds and give higher extent of crosslinking. The order of the vulcanisation reaction and the temperature coefficient of vulcanisation were not affected. The flow properties of the compounds at different temperatures indicated that the compounds are pseudoplastic in nature and have lower viscosity compared with HAF and acetylene black-filled ones. The aluminium powder-filled compounds were having lower die swell. The extrudate deformation was least when these compounds were processed at an apparent shear rate range of 333 S^{-1}. Low viscosity of aluminium powder-filled compounds at 90°C and below indicated that this filler may be affecting the stress induced crystallisation of natural rubber during flow through a capillary.

Evaluation of the technological properties of the aluminium powder-filled vulcanisates showed that it is not a reinforcing filler. But it gives properties comparable to those of HAF and acetylene black-filled vulcanisates due to higher extents of crosslinking achieved. These vulcanisates had lower set, higher resilience and lower heat build up. Higher loadings of aluminium powder beyond 15 volume per cent reduced the strength properties of vulcanisates. The heat ageing resistance of the aluminium powder-filled vulcanisates at 70°C and 100°C was similar to that of the HAF and acetylene black-filled ones. The γ-radiation resistance of aluminium powder-filled vulcanisates was slightly lower than that of the HAF and acetylene black-filled ones, especially at higher loadings of the filler. Thermal conductivity measurements of the vulcanisates showed that aluminium powder imparts much higher conductivity to the vulcanisate compared with the so called conductive black, acetylene black. Conductivity decreases with increase in temperature. In the range of loadings of filler evaluated, it was found that conductivity increase was linear with filler content. Addition of aluminium powder in truck tyre retread compound increased the conductivity to a very high level. However higher loadings of aluminium powder adversely affected the properties especially tear strength and abrasion resistance. Incorporation of aluminium powder in the polybutadiene rubber initially and then preparing the blend was helpful in improving the abrasion resistance of the retread. Prolonged curing of NR compounds adversely affects its abrasion resistance. Higher thermal conductivity of the retread compounds containing aluminium powder enables it to get cured at lower periods of time. Hence it is expected that appropriate loading of aluminium powder in retread compounds can reduce the retreading time without adversely affecting the service performance.

Scope for Further Work

Incorporation of aluminium powder was found to increase the thermal conductivity to a very high level. Products such as dock fenders, solid tyres, etc. are vulcanised for several hours to achieve any reasonable level of curing. Hence compounds containing aluminium powder may be evaluated for such applications. Since properties such as damping and dynamic mechanical behaviour of the vulcanisate are important in such cases, there is scope for a detailed study of these properties.

List of Publications Connected with this Work

1. Effect of retarders on cure characteristics, kinetics of vulcanisation and physical properties of natural rubber. Chandy, S. and Kuriakose, B. (1990). *Indian Journal of Natural Rubber Research*, **3(2)**, 116.

2. Use of aluminium powder in natural rubber compounds for improved thermal conductivity. Accepted for presentation in 150th Meeting of the Rubber Division, American Chemical Society, Scheduled During October 8-11, 1996 at Louisville, USA.

3. Developments of truck tyre retread compounds for reduced vulcanisation time. Accepted for presentation in Symposium on truck tyre tread wear and retreading, scheduled on 8th and 9th October 1996 at Louisville, USA.

4. Degradation behaviour of natural rubber vulcanisates containing aluminium powder. *Polymer Degradation and Stability* (communicated).

5. Melt flow behaviour of aluminium powder-filled natural rubber compounds. Plastics, *Rubber and Composites Processing and Applications* (Communicated).