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

<table>
<thead>
<tr>
<th>Black</th>
<th>Name</th>
<th>Surface area (m²/g)</th>
<th>Average particle size (nm)</th>
<th>DBP absorption (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N110</td>
<td>Super abrasion furnace</td>
<td>140</td>
<td>20-25</td>
<td>1.13</td>
</tr>
<tr>
<td>N220</td>
<td>Intermediate super abrasion furnace</td>
<td>120</td>
<td>24-33</td>
<td>1.14</td>
</tr>
<tr>
<td>N330</td>
<td>High abrasion furnace</td>
<td>80</td>
<td>28-36</td>
<td>1.02</td>
</tr>
<tr>
<td>N550</td>
<td>Fast extrusion furnace</td>
<td>45</td>
<td>39-55</td>
<td>1.21</td>
</tr>
<tr>
<td>N660</td>
<td>General purpose furnace</td>
<td>37</td>
<td>50-60</td>
<td>0.91</td>
</tr>
<tr>
<td>N774</td>
<td>Semi-reinforcing furnace</td>
<td>28</td>
<td>70-96</td>
<td>0.70</td>
</tr>
</tbody>
</table>

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 compoundinger 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

<table>
<thead>
<tr>
<th>Product types and grades</th>
<th>Average particle size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Specific gravity</th>
<th>Volume specific surface area (m²/cm³)</th>
<th>pH</th>
<th>Oil absorption (g/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica precipitated, hydrated</td>
<td>16-100</td>
<td>40-170</td>
<td>1.93-2.05</td>
<td>77-332</td>
<td>5.7-9.5</td>
<td>160-240</td>
</tr>
<tr>
<td>Silica anhydrous, fumed</td>
<td>8-15</td>
<td>200-380</td>
<td>2.10</td>
<td>420-798</td>
<td>3.9-4.0</td>
<td>150-200</td>
</tr>
<tr>
<td>Aluminium silicate precipitated, hydrated</td>
<td>25</td>
<td>130</td>
<td>2.10</td>
<td>273</td>
<td>10.0</td>
<td>140</td>
</tr>
<tr>
<td>Clays</td>
<td>300-1500</td>
<td>8-22</td>
<td>2.60-2.68</td>
<td>21-58</td>
<td>4.1-7.0</td>
<td>29-52</td>
</tr>
<tr>
<td>Talcs</td>
<td>100-15000</td>
<td>1.3-17</td>
<td>2.80-2.90</td>
<td>3.8-48</td>
<td>9.8-10</td>
<td>80</td>
</tr>
<tr>
<td>Calcium carbonate precipitated</td>
<td>50-700</td>
<td>8-74</td>
<td>2.42-2.71</td>
<td>22-179</td>
<td>9.4</td>
<td>28.60</td>
</tr>
</tbody>
</table>

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.

\[
A_s = \frac{6}{d^2 \rho} \quad \ldots \ldots (I.1)
\]

where \( d \) is the diameter and \( \rho \) 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.

\[ I.3.2 \quad \textit{Effect of Structure of the Filler on Reinforcement} \]

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]. Nonspherical 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 'Sf' 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 Sf 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

<table>
<thead>
<tr>
<th>Vulcanisate properties</th>
<th>Decreasing particle size</th>
<th>Increasing structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of cure</td>
<td>Decreases</td>
<td>Little</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Modulus</td>
<td>Increases to maximum and then decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Hardness</td>
<td>Increases</td>
<td>&quot;</td>
</tr>
<tr>
<td>Property</td>
<td>Decreasing particle size</td>
<td>Increasing structure</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>--------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Loading capacity</td>
<td>Decreases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Incorporation time</td>
<td>Increases</td>
<td>Increases</td>
</tr>
<tr>
<td>Oil extension potential</td>
<td>Little</td>
<td>Increases</td>
</tr>
<tr>
<td>Dispersability</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Mill bagging</td>
<td>Increases</td>
<td>&quot;</td>
</tr>
<tr>
<td>Viscosity</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Scorch time</td>
<td>Decreases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Extrusion shrinkage</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Extrusion smoothness</td>
<td>Increases</td>
<td>Increases</td>
</tr>
<tr>
<td>Extrusion rate</td>
<td>Decreases</td>
<td>Little</td>
</tr>
</tbody>
</table>
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 absorption 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.

1.3.4 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 (~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 up to 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.

1.6 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.

1.6.1 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

\[ \sigma_b = \left( \frac{T_C E}{\pi C} \right)^{\frac{1}{2}} \]  

and the elongation at break, by

\[ e_b = \left( \frac{T_C}{\pi CE} \right)^{\frac{1}{2}} \]  

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 1.2, accounting for the catastrophic nature of the rupture.

Since modulus enters in the numerator of Equation 1.2, 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 m²/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 up to 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 \( \varepsilon = 100 \text{ sec}^{-1} \) 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 \( \varepsilon = 150 \text{ sec}^{-1} \).

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

\[
A/\mu \approx C/U_b
\]  \hspace{1cm} \text{...(I.4)}

where,

- \( A \) - volume abraded
- \( \mu \) - 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 $\mu$ 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 combustible 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 combustible 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 effective smoke suppressant. Application of magnesium hydroxide as a flame retardant
and smoke suppressant in two EVA copolymers was studied by Holloway [131].

1.7.2 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 aluminium, 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].

1.7.3 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.

1.7.4 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].

1.8 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

\[ \frac{\partial t}{\partial \theta} = \frac{k \partial^2 t}{c \rho \partial x^2} \]  

... (I.5)

where

- \( t \) - temperature
- \( \theta \) - time
The expression \( k/c\rho \) is called '\( \alpha \)' 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 '\( \alpha \)' of all substances quoted which include metals, insulating materials, soils, woods, liquids and gases. This low value of '\( \alpha \)' 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.
d) 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 up to 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].

1.9 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 interior 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 moderately 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 reasonable 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.
References


93. Technical Report RG-130, Cabot Corporation, Boston, USA.


