STUDIES ON ALUMINIUM POWDER FILLED NATURAL RUBBER AND STYRENE BUTADIENE RUBBER COMPOSITES

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BY

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..... dedicated to my parents and teachers.

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Certificate

This is to certify that the thesis entitled ***'Studies on Aluminium Powder Filled Natural Rubber and Styrene Butadiene Rubber Composites'*** *is an authentic record of the research work carried out by Mr* ***V. S. Vinod*** *under our joint supervision and guidance in partial fulfilment of the requirements for the award of the degree of* ***Doctor of Philosophy*** *in Polymer Chemistry under the faculty of science of Mahatma Gandhi University, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma earlier. It is also certified that Mr V. S. Vinod has fulfilled the course requirements and passed the qualifying examination for the* ***Ph.D*** *degree of Mahatma Gandhi University.*

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Declaration

I hereby declare that the thesis entitled ***'Studies on Aluminium Powder Filled Natural Rubber and Styrene Butadiene Rubber Composites'*** *is an authentic record of the research work carried out by me under the joint supervision of* ***Dr Baby Kuriakose*** *and* ***Dr Siby Varghese*** *of Rubber Research Institute of India, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma earlier.*

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Preface

Generally, rubbers are non-conducting, but can be made anti-static and even conductive by the addition of suitable fillers. This widens the applicability of rubber in new areas like discharging static electricity, electromagnetic interference shielding, electrical heating etc. In rubber composites the incorporation of conductive fillers has advantages in the moulding of thick articles like dock fenders. Since metal powders are best conductors of heat, addition of metal powders to rubber compounds will enhance the heat conduction, which minimise the vulcanization time of thick rubber articles and gave uniform curing throughout the material. However this technique has not been fully absorbed by the industry due to the lack of technology and related informations in this field. Hence, a detailed investigation has been carried out on the vulcanization behaviour and mechanical properties of aluminium powder filled natural rubber and styrene butadiene rubber composites with special reference to the effect of bonding agents.

The subject matter of the thesis is presented in eleven chapters. The first chapter consists of a detailed review of the earlier work in this field, especially with conductive rubber compounds. The experimental techniques and details of the equipments used for the study are described in chapter two. Chapter three discusses the effect of various bonding agents on the properties of natural rubber-aluminium powder composites. Equilibrium swelling of the vulcanizates has been taken as a means to assess the adhesion between aluminium powder and natural rubber and is explained in the fourth chapter. Chapter five comprises the effect of aluminium powder in combination with other fillers. The stress relaxation behaviour and dynamic mechanical properties of the composites are described in chapters

six and seven respectively. Chapter eight discusses the thermal, ozone and high energy radiation on the properties of these composites.

Based on the properties of the composites discussed in earlier chapters, the role of aluminium powder in the uniform curing and in minimising the total vulcanization time of thick rubber articles are presented in chapter nine. The effect of aluminium powder on the mechanical properties of styrene butadiene rubber is summarised in chapter ten. Chapter eleven describes the effect of various bonding agents on styrene butadiene rubber-aluminium powder composites. And finally, we included the summary and conclusions of the study carried out in this Ph.D. programme.

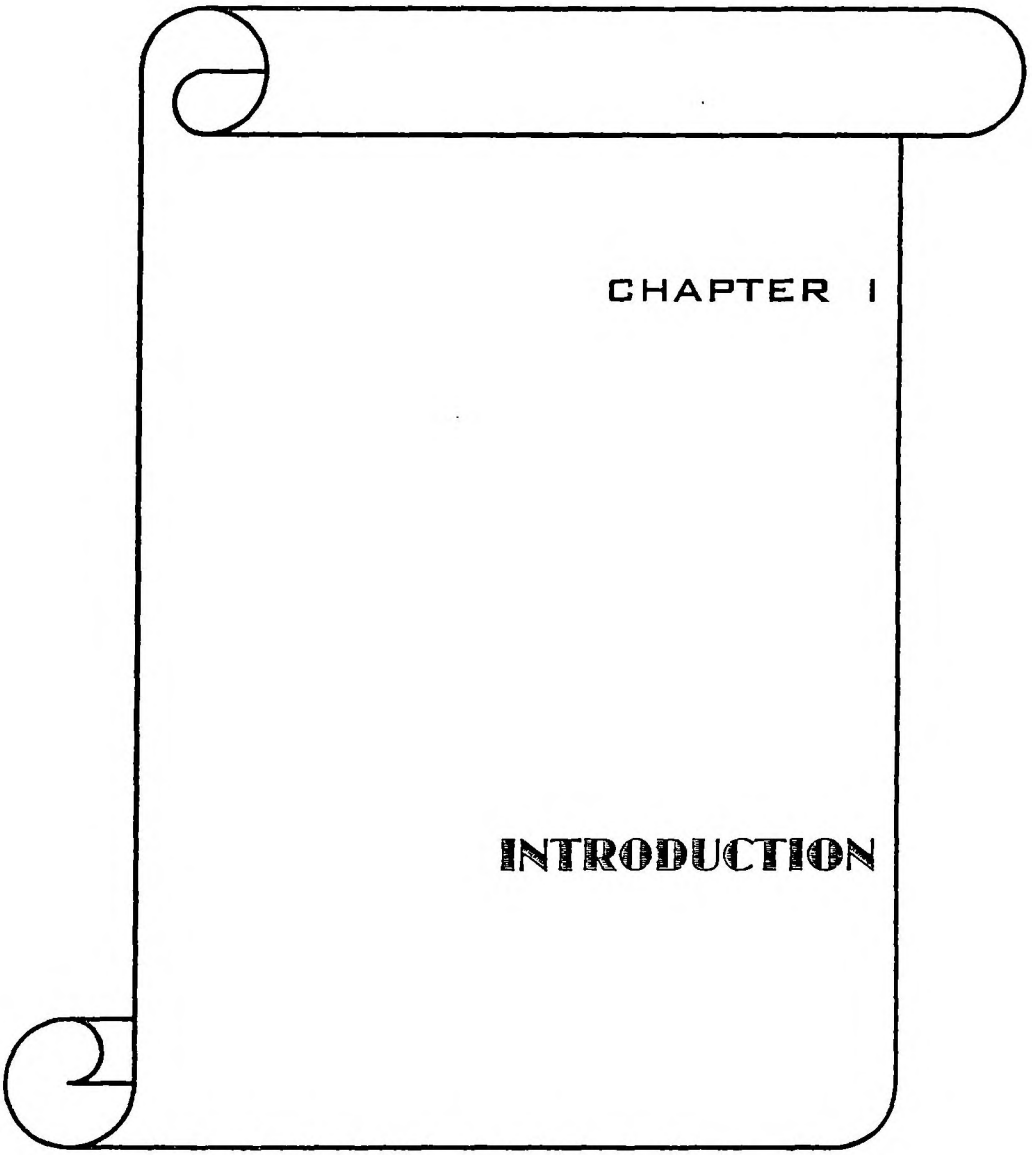
CONTENTS

Glossary of Terms

ACB	- Acetylene black
Al	- Aluminium
ASTM	- American standard for testing materials
CBS	- N-cyclohexyl 2-benzthiazyl sulphenamide
cm	- Centimetre
CoN	- Cobalt naphthenate
CRI	- Cure rate index
CTP	- N-(cyclohexyl thio) phalimide
CV	- Conventional vulcanization
D	- Diffusivity constant
DCBS	- N,N′-dicyclohexyl 2-benzothiazyl sulphenamide
DCP	- Dicumyl peoxide
DEG	- Diethylene glycol
DMA	- Dynamic mechanical analysis
E′	- Storage modulus
E″	- Loss modulus
ENR	- Epoxidised natural rubber
EV	- Efficient vulcanization
GPF	- General purpose furnace black
h	- Hour
HAF	- High abrasion furnace black
Hexa	- Hexa methylene tetramine

HR	- Hexa-resorcinol
HRH	- Hexa-resorcinol-hydrated silica
ISNR	- Indian standard natural rubber
LOI	- Limiting oxygen index
M_H	- Maximum torque
M_L	- Minimum torque
mm	- Millimetre
MOR	- 2-(morpholino thio) benzothiazole
MPa	- Mega pascal
nm	- Nanometer
NR	- Natural rubber
OCT	- Optimum cure time
P	- Permeability constant
Phr	- Parts per hundred
Qt	- mol percent uptake
RIT	- Rheometric induction time
S	- Sorptivity constant
SBR	- Styrene butadiene rubber
SEM	- Scanning electron microscopy
Si-69	- Bis [(3-triethoxy silyl) propyl] tetrasulphide
Sufassan R	- 4,4'-dithiomorpholine
tanδ	- Dissipation factor
TDI	- Toluene diisocyanate
TDQ	- Polymerised 1,2-dihydro 2,2,4-trimethyl quinoline

UTM	- Universal testing machine
UV	- Ultra violet
V_r	- Volume fraction of rubber
WOB	- Without bonding agent
ZnO	- Zinc oxide
ΔG	- Change in free energy
ΔH	- Change in enthalpy
ΔS	- Change in entropy
%	- Percentage
β	- Interaction parameter.
γ	- Gamma
^0C	- Degree celcius
Φ	- Volume fraction of filler
σ_o	- Stress at zero time
σ_t	- Stress at time 't'
λ	- Thermal conductivity
χ	- Rubber-solvent interaction parameter
ρ	- Density



CHAPTER I

INTRODUCTION

Polymer composite is one of the fast growing sectors of industry, which finds various applications due to their wide range of properties. Various additives are incorporated to these materials to modify their properties in the processing stage. Fillers constitute the largest bulk of these additives, especially in the case of rubber products. The introduction of mineral fillers, which are finally dispersed in rubbers induce substantial changes in their physicochemical and mechanical properties, which are caused by behaviour in the mobility of the macromolecules in the boundary layers, the orienting behaviour of the filler surface and different types of filler-polymer interactions. Filler characteristics such as size and shape of particles, size distribution, pattern of particle packing, specific surface area, porosity of surface, chemical nature, dispersibility and tendency to agglomerate etc. determine its effect on rubber compounds.

For many material applications, information is needed on their thermal and electrical properties; in such cases conductive polymers acquire wide acceptability [1]. Reports are available on the electrical and thermal properties of various composites [2-4]. Various methods exist to increase the conductivity of rubber compounds, among which an economically feasible and easy method is to fill them with specific conductive fillers like metal powders. The relation of these particulate fillers with the properties of composites has recently received particular attention. Interfacial interaction between the matrix and filler particles governs a number of the final product properties [5,6]. There exist many coupling/bonding agents to enhance

surface interaction between the components by better adhesion [7-9]. However, only a limited number of publications are available on metal powder incorporated composites [10-13]. Interest in this field is driven by an increasing industrial demand for these materials and to enlarge their areas of applications and potential.

1.1. Definition and Importance of Composites

Composites are combinations of two or more materials; namely a selected filler or reinforcing element and a polymer to take advantage of certain desirable properties of each component. The constituents can be organic, inorganic or metallic in the form of particles, fibres, plates, rods etc. and do not dissolve or otherwise merge completely into each other. Normally the components can be physically identified along with the interface between components. Composite materials consist of a continuous matrix phase that surrounds the reinforcing phase. The reinforcing materials have high strength and stiffness and the matrix serves to transfer stress from one to the next and produce a fully dense structure. The matrix has many desirable intrinsic physical, chemical or processing characteristics and the reinforcing material serves to improve certain other important engineering properties, such as tensile strength, abrasion, tear strength etc. Also by mixing or diluting rubber with fillers improve its appearance, processability or cost advantages while maintaining adequate performance.

Composites can be classified according to the type of materials embedded. Particulate filled composites consist of a continuous matrix phase and a three dimensional distribution of randomly oriented discontinuous filler phase made up of discrete particles. Fibre filled composites consist of a two dimensional distribution of randomly oriented chopped fibre as the discontinuous phase, and the interpenetrating network or skeletal

composites, consisting of two continuous phases. Certain properties such as colligative thermodynamic ones can be calculated from knowledge of the volume fraction and chemical composition of the constituent phase. Other properties such as thermal and electrical conductance and the elastic properties can be calculated from idealized models, which closely approximate real composite behaviour. Other important properties such as failure strength and failure toughness can only be approximated roughly.

I.2. Component Materials

I.2.1. Elastomer types

Various types of polymers are used for making composite matrices. Among these rubber is one of the most fascinating material on account of its range of applications in everyday life, defence and civilian purposes and its behaviour under the most diverse conditions of applications. These polymers have unique properties of deformation and elastic recovery after vulcanization with sulphur or other crosslinking agent, which in effect change the polymer from thermoplastic to thermosetting. Natural rubber (NR) is a commonly used rubber and has been produced in various forms and types to meet the specific requirements of consumers. These have usually involved chemical modification of the polymer chains or simple changes in the production process. Some of the modified forms of natural rubber include superior processing rubber, thermoplastic natural rubber, chlorinated rubber, epoxidised natural rubber and grafted rubber. Thermoplastic natural rubber is a physical blend of natural rubber and polypropylene, mixed in a particular proportion to impart rubbers having specific stiffness properties. The properties of silica reinforced epoxidised natural rubber are comparable to black filled natural rubber. These

reinforcement properties of epoxidised NR can be achieved without any expensive coupling agent [14].

Styrene butadiene rubber (SBR), the world's widely used synthetic rubber and easily available worldwide, has unique place among elastomers. This is because practically all automotive tires use SBR, especially in the tread, due to its wear advantage over natural rubber treads. SBR is produced by the copolymerisation of butadiene and styrene. The sequence or the arrangement of the monomer is irregular in the chain of the polymer. Due to the irregularity of the arrangement of monomers, the tensile strength is not high for SBR. Irregularity of the chain structure causes weak interchain forces. To increases the tensile strength carbon black or other reinforcing pigment is required.

Silicon rubbers constitute one of the new classes of rubber like polymers. These exhibit unique physical and chemical properties. The unique property of silicone polymers is partially explained by the fact that the bond energy of silicon-oxygen linkage is about 1.5 times as strong as the C-C linkage in hydrocarbon polymers. Although the polymer is saturated. it can be vulcanized by heating with a source of free radicals such as benzoyl peroxide. The outstanding characteristic of silicon rubbers is their broad useful temperature range. In this range flexibility, resilience and tensile strength are retained to an amazing degree.

Other elastomers like polybutadiene, polychloroprene, butyl rubbers, ethylene propylene rubbers, and nitrile rubbers have also received much attention. Butyl rubber is commonly produced by cationically copolymerising isobutylene with small amount of isoprene. The halogen derivatives provide more active functionality to the butyl molecule. Butyl rubber has good abrasion resistance, excellent impermeability of gases, resistance to oxidation and weathering. Nitrile rubbers are characterised by

their excellent resistance to solvents. They are copolymers of butadiene and acrylonitrile. The rubbers are now available in a number of types differing mainly in the relative proportion of the two monomers. Flouro carbon rubbers are highly specialised rubber, distinguished by their outstanding resistance to heat and chemical attack. For a particular application a suitable rubber is selected based on its properties.

I.2.2. Compounding ingredients

In most formulations there are many ingredients, which are meant for specific purposes. Developments of rubber formulations that are environmentally safe, factory-processible, cost-competitive with other compounds in the same applications and able to provide satisfactory properties and service life are getting much importance. These requirements put considerable demands on the compounder, who must have extensive knowledge of materials, which can provide these properties in elastomer compounds. Generally in rubber compounding, we can classify the materials based on the functions they serve. These include, vulcanizing or crosslinking agents, accelerators, activators, retarders, process aids, softners and plasticizers, fillers and other miscellaneous materials.

The crosslinking efficiency of some vulcanizing agents in natural rubber was assessed by Lorenz and Parks [15,16]. It is generally assumed that the presence of a filler might affect the efficiency of the curing agent. The filler-curing agent interaction might influence the rate of crosslinking, which give vulcanization rates in filled stocks different from those in gum stocks. Pal *et al.* [17.18] have studied the effect of reinforcing black, silica and clay on vulcanisation.

Zinc oxide is one of the basic components of rubber compounds, it act as an activator of rubber crosslinking by sulphur or sulphur donors. It

increases the amount of bound sulphur as well as the efficiency of crosslinking system. Borros and Agullo [19] made an investigation on sulphenamide accelerating system on natural rubber vulcanization, and the active role of zinc oxide and the olefinic chain in NR. Recently Kruger and Mc Gill have published papers on the interactions between the components of the crosslinking systems [20, 21].

I.3. Importance and Classification of Fillers

Among the various compounding ingredients, fillers become one of the most important components in the manufacture of rubber products. with consumption second to rubber. Fillers are widely used to enhance the performance of rubbers and other polymeric materials. In certain cases they lower the cost of production of the final products. They influence almost all properties, including density, hardness, tensile strength, impact strength, chemical resistance, heat distortion temperature, processability and even the appearance of the final products.

Filler may either be active or inactive according to the mutual interaction between filler and polymer. This classification is rather arbitrary since it is based on the difference in chemical composition and characteristics of filler-particle surfaces, particle shape, size and treatment of surfaces by coupling agents. The filler activity is controlled by the mutual adhesion of the polymer and filler; it corresponds to the physicochemical character of the polymer-filler interface, which determines the extent of sorption process on the solid surface as well as the type of polymer-filler bonds. The results of many studies describing the different aspects of filler-polymer interaction are available in the literature [22,23].

Today there are hundreds of commercial fillers providing a performance range from non-reinforcing to highly reinforcing; giving the

rubber compounder a wide choice of cost benefit option. Fillers used in rubber compounds are generally classified into black and non-black fillers.

1.3.1. Carbon blacks

The primary purpose of using carbon black with rubber is to reinforce it. Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall performance. Five types of carbon blacks, based on manufacturing method, are used in rubber compounds, which are,

1. Lamp black
2. Channel black
3. Thermal black
4. Acetylene black
5. Oil furnace black

The acetylene carbon is a coarse, very high-structure black, produced from acetylene gas in an exothermic reaction. Its principal use in the rubber industry has been that of a conducting carbon. Thermal blacks are made by the thermal decomposition of natural gas and are of two types medium thermal (MT) and fine thermal (FT). Today the channel process furnishes two grades of carbon blacks differing essentially in fineness, they are easy processing channel (EPC) and medium processing channel (MPC). The most popular blacks are those made by the oil furnace process. The furnace process produces a series of carbon blacks such as general-purpose furnace (GPF), fast extrusion furnace (FEF), high abrasion furnace (HAF), super abrasion furnace (SAF) etc.

As surface area of the black particle increases, the viscosity of the uncured stock increases, mixing takes longer and the smoothness of the

extrusion increases. In the vulcanizate, abrasion resistance, tear strength, cut growth and flex resistance increase along with tensile strength and modulus. Increasing structure decreases tensile strength but increases modulus, hardness and abrasion resistance. In the ASTM D 1765 classification for carbon blacks about 42 commercial blacks were recognized.

I.3.2. Non-black fillers

Non-black reinforcing fillers for rubber include hydrated silica, calcium silicate, zinc oxide, the fine particle size precipitated calcium carbonate etc. The use of coupling agent is more relevant with these non-black fillers [24-27]. Reinforcement by silica and silicates has been reviewed by Wagner [28].

There is another category of materials used principally for bulk. Materials in this class are inert, cheap and are really diluents. Some of the non-black inert fillers are soft clay, ground whiting, barites and talc. Inert fillers are also used to impart processing characteristics such as extruding or calendaring properties of uncured compounds. A third class of non-black pigments consists of the materials used to produce colour to vulcanizates. This class includes both inorganic mineral compounds and organic colour and dyes. From the physical stand point, one must consider its size, surface area per unit weight, the activity of the pigment surface and perhaps the electrical charge it carries. Chemically it is important to know whether the material is acidic or basic and whether it will react chemically with the accelerator. Brief descriptions of the properties of various non-black fillers are given in Table I.1.

Table I.1. Classification and properties of non-black fillers

Product types and grades	Average particle size (nm)	Surface area (m^2/g)	Specific gravity	pH	Oil absorption (g/100g)
Silica, precipitated, hydrated	16 - 100	40 – 70	1.93 – 2.05	5.7 - 9.5	160 – 240
Silica anhydrous	8 – 50	200 - 300	2.10	3.9 – 4.0	150 – 200
Clay	300 -1500	8 – 22	2.6 – 2.7	4.1 – 7.0	29 – 52
Talc	100 - 15000	1.3 – 17	2.8 – 2.9	9.8 – 10.0	80
Calcium carbonate, precipitated	50 -700	8 – 74	2.4 – 2.7	9.4	28 – 60
Titanium dioxide	30	50	3.8	3.5	_
Calcium silicate	85	35	2.1	10.0	_
Aluminium silicate	25	130	2.10	10.0	140

I.4. Reinforcement by fillers

Reinforcement is the enhancement of tensile strength, modulus, abrasion and tear resistance obtained by adding a material like fillers. Active fillers called reinforcing fillers, interact with polymer molecules through Van der Waals forces, chemisorption forces, and eventually covalent forces. It is possible to create chemical bonds with the surface of the filler particles using coupling agents. Reinforcing agents are substances having shape and structures such as short fibrous forms or powdery form, and are impregnated with polymers and the moulded product thus obtained possess remarkable mechanical properties. Interaction between carbon black and polymer are one of the most important mechanisms of carbon black reinforcement, often measured as bound rubber [29]. Bellander *et al.* studied the influence of

pressure and temperature on bound rubber for carbon black-polybutadiene composites and concluded that elevated pressure and temperature increased the amount of bound rubber. The reinforcement of elastomers by particulate fillers, to a large extent depends on polymer properties, filler characteristics and processing methods [30]. The various filler characteristics that influence the elastomer reinforcement are as follows.

1.4.1. Surface area

The total surface area of the filler is the most important parameter that influences the reinforcement. Particle size naturally is directly related to surface area by simple geometric considerations, in the absence of porosity. Other factors like shape of particle, size distribution and pattern of particle packing etc. affect the total surface area of a given quantity of filler. In reality there is always a distribution of sizes that can be averaged in various ways [31] and particles are usually far from round [32].

1.4.2. Porosity

Frequently particles are porous. In particular the presence of microspores, of diameters below 0.5nm. excludes part of the particle surface from direct interaction with the larger elastomers molecules or segments, thereby influencing reinforcement. 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 blacks gives decreased resilience and increased electrical conductivity when compared with equal weight loadings of non-porous blacks.

Wolff studied the chemical aspects of rubber reinforcement by fillers [33]. Bound rubber is regarded to be the result of rubber-to-filler interaction

and is therefore often taken as a measure of surface activity of the filler which also a function of specific surface area [34-36]

I.4.3. Morphology of aggregates

While elementary filler particles may be spherical, such particles have often coalesced into larger, irregular shaped aggregates. Moreover, such aggregates are most frequency united into larger agglomerates by attractive forces of the Van der Waals types. The extent of aggregation and agglomeration has a marked influence on the reinforcing properties of fillers. By comparing the reinforcing action of fillers in the same surface area range, the morphology is the major factor determining reinforcement. 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 [37].

Structure is found to be very closely related to oil absorption characteristics. By oil absorption is meant the ability for a mass of filler to absorb and hold within its structure certain amount of oil before the mass becomes thin enough to flow. The internal void volume may also be measured by the compressibility of the carbon blacks at high pressures [38]. High structured carbon blacks have high oil absorption and lower compressibility [39].

I.4.4. Surface chemical characteristics

Besides the presence of chemically active groups. surface sites on the particle have great importance. these permit chemical interaction between

elastomers and filler particles. The elimination of such active sites by heat treatment reduces the reinforcing properties of the filler.

1.4.5. Polymer-filler interaction

The reinforcement of elastomers by fillers is the physical expression of the microscopic balance at the rubber-filler interface and the interactions between the filler particles making up a filler network. The rubber-filler interface formed during the mixing process is primarily responsible for properties such as abrasion resistance, tensile stress at break, tear propagation resistance etc. The dispersion of the fillers depends on both the particle size and the structure of the primary aggregates and agglomerates [40-42]. During mixing fracture of filler aggregates takes place [43]. Continued mixing decreases the number of inter-aggregate 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 break down increasing with increased structure and increased polymer-filler interaction [44].

The effects of interaction between the rubber and filler on the adhesion characteristics of elastomer compositions were studied by Kiselev and Vnukova [5]. When filler is introduced adhesion interactions between the elastomer and the filler increase with decreasing size of the filler particles. 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 [45]. In all cases, physical adsorption undoubtedly occurs to varying degrees depending on particular surface and molecular segments. Evidence for chemical bonding at the interface is also conclusive for some systems [46]. Extreme physical

interaction takes place between the chain segments and active centres on filler surfaces and these lead to the formation of adsorbent polymer layers with restricted chain mobility and dynamics. The relative contributions to reinforcement by physical and chemical interactions, differ both with the nature of the filler and the elastomer.

1.5. Role of Coupling/Bonding Agents

1.5.1. Coupling agents

Coupling agents are defined primarily as materials that improve the adhesive bond of dissimilar surfaces. These involve an increase in true adhesion between the filler and polymer, better wetting, rheology and other handling properties. Better adhesion strength in these cases has been explained by a coupling mechanism through interfacial diffusion and interpenetrating crosslinking networks. The coupling agent creates a strong bond between the two at their interface and modifies the interface region to strengthen the organic and inorganic boundary layers [47]. Surface-active agents can be used to favour interactions between hydrophilic filler and a hydrophobic polymer, but this type of coupling is not very effective. Stearic acid and its metallic salts are good examples of surface-active agents. Their effect may be simply described as an increase in the wetting of filler particle surfaces by polymer molecules. Even though the properties of polymers are improved by the addition of surface-active agents their effect does not last long in humid atmosphere or for a long storage period and the physical properties deteriorate.

Surface treatment of fillers to improve polymer-filler interaction has become common during the last decade and a number of publications in this regard, are available [48-55]. Improvement in dispersion level and processability can be attained through the use of surface treated fillers.

Coupling agents may be fixed to fillers prior to their addition to polymers or they may be added directly to polymers. The problem of compatibility between the filler and polymer matrix can be overcome by modifying the filler-matrix interface [56,57].

Coupling agents, usually have dual reactivity since they are capable of reacting both with polymer and with the filler surfaces. The stability of composite appears to be related to the strength of the covalent bonds between the polymer and the filler via. the coupling agents. Although the exact mechanism of bonding may still be controversial, it is believed that the organo functional portion of the coupling agent reacts with polymer and becomes covalently bonded to the matrix. There exist many coupling agents for these applications and among these. silane [7] and titanate-coupling agents [58], phosphorous esters [59] and chromium-acid complexes [60] etc. have been found to form strong assemblies.

Marked increase in reinforcement is observed with silane coupling agents in silica filled rubber vulcanizates [49,50]. Wang and Wolf [61] showed that silane modified silica increases its compatibility with hydrocarbon elastomers, hence, improves filler dispersion, compound processability and certain vulcanizate properties. Now a series of silane coupling agents are available with general formula $YRSiX_3$, in which Y is the organo functional radical, R represents the alkyl group and X represents the hydrolysable groups, such as chloro. alkoxy or acetoxy groups. The hydrolysable groups allow them to form strong bonds with the polymer matrix and with the filler particles. Plueddemann [7] gives a detailed account of silanes, in bonding thermoplastic polymers to mineral surfaces. The silane by co-reacting with the polymers modifies the polymer morphology at the interface to improve stress-transfer at the interface. The silane-triol formed by hydrolysis of trialkoxy silane coupling agents has unique bonding

capability with silica, glass and some other mineral surfaces. Pickwell [62] studied the use of the bis[triethoxysilyl toluene] polysulphide as a scorch resistant silane coupling agent for mineral-filled elastomers.

Organo titanate coupling agents are unique in that their reaction with the free protons at the inorganic interface results in the formation of organic monomolecular layers on the inorganic surface. The absence of polymolecular layers at the interface together with the chemical structure of the titanates create novel substrate surface energy modifications and polymer phase interactions often resulting in viscosity reductions in unfilled, as well as filled polymer composites. Titanate-treated inorganics are hydrophobic and organofunctional. When incorporated into polymer systems they often promote adhesion, improve dispersion, rheology, impact strength and mechanical properties. Titanate coupling agents react with the filler surface resulting in the formation of extractable organic monomolecular layers providing compatibilization and a molecular bridge between the interface of the inorganic filler and the organic matrix. Reports are available regarding the use of these types of coupling agents [63,64].

Yamaguchi *et al.* [65,66] developed some non-nitroso coupling agents and claimed improved dynamic properties in natural rubber, synthetic polyisoprene, styrene butadiene rubber and poly butadiene rubber. Furukawa *et al.* [67] claimed that modification of carbon black with ethylene glycol, ethanolamine, hexa methylene diamine, 1,2-dimercapto propyl alcohol or phenyl isocyanate improved SBR vulcanizate properties as a function of active hydrogen content of carbon black.

1.5.2. Bonding systems

Polymer-filler interaction is a key factor in the reinforcement of the composites, which in turn is related to the adhesion between the filler and

the polymer. A good level of adhesion between filler and rubber is obtained by the incorporation of an external bonding agent. The bonding agent may either be a liquid or a solid (dry form) one. We can pre-treat the filler with the bonding system prior to mixing or can be incorporated directly in to the compound during mixing. Hexamethylene tetramine-resorcinol-hydrated silica (HRH), resorcinol-formaldehyde latex (RFL) etc. are commonly used bonding systems. The major additives of these systems are resorcinol and methylene donor. The most widely used donors are hexamethylene tetramine, hexamethoxy methyl melanin and formaldehyde. Essentially this system works by the production of resorcinol formaldehyde resin, which migrates to the rubber-filler interface, where it reacts to bond the two components together [68]. The role of silica in this system is not fully explained. It would appear to act by retarding the cure of the rubber, thereby allowing longer time for the migration of resin to the filler-rubber interface.

Buchan [69] gives a detailed account of a variety of rubber to metal bonding agents. These bonding agents include ebonite bonding, brass plating and chemical agents such as proprietary rubber-to-metal adhesives. isocyanates, and post vulcanization bonding agents. Isocyanate bonding agents can achieve good adhesive bonds and commonly used isocyanates are triphenyl methane triisocyanate (TPMTI), toluene diisocyanate (TDI) and polymethyl polyphenyl isocyanate (PMPPIC). Certain cobalt salts are used commercially in elastomeric compounds to promote adhesion to metal. The detailed mechanism of improved adhesion in presence of cobalt salt is unknown, but it is assumed that these will create an increased polarity. which would improve the adhesion properties. The combined effect of cobalt and resorcinol bonding agents in rubber-brass adhesion is reported by Hamed and Huang [70]. Tomilson [71] described the use of two adhesion

promoting additives, 5-norbornene-2,3-dicarboxylic anhydride (NCH) and cobalt naphthenate (CoN) in EPDM- carbon black filled vulcanizates.

Evaluation of various cobalt additives for their effectiveness in improving adhesion between natural rubber and brass-plated steel tyre cords were reported [72]. The pro-oxidant activity of cobalt is potentially a serious disadvantage, but this has not stopped its use and, normally available antioxidants would be effective in preventing excessive rubber degradation [73]. Effects of modified carbon black on the properties of natural rubber vulcanizates were evaluated [74]. It is observed that surface modified blacks provide better processing behaviour, with out any processing aid, such as easy incorporation and uniform dispersion in the rubber phase without abnormal heat generation and also improved vulcanizate properties such as tensile strength, flex cracking resistance and lower abrasion loss, without affecting other properties significantly.

I.6. Effect of Filler on Vulcanizate Properties

The effects of various fillers on the mechanical and other physical properties of polymeric composites have been reviewed by several authors [75-78]. In filler reinforced rubber composites, bound rubber, that is the portion of elastomers non extractable by a good solvent, is a major factor in reinforcement by active fillers like carbon black and its significance is discussed by Kraus [79] and Dannenberg [80]. Bound rubber is regarded to be the result of rubber-to-filler interaction and is therefore often taken as a measure of the surface activity of the filler. Much attention has therefore been paid to the factors influencing the bound rubber content, the mechanism of its formation and its influence on vulcanizate properties. Literature supply the detailed account of rubbers containing reinforced fillers and their properties like stress-relaxation behaviour [81-83] and

dynamic mechanical properties [84-87]. A wide range of physical and mechanical properties may be developed by selecting a proper filler and polymer. Some of the developments on the properties of elastomeric compounds by fillers are discussed below.

1.6.1. Effect of filler on crosslinking process

Most of the properties of the vulcanizates undergo a pronounced change with degree of crosslinking. The influence of fillers on the degree of crosslinking of natural rubber was studied and found that the crosslink density increased proportional to the concentration of carbon black [88]. The change in concentration of the effective chains of a rubber network caused by the presence of the filler in vulcanized rubbers has been investigated [89-91]. The ability of the filler to affect the degree of crosslinking as well as the proportion of mono, di and poly sulphidic linkage are of particular relevance since these factors greatly affect the composite properties [92.93]. Kraus [79] determined the crosslink density of a variety of vulcanizates. both filled and unfilled. From the increase in crosslink density of the filled vulcanizates, he deduced the number of polymer-filler bonds formed during mixing and vulcanization as well as the catalytic effect of the filler in the course of the crosslinking reaction. Lorentz and Parks [16] also investigated the restriction from swelling exerted by a filler, using carbon black in natural rubber vulcanizates and suggest an increased polymer-filler attachment.

1.6.2. Effect on modulus and elongation at break

Particle surface, structure, nature and loading of fillers affect the modulus of elastomeric compounds. The finer carbons enhance modulus to a greater degree than the coarser carbons. Also the modulus of a compound increased with increased loading and structure of carbon blacks. Mineral

filled vulcanizates have considerably lower modulus values compared to carbon black filled vulcanizates at equivalent hardness. This is due to the lower polymer-filler interaction and larger particle size of their fillers. Among the non-black fillers lower particle size silica has higher modulus values. In presence of silane coupling agents silica filled compounds show modulus as that of carbon black at the same loading.

Elongation has the inverse function of modulus and those characteristics of carbon black, which promote modulus, also act to detract from the elongation properties of the vulcanizate.

1.6.3. Effect on tensile strength

It is generally agreed that tensile strength of filled rubbers is one of the most important criteria of reinforcement. In amorphous rubbers, the tensile strength reaches an optimum value as filler loading increases. The maximum tensile values increase as the average particle size decreases, and for the same material, there is a correlation between particle size and tensile strength in amorphous rubbers. Weak bonding, low interaction with the rubber phase, poor dispersion and cure retardation due to acidic surface characteristics etc. of certain inorganic fillers make it unable to reinforce rubbers as that of carbon black filled composites.

Boonstra *et al.* and Greensmith [94-96] tried to establish correlation of reinforcement with particle size in carbon black reinforced vulcanizates. Tensile strength and modulus of carbon black- filled rubber vulcanizates were reported by Neogi *et al.* [97]. The exact reaction why carbon blacks reinforce these rubbers is still obscure. It is usually mentioned. that this is due to high hysterisis and interaction. It has been reported that NR shows an optimum strength at around 30-40 phr loadings and SBR at around 50-60 phr loading for room temperature testing [98]. This is due to the fact that

two opposing factors are in action when reinforcing filler like carbon black is added to rubber. One is the increase in tensile strength and modulus dependent on the particle size of carbon black, and the other is the reduction in properties at higher loading due to diminishing volume fraction of rubber in the composite.

The tensile strength depends on molecular weight of the polymer, its distribution, morphology, test temperature and extension rate [99,100]. The effects of filler structure and loading have been studied by Kraus [101] using blacks of approximately the same surface area. Results confirmed that with reinforcing blacks, the net effect of loading on tensile strength is that of carbon black and the occluded rubber.

1.6.4. Effect on other mechanical properties

The introduction of fillers into rubber compound markedly affects its various mechanical properties like abrasion, heat build-up, fatigue etc. Abrasion is a complicated process of repeated straining of small volumes at the surface resulting finally in tearing and their separation from the bulk of the rubber [102]. Carbon blacks primarily improve abrasion resistance and found that abraded volume falls with carbon black loading [103]. It is now 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 [104-106]. Abrasion gives best performance in one polymer may not do so in another. In natural rubber, those factors in carbon black, which develop highest tensile, normal to low modulus and low heat build-up, tend to give best abrasion performance. Modulus development is a positive factor for improved abrasion in an inherently weak polymer like SBR.

The polymer-filler attachment has a prime effect on heat build-up. Increased carbon surface accomplished primarily through the use of finer

carbons is a main characteristic of the carbon black affecting the heat build-up of these composites. In certain tests and in certain applications, modulus can act either as a contributor or as a deterrent to heat build-up. If the rubber part is flexed under constant load conditions, the amount of deflection will be dependent on the modulus.

Fatigue performance of a compound is obtained by measuring the cracking on a De Mattia, Goodrich or Firestone flexometer. Cracking generally will be adversely affected with increased loadings for any given carbon black. This statement must be amplified by recognizing that certain minimum modulus and hardness levels are needed for a successful operation of a particular part. In natural rubber, for the furnace carbons those factors that promote high modulus in carbon blacks act in an unfavourable role towards cracking performance. Improved cracking may be observed from HAF to ISAF. In SBR the reverse pattern appears to be true and this most probably is a function of dispersion.

Air permeability of polymer composites is affected by the presence and nature of fillers, Van Amerongen [107] has evaluated the effect of carbon black at 50 phr and mineral filler at 20 vol % on gas permeability of natural rubber and showed that incorporation of filler reduced permeability of the base polymer. It is reported that no remarkable difference exists between reinforcing and non-reinforcing filler as far as permeability is concerned as evidenced by the study using a series of fillers like high abrasion furnace black, precipitated silica, calcium carbonate, china clay, mica powder and graphite powder in natural rubber [108].

I.6.5. Effect of filler on degradation

Oxygen, ozone, heat, solvents and chemicals are the most common agents, which cause degradation of elastomers. Unsaturation in elastomer

makes it susceptible to attack by oxygen. 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 by the main chain scission or crosslink scission. It is reported that carbon black accelerates main chain scission and crosslink scission by surface catalysis [109,110]. In routine technological evaluation, rubber compounds are subjected to accelerated ageing tests to get information about the service life. This problem was well recognised by Baker [111] who examined the effect of temperature on the ageing behaviour of natural rubber vulcanizates.

All chemically unsaturated rubbers are prone to attack by minute quantities of ozone present in the atmosphere. Such attack not only detracts from the surface appearance of rubber products but also causes loss of physical properties, especially in thin walled articles [112]. Unstretched rubber surfaces are degraded by ozone, but the characteristic cracking is not observed unless a tensile strain is imposed during exposure. Once the critical strain is exceeded a crack will grow at a constant rate independent of additional strain and for many rubbers in direct proportion to ozone concentration. There are ways of increasing the resistance of polymers to ozone cracking [113]. One obvious way is to coat the rubber surface with some unreactive protective layer, and this is often done by the incorporation of wax, which blooms to the surface of a moulded specimen. Another efficient method involves the use of antiozonants. The selectivity of antiozonants and waxes varies as they may not protect against all forms of degradation. Surface cracking may not necessarily be due to ozone-mechanico-oxidative fatigue, sunlight crazing, heat ageing etc. may also be involved. Lake [114] had studied the mechanical fatigue of rubber in detail. Several reports [115-119] regarding the oxidative ageing of elastomers have

been appeared in the literature. The activity of the protective systems is influenced by fillers and oils by changing one or more of the following (i) the proportion of protective agent to total formulation by volume, (ii) the diffusion coefficient and solubility, (iii) the bloom quality, (iv) hardness and modulus, (v) introduction of filler flaws.

The mechanical properties of polymers are changed considerably by high-energy radiation. This may be the result of either crosslinking or degradation of the polymer chain. Properties such as tensile strength, elongation, modulus and hardness are decreased as a result of chain scission, while crosslinking has the opposite effect on these properties. The effect of radiation on polymeric materials have been reported by many research groups [120-124]. The fillers have great influence on the degradation by high-energy radiation.

1.6.6. Effect on solvent resistance

Elastomers have been used in a number of barrier applications in which it comes under the influence of solvents. Aminabhavi and co-workers have published a series of articles relating the various rubber-solvent interactions [125-128]. Dannenberg [129] investigated the effect of a variety of carbon blacks. having a wide range of surface areas, on the reduction of the equilibrium swelling volume of synthetic rubber. Later Boonstra and Dannenberg [130] presented equilibrium swelling of a series of solvents in natural rubber, SBR, butyl rubber, neoprene and nitrile rubber containing carbon blacks, silica and hard clays as fillers. It was observed that certain fillers, cause a reduction in swelling of the membranes which is commensurate with the volume loading of the filler, and the effect of different carbon blacks and varying loadings were reported [131-134]. The

kinetics of swelling of rubber and black-filled SBR vulcanizates in the presence of iso-octane has been studied [135].

1.6.7. Effect on flame resistance

Dilution of the polymer with a filler having strong endothermic transitions is related to the flammability of the rubber compound. For flame resistant applications, usually the polymers selected are fluoroelastomers, chlorinated polyethylene rubbers, chloroprene rubber and silicone rubbers. Other polymers can be made flame-retardant by he incorporation of suitable fillers like alumina trihydrate. Alumina trihydrate and magnesium hydroxide exhibited both smoke suppressant and flame retardant effect in a wide variety of elastomers [136,137].

Flammability of a material is characterised by its ability to supply one or more ingredients needed to bring about combustion. Ease of ignition, surface flame spread, fuel contribution, fire endurance and smoke evolution etc. are taken into consideration for evaluating the flammability characteristics of a composite. Flammability ratings based on these are expressed in terms of oxygen needed to allow burning for specific time, length of flame travel under given conditions of burning, rise in temperature, lowest ignition temperature and duration of burning in terms of time.

The limiting oxygen index (LOI) value has been widely accepted as a measure of polymer flammability [138]. The LOI is defined as the volume fraction of oxygen in an oxygen-nitrogen atmosphere that will just support steady candle like burning of a material. The effect of a variety of commonly used fillers and flame retardant additives was examined by Bolibar [139]. Among the inorganic fillers alumina and kaolin were found to be best in improving the flame retardance of polymers. Bautista [140] studied the use of aluminium trihydrate as a powerful additive for track and flame

retardancy of reinforced plastics. Measurements of thermal conductivity and limiting oxygen index of a basic rubber blend/aluminium hydroxide particulate composite have been made by Barta *et al.* [141].

Analysis of fire retardancy of filled polymers was reported [142-145]. Comparing results of the two 'inert' non-hydrated fillers studied, magnesium oxide filled polypropylene gave a significantly higher LOI value than the glass bead filled polymer. Dilution effect showed only a slight increase in LOI relative to unmodified polypropylene.

1.7. Electrical/Thermal Properties of Elastomers

1.7.1. Electrical properties

Electrical conductivity in carbon black filled compound is controlled by cleanness of carbon surface, fineness and structure. The finer the carbon black, the greater will be the number of particles present in a compound and the more will be the chains, channels, or paths for the electricity to travel through the stock. Therefore the greater the fineness, the lower the resistivity. Similarly for structure, if the carbon particles line-up in chains, the resistance between particles is considerably reduced. Conductivity improved with increased loading up to a certain point. The acetylene carbon obtains its conductivity through its very high structure. The network can be easily destroyed either by over milling or by flexing of the final vulcanizate. In both cases the result is a loss of conductivity. ISAF obtains its conductivity through modest structure, extreme fineness and cleanliness of surface.

Electrical conductivity of short carbon fibre-reinforced polychloroprene rubber and its mechanism of conduction are reported by Jana *et al.* [146]. Dielectric studies in epoxy and epoxy composites containing different volume fractions of three different dielectric fillers have

been performed by Wu and Tung [147]. Hashem [148] studied the current voltage characteristics of samples of butyl rubber loaded with two different types of carbon black at different temperatures. It is found that the electrical conduction process in carbon black-polymer composites is complicated depending on a large number of parameters like particle size, surface area, surface condition and dispersion of carbon particles [149,150]. Electrical conductivity is essentially explained by a combination of percolation and quantum mechanical tunnelling that control the current flow via the carbon particles [151]. The interaction between carbon black and polymer plays an important role in the electrical conductivity of these composites.

1.7.2. Thermal properties

Thermal conductivity may be defined as the quantity of heat passing per unit time normally through unit area of a material of unit thickness for unit temperature difference between the faces. In a review of thermal conductivity of polymers, Hands [152] discusses methods of measurement of thermal conductivity, which can be divided into steady state methods and transient methods. The thermal conductivity of solid rubbers is in the order of 1-2 $x10^{-10}$ W/mK, which is in the region of fairly low conductivity. Lu and Xu [153] prepared polyurethane composites filled with alumina or carbon fibres to study the thermal conductivities under humid environments. The thermal conductivities of those polymer composites in relation to filler concentrations and filler sizes were investigated and it was found that the thermal conductivity can increase up to 50 times that of polyurethane. The formation of heat-conductivity bridges in the polymer composites, as well as the crystallization of polymer chains have been observed which also have large effects on the thermal conductivity of polymer composites.

Maxwell and Eucken [154] obtained an exact solution for the conductivity of randomly distributed and non-interacting spheres in a continuous medium, and is frequently used because of its simplicity,

$$k_c = k_m \left(\frac{k_f+2k_m+2\varphi\,(k_f-k_m)}{k_f+2k_m-\varphi\,(k_f-k_m)} \right)$$

where k_c, k_m and k_f are thermal conductivities of composite, matrix and filler respectively and φ is the volume fraction of filler. Based on different assumptions Bruggeman [155] developed an implicit correlation

$$1-\varphi = \left(\frac{k_f-k_c}{k_f-k_m} \right) \left(\frac{k_m}{k_c} \right)^{1/3}$$

Tsao [156] developed a model relating the conductivity of two experimentally determined parameters, which describe the spatial distribution of the two phases. Cheng and Vachon [157] extended Tsao's [156] model assuming a parabolic distribution of the discrete phase (filler) in the continuous phase.

$$\frac{1}{k_c} = \left(\frac{1}{MN} \right) \ln \left(\frac{2N+BM}{2N-BN} \right) + \left(\frac{1-B}{k_m} \right)$$

where

$$B = \left(\frac{3}{2}\varphi \right)^{1/2}, \qquad C = 4 \left(\frac{2}{3}\varphi \right)^{1/2}$$

$$M = [\,C\,(k_f-k_m)\,]^{1/2}$$

$$N = [k_m + B\,(k_f-k_m)]^{1/2}$$

From experimental results, Sundstrom and Lee [158] concluded that the Bruggeman equation gave better results upto 10% of filler by volume, where as the Cheng-Vachon equation was more accurate in the range of 15-20% by volume. It is indicated that their data could be fitted by the Lewis and Nielson equation [159], in which effects of the shape of particles and type of packing were included.

$$K_c = k_m \left(\frac{1+AB\varphi}{1-B\psi\varphi} \right)$$

where

$$B = \frac{k_f/k_m - 1}{K_f/k_m + A}, \qquad \psi = 1 + \left(\frac{1-\varphi_m}{\varphi_m^2} \right) \varphi$$

where A is a constant related to the generalized Einstein coefficient and φ_m, the maximum packing fraction of the filler.

During the vulcanization process, rubber compounds are heated to high temperature. This temperature increase can be so high that it can cause tyre destruction. Knowledge of thermal diffusivity data of rubber compounds and reinforced rubber is important in such cases. Bafrnec *et al.* [160] described a method to find the thermal diffusivity of a compound, which is developed especially for determining thermal diffusivity of thick fibre composite materials and reinforced rubber.

1.8. Heat Transfer and Vulcanization of Thick Articles

The heating and cooling of solids is known as heat transfer in the unsteady state since the temperature at any point within the body varies with both time and position. For example in the vulcanization of rubber, heat transfer is especially important since the rate of reaction increases rapidly

with comparatively small changes in temperature. In the vulcanization 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 of 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 of conduction occurs during the entire cure. Knowledge of the temperature changes within a heated body can be gained in many ways.

The existing methods of estimating the degree and time of vulcanization of thick–walled rubber articles are based on calculation or experimental determination of the temperature field and finding the equivalent time by analytical or graphical methods [161]. Also the analytical relationship obtained by Sverdel and Aronovich [162] makes it possible to determine the equivalent time and duration of vulcanization of thick walled rubber articles with constant temperature on the heating surface without complete calculation of the temperature field. Joshi and Astarita [163] made a mathematical modelling of the coupled heat transfer-phase transition phenomena in polymeric composites containing thermally active fillers.

Rubber is a poor conductor of heat and thick articles may require long periods of heating during vulcanization. As the temperature of vulcanization increases, certain properties of rubber vulcanizates tend to deteriorate. Natural and some synthetic rubbers are especially sensitive to high temperature curing because of their poor resistance to overcure. Large articles are normally cured by one or a combination of the following methods.

1. Using lower temperature than for smaller articles.

2. Soak cures, where the external heating is discontinued and heat is allowed to penetrate to the centre while the article is held under pressure.
3. Step-up cures, starting at a low temperature and rising at intervals to the final curing temperature.
4. Where possible, in the case of open steam curing of rubber on metal base or former by the use of hollow mandrels, thus allowing heat from 'inside' and hence shorter cure times.
5. Post curing during cooling, where the exterior of the article is allowed to cool after removal from the heating equipment. This effect is often overlooked in production where additional curing (and possibly over curing) takes place when hot articles are stacked or not cooled adequately.

In order to make a balance between the uneven state of cure between the outer and inner surfaces of a thick article and to ensure adequate processing safety, cure retarders are used in rubber compounds [164]. Retarders prolong the induction period before the onset of vulcanization. In the vulcanization of thick articles, a high ratio of accelerator to sulphur (EV system) reduces the reversion in the outer portion during the long period of heating to cure the inner portion. A nomogram for establishing the additional curing time for various sizes of slabs, blocks, bars, cubes, spheres and cylinders were published [165]. The additional time was assumed to be independent of the compressed temperature and the error is negligible for a reasonable range of curing temperatures.

A balance must be achieved between too low state of cure at the inner portion giving porosity or blows, and gross overcure at the outer surface leading to degradation. One way to achieve this balance is by reducing the cure time by increasing the heat transfer of the compound. Increased thermal

conductivity of the rubber compound will improve the heat transfer and reduce the cure time for thick articles. Incorporation of suitable filling materials, like metal powders, having high thermal conductivity will improve the thermal conductivity of polymers [166].

1.9. Conductive Polymers

In recent years conductive polymers have attained wide applicability in many areas. The methods currently used to increase the conductivity of polymers are to fill them with specific conductive additives such as metallic powders [167] metallic fibres [168] carbon black [169], ionic conductive polymers [170] and intrinsically conductive polymeric powders eg. Polypyrrole [171]. In addition to these techniques, synthesis of electro-active polymers, use of dopants and charge transfer salts, deposition of metallic elements in polymers by thermal decomposition of specific metallo-organic compounds, metallic ion implantation techniques and vacuum metallization of polymers are also used to prepare conductive polymers [1].

Heeger [172] pointed out that iodine added to the polymer increased conductivity more than 10 orders of magnitude. It should also be noted that the number of organic electrical conductors has been growing and that conductivity is influenced by organic charge transfer compounds. Polyacetylene and poly (*p*-phenylene) are conductive due to their specific structure itself. Heeger reported on techniques for studying charge transfer doping reactions in conducting polymers. These techniques have made it possible to monitor the kinetics of charge transfer reaction. Delmonte [1] in his book gave a list of electro active polymers. High temperature treatment of polyoxidiazole yielded a flexible film of high electrical conductivity. Polymers of N-substituted carbozoles and substituted benzaldehydes when doped with charge transfer acception show acceptable level of conductivity.

Electrochemical doping of various quinoline polymers and polymer complexes, consisting of ionized polymer backbones with appropriate counter-ions interdispersed between the charged chains, is also a method to improve the conductivity of polymers. The introduction of metal atoms into a polymer matrix is believed to result in a sharp change in their electrical/thermal properties. Pomogailo and Savostyanov [173] reported the advances in the synthesis and polymerisation of metal-containing monomers. Kurnoskin [174] gave a detailed account of the chemistry and production of epoxy chelate copper containing polymers.

I.10. Metal Powders as Conductive Fillers

The conductive polymers so far discussed suffer many disadvantages. The preparation of such polymers involves tedious and time-consuming processes. The product obtained is of very low conductivity in quantitative means and is costly. These methods are applicable only in some selected polymeric system. The incorporation of conductive fillers in polymers is a very easy and cost effective method to introduce thermal/electrical properties and also overcomes the above-mentioned problems. Carbon blacks and metal powders are the fillers used for this purpose, among them metal powder is unique. A polymer filled with metal powder has considerably good mechanical properties and it also acquires specific properties like thermal/electrical conductivities.

There exist various methods for the preparation of metal filled polymers, which include electrolytic, electroflotational, thermal and mechanical methods. In electrolytic method, during electrolysis of aqueous solutions of suitable salts, the metal particles released on a horizontally revolving cathode pass to an external, organic layer of the tank containing polymer solution, where they interact with polymer molecules. In

electroflotation method high-dispersion metals and metallo polymers are obtained in an apparatus provided with a stationary vertical cathode. The thermal method makes use of the fact that if certain organic and inorganic metal compounds are heated to a certain temperature in an oxygen free atmosphere or vacuum, they decompose and release high dispersion metal particles. If such compounds are decomposed in an organic medium, concentrated high dispersion organosols of metals can be produced. The different mechanics or mechano chemical methods are as follows.

1. Mixing the polymer and metal powder in a mill. During this, breaking of polymer molecules takes place due to mechanical action with release of free radicals, which may interact with the metal surface leading to a metal polymer combination.
2. Polymerisation of monomers on the newly formed surface of metal particles.
3. Polymerisation of monomers on the surface of vacuum pre-dispersed metal particles.
4. Mechanical dispersion of metals in a polymer medium.
5. Predispersion of metal in a medium of low molecular surface-active substances followed by introduction of polymers containing active functional groups or multiple bonds.
6. Simultaneous evaporation of metal and monomer leading to the formation of metal polymer composite.

Bhattacharya and Chaklader gave previews on the electrical conductivities and thermal properties of metal filled polymers [10,11]. The effect of brass powder in rubber composites was reported by Parks [12]. The effect of filler content and applied electric field on the electrical resistivity of poly (methyl methoxylate) filled with aluminium particles was investigated [13]. The resistivity of such composites suddenly decreases by

several orders of magnitude at a critical volume concentration of metal powder (φ_c). In addition, for filler contents lower than φ_c, it undergoes a transition from a low to high resistance material. This value has been related to thermal breakdown occurring in the regions between conductive particles. Maity and Mahapatro [175] studied the thermal properties of aluminium powder filled polypropylene composites. They reported that the thermal conductivity showed an increase with increase in filler content. Both crystallinity and tensile properties decreased with increased aluminium powder loading. The presence of aluminium powder increased the thermal stability of polypropylene through an increase in activation energy.

I.11. Applications of Metal Powder Filled Composites

The application of polymers has been widened with the recent discovery of metal-filled polymers, in which the inherent thermal and electrical characteristics of polymers have been substantially modified. The increased electrical/thermal conductivity due to the incorporation of metal powders makes it suitable for various specific applications, some of which are briefly discussed below.

I.11.1. Uniform curing of thick rubber products

Incorporation of conductive fillers like metal powders in rubber has advantage in moulding of thick articles like dock fenders, tyre retreads, roll covers, solid tyres etc. Since rubbers are poor conductors of heat, the level of cure may not be the same throughout the material even after the optimum vulcanization time, especially when the articles are thick. Thick articles require additional time (5minutes additional for every additional 6mm thickness at 150^0C) to complete the vulcanization of the bulk of the material. As a result, the surface, which is in contact with the mould becomes over

cured (highly crosslinked) whereas the inner portion may be in a state of under cure (poorly crosslinked). Moreover it requires additional time for moulding and thus expending additional energy, which reduces the output. This can be successfully overcome by the addition of metal powder, which gives uniform curing through out the material due to the increased conductivity. Thus it helps to save energy by reducing the vulcanization time for thick rubber products and thus increases the output.

I.11.2. As shielding materials

Electromagnetic interference (EMI) and radio frequency interference (RFI) shielding has got importance as they can affect critical electronic equipments such as computers, medical instruments, navigation equipment and process control equipments. The metal powder filled polymers offer good shielding property against these. Simon [176] and Regan [177] have reported the EMI shielding through conductive plastics and its practical aspects.

I.11.3. As antistatic materials

In many industrial process antistatic conveyor belts, made of conductive rubber, are used to eliminate static electricity. Semiconducting walls and floors have been developed from metal-filled rubber, which are especially used in hospital operating rooms to bleed off static electricity. Another important use of metal-filled rubbers as antistatic materials is in aeroplane tyres and blades to dissipate the substantial electrostatic charges accumulated during flight. These composites also find application in the field of marine engineering as antistatic materials. Seanor [178] described the techniques for the prevention and elimination of static electricity from polymers.

I.11.4. In electrical and electronic industries

Metal-polymer composites are extensively used for encapsulating electrical and electronic components, for making resistors and capacitors and also as semiconductors. Silver and copper in phenolic resins are used as printed circuits and find use in many communication apparatus, in TV equipments and in computers [1]. A recent development is their use as thermistors, where copper-filled polystyrene showed promising results [179]. Metal-filled polymers are also used in making heating pads and radiant heating panels for domestic needs.

I.11.5. As magnetic materials

Metallic and magnetizable powders in combination with plastics are widely used as magnetic material for various applications, especially for making magnetic tapes. Powdered iron and iron oxides in a polymer matrix are mostly used for this purpose. Powdered iron, cobalt and nickel coupled with varnishes are used for printing inks for electronic sensing for the automatic sorting of printing materials such as bank cheques, postage stamps and business forms.

I.11.6. In marine applications

Copper powder and its alloys are used in bottom paints of ocean going vessels to prevent the growth of marine organisms which otherwise form a thick encrustation on the vessels. This interferes with the accuracy of signal response and retards the speed of the vessel. Possible many other future applications of these materials have been discussed by Delmonte [1].

1.12. Scope and Objectives of the Work

Fillers generally used in rubber compounding are carbon blacks, silica, calcium carbonate, clay and fibrous materials such as nylon, sisal, jute etc. Role of these fillers in imparting special properties such as thermal/electrical properties has great importance in certain applications. However, use of metal powder as a filler in rubber compounds was examined only to a very limited extend. Among the metal powders available, silver, copper and aluminium are the best conductors of heat. But silver is costly and copper is a pro-oxidant of rubber. Aluminium is neutral towards rubber and is available in powder form. Its specific gravity (2.69) is in the range of other fillers such as china clay (2.60), calcium carbonate (2.65) etc. One of the cost effective methods to increase the thermal conductivity of natural rubber compounds indented for thick rubber articles is to use aluminium powder as a filler. Hence it is worth to take up a detailed study on the use of aluminium powder as a filler in rubber compounds.

Natural rubber and styrene butadiene rubber are the most exploited and widely used commercial elastomers. They have a number of desirable properties and the incorporation of different metal powders, especially aluminium powder, improves the conductivity of the compounds, which is suitable for various specific applications. A detailed study in this area will increase their applications and offer the possibility of substituting some of the costly materials with natural rubber or SBR composites containing desired quantity of aluminium powder. The electrical study of these composites is expected to give an idea about their applicability as a shielding material towards electromagnetic interference and radio frequency interferences. These composites are light-weight compared to metals and have wide applicability in protecting aerospace components. The uniform curing of thick rubber articles containing aluminium powder will lead to

high industrial output, energy saving and enhanced service life to such products. Therefore research in this field will lead to successful implementation of new ideas and formulations, which will open up new avenues for our natural resources.

The primary objective of the study is to modify the properties of natural rubber and styrene butadiene rubber with the incorporation of aluminium powder. To throw light on the technological properties of aluminium powder filled rubber composites various phases of experiments were undertaken. In metal powder-filled composites, the major problems faced are the poor interface adhesion between the component materials and the non-uniform dispersion of the discrete phase in the matrix. Partial modification of the filler surface by a suitable coupling/bonding agent reduces such problems. Effect of various coupling/bonding agents viz. hexamethylene tetramine-resorcinol (HR), bis[3-(triethoxy silyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene 2,4-diisocynate (TDI) on the mechanical properties of aluminium powder filled natural rubber composites have been investigated to find out the optimum loading of aluminium powder in natural rubber and also to identify the best bonding agent, which imparts maximum properties to the composites.

In the case of aluminium powder filled-rubber composites, the level of adhesion cannot be ascertained quantitatively and hence a qualitative assessment of the same is to be made. Equilibrium swelling of natural rubber composites containing aluminium powder has been investigated in a series of aromatic hydrocarbon solvents such as, benzene, toluene, xylene and mesitylene and aliphatic hydrocarbon solvents like *n*-pentane, *n*-hexane and *n*-heptane. These vulcanizates were prepared using four different vulcanizing systems viz. conventional (CV), efficient (EV), dicumyl peroxide (DCP) and a mixture consisting of sulphur and dicumyl peroxide

(Mixed). In each vulcanizing system, the effect of aluminium powder was studied both in the presence and absence of a bonding agent. The bonding system consisted of a combination of hexamethylene tetramine, resorcinol and precipitated silica.

The effect of aluminium powder on the properties of natural rubber containing various fillers viz. high abrasion furnace black (HAF), general purpose furnace black (GPF), acetylene black, china clay and precipitated silica were studied. In all cases the total filler content including aluminium powder is kept at 40 parts per hundred rubber. These composites were characterized by analysing mechanical properties such as tensile strength, hardness, rebound resilience, heat build up, compression set etc.

Stress relaxation characteristics and dynamic mechanical analysis were carried out for aluminium powder filled natural rubber vulcanizates and are compared with those containing conventional fillers such as HAF, GPF, acetylene black, china clay and precipitated silica. The effects of various bonding/coupling agents viz. HR, Si-69, CoN and TDI on stress relaxation behaviour and dynamic mechanical properties of natural rubber-aluminium powder composites were investigated.

During service, the products may expose to elevated temperature, gamma irradiation or ozonized air. Therefore there is a need to study the effect these degrading agents on these composites. The ageing properties like resistance towards heat, ozone, high-energy radiation and flame resistance of aluminium powder filled natural rubber composites were studied. Effects of various bonding agents on the degradation behaviour of these composites were also investigated.

Vulcanization of thick rubber articles is a tedious process as they undergo uneven curing at the outer and interior portions of the material due to the non-uniform distribution of heat in rubber compound. In the

conventional process complete and uniform curing of these materials require additional time of vulcanization, which finally leads to poor properties to the product. This can be successfully overcome by the use of conductive fillers. The role of aluminium powder in uniform curing and thus the reduction in vulcanization time of thick rubber articles was studied in detail. The thick articles selected for this study were dock fender (used for gentle docking of ships) and rice polisher brake, which were moulded according to standard specifications. In order to follow-up the heat flow and crosslinking pattern in thick rubber articles experiments were conducted using vulcanized rubber cubes of 5 cm in size, which were crosslinked to different levels by changing the vulcanization time. Crosslink density assessments of the outer and central portions were done by equilibrium swelling method.

In cases where natural rubber cannot be used, a blend of NR with synthetic rubber or synthetic rubber alone is used according to the requirements. Hence, the effects of aluminium powder on the properties of styrene-butadiene rubber (SBR) composites were also studied. Conventional fillers such as HAF and acetylene black were included in this study for comparison. Effects of various bonding agents on the properties of SBR-aluminium powder composites were studied. The bonding agents selected were hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl) propyl] tetrasulphide (Si-69) and cobalt naphthenate (CoN). Studies were conducted to find out the optimum aluminium powder loading and the suitable bonding system for the new compositions.

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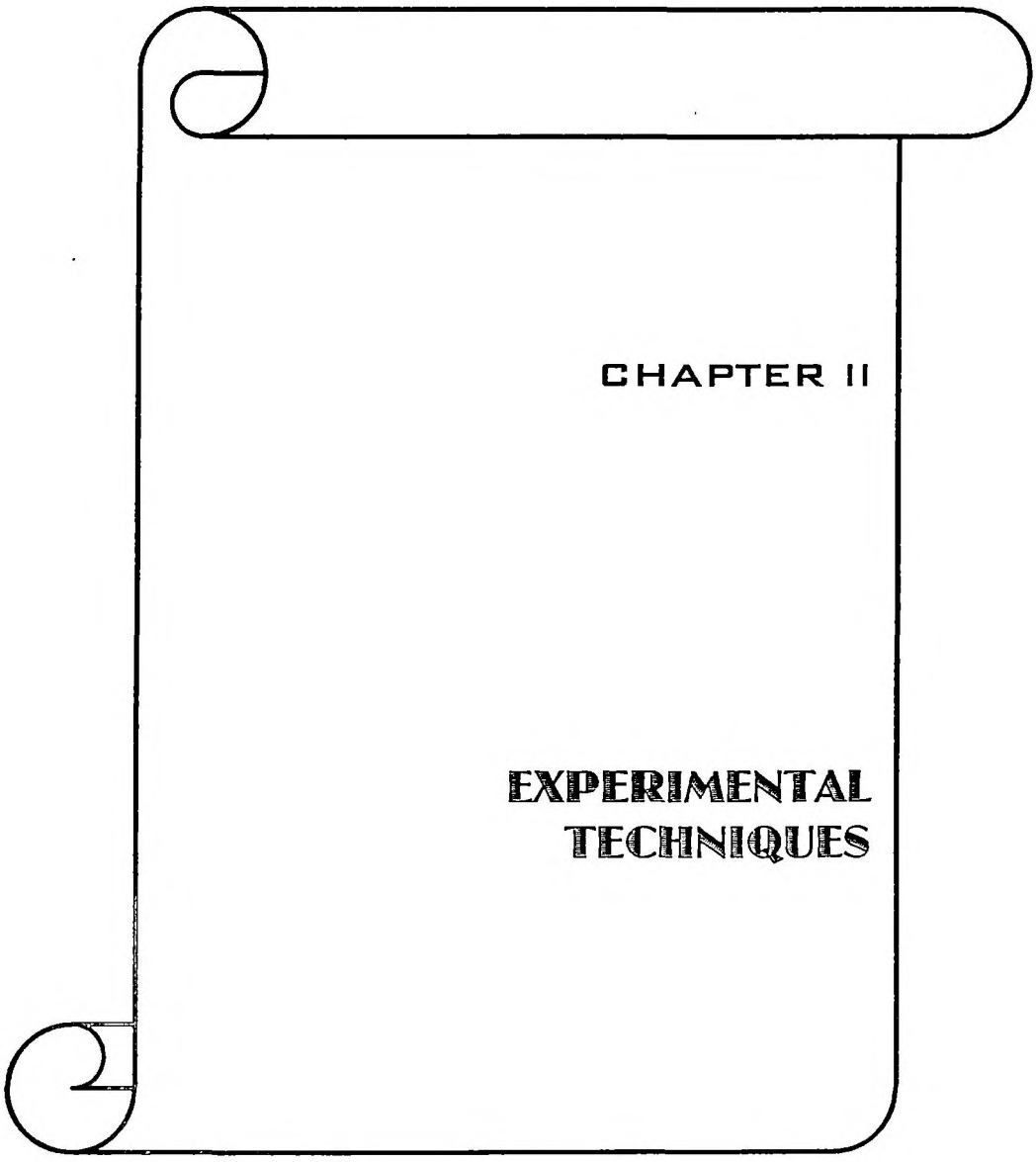

CHAPTER II

EXPERIMENTAL TECHNIQUES

II.1. Materials Used

II.1.1. Natural rubber

Natural rubber (NR) used in this study was the ISNR-5 (Indian Standard Natural Rubber-5) grade rubber supplied by Rubber Research Institute of India, Kottayam. Kerala. The specifications of ISNR-5 grade NR and their limits are given in Table II.I. 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 [1,2]

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

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

II.1.2. Styrene butadiene rubber

Styrene butadiene rubber (SBR) used was Synaprene 1502 having 25% styrene, which was supplied by Synthetics and Chemicals Ltd.. Bareilly, Uttar Pradesh, India. The basic characteristics of SBR are given in Table II.2.

Table II. 2. Characteristics of SBR-1502

Chemical constituents (%)	Minimum	Maximum
Styrene	21.5	25.5
Volatile matter	--	0.75
Organic	4.75	7.0
Soap	--	0.5
Ash	--	1.5
Antioxidant	0.5	1.5
Cis-1,4 content	--	18
Trans-1,4 content	--	65
Vinyl-1,2 content	--	17

II.1.3. Fillers

II.1.3.1. Aluminium powder

Aluminium powder used for the study was obtained from M/s Kosla Metal Powders Pvt. Ltd., Pune, India. The technical details are given below.

Specific gravity	2.69
Bulk density	0.36 g/cc
Particle size	127- 200 nm
pH	7.0

II.1.3.2. Carbon blacks

High abrasion furnace black (HAF), general purpose furnace black (GPF) and acetylene black (ACB) are the black fillers used for this study. The suppliers and characteristics of these fillers are given in Table II. 3

Table II.3. Characteristics of carbon black fillers

Characteristics	HAF	GPF	Acetylene black
Supplier	Philips Carbon Black. Ltd., Durgapur.	Philips Carbon Black Ltd., Durgapur.	Tecil Chemicals and Hydro Power Ltd., Kottayam.
Particle size, nm	29-38	59-68	40-50
Specific gravity	1.81	1.81	1.81
Bulk density, g/cc	0.39	0.26	0.06
Ash content, % by mass	0.40	0.40	0.20
pH	7.1	7.0	6.5

II.1.3.3. Non-black fillers

Commercial grade precipitated silica and china clay are the non-black fillers used for this study. Precipitated silica has a specific gravity of 1.95, pH of 6.7 and an average particle size of 40-60 nm. Specific gravity of china clay is 2.62, which has a pH of 5.2 and an average particle size of 300-325 nm.

II.1.4. Rubber chemicals

The rubber chemicals used for the study were supplied by M/s ICI India Limited and were of chemically pure grade.

II.1.4.1. Accelerators

2-(morpholinothio) benzothiazole (MOR), N-cyclohexyl benzthiazyl sulphenamide (CBS), 4,4^1-dithiomorpholine (Sulfassan-R) and N-N^1-dicyclohexyl-2-benzothiazyl sulphenamide (DCBS) are the accelerators used for this study. The melting point and specific gravity of these chemicals are given in Table II.4.

Table II.4. Characteristics of accelerators

Accelerators	Melting point in ^{0}C	Specific gravity at 25^{0}C
MOR	82	1.36
CBS	96	1.28
Sulfassan-R	126	1.35
DCBS	90	1.20

II.1.4.2. Antioxidant

Polymerised 1,2-dihydro-2,2,4-trimethyl quinoline (TDQ) was used as an antioxidant. It has a softening point of 75^{0}C, specific gravity 1.06 at 25^{0}C and is soluble in benzene and acetone.

II.1.4.3. Retarder

N-(cyclohexyl thio)- phthalimide (CTP) having a melting point 90^{0}C and specific gravity 1.30 at 25^{0}C was used as retarder.

II.1.4.4. Other chemicals

Zinc oxide (ZnO) used for the study has a specific gravity of 5.6 at 25^{0}C and a purity of 99.6 %.

Stearic acid having a melting point 70^{0}C, iodine value 9.5 and specific gravity 6.84 at 25^{0}C was used.

Sulphur used for the study has a melting point of 114^{0}C and specific gravity 2.07 at 25^{0}C. The material is completely soluble in CS_2.

Dicumyl peroxide used for the study has a specific gravity of 1.00 at 25^{0}C and contains 5.4 % active oxygen.

II.1.5. Plasticizer

Naphthenic oil was used as the plasticizer in this study. It has a specific gravity of 0.9 at 25^{0}C, aniline point 77.8^{0}C, pour point 6^{0}C and flash point 180^{0}C.

II.1.6. Special chemicals

Resorcinol (specific gravity 2.36) and hexa methylene tetramine (specific gravity 1.33) were of chemically pure grades and were obtained from Aldrich Chemical Company Inc., U S A.

Bis [3-(triethoxy silyl) propyl] tetrasulphide (Si-69) used for the study had a specific gravity of 1.095 at 25^{0}C and was supplied by the Shephard Chemical Co. Toluene diisocyanate was supplied by Poly Science Inc., USA.

Diethylene glycol (DEG) used for the study was obtained from E.merck India Limited. Mumbai. It has a specific gravity of 1.11 at 25^{0}C and boiling point of 197^{0}C.

II.1.7. Solvents

The solvents used were supplied by Nice India Ltd. and their characteristics are given Table II.5. All the solvents are distilled before use.

Table II.5. Characteristics of solvents

Solvent	Purity	Specific gravity at 25^{0}C	Boiling point, ^{0}C
Benzene	99.7	0.878	80
Toluene	99.6	0.867	110
p-xylene	99.5	0.866	137
Mesitylene	99.8	0.864	163
n-pentane	99.4	0.626	36
n-hexane	99.6	0.675	69
n-heptane	99.7	0.680	98

II.2. Test Sample Preparation

II.2.1. Preparation of composites

Formulations used for the study were given in respective chapters. The codes used to distinguish the composites are also given along with the formulation table. The composites were prepared in a two-roll laboratory model-mixing mill (300 x 150 mm) at a nip gap of 1.3 mm and at a ratio 1:1.25 [3]. Nip gap, mill roll speed ratio, time of mixing and temperature of the rolls were kept at the same for all mixes. In the case of composites containing bonding/coupling agents, these were added at the time of mixing. All the chemicals were finely powdered for the purpose of homogeneous mixing.

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.2.2. Time of optimum cure

Optimum cure time was measured using an oscillating disc rheometer supplied by 'Monsanto' (model R-100), according to ASTM D- 2084-93 test method. The optimum cure time corresponds to the time to achieve 90% of the cure, calculated using the formula,

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

where M_H and M_L are the maximum and minimum torque respectively for the rheograph. In this study, the optimum cure time was determined at 150^0C, at a chart speed of 60 min.

II.2.3. Rheometric induction time and cure rate index

Rheometric induction time is the time required for the torque values to increase by one unit above the minimum torque. Cure rate index is a direct measure of the cure nature of the rubber compound and is calculated as follows,

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

where scorch time is the total time from the start to get 2 units rise from the minimum torque.

II.2.4. Moulding of test samples

Test pieces were compression moulded at 150^0C by placing 5 % excess of the uncured stock in the cavity of a suitable mould and curing in a hydraulic press having electrically heated platens, to their respective optimum cure time as obtained from Monsanto Rheometer.

II.3. Testing for Vulcanizate Properties

At least five specimens per sample were tested for each property and the mean of these values was reported.

II.3.1. Modulus, tensile strength and elongation at break

These three parameters were determined according to ASTM D-412-87 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 vulcanized sheets. The thickness of the narrow portion of the specimen was measured using a dial gauge. The specimens were tested in a Universal Testing Machine (UTM model-1474 supplied by 'Zwick', Germany) at 25 ± 2^0C with a crosshead 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.3.2. Tear strength

This property was tested as per ASTM D624-81 test method, using unnicked 90^0 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 crosshead speed of 500 mm per minute and at 25± 2^0C. The tear strength values are reported in kN/m.

II.3.3. 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.3.4. 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 50^0C. 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.

II.3.5. Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader as per DIN 53516 specifications. 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 m. 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 weights 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:

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

where Δm = mass loss

ρ = density

V = abrasion loss in mm^3

To ensure 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 [3].

$$\left\{\begin{array}{l}\text{DIN Abrasion}\\ \text{loss of specimens}\\ \text{in } mm^3\end{array}\right\} = \left\{\begin{array}{l}\text{DIN abrasion}\\ \text{loss of test}\\ \text{specimen}\end{array}\right\} \quad X \quad \left\{\begin{array}{l}\text{abrasion index}\\ \text{of standard}\\ \text{specimen}\end{array}\right\}$$

where

$$\text{Abrasion index of standard specimen} = \frac{200}{\text{Abrasion loss for standard specimen}}$$

II.3.6. Rebound resilience

The rebound resilience of the vulcanizate 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 (45^0). The pendulum rebounded and the rebound angle was noted. The temperature of the specimen holder and the sample was kept constant at 30^0C. Rebound resilience was calculated as,

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

where θ_1 and θ_2 are the initial and rebound angles respectively, θ_1 was 45^0 in all cases.

II.3.7. 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 percent deflection between two parallel plates provided with spacers and kept in an air oven at 70^0C for 22 h (ASTM D-395-71, Method B). After the heating period, the deflection was released; the sample was cooled to room temperature for half an hour and final thickness was measured. The compression set was calculated as follows

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

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

II.4. Measurement of Resistance to Degradation

II.4.1. Hot air ageing

Dumb-bell shaped tensile test samples (2 ± 0.2 mm thick) were aged at 70^0C and 100^0C 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

$$\text{Tensile strength retention (\%)} = \frac{\text{Tensile strength after ageing}}{\text{Tensile strength before ageing}} \text{X } 100 \quad \text{....(II.6)}$$

II.4.2. Exposure to ϒ- radiation

Dumb-bell shaped tensile test samples (2 ± 0.2 mm thick) were irradiated with ϒ- rays from a ^{60}Co source in a gamma chamber. The samples were irradiated for different radiation doses at a dose rate of 0.321 Mrad/ 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.4.3. Exposure to ozonized air

The ozone test chamber manufactured by MAST Development Company, USA, was used to study ozone cracking. The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration used was 50 pphm, which is generated by a UV-quartz lamp. The test was carried out as per ASTM D-1149-81 specification. The test was conducted at 38.5 $\pm 2^0$C.

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

II.5. Swelling Studies

For swelling studies, vulcanized composites were cut using a sharp edged circular die of 1.98 cm diameter. The thickness of the sample was measured using a micrometer screw gauge. The initial weight of the specimen was taken and immersed in solvents contained in test bottles, kept at four different temperatures, say 27, 40, 55 and 70^{0}C. The samples were removed from bottles at periodic intervals and weighed immediately in an

air tight weighing bottle after the wet surface of the sample was dried using a piece of blotting paper. The uptake of the solvent sorbed by 100 g of composite was calculated. This method was found to be more convenient for the comparison of sorption data as adopted by many researchers [4-6].

II.6. Measurement of Thermal Conductivity

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, $^0C/m$, λ is expressed as W/m k. The thermal conductivity of the vulcanized samples was measured by a Quick Thermal Conductivity Meter, 'Kemtherm' QTM-D3 supplied by Kyoto Electronics, Japan. The measurements were made on a vulcanized rubber sample having 10 x 5 x 1 cm^3 size. 'Kemtherm' QTM-D3 makes measurements using a probe based on the transient hot wire method. Thermal conductivity of a sample by probe method will be given by the equation.

$$\lambda = \frac{K I^2 \ln (t_2/t_1)}{(V_2-V_1)} \qquad \ldots\ldots\ldots \text{(II. 7)}$$

where K is a constant, V_1 and V_2 are electro motive forces (mV) at time t_1 and t_2 respectively. I is the heating current (A). The probe of QTM- D3 consists of an elastic base of which thermal conductivity is already known and a hotwire with a thermocouple embedded on the surface of the base. 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 60 seconds.

II.7. Measurement of Electrical Properties

Rectangular pieces of the composites having dimension 1.0 x 1.0 x 0.25 cm^3 were used for the measurement. The samples were coated with conductive silver paint on both sides. Copper wires were fixed as electrodes on either side. The measurement was carried out at room temperature using a 4192 LF Impedance Analyser (Hewlett- Packard Co., Palo Alto, CA, USA) at a frequency range of the 10 kHz to 10 MHz, The volume resistivity of the composites is given by the following equation

$$\rho_v = \frac{RA}{t} \ \Omega \text{ cm} \qquad \ldots\ldots\ldots \text{(II.8)}$$

where R is the volume resistance

A is the area of the sample

and t is the thickness of the sample.

II.8. Scanning Electron Microscopy Studies

The scanning electron microscopic (SEM) photographs given in this work were obtained using a 'JEOL' (model 35 C) scanning electron microscope. The fracture surfaces were carefully cut from the failed test specimens without touching the surface and were sputter coated with gold within 24 h. of testing. The SEM observation was made within 24 h of gold coating. The fractured specimens and the gold-coated samples were stored in a desiccator till the SEM observations were made. It is reported that, there will not be any change in the fracture pattern even if the SEM observations were made one month after gold coating [7]. The operating conditions of the SEM are summarised in Table II.6.

Table II.6. Operating conditions of the SEM

Specification position, tilt, degree	Adjustable
Maximum resolution, mm	0.5
Spot size, angstrom	640
Emission current, amp.	26
Aperture, microns	200
H.T, kV	25
Depth of focus	High

II. 9. Stress Relaxation Studies

The stress relaxation measurements were carried out in a 'Zwick' Universal Testing Machine.(UTM model 1474). The dumb-bell shaped specimens (die C, ASTM D-412-87) were pulled to desired strain level and the test was carried out at room temperature according to ASTM D-638-87. The stress was recorded as a function of time on a chart paper. The ratio σ_t/σ_0 is plotted against logarithm of time, where 'σ_t' and 'σ_0' being stresses at time 't' and that at zero time, respectively.

II.10. Dynamic Mechanical Analysis

The dynamic mechanical properties of the composites were measured using a dynamic mechanical thermal analyser, DMTA-MKII of Polymer Laboratories, UK. Samples of dimension 5 x 1 x 0.5 cm^3 were used for testing. The testing was done at a temperature range of 30 to 150^0C and at a heating rate of 2^0C per minute. The experiment was conducted at a dynamic strain of 0.325 % and at frequencies 0.1, 1.0 and 10 Hz. The instrument measures dynamic moduli (both storage and loss modulii) and the damping of the specimen under an oscillatory load as a function of temperature.

Mechanical loss factor (tanδ) and dynamic moduli (E′ and E″) were calculated with a microcomputer. The storage modulus, E′ and loss modulus, E″ are obtained from E* and δ using the following equations [8].

$$E' = E^* \cos \delta \quad \text{.....(II.9)}$$

$$E'' = E^* \sin \delta \quad \text{.....(II.10)}$$

where E* is the dynamic complex modulus.

The loss tangent is obtained as,

$$\text{Tan}\delta = E''/E' \quad \text{.....(II.11)}$$

II.11. Limiting Oxygen Index

The above test was carried out using a Limiting Oxygen Index (LOI) apparatus manufactured by Appareillage Industrialet Scientifique Company, France [9], according to ASTM- D-2863-77. Both oxygen and nitrogen were connected to the equipment through pressure regulations (about 2 bars). The flow of gases was regulated at 17 litres per minute.

The specimens of 70 to 150 mm long, 6.5 mm wide and 3 mm thick were cut from vulcanized sheets and clamped vertically in the specimen holder at centre of the column with the top of the specimen at least 100 mm below the top of the open column.

A definite concentration of oxygen for the gas mixture was selected and the flow valves were adjusted so as to read the set oxygen concentration. The test chamber was purged with the mixture for 30 seconds and the specimen was ignited so that it was well lit and the entire top was burning. Subsequent trials were carried out with new specimens and changed concentrations of oxygen. The level of oxygen flow was adjusted to

the minimum at which the specimen burned for 3 minutes or more than 30 mm length whichever is earlier. The test specimen was changed after each trial and the test continued until reaching the minimum oxygen concentration with a precision of at least 0.2 %.

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CHAPTER III

EFFECT OF BONDING AGENTS ON THE PROPERTIES OF NATURAL RUBBER-ALUMINIUM POWDER COMPOSITES

Result of this chapter is accepted for publication in Journal of Adhesion Science and Technology

Fillers are usually added to polymers to obtain composite materials with improved physical properties. Incorporation of conductive fillers in rubber increased the conductivity, which made it suitable for various specific applications. Material engineers have long sought to combine the versatility of polymers with the thermal/electrical properties of metals. Among the various methods to increase the conductivity of polymers, incorporation of metals in the powder form is the best. Among the available metal powders silver, copper and aluminium are the best conductors of heat, but silver is costly and copper is a pro-oxidant in natural rubber. Aluminium is neutral towards natural rubber and is available in powder form, which can be used as a filler to improve the thermal conductivity of rubbers.

A large number of variables, viz., size, shape, nature, and state of distribution of the filler, adhesion and thermal compatibility of the phases, etc., affect properties of the composites. It is difficult and perhaps impossible to discuss the effect of each of the variables on the final properties of the composites [1]. In metal powder filled polymer systems the major problems are due to the poor adhesion and the non-uniform dispersion of discrete phases in the matrix [2,3]. There are many methods to achieve better rubber to metal adhesion. These include chemically or physically modifying the existing metal surface or the polymer and also by incorporating special additives which promote chemical bonding. There are suitable coupling agents, which enhances the surface interaction between the two phases. Better adhesion strength in the case of coupling agents have

been explained by a coupling mechanism through interfacial diffusion and interpenetrating crosslinking networks. The use of efficiently dispersed resorcinol-formaldehyde resin in rubber compound, along with methylene donor for improving the bonding of rubber to the reinforcing materials, is reported by Rajan and colleagues [4]. Varghese *et al.* [5] concluded that a bonding system consisting of hexamethylene tetramine and resorcinol is sufficient for getting good fibre-rubber adhesion. Buchan [6] gives a detailed study of various bonding agents for rubber and metal. The combined effect of cobalt and resorcinol bonding agents in rubber-brass adhesion is reported by Hamed and Huang [7]. Several reports about coupling agents, their use, types of agents studied, mechanisms by which they act, substrates, adhesive systems, and mechanism of adhesion are available in the literature [8-14]. The most common system is silane-coupling agent on a glass substrate and a covalent linkage is proposed as the operative mechanism. Phosphorous esters and chromium-acid complexes are also known to be effective and similar mechanisms are postulated.

One of the cost effective methods to increase the thermal conductivity of thick natural rubber articles is to use aluminium powder as filler. Bonding between the filler and polymer is essential to achieve better technological properties for the composites. Hence a study is conducted to evaluate the effects of various bonding agents on the properties of natural rubber-aluminium powder composites. The selected bonding agents included, a combination of hexamethylene tetramine and resorcinol (HR), bis[3-(triethoxysilyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI). The base formulation selected for studying the effect of various bonding/coupling agents on natural rubber-aluminium powder composites are given in Table III.1. The proportion of hexamethylene tetramine and resorcinol is in the ratio 1:2 for this system.

Table III.1. Base formulations of mixes for the evaluation of bonding agents

Ingredients	Quantity (phr)					
	GUM	WOB	HR	Si-69	CoN	TDI
Natural rubber	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0
Aluminium powder	-	10	10	10	10	10
Hexa	-	-	1.0	-	-	-
Resorcinol	-	-	2.0	-	-	-
Si-69	-	-	-	1.0	-	-
Cobalt naphthenate	-	-	-	-	1.0	-
Toluene diisocyanate	-	-	-	-	-	1.0
CBS	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

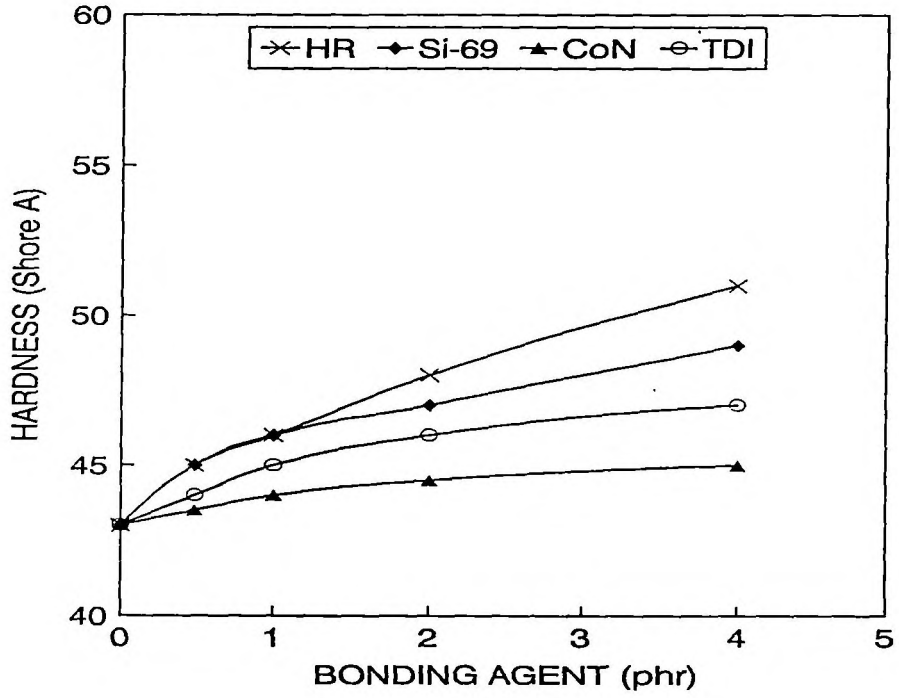
TDQ - 2,2,4-Trimethyl-1,2-dihydroquinoline
Si-69 - bis[3-(triethoxysilyl)propyl]tetrasulphide
CBS - N-cyclohexyl benzothiazyl sulphenamide
Hexa - Hexamethylene tetramine

The amount of bonding agent varied according to the loading of aluminium powder. The effect of bonding agent was studied at a constant aluminium powder loading of 10 phr. The effect of loading of aluminium powder was studied by varying the aluminium powder content from 0 to 40 phr. While plotting the figures, in the case of HR system we have taken the amount of hexamethylene tetramine on the abscissa, whereas the resorcinol varied proportionately by keeping the above ratio. Mechanical properties such as hardness, rebound resilience, heat build-up, tensile strength, abrasion loss, etc. have been evaluated, the experimental procedures of which are given in Chapter II. The effect of various bonding agents on the interaction

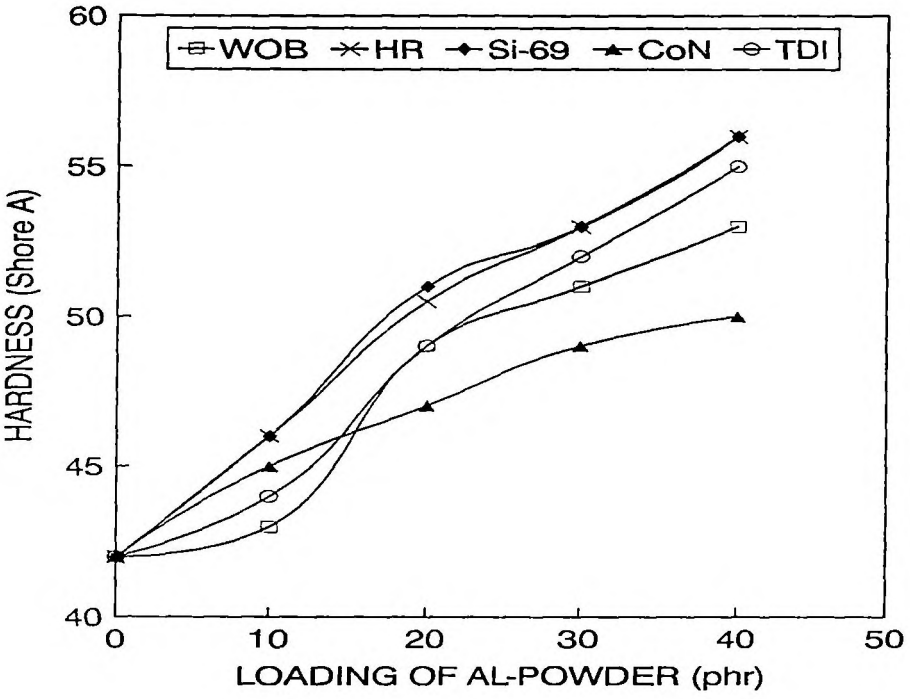
between rubber and aluminium powder was evaluated by equilibrium swelling in toluene.

III.1. Effect of Bonding Agents on Hardness and Resilience

Shore A hardness values of the composites are shown in Figure III.1a. As the bonding agent concentration increased, the hardness also increased and is maximum with HR system. The improved adhesion in presence of bonding agent may be the reason for the higher hardness of the composites, which follows the order, HR system > Si-69 > TDI > CoN. Figure III.1b shows that as the aluminium powder content increased, the hardness increased. Increase in hardness can be due to reinforcement effect of the filler as well as higher extent of crosslinking of the rubber. The presence of bonding agent increased the hardness due to the increased adhesion of aluminium powder with natural rubber compared to that with out bonding agent. The rebound resilience of NR-aluminium powder composites increased when HR and Si-69 were used as the bonding agents whereas it decreased on adding cobalt naphthenate and TDI as evident from Figure III.2a, where the loading of aluminium powder was kept at 10 phr. A change in this trend is observed at higher loading of aluminium powder (Figure III.2b). In presence of Si-69 and HR the rebound resilience first increased and then decreased, and this effect was more pronounced in the case of Si-69. The presence of TDI and cobalt naphthenate increased the resilience at higher loadings. The difference may be due to the different extent of interaction between natural rubber and aluminium powder towards various bonding agents as indicated by lower hardness values of the samples containing CoN and TDI bonding agents.

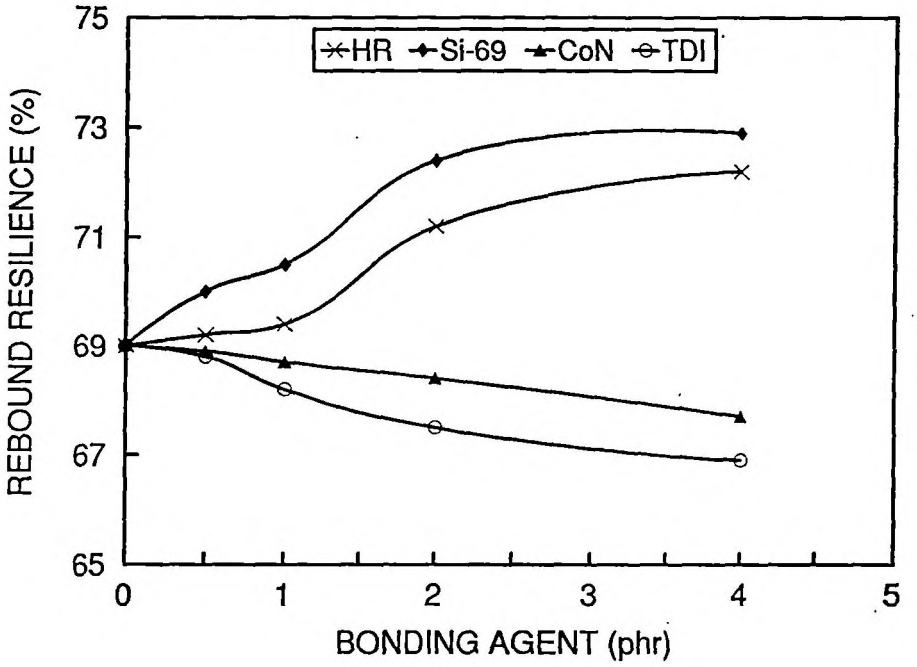


(a)

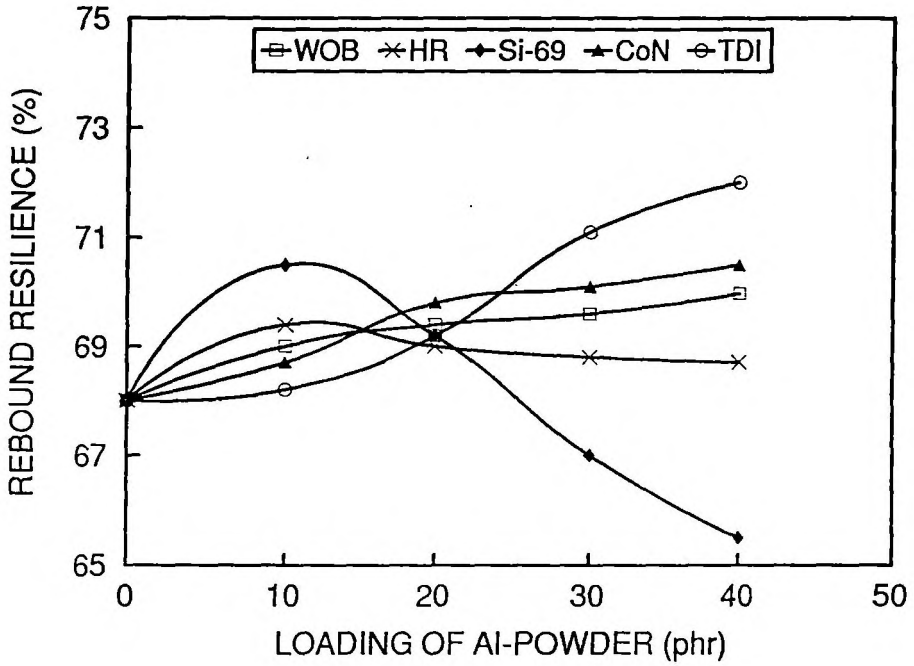


(b)

Figure III.1. Variation in Shore A hardness as a function of (a) the amount of bonding agents on natural rubber-aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR



(a)

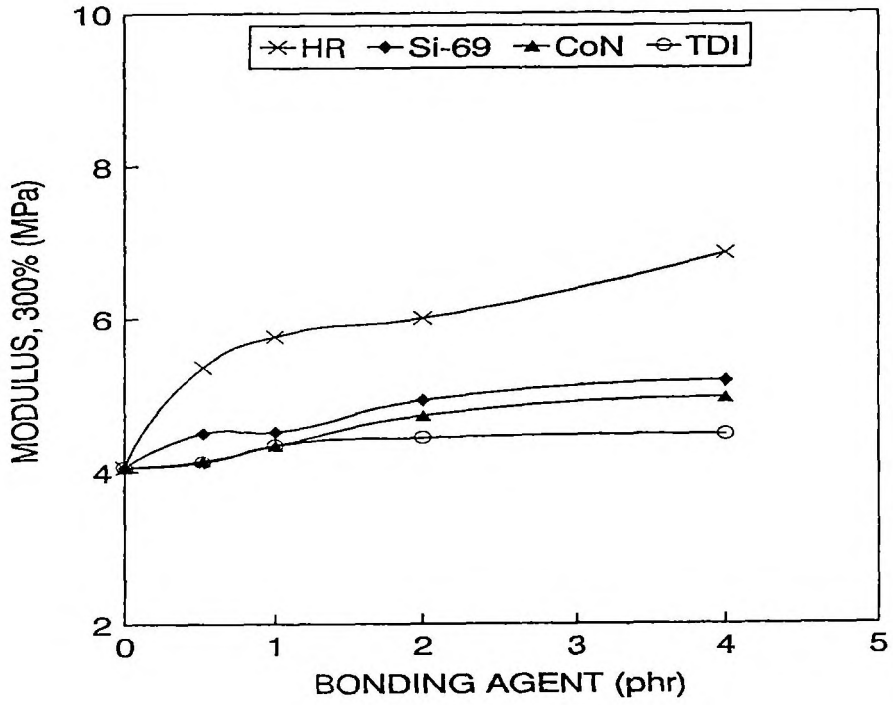


(b)

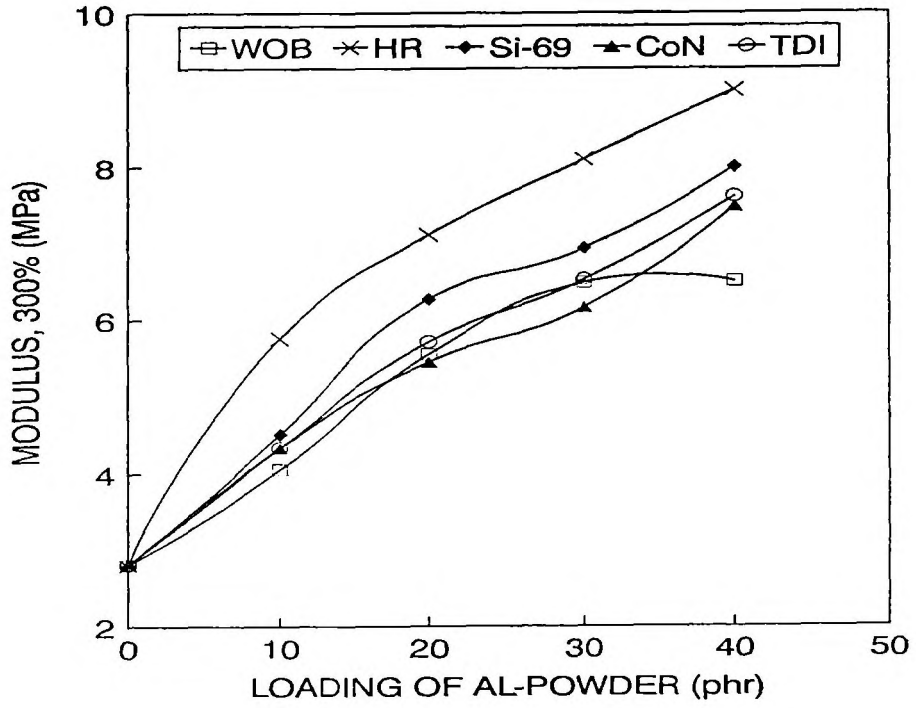
Figure III.2. Variation in rebound resilience as a function of (a) the amount of bonding agents on natural rubber - aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR

III.2. Effect of Bonding Agents on Tensile Properties

Figure III.3 shows the modulus at 300% elongation of aluminium powder filled natural rubber composites in presence of various bonding agents. Addition of bonding agent increased the modulus of the composites and the increase is maximum with HR bonding system followed by Si-69. The increased modulus is an evidence of strong interaction between natural rubber and aluminium powder, which results from the improved adhesion of the aluminium powder with the matrix. The tensile strength of these composites is presented in Figure III.4. At 10 phr of aluminium powder the bonding agent increased the tensile strength values, in the order, Si-69 > HR > TDI > CoN. It indicated that the natural rubber-aluminium powder interaction was maximum with Si-69 and HR systems among the bonding agents evaluated in this study. When aluminium powder loading is increased, maximum tensile strength is observed at 20 phr with Si-69 as the bonding agent, followed by HR system. Figure III.5 shows the elongation-at-break of the NR-aluminium powder composites with and without bonding agents. At 10 phr aluminium loading, as the bonding agent increases, the elongation-at-break decreases and, the order of decrease is opposite to that of tensile strength. This is because an increased crosslinking and interaction of rubber with filler leads to a lower elongation. At higher loadings of aluminium powder (Figure III.5b) the elongation-at-break decreases and the reduction is more in the presence of bonding agents. The action of bonding agents in rubber-metal powder interaction is expected to be similar to those in the case of other fillers, which is described below.



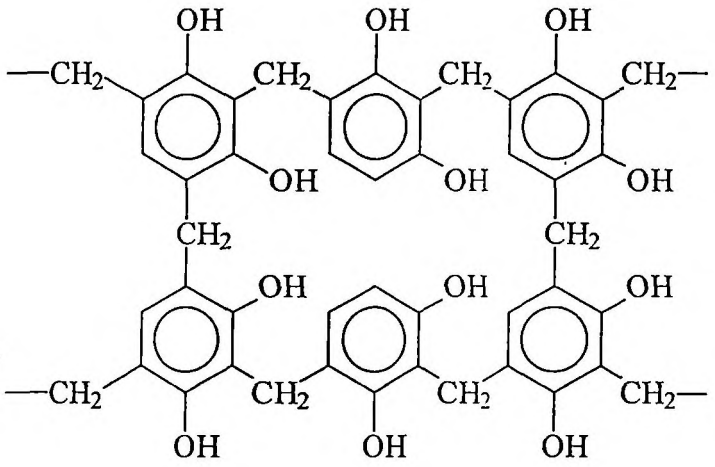
(a)



(b)

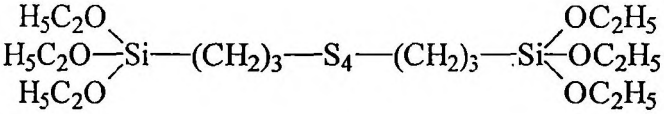
Figure III.3. Variation in modulus at 300 % elongation as a function of (a) the amount of bonding agents on natural rubber-aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR

In the case of HR system, resorcinol combines with methylene donor (hexa) to give a resin with the following structure.



After the bonding ingredients are intimately mixed with rubber, they react together during vulcanization and produce the resin, which binds the rubber and the metal powder. This is due to the increased polarity of the rubber, which arises from the hydrogen bonding characteristics of the resorcinol resin. This makes great improvements in bonds between rubber and various materials such as aluminium powder [4].

The silane-coupling agents are quite effective in reactive polymer systems. They contain polar silanol groups capable of interacting with the surface of glass, metals, etc. and a hydrocarbon part, which interacts with the rubber matrix. The silane coupling agent, bis-[3-(triethoxysilyl) propyl] tetrasulphide has the following structure ,



This coupling agent has dual functionalities. Hydrolyzable alkoxy groups attached to a silicon atom react with or otherwise condense on the

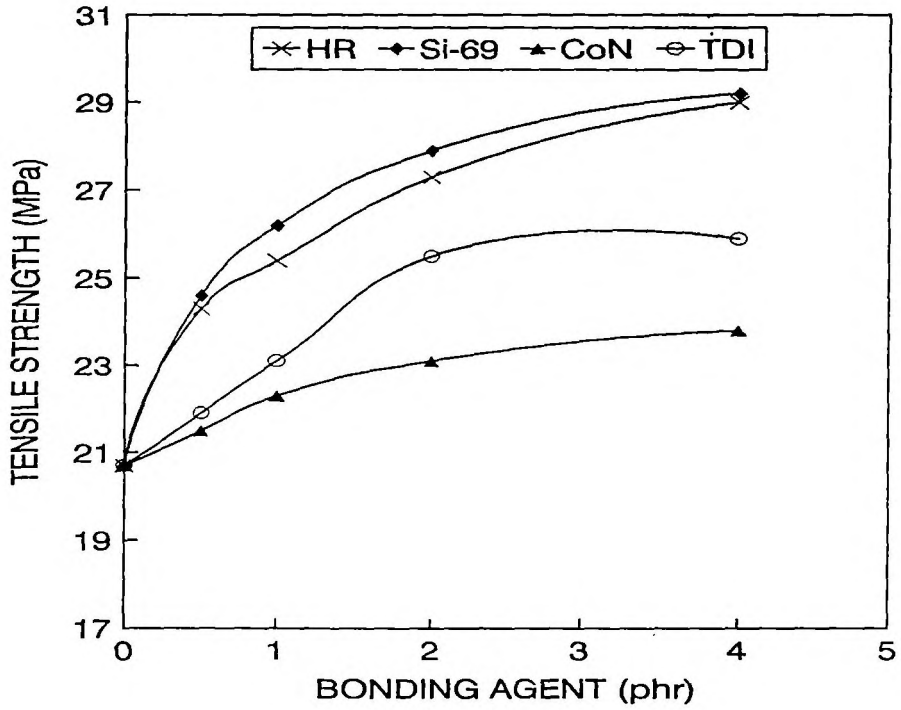
surface of metal powders. The organic functional groups attached to the silicon can react with polymers, establishing effective bonding between metal powder and the rubber matrix.

It would appear that addition of isocyanate to rubbers initiates a chemical reaction, and this might account for the bond, between rubber and the isocyanates. It is suggested that the isocyanate itself unites with the hydrated oxide layers on the surface of the metal.

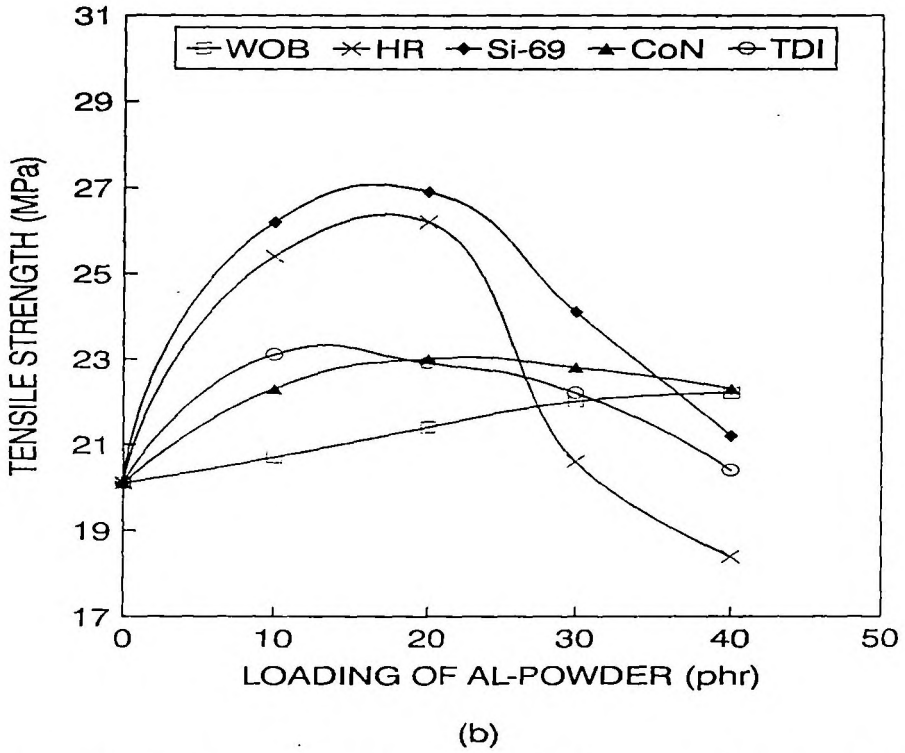
Cobalt naphthenate, as well as other cobalt salts, are used commercially in elastomeric compounds to promote adhesion to metal. The detailed mechanism of improved adhesion in presence of cobalt salts is unknown, but it is assumed that these will create an increased polarity, which would improve the adhesion properties. It is also reported that CoN is an effective oxidation catalyst for natural rubber [15]. The comparatively lower tensile properties, hardness etc. of the vulcanizates containing CoN may be due to the degradation of natural rubber by CoN.

III.3. Effect of Bonding Agents on Other Mechanical Properties

The heat build-up values are presented in Figure III.6. As the amount of bonding agent increased, the heat build-up values also increased, and the increase is also reflected at higher loading. As the interaction between aluminium powder and natural rubber increases the heat build-up also increases due to the higher amount of energy to be expended for effecting the same deformation. Figure III.7 shows the DIN abrasion loss of the composites. At 10 phr loading of aluminium powder, the abrasion loss can be minimized by the addition of Si-69 or HR system as the bonding agent.



(a)



(b)

Figure III.4. Variation in tensile strength values as a function of (a) the amount of bonding agents on natural rubber-aluminium powder (10phr) composites and (b) the amount of aluminium powder in NR

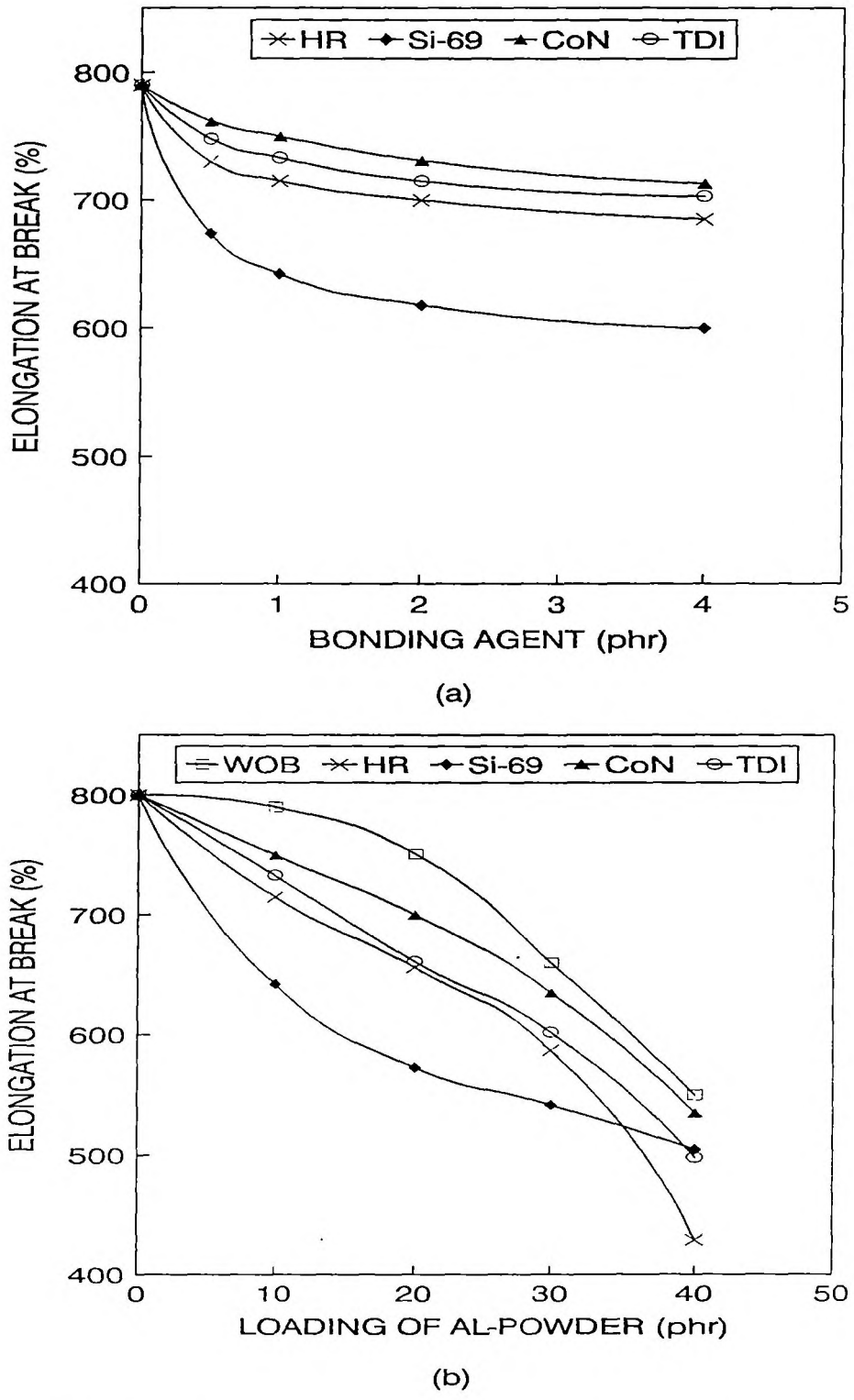
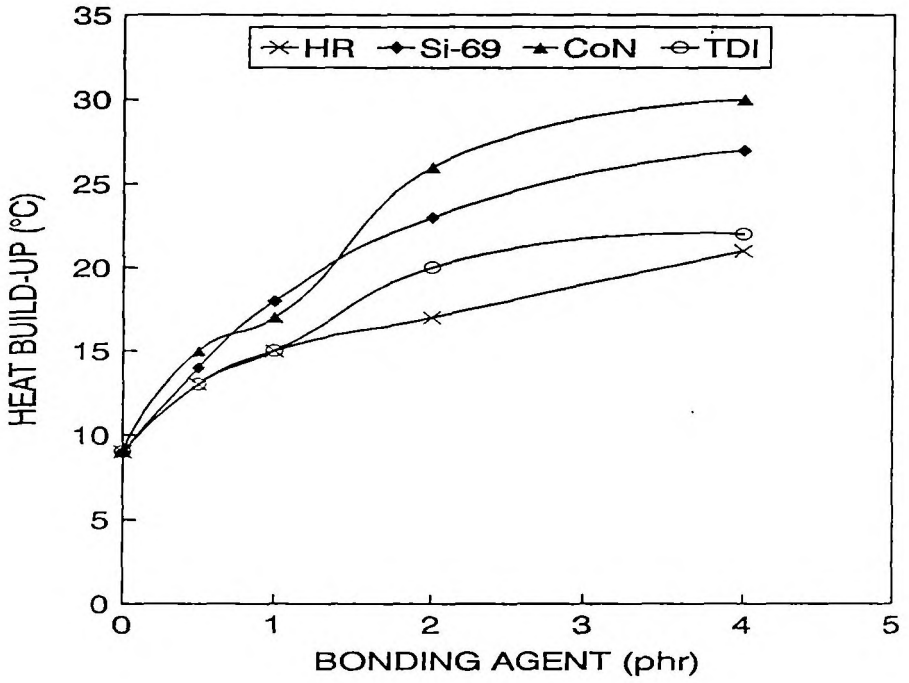
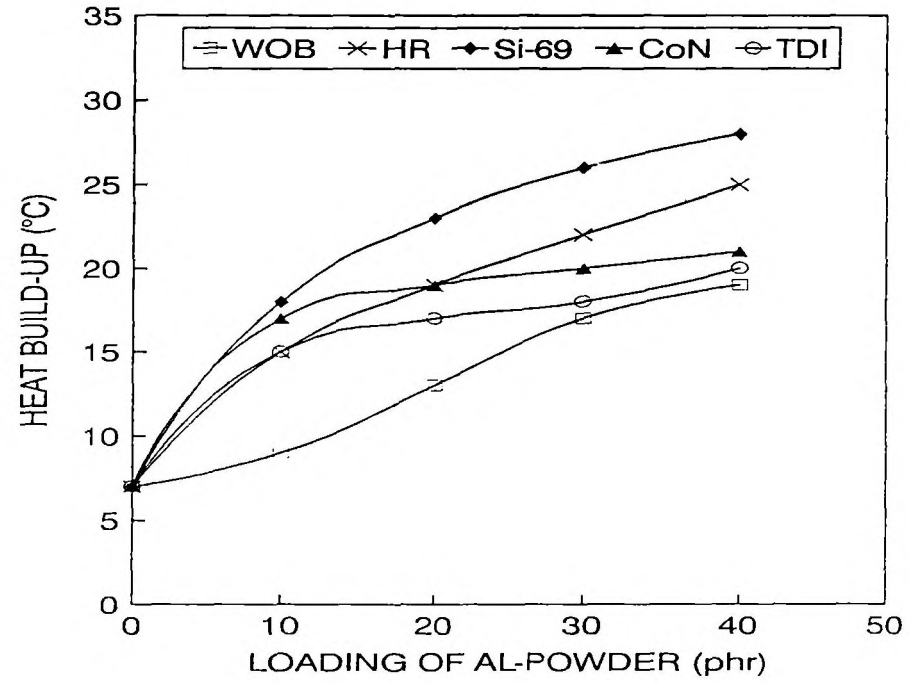


Figure III.5. Variation in elongation at break as a function of (a) the amount of bonding agents on natural rubber-aluminium powder (10 phr) composites and (b) the amout of aluminium powder in NR

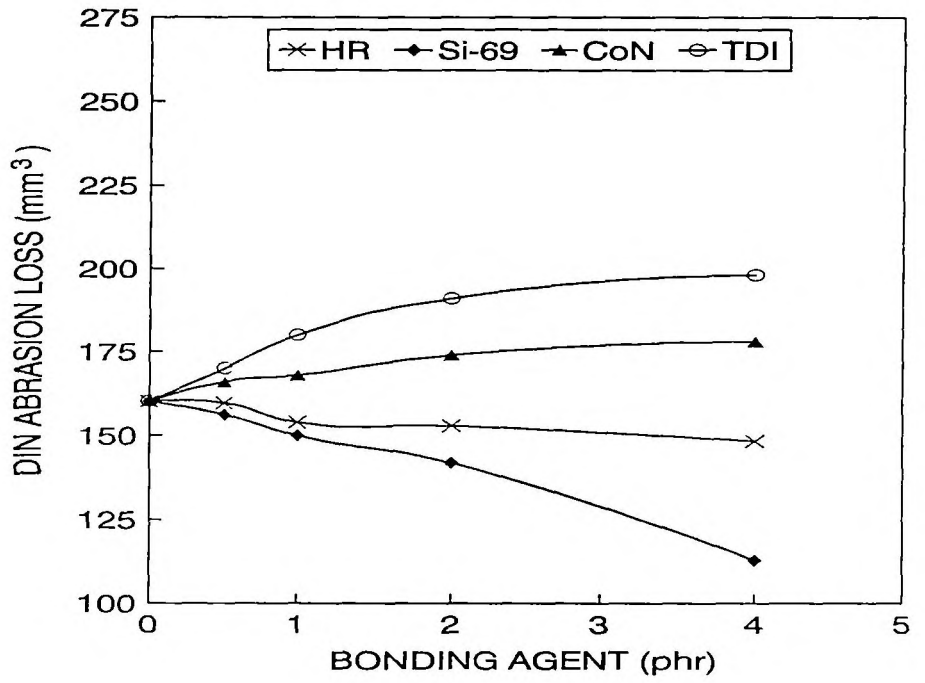


(a)

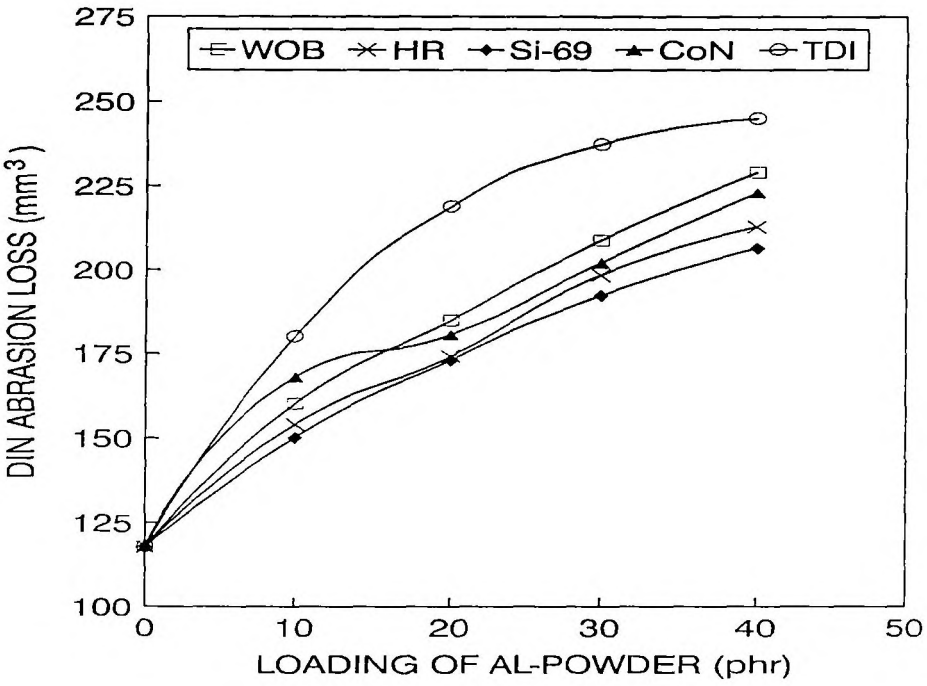


(b)

Figure III.6. Variation in heat build-up as a function of (a) the amount of Bonding agents on natural rubber - aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR



(a)



(b)

Figure III.7. Variation in DIN abrasion loss as a function of (a) the amount of bonding agents on natural rubber-aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR

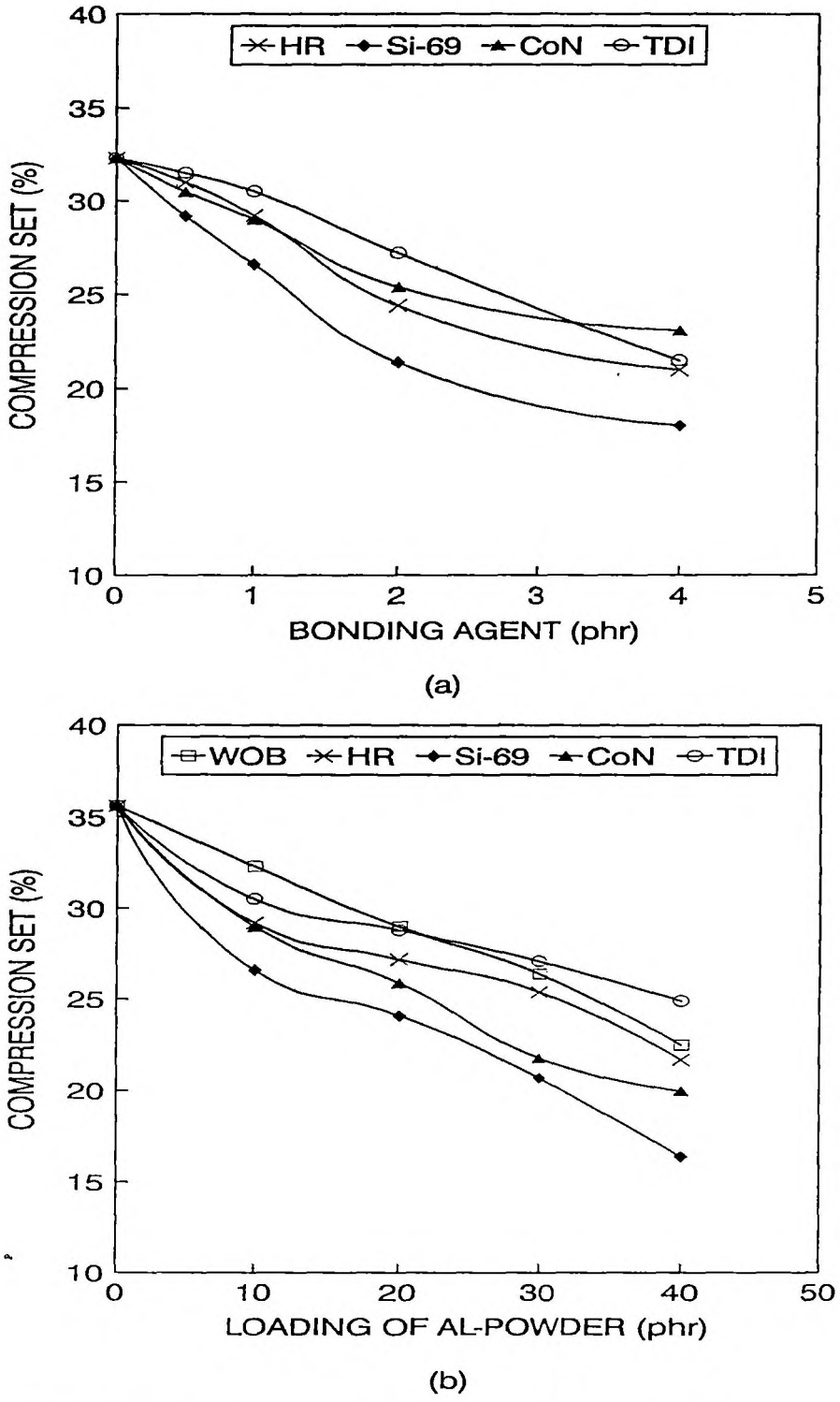
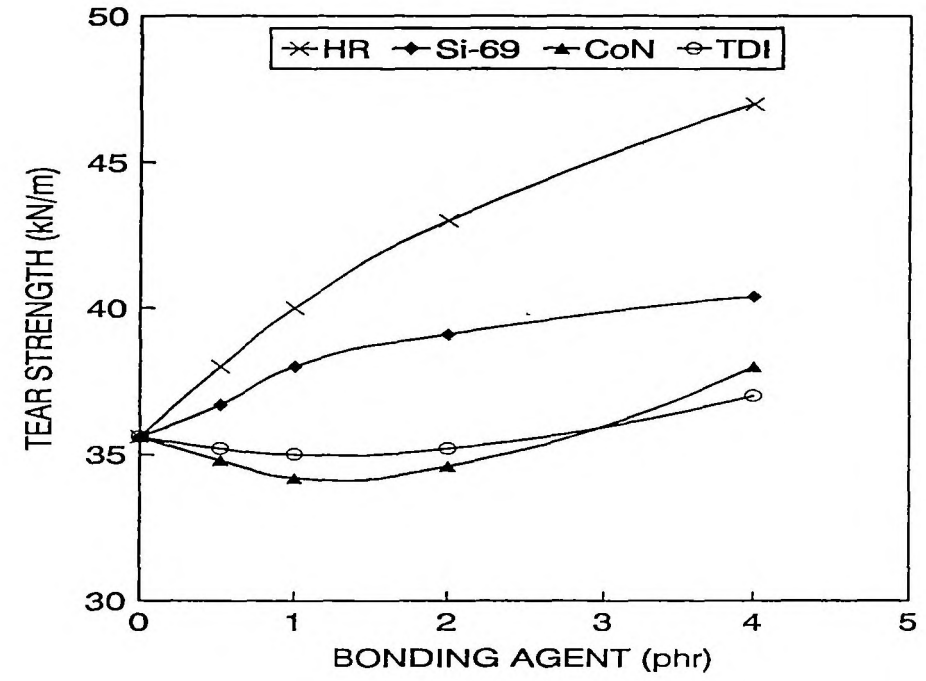
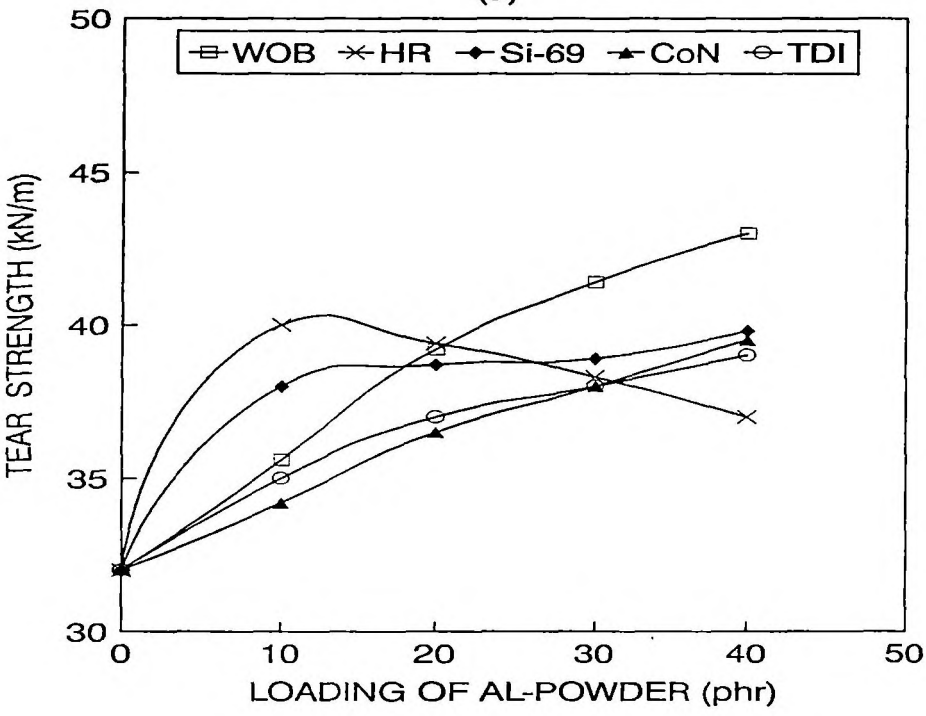


Figure III.8. Variation in compression set as a function of (a) the amount of bonding agents on natural rubber-aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR

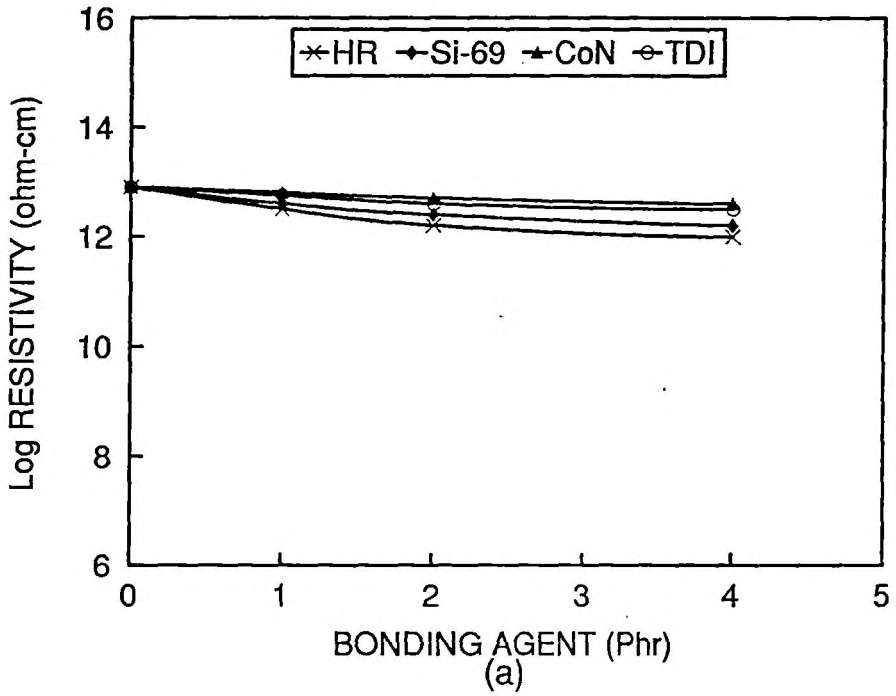


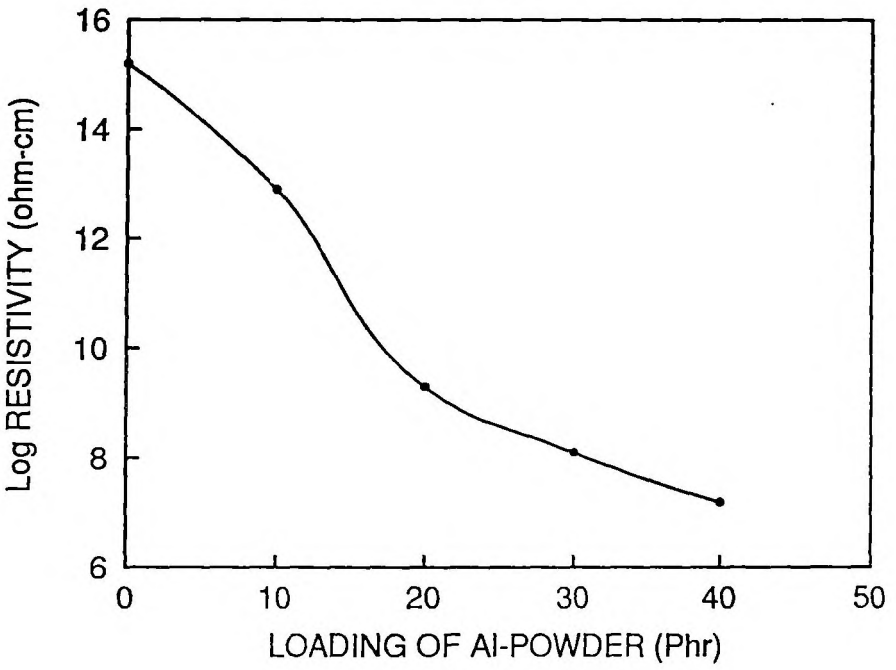
(a)



(b)

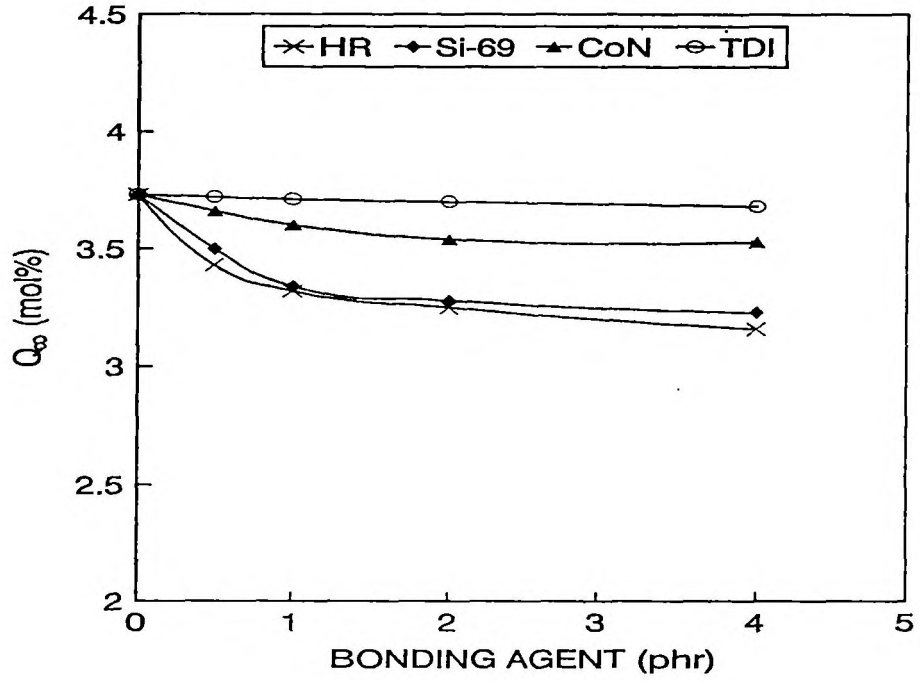
Figure III.9. Variation in tear strength as a function of (a) the amount of bonding agents on natural rubber aluminium powder(10 phr) composites and (b) the amount of aluminium powder in NR



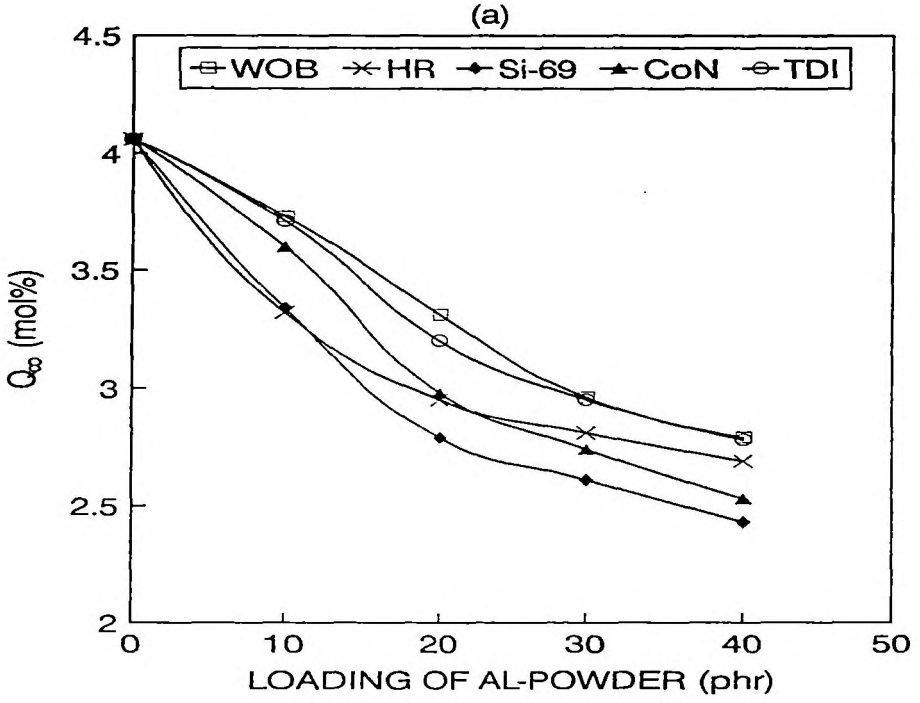


(b)

Figure III.10. Volume resistivity of NR-aluminium powder composites as a function of (a) the amount of bonding agent and (b) the amount of aluminium powder without bonding agent



(a)



(b)

Figure III.11. Variation in equilibrium swelling as a function of (a) the amount of bonding agents on natural rubber – aluminium powder (10 phr) composites and (b) the amount of aluminium powder in NR [solvent – Toluene at 27°C]

Cobalt naphthenate is not very effective in minimizing the abrasion loss whereas TDI increases the abrasion loss. As the loading of aluminium powder increases the abrasion loss also increased, which is due to the higher particle size of aluminium powder used in this study. This increase in abrasion loss can be reduced by the addition of HR or Si-69 (Figure III.7b).

The compression set of aluminium powder filled natural rubber composites in presence of various bonding agents is shown in Figure III.8. At a given loading of aluminium powder (10 phr) the compression set values decrease by the addition of bonding agent. The adhesion of natural rubber to the filler is maximum with Si-69 and least with CoN. At higher loading of aluminium powder, the compression set values decreases by the addition of the bonding agents, especially with Si-69. Normally as the filler content in composite increases, the compression set values also increase due to polymer dilution effect. But in the case of natural rubber-aluminium powder composites the compression set values decreased with increase of aluminium powder content. As the aluminium powder content increases the crosslink density also increases due to the increased thermal conductivity. Thus the decrease in compression set values of the composites containing the bonding agent may be due to the combined effect of better rubber-filler adhesion and higher crosslink density achieved in these composites. Among the bonding agents used Si-69 is the most effective one in reducing the compression set values. Tear strength values of the composites are given in Figure III.9. At 10 phr loading of aluminium powder, HR and Si-69 show high tear strength and this effect is more pronounced with the former.

The volume resistivity of aluminium powder filled natural rubber composites are shown in Figure III.10. The volume resistivity is found to be decreased as the loading of aluminium powder (Figure III.10b). At 10 phr

loading of aluminium powder, the presence of bonding agents decreased the resistivity values (Figure III.10a). The maximum decrease is with HR system followed by Si-69. The results showed that improvement in adhesion between rubber and aluminium powder would increase the conductivity (which is the inverse of resistivity) of these composites.

III.4. Effect of Bonding Agents on Equilibrium Swelling

The swelling of these composites was conducted in toluene at 27°C. The equilibrium swelling values give an idea about the degree of crosslinking in the composites. The lower the equilibrium swelling (Q_∞) value, the greater the extent of crosslinking. Figure III.11 shows the Q_∞ values of natural rubber-aluminium powder composites in presence of various bonding agents. At a given loading of aluminium powder (10 phr) the equilibrium swelling decreases as the amount of bonding agent increases, which follows the order, HR system > Si-69 > CoN > TDI. At higher loadings of aluminium powder this order is no more retained, but all the bonding agents decreased equilibrium swelling of the composites. Equilibrium swelling values can also be taken as a measure of adhesion between polymer and the filler as reported by Varghese *et al.* [5]. In NR-aluminium powder composites, the decreased swelling in presence of bonding agents can also be due to the improved adhesion. A strong polymer-filler interaction reduces the voids at the interface which, in turn, leads to less solvent pockets.

III.5. Conclusions

The effects of various bonding agents on the mechanical properties of aluminium powder filled natural rubber composites were studied. The

various bonding agents used were hexamethylene tetramine-resorcinol (HR) system, bis [3-(triethoxysilyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI). Addition of aluminium powder increased the Shore A hardness of NR-vulcanizates and the bonding agent further increased the hardness value, due to the improved natural rubber-aluminium powder adhesion as evident from the reduced swelling in toluene. At low loading of aluminium powder (10 phr) the addition of HR and Si-69 increased the rebound resilience whereas CoN and TDI caused a decrease in resilience. The heat build-up values were increased by the addition of the bonding agents. The compression set values decreased by the incorporation of aluminium powder due to the increase in degree of crosslinks formed through improved thermal conductivity. The addition of bonding agents further reduced the compression set values, and Si-69 was found to be the most effective among the bonding agents used. At low loading (10 phr) of aluminium powder the bonding agents increased the tensile strength in the order, Si-69 > HR > TDI > CoN. At higher aluminium powder loading, along with bonding agents, a reversion in tensile strength was obtained, around 20 phr aluminium loading after attaining the maximum value.

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CHAPTER IV

ASSESSMENT OF ADHESION IN NATURAL RUBBER-ALUMINIUM POWDER COMPOSITES BY EQUILIBRIUM SWELLING

Result of this chapter is published in the Journal of Applied Polymer Science, 70, 2427, 1998

Conducting polymer composites made by the incorporation of metal powders into polymers have become an emerging group of engineering materials suitable for a number of applications. In metal powder filled systems, as we discussed in chapter III, the major problems are non-uniform dispersion of the powder and poor adhesion between the polymer and the filler surfaces. The non-uniform dispersion of the discrete phase in the matrix, results in fluctuations of composite properties [1-3]. Partial surface modification of the filler by a suitable coupling agent reduces this problem by enhancing surface interaction between the two phases. Many coupling agents are available for this application and among these, silane coupling agents [4], titanate coupling agents [5] and chromium (III) fumarato compounds [6] have been found to form strong assemblies. Better adhesion strength in these cases has been explained by a coupling mechanism through interfacial diffusion and interpenetrating crosslinking networks. Earlier works done in this field are already discussed in Chapter I.

To measure the adhesion in rubber composites many techniques such as H-block and strip adhesion have been used. Although these measurements gave a good relative indication of adhesion, the real effect was overshadowed by the time-dependent nature of the viscoelastic materials. Equilibrium swelling in solvents is another technique that has been used to assess rubber-filler adhesion, because filler-if bonded-is supposed to restrict the swelling of the elastomers. Swelling of rubber vulcanizates in a wide range of solvents has been studied by Whitby and colleagues [7]. The

sorption and transport of organic solvents by polymer membranes have been studied extensively by Aminabhavi *et al.,* [8-9]. Unnikrishnan and Thomas [10] studied the transport of aromatic hydrocarbons through the natural rubber vulcanizates with different vulcanizing systems. Kraus [11] determined the degree of cure in particulate filler reinforced vulcanizates by the swelling method. Lorentz and Parks [12] also investigated the restriction from swelling exerted by a filler using carbon black in NR vulcanizates. Based on swelling measurements, Parks [13] reported that NR vulcanizates loaded with brass powder showed an increase in crosslink density, indicating an interaction or bonding between rubber and brass.

In this chapter, the equilibrium swelling was evaluated as a means to measure the degree of adhesion between NR and aluminium powder, with and without the presence of hexa-resorcinol-silica bonding system. Efforts were also made to investigate the effect of different types of crosslinking systems on the phenomenon of diffusion and adhesion. NR was vulcanized by four vulcanizing systems viz. dicumyl peroxide (DCP), conventional (CV), efficient (EV) and a mixture of sulphur and dicumyl peroxide (mixed). The formulations used are given in Table IV.1. The quantity of resorcinol, silica and hexa was varied according to the filler content. To study the effect of different vulcanizing systems on diffusion, the samples were cured to the extend that all of them developed the same rheometric torque [10] (40 dNm). Since torque is proportional to the crosslink density, it is assumed that all the samples have nearly the same crosslink density. However this assumption is not always true in the absolute sense, when we compare samples with different crosslinking systems. Hence, samples were cured also to their optimum cure time (t_{90}) and subjected to swelling measurements. The experimental details of swelling studies are given in Chapter II.

Table IV.1 Formulations of mixes

Ingredients	DCP			MIXED			EV			CV						
	A	E	I	D	H	L	C	G	K	B	F	J	F_2	J_2	F_3	J_3
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	-	-	-	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	-	-	-	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
MOR	-	-	-	0.6	0.6	0.6	1.5	1.5	1.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulfassan-R	-	-	-	-	-	-	1.0	1.0	1.0	-	-	-	-	-	-	-
DCP	4.0	4.0	4.0	1.5	1.5	1.5	-	-	-	-	-	-	-	-	-	-
Sulphur	-	-	-	2.5	2.5	2.5	0.6	0.6	0.6	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Al-powder	-	10	10	-	10	10	-	10	10	-	10	10	25	25	50	50
Resorcinol	-	-	2.0	-	-	2.0	-	-	2.0	-	-	2.0	-	5	-	10
Silica	-	-	2.0	-	-	2.0	-	-	2.0	-	-	2.0	-	5	-	10
Hexa	-	-	0.75	-	-	0.75	-	-	0.75	-	-	0.75	-	1.88	-	3.75

TDQ - 2,2,4-trimethyl 1,2-dihyrdoquinoline MOR - Morpholine benzthiazyl sulfenamide Al-powder - Aluminium Powder
Sulfassan-R - 4,4'-dithiodimorpholine DCP - Dicumyl peroxide Hexa - Hexamethylene tetramine.

The swelling studies were conducted in a series of aromatic (ie., benzene, toluene, xylene and mesitylene) and aliphatic (*n*-pentane, *n*-hexane and *n*-heptane) hydrocarbons.

IV.1. Effect of Aluminium Powder on Cure Characteristics

Rheometric data of aluminium powder loaded natural rubber compounds containing conventional vulcanizing systems are shown in Figure IV.1. Aluminium powder incorporation causes a decrease in scorch time and optimum cure time and an increase in maximum torque. The cure characteristics are presented in Table IV.2.

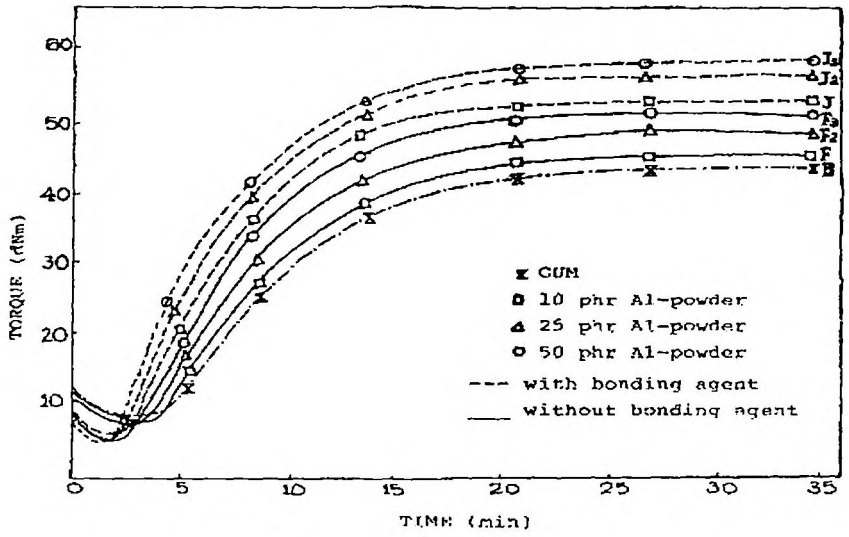


Figure IV.1. Rheometric data of aluminium powder loaded natural rubber composites containing conventional vulcanizing systems.

Westlinning and Wolff treated the rheometric data in terms of α_F values to describe the rubber-filler interaction. The α_F is given as

$$\alpha_F = [\Delta L_F/\Delta L_g)-1]/w \qquad \ldots\ldots\ldots \text{(IV.1)}$$

where L_F and L_g stand for torque measured with filled stock and gum stock, respectively and w represents the weight of the filler. Figure IV.2 shows the Westlinning plot, which indicates that the aluminium powder promotes or accelerates the crosslinking process and the effect is more pronounced in presence of hexa-resorcinol-silica as the bonding system.

Table IV.2. Cure characteristics

Mixes	Max. Torque (dNm)	Min. Torque (dNm)	Optimum Cure Time at 150°C (min)	Cure Time for 40 dNm at 150°C (min)
A	42	14	26.5	40.0
E	42	13	27.5	33.0
I	47	12	30.0	27.0
B	43	8	16.0	17.0
F	45	7	16.0	15.5
J	52.5	8	13.5	8.5
C	44	5	3.5	3.5
G	46	4	3.5	3.5
K	49	3	2.5	2.5
D	47	10	14.0	12.0
H	47	9	13.5	12.0
L	56	6	13.5	8.0
F_2	47.8	6	15.0	12.0
J_2	55.5	6.5	13.0	8.5
F_3	52	4	14.5	10.5
J_3	59.8	4	13.5	8.0

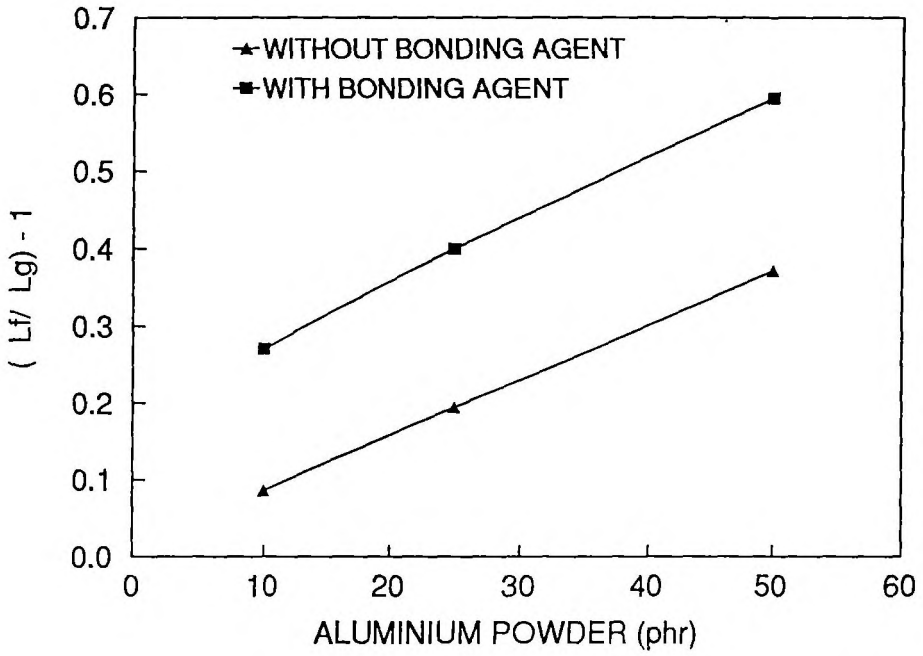


Figure IV.2. Westlinning plots of rheometric data. Effect of aluminium Powder with and without bonding agent

IV.2. Effect of Aluminium Powder on Sorption and Diffusion

IV.2.1. Type of vulcanization

The sorption curves were obtained by plotting Q_t, mol per cent solvent uptake per 100g of polymer against square root of time. The experiments were carried out in benzene, toluene, xylene, mesitylene, n-pentane, n-hexane and n-heptane at 27^0C. Since, all the solvents followed the same diffusion pattern as evident from the shape of sorption curves, the discussion is limited to the diffusion of toluene. It is seen from the sorption curves that in each system, viz. DCP (mixes A, E and I), CV (mixes B, F and J), EV (mixes C, G and K), mixed (mixes D, H and L) the gum compounds absorbed the maximum amount of solvent at equilibrium swelling (Figures IV.3a. – IV.3d.). This was expected since there is less restriction for the penetrant to diffuse into the vulcanizate. The Q_∞ values as from Table IV.3

follow the order DCP < EV < mixed < CV for the gum samples, which may be due to the different types of crosslinks. i.e. polysulphidic linkage in CV, polysulphidic along with C-C linkage in mixed, predominantly mono or disulphidic in EV and the C-C bonds in DCP. For the composites containing aluminium powder with and without bonding agents, the above order is no more retained. This was due to the effect of aluminium powder towards different vulcanizing systems. The same trend was obtained when the sorption experiments were conducted using samples cured to their respective optimum cure time.

The decreased swelling in filled polymeric systems may results from one or more of the following reasons [14]. (i) The filler may cause an increase in crosslinking efficiency of the vulcanizing agent, thus leading to additional polymer to polymer crosslinks; (ii) the presence of filler may enhance the polymer to polymer crosslinks or physical chain entanglements (or both), which restrict swelling of the rubber; (iii) the filler may alter the affinity of the swelling agents with the rubber; (iv) the filler may restrict the swelling of the rubber because of adhesion of rubber to the filler surface either by physical interactions or through the formation of rubber to filler bonds. The presence of bonding agents again complicates the system and may affect all these factors. In the present case the loading of aluminium powder is kept constant and the compound is cured to the same level in such a way that all of them develop the same rheometric torque. Thus the qualitative measurement of the enhanced adhesion in presence of a bonding agent in a filler-rubber composite is reasonable.

Table IV.3. Amount of solvent sorbed at equilibrium swelling (27°C) in mol%

Solvents	Cure system	Gum	Unbonded	Bonded
Benzene	DCP	4.40	4.28	3.96
	CV	5.21	4.78	3.86
	EV	4.50	4.06	3.82
	Mixed	4.71	4.52	4.36
Toluene	DCP	4.07	3.73	3.55
	CV	4.64	4.25	3.42
	EV	4.09	3.51	3.36
	Mixed	4.24	4.01	3.77
Xylene	DCP	3.77	3.55	3.44
	CV	4.20	3.87	3.43
	EV	3.81	3.34	3.24
	Mixed	3.99	3.61	3.49
Mesitylene	DCP	2.79	2.65	2.53
	CV	3.26	2.95	2.47
	EV	2.81	2.57	2.47
	Mixed	3.08	2.86	2.75
Pentane	DCP	1.42	1.30	1.29
	CV	1.88	1.68	1.38
	EV	1.50	1.46	1.37
	Mixed	1.68	1.58	1.48
Hexane	DCP	1.58	1.47	1.38
	CV	2.19	1.94	1.57
	EV	1.69	1.66	1.52
	Mixed	2.02	1.85	1.77
Heptane	DCP	1.93	1.84	1.73
	CV	2.69	2.48	2.01
	EV	2.01	2.00	1.92
	Mixed	2.41	2.33	2.23

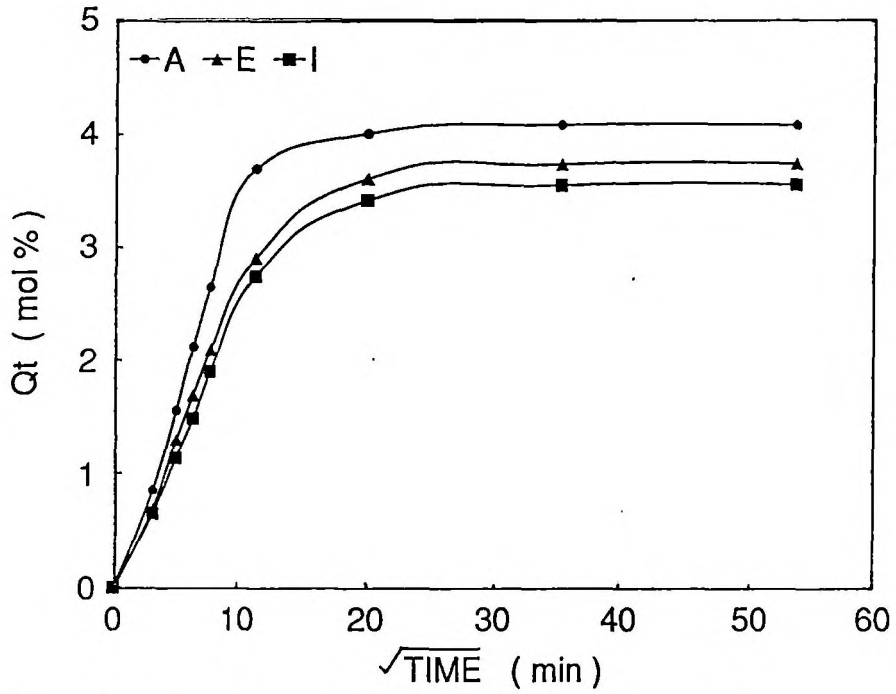


Figure IV.3a. Sorption curves for DCP system in toluene at 27°C

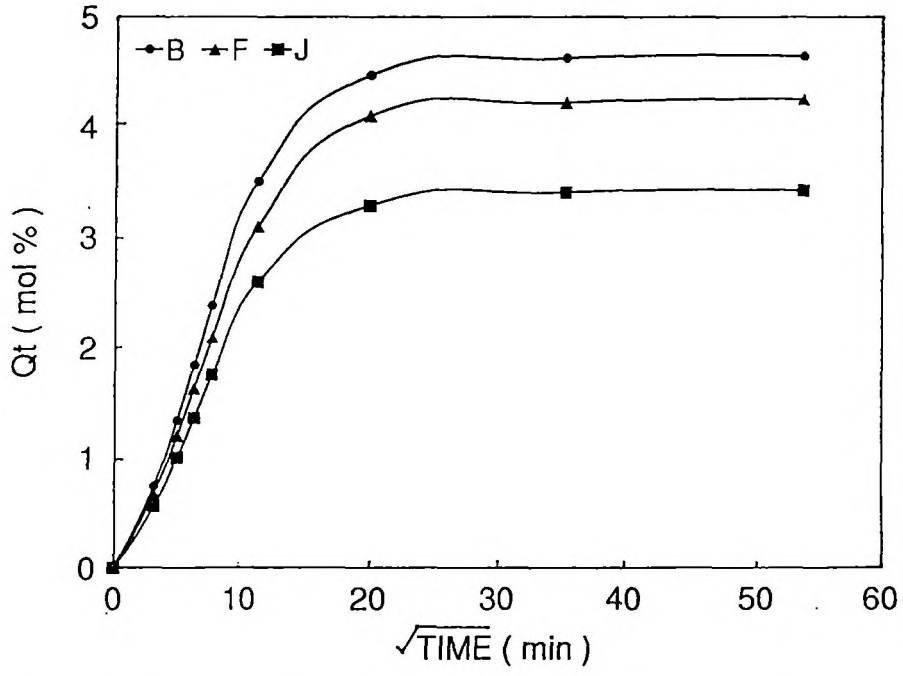


Figure IV.3b. Sorption curves for CV-system in toluene at 27°C

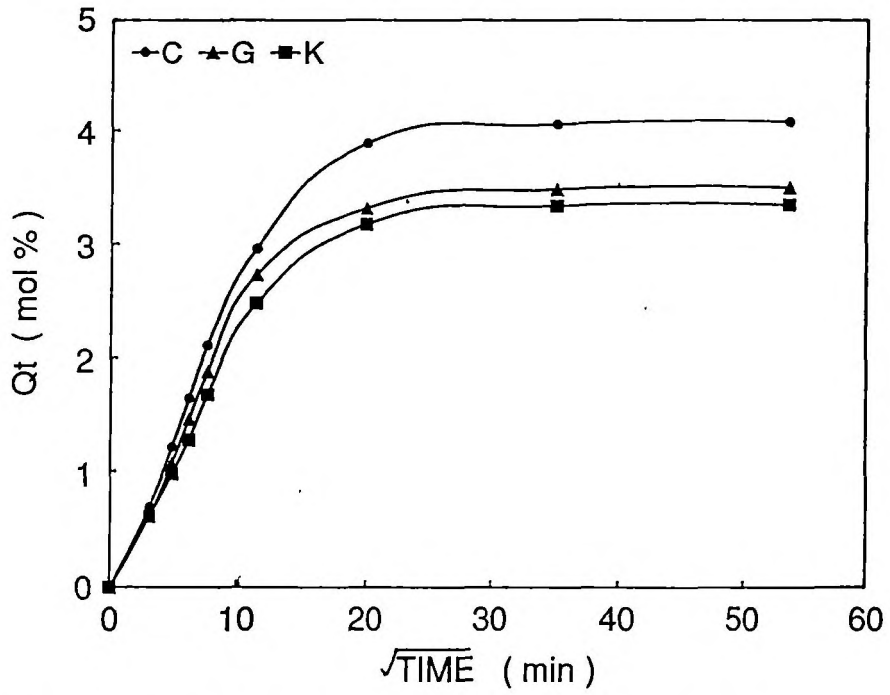


Figure IV.3c. Sorption curves for EV-system in toluene at 27°C

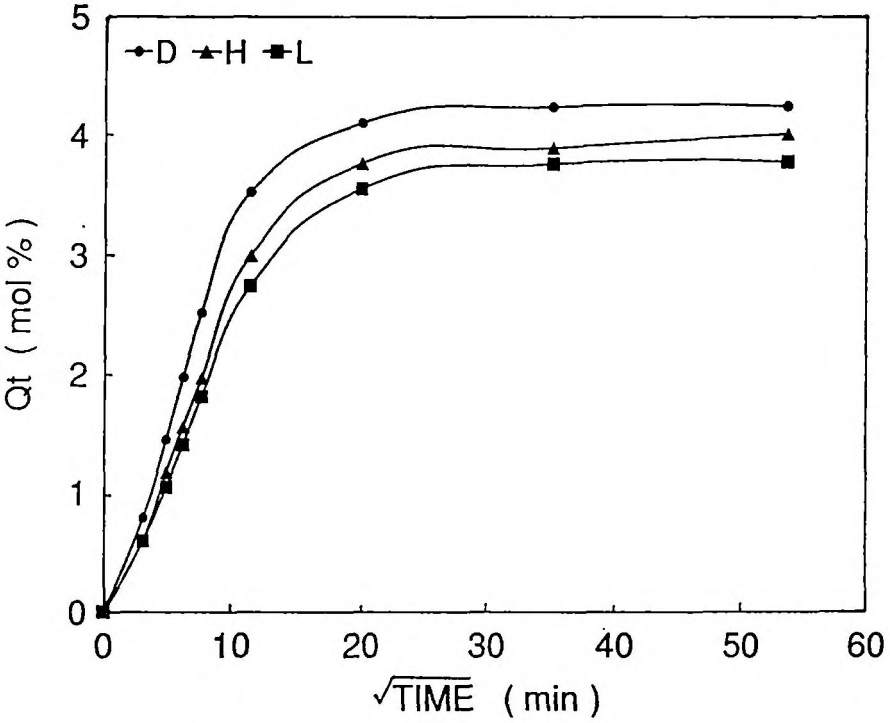


Figure IV.3d. Sorption curves for mixed system in toluene at 27°C

IV.2.2. Effect of bonding agents

The effect of hexa-resorcinol-silica bonding system on the equilibrium swelling with each vulcanizing system is shown in Figure IV.4. In each vulcanizing system, with same loading of aluminium powder the equilibrium sorption is less for composites containing hexa-resorcinol-silica as bonding system compared to composites containing no bonding agents. This is because in unbonded rubber-aluminium powder composites the voids at the interface is higher compared to composites containing bonding agent. The weak interface allows easy entrance of the penetrant, which act as solvent pockets at equilibrium. The effect in reducing the solvent uptake is maximum in conventional vulcanization and this may be due to the presence of excess sulphur present in the conventional system, which may assist the bonding phenomenon. The effect of bonding agent in composites containing higher loadings of aluminium powder, on equilibrium swelling is given in Figure IV.5. At high loadings, only CV-system is selected for further study since the effect of bonding agent is more clear in CV-system and also the conventional vulcanization is widely used for vulcanization. As the loading of metal powder increased, the equilibrium sorption of the specimens decreased. This was due to the increased hindrance exerted by the filler and the better heat conduction of the aluminium powder, which causes high crosslinking. The reduction in equilibrium sorption is sharp in the case of bonded composites than unbonded, which shows the improved adhesion on adding hexa-resorcinol-silica bonding system. Another interesting observation is the differences in initial rates of diffusion for different composites. The initial rate of diffusion is faster for composites without bonding agent compared to that containing bonding agent.

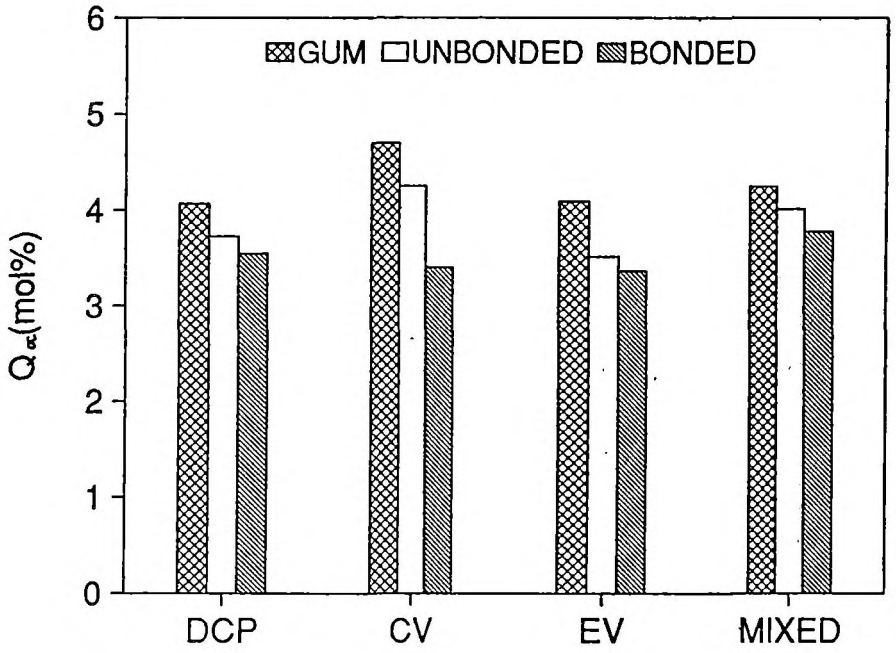


Figure IV.4. Effect of aluminium powder (10 phr) on equilibrium swelling of NR vulcanizates with and without bonding agents (solvent – toluene at 27°C)

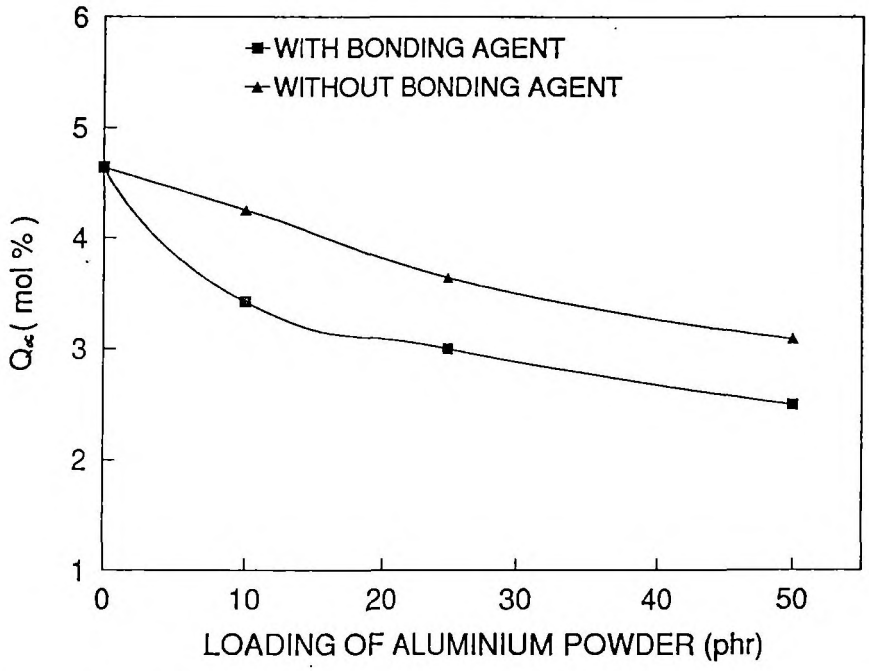


Figure IV.5. Effect of aluminium powder on equilibrium sorption (swelling solvent – toluene at 27°C)

IV.2.3. Effect of penetrant size and temperature

The pattern of the diffusion curves obtained for all the solvents is similar. However, as the penetrant size increased the uptake (Q_t) decreased in the case of aromatic solvents and whereas it increased in the case of aliphatic solvents (Figure IV.6a. and IV.6b.). This type of absorption was also reported by Salmon and Van Amerongen [15].

The temperature dependence of the diffusion process is investigated for the temperature range 27 to 70 ^{0}C, which clearly supported the fact that temperature activates the diffusion process (Figure IV.7). The rubber-solvent interaction parameter χ has been calculated using the equation [16].

$$\chi = \frac{(d\phi/dT)\{[\phi/(1-\phi)+ N\ln(1-\phi)]+N\phi\}}{2\phi(d\phi/dT)-\phi^2 N(d\phi/dT)-\phi^2/T} \qquad \ldots\ldots\ldots \text{(IV.2)}$$

where ϕ is the volume fraction of rubber in the solvent swollen sample at equilibrium swelling and N is calculated from ϕ using,

$$N = \frac{\phi^{2/3} - 2/3}{\phi^{1/3} - 2\phi/3} \qquad \ldots\ldots\ldots \text{(IV.3)}$$

These values are listed in Table IV.4. In each system the χ values are highest for the bonded composites suggesting the lowest rubber-solvent interaction in the bonded composites.

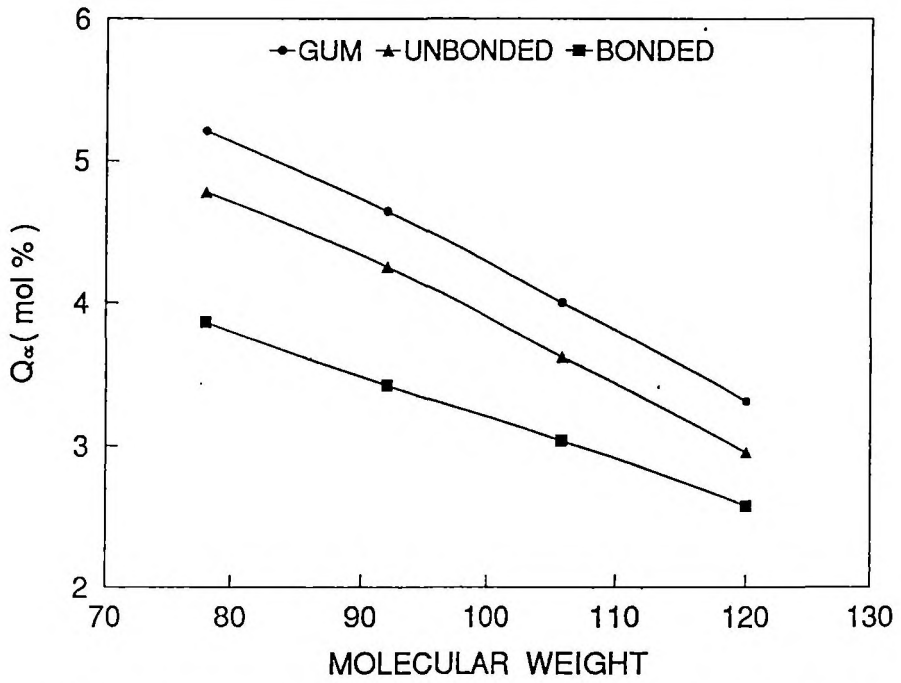


Figure IV.6a. Dependence of maximum mol% uptake on molecular weight of solvent on CV system for aromatic solvents

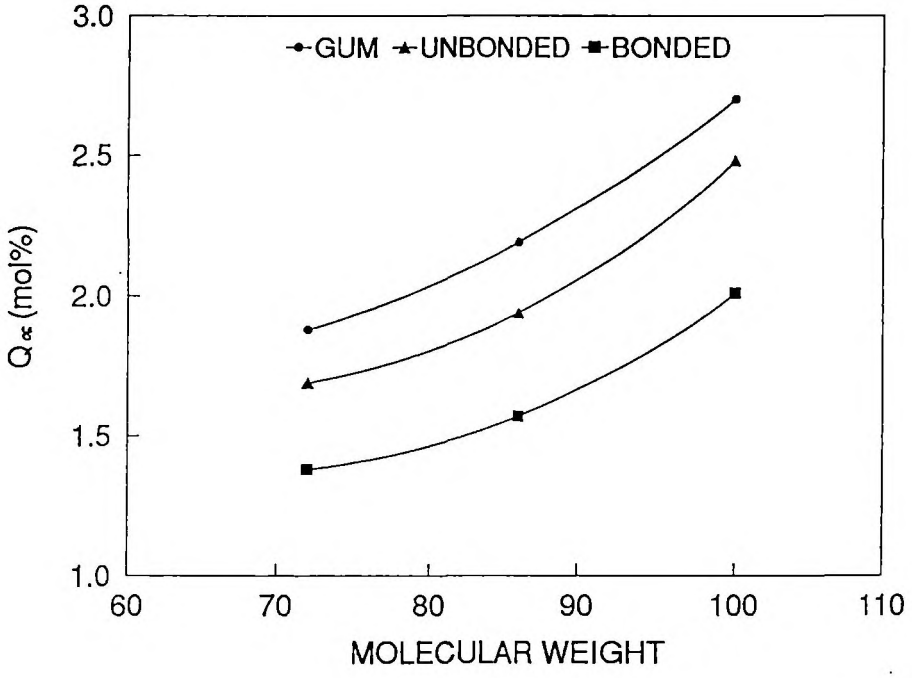


Figure IV.6b. Dependence of maximum mol% uptake on molecular weight on CV system for aliphatic solvents

The enthalpy and entropy of these composites were calculated using Van Hoffs equation,

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303RT} \qquad \ldots\ldots\ldots \text{(IV.4)}$$

where K_s is the maximum mole per cent uptake of the solvent. The values of ΔH and ΔS are given in Table IV.4. The negative sign of entropy of sorption data suggests the retainment of liquid structure of solvent molecules even in the sorbed state [16].

Table IV.4. Values of diffusion constant (D), permeation coefficient (P), interaction parameter (χ) and thermodynamic functions (swelling solvent, toluene)

System		$D \times 10^7$ cm^2/sec	$P \times 10^7$ cm^2/sec	χ	ΔH kJ/mol	ΔS Jmol/K
DCP	Gum	9.39	18.15	0.366	0.968	-23.41
	Unbonded	8.56	15.76	0.379	0.998	-24.39
	Bonded	8.31	14.42	0.456	0.919	-23.45
CV	Gum	6.20	16.74	0.359	0.995	-24.28
	Unbonded	4.84	11.99	0.379	0.935	-23.13
	Bonded	4.59	9.25	0.414	0.901	-25.06
EV	Gum	7.65	15.41	0.386	0.899	-23.56
	Unbonded	5.67	11.37	0.413	0.888	-24.89
	Bonded	5.55	10.65	0.424	0.899	-25.08
Mixed	Gum	6.33	15.28	0.377	0.893	-23.30
	Unbonded	4.69	10.94	0.388	0.889	-23.98
	Bonded	4.58	10.25	0.443	0.872	-24.33

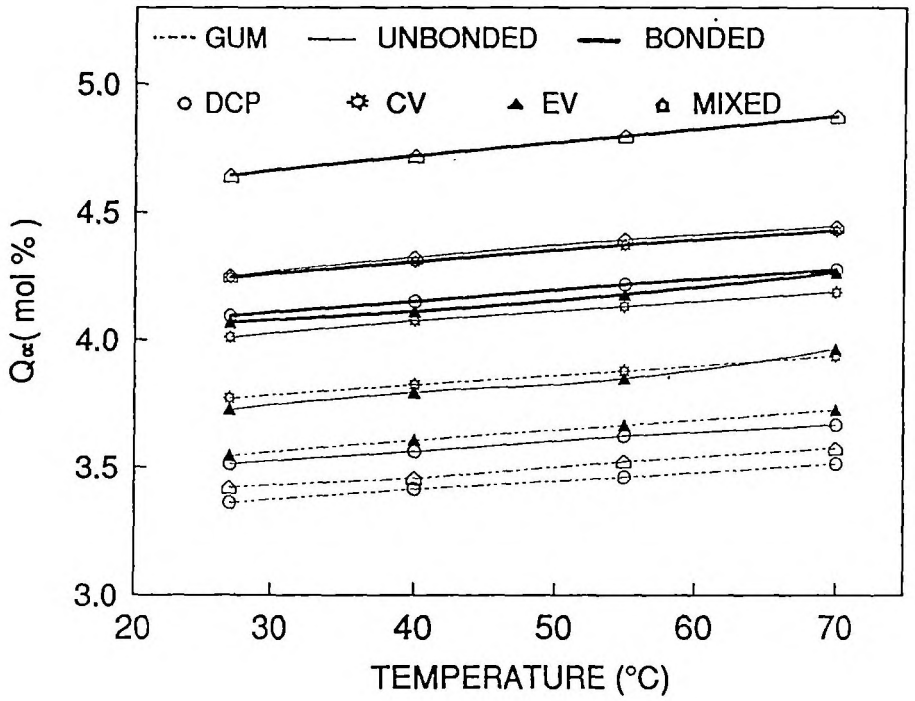


Figure IV.7. Dependence of temperature on the maximum uptake of toluene

IV.3. Analysis of Sorption Data

From the initial linear portion of the sorption curves, the effective diffusivity 'D' of the polymer-solvent system was calculated using the following equation [17].

$$D = \pi (h\theta/4Q_\infty)^2 \qquad \ldots\ldots\ldots \text{(IV.5)}$$

where θ is the slope of the linear portion of the sorption curve and h is the initial thickness of the polymer sample. The variation of diffusion depends on the nature of the penetrant molecule, in addition to the different crosslinks present in the polymer. The calculated values of D, given in Table IV.4, indicate that DCP system has the highest value of D and CV has the lowest. Comparing the bonded and unbonded composites, lowest values of D are with the bonded vulcanizates. The permeability coefficient P can be computed from the following equation [18]

$$P = D.S \qquad \text{..... (IV.6)}$$

where 'S' is the solubility or sorptivity, which is the maximum saturation sorption value and has been calculated as

$$S = M_s/M_p \qquad \text{..... (IV.7)}$$

where 'M_s' is the mass of the penetrant at equilibrium swelling and 'M_p' is the mass of the polymer sample. The permeability coefficient shows the net effect of sorption and diffusion process. The values of 'P' are included in Table IV.4, which show that the bonded composites have lower values than the unbonded composites. According to Lorentz and Parks [12]

$$Q_f/Q_g = ae^{-z} + b \qquad \text{..... (IV.8)}$$

where Q is defined as grams of solvent per gram of hydrocarbon and is calculated by

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100 / \text{formula weight}} \qquad \text{..... (IV.9)}$$

The subscripts 'f' and 'g' of the above equation refer to filled and gum vulcanizates respectively. 'z' is the ratio by weight of filler to rubber hydrocarbon in the vulcanizate while 'a' and 'b' are constants. Higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix. Parks [13] also suggested that the value of 1/Q, the degree of crosslinking, could be used to study the adhesion effects. Table IV.5 shows the Q_f/Q_g and 1/Q values for the composites with different vulcanizing systems. The lowest value of Q_f/Q_g in each crosslinking system is for the composites with bonding agent, which confirms that maximum aluminium powder-rubber interaction has occurred when the bonding agent is present in the composite. Among the different crosslinking systems, the CV system

has the highest Q_f/Q_g value and lowest 1/Q value suggesting that hexa-resorcinol-silica, bonding system suits well with aluminium powder in natural rubber.

Table IV.5. Values of 1/Q and Q_f/Q_g, heptane at 27°C

System	Sample	1/Q	Q_f/Q_g
DCP	Unbonded	0.4663	1.044
	Bonded	0.4748	1.025
CV	Unbonded	0.3319	1.041
	Bonded	0.3921	0.846
EV	Unbonded	0.4075	1.085
	Bonded	0.4088	1.081
Mixed	Unbonded	0.3476	1.052
	Bonded	0.3494	1.046

The interaction between rubber and carbon black has been investigated by a number of researchers using a swelling technique. Assuming the swelling to be completely restricted at the rubber-filler interface due to adhesion, Kruas [19] has shown that the degree of restriction on the volume concentration of a reinforcing filler follows an equation of the form,

$$\frac{V_{ro}}{V_{rf}} = 1-[3c(1-V_{ro}^{1/3}) + V_{ro} - 1] \frac{\theta}{1-\theta} \qquad \ldots\ldots\ldots \text{(IV.10)}$$

where 'θ' is the volume fraction of filler and 'c' is a constant characteristic of the filler and indicative of the degree of adhesion.

$$\theta = \frac{\text{Volume of filler}}{\text{Total volume of the vulcanizate}} \quad \ldots\ldots\ldots \text{(IV.11)}$$

V_r is the volume fraction of rubber which was calculated from the equilibrium swelling data using the equation,

$$V_r = \frac{(d - fw)\rho_r^{-1}}{(d - fw)\rho_r^{-1} + A_0\rho_s^{-1}} \quad \ldots\ldots\ldots \text{(IV.12)}$$

where 'd' is the weight after drying out the sample, 'w' is the weight of the swollen sample. 'A_0' is the weight of the absorbed solvent, 'f' is the fraction of the insoluble components and 'ρ_r' and 'ρ_s' are the densities of the rubber and solvent respectively.

Table IV.6 Values of V_{ro}/V_{rf} for the composites, toluene at 27°C

System	Sample	V_{ro}/V_{rf}
DCP	Unbonded	0.9523
	Bonded	0.9145
CV	Unbonded	0.9524
	Bonded	0.7979
EV	Unbonded	0.9303
	Bonded	0.8936
Mixes	Unbonded	0.9800
	Bonded	0.9325

When the above equation is applied to rubber containing reinforcing filler, it is found that V_{rf} of the rubber phase in the swollen gel is always much higher compared to pure gum V_{ro}. So the ratio V_{ro}/V_{rf} decreases with filler

loading. The ratio represents the degree of restriction of the swelling of rubber matrix due to the presence of filler. From Table IV.6, it is seen that in each crosslinking system the lowest V_{ro}/V_{rf} values are for composites with bonding agent, which is associated with enhanced rubber-filler adhesion due to the presence of bonding agent.

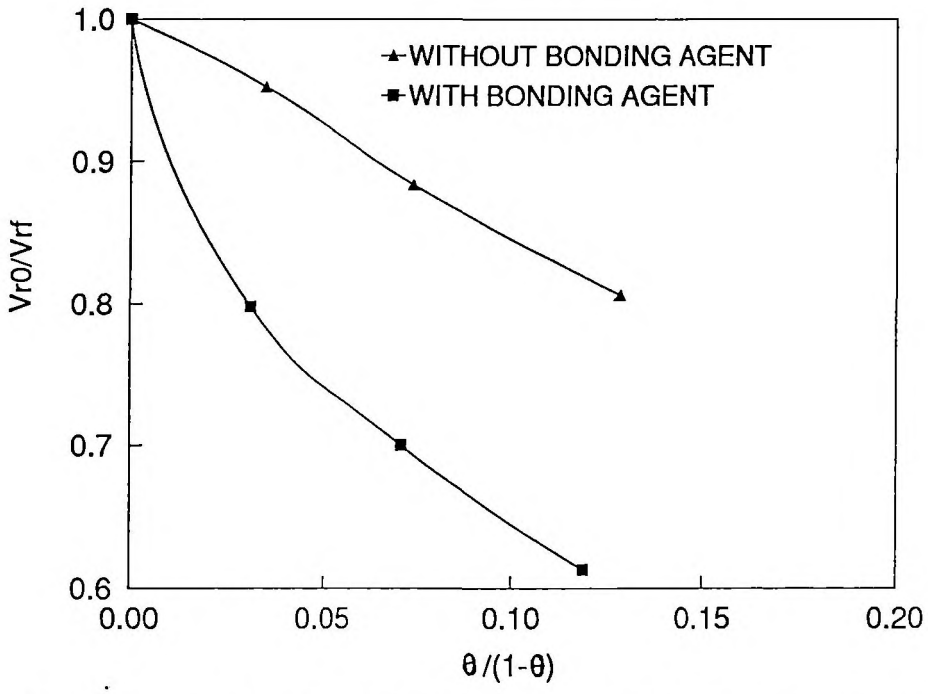
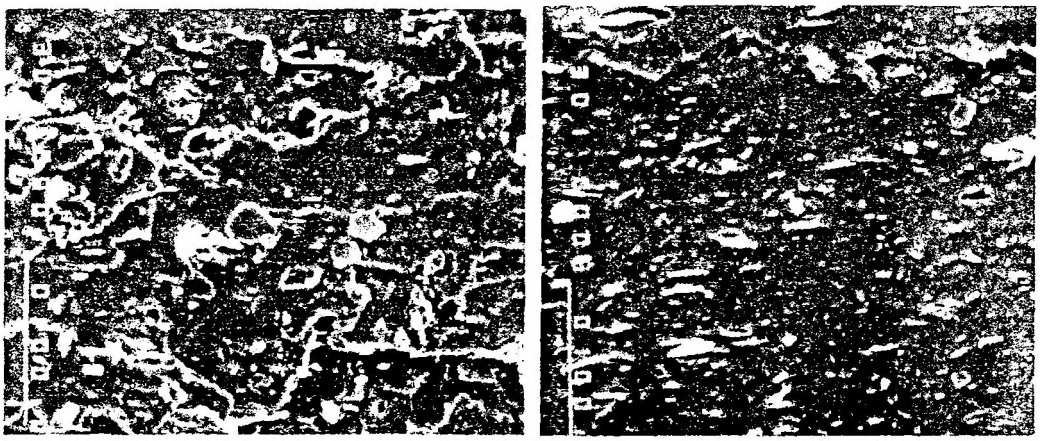


Figure IV.8. Kraus plots of swelling data. Effect of bonding agent on NR-aluminium powder composites

Equation (IV.10) predicts that V_{ro}/V_{rf} should vary linearly with θ/1-θ. At high filler loading the line deviates from linearity. The theory assumes that the filler particles are far enough, so as not to interact with each other. This is obviously not true at higher loading. According to Kraus theory, the slope of the straight line will be a direct measure of reinforcing ability of the filler used. The more the adhesion ability, the more will be the swelling resistance. Negative higher slope values indicate a better adhesion effect.

From Figure IV.8, the composites with bonding agent have higher slope than composites without bonding agent, which shows the increased adhesion. According to this, aluminium powder showed an improved adhesion to the rubber when hexa-resorcinol-silica as a bonding agent.



(a) *(b)*

Figure IV.9. Scanning electron microphotographs (magnification, X1000) of Tensile fractured surface of 10 phr aluminium powder filled NR Vulcanizates (a) having no bonding agent and (b) having bonding agent.

The fractured surfaces of tensile pieces of the composites with and without bonding agent at 10 phr loading of aluminium powder were examined by means of a scanning electron microscope and the photomicrographs are presented in Figures IV.9a and IV.9b. It can be seen from the SEM photographs that with the addition of bonding agent, the aluminium powder is more firmly bonded to the rubber matrix, which gave a smooth surface on failure. Whereas in the unbounded composites the metal powder is seen to exist as loose aggregate which results in a non-uniform rough surface. Moreover the filler particles are found to be more aligned in vulcanizates containing the bonding agent.

IV. 4. Conclusions

The swelling behaviour of aluminium powder filled natural rubber composites influenced the type of crosslinking systems used. The crosslinking system has an important role in the maximum uptake value which is in the order CV system> mixed system>EV system> DCP system for gum composites. However, the order of maximum uptake value changed in composites filled with aluminium powder. In all the samples temperature activates the diffusion process. In all crosslinking systems the maximum uptake for composites containing bonding agent is substantially lower compared to composites without bonding agent, and is more pronounced in CV system. The increased aluminium powder content brings about a greater restriction to swelling and the use of a bonding agent further reduced the swelling considerably. The χ values for the composites indicate that the rubber-solvent interaction decreases when hexa-resorcinol-silica is used as the bonding agent in each crosslinking system, for the aluminium powder filled natural rubber vulcanizates.

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CHAPTER V

PROPERTIES OF NATURAL RUBBER VULCANIZATES CONTAINING ALUMINIUM POWDER IN COMBINATION WITH OTHER FILLERS

Result of this chapter is accepted for publication in Rubber Chemistry and Technology

Fillers are widely used to enhance the performance of rubbers and also to reduce the cost of the material. Properties imparted to the rubber vulcanizates by the addition of fillers depend on the type and the quantity of filler added. The quantity of filler required to impart the maximum property to the vulcanizates varies with type of filler; the reinforcing ones give the maximum property with minimum quantity [1]. The vulcanizate properties also depend on extend of crosslinking and types of crosslinks formed during vulcanization [2,3].

A single material may not meet all the requirements necessary for a potential filler. Since the final performance of the composites is controlled by the properties and proportion of the component materials, the choice of the filler plays a very important role in polymer composites. The use of various fillers in composites has been reviewed by Seymour [4]. The advantage of metal powders over other fillers is that they provide good electrical and thermal conductivity to the composite [5-9]. A large number of variables, viz., size, shape, nature and state of distribution of the filler, adhesion and thermal compatibility of the phases, etc., characterize the system and some of them have strong influence on the properties of the composites. Many research groups [10-14] have made attempts to increase the thermal and electrical conductivity of the polymers by incorporating conductive fillers.

Table V.1a. Base formulation

Ingredients	Quantity (phr)
Natural rubber	100
Stearic acid	1.5
Zinc oxide	5.0
2,2,4-Trimethyl 1,2-dihydroquinoline	1.0
Morpholine benzothiazyl sulfenamide	0.6
Sulphur	2.5
Filler	40

Table V.1b. Sample code and illustrations

H1 - 10 HAF + 30 Al-powder	**G1** - 10 GPF + 30 Al-powder	**A1** - 10 Acetylene black + 30 Al-powder	**S1** - 10 Silica + 30 Al-powder	**C1** - 10 Clay + 30 Al-powder
H2 - 20 HAF + 20 Al-powder	**G2** - 20 GPF + 20 Al-powder	**A2** - 20 Acetylene black + 20 Al-powder	**S2** - 20 Silica + 20 Al-powder	**C2** - 20 Clay + 20 Al-powder
H3 - 30 HAF + 10 Al-powder	**G3** - 30 GPF + 10 Al-powder	**A3** - 30 Acetylene black + 10 Al-powder	**S3** - 30 Silica + 10 Al-powder	**C3** - 30 Clay + 10 Al-powder
H4 - 40 HAF	**G4** – 40 GPF	**A4** - 40 Acetylene black	**S4** - 40 Silica	**C4** - 40 Clay
A - 40 Al-powder				

In this chapter, the effects of aluminium powder on the vulcanization of natural rubber containing various fillers are presented. The fillers selected were high abrasion furnace black (HAF), general purpose furnace black (GPF), acetylene black, china clay and precipitated silica. Formulations used are given in Tables V.1a and V.1b. The total quantity of the filler including aluminium powder is fixed to 40 phr so as to avoid polymer dilution effect.

The fillers are partly and successively substituted by aluminium powder. The details of the instruments and test procedures adopted are given in chapter II. The cure rate index and cure reaction rate constant were calculated from the cure curves and thus the kinetics of vulcanization was studied. Efforts were also made to investigate the reduction in cure time for thick articles by the addition of aluminium powder.

V.1. Effect of Aluminium Powder on Cure Characteristics

The cure characteristics of NR-compounds containing aluminium powder along with other fillers are given in Table V.2. Rheometric induction time (time required for the torque values to increase one unit above the minimum torque) is the time available before the onset of vulcanization. It is clear from Table V.2. that as the aluminium powder contents increases, time required to initiate the vulcanization become low. Cure rate index (which is a direct measure of the cure nature of the rubber compound) values showed an increase with increased loading of aluminium powder. The kinetics of cure reaction is analysed by considering the equation for the kinetics of a first order chemical reaction [15],

$$\ln (a-x) = -kt + \ln a \qquad \ldots\ldots\ldots (V.1)$$

where 'a' is initial reactant concentration, 'x' is consumed reactant at time 't' and 'k' is first order reaction rate constant.

We can follow the rate of crosslink formation by measuring the torque developed, during the vulcanization process. The torque values so obtained are proportional to the modulus of the rubber. So if the change in a physical property such as modulus is measured rather than the change in reactant concentration, the following substitution can be made,

Table V.2. Analysis of rheometric curves

Sample code	Rheometric induction time (min)	Cure rate index (min^{-1})
A	2.0	8.30
H_1	2.0	9.09
H_2	2.25	8.89
H_3	2.5	8.69
H_4	2.5	8.00
G_1	2.0	9.09
G_2	2.25	8.69
G_3	2.5	8.51
G_4	2.5	7.55
A_1	2.0	8.69
A_2	2.0	8.00
A_3	2.0	7.69
A_4	2.0	7.41
S_1	2.25	9.30
S_2	2.15	9.09
S_3	2.75	8.69
S_4	3.0	7.02
C_1	1.75	9.09
C_2	2.75	8.33
C_3	3.0	7.27
C_4	4.0	6.45

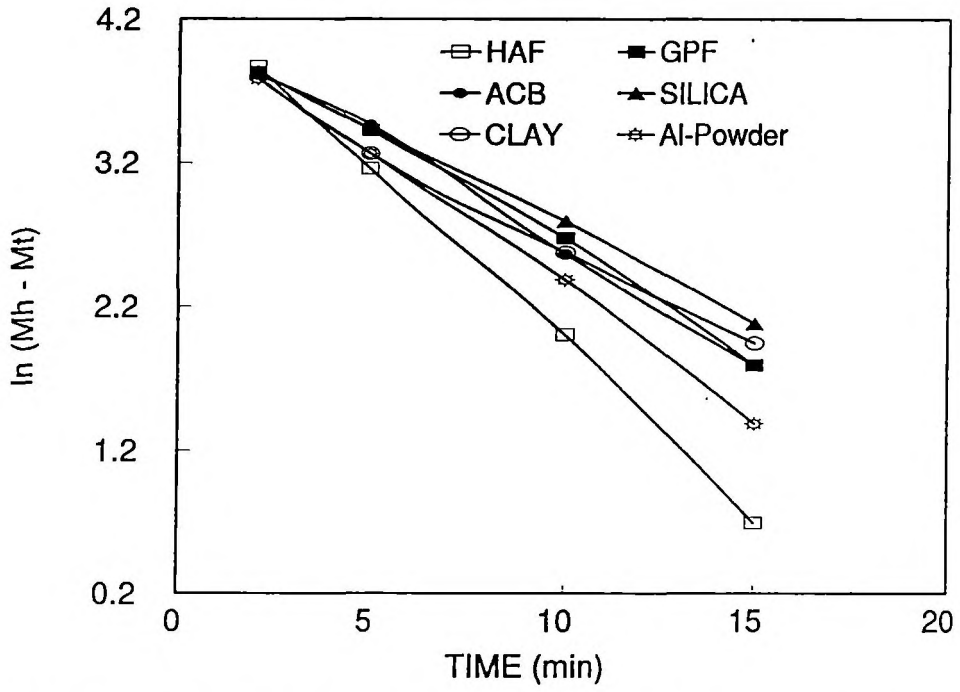

Figure V.1. Kinetic plot for the cure reaction of various filler (40 phr) incorporated natural rubber composites

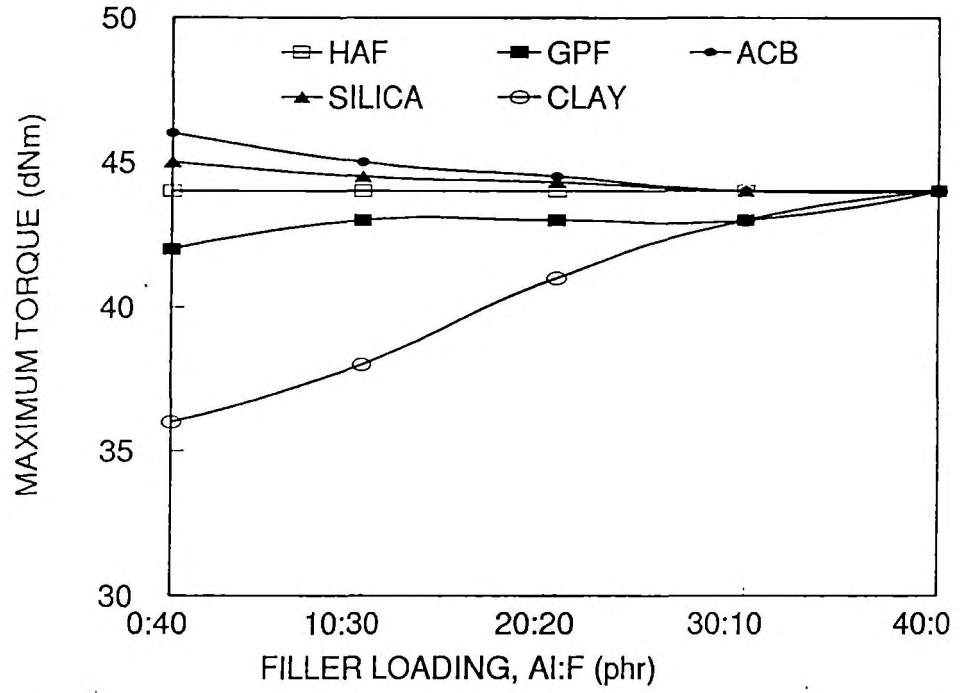

Figure V.2. Effect of aluminium powder substitution on torque values of NR-composites containing various fillers

$$(a-x) = M_h - M_t \qquad \ldots\ldots\ldots \text{(V.2)}$$

$$a = M_h - M_0 \qquad \ldots\ldots\ldots \text{(V.3)}$$

where 'M_h' is the maximum torque, 'M_t' is the torque at time 't', and 'M_0' is the minimum torque. When ln (M_h-M_t) is plotted against, 't', an almost straight-line graph is obtained as shown in Figure V.1, which proves that the cure reaction follows first order kinetics. Figure V.2 shows the effect of aluminium powder substitution on the maximum torque values in presence of various fillers.

V.2. Effect of Aluminium Powder on Mechanical Properties

V.2.1. Hardness and rebound resilience

Shore A hardness of the composites is shown in Figure V.3. It is clear that as aluminium powder substitutes other fillers successively, the hardness increase linearly. Increase in hardness can be due to reinforcement effect of the filler as well as higher extents of crosslinking of the polymeric material. The composite with 40 phr aluminium powder has the highest hardness and is attributed to the higher extents of crosslinking through better heat conduction. Since the particle size of the aluminium powder used is much higher than that of HAF and silica, the contribution to the hardness increase by reinforcement is considered to be lower for aluminium powder. This is also reflected in the higher rebound resilience of the aluminium powder filled composites (Figure V.4). On successive substitution of HAF and acetylene blacks by aluminium powder an increase in resilience value is noted. Resilience of vulcanizates at 40 phr filler loading increased in the order aluminium powder > china clay > GPF > acetylene black > silica > HAF. Normally, for rubber vulcanizates, with increasing reinforcing filler content, its rebound resilience decreases.

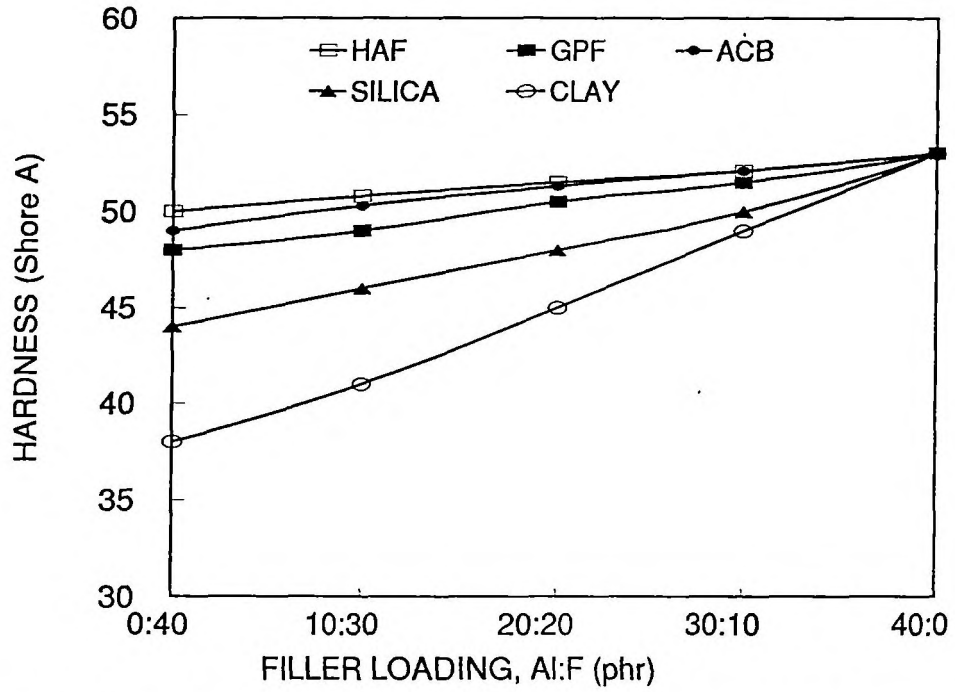

Figure V.3. Variation of hardness with aluminium powder in presence of various fillers

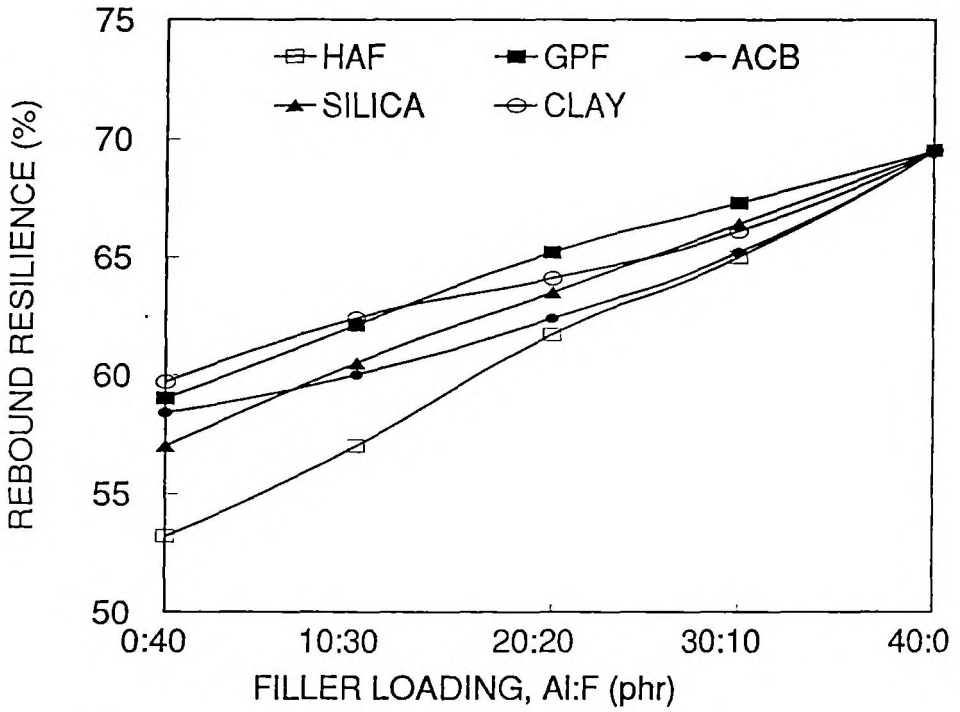

Figure V.4. Variation of resilience with aluminium powder in presence of various fillers

Thus higher hardness value coupled with higher rebound resilience observed for aluminium powder filled composites is mainly due to higher extent of crosslinking achieved through better thermal conductivity of the aluminium powder.

V.2.2. Tensile and tear properties

Table V.3 shows the variation of tensile properties with various filler combinations. At equal loading (40 phr) HAF and acetylene black filled vulcanizates have higher tensile strength compared to the aluminium powder filled one, whereas clay filled composites have lower tensile strength values.

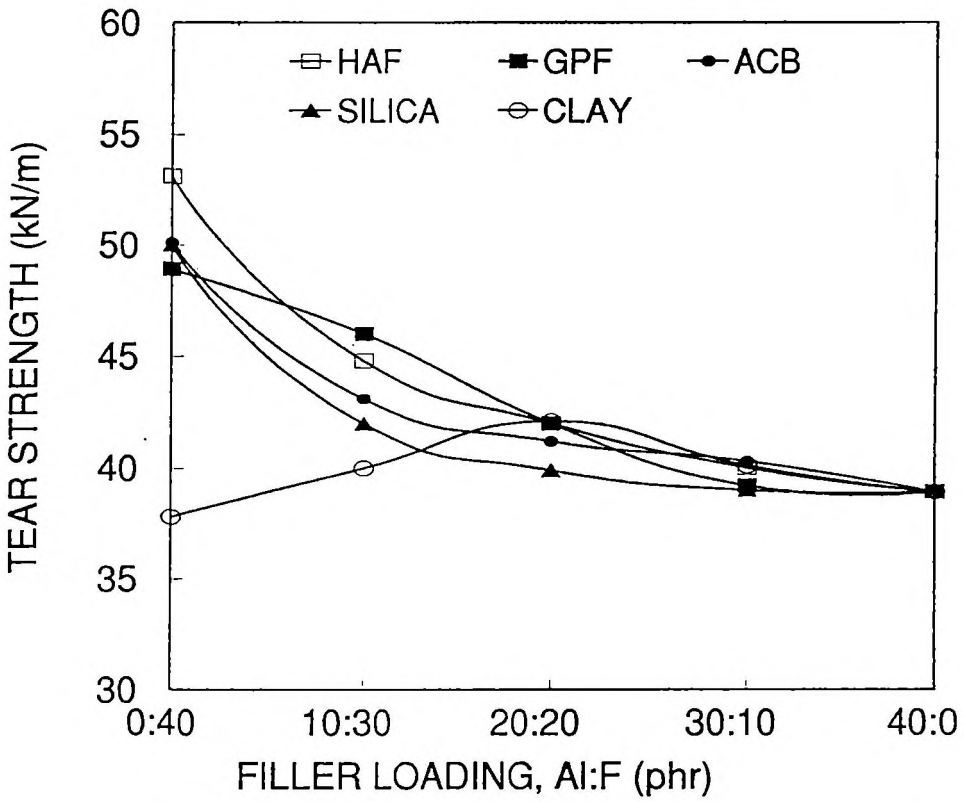

Figure V.5. Variation of tear strength with aluminium powder in presence of various fillers

This shows that aluminium powder is a low reinforcing filler compared to HAF or acetylene black. The elongation at break decreases with aluminium powder content in the composites in the presence of non-reinforcing fillers (clay). The modulus for 300% elongation showed the same trend as that of tensile strength.

Table V.3. Tensile properties of the vulcanizates

Sample Code	Modulus 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)
A	8.6	22.2	448
H_4	18.0	27.9	375
H_3	14.9	25.7	419
H_2	12.3	24.4	443
H_1	12.2	22.7	444
G_4	17.0	25.5	356
G_3	16.3	24.4	398
G_2	12.2	23.8	419
G_1	8.8	23.1	434
A_4	15.6	24.0	378
A_3	14.4	23.9	413
A_2	12.6	23.7	421
A_1	11.9	22.6	469
S_4	8.3	26.0	445
S_3	7.4	24.8	471
S_2	7.6	22.6	479
S_1	6.9	22.5	480
C_4	6.3	20.0	490
C_3	7.3	21.9	461
C_2	8.0	23.3	455
C_1	7.3	22.5	454

Figure V.5 shows the variation of tear strength of vulcanizates containing aluminium powder along with other fillers in NR. From the figure it is clear that the tear strength follows the order HAF > acetylene

black > silica > GPF > aluminium powder > clay. Combination of aluminium powder with other fillers gives tear strength values intermediate between that of pure aluminium powder or the pure filler incorporated vulcanizates.

V.2.3. Heat Build-up, abrasion and compression set

The heat build up values of the composites are shown in Figure V.6. The aluminium powder filled (40 phr) composites have only half the heat build-up value compared to corresponding HAF or acetylene black filled composites. As aluminium powder substitutes other fillers, the heat build up decreases and this effect is more pronounced in the case of HAF and acetylene black fillers. This indicates that use of aluminium powder in rubber compounds can reduce the heat build-up in products. DIN abrasion loss for these composites is presented in Figure V.7. It is clear from this figure that the abrasion resistance is in the order, HAF > GPF > silica > acetylene black > aluminium powder > clay. As the aluminium powder content increases, the abrasion loss increases in NR composites containing various fillers except clay. The increase in abrasion loss by the increase of aluminium powder may be due to the larger particle size of the aluminium powder, compared to other fillers used, except clay.

Compression set values of these composites is presented in Figure V.8. It is interesting to note that the percentage of set is minimum in the case of aluminium powder filled natural rubber composites than those containing other fillers. Also as the percentage of aluminium powder in the total filler content is increased, the set value decreased. The reduction in set value is due to the higher crosslinking in presence of aluminium powder, which in turn is related to the higher thermal conductivity.

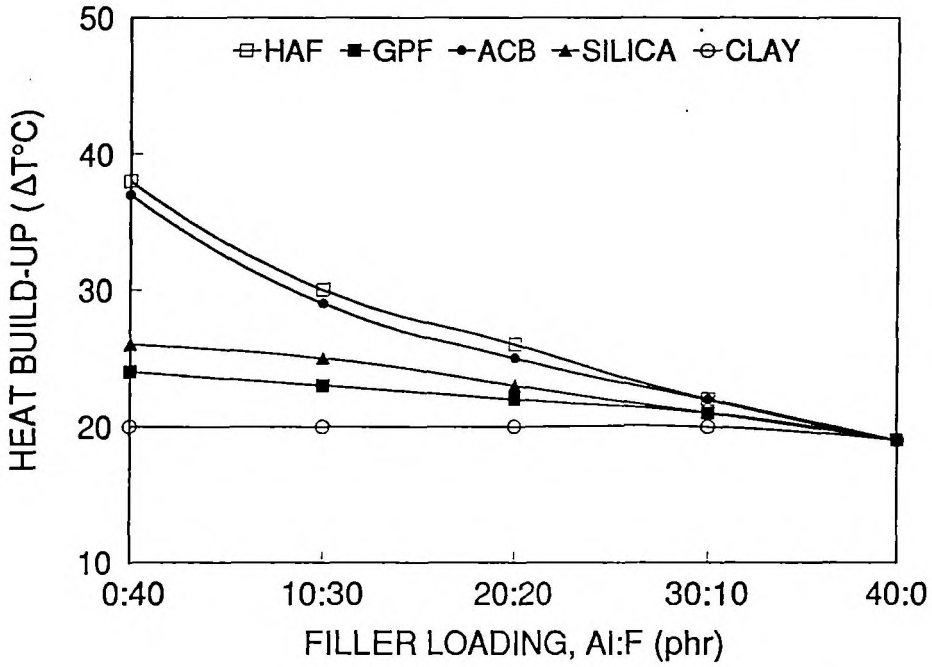

Figure V.6. Heat build-up of aluminium powder incorporated NR-composites in presence of various fillers

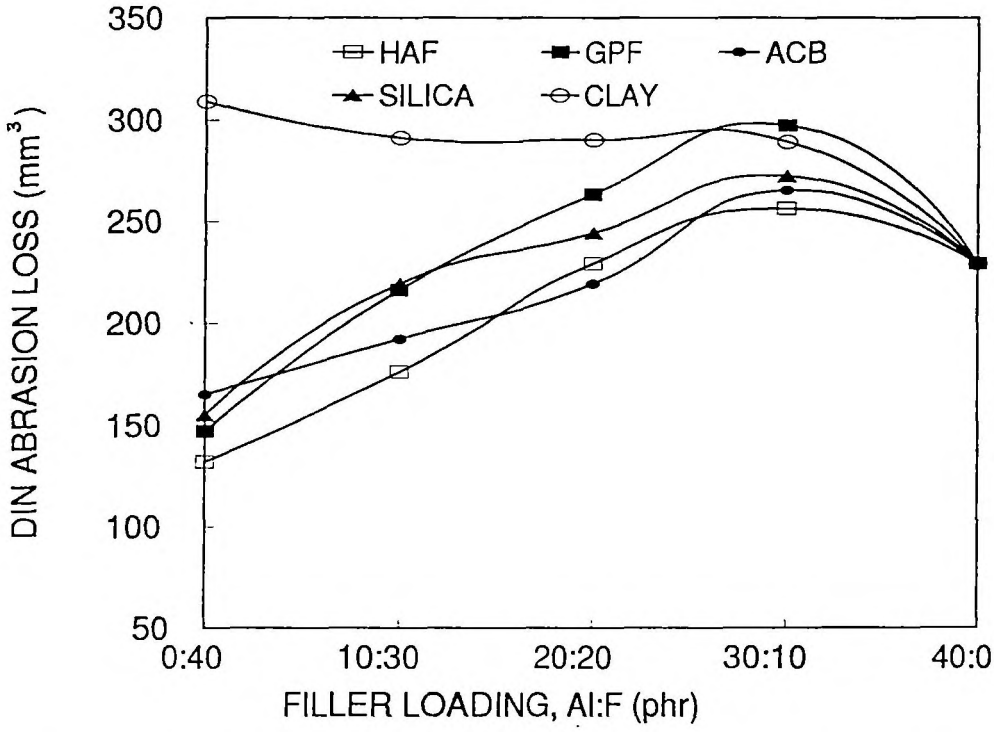

Figure V.7. Dependence of abrasion loss with aluminium powder on various filler incorporated NR-composites

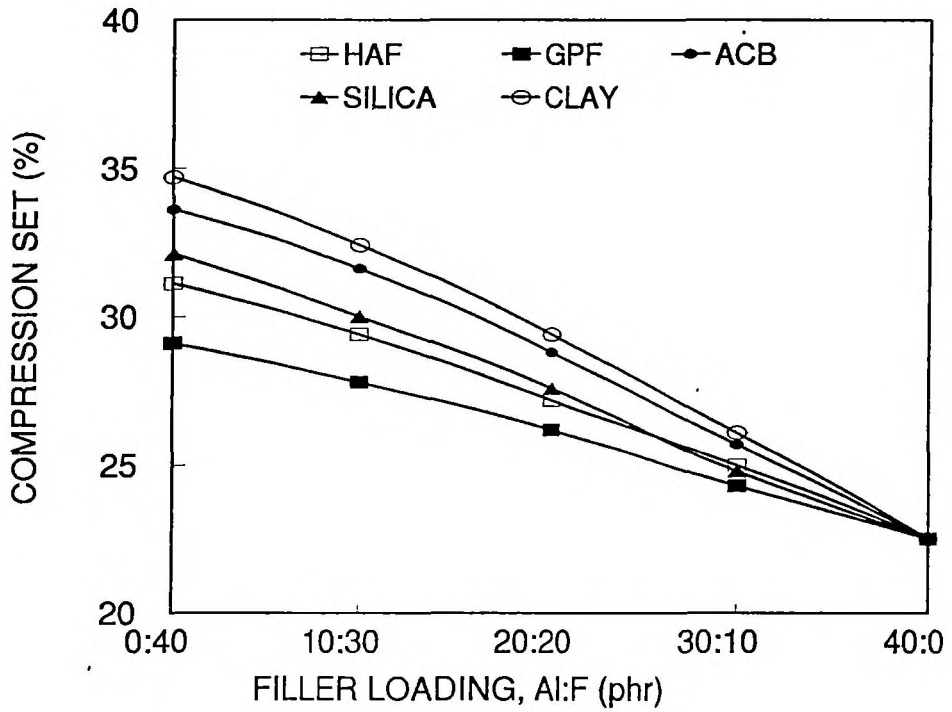

Figure V.8. Dependence of compression set with aluminium powder on various filler incorporated NR-composites

V.3. Effect of Aluminium Powder on Equilibrium Swelling

The higher extent of crosslinking of the vulcanizates containing aluminium powder is also reflected in the equilibrium swelling values. The Q_∞ values at equilibrium swelling of these composites in toluene at 27°C are plotted in Figure V.9. From the figure it is clear that the equilibrium swelling, Q_∞, for NR composites is in the order clay > silica > GPF > acetylene black > HAF > aluminium powder. As the aluminium powder substitutes the other fillers, gradually the equilibrium swelling decreases, which reflects that higher extent of crosslinks are formed in presence of aluminium powder. Higher extent of crosslinking of aluminium powder filled composites may be due to the better heat conduction of the composites through higher thermal conductivity of the metal powder.

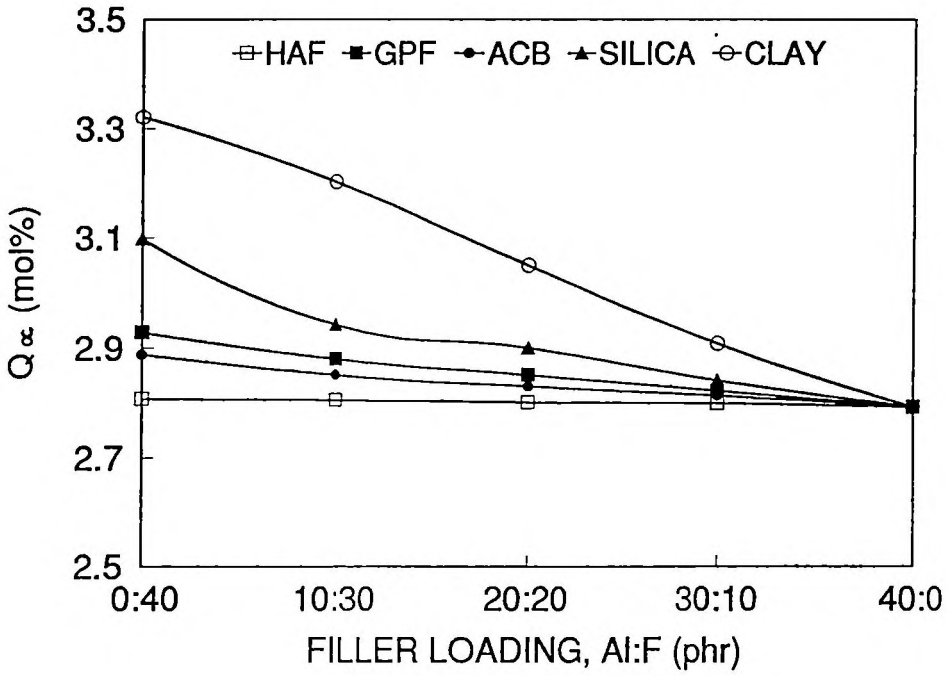

Figure V.9. Variation of equilibrium-swelling with aluminium powder in presence of various fillers (swelling in toluene at 27°C)

V.4. Thermal Conductivity and Uniform Curing of Thick Articles

Thermal conductivity values of these composites are presented in Figure V.10. It is clear that the thermal conductivity is much higher for aluminium powder filled composites compared to other fillers. Thermal conductivity is increased almost linearly as the aluminium powder loading is increased. In the vulcanization of thick articles, thermal conductivity plays an important role. Hence, test pieces were taken from the outer surface and central portion of a rubber cube having 25.4 mm size. which was vulcanized with 5 min additional time. These specimens were assessed for their crosslink density by swelling method. Parks [16] suggested that the value of 1/Q, gives an idea about the degree of crosslinking, as follows,

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100 / \text{Formula weight}} \qquad \ldots\ldots\ldots \text{(V.4)}$$

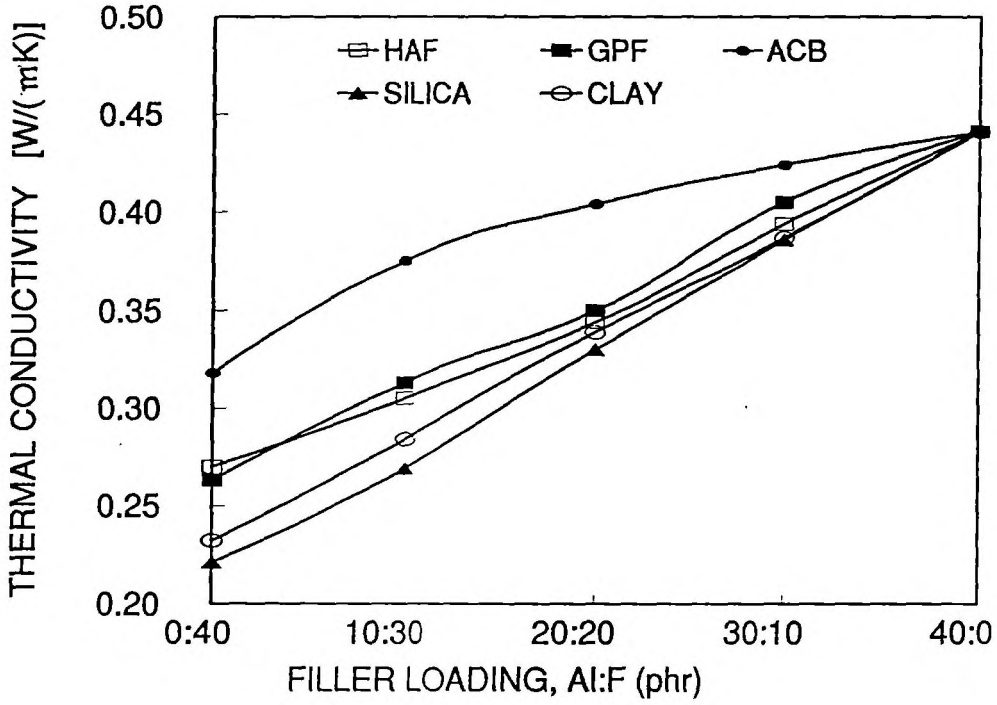

Figure V.10. Variation of thermal conductivity with aluminium powder in presence of various fillers

The effect of aluminium powder on the 1/Q values of the centre and outer layers of the rubber cube containing china clay as filler is shown in Table V.4.

Table V.4. Q_∞ and 1/Q values of inner and outer layers of the cube

Sample code	Al: Clay	Q_∞ Inner	Q_∞ Outer	Difference in Q_∞ (%)	1/Q Inner	1/Q Outer	Difference in Q_∞ (%)
C_4	0:40	3.69	2.05	17.3	0.195	0.235	17.1
C_3	10:30	3.28	2.93	10.7	0.278	0.245	10.9
C_2	20:20	3.00	2.84	5.3	0.239	0.254	5.6
C_1	30:10	2.80	2.73	2.5	0.255	0.264	3.3
A	40:0	2.72	2.71	0.3	0.262	0.265	0.8

As the aluminium powder content increased the difference between 1/Q values of the centre and surface layers decreased. Lower difference means the surface and centre portions have almost same crosslink density. In principle the 25.4 mm cube needs more than 5 min additional time for the complete vulcanization. The difference between the equilibrium swelling values, Q_∞ (which is also an indication of the extent of crosslinking) of the centre and outer layers of the rubber cube also decreased as the aluminium powder content increased. The percentage differences in 1/Q and Q_∞ values of the centre and surface layers show that use of aluminium powder increases the extent of crosslinking of thick articles through increased thermal conductivity. The vulcanization time of thick rubber articles can be reduced considerably and uniform curing can be attained throughout the material by making use of this technique.

V.5. Conclusions

The effects of aluminium powder on the properties of natural rubber vulcanizates containing various fillers, viz., HAF, GPF, acetylene black, china clay and precipitated silica, were studied. Analysis of rheometric curves showed that for compounds containing aluminium powder the vulcanization reaction was much faster and followed a first order reaction kinetics. Hardness values of aluminium powder filled vulcanizates were higher than those containing HAF and acetylene black. As the proportion of aluminium powder in total filler content increased the rebound resilience increased and the heat build-up decreased. Tensile strength and tear strength decreased with aluminium powder loading. The DIN abrasion loss of aluminium filled composites were in between that of acetylene black and clay filled composites, due to the higher particle size of aluminium powder. Compression set was minimum in the case of aluminium powder filled vulcanizates and a corresponding reduction in set was observed on

substituting other fillers by aluminium powder. The Q_∞ values gradually decreased on substituting the other fillers by aluminium powder, due to the increased thermal conductivity, which led to an increase in the extent of crosslinking. Thermal conductivity of aluminium powder filled vulcanizates is much higher than those containing other fillers and hence it was possible to reduce the vulcanization time of thick articles, which also imparts more uniform cure throughout the material.

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CHAPTER VI

STRESS-RELAXATION BEHAVIOUR OF NATURAL RUBBER-ALUMINIUM POWDER COMPOSITES

Results of this chapter have been communicated to Journal of Polymer materials

Stress relaxation properties assume importance in static and dynamic applications under stress. The stress under a constant deformation decays by an amount substantially proportional to the logarithm of the period of the deformed state. Stress relaxation of a material is found to be dependent on various factors such as composition of the mix including the amount and type of fillers [1,2], nature and type of cross links, crosslinks density [3], hysterisis behaviour of the compound [4], type of plasticizers and antioxidants used and testing conditions such as temperature, strain level and strain rate [5,6]. Kalfayan *et al.* [7], described stress relaxation as a tool to study ageing characteristics since it gives an idea about the rates of network scission and formation during ageing. The stress relaxation behaviour of short jute fibre-nitrile rubber composites has been studied by Bhagawan *et al.* [8], and reported the existence of a two-stage relaxation pattern. Stress relaxation behaviour of short Kevlar-fibre reinforced thermoplastic polyurethane has been reported by Kutty *et al.* [6], they reported a two-step relaxation mechanism for the unfilled stock and a three-stage relaxation process for the filled stock. Varghese *et al.* [9], have studied the behaviour of sisal fibre reinforced natural rubber composites and reported the existence of a single-relaxation pattern in the unfilled stock and a two-stage mechanism to the short fibre filled composites. It is also reported that bonding agents influence the relaxation process. The cross over time from one mechanism to the other is less for composites containing bonding agents compared to those without bonding agents [10]. Stress relaxation in rubber containing reinforcing fillers was studied by Cotton and

Table VI.1. Formulations of mixes

Ingredients	GUM	HAF	GPF	ACB	CLY	SIL	10Al	20Al	30 Al	40 Al	HR	Si-69	CoN	TDI
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Aluminium powder	-	-	-	-	-	-	10	20	30	40	10	10	10	10
HAF	-	40	-	-	-	-	-	-	-	-	-	-	-	-
GPF	-	-	40	-	-	-	-	-	-	-	-	-	-	-
Acetylene black	-	-	-	40	-	-	-	-	-	-	-	-	-	-
China clay	-	-	-	-	40	-	-	-	-	-	-	-	-	-
Precipitated silica	-	-	-	-	-	40	-	-	-	-	-	-	-	-
Hexa	-										1.0	-	-	-
Resorcinol	-										2.0	-	-	-
Si-69	-										-	1.0	-	-
Cobalt naphthenate	-										-	-	1.0	-
TDI	-										-	-	-	1.0
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

TDQ - 2,2,4-trimethyl-1,2-dihydroquinoline Hexa – hexamethylene tetramine TDI – toluene diisocyanate
Si-69 - bis[3-(triethoxysilyl) propyl] tetrasulphide CBS - N-cyclohexyl benzothiazyl sulphenamide

Boonstra [11] and summarized that, in raw rubber, reinforcing carbon blacks decrease the rate of relaxation; while in cured rubbers the effect of carbon black is very small.

In this chapter, the stress relaxation behaviour of aluminium powder filled natural rubber composites is reported in comparison with compounds containing conventional fillers such as HAF, GPF, acetylene black, precipitated silica and china clay. Efforts were also made to investigate the effect of various bonding agents such as hexamethylene tetramine-resorcinol system (HR). bis[3-(triethoxysilyl) propyl)] tetrasulphide (Si.-69), cobalt naphthenate (CoN) and toluene diisocynate (TDI) on the stress relaxation behaviour of natural rubber-aluminium powder composites. The base formulations used are given in Table VI.1. The experimental procedures are given in section II.9. The fractured surfaces of the tensile specimens were examined by a Scanning Electron Microscope.

VI.1. Effect of Strain Level on Stress-Relaxation

Figure VI.1 gives the stress relaxation plot, (σ_t/σ_0) versus log t, of the gum vulcanizate at different strain levels. σ_t is the stress at a particular time and σ_0 is the stress at t=0. It is seen that the experimental points for the gum compound fall on a straight line, showing that the relaxation process involved only a single mechanism. There are two important mechanisms that can lead to stress relaxation in a crosslinked elastomer [12]. Chemical stress relaxation due to chain scission, crosslink scission or crosslink formation and physical stress relaxation due to molecular rearrangement requiring little primary bond formation or breakage. Under normal condition, both physical and chemical stress relaxation will occur simultaneously. However, at typical ambient temperatures, the rate of chemical relaxation in a rubber like substance is very small, and the

relaxation behaviour is dominated by a physical process except for very long periods. Here the relaxation patterns of the samples were studied at different elongations. However, it is interesting to note that the rate of stress relaxation at all the extensions studied are almost constant. According to Mackenzie and Scanlan [13] the slope of stress relaxation plot of unfilled natural rubber was independent of strain upto stress-induced crystallisation occurs. It was also concluded that the mechanism is a physical one probably involving the protracted rearrangement of molecular chains or aggregates [5]. It is seen that in the present case also, the stress relaxation of the gum vulcanizates is independent of strain levels as indicated by almost parallel straight-line plots.

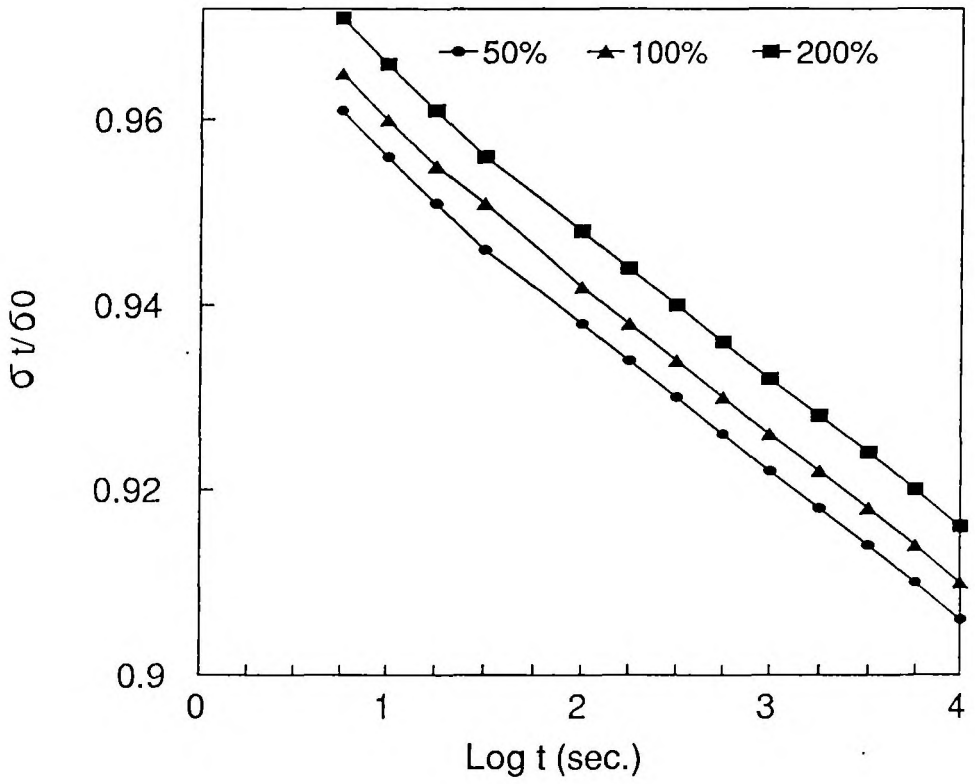

Figure VI.1. Stress relaxation curves of natural rubber (mix gum) at various strain levels

Figure VI.2 shows the stress relaxation plots for natural rubber composites containing 40 phr aluminium powder. Unlike the gum composites, the experimental points fall on two intersecting straight lines. The stress relaxation curves consisting of two straight lines of unequal slopes indicate the existence of a different relaxation mechanism in the case of filled composites, one that operates at shorter time and another is prominent at the later stages of relaxation. The point of intersection of these two straight lines is the time at which a change over from one mechanism to another takes place.

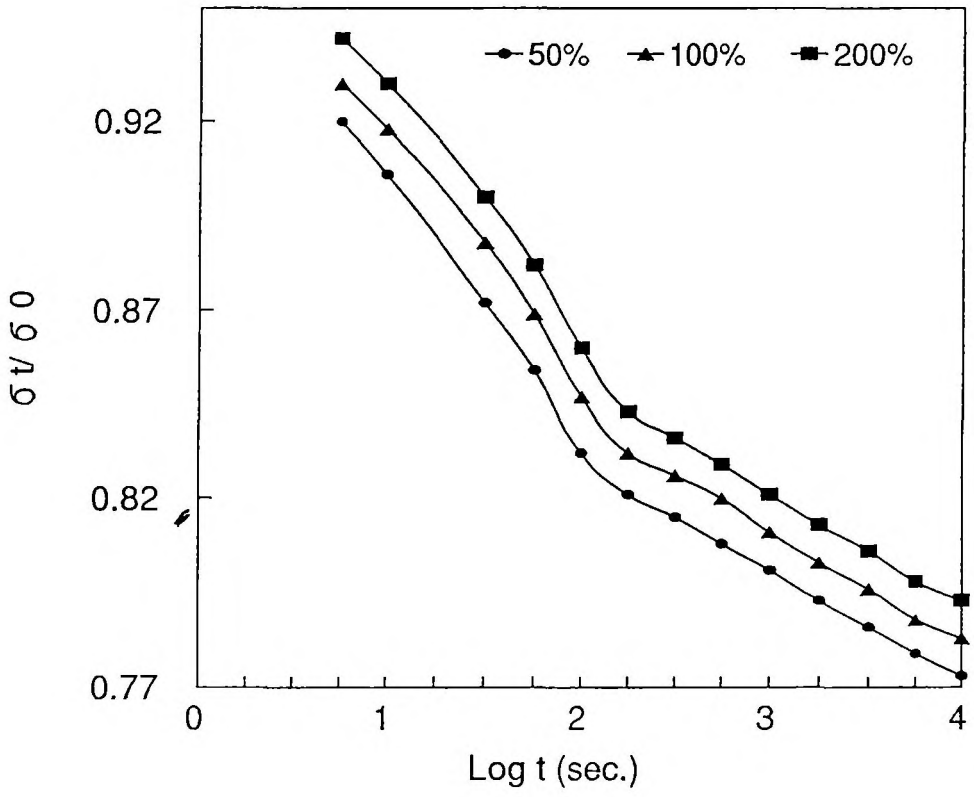

Figure VI.2. Stress relaxation curves of 40 phr aluminium powder filled NR composites at various strain levels

VI.2. Effect of Fillers on Stress-Relaxation

The stress relaxation plots for various filler incorporated natural rubber vulcanizates are presented in Figure VI.3. All the filled vulcanizates followed a two-stage relaxation mechanism. It must arise from the progressive failure of rubber-filler attachment either at the surface of the filler or by rupture of the rubber molecules attached to them. The relaxation properties of filled vulcanizates must in some way be related to the relaxation characteristics of filled rubber. This agrees with the concepts of Mullins and Tobin [14] that the deformation behaviour of filled rubbers can be represented by models in which the rubbery portion of filled vulcanizate is made up of two parts, 'soft' and 'hard' domains. The principal deformation occurring in the soft component displays the same deformation characteristics as seen in unfilled vulcanizates. The effect of filler is manifested in the rise of actual deformation in the soft domains. At the same time, in the hard domains the effective volume of the filler is the volume of the filler itself as well as the volume of the combined rubber layer, ie., the rubber adsorbed on the filler particles. The greater the activity of the fillers, the greater the combined layer and the effective size of the particles. These adsorbed (bound) layers of rubber seem to be less elastic and tough than the unbound rubber in the soft domains. In the filled portion of rubber domain there are relaxation nodes or knots formed through contacts between filler and rubber chains. Here the relaxation process takes place through a breaking away or through adhesion of segments of the rubber chains to the filler particles. The initial relaxation may be arising out of the combined effect of the orientation at the hard, soft and filler-matrix interfaces, whereas the second one may be due to the flow of soft matrix under tension at longer times.

The slope and intercept of the relaxation curve give the characteristics of the mixes. The slopes and intercepts were calculated using a linear regression method. The contribution by an earlier process of relaxation is calculated as reported by Mackenzie and Scanlan [13] by dividing the difference of the two intercepts by the intercept of the first line at t = 1. The values obtained by this method are given in the Table VI.2.

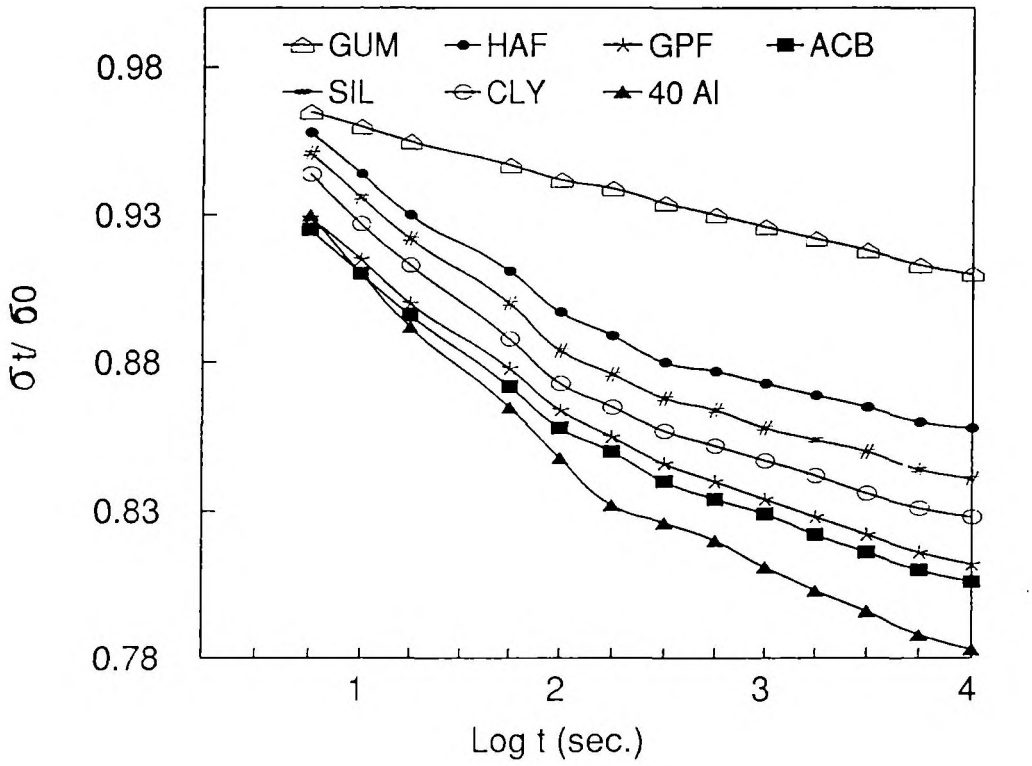

Figure VI.3. Stress relaxation curves of natural rubber composites with various fillers (at 100% elongation)

It is seen that in all cases the earlier slope is greater than the later. The rate of relaxation is faster in the case of first stage of relaxation process. This shows that relaxation as indicated by the slopes, is independent of the strain levels upto 200%. The independence of relaxation at lower strain levels has been reported earlier in the case of natural rubber [4].

Table VI.2. Results of stress-relaxation measurements

Sample	Slope			Intercept			Contribution to initial mechanism, %	Cross over time, sec.
	Early	Later	Difference	Early	Later	Difference		
GUM, 50%	0.0167	-	-	0.9727	-	-	-	-
GUM, 100%	0.0167	-	-	0.9766	-	-	-	-
GUM, 200%	0.0167	-	-	0.9827	-	-	-	-
40 Al, 50%	0.0656	0.0297	0.0359	0.9702	0.8918	0.0784	8.08	210
40 Al, 100%	0.0609	0.0297	0.0312	0.9700	0.9018	0.0682	7.03	199
40 Al, 200%	0.0606	0.0297	0.0309	0.9815	0.9128	0.0687	7.00	191
HAF	0.0442	0.0157	0.0285	0.9882	0.9109	0.0773	7.82	273
GPF	0.0474	0.0227	0.0247	0.9620	0.8932	0.0688	7.15	223
ACB	0.0484	0.0231	0.0253	0.9587	0.8884	0.0703	7.33	236
CLY	0.0519	0.0194	0.0315	0.9725	0.9044	0.0681	7.00	188
SIL	0.0483	0.0184	0.0299	0.9847	0.9146	0.0701	7.12	211
40 Al	0.0609	0.0297	0.0312	0.9700	0.9018	0.0682	7.03	199

The rate of relaxation is minimum with gum vulcanizates and maximum with aluminium powder filled sample. The contribution to initial mechanism and cross over time of natural rubber with various fillers followed the order, HAF>acetylene black>GPF>silica> aluminium powder>clay.

VI.3. Loading of Aluminium Powder on Stress-Relaxation

Figure VI.4 illustrates the effect of aluminium powder loading on stress relaxation at 100% strain level in natural rubber vulcanizates. The slope and intercept values of these composites are presented in Table VI.3.

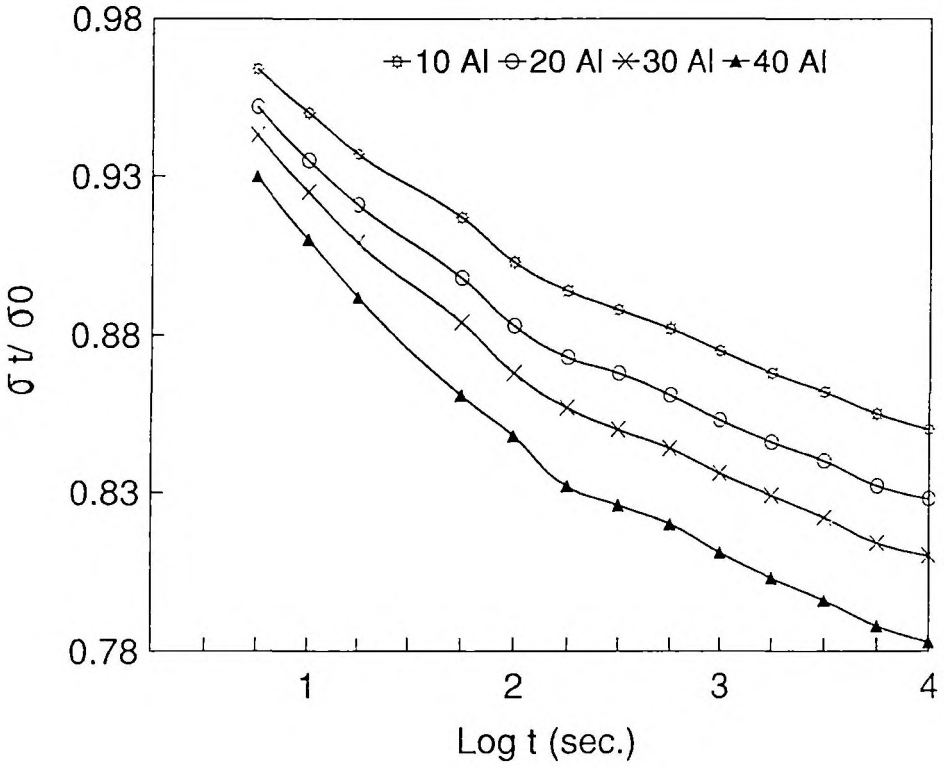

Figure VI.4. Stress relaxation curves of natural rubber composites containing aluminium powder (at 100% elongation)

All the stocks show a two-step relaxation mechanism as indicated by two intersecting straight lines of different slopes. The rate of relaxation in the

second stage is always lower than in the first stage. As the aluminium powder content is increased the earlier slope is increased. This shows that the rate of relaxation increases with aluminium powder content. At a lower aluminium powder content, though the filler matrix interface is higher compared to the unfilled stocks, the matrix gets diluted, resulting in less reinforcement, whereas at higher filler loading the matrix get reinforced, which results in higher relaxation. Similar observations have been reported earlier [11] for highly reinforced rubber vulcanizates. From Table VI.3. it is clear that the contribution to initial mechanism and the cross over time are gradually increased as the aluminium powder loading is increased ie., the time at which the earlier relaxation mechanism stops and is shifted to a second mechanism.

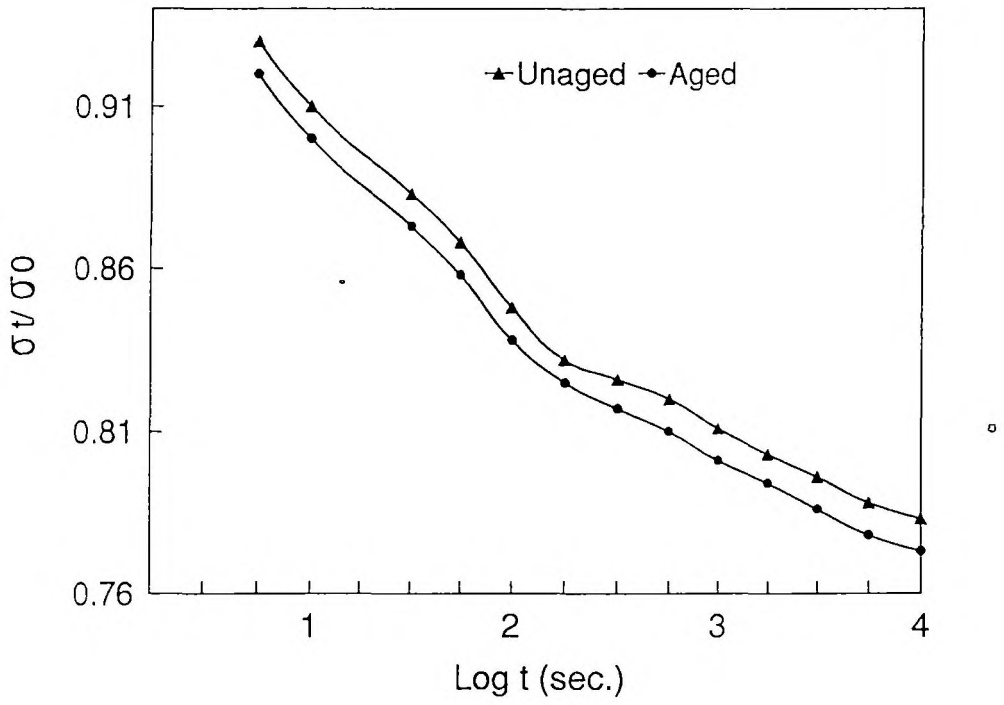

Figure VI.5. Stress relaxation curves of natural rubber composites containing 40 phr aluminium powder (after ageing, at 100% elongation)

Stress relaxation measurement for 40 phr aluminium powder filled NR-composite has been made after ageing the sample at 70°C for 7 days (Figure VI.5). It is seen that the aged sample registered maximum cross over time and the contribution to the initial relaxation. On ageing there are two possibilities (1) formation of extra crosslinks and (2) chain scission due to higher temperature. In the case of aluminium powder incorporated sample better ageing resistance is reported which is reflected in the stress relaxation data also. The degradation starts only on longer periods of ageing.

VI.4. Effect of Bonding Agents on Stress-Relaxation

The variation of relaxation behaviour with various bonding agents is shown in Figure VI.6. and the corresponding slope and intercept values are given in TableVI.3. All the composites contain 10 phr of aluminium powder and the experiment was conducted at 100% elongation. The mixes with bonding agents show a two-stage relaxation pattern, indicating that two types of mechanisms are operating in the process. However, the early relaxation rate of the composites is found to be affected by the presence of bonding agents. This is because compared to the composites without bonding agents; the filler-matrix bond in composites containing bonding agent is stronger. Composites containing bonding agents show a slower rate of relaxation than composites having no bonding agents. This reflects the increased adhesion between natural rubber and aluminium powder in presence of these bonding agents. Improved adhesions by the use of various bonding agents are reported earlier [9,10], which supported the present observation. By comparing the crossover times of various mixes with and without bonding agents, we can have a clear idea about the level of adhesion between the aluminium powder and natural rubber in these compounds.

Table VI.3. Results of stress-relaxation measurements at 100% elongation

Sample	Slope			Intercept			Contribution to initial mechanism, %	Cross over time, sec.
	Early	Later	Difference	Early	Later	Difference		
10 Al	0.0442	0.0257	0.0185	0.9945	0.9532	0.0413	4.15	133
20 Al	0.0495	0.0267	0.0228	0.9856	0.9345	0.0511	5.18	158
30 Al	0.0541	0.0277	0.0264	0.9799	0.9206	0.0593	6.05	177
40 Al	0.0609	0.0297	0.0312	0.9700	0.9018	0.0682	7.03	199
HR	0.0438	0.0248	0.0190	0.9696	0.9186	0.0510	5.26	223
Si-69	0.0406	0.0241	0.0165	0.9802	0.9297	0.0505	5.14	201
CoN	0.0387	0.0221	0.0166	0.9683	0.9197	0.0486	5.01	198
TDI	0.0348	0.0203	0.0145	0.9889	0.9401	0.0488	4.93	191

Vulcanizates containing bonding agents always registered a higher crossover time. Initial relaxation is fast in a weak interface and hence a low crossover time for unbonded composite. In a strong interface as that exists in mixes with bonding agents, the initial relaxation process is long and takes more time for the initiation of the second phase of the relaxation process.

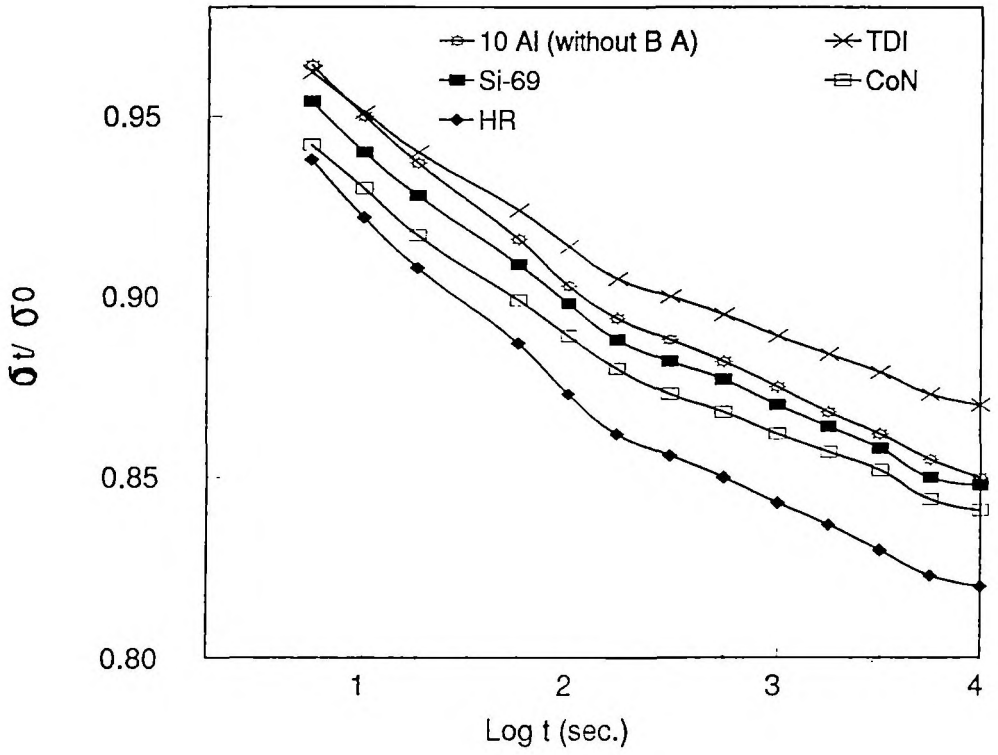

Figure VI.6. Effect of bonding agents on the stress relaxation curves of NR-aluminium powder composites (at 100% elongation)

VI.5. Analysis of SEM Photographs

The fractured surface of the tensile pieces of the composites was examined by means of Scanning Electron Microscope (SEM). The SEM photographs are given in Figures VI.7(a-e). It is seen that in the unbonded composite the aluminium powder exists as loose aggregate resulting in a

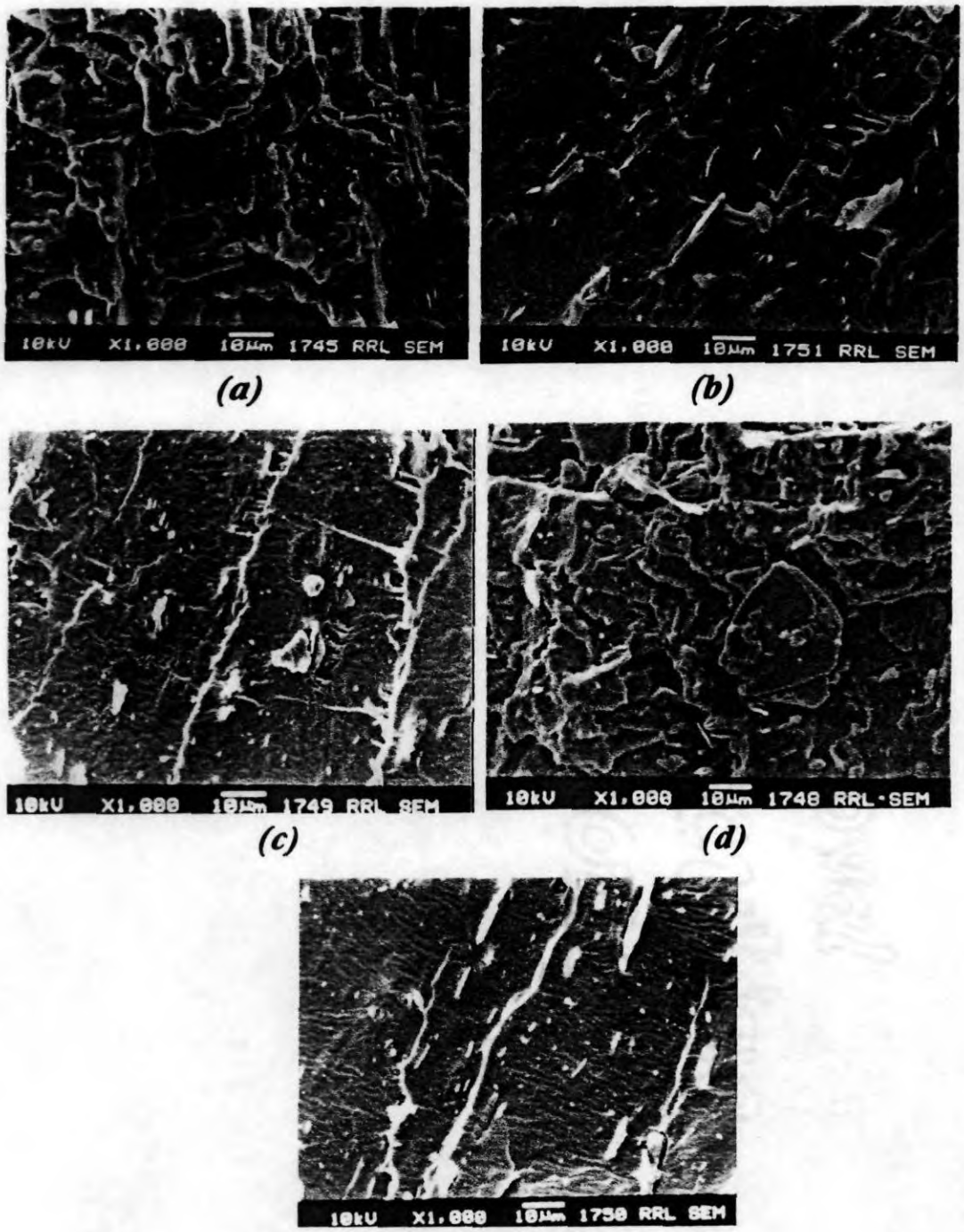

Figure VI.7. SEM photographs of tensile fractured surface of aluminium powder filled (10 phr) natural rubber composites (magnification, x 1000) (a) without bonding agent (b) with HR syste (c) with Si-69 (d) with CoN (e) with TDI

VI.6. Conclusions

The natural rubber gum vulcanizates showed only one relaxation pattern, the rate of which was almost independent of the strain level. The incorporation of filler changes the relaxation pattern from a single-stage to a two-stage mechanism. The initial mechanism is due to the filler-rubber attachment and the latter one due to relaxation process of natural rubber molecules. The rate of stress relaxation is fast in the first stage compared to the latter in all cases. It is found that the rate of stress relaxation is increased with the loading of aluminium powder. It is also noted that the cross over time and the contribution to initial mechanism are gradually increased as the aluminium powder loading increased. Initial relaxation process is found to be decreased by ageing. The use of various bonding agents, namely hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl)propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocynate (TDI) in natural rubber- aluminium powder composites have been studied. The relaxation processes are influenced by bonding agents, which indicated an increased natural rubber-aluminium powder interaction through improved adhesion. The scanning electron microphotographs showed that the aluminium powder is more uniformly aligned in natural rubber in presence of bonding agents.

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CHAPTER VII

DYNAMIC MECHANICAL PROPERTIES OF NATURAL RUBBER-ALUMINIUM POWDER COMPOSITES

Results of this chapter have been communicated to Journal of Polymer Science

Rubber products generally undergo dynamic stress during service and hence their behaviour under dynamic loading is highly important. The informations obtained from dynamic mechanical measurements are of importance to manufactures and users of polymers in structural applications. Of these greater importance is the information provided by the damping, since end-use properties such as vibration dissipation, heat build up, impact resistance and noise abatement are all related to mechanical damping. The dynamic mechanical properties of elastomers are greatly dependent on temperature, frequency, type and concentration of filler and the extent of deformation. Several investigators have studied the dependence of dynamic mechanical properties of rubber vulcanizates on the type and concentration of fillers [1-4] under different test conditions [5]. Studebaker and Beatty [6] studied the effect of compounding on dynamic mechanical properties of rubber. The major compounding variables in this study are the nature of the rubber, nature and amount of ingredients in the curing system, nature and amount of fillers and presence of plasticizers. Viscoelastic studies of short sisal fibre reinforced natural rubber composites have been studied by Varghese *et al.* [7]. Dynamic mechanical properties of a variety of carbon black–loaded compound over a wide range of frequency and temperature have been reported [8-12]. Manna *et al.* [13] studied the effect of strain on the dynamic mechanical properties of ENR-carbon black mixture with special reference to the role of oxidation of the filler surface in the formation of rubber-filler bonds. Blaine [14] gives a good report on dynamic mechanical analysis for the characterization of physical properties.

Table VII.1. Formulations of mixes for dynamic mechanical analysis

Ingredients	GUM	HAF	GPF	ACB	CLY	SIL	10Al	20Al	30 Al	40 Al	HR	Si-69	CoN	TDI
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Aluminium powder	-	-	-	-	-	-	10	20	30	40	10	10	10	10
HAF	-	40	-	-	-	-	-	-	-	-	-	-	-	-
GPF	-	-	40	-	-	-	-	-	-	-	-	-	-	-
Acetylene black	-	-	-	40	-	-	-	-	-	-	-	-	-	-
China clay	-	-	-	-	40	-	-	-	-	-	-	-	-	-
Precipitated silica	-	-	-	-	-	40	-	-	-	-	-	-	-	-
Hexa	-										1.0	-	-	-
Resorcinol	-										2.0	-	-	-
Si-69	-										-	1.0	-	-
Cobalt naphthenate	-										-	-	1.0	-
TDI	-										-	-	-	1.0
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

TDQ - 2,2,4-trimethyl-1,2-dihydroquinoline
Hexa – hexamethylene tetramine
TDI – toluene diisocyanate
Si-69 - bis[3-(triethoxysilyl) propyl] tetrasulphide
CBS - N-cyclohexyl benzothiazyl sulphenamide

Effect of silica filler on the dynamic mechanical properties of ionic elastomer based on carboxylated nitrile rubber was reported [15] and found that the rubber-filler interaction in the cluster region causes striking changes in the variation of E' and tanδ with double strain amplitude.

In this chapter, the dynamic mechanical properties of aluminium powder filled natural rubber composites over a wide range of temperatures (30 to 150^0C), and also at different frequencies are reported. The effects of loading of aluminium powder and various bonding agents such as hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocynate (TDI) on viscoelastic properties have been investigated. For comparison, results of vulcanizates containing conventional fillers are also included. Formulations of the mixes are given in Table VII.1. The experimental viscoelastic data have been compared with theoretical predictions.

VII.1. Effect of Fillers on Dynamic Mechanical Properties

The dynamic storage modulus (E′), loss modulus (E″) and loss factor (tan δ) were measured as a function of temperature at three frequencies viz. 10, 1.0 and 0.1 Hz. All these parameters have the same pattern of change with temperature at all frequencies. Figure VII.1 shows the effect of temperature on the storage modulus (E′) of the composites containing different fillers. The measurements were carried out at a frequency of 1.0 Hz over a wide temperature range from 30 to 150^0 C. Increase in storage modulus by the addition of carbon black is also reported by Gandhi *et al.* [8]. The storage modulus of natural rubber composites with various fillers increased in the order, china clay < aluminium powder < acetylene black < GPF < precipitated silica < HAF.

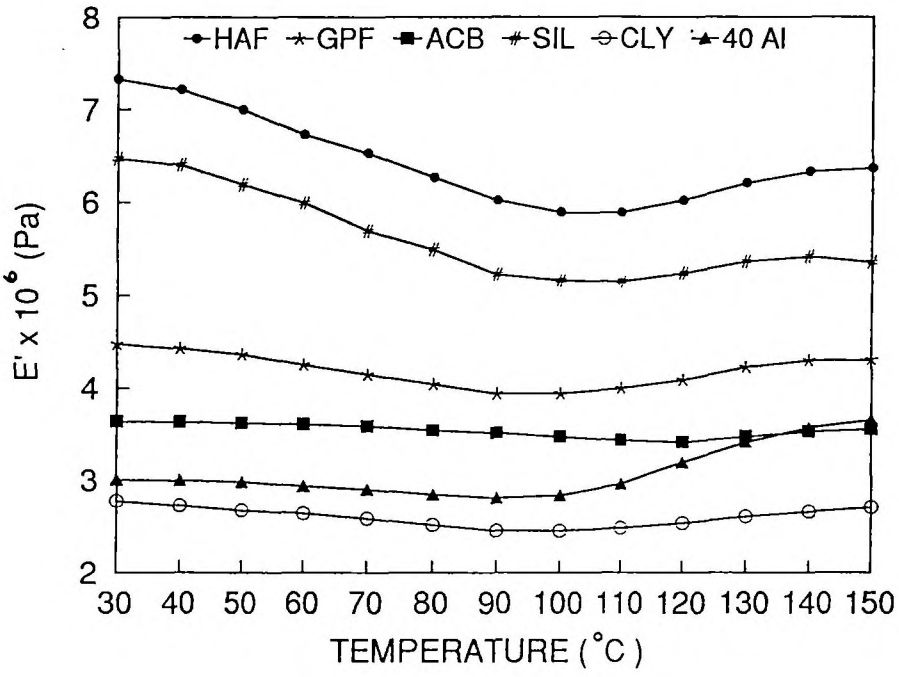

Figure VII.1. Variation E' with temperature of natural rubber composites with various fillers at a frequency of 1.0 Hz

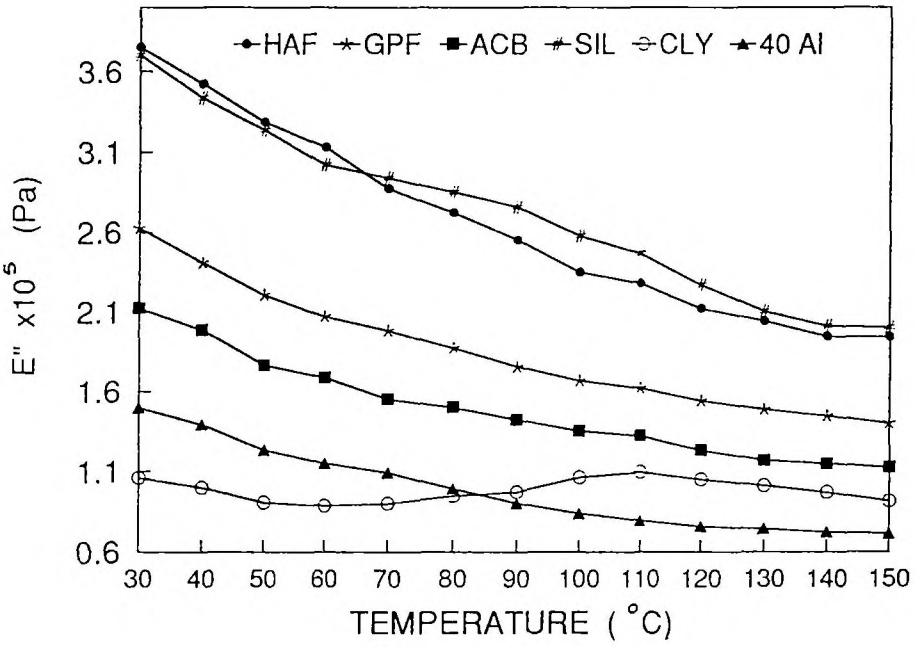

Figure VII.2. Dependence of E'' with temperature of various fillers incorporated natural rubber composites at a frequency of 1.0 Hz

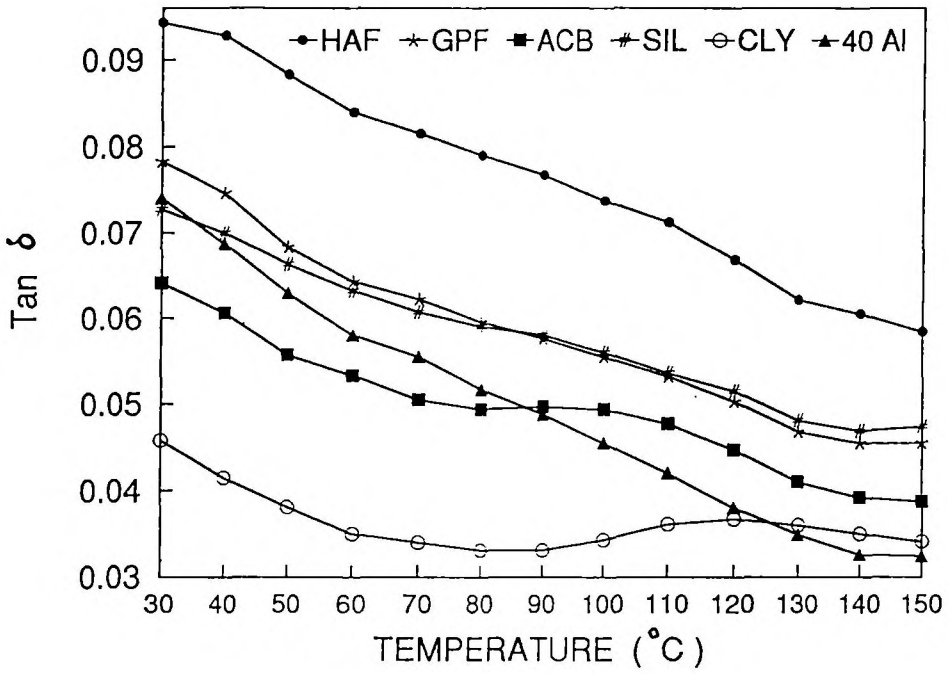

Figure VII.3. Variation of tanδ with temperature of natural rubber with various fillers at a frequency of 10 Hz

Similar trends are reflected in the loss modulus (E″) and tanδ values of the natural rubber composites containing various fillers and these are shown in Figures VII.2 and Figure VII.3 respectively. Storage modulus (E′) is a measure of the elastic energy stored or recovered in a cycle of deformation. The loss modulus (E″) measures the energy dissipated or lost as heat. Loss tangent (tanδ) is a dimensionless parameter. which is a measure of the ratio of energy lost (E″) to energy stored (E′) in a cyclic deformation. The storage modulus, loss modulus and tan δ are increased in the same order as that the reinforcing capacity of these fillers in natural rubber vulcanizates. Rubber-filler interaction is a major factor, which influences the dynamic mechanical properties of a compound to greater extend. The rubber-filler interaction increases as the reinforcing capacity increases. Silica filled vulcanizates show modulus and tanδ values close to HAF filled ones. The storage

modulus, loss modulus and tanδ values of aluminium powder filled composites are in between those of acetylene black and clay.

VII.2. Effect of Aluminium Powder Loading

Figure VII.4 shows the effect of temperature on storage modulus of aluminium powder filled natural rubber vulcanizates at 0.1 Hz. The gum vulcanizate has the lowest storage modulus. As the loading of aluminium powder increased the storage modulus increased. There is a continuous increase in the storage modulus of the composite as temperature is increased above 100^0C.

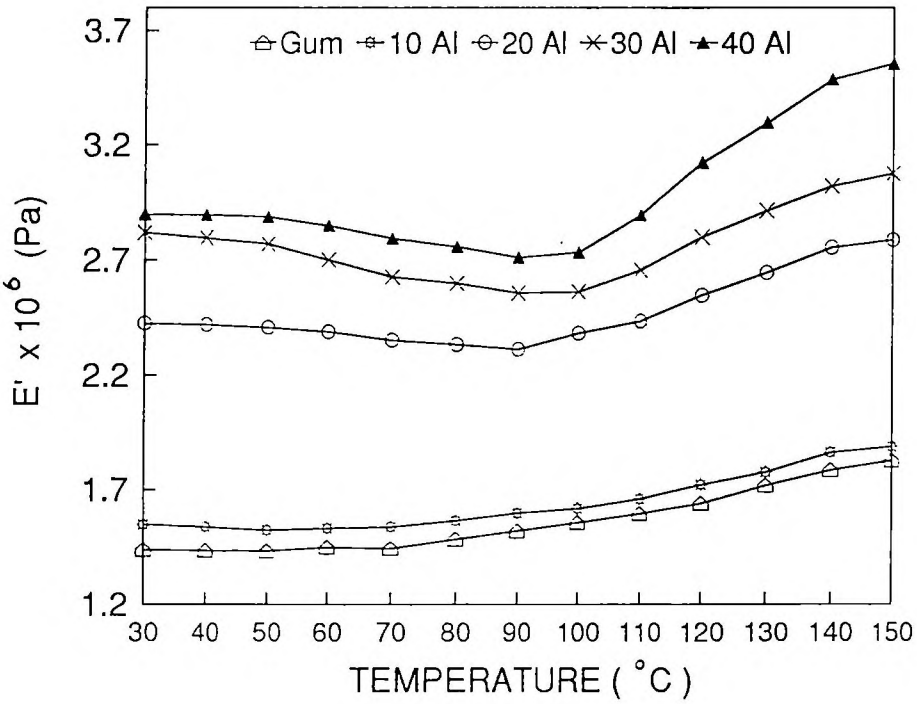

Figure VII.4. Variation E' with temperature of natural rubber composites with aluminium powder at a frequency of 0.1 Hz

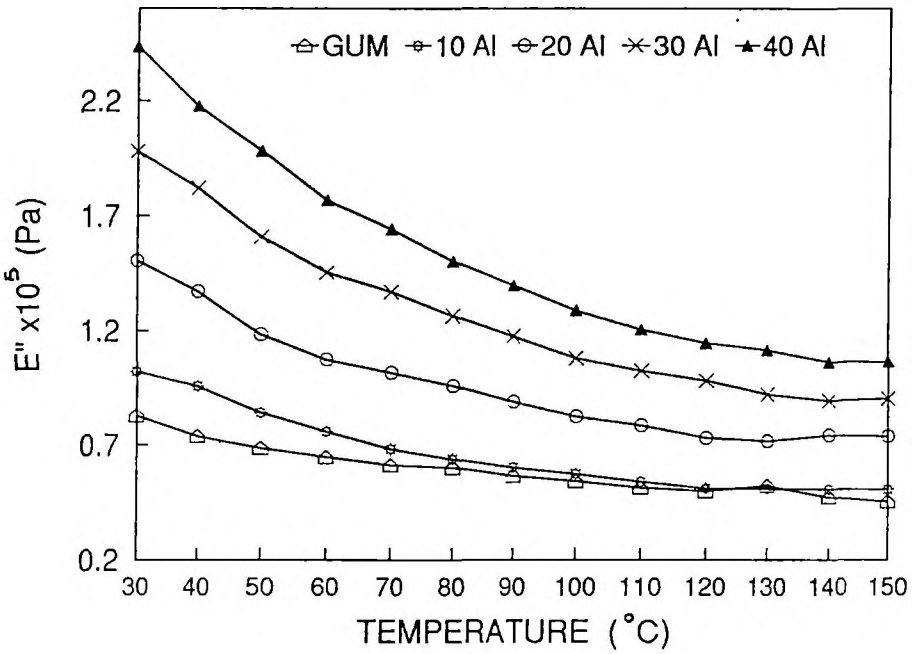

Figure VII.5. Dependence of E'' with temperature of aluminium powder filled natural rubber composites at a frequency of 10 Hz

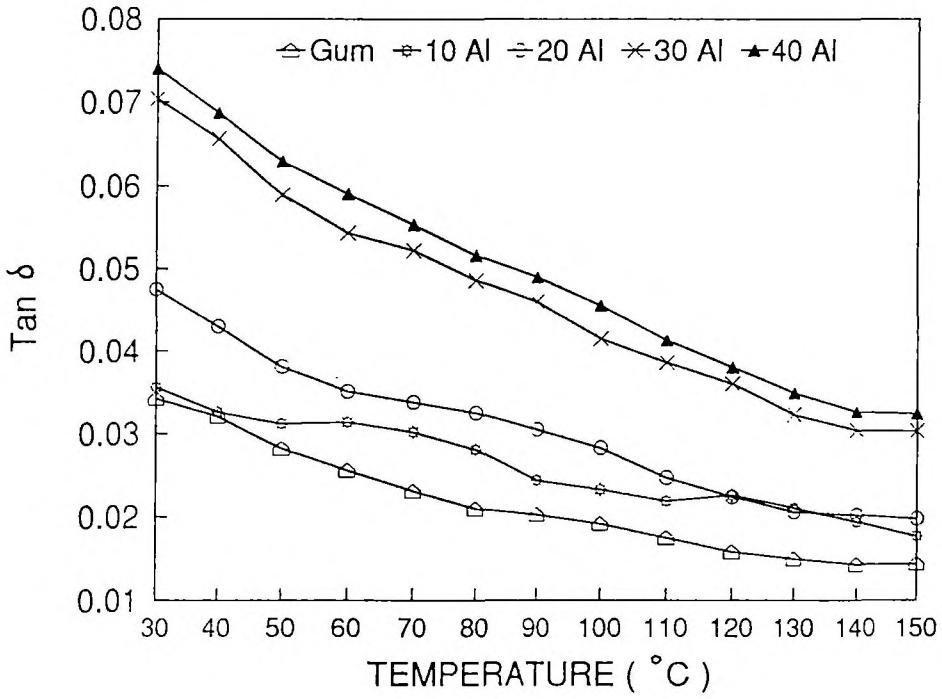

Figure VII.6. Variation of tanδ with temperature of natural rubber composites with aluminium powder at a frequency of 10 Hz

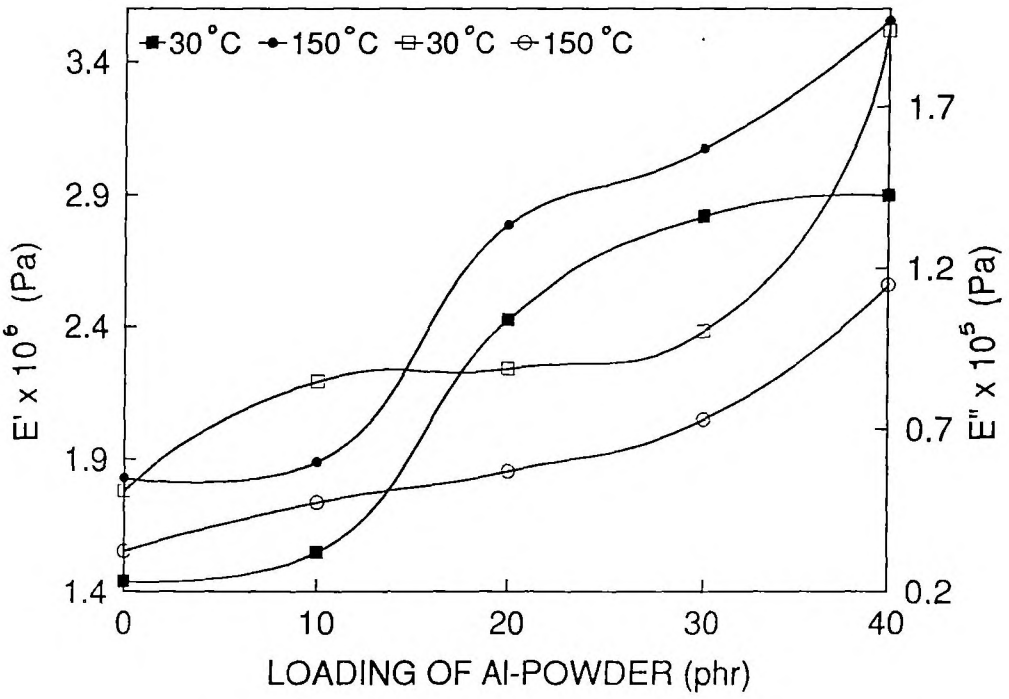

Figure VII.7. Variation of E' with loading of aluminium powder in natural rubber at different temperatures at 0.1 Hz

The variation of loss modulus (E″) of the same composites at 10 Hz is presented in Figure VII.5. The minimum loss modulus is observed with gum vulcanizate. Presence of aluminium powder in natural rubber composites resulted a higher loss modulus and as the loading of aluminium powder increased the loss modulus also increased. In all cases, as temperature increased, the loss modulus decreased gradually. The damping properties of the vulcanizates can be understood from the plot of tanδ versus temperature (Figure VII.6). It is interesting to note that the tanδ values are minimum with gum natural rubber vulcanizates and increased with aluminium powder loading. The variation of storage modulus and loss modulus as a function of aluminium powder loading in natural rubber is shown in Figure VII.7. As the loading of aluminium powder increased, both E′ and E″ are increased. A similar increase is also observed in the tanδ values with increased loading of aluminium powder (Figure VII.8). Depending on the strength of natural

rubber-aluminium powder interaction, physical adsorption and/or chemisorption of rubber molecules on the surface of aluminium powder may takes place. This interaction leads to an immobilization of the rubber segments. Kaufman *et al.* [16] demonstrated the presence of three distinct regions within the polymer characterised by different degrees of molecular mobility: a region of mobile rubber, an outer shell surrounding the filler which is less mobile, and a hard inner shell where the motion of rubber segments is extremely restricted. This resembles a rubber shell model of definite thickness around the filler. This would result in a rubber shell on the filler surface in which the polymer viscosity is increased and the modulus would be increased. Generally, it can be assumed that the modulus of the inner shell is very high and decreases gradually with increasing distance from the filler surface (Figure VII.9).

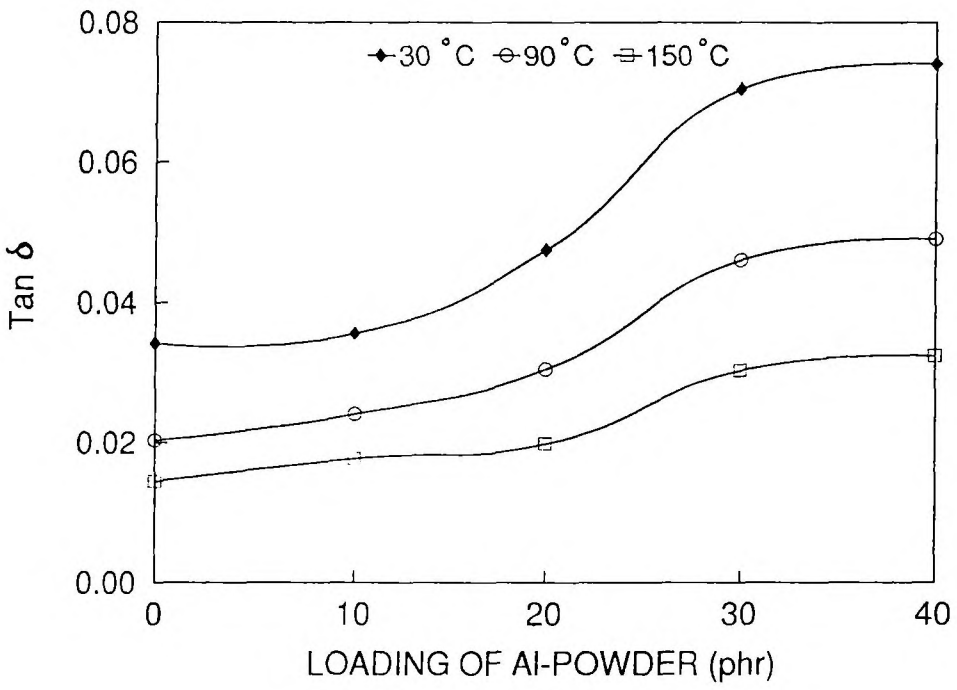

Figure VII.8. Variation of tanδ with loading of aluminium powder in natural rubber at different temperatures at a frequency of 10 Hz

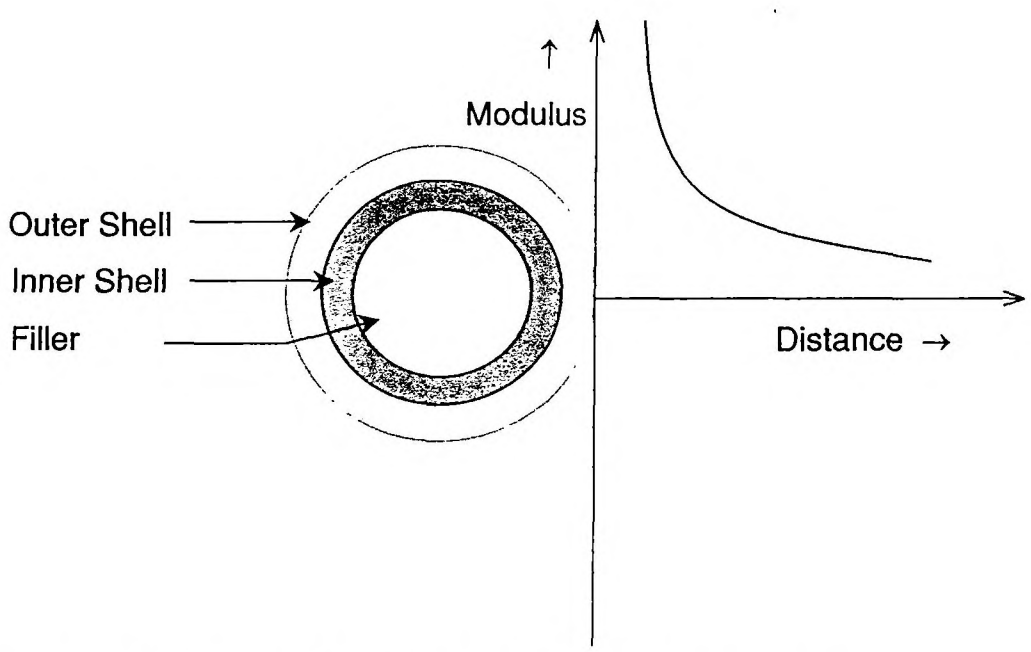

Figure VII.9. Schematic representation of rubber shell model

In the case of natural rubber-aluminium powder composites, as the aluminium powder loading increases, the mobile region decreases and the sites for natural rubber-aluminium powder interaction increase. This results a higher storage modulus and tanδ in vulcanizates containing higher loading of aluminium powder.

VII.3. Effect of Bonding Agents

Figures VII.10 and VII.11 show the effect of various bonding agents on storage modulus and loss modulus of natural rubber containing 10phr aluminium powder respectively. By the addition of bonding agents, the storage modulus and loss modulus are increased, in the order cobalt naphthenate (CoN) < toluene diisocyanate (TDI) < bis[3-(triethoxy silyl)propyl]tetrasulphide (Si-69) < resorcinol-hexa system (HR).

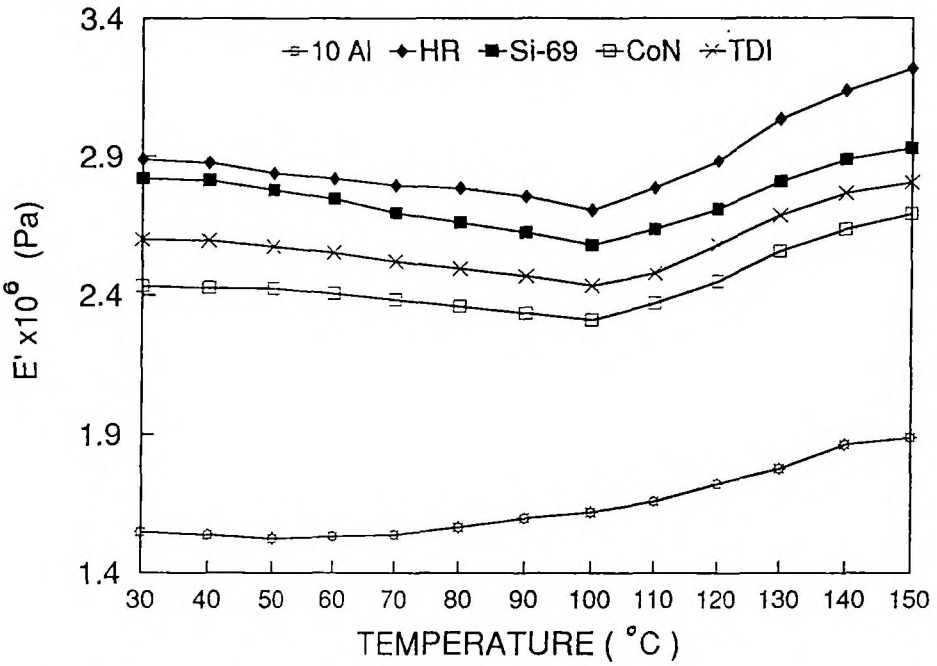

Figure VII.10. Variation of E' with temperature of natural rubber-aluminium powder filled composites with various bonding agents at a frequency of 0.1 Hz

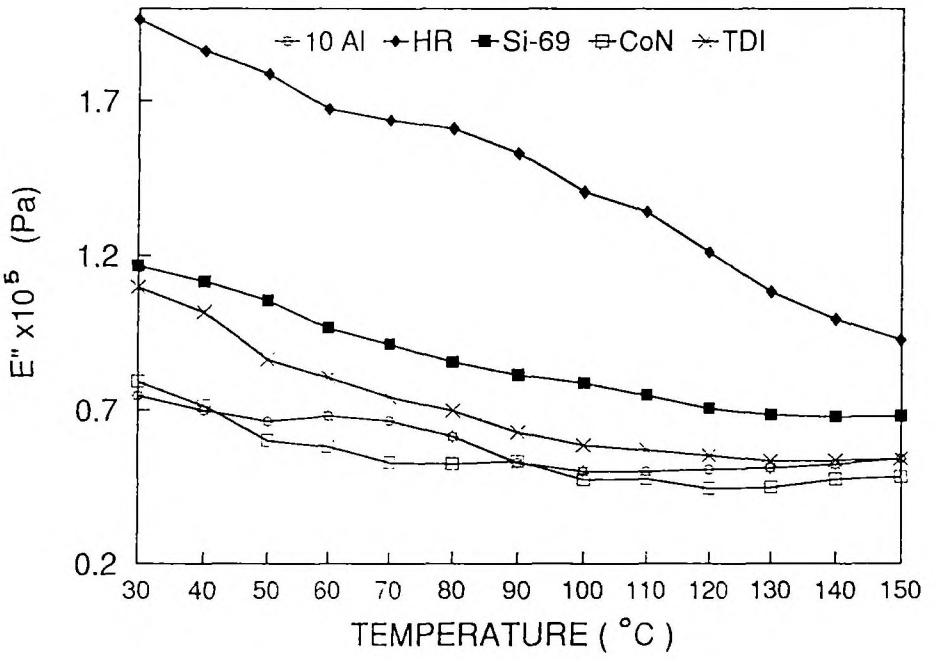

Figure VII.11. Dependence of E" with temperature of NR-aluminium powder filled composites with various bonding agents at a frequency of 1.0 Hz

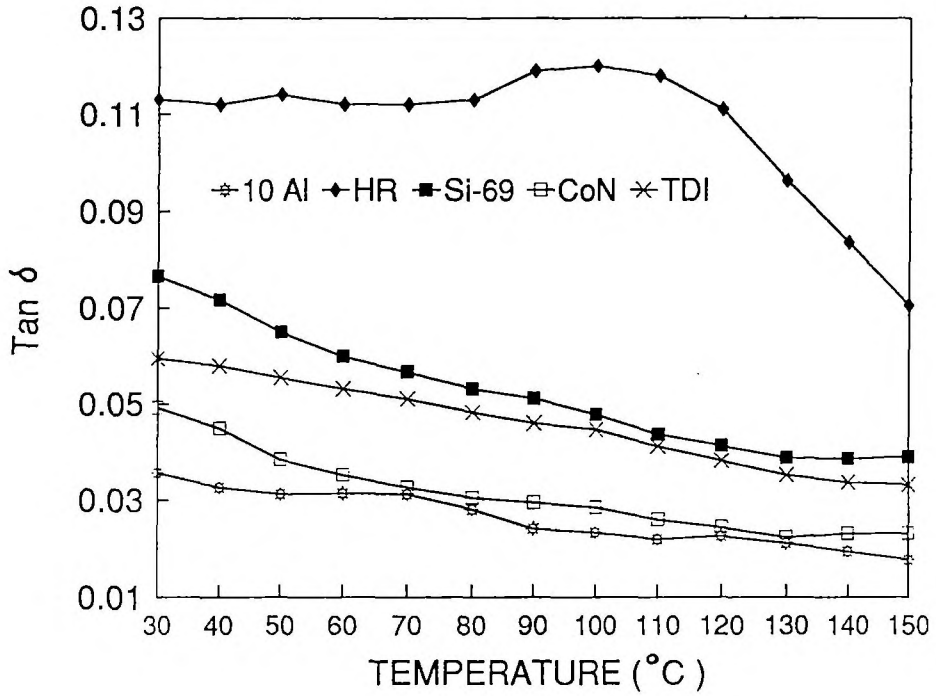

Figure VII.12. Variation of tanδ with temperature of NR-aluminium powder composites with various bonding agents at a frequency of 10 Hz

The increase in storage modulus by the addition of bonding agent is due to the improved adhesion between aluminium powder and the matrix. The damping behaviour of natural rubber vulcanizates containing aluminium powder with various bonding agents is shown in Figure VII.12. The addition of bonding agent increased the tanδ values. The presence of coupling/bonding agent in the filled vulcanizates caused significant reduction in the polymer mobility due to the strong rubber-filler interaction. This improved adhesion between filler and rubber in presence of bonding agent restricts the easy slippage of the polymer molecules along the filler surface. The mechanism of the adhesion between natural rubber and these bonding agents are described in section III.

VII.4. Temperature and Frequency on Dynamic Mechanical Properties

In all cases as the temperature increases. the tanδ values of composites decreased (Figure VII.8). This is due to the increased storage modulus by the continued crosslinking of the rubber composites as the temperature increased. The increased interface adhesion in presence of bonding agents again increased the storage modulus. With increase in temperature the free volume increases and the polymer chain mobility is increased. When the temperature reaches a certain level, the free volume of the polymer increases more rapidly than the volume expansion of the molecules, facilitating the segmental motion. The viscosity of the polymer decreases and the molecular adjustments take place easily, so that the modulus is decreased and the energy dissipation among polymer molecules will increase with temperature. Also at high temperature the brownian motion increases and the viscosity is low in the polymeric solid permitting an easy segmental movement.

Effects of frequency on dynamic mechanical properties are shown in Figure VII.13. A decrease in storage modulus (E'). loss modulus (E'') and tanδ are observed as the frequency is decreased. This phenomenon may be explained by the pseudo-rigidity effect of the frequency. In this effect, the relaxation time (which may be considered as the inverse of frequency) responsible for chain mobility reduces drastically with increasing frequency, which results in temporary "freezing" of the amorphous region.

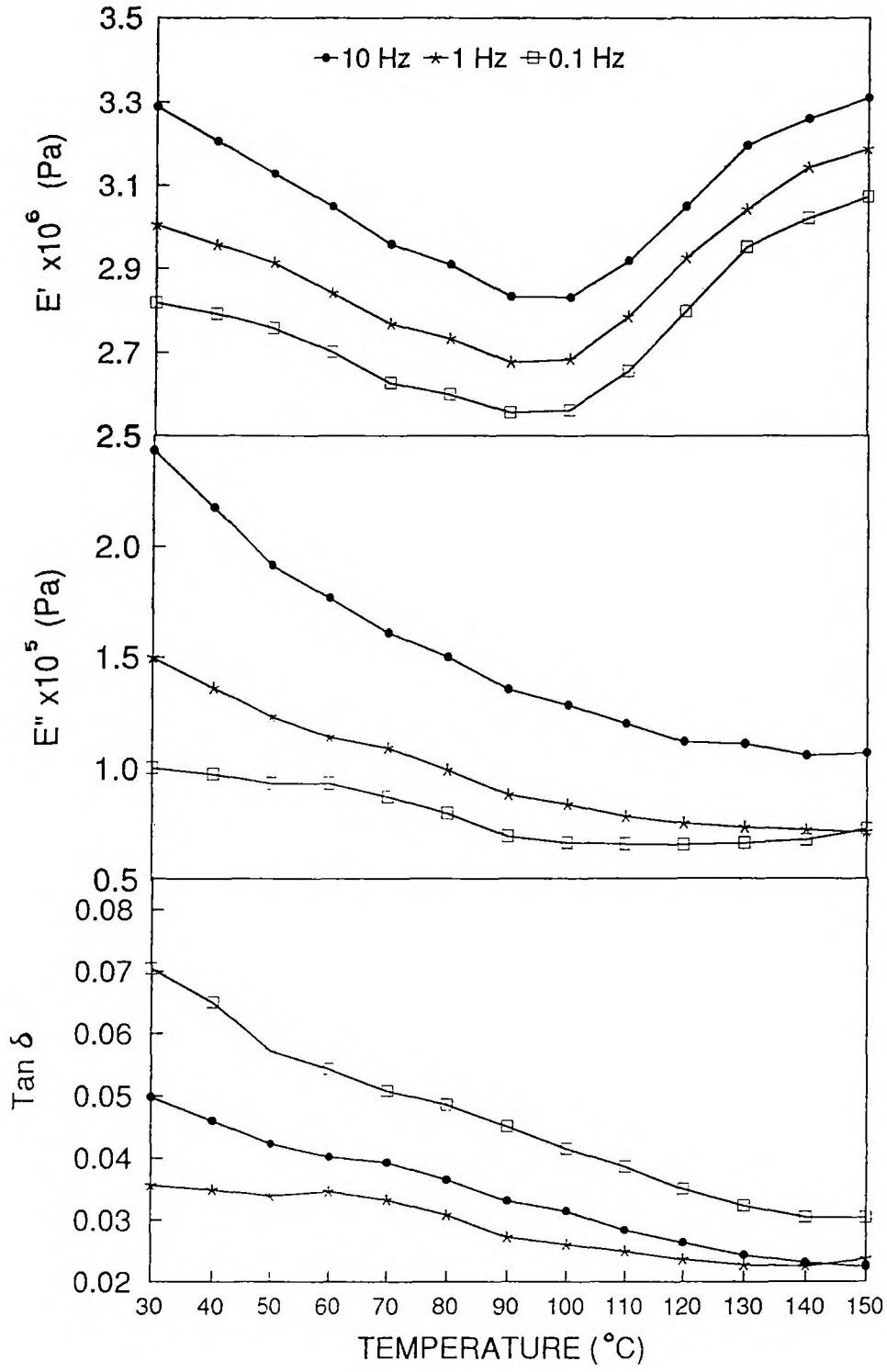

Figure VII.13. Frequency dependence of E', E" and tanδ for natural rubber composites containing 30 phr aluminium powder

VII.5. Comparison with Theoretical Models

Relative moduli; defined as E'_f/E'_m , where E'_f is the elastic modulus of the filled vulcanizate and E'_m is that of the gum vulcanizate, can be plotted as a function of volume fraction of the filler. The experimental value can be compared with the modified Kerner equation [17]. Kerner considered that a filler particle is surrounded by a shell of matrix material, which merges into a medium that has the elastic properties of the composite. Particles are adhere to the matrix, but do not interact with one another. The complexity of the Kerner equation has been simplified by restricting its applicability to the rubbery state of the filled compounds and assuming that the dynamic modulus of the filler greatly exceeds that of the polymer matrix. Now, assuming the Poisson's ratio for the rubber as 0.5, at a given volume fraction of filler, ϕ, the modified Kerner equation can be written as,

$$\frac{E'_f}{E'm} = \frac{1+1.5A\phi}{1-A\phi} \qquad \text{..... (VII.1)}$$

where 'A' is the filler-rubber interaction parameter. The value of 'A' can be obtained from the comparison of the loss moduli E'' of unfilled and filled specimens at the reference temperature. Figure VII.14. shows the plot of E''_m/E''_f versus the volume fraction of the filler at 35^0C. A linear decrease in E''_m/E''_f with volume fraction was observed according to the following equation.

$$E''_m/E''_f = 1 - A\phi \qquad \text{..... (VII.2)}$$

where 'A' is the same interaction parameter term used in the first equation. The value of 'A' is obtained from the slope of the line and is found to be 7.4. Using this value we can calculate E'_f/E'_m theoretically.

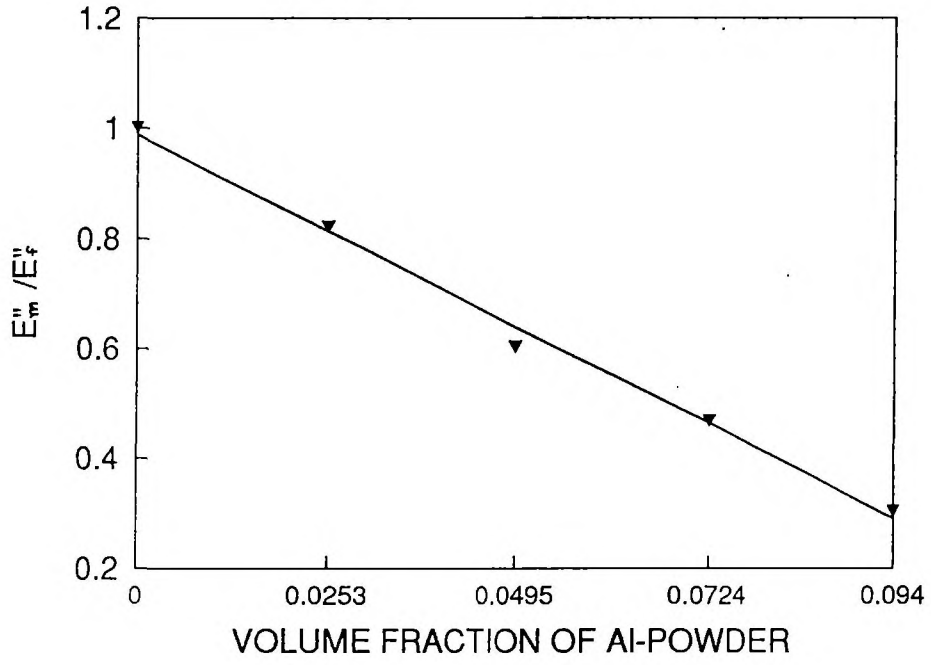

Figure VII.14. E_m''/E_f'' as a function of aluminium powder concentration at 35°C, 10 Hz

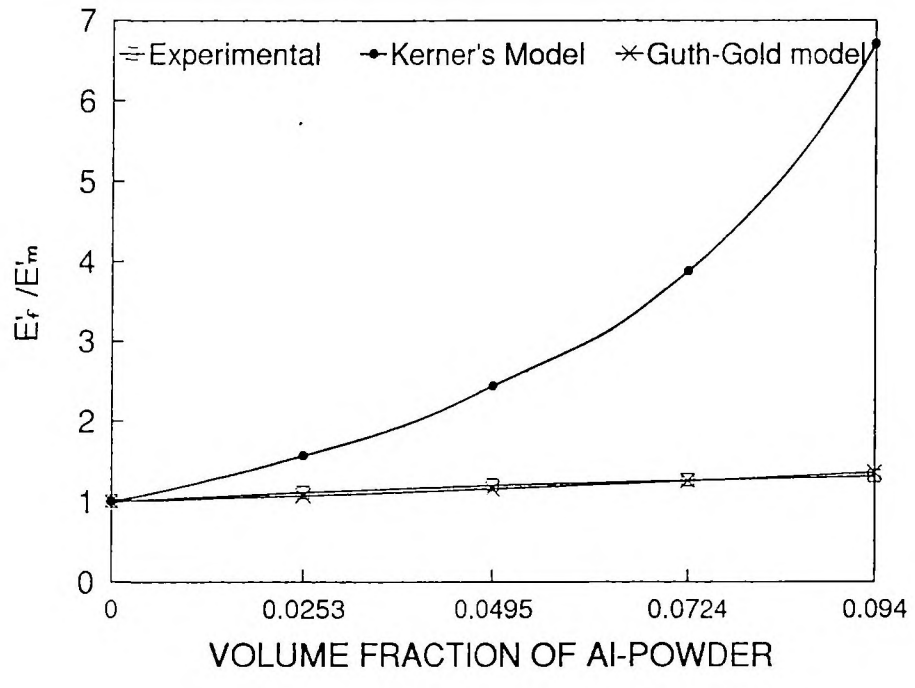

Figure VII.15. Relative modulus E'_f/E'_m as a function of aluminium powder concentration at 35°C, 10 Hz

The hydrodynamic interaction model for rubber reinforcement was developed by Guth and Gold [18,19]. The model is described by the equation

$$E'_f = E'_m (1+ \alpha\phi + \beta\phi^2) \quad \ldots\ldots \text{(VII.3)}$$

E'_f, E'_m and ϕ has the same meaning as the above equation. For Vander Walls types of interaction between rubber and the dispersed filler particles, α=2.5 and β=14.1.

Figure VII.15. shows the experimental and theoretical curves of the storage modulus of NR-aluminium powder composites as a function of volume fraction of aluminium powder. It is seen that the experimental values are close to the Guth and Gold model. It is well known that the term 'α' depends on dispersion of the filler particles in the matrix and 'β' depends on molecular interaction [19]. Hence, the value of 'β' can be used to study the interaction of filler with matrix. In the present case, α, the degree of dispersion is taken as constant (2.5) for a particular loading of aluminium powder since we are given the same procedure and time for mixing. The variation in β with various bonding agents in 10 phr loading of aluminium powder is shown in Table VII.2. It is seen that the β values are remarkably increased by the use of bonding agents due to the increased interaction of aluminium powder with natural rubber in presence of bonding systems.

Zhou *et al.* [20] introduced a new concept as that of equivalent interfacial thickness, R, as derived from the Halpin-Tsai equation [21]. This concept substantiates the idea that the interface can be understood as a uniform layer, assuming that property variation in filler-reinforced materials generated at the interface is a consequence of an increment in filler radius in such a way that greater ΔR will stand for stronger interfacial action. ΔR is expressed as

$$\Delta R = R_0 \sqrt{(B-1)} \quad \ldots\ldots\ldots \text{(VII.4)}$$

where R_0 is the filler radius and B can be determined using the equation,

$$\frac{(E'_f/E'_m) - 1}{(E'_f/E'_m) + 2} = B\phi \quad \ldots\ldots\ldots \text{(VII.5)}$$

where the parameters has the same meanings as above equations. It is clear that 'ΔR' is proportion to the value of 'B'. A comparison of 'B' values will give an idea about the rubber-filler interaction. The calculated 'B' values for NR-aluminium powder (10phr) composites with various bonding agents are given in Table VII.2. The B values increased with the use of bonding agents which follow the order, HR-system >Si-69 > TDI >CoN. This again supported the increased interaction of aluminium powder with natural rubber by the use of bonding agents.

Table VII.2. Values of β and B of NR-aluminium powder composites with bonding agents

Sample	β	B
10 Al (with out bonding agent)	15.50	1.027
HR	1471.0	9.917
Si-69	1401.4	9.584
CoN	980.00	7.396
TDI	1165.0	8.395

VII.6. Conclusions

Dynamic mechanical properties of natural rubber vulcanizates containing aluminium powder have been investigated and are compared with those of vulcanizates containing conventional fillers. Presence of

aluminium powder increased the storage modulus, loss modulus and tanδ value of natural rubber composites. These properties are also increased with the loading of aluminium powder. Additions of other fillers like HAF, GPF, acetylene black, china clay and precipitated silica to natural rubber increased the storage modulus, loss modulus and tanδ values of rubber vulcanizates. The increase follows the same order as that of the reinforcing capacity of these fillers. The filler-rubber interface has a vital role in determining the viscoelastic properties of the composites. The effect of various bonding agent viz. hexamethylene tetramine- resorcinol system (HR), bis [3-(triethoxysilyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN), toluene diisocyanate (TDI) have been investigated. Presence of bonding/coupling agents increases the tanδ values, due to the improved adhesion between rubber and aluminium powder. With increase in temperature, tanδ decreased gradually. Dynamic mechanical properties are also influenced by the frequency of measurements.

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CHATPER VIII

DEGRADATION BEHAVIOUR OF NATURAL RUBBER-ALUMINIUM POWDER COMPOSITES

Results of this chapter have been communicated to Polymer Degradation and Stability

Natural rubber (NR), unlike many other polymers, is highly susceptible to degradation, due to the presence of active double bonds in the main chain. Degradation of NR is accelerated mainly by heat, humidity, light, ozone, oxygen, radiation etc. In routine technological evaluation, rubber vulcanizates are subjected to accelerated ageing tests to get information about their service life. This problem was well recognized by Baker [1] who examined the effect of temperature on the ageing behaviour of natural rubber compounds. Effects of high-energy radiation, thermal and ozone exposure in natural rubber composites containing short sisal fibre were reported [2]. Many of the chemically unsaturated rubbers are prone to attack by even the minute quantities of ozone present in the atmosphere. Such attack affects the surface appearance of rubber products and it causes loss of physical properties, especially in thin-walled articles. Natural rubber when properly compounded either with suitable waxes or antiozonants, will get ozone resistance as good as or even better than many synthetic rubbers [3]. Degradation of NR by radiation is also a serious problem, mainly from gamma-ray irradiation, which is usually applied in sterilization process. With gamma ray irradiation high molecular weight materials may decompose. The mechanism of characteristic changes in gamma ray irradiated polymer, including degradation and crosslinking has been studied by Shintani and Jakamura [4]. The effects of temperature and environmental factors on the performance of polymers and various degradation reactions including their mechanisms are available in the literature [5-10].

Table VIII.1 Formulations of mixes

Ingredients	GUM	HAF	GPF	ACB	CLY	SIL	10Al	20Al	30 Al	40 Al	HR	Si-69	CoN	TDI
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Aluminium powder	-	-	-	-	-	-	10	20	30	40	10	10	10	10
HAF	-	40	-	-	-	-	-	-	-	-	-	-	-	-
GPF	-	-	40	-	-	-	-	-	-	-	-	-	-	-
Acetylene black	-	-	-	40	-	-	-	-	-	-	-	-	-	-
China clay	-	-	-	-	40	-	-	-	-	-	-	-	-	-
Precipitated silica	-	-	-	-	-	40	-	-	-	-	-	-	-	-
Hexa	-										1.0	-	-	-
Resorcinol	-										2.0	-	-	-
Si-69	-										-	1.0	-	-
Cobalt naphthenate	-										-	-	1.0	-
TDI	-										-	-	-	1.0
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

TDQ - 2,2,4-trimethyl-1,2-dihydroquinoline
Hexa – hexamethylene tetramine
TDI – toluene diisocyanate
Si-69 - bis[3-(triethoxysilyl) propyl] tetrasulphide
CBS - N-cyclohexyl benzothiazyl sulphenamide

Introduction of filler into polymers leads to a wide range of interactions arising at the polymer-filler interface. These dispersed fillers considerably influence the properties of the polymer composites, including their degradation and stability. The major factors that control these properties are the surface chemistry of the filler, nature, shape and size of particles, size distribution and specific surface area etc. [11]. This chapter contains the ageing properties of aluminium powder filled natural rubber composites.

The formulation of mixes used for the study was given in Table VIII.1. Resistance towards heat, ozone, gamma-irradiation and flame resistance were studied, the procedures of which are described in section II.4. Effects of loading of aluminium powder and various bonding agents have been investigated. For comparison of results, vulcanizates containing conventional fillers are also included in the study.

VIII.1. Effect of Heat Ageing

Figure VIII.1 illustrates the percentage decrease in tensile strength and modulus (300%) due to thermal ageing for natural rubber composites containing 40 phr loading of various fillers. After keeping at 70^0C for 14 days, the percentage decrease in tensile strength followed the order clay<aluminium powder <GPF < acetylene black<HAF<silica. The results showed that clay and aluminium powder incorporated vulcanizates have better retention of mechanical properties after ageing compared to other fillers. The action of oxygen on natural rubber is activated by heat. For assessing the long-term serviceability of the vulcanizates, variation in modulus along with the variation in tensile strength is helpful. From the figure it is clear that the percentage decrease in 300% modulus due to ageing follows the order, aluminium powder<clay<acetylene black <GPF<HAF

<silica. This showed that aluminium powder filled natural rubber composites have the minimum loss in its properties compared to other fillers. The influence of temperature is not direct, as in normal chemical reactions in promoting the reaction but it is mainly an indirect effect, which finally leads to polymer degradation.

Variation in tensile strength of natural rubber vulcanizates containing different loadings of aluminium powder after thermal ageing is shown in Figure VIII.2. An increase in tensile strength is observed with aluminium powder filled samples at all loadings.

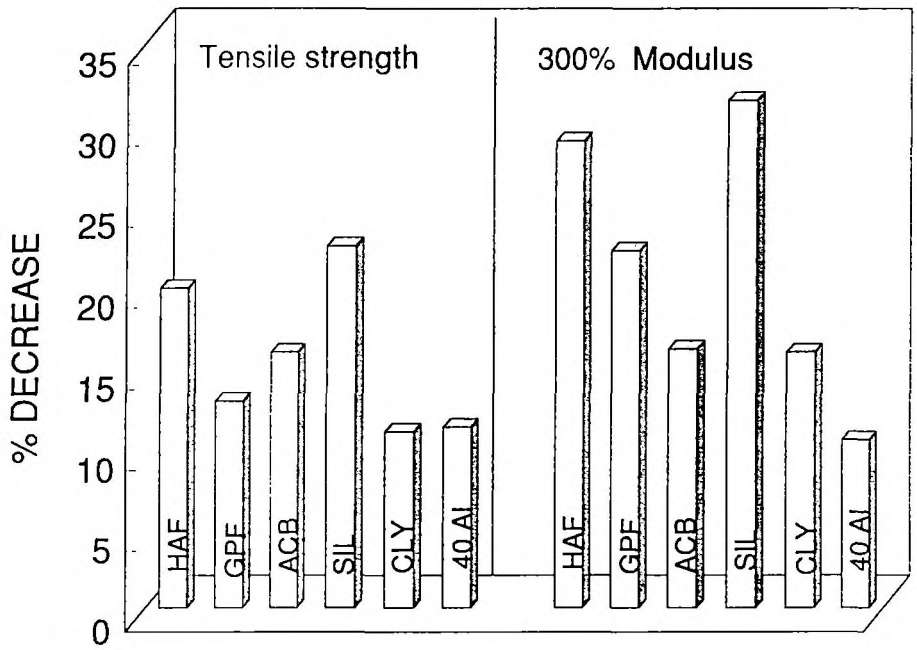

Figure VIII.1. Percentage decrease in tensile strength and modulus (300%) of NR vulcanizates containing various fillers, after ageing at 70°C for 14 days

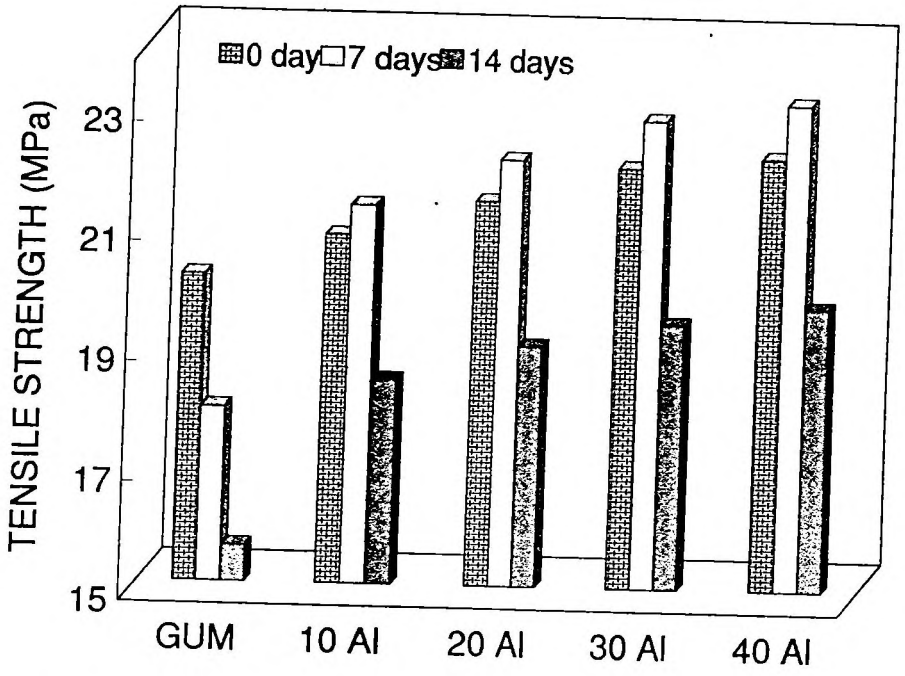

Figure VIII.2. Variation in tensile strength of aluminium powder filled natural rubber composites after ageing at 70°C

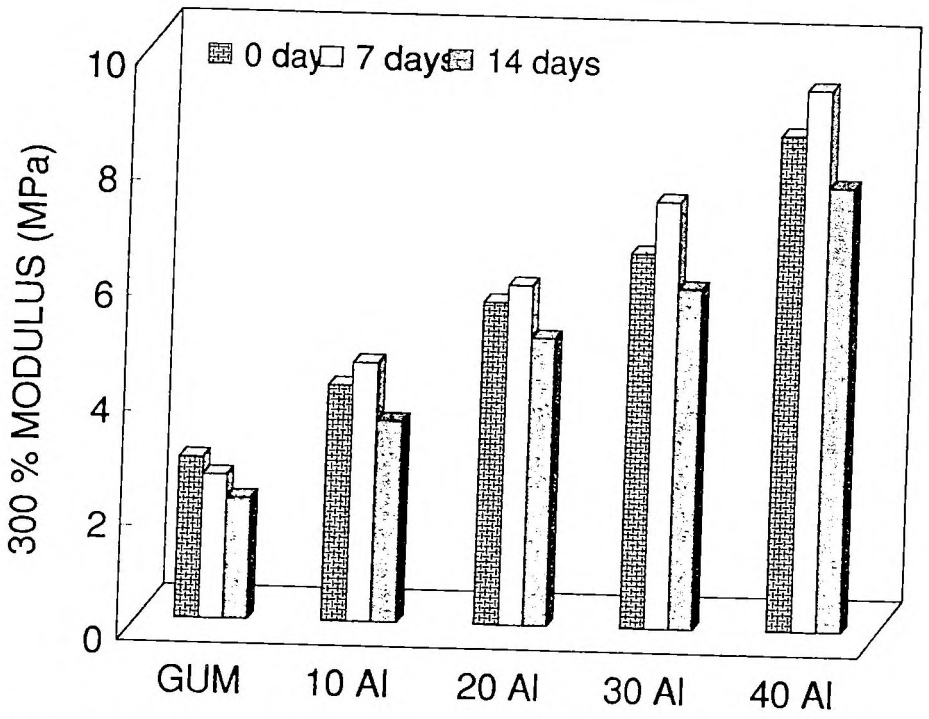

Figure VIII.3. Variation of modulus (300%) of aluminium powder filled natural rubber composites after ageing at 70°C

The higher retention in tensile strength (>100%), after ageing at 70^0C for 7 days of the vulcanizates could be due to the continued cross-linking of the elastomer. Ageing for 14 days at 70^0C results in a decrease of tensile strength at all loadings. However, the filled samples showed better retention than the gum sample. Figure VIII.3 shows the variation in modulus (300%) of the aluminium powder filled vulcanizates. From the figure it is clear that as the loading of aluminium powder increased, the modulus also increased. The increase in modulus is due to the higher extending of cross-links formed in the composites, in presence of aluminium powder. Due to thermal ageing the gum composite gradually loses the modulus due to polymer degradation. In aluminium powder filled vulcanizates an increase in modulus is observed after 7days ageing and a decrease after 14 days ageing at 70^0C, the same trend as in the case of the tensile strength values after ageing. In rubber compounds, high temperature causes two competing reactions namely the cross-link formation and scission of chains. The slight increase and then the decrease in tensile strength and modulus values of these composites can be explained on the basis of these processes. At lower periods of ageing the extent of main chain scission is less and effect of cross-linking predominates but at longer periods the reverse situation occurs resulting in lower retention of tensile strength and modulus.

Figure VIII.4 shows the tensile strength of natural rubber-aluminium powder composites containing different bonding agents. after ageing. The bonding/coupling agents used were hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl)propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI). The 300% modulus of these composites and its variations due to thermal ageing are presented in Figure VIII.5.

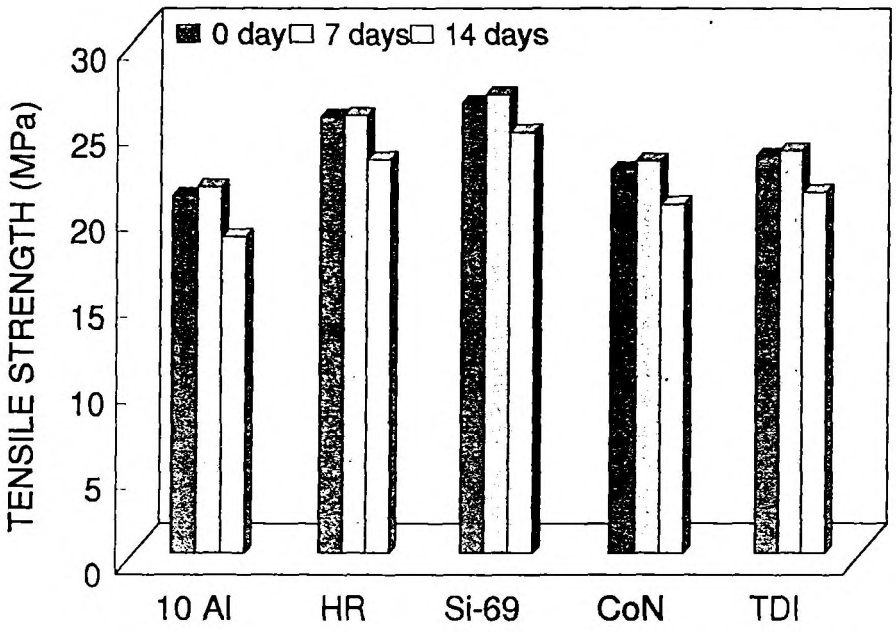

Figure VIII.4. Dependence of tensile strength with ageing at 70°C for NR-aluminium powder (10 Phr) composites containing different bonding agents

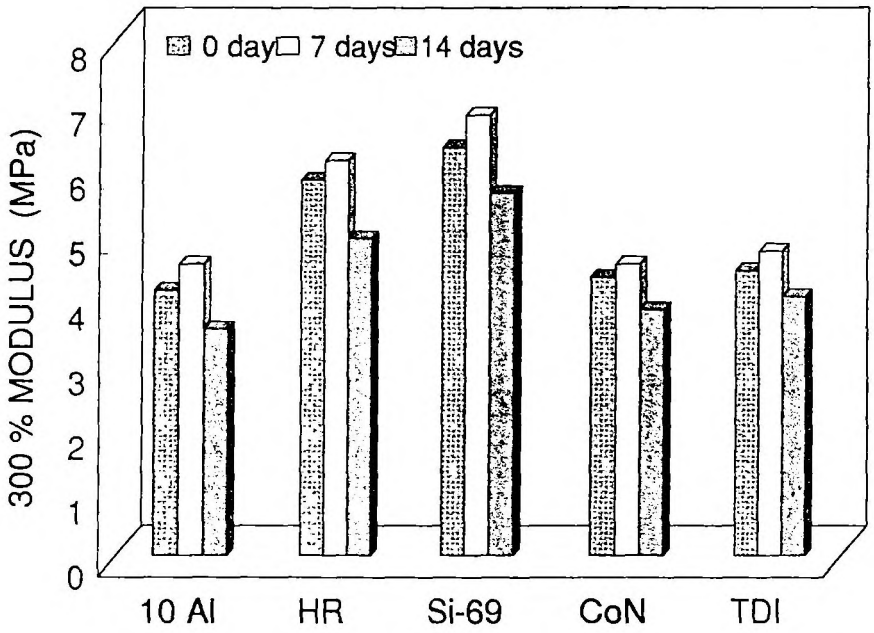

Figure VIII.5. Dependence of 300% modulus with ageing at 70°C for NR-aluminium powder (10 Phr) composites containing different bonding agents

It is seen that both the tensile strength and modulus slightly increased in all cases after ageing at 70^0C for 7 days. Further ageing at the same temperature caused more polymer degradation than crosslink formation resulting in a decrease of tensile strength and modulus.

Table VIII.2. Variation in the elongation at break values (%) of the composites after ageing at 70°C.

Sample	0 day	7 days	14 days
GUM	800	788	760
HAF	374	371	362
GPF	356	344	328
ACB	378	371	346
SIL	445	439	425
CLY	490	479	468
10 Al	790	785	779
20 Al	751	745	730
30 Al	660	642	620
40 Al	550	544	539
HR	715	702	695
Si-69	642	631	620
CoN	750	729	710
TDI	733	719	700

The elongation at break (%) values of the composites are presented in Table VIII.2. It is seen that the elongation at break (EB) is maximum for gum vulcanizate and the loading of aluminium powder decreased the elongation at break. Presence of bonding agent further decreased the EB. The improved adhesion in presence of bonding agent restricts the mobility of polymer segment, which finally results a reduction in elongation. The thermal ageing caused a slight reduction in the elongation at break in all

cases. Both the cross-link formation and main chain scission at high temperature causes reduction in polymer elongation. We have seen that the tensile strength and modulus are slightly increased by ageing due to additional (7days at 70^0C) crosslinks formed during the ageing period. This additional crosslinks reduced the elongation of the composites. Ageing at 70^0C for 14 days further decreased the maximum elongation, but here the main mechanism involves the chain scission due to polymer degradation as evident from the loss in tensile strength values.

VIII.2. Effect of Gamma Radiation

The effect of γ-radiation on the tensile properties of various filler incorporated vulcanizates is given in Figure VIII.6. Gamma irradiation caused a decrease in tensile strength of all compounds, but the extent of decrease is different. From the figure it is clear that the percentage decrease is minimum for aluminium powder filled compounds, whereas in other cases a sharp fall in tensile strength was observed. Though gamma irradiation can cause crosslinking and polymer degradation, the reduction in tensile value shows that chain scission leading to polymer degradation is the main reaction here. Figure VIII.7 shows the effect of gamma radiation on tensile strength of natural rubber-aluminium powder composites at different loadings of aluminium powder. The tensile strength of the gum sample was reduced sharply from the initial value after a radiation dose of 18 M rads. At all loadings, aluminium powder incorporated samples showed better resistance towards γ-radiation than the gum samples. The effect of various bonding agents on NR-aluminium powder composites towards gamma irradiation is shown in Figure VIII.8. Here also the irradiation caused a reduction in the tensile strength, the same trend as observed in composites having no bonding agent.

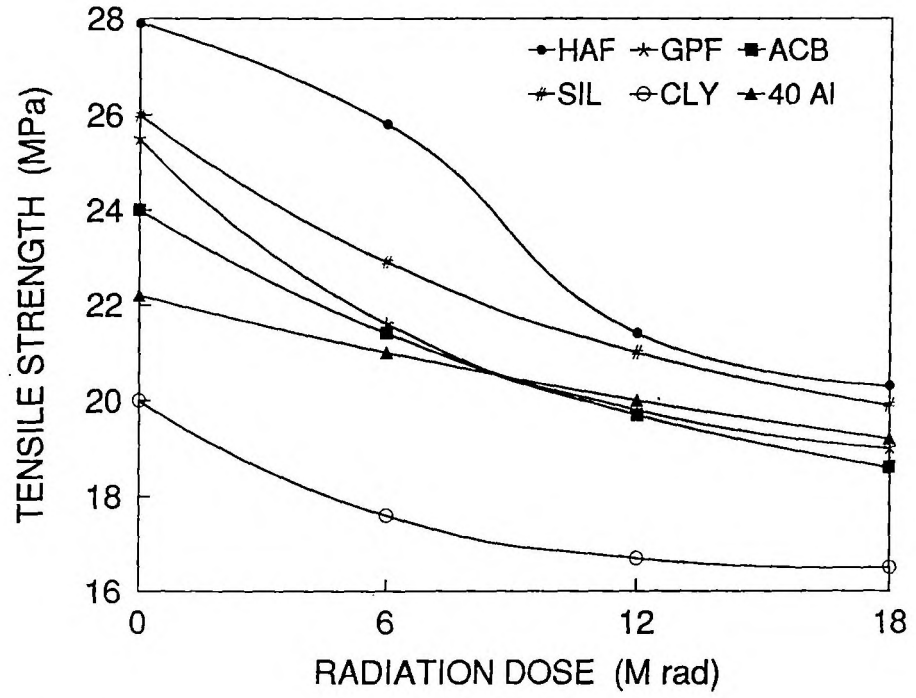

Figure VIII.6. Variation in tensile strength with gamma irradiation for NR-vulcanizates containing different fillers

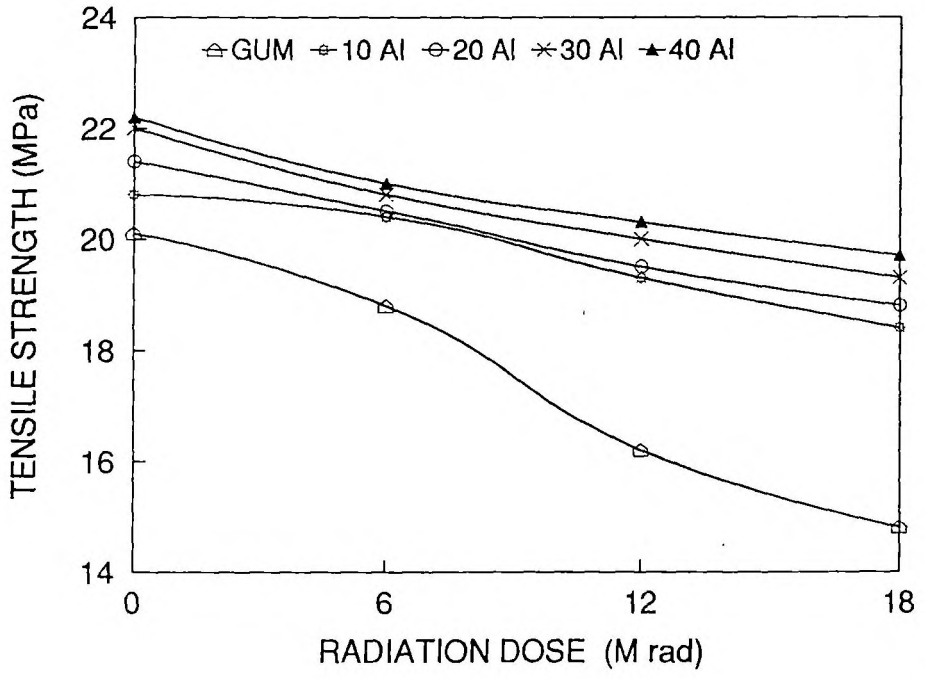

Figure VIII.7. Effect of gamma radiation on natural rubber-aluminium Powder Composites

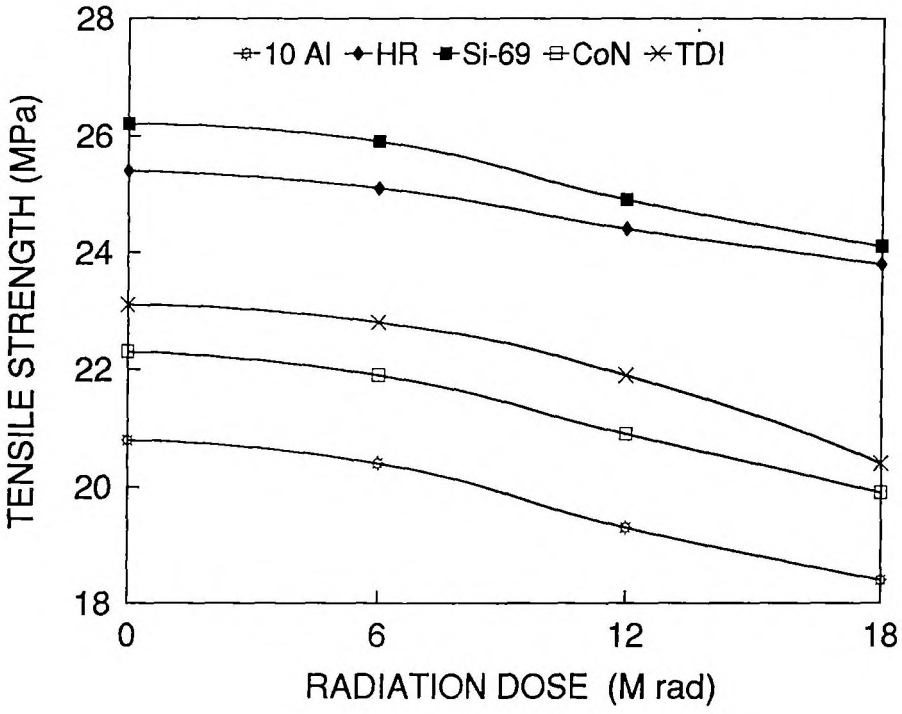

Figure VIII.8. Variation in tensile strength with gamma irradiation for NR-aluminium powder (10Phr) composites containing different bonding agents

VIII.3. Ozone Resistance of NR-Aluminium Powder Composites

For assessing the ozone resistance of the aluminium powder filled vulcanizates, test samples having 20% strain were exposed to ozonized air having 50 pphm ozone concentration. Characteristic cracking in rubber is not observed unless a tensile strain is imposed during exposure, and once the strain is exceeded, a crack will grow at a constant rate independent of additional strain, and for many rubbers in direct proportion to ozone concentration [3].

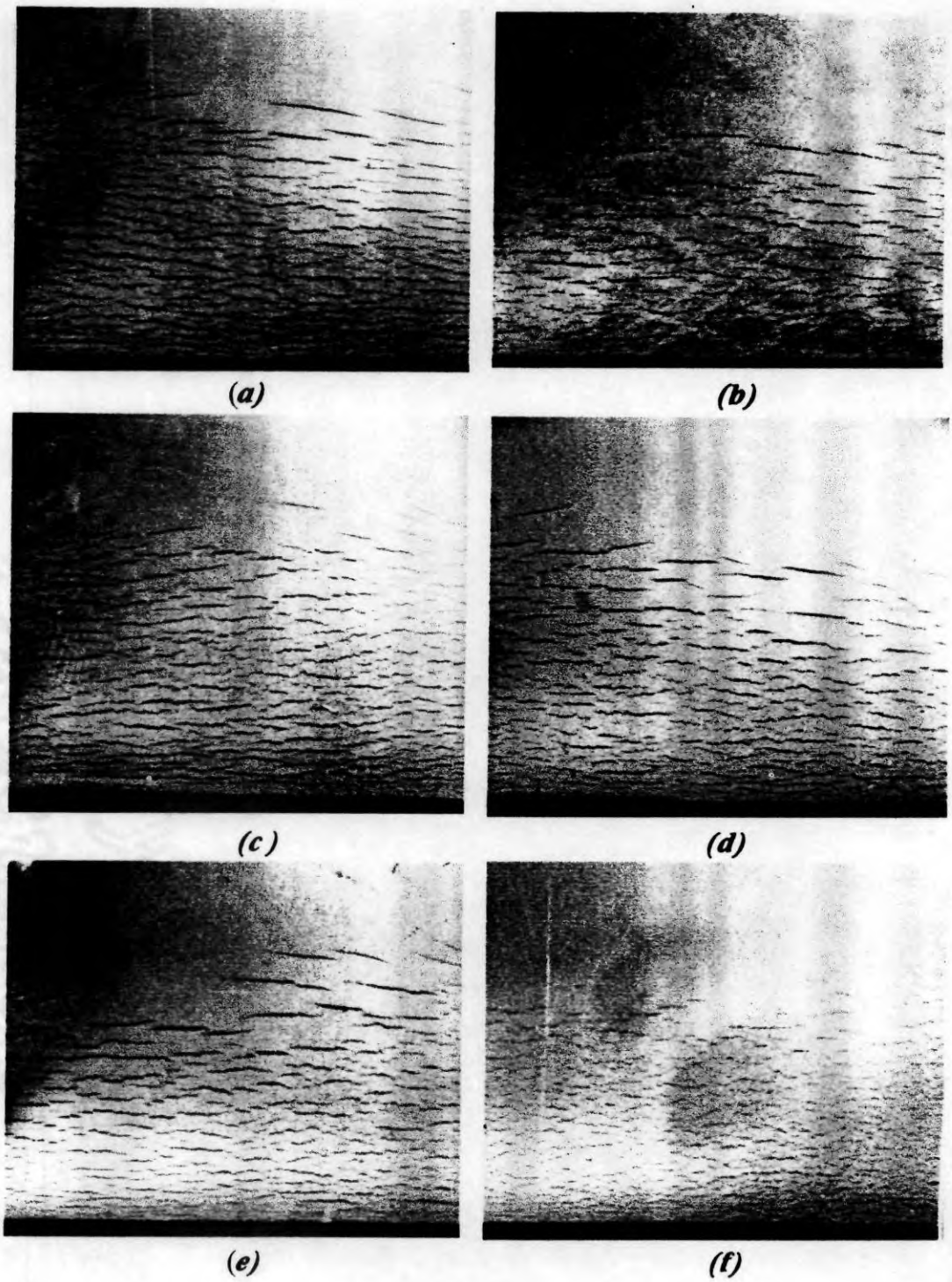

Figure VIII.9. Optical photomicrographs of ozone exposed (10 hrs) NR-vulcanizates containing 40phr fillers (a) HAF (b) GPF (c) acetylene black (d) precipitated silica (e) china clay and (f) aluminium powder

In the case of NR-aluminium powder composites it is seen that cracks were developed on the surface of all the samples immediately after two hours of exposure to ozone. However, the nature and intensity of cracks due to ozone attack are different for various vulcanizates. Optical photographs of the surfaces of vulcanizates after 10 h of ozone exposure are presented in Figures VIII.9(a-f). In the case of aluminium powder incorporated samples the cracks are small and discontinuous whereas a lot of continuous, deep cracks are observed in the vulcanizate having no aluminium powder. It may due to the higher extent of cross-links formed in these composites, due to the higher thermal conductivity of aluminium powder. The presence of aluminium powder as an inert particle in the elastomer prevents the growth of cracks along the polymer. A growing crack in the reactive phase must, sooner or later encounter an inert particle and come to a halt, further propagation being possible only by the crack circumventing the particle or jumping over it. Except for very small particles circumvention is unlikely, since it would involve the crack propagating parallel to the applied stress, ie., in a direction involving a minimum release of elastic stored energy [12]. The length of cracks in the reactive phase is governed by the density and nature of the unreactive particles present in the polymer. From the photograph it is clear that incorporation of aluminium powder will impart better ozone resistance compared to other filler incorporated vulcanizates. The same trend is observed with vulcanizate containing bonding agents.

VIII.4. Limiting Oxygen Index Values of the Vulcanizates

The limiting oxygen index (LOI) values of natural rubber composites containing aluminium powder are given in Table VIII.3. The LOI is defined as the volume fraction of oxygen in an oxygen-nitrogen atmosphere that will just support steady candle like burning of a material. It has been widely

applied as a measure of the polymer flammability. All fillers including aluminium powder increased the LOI value of the gum compound and LOI value increased with aluminium powder loading. But the addition of bonding agent was found to have less effect on the LOI values.

Table VIII.3. LOI Values of the Composites

Sample	LOI (%)
GUM	16.4
HAF	18.4
GPF	18.2
ACB	18.0
SIL	18.1
CLY	18.2
10 Al	17.3
20 Al	17.4
30 Al	17.8
40 Al	18.2
HR	17.3
Si-69	17.5
CoN	17.4
TDI	17.4

VIII.5. Conclusions

Compared to other fillers, aluminium powder filled natural rubber composites retained the mechanical properties after thermal ageing. Ageing at 70^0C for 7days slightly increased the tensile strength due to the continued crosslinking in the composites, but degradation predominates on prolonged

ageing, resulting a decreased tensile value. The elongation at break is found to decrease on prolonged ageing. Gamma irradiation caused a decrease in tensile strength for all compounds and is minimum for aluminium powder incorporated samples. The trend remains same irrespective of aluminium powder loading and presence of various bonding agent. Optical photographs of ozone exposed samples showed that cracks were developed on the surface after two hours of ozone exposure. In the case of aluminium powder filled vulcanizates, the cracks developed are small and discontinuous, whereas in other samples the cracks are deep, wide and continuous. There is no adverse effect due to the presence of bonding agents like hexamethylene tetramine-resorcinol system, bis[3-(triethoxy silyl) propyl] tetrasulphide, cobalt naphthenate and toluene diisocyanate, on the ageing performance of natural rubber-aluminium powder composites. However HR system shows a better retention of properties after the ageing period due to the continued resin for the ageing process. The LOI values are increased by the incorporation of various fillers including aluminium powder.

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CHAPTER IX

UNIFORM CURING AND REDUCTION IN VULCANIZATION TIME OF THICK RUBBER ARTICLES USING ALUMINIUM POWDER

Results of this chapter have been communicated to NR Technology

Natural rubber compounds found use in various engineering application for decades due to their outstanding properties. They occupy the lion's share in moulded thick rubber articles for a number of reasons. However, uneven curing of the surface and interior portions of thick rubber articles is a serious problem. Since rubbers are poor conductors of heat, the interior portion of thick rubber articles may not be sufficiently cross-linked, and hence additional time is given for their vulcanization [1]. As a result, the surface of the article becomes overcured (highly cross-linked) whereas the interior portion may be in a state of undercure (poorly cross-linked). Moreover it requires additional time for moulding and thus expending additional energy, which reduces the output. Several methods have been adopted to get a uniform cure in thick articles. These include microwave heating [2], use of heat resistant, efficient vulcanization systems [3], use of delayed action accelerators [4], use of retarders [5], 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 [6]. Work has been reported on heat transfer and vulcanization of rubber products [1] and on the influence of degree of vulcanization on thermal conductivity [7,8]. Addition of conductive fillers like metal powders to rubber compounds will enhance the heat conduction and lead to uniform curing of thick articles.

Here, two products namely dock fender and brake of rice polisher were selected as thick rubber articles to investigate the role of aluminium powder in reducing the vulcanization time and thus attaining uniform in

curing of the surface and interior portions of the products. Dock fender [9] is used for gentle docking of ships at ports. When a ship docks, the fender system must be able to withstand sudden heavy load in various directions. The energy-absorbing medium is a large cylinder made up of vulcanized natural rubber. Rice polisher brake is a long rectangular soft rubber block placed in an abrasive cone polisher between the wire mesh segments for restricting motion of brown rice around the rotating abrasive cone. Both these products suffer serious problems due to the uneven curing of the surface and interior portions during vulcanization. Here, efforts are made to solve the uneven curing by the incorporation of aluminium powder, which is a conductive filler.

Formulations used are given in Table IX.1. To study the crosslinking pattern in thick rubber articles, rubber cubes of 5cm in size were moulded by giving different periods of cure. The cubes were then sliced and the outer and central layers were subjected to swelling in toluene upto equilibrium. Rice polisher brake was moulded with a size of 4 x 4.5 x 46 cm at 150^{0}C in a hydraulic press. Dock fender samples with 12.5 cm (inner diameter) x 25 cm (outer diameter) and having a length of 250 cm, were moulded by winding the compounded sheet on a steel mandrel and then steam curing at 55psi pressure in an autoclave. The vulcanized pieces were then sliced to obtain outer and inner layers for studying the cross-link density.

IX.1. Properties of Aluminium Powder Incorporated Compounds

The standard specifications suggest that the dock fender material requires a minimum tensile strength of 16 MPa, elongation at break 350%, a maximum hardness of 72 IRHD, and a compression set of not more than 25 per cent after 22 h at 70^{0}C. The base formulation was designed to meet all these technical requirements. Substitution of a part of the filler by aluminium powder marginally improved the properties like compression set

and heat build-up. This is due to the increased amount of crosslinking with the better conduction of heat, as indicated by reduced swelling values. In the case of aluminium powder incorporated vulcanizates, hexamethylene tetramine-resorcinol system was used as a bonding agent to minimise the abrasion loss. Resorcinol combines with methylene donor *insitu* during vulcanization, which binds the rubber and the metal powder [10]. The important properties of the vulcanizates are given in Table IX.2.

Table IX.1. Formulations of mixes for dock fender and rice polisher brake

Ingredients	DSD	DAL	RSD	RAL
Natural rubber	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0
HAF	30	30	--	--
FEF	40	20	--	--
Silica	--	--	30	20
China clay	--	--	20	10
Aluminium powder	--	20	--	20
Diethylene glycol	--	--	1.0	1.0
Naphthenic oil	2.0	2.0	2.0	2.0
Resorcinol	--	2.0	--	2.0
Hexamethylene tetramine	--	0.75	--	0.75
DCBS	0.8	0.8	1.0	1.0
PVI-50	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.25	2.25

TDQ - 2,2,4-trimethyl 1,2-dihydroquinoline
HAF - high abrasion furnace black
DCBS - dicyclohexyl benzothiazyl sulphenamide
FEF - fast extrusion furnace black
PVI - pre vulcanization inhibitor

The optimum cure time did not change with the addition of aluminium powder in both, dock fender and rice polisher brake compounds.

The hardness and rebound resilience are increased whereas the equilibrium swelling decreased for the aluminium powder incorporated sample. These are due to the increased amount of crosslinking with the better conduction of heat, and also due to the increased adhesion between natural rubber and aluminium powder in presence of hexamethylene tetramine-resorcinol system.

Table IX.2. Properties of vulcanizates

Property	DSD	DAL	RSD	RAL
Optimum cure time, T_{90}, min.	12.5	12.5	18.0	18.0
Max torque, dNm.	100	99	63	65
Rheometric induction time, min.	3.0	2.5	3.0	2.5
Cure rate index, min^{-1}.	12.5	12.5	7.1	7.1
Hardness, IRHD	70	72	49	51
Modulus (300%), M Pa	18.1	17.5	3.7	6.3
Tensile strength, M Pa	23.6	21.6	19.0	19.6
Elongation at break, %	357	367	788	735
Tear strength, kNm^{-1}	56.4	54.6	52.1	50.4
Compression set, %	23.8	21.7	32.0	30.5
Heat build up, $\Delta T\ ^0C$	39	37	21	20
Rebound resilience, %	53.2	54.0	59.7	60.3
DIN abrasion loss, mm^3	83	139	164	169
Equilibrium swelling (mol %)	1.705	1.669	3.150	2.901
Retention in tensile strength, %	78	88	85	87

It is seen that, the resistance towards thermal ageing of the composites are improved by the addition of aluminium powder. After keeping at 70^0C for 7 and 14 days, the percentage retention of tensile strength is higher in the case of aluminium powder incorporated compound. This is true for both dock fender and rice polisher compounds. Ozone exposure of the samples showed that cracks were developed on the surface

of both samples after two hours. However, in the control compound, the cracks were deep, wide and continuous, whereas in DSD and RSD samples the cracks were small and discontinuous.

Substitution of a part of the filler (20 parts) by aluminium powder markedly increased the thermal conductivity (Figure IX.1). Between the control compounds, 'DSD' showed better thermal conductivity due to the presence of carbon blacks. Compound 'RSD' contained silica and china clay, which are having lower conductivity compared to carbon black. The increase in thermal conductivity due to addition of aluminium powder is almost identical in both the compounds.

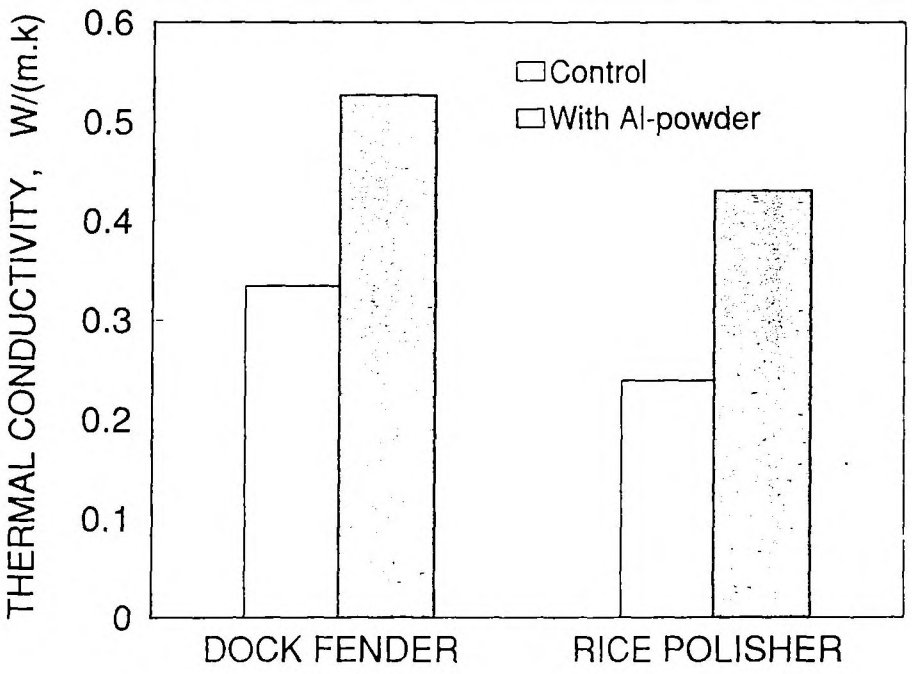

Figure IX.1. Thermal conductivity increase of the composites by the replacement of 20 phr HAF with Aluminium powder

IX.2. Uniform Curing of Thick Articles Using Aluminium Powder

Thermal conductivity of rubber compound is very important in the vulcanization of thick article as it helps to achieve uniform crosslinking. To follow the extent of crosslinking in thick articles, rubber cubes having 5 cm in diameter and different crosslink densities were prepared. Test pieces from the surface and central portions were taken [Figure IX.2] and were assessed for crosslink density by swelling method. Parks [11] suggested that the value of 1/Q gives an idea about the degree of crosslinking, where Q is given by

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100/\text{Formula weight}} \quad \ldots\ldots\ (IX.1)$$

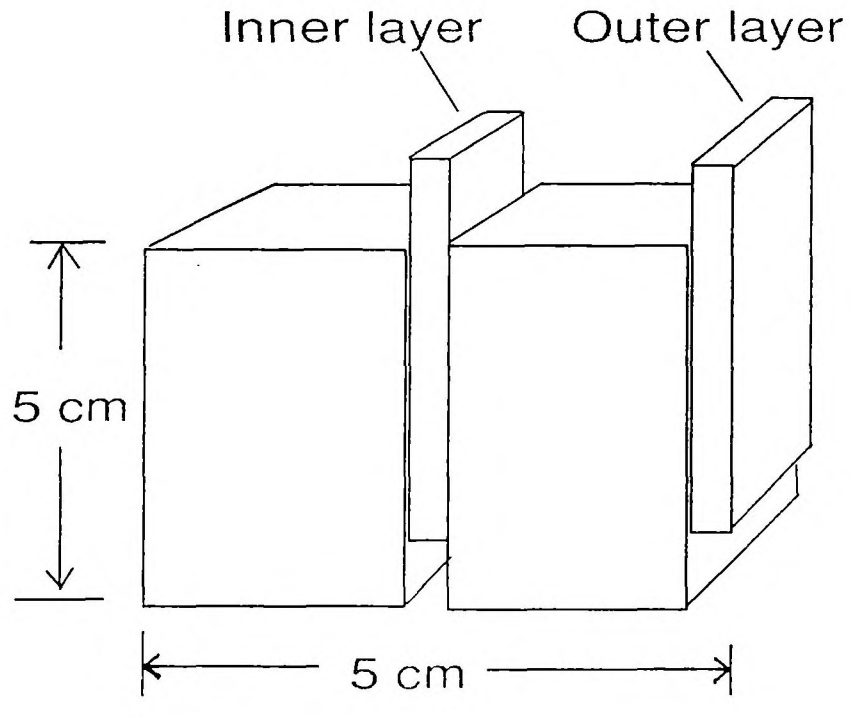

Figure IX.2. Samples from inner and outer layers of a rubber cube for swelling studies

The effect of aluminium powder on the 1/Q values of the centre and outer layers of the 5 cm rubber cube of dock fender and rice polisher brake compounds are shown in Figures IX.3 and IX.4 respectively. As the additional time given for vulcanization increases, the difference between 1/Q values of the centre and surface layers decreased. Less difference in 1/Q values suggests that the surface and centre portions have almost same cross link density. It is very interesting to note that this difference is decreased by the substitution of a part of the filler (20 phr) by aluminium powder. Measurements with the inner layer, sliced from the rice polisher brake compound (10 min additional curing), could not be made as the sample dissolves in the solvent because it is almost in an uncrosslinked state. Even after giving 30 minutes additional time over the optimum cure time, the control compounds of both the dock fender and rice polisher brake, had appreciable differences in cross link density between the outer and inner portions. Aluminium powder incorporated compound attained almost the same crosslink density in the inner and outer portions after giving 30 minutes additional vulcanization time. The same result can be observed on comparing the equilibrium swelling data. This result confirms that the use of aluminium powder imparts uniform crosslinking in thick articles through increased thermal conductivity. This technique also helps to reduce the vulcanization time of thick rubber articles.

Usual procedure for the vulcanization of thick articles is to give additional time over the optimum cure time for vulcanizing the interior portions. Conventionally 5 min additional time is given for every additional 6 mm thickness of the material at 150^0C. By this practice, the surface which is in contact with the hot mould becomes over cured and get degraded, as evident from the decrease in percentage retention of tensile strength after giving additional time for moulding (Table IX.3).

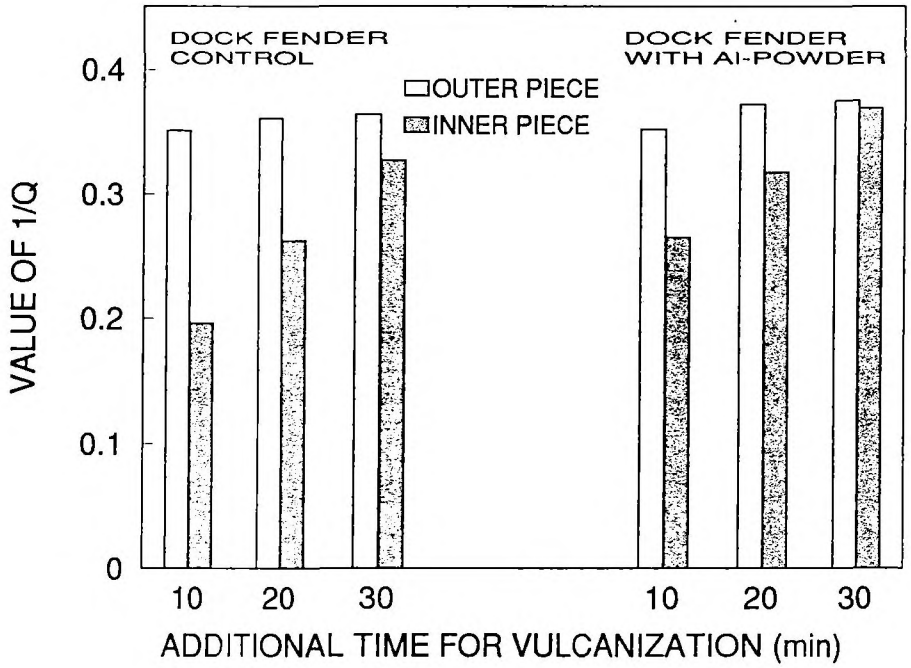

Figure IX.3. 1/Q values of inner and outer pieces of 5 cm cube of dock fender compound with and without aluminium powder

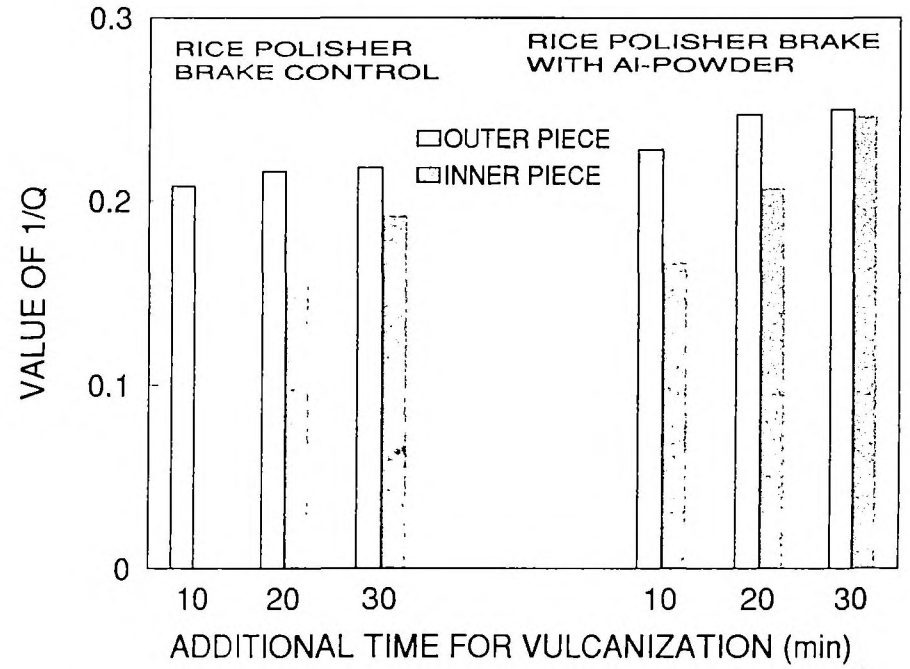

Figure IX.4 1/Q values of inner and outer pieces of 5 cm cube of rice polisher brake compound with and without aluminium powder

Table IX.3. Percentage retention of tensile strength after over curing

Sample	Additional time given for moulding (over curing)		
	15 min	30 min	45 min
Dock fender standard (DSD)	99	85	70
Dock fender with Al-Powder (DAL)	101	96	78
Rice polisher standard (RSD)	100	95	86
Rice polisher with Al-powder (RAL)	101	96	88

This reduction in tensile strength is due to the degradation of the polymer chain exposed to higher temperature for longer period. The same trend is reflected in other properties also. This observation emphasises the need for vulcanization of thick articles, in the minimum possible time.

IX.3. Uniform Curing of Dock Fender and Rice Polisher Brake

Figures IX.5 and IX.6 shows the photographs of dock fenders and rice polisher brakes, which were moulded to study the effect of aluminium powder in respective compounds. Here also, the slices from surface and central portions were taken for testing and were subjected to swelling studies to assess the crosslink density. The results are presented in Table IX.4.

The Q_α and 1/Q values were decreased on increasing the vulcanization time from 45 min to 60 min for the standard compound (DSD). The substitution of 20 phr of black with aluminium powder in this compound decreased the difference in crosslink-density between the outer and interior portions, as evident from the Q_α and 1 Q values of DAL.

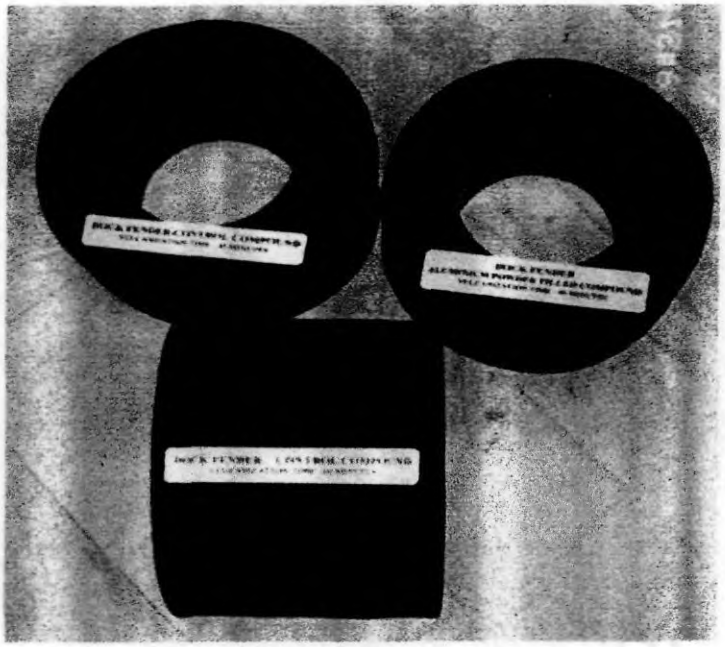

Figure IX.5 Photograph of Dock Fenders

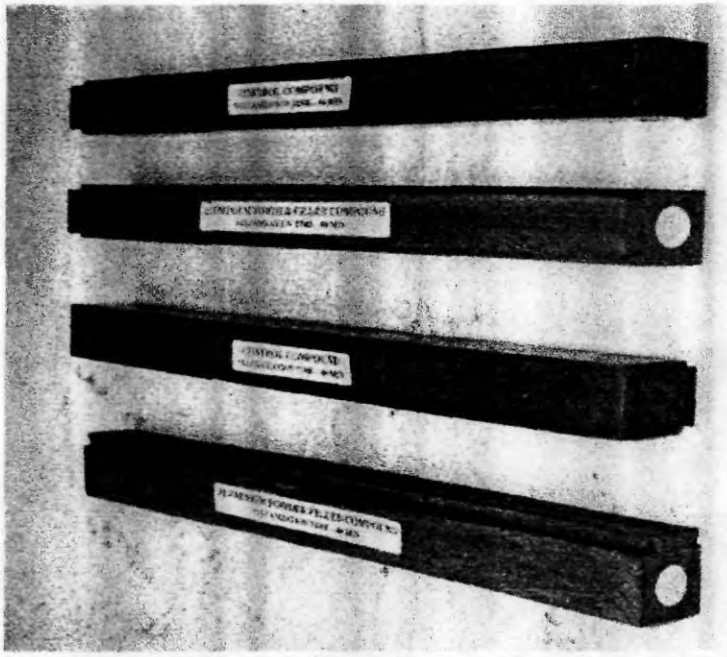

Figure IX.6 Photograph of Rice Polisher Brake

Table IX.4. Swelling values of inner and outer portions of dock fender and rice polisher brake

Sample	Cure time (min)	Q_α outer	Q_α inner	Differ. in Q_α	1/Q outer	1/Q inner	Differ. in 1/Q
Dock fender standard	45	1.604	1.693	0.089	0.362	0.342	0.020
	60	1.590	1.648	0.058	0.363	0.351	0.012
Dock fender with Al-powder	45	1.589	1.638	0.049	0.364	0.353	0.011
Rice polisher standard	40	3.151	3.927	0.776	0.208	0.167	0.041
	50	3.020	3.272	0.252	0.216	0.200	0.016
Rice polisher with Al-powder	40	2.700	2.817	0.177	0.244	0.234	0.010
	50	2.543	2.555	0.012	0.257	0.255	0.002

It is evident that the DAL compounds attained almost uniform cross-linking at a lower vulcanization time compared to that without aluminium powder. This is true in the case of rice polisher brake compound also. It is seen that vulcanization at 150^0C for 40 minutes gives better uniformity in cross-linking in the RAL compound compared to the control compound vulcanized for 50 minutes. This again confirms that aluminium powder imparts uniform curing and reduces the vulcanization time for thick articles. It is also noted that the effect of aluminium powder is best reflected when it is used in combination with non-black fillers, which are less conductive compared to carbon blacks.

IX.4. Conclusions

Uniform curing and reduction in vulcanization time of thick rubber articles such as dock fender and rice polisher brake were successfully achieved with the use of aluminium powder as a conductive filler. The mechanical properties of vulcanizates were determined and found that substitution of a part of the filler with aluminium powder did not affect the

properties to any significant level. However, it imparts better results against oxidative degradation and thermal ageing. Marked increase in thermal conductivity is obtained by the replacement of 20 phr of the filler by aluminium powder, which helps to attain uniform curing of thick rubber products, as indicated by swelling experiment conducted using test pieces taken from surface and central portions. All these results strongly supported the findings that increased thermal conductivity of aluminium incorporated rubber compound imparts uniform curing through out the material, which in turn reduces the total vulcanization time of thick rubber products. Thus use of aluminium powder in rubber compounds can considerably save the amount of heat energy required for the vulcanization of thick articles and uniform curing is achieved which enhances the service life of thick rubber articles.

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CHAPTER X

PROPERTIES OF ALUMINIUM POWDER FILLED STYRENE BUTADIENE RUBBER COMPOSITES

Results of this chapter have been communicated to Kautschuk Gummi Kunststoffe

Styrene Butadiene Rubber (SBR) is a versatile polymer widely used in many engineering applications and it accounts for 42% of the world market of elastomers because of its low cost, good abrasion resistance, and high level of uniformity compared to other rubbers. Reinforcement of SBR with carbon black leads to vulcanizates, which have high strength. The most important application of SBR is in tire products. The incorporation of carbon black into rubber vulcanizates gives improved properties like strength, extensibility, fatigue resistance, abrasion resistance etc. [1-3]. In certain applications, increased thermal and electrical conductivity of rubber compound is essential. During vulcanization, increased thermal conductivity helps to attain uniform curing and reduction in vulcanization time of thick articles. Investigations have been carried out to increase the thermal and electrical conductivity of the polymers., which are available in the literature [4-8]. Lu and Xu [9] reported that thermal conductivity of polyurethane composites filled with carbon fibres is about 50 times more than that of pure polyurethane. The advantage of metal powders over other fillers is that they provide good electrical and thermal conductivity to the composite [10-12].

In this chapter, the effects of aluminium powder on styrene butadiene rubber composites were studied in detail. For comparison, the properties of commonly used high abrasion furnace black (HAF) and conductive acetylene black incorporated SBR vulcanizates were also studied. Formulations used are given in Tables X.1a and X.1b. The procedures adopted for finding the hardness, tear strength, tensile properties, thermal conductivity etc. are given in chapter II.

Table X.1a. Formulations of mixes

Ingredients	GUM	HF1	HF2	HF3	HF4	AC1	AC2	AC3	AC4
SBR	100	100	100	100	100	100	100	100	100
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF	--	10	20	30	40	--	--	--	--
Acetylene black	--	--	--	--	--	10	20	30	40
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2

SBR - Styrene butadiene rubber TDQ - 2,2,4-Trimethyl-1,2-dihydroquinoline
HAF - High abrasion furnace black CBS - N-cyclohexyl benzthiazyl sulphenamide

Table X.1b. Formulationsof mixes

Ingredients	Al 1	Al 2	Al 3	Al 4	HAA	HAB	HAC
SBR	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF	--	--	--	--	30	20	10
Aluminium powder	10	20	30	40	10	20	30
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	2.2	2.2	2.2	2.2	2.2	2.2	2.2

SBR - Styrene butadiene rubber TDQ - 2,2,4-Trimethyl-1,2-dihydroquinoline
HAF - High abrasion furnace black CBS - N-cyclohexyl benzthiazyl sulphenamide

X.1. Effect of Aluminium Powder on Cure Characteristics

The cure characteristics of the SBR composites are given in Table X.2. The maximum torque values are found to be increased by the use of fillers namely HAF, acetylene black and aluminium powder. The optimum cure time decreased as the loading of fillers increased and is more pronounced in aluminium powder filled vulcanizates. Rheometric induction time (RIT) - the time available before the onset of vulcanization - was decreased in the same trend as shown by the optimum cure time. The cure rate index (CRI) was increased with HAF and aluminium powder while it decreased with acetylene black.

Table X.2. Analysis of rheometric curves

Sample	Max.Torque, dNm	t_{90} (min)	RIT (min)	CRI (min^{-1})
GUM	64	30.0	10.0	5.26
HF1	66	27.0	6.5	5.32
HF2	78	25.0	5.0	5.43
HF3	85	24.0	4.5	5.55
HF4	92	21.0	4.0	5.70
AC1	65	30.0	7.5	5.20
AC2	76	30.0	7.0	5.16
AC3	84	29.0	6.0	5.10
AC4	91	28.0	5.5	5.00
Al 1	65	28.0	7.0	5.72
Al 2	66	24.0	6.0	6.45
Al 3	68	21.0	5.0	6.89
Al 4	70	17.0	4.0	7.60

X.2. Effect of Aluminium Powder on Mechanical Properties

Figure X.1 shows the Shore A hardness of SBR vulcanizates containing HAF, acetylene black and aluminium powder as fillers. The increase in hardness is in the order HAF>acetylene black>aluminium powder. Since the particle size of aluminium powder used is much higher than that of HAF and acetylene black, the contribution to hardness increase by reinforcement is found to be lower for aluminium powder. The hardness of aluminium powder filled SBR–composites is mainly due to the higher extent of crosslinking achieved through better thermal conductivity.

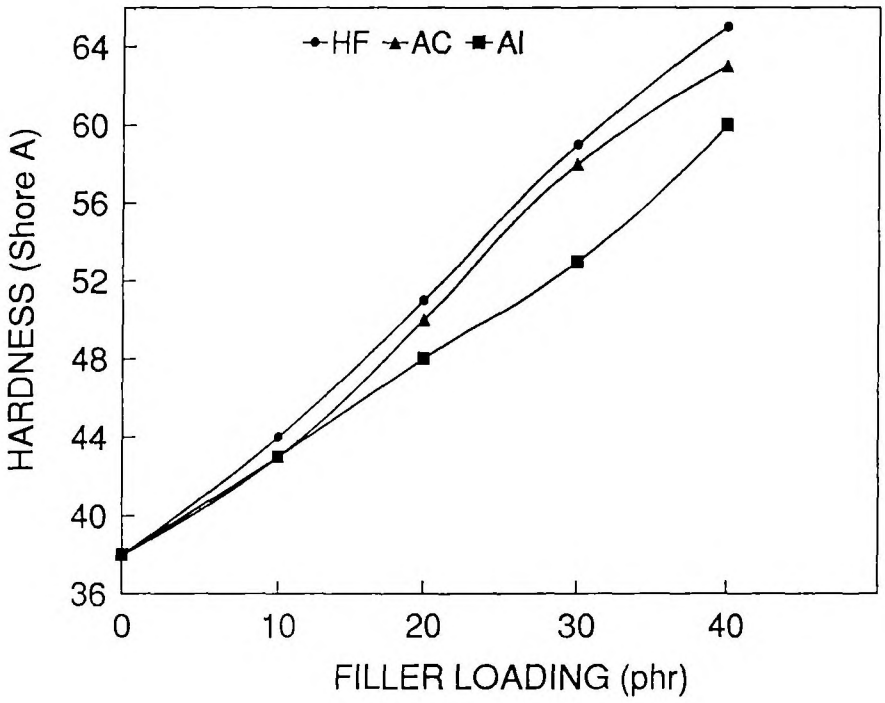

Figure X.1. Variation in hardness with filler loading in SBR-vulcanizates

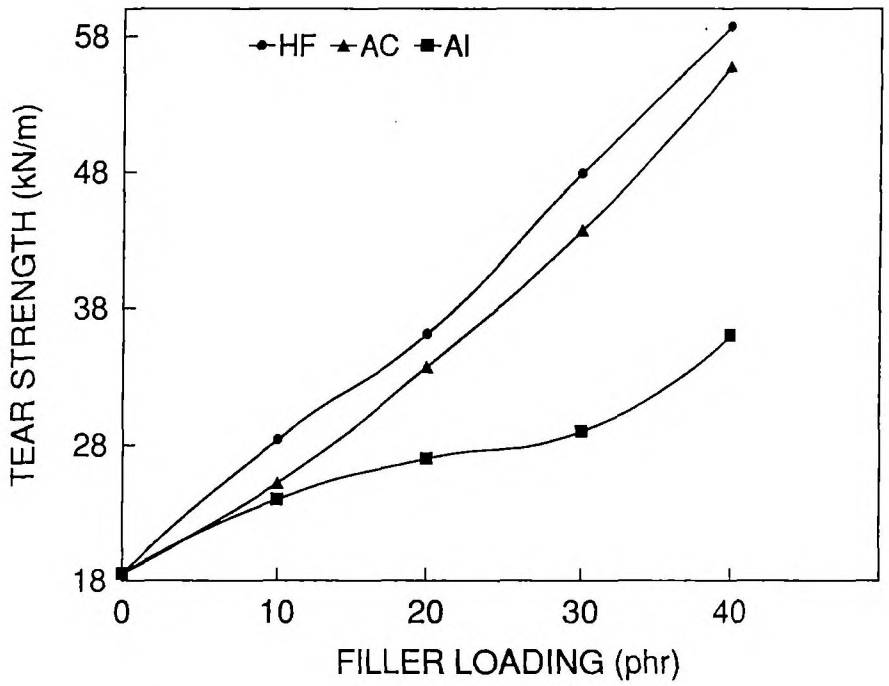

Figure X.2. Effect of filler on the tear strength of SBR vulcanizates

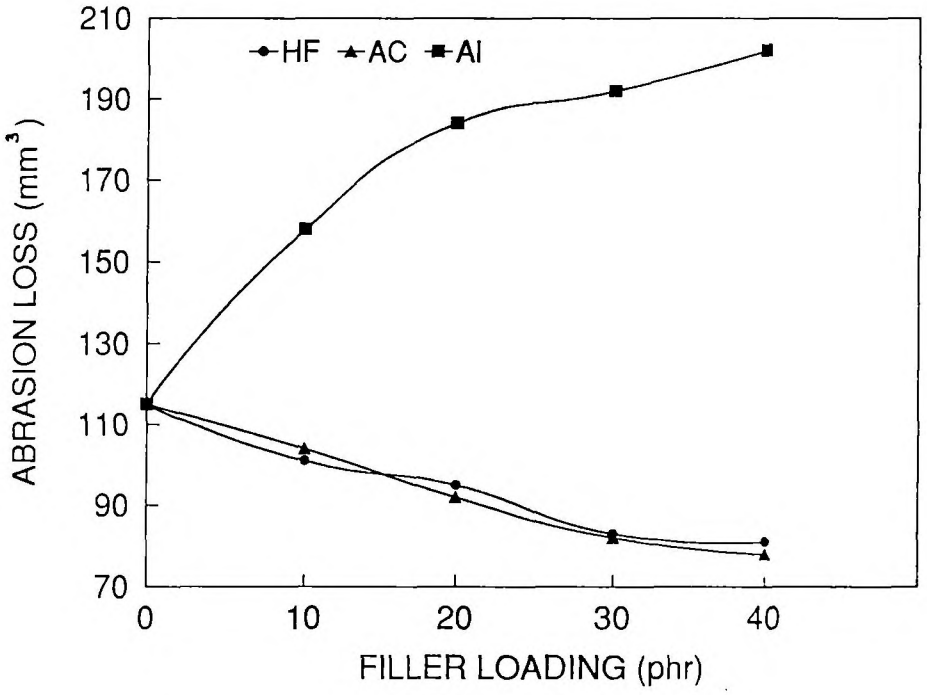

Figure X.3. Abrasion loss due to loading of HAF, acetylene black and aluminium powder on SBR

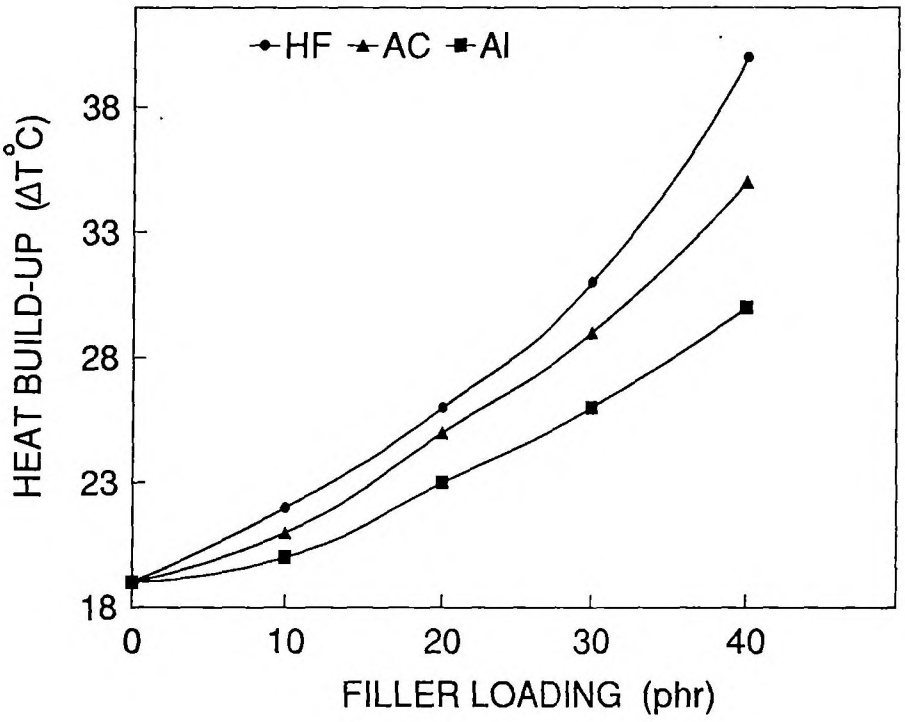

Figure X.4. Heat build-up values of SBR-vulcanizates containing HAF, acetylene black and aluminium powder

Variation in tear strength of SBR vulcanizates with loading of HAF, acetylene black and aluminium powder is shown in Figure X.2. The tear strength of HAF and acetylene black filled vulcanizates are higher than that of aluminium powder filled one, due to the higher reinforcing capacity of these fillers. In all cases, the tear strength increased with loading of the fillers [13]. DIN abrasion loss of these composites is presented in Figure X.3. The presence of HAF and acetylene black caused a decrease in abrasion loss. Whereas in the case of aluminium powder filled compounds, the abrasion loss increased with loading.

Table X.3. Tensile properties of the vulcanizates

Sample	Modulus (200%) Mpa	Tensile Strength, MPa	Elongation at break, %
GUM	1.81	2.42	367
HF1	2.83	7.30	340
HF2	3.20	10.6	310
HF3	6.20	21.2	300
HF4	8.60	23.7	253
AC1	2.02	5.40	360
AC2	3.10	8.70	350
AC3	5.90	14.3	326
AC4	7.01	16.1	310
Al 1	2.02	2.90	362
Al 2	2.47	3.50	354
Al 3	2.60	4.20	347
Al 4	3.24	5.60	340

This is due to the larger particle size of aluminium powder used. Kraus [13] reported that the more reinforcing fillers have much smaller primary particles, fused together to form primary aggregates. The size of the primary particle determines the surface area of aggregates since the area used up by the fusion of particles is relatively low. The larger particle size of aluminium powder has low surface area, which explains the higher abrasion loss. The heat build up values of these composites are presented in Figure X.4. The maximum heat build up is for HAF filled composites followed by acetylene black and then aluminium powder. Lower reinforcement and the higher thermal conductivity of aluminium powder filled compounds accounts for the low heat build-up value.

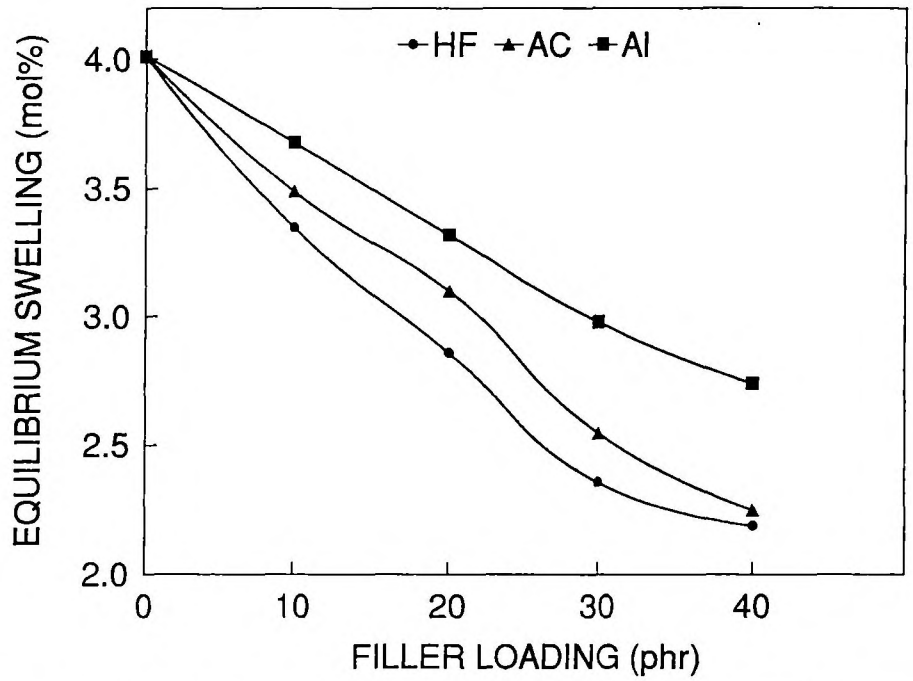

Figure X.5. Equilibrium swelling values of SBR composites with different fillers (swelling solvent, toluene at 27°C)

Tensile properties of the composites are given in Table X.3. Addition of HAF, acetylene black and aluminium powder increased the tensile strength. The maximum increase is observed with HAF black followed by acetylene black and minimum for aluminium powder. This is due to the difference in reinforcing capacity of these fillers as a result of their particle size. It is observed that as the particle size decreased the tensile strength increased. Lower particle size gives higher surface area, which enhances the reinforcement. In the case of aluminium powder. the particle size is higher than that of HAF and acetylene black. The modulus for 200% elongation, presented in Table X.2. follows the same trend as that of tensile strength. The maximum elongation value of the composite is decreased with filler loading. The mole percent absorption of toluene at 27^0C is given in Figure X.5. Incorporation of filler decreased the equilibrium swelling. The aluminium powder filled SBR vulcanizates showed a higher equilibrium

swelling value than HAF and acetylene black filled compounds due to the lower extent of reinforcement

X.3. Effect of Aluminium Powder on Heat Ageing

Ageing effects of these vulcanizates are presented in Figure X.6. The action of oxygen on rubber is slow at room temperature, but is activated by heat.

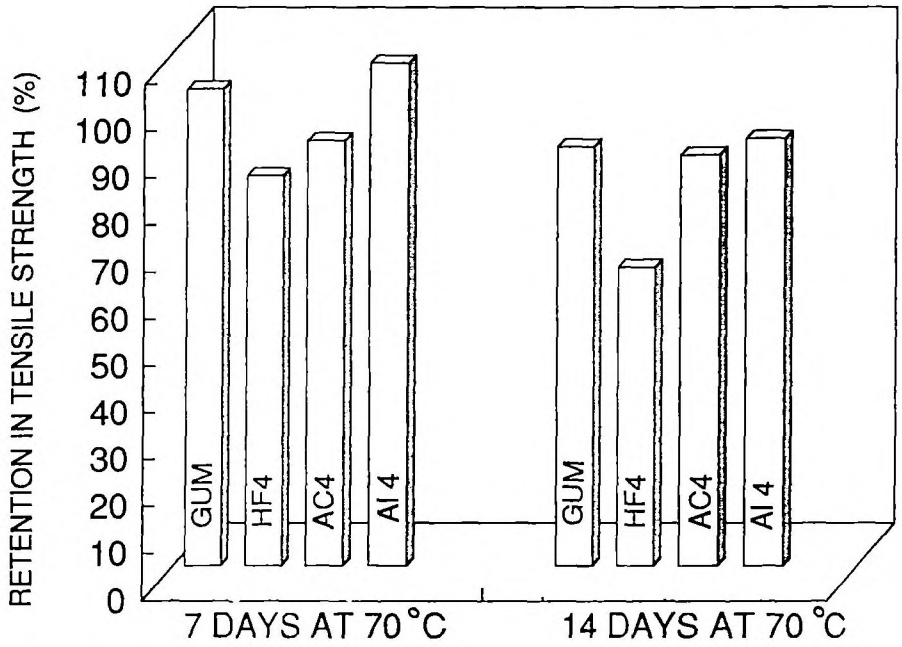

Figure X.6. Percentage retention in tensile strength after ageing at 70°C

To assess the ageing resistance, the samples were aged at 70^0C for 7 and 14 days in an air oven, and the retention of tensile strength was evaluated. The gum composite retained the tensile strength after ageing for 7 days at 70^0C, however black filled SBR vulcanizates did not retain their original tensile strength. It is interesting to note that the tensile strength values of aluminium powder filled compounds (with and without bonding agent)

increased after ageing at 70^0C for 7 days. On prolonged ageing (14 days at 70 ^{0}C), a decrease in the percentage retention of tensile strength and maximum retention is with the aluminium powder filled vulcanizates compared to HAF and acetylene black. The high retention of tensile strength after ageing at 70^0C for 7 days of aluminium powder filled vulcanizates could be due to slow, continued crosslinking of the elastomer, but on prolonged ageing the polymer degradation overcomes the crosslinking, resulting in a decrease of tensile strength.

X.4. Thermal Conductivity and Vulcanization of Thick Articles

Figure X.7 shows the thermal conductivity values of the SBR compounds. It is clear from the figure that the filler loading increased the thermal conductivity of the vulcanizates. The thermal conductivity increase is in the order, aluminium powder>acetylene black>HAF. The aluminium powder filled compounds have the thermal conductivity much higher than that of acetylene black filled ones. 40 phr aluminium powder filled SBR compound has a thermal conductivity value which is twice that of HAF filled compound. Higher thermal conductivity of rubber compound is very important in the vulcanization of thick articles, since it results a material with more uniform crosslinking. To follow the vulcanization in thick articles, test pieces were taken from the surface and central portions of a rubber cube having 25.4 mm size, which was vulcanized with 5 min additional time over the optimum cure time. The extent of crosslinking in these specimens was assessed by equilibrium swelling (Q_∞). The results are given in Figure X.8. In the gum compound, there exists a large difference in the Q_∞ values, of the central and surface layers of the cube. A higher difference in Q_∞ values indicates uneven curing of the inner and outer portions of the cube. This difference is less in the case of HAF and

acetylene black filled vulcanizates, but these vulcanizates also did not attain a uniform crosslinking. In the case of aluminium powder filled compound the extend of crosslinking in the inner and surface portions becomes almost same as evident from the Q_{∞} values. In principle the 25.4 mm cube needs more than 5 min additional time for complete vulcanization. The increased thermal conductivity of the aluminium powder filled compound thus helps to reduce the vulcanization time of thick rubber articles and gave uniform curing throughout the material.

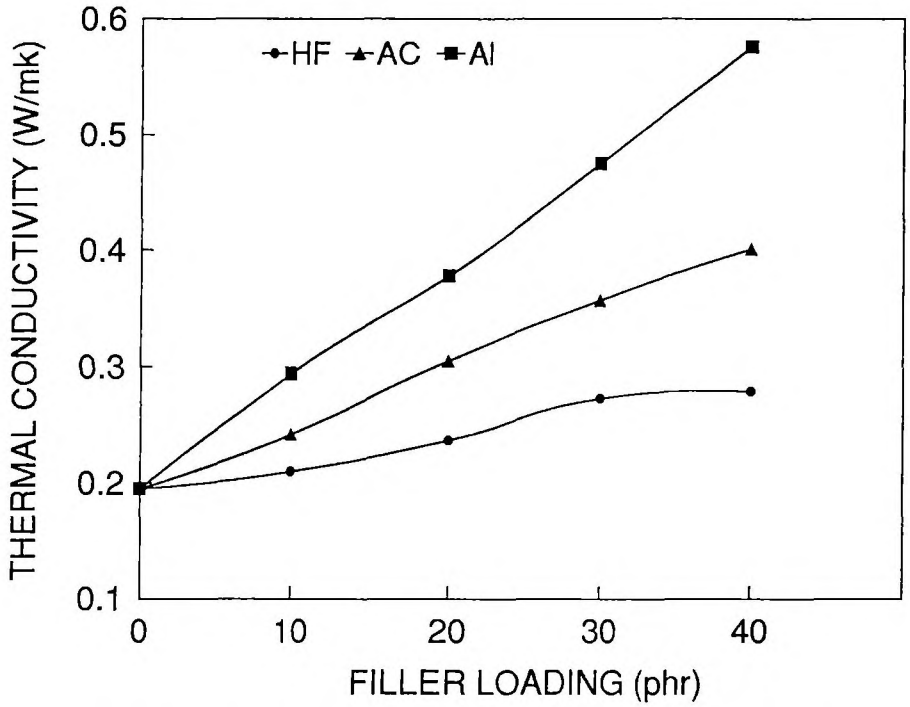

Figure X.7. Thermal conductivity of SBR composites with different fillers

The thermal conductivity values have a good correlation with the electrical conductivity [14]. The volume resistivity of SBR composites with different loadings of HAF, acetylene black and aluminium powder are given in Figure X.9. The volume resistivity found to be decreased with loading of fillers.

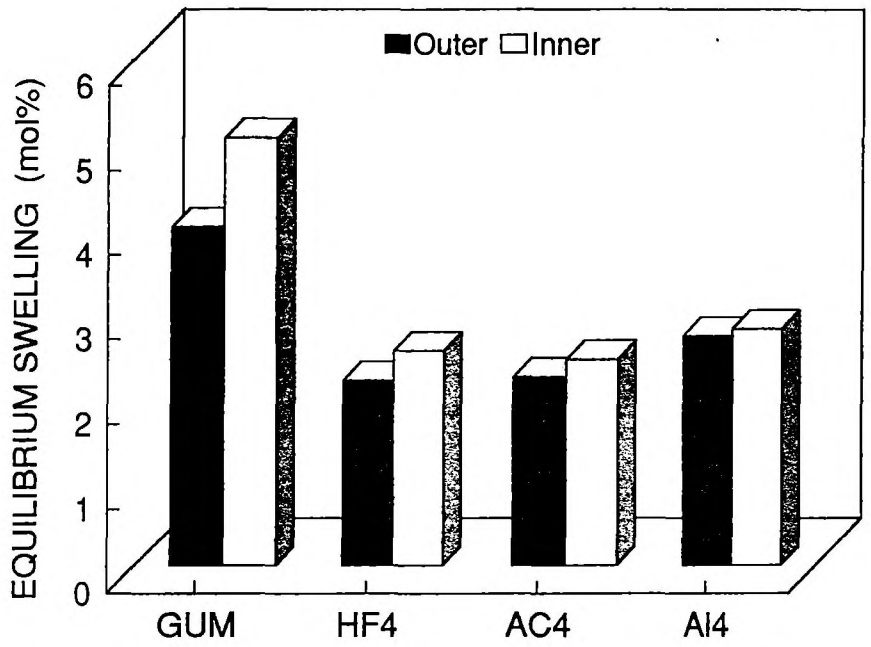

Figure X.8. Equilibrium swelling (Qα) values of inner and outer layers of 25.4 mm cube of SBR compounds, vulcanized for additional 5 min over optimum cure time

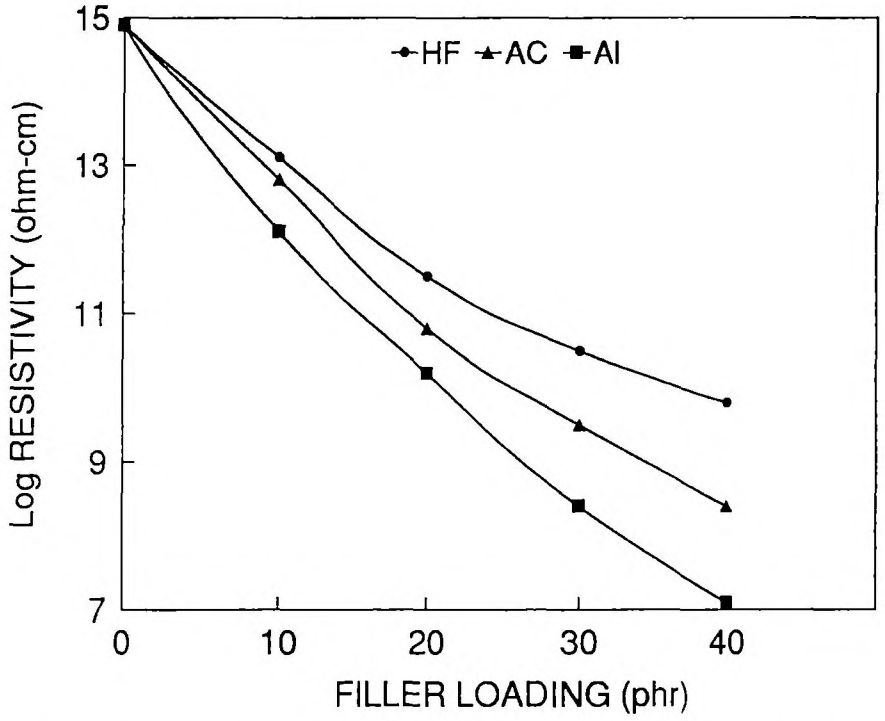

Figure X.9. Volume resistivity of SBR composites with HAF, acetylene black and aluminium powder fillers

The aluminium powder filled compound has the lowest resistivity values compared to HAF or acetylene black filled composite. This indicated that the electrical conductivity (which is the inverse of resistivity) showed the same trend as that of thermal conductivity with the addition of aluminium powder.

X.5. Effect of Aluminium Powder Along with HAF in SBR

In most cases, a single material may not meet all the requirements for a potential filler in a rubber compound. SBR vulcanizates having higher thermal conductivity and better strength can be obtained by a combination of aluminium powder and HAF. Properties of SBR vulcanizates containing different proportions of HAF and aluminium powder are given in Table X.4. In all cases, the total filler content is fixed to 40 phr. Maximum torque, optimum cure time, hardness, tear strength, heat build-up and tensile strength were decreased by the successive replacement of HAF by aluminium powder. A marked increase in thermal conductivity is observed with the successive substitution of HAF by aluminium powder. Other properties like cure rate index (CRI), rebound resilience, DIN abrasion loss, equilibrium swelling and elongation at break were also increased by the substitution of HAF by aluminium powder. The above property changes reveal the combined effect of the thermal conductivity and reinforcement ability of these fillers. If we have a good knowledge of the combined effect of these fillers, selection of a particular combination that suits for a specific application is quite easy.

Table X.4. Properties of SBR vulcanizates containing different proportions of HAF and aluminium powder

Properties	Al 4	HAA	HAB	HAC	HF4
Aluminium powder, phr	40	30	20	10	0
HAF, phr	0	10	20	30	40
Maximum torque, dNm	70	75	80	84	92
t_{90}, min.	17	18	19	20	21
RIT, min.	4.0	4.0	4.0	4.0	4.0
CRI, min^{-1}	8.33	7.69	7.14	6.67	5.70
Hardness, IRHD	60	62	63	64	65
Tear strength, k Nm^{-1}	39.1	41.2	48.0	55.5	58.7
Rebound resilience, %	55.1	54.7	54.4	53.2	52.2
Heat build-up, $\Delta T\ ^0C$	30	32	34	37	40
DIN abrasion loss, mm^3	202	181	104	86.5	84
Thermal conductivity, W/(mk)	0.576	0.550	0.445	0.314	0.279
Equilibrium swelling, mol %	2.74	2.70	2.62	2.55	2.19
Modulus, (200%), MPa	3.24	3.6	4.6	5.2	8.6
Tensile strength, MPa	5.6	9.3	19.7	22.8	23.7
Elongation at break, %	344	323	309	293	283

X.6. Conclusions

The presence of aluminium powder as a filler in SBR composites results an increase in rheometric torque and a decrease in optimum cure time. Hardness, tear strength, tensile strength etc are higher for HAF filled vulcanizates followed by acetylene black and aluminium powder. The heat build up is minimum for aluminium powder filled compounds. Ageing studies of these composites revealed that aluminium powder filled SBR

vulcanizates have better resistance towards heat ageing compared to HAF and acetylene black. A marked increase in thermal conductivity is observed with aluminium powder filled composites. The higher thermal conductivity helps to reduce the vulcanization time of thick rubber articles and also imparts uniform curing throughout the material. The coupled effect of strength and other technological properties along with higher thermal conductivity can be obtained by the use of appropriate combinations of both HAF and aluminium powder in the compound.

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CHAPTER XI

EFFECT OF BONDING AGENTS ON THE PROPERTIES OF STYRENE BUTADIENE RUBBER-ALUMINIUM POWDER COMPOSITES

Results of this chapter have been communicated to Journal of Applied Polymer Science

The physicomechanical properties of the metal powder filled polymer composites are inferior due to the lack of proper adhesion and poor dispersion of the filler in the polymer phase [1]. In order to get beneficial properties of rubber vulcanizates, the filler must be uniformly dispersed therein. In addition, poor dispersion may results in certain detrimental effects [2]. These can be summarised as follows (i) reduced product life, (ii) poor performance in service, (iii) poor product appearance, (iv) poor processing characteristics, (v) poor product uniformity, (vi) raw material waste and high finished-product rejection rates and (vii) excessive energy usage. The application of coupling agents, for the surface modification of fillers and reinforcement in polymers, has generally been suggested for improving the mechanical strength and chemical resistance of composites. Coupling agents may be mixed with fillers prior to their addition to polymers or they may be added directly to the polymers. Several reports on coupling agents, their uses, mechanism by which they act, substrates, adhesive systems, and theories of adhesion are available [3-7] and most of them are discussed in Chapter III. Wolff [8] made a detailed study on the optimisation of silane-silica compounds, variations of mixing temperature and time during the modification of silica with a silane-coupling agent. The effects of some carbon black/rubber-coupling agents without nitrosogroups have been investigated, and the correlation between the efficiency and chemical structure of coupling agents was discussed by Klasek *et al.* [9]. To get an acceptable level of adhesion strength, in cases where the adhesion between the materials is usually low due to the low polarity of the polymer, modifications of the polymer is reported [10]. Partial epoxidation of natural

rubber has been carried out in order to assess its effect on rubber to brass adhesion [11].

Table XI.1. Base Formulations of mixes

Ingredients	Mixes				
	G	W	H	S	C
SBR	100	100	100	100	100
Stearic acid	2.0	2.0	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0
Aluminium powder	--	10	10	10	10
Hexamethylene tetramine	--	--	1.0	--	---
Resorcinol	--	--	2.0	--	---
Si-69	--	--	--	2.0	----
Cobalt naphthenate	--	--	--	--	2.0
CBS	1.0	1.0	1.0	1.0	1.0
Sulphur	2.2	2.2	2.2	2.2	2.2

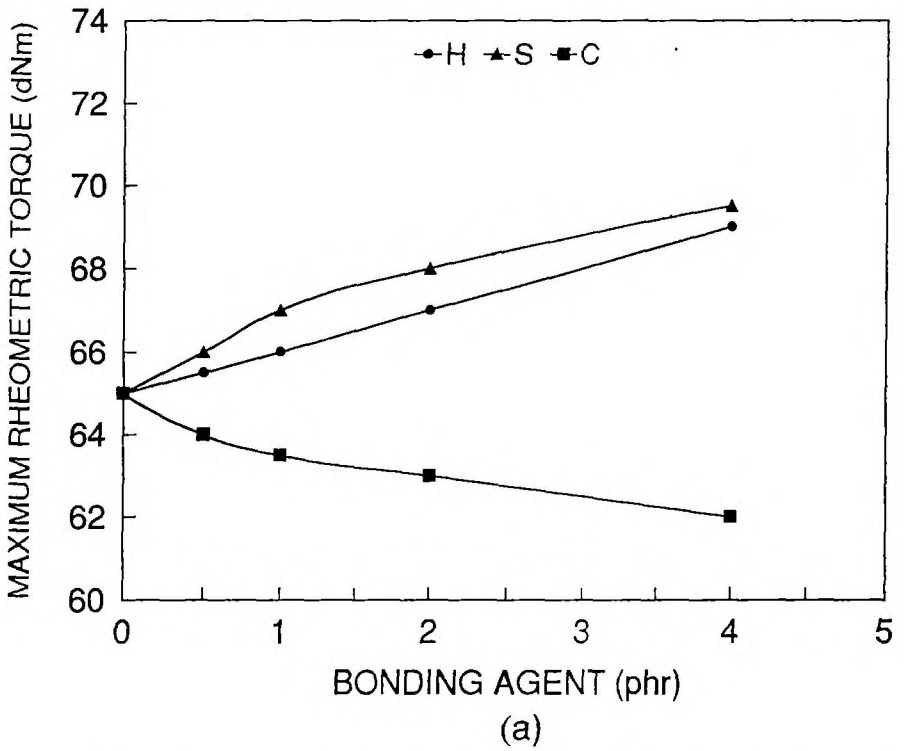
SBR - Styrene butadiene rubber
TDQ - 2,2,4-Trimethyl-1,2-dihydro quinoline
Si-69 - bis[3-(tricthoxysilyl) propyl] tetrasulphide
CBS - N-cyclohexyl benzthiazyl sulphenamide

In this chapter, the effect of various bonding/coupling agents in aluminium powder filled styrene butadiene rubber composites is presented. The selected systems include, hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl) propyl] tetrasulphide (Si-69) and cobalt naphthenate (CoN). The base formulations used are given in Table XI.1. The ratio of hexamethylene tetramine and resorcinol used in this study is in the ratio 1:2. While plotting figures, in the case of HR system. we have taken the amount of resorcinol in the abscissa. whereas the amount of hexa varies according to the ratio. The effect of bonding agents was studied at a

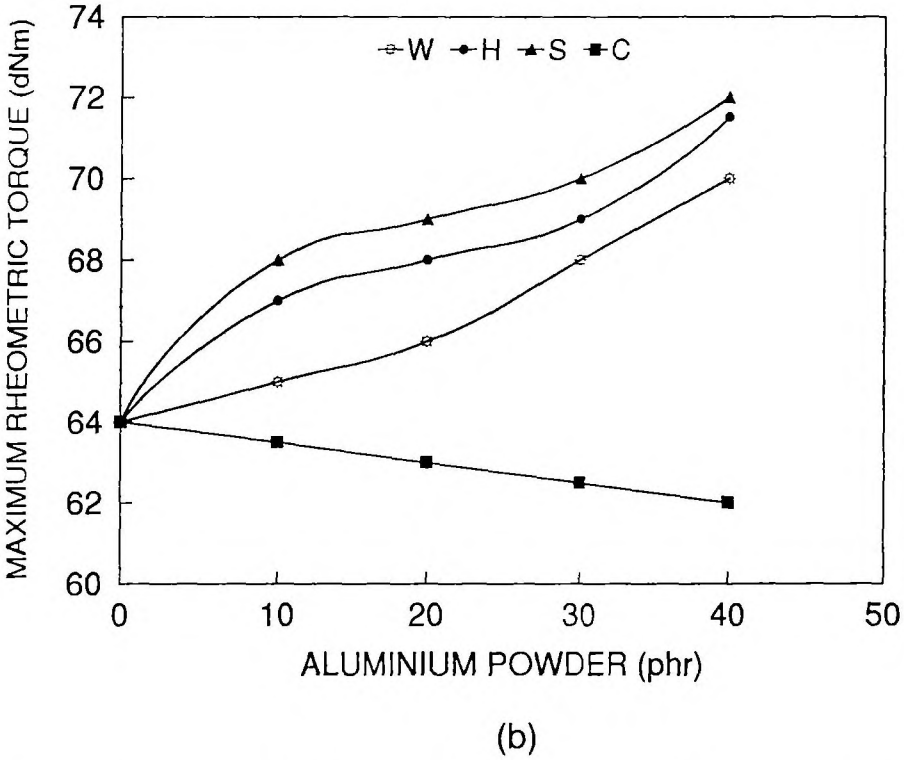
constant aluminium powder loading of 10 phr. The effect of loading of aluminium powder was studied by varying the aluminium powder content from 0 to 40 phr. At higher loadings of aluminium powder, the concentration of bonding agent varied as the multiples of the ratio of filler to bonding agent used in the base formulation. Mechanical properties like Shore A hardness, rebound resilience, heat build-up, tensile strength etc. have been evaluated, according to the standard procedures as given in Chapter II. Enhancement in adhesion between rubber and aluminium powder is studied by equilibrium swelling in toluene.

XI.1. Effect of Bonding Agents on Cure Characteristics

The maximum rheometric torque obtained at 150^0C for aluminium powder filled SBR composites are given in Figure XI.1. For 10 phr aluminium powder loaded composites with hexa-resorcinol and Si-69 as bonding agent, the maximum torque, increased continuously whereas in the case of cobalt naphthenate the trend is reversed. From Figure XI.1b it is clear that without the use of any bonding agent the maximum torque increases with aluminium powder loading. At higher loading, both HR-system and Si-69 increased the maximum torque of aluminium powder filled SBR composites. With HR and Si-69, the adhesion between aluminium powder and SBR improved considerably, which increased the maximum torque. The decrease in torque with cobalt naphthenate may be due to its catalytic activity in the oxidation of rubber. The cure rate index (CRI) values, which is a measure of the level of cure of rubber vulcanizate, are shown in Figure XI.2.



(a)



(b)

Figure XI.1. Variation of maximum rheometric torque in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

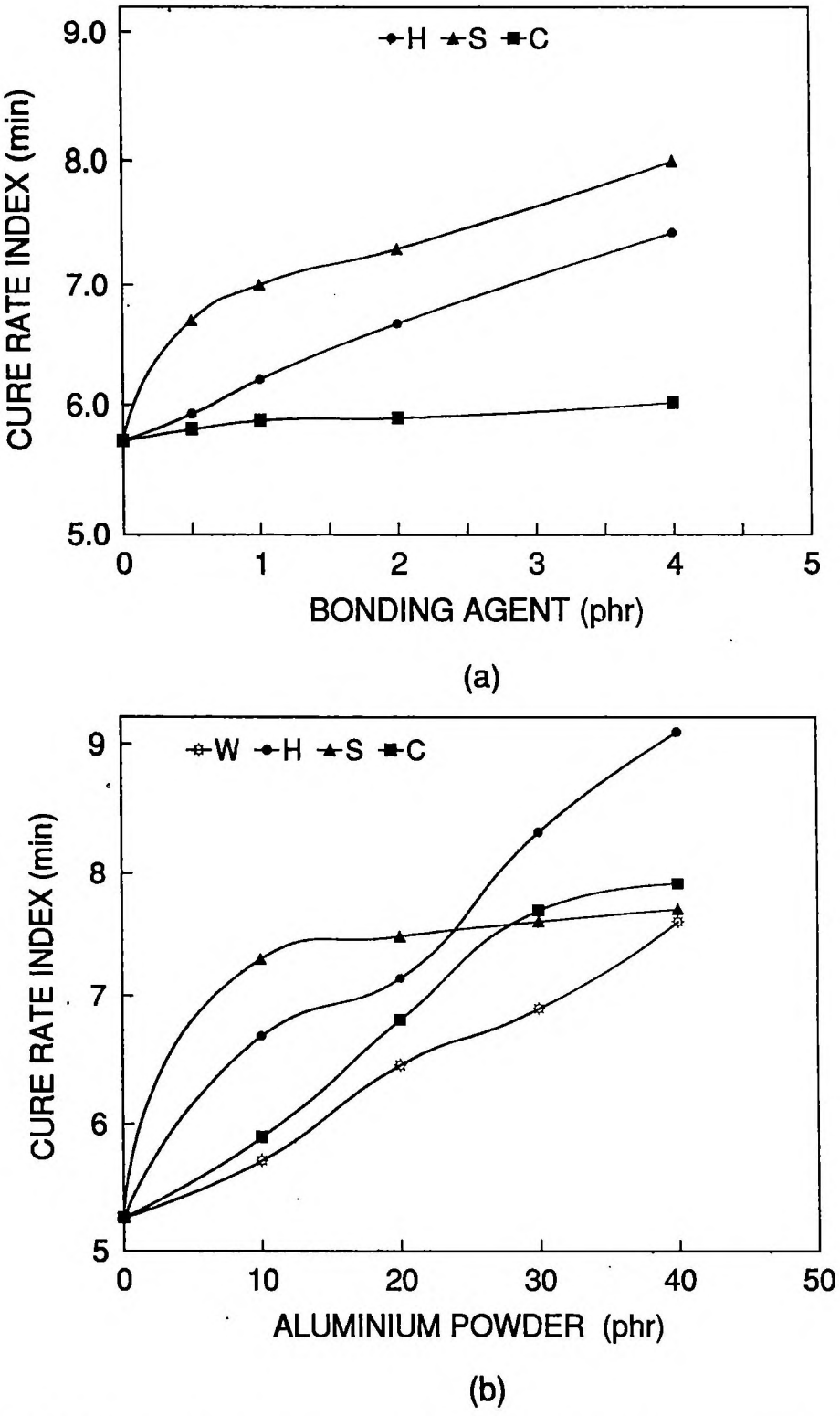
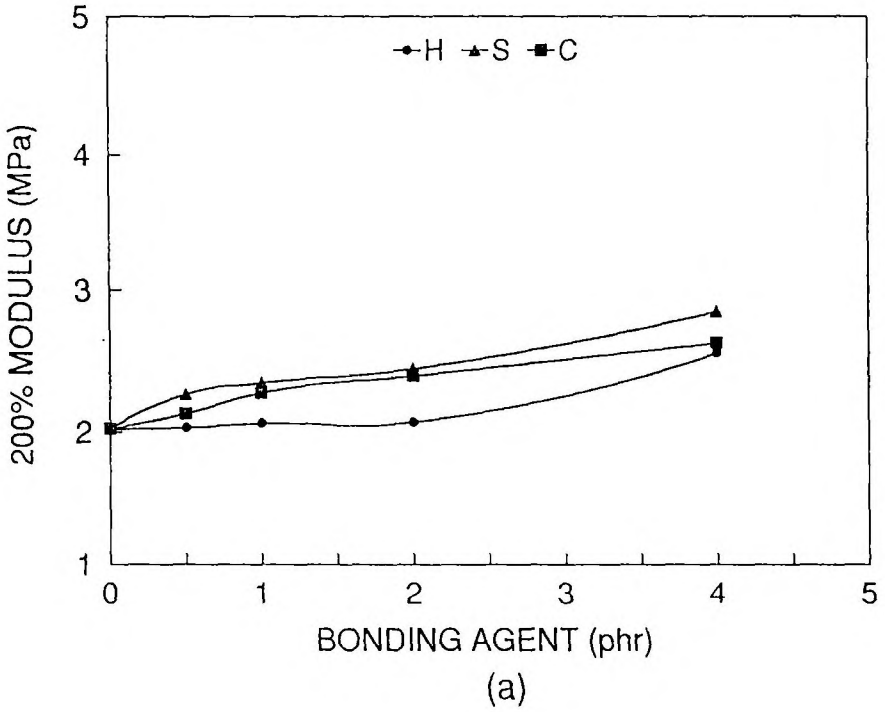


Figure XI.2. Variation of cure rate index in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

It is found that all the bonding agents increased the CRI. At 10 phr of aluminium powder loading the CRI is in the order Si-69>HR>CoN. But at higher loadings, HR is found to be better in increasing the CRI, which may be due to the action of hexa as a secondary accelerator.

XI.2. Effect of Bonding Agents on Tensile Properties

Figure XI.3 shows the modulus at 200% elongation of aluminium powder filled SBR composites in presence of various bonding agents. The modulus values are found to be increased by the addition of bonding agents. The tensile strength of the composites is given in Figures XI.4a and XI.4b. As in the case of modulus, here also the presence of bonding agents increased the tensile strength and maximum effect is observed with silane coupling agent. It is also noted that even without any bonding agent, the addition of aluminium powder increased the tensile strength of SBR-vulcanizates. This is further increased by the addition of bonding agents. The increase in modulus and tensile strength for these composites in presence of bonding agents are due to better interactions between the filler and the matrix. The elongation at break of the aluminium powder filled SBR compound with and without bonding agents is presented in Figure XI.5. At 10 phr loading of aluminium powder, the elongation at break decreased gradually as the bonding agent increased and the decrease is sharper at higher loading of bonding agent. From Figure XI.5b, we can see that, the aluminium powder loading decreased the elongation continuously due to the decrease in polymer fraction in the composite. The bonding agents again decreased the elongation at break, since the presence of bonding agents caused additional interaction between the aluminium powder and rubber which restrict the elongation of the polymer net works.



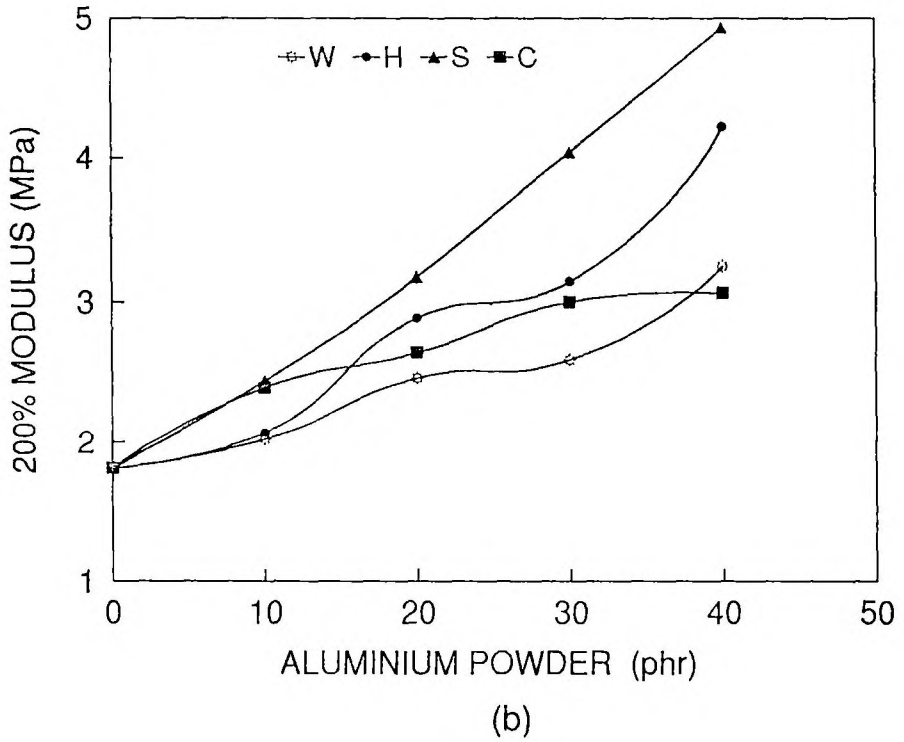
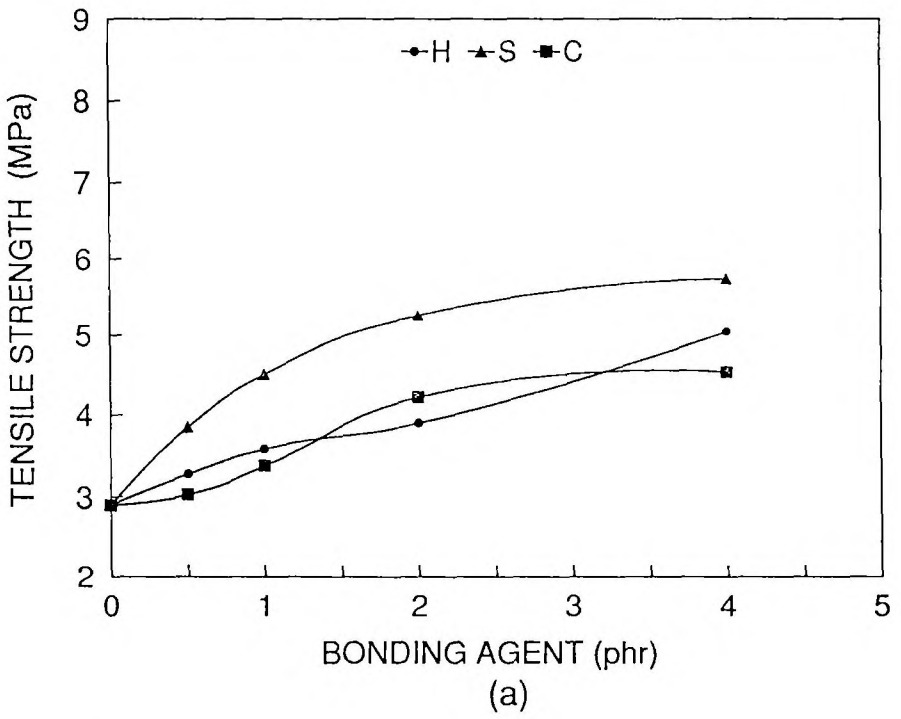


Figure XI.3. Variation of 200% modulus in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder



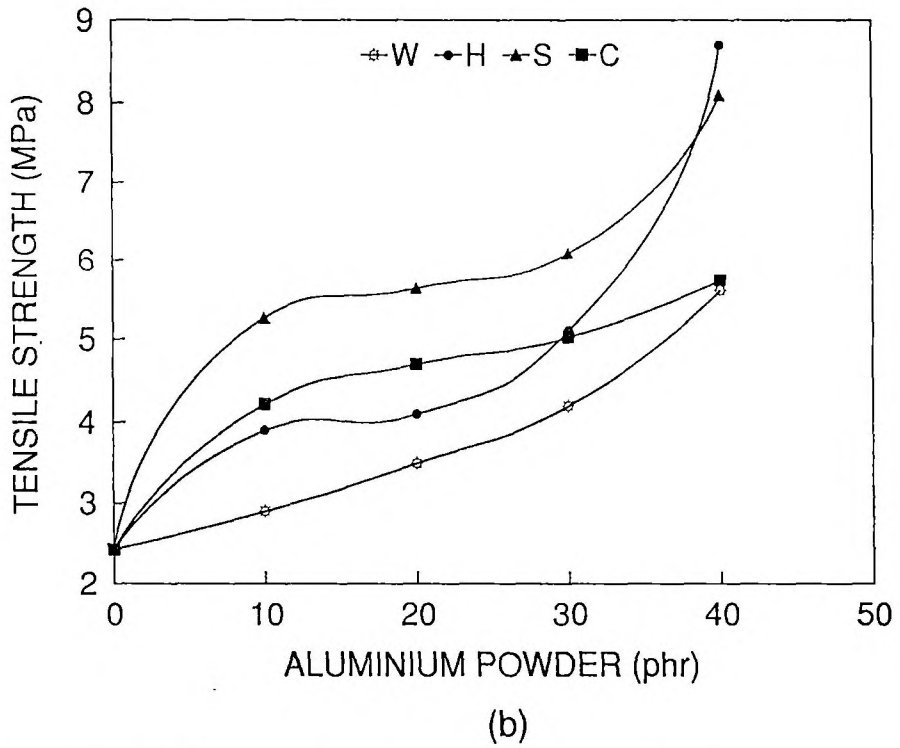
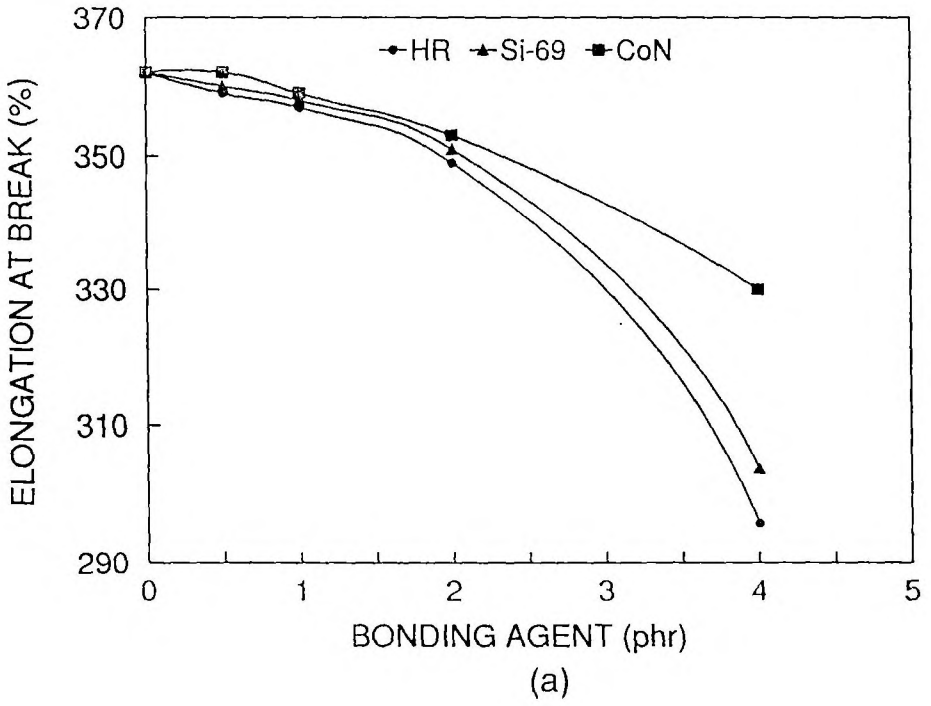


Figure XI.4. Variation of tensile strength in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder



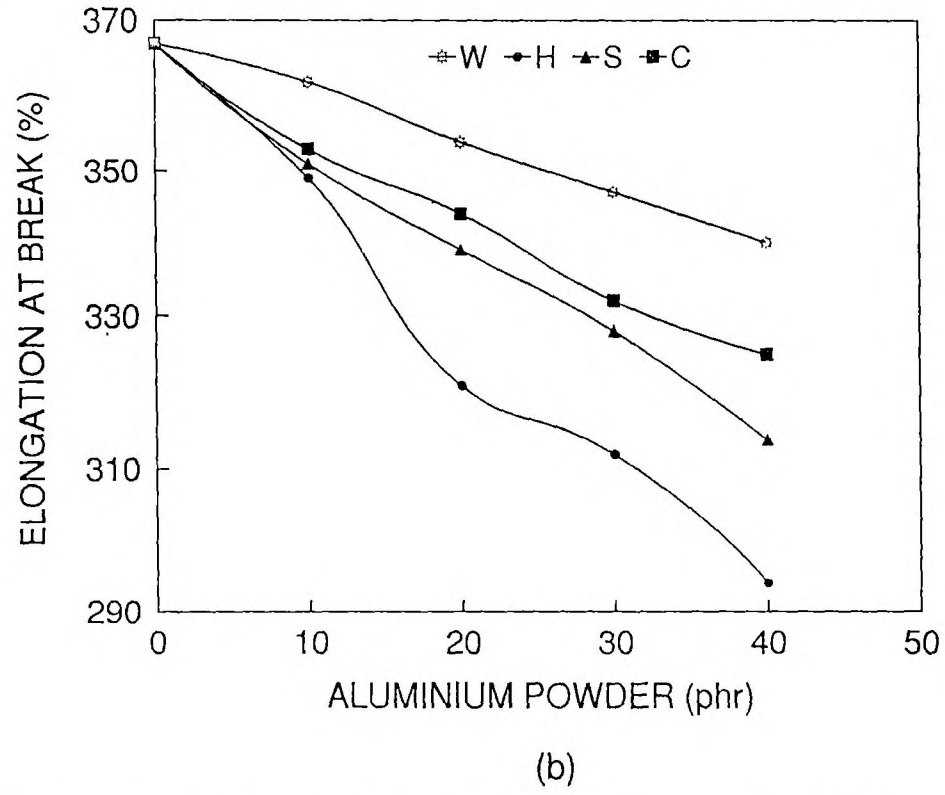


Figure XI.5. Variation of elongation at break in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

XI.3. Effect of Bonding Agents on Swelling Behaviour

Equilibrium swelling (Q_α) of aluminium powder filled SBR-vulcanizates with and without bonding agents is presented in Figures XI.6a and XI.6b. Aluminium powder filled SBR having no bonding agent decreased the Q_α values. This is due to the combined effects of reinforcement, additional crosslinking in presence of filler and the decrease in polymer fraction in the composite. The presence of bonding agent again decreased the Q_α values. The maximum decrease is found with HR system followed by Si-69. Equilibrium swelling in solvents can be taken as a means to assess rubber- filler adhesion, because filler - if bonded - is supposed to restrict the swelling of the elastomers. Swelling of rubber vulcanizates in a wide range of solvents has been studied by Hargopad and Aminabhavi [12]. The degree of cure in a particular filler reinforced vulcanizates can also be calculated by swelling methods. Here also the decrease in equilibrium swelling of aluminium powder filled SBR-compounds in presence of various bonding agents can be explained on the improved adhesion. The value of 1/Q, the degree of crosslinking, can also be used to study the enhancement in adhesion, where Q is defined as grams of solvent per gram of hydrocarbon at equilibrium swelling and is calculated by

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100 / \text{Formula weight}} \quad \ldots\ldots \text{(XI.1)}$$

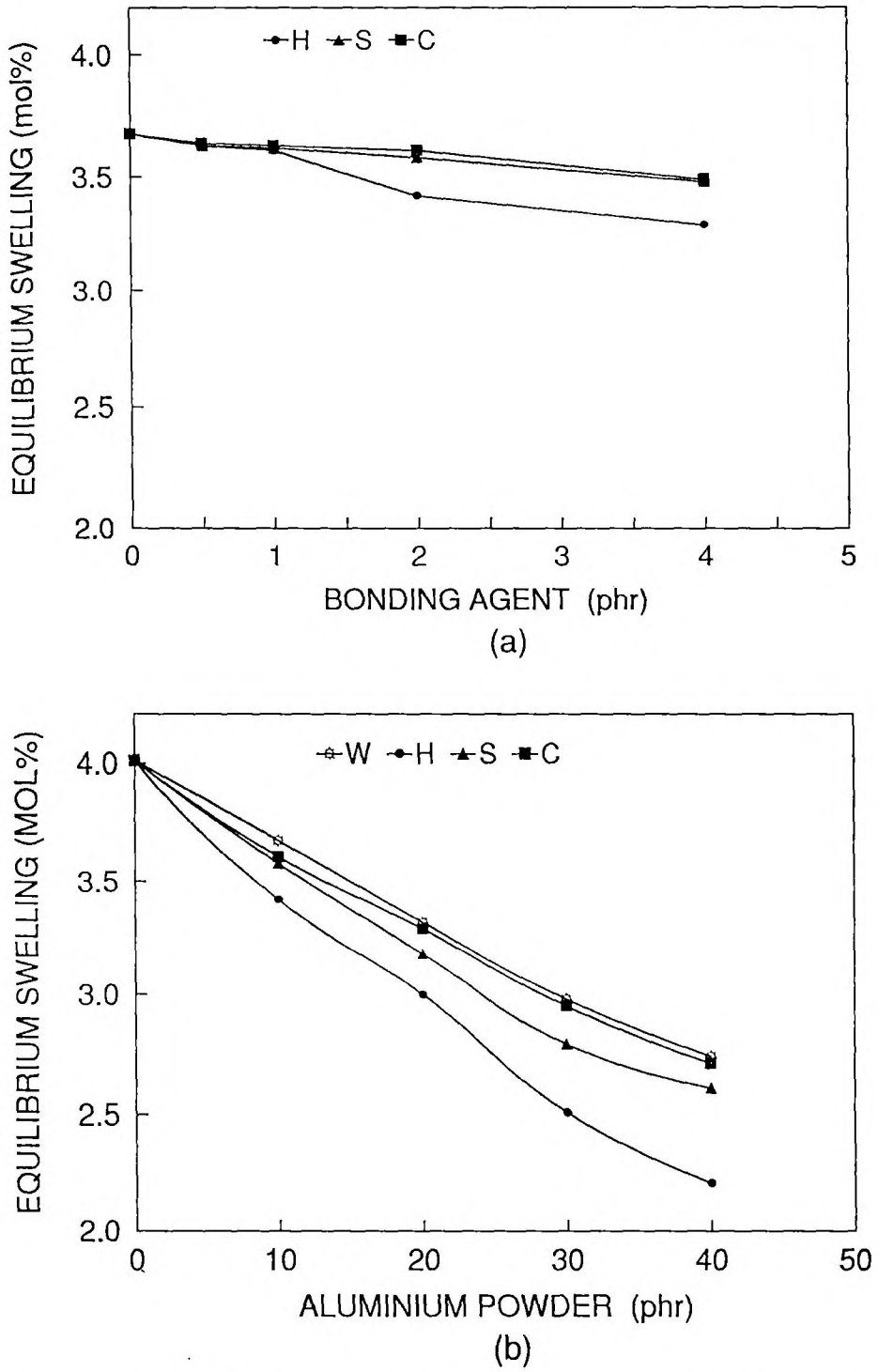


Figure XI.6. Variation of equilibrium swelling in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder (solvent, toluene at 27°C)

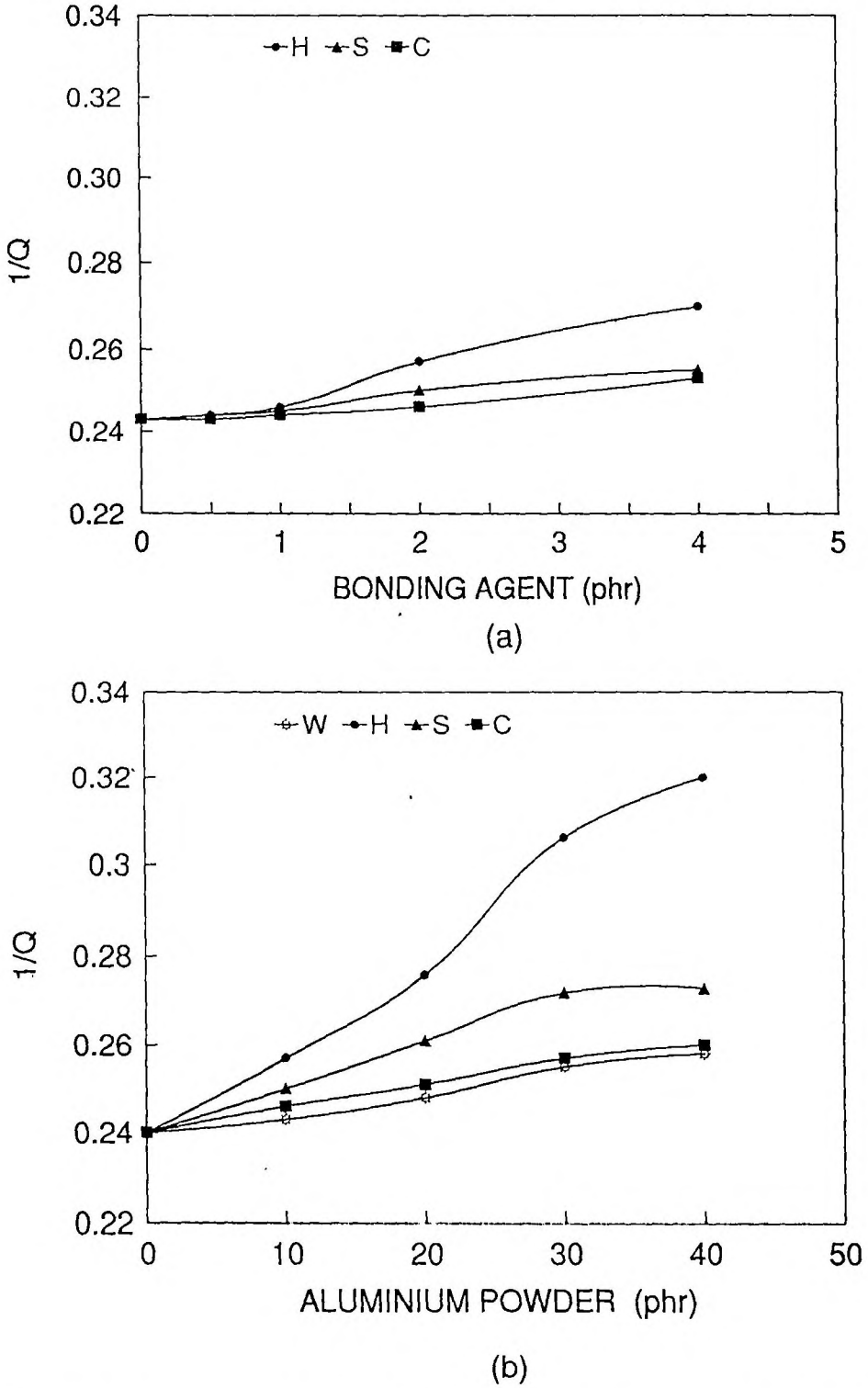
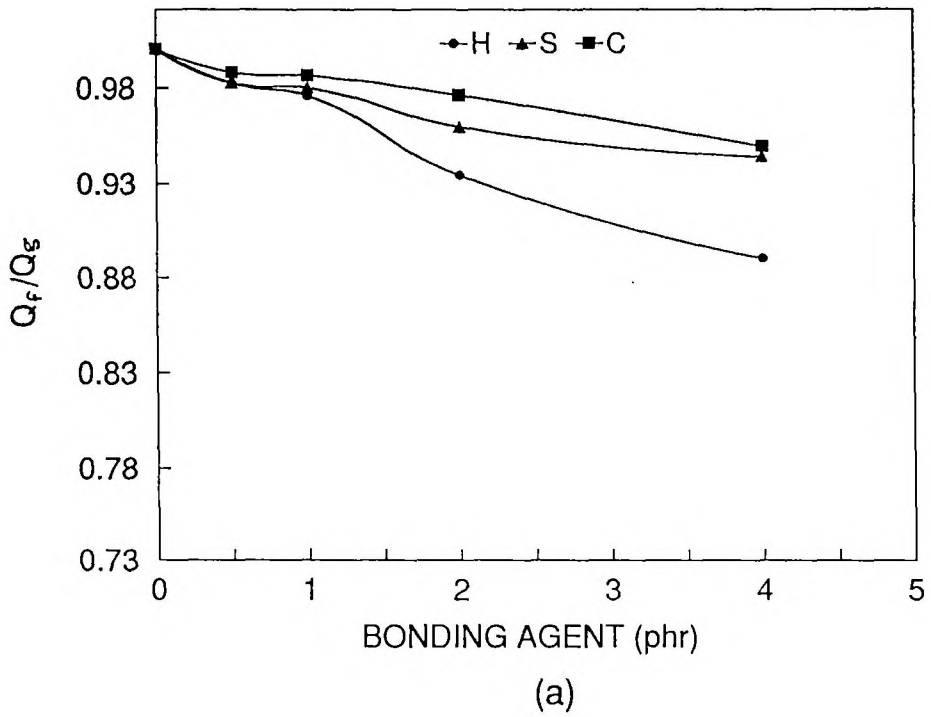


Figure XI.7. Variation of 1/Q values in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder



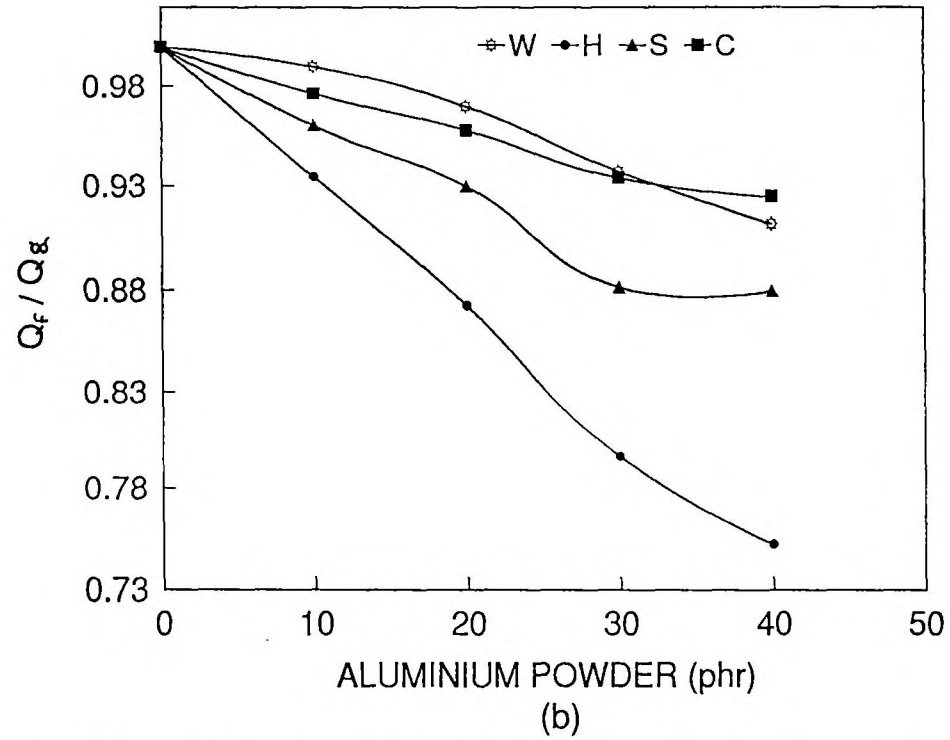


Figure XI.8. Variation of Q_f/Q_g values in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

Figures XI.7a and XI.7b show the 1/Q values of the composites with different bonding systems. In all cases the 1/Q values follow the order, HR>Si-69>CoN. This showed that adhesion is maximum with HR system followed by Si-69. According to Lorentz and Parks [13],

$$Q_f / Q_g = a\, e^{-z} + b \qquad \ldots\ldots \text{(XI.2)}$$

where Q has the same meaning as above, the subscripts 'f' and 'g' of the equation refer to filled and gum vulcanizates respectively. 'z' is the ratio by weight of filler to rubber hydrocarbon in the vulcanizate, whereas 'a' and 'b' are constants. Higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix. Figure XI.8 gives the Q_f/Q_g values of the SBR-compounds. At 10 phr of aluminium powder loading (Figure XI.8a) the addition of bonding agents decreased the Q_f/Q_g values, suggesting greater rubber-filler interaction in the composites. At higher aluminium powder loadings (Figure XI.8b), the presence of bonding agent decreased the Q_f/Q_g values, and the maximum effect is with the HR system. Among the cases studied the ability of the bonding agents to decrease the Q_f/Q_g values is in the order, HR>Si-69>CoN. Stronger the polymer-filler interaction lesser will be the voids at the interface, which in turn form less solvent pockets. This confirms that maximum aluminium powder-rubber interaction has occurred when bonding agents are present in the composites. These bonding agents are supposed to act differently to affect the bonding between the filler and rubber. The bonding mechanisms are illustrated in Chapter III.

XI.4. Effect of Bonding Agents on Mechanical Properties

Figure XI.9 shows the Shore A hardness of the composites. As the bonding agent concentration increased, the hardness also increased. From

Figure XI.9b, it is clear that even without any bonding system aluminium powder increased the hardness. This is due to the higher extent of crosslinking in the polymeric phase. The presence of bonding agents further increased the hardness due to the increased adhesion of the aluminium powder with SBR.

Tear strength for SBR-composites containing aluminium powder is shown in Figure XI.10. At 10 phr level of aluminium powder, Si-69 and HR increased the tear strength and is higher in the former case. Aluminium powder increased the tear strength of the SBR composites which is in proportion with its loading. In the case of cobalt naphthenate, a lower value of tear strength is recorded compared to the control compound. The enhancement of tear strength with HR and Si-69 are due to the improved adhesion. But with CoN, the adhesion effect might have been over shadowed by the catalytic oxidation reaction of the polymeric chains. This dual functionality of cobalt naphthenate is reflected in the properties of its compounds.

The heat build-up values, in Figure XI.11, showed a marked increase with Si-69 at 10 phr loading of aluminium powder. Heat build-up increased as the loading of aluminium powder increased. Composites bonded with HR and Si-69 have high value of heat build-up especially, at high loading of aluminium powder. Cobalt naphthenate increased the heat build-up upto 30 phr of aluminium and then a slight decrease is observed.

Rebound resilience of the composites is given in Figure XI.12. The maximum decrease in resilience is observed with vulcanizates containing Si-69 followed by HR system, at 10 phr loading of aluminium powder. At higher loadings also the rebound resilience is decreased with aluminium powder for composites with and without bonding agents. As the loading of filler increased, the polymer fraction in the compound decreased, resulting a decreased resilience.

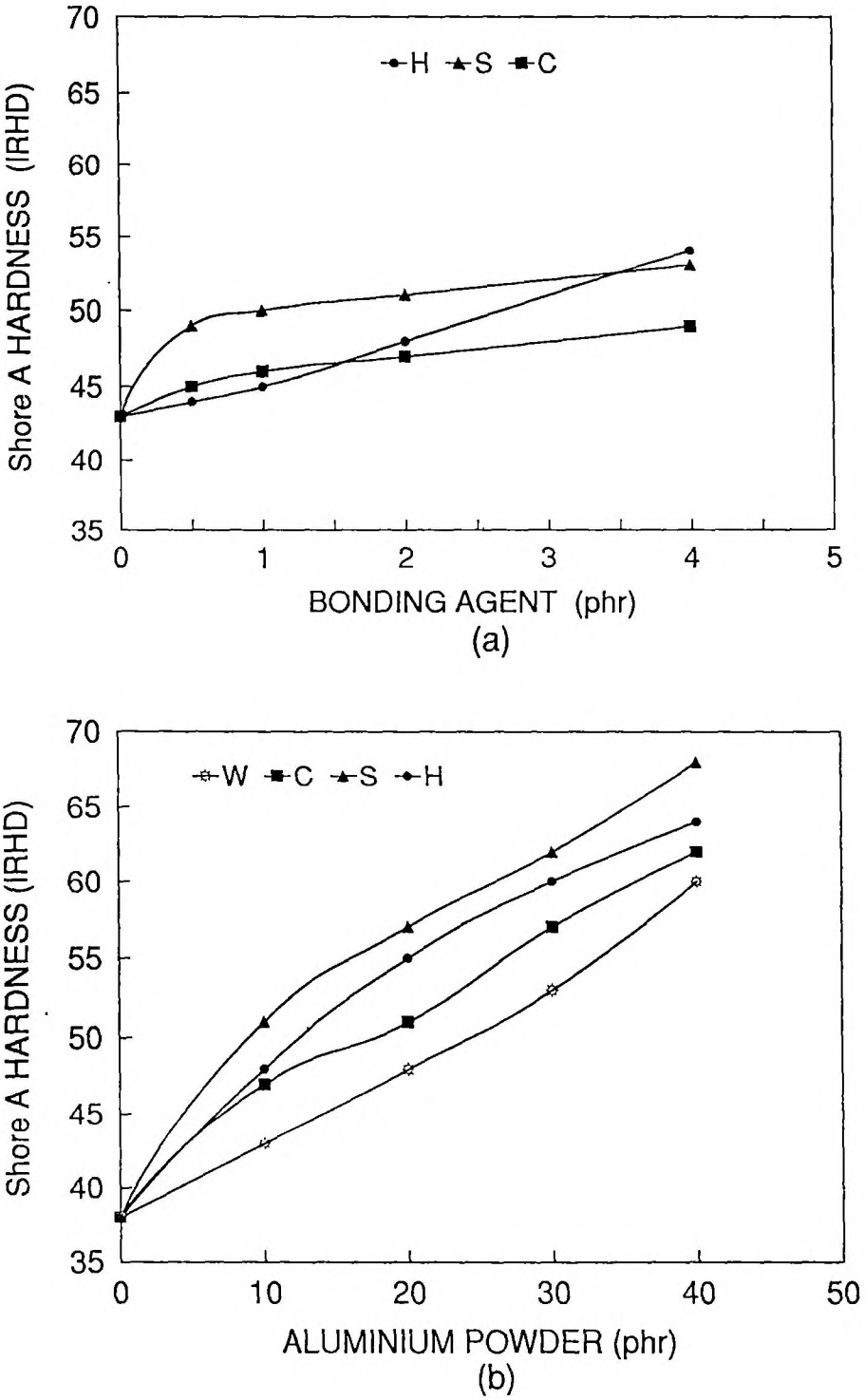


Figure XI.9. Variation of hardness in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

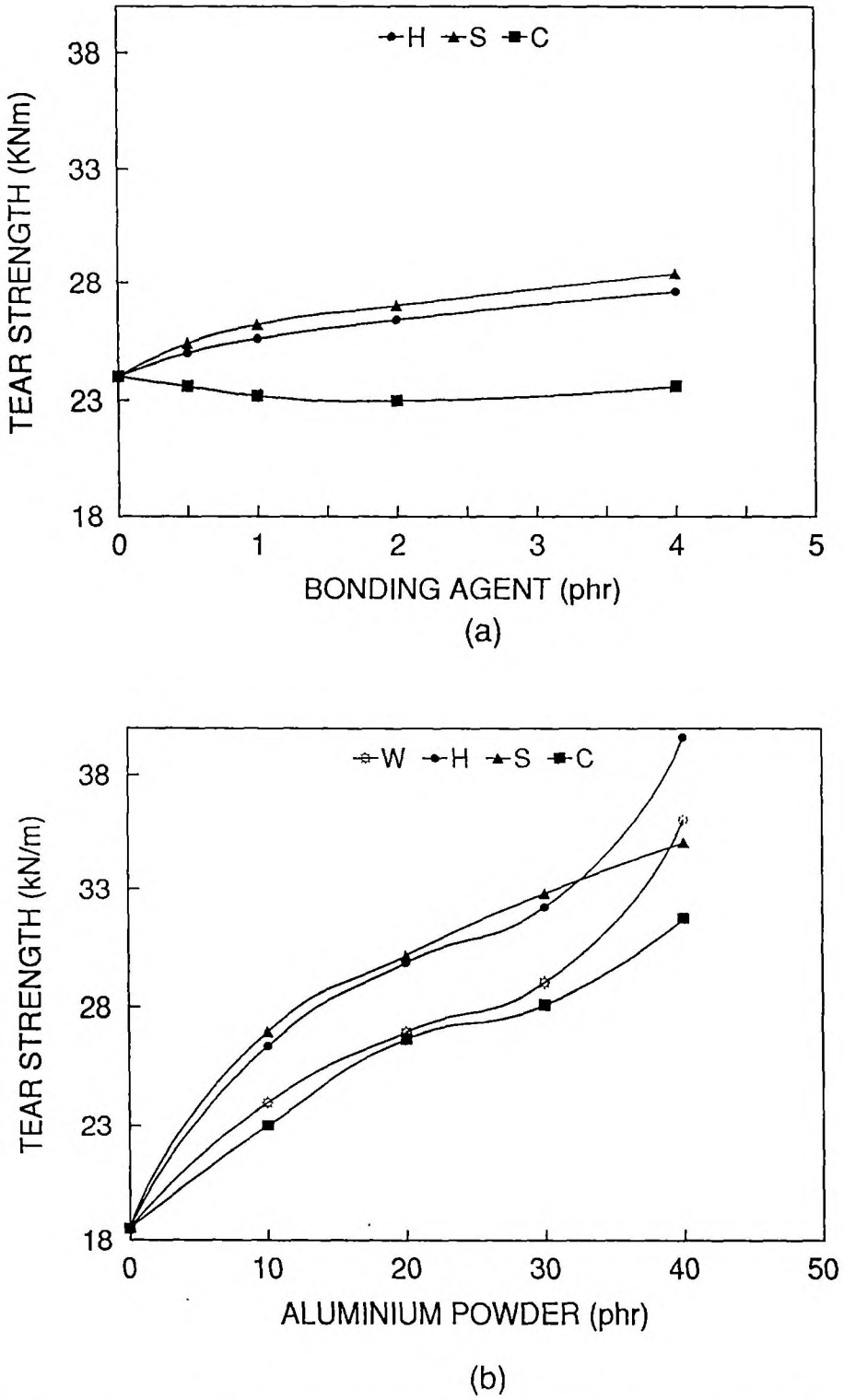


Figure XI.10. Variation of tear strength in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

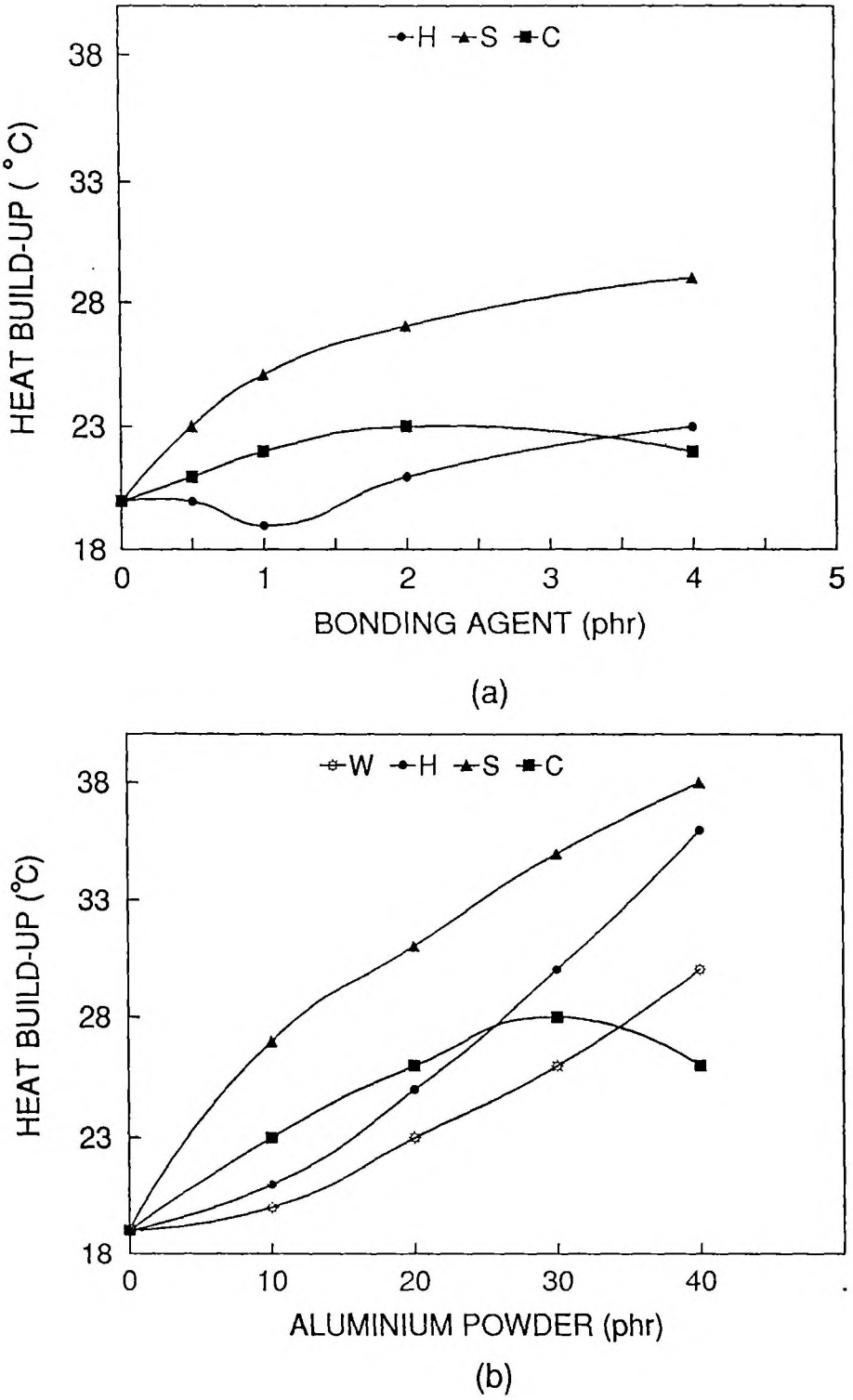


Figure XI.11. Variation of heat build-up in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

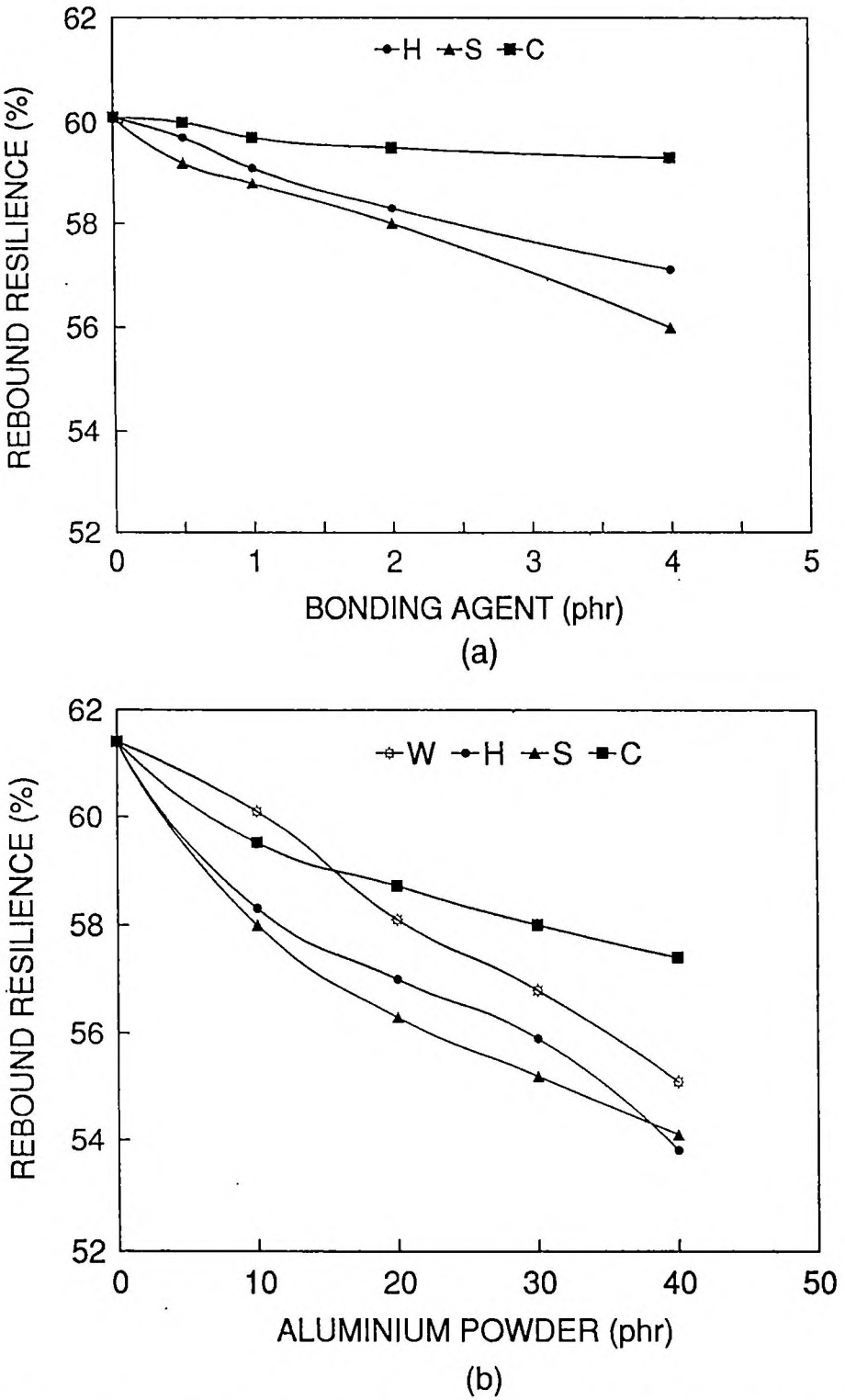
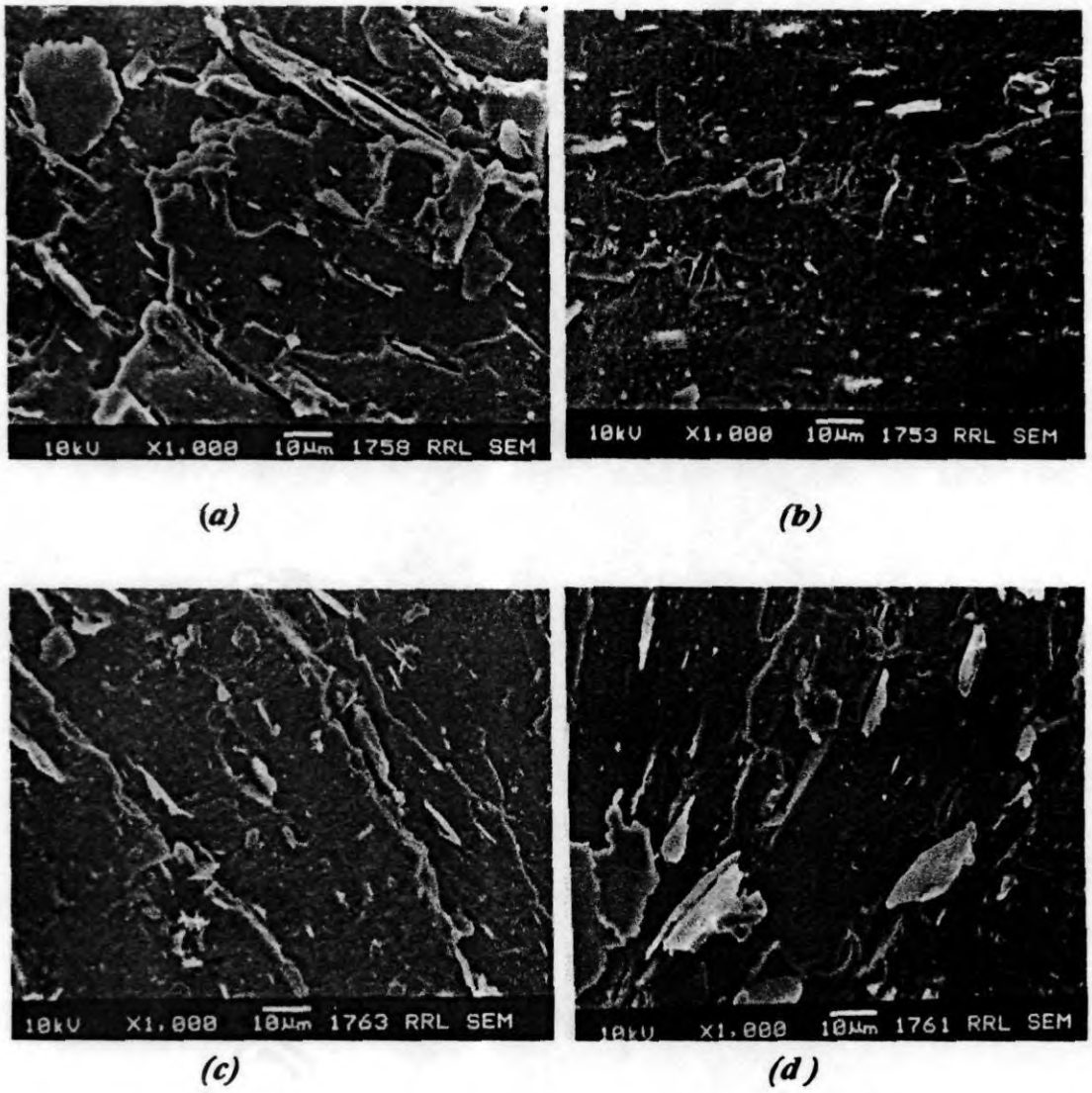


Figure XI.12. Variation of rebound resilience in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder

XI.5. Analysis of SEM Photographs

The fractured surface of the tensile pieces of the composites was examined by Scanning Electron Microscope (SEM). The SEM photographs are given in Figures XI.13(a-d).



(a) *(b)*

(c) *(d)*

Figure XI.13. SEM photographs of tensile fractural surface of 10 phr aluminium powder filled SBR vulcanizates with and without the presence of bonding agents.
(a) having no bonding agent (b) with HR-system
(c) with Si-69 (d) with CoN

These SEM photographs support the improved properties of aluminium powder filled styrene butadiene rubber composites in presence of bonding agents. In the unbonded composite the aluminium powder exists as loose aggregates where as in the bonded composites, aluminium particles are more aligned as compared to unbonded composites. Aluminium powder is more firmly bonded to the rubber matrix with hexamethylene tetramine-resorcinol system (HR) and with silane (Si-69) coupling agent.

XI.6. Conclusions

The cure characteristics of aluminium powder filled SBR-composites showed an increase in maximum rheometric torque and cure rate index with aluminium powder loading. Hexa-resorcinol and Si-69 increased the maximum torque while CoN decreased it. Shore A hardness of SBR-aluminium powder composites is increased with loading and is more pronounced in presence of bonding agents. Equilibrium swelling studies showed an improved adhesion between aluminium powder and SBR in presence of bonding agents. The modulus, tensile strength and tear strength increased with aluminium powder loading, and these properties were further improved with HR and Si-69 bonding systems. The improved adhesion restricts the chain movements, which caused a decrease in elongation at break in presence of bonding agents. SBR-aluminium powder composites showed a marked increase in heat build-up value especially with silane coupling agent. Aluminium powder caused a decrease in rebound resilience of SBR compounds and the decrease is maximum with Si-69 followed by HR system.

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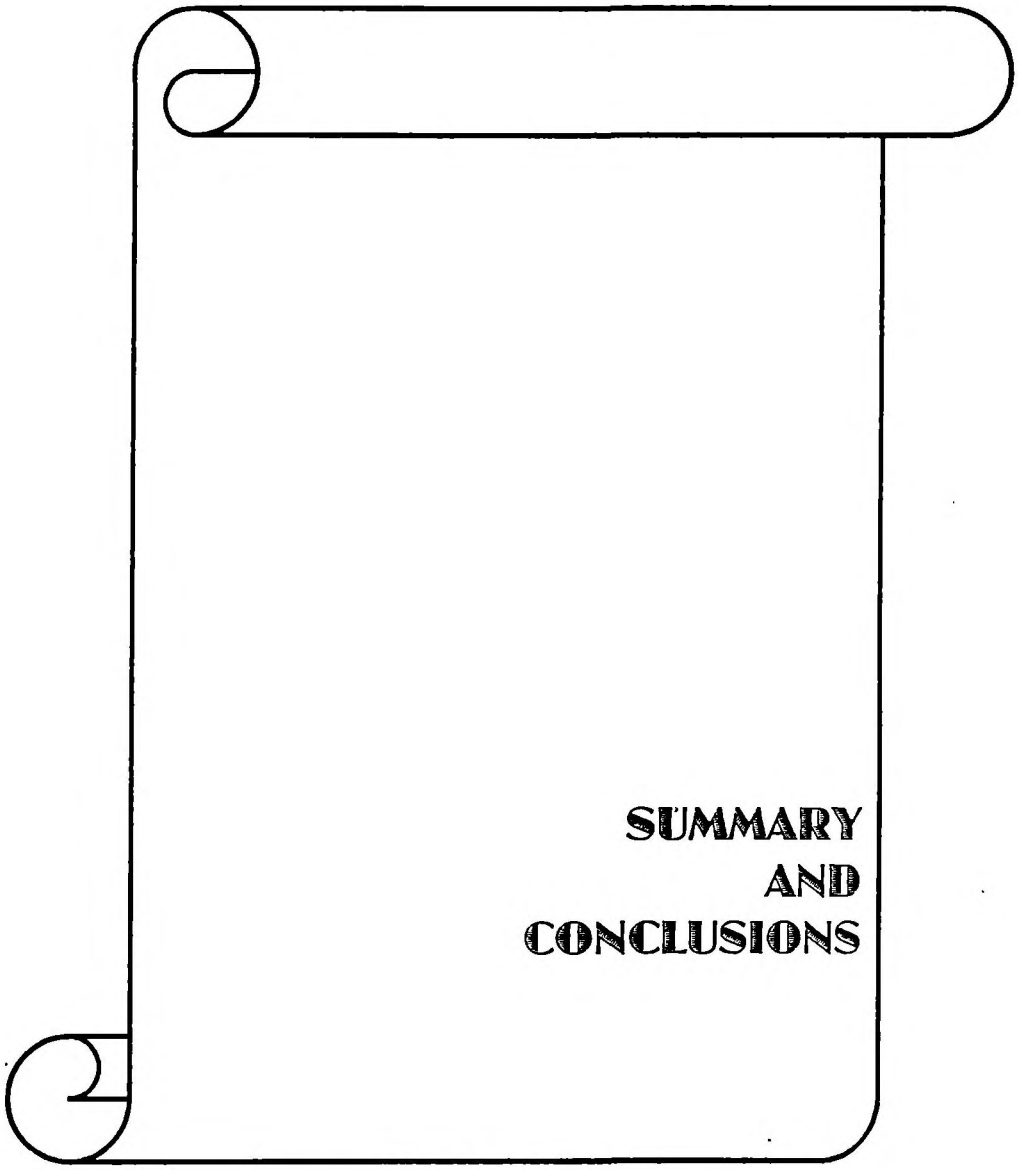

SUMMARY AND CONCLUSIONS

Polymers can act as thermal and electrical insulators, which is the basis for their application in many areas. But in certain special applications like discharging static electricity, electrical heating, friction–antifriction materials etc. the polymeric materials require thermal and electrical conductivity. The increased thermal conductivity has also advantages in the moulding of thick rubber articles. The increased thermal conductivity reduces the total vulcanization cycle of thick rubber articles and gives uniform curing throughout the material. Addition of metal powders is one of the best methods to improve the thermal conductivity of rubber compounds. Among the commercial metal powders, silver, copper and aluminium are the best conductors of heat, but silver is costly and copper is a pro-oxidant of many elastomers. Hence, the use of aluminium powder for improving the thermal conductivity of natural rubber and styrene butadiene rubber has been attempted in this study.

In metal powder filled composites, a major problem is caused due to the poor adhesion and the non-uniform dispersion of the discrete phase in the matrix. Partial modification of the filler or the polymer reduces this problem. Effect of various bonding agents namely hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl)propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisosyanate (TDI) on mechanical properties of aluminium powder filled natural rubber composites has been investigated. Shore A hardness, rebound resilience, heat build-up

etc. are found to be increased by the use of bonding agents due to the improved adhesion. Addition of bonding agent minimizes the DIN abrasion loss and compression set. Better adhesion between the elastomer and aluminium powder in presence of bonding agents is evident from the reduced swelling data. Among the various bonding agents silane coupling agent and the hexa-resorcinol system are found to be better for natural rubber-aluminium powder vulcanizates.

Equilibrium swelling was tried as a means to measure the adhesion between natural rubber-aluminium powder composites. This is based on the assumption that components of the composites, if bonded well have a decreased swelling in solvents. Equilibrium swelling has been investigated in a series of aromatic hydrocarbons like benzene, toluene, xylene and mesitylene, and aliphatic hydrocarbons like pentane, hexane and heptane. The natural rubber-aluminium powder composites were vulcanized by four vulcanizing systems, viz. conventional, efficient, dicumyl peroxide and a mixture consisting of sulphur and dicumyl peroxide. The crosslinking systems has an important role in the maximum solvent uptake value, which is in the order CV system>mixed system>EV system≥ DCP system for gum vulcanizates. In each system, the effect of a bonding agent consisting of hexamethylene tetramine-resorcinol-silica was studied. The results showed that addition of bonding agent reduced the swelling considerably and its effect is more pronounced in the conventional system due to increased adhesion. In all the samples temperature activates the diffusion process. The dependence of diffusion coefficient on the crosslinking system and the solvent-polymer interaction parameter were calculated from diffusion data. The results are also indicative of the improved adhesion with hexa-resorcinol-silica bonding system in these composites. The scanning electron

microphotographs showed that the metal powders are uniformly aligned throughout the matrix in the presence of bonding agent.

The effect of aluminium powder on the properties of natural rubber compounds containing various fillers namely, high abrasion furnace black (HAF), general purpose furnace black (GPF), acetylene black, china clay and precipitated silica were studied. As the proportion of aluminium powder in the total filler content increased, both Shore A hardness and rebound resilience increased. At equal loading (40 phr), HAF and acetylene black filled vulcanizates have higher tensile strength compared to the aluminium powder filled one. Compression set and heat build-up values were minimum with aluminium powder filled vulcanizates and a corresponding reduction in compression set and heat build-up was observed on substituting a part of the total filler content by aluminium powder. Substitution of other fillers with aluminium powder decreased the equilibrium swelling, which is an indication of higher extent of crosslink formation in presence of aluminium powder through better heat conduction. Among the various fillers used, aluminium powder filled composites showed the maximum thermal conductivity. Successive replacement of various fillers by aluminium powder showed a marked increase in thermal conductivity.

Stress-relaxation measurements have been carried out for aluminium powder filled natural rubber vulcanizates and are compared with those containing conventional fillers such as HAF, GPF, acetylene black, china clay and precipitated silica. The results showed that the gum natural rubber vulcanizates has a single stage relaxation pattern whereas the filled natural rubber composites followed a two-stage relaxation mechanism. The two-stage mechanism arises either from the progressive failure of rubber-filler attachment at the interface or by the rupture of the rubber molecules attached to them. The rate of stress relaxation is increased with aluminium

powder loading in natural rubber vulcanizates. Stress relaxation measurements of aged samples showed that ageing decreased the initial relaxation process of natural rubber composites containing aluminium powder. The relaxation processes are influenced by the presence of bonding/coupling agents like HR, Si-69, CoN and TDI, which indicated an increased natural rubber-aluminium powder interaction through improved adhesion. Composites containing bonding agents showed a slower rate of relaxation and higher crossover time compared to composites without bonding agents. The scanning electron photographs taken from the fractured surface of the tensile pieces again supported the improved adhesion in presence of bonding agents.

The dynamic mechanical properties of natural rubber vulcanizates containing aluminium powder have been investigated and are compared with vulcanizates containing conventional fillers. The effect of loading, presence of bonding agents, temperature, frequency etc. were analysed. As the loading of aluminium powder increased storage modulus, loss modulus and tanδ were increased. The use of various bonding agents like HR, Si-69, CoN and TDI, influenced the dynamic mechanical properties. The strong rubber-filler interaction in presence of bonding agents caused significant reduction in polymer mobility. Studies on the effect of frequency on dynamic mechanical properties showed that as the frequency decreased the storage modulus (E′), loss modulus (E″) and tanδ were decreased. The experimental values of the dynamic mechanical analysis were compared with theoretical models and found that the system is more close to 'Guth and Gold' model.

Ageing studies of the composites showed that incorporation of aluminium powder imparts better resistance towards heat ageing, gamma radiation, flammability and ozone degradation compared to other filler

incorporated natural rubber vulcanizates. During thermal ageing the gum vulcanizate gradually loses the modulus and tensile strength, but in aluminium powder filled vulcanizate an increase in modulus and tensile strength was observed after 7 days ageing at 70^0C and on prolonged ageing these properties slowly decreased. This is due to the competing reactions of crosslink formation and chain scission, which occur during thermal ageing. Aluminium powder increased the limiting oxygen index (LOI) values of natural rubber compounds. Ozone exposure of samples revealed that cracks were developed on the surface of all the samples, but the nature and density of cracks were different. In the case of aluminium powder filled vulcanizates a large number of small cracks were observed whereas in the samples containing other fillers the cracks were wide and deep. Composites containing bonding agents also followed the same trend.

Vulcanization of thick rubber articles is a tedious process as they undergo uneven curing due to the non-uniform distribution of heat in rubber compound. In conventional process complete and uniform curing of these materials requires additional time of vulcanization, which finally leads to poor properties to the product. This can be successfully overcome by the use of aluminium powder, as evidenced by the studies done in two thick products namely dock fender and rice polisher brake. Replacement of a portion of the filler content by aluminium powder showed a marked increase in thermal conductivity. Crosslink density assessment of the outer and central portions of a 5 cm cube confirmed that the use of aluminium powder imparted uniform crosslinking throughout the material within a limited time. The results with dock fender and rice polisher brake by substitution of 20 phr of the filler by aluminium powder supported the above findings. It is also noted that this replacement did not adversely affect the mechanical properties. Thus, use of aluminium powder in rubber compounds can

considerably save the amount of heat energy required for the vulcanization of thick articles imparts uniform curing which in turn can enhance the service life of such products.

The effects of aluminium powder on the properties of styrene butadiene rubber (SBR) composites were studied, and are compared with those containing HAF and acetylene black filled composites. All these fillers increased the Shore A hardness, modulus, tensile strength, tear strength and heat build-up of SBR compounds which followed the order HAF> acetylene black>aluminium powder. The maximum thermal conductivity is observed with aluminium powder filled composites. The electrical resistivity decreased as the loading of aluminium powder increased. A combination of HAF and aluminium powder in SBR showed properties in between the corresponding pure filler incorporated samples. Various bonding agents like HR, Si-69 and CoN were used in SBR-aluminium powder composites. The presence of bonding agents decreased the equilibrium swelling in toluene due to the improved adhesion between rubber and aluminium powder. Aluminium powder increased the modulus, tensile strength, tear strength and Shore A hardness. The bonding agents further enhanced these properties. The improved adhesion does not allow easy slippage of polymer segments, which caused a decreased elongation at break in presence of bonding agents. The SEM photographs taken from the fractured surfaces of tensile pieces showed that addition of bonding agent improved the adhesion and dispersion of aluminium powder in styrene butadiene rubber.

List of Publications

1. Effect of Adhesion on the Equilibrium Swelling of Natural Rubber-Aluminium Powder Composites, V. S. Vinod, Siby Varghese and Baby Kuriakose, *J. Appl, Polym. Sci.*, **70**, 2427, 1998.
2. Effect of Bonding Agents on Natural Rubber-Aluminium Powder Composites, V. S. Vinod, Siby Varghese and Baby Kuriakose, *J. Adhesion Sci. Technol.*, (In press).
3. Assessment of Adhesion in Natural Rubber-Aluminium Powder Composites by Equilibrium Swelling in Aliphatic Solvents, V. S. Vinod, Siby Varghese and Baby Kuriakose, *J. Mater. Sci.*, (In press).
4. Effect of Aluminium Powder on Filled Natural Rubber Composites, V. S. Vinod, Siby Varghese, Rosamma Alex and Baby Kuriakose, *Rubber Chem. Technol.*, (In press).
5. Dynamic Mechanical Properties of Aluminium Powder Filled Natural Rubber Composites., V. S. Vinod, Siby Varghese and Baby Kuriakose, *J. Polym. Sci.*, (Submitted).
6. Stress Relaxation in Aluminium Powder Filled Natural Rubber Composites, V. S. Vinod, Siby Varghese and Baby Kuriakose, *J. Polym. Mater.*, (Submitted).
7. Degradation Behaviour of Natural Rubber-Aluminium powder Composites; Effect of Heat, Ozone and High Energy Radiation., V.S. Vinod, Siby Varghese and Baby Kuriakose, *Polym. Degrad. Stab.*, (Submitted).
8. Natural Rubber-Aluminium powder Composites; Uniform and Fast Curing of Thick Rubber Articles, V. S. Vinod, Siby Varghese and Baby Kuriakose., *NR Technology*, (Submitted).
9. Properties of Aluminium Powder Filled Styrene Butadiene Rubber Composites, V. S. Vinod, Siby Varghese and Baby Kuriakose, *Kauts. Gummi Kunst.*, (Submitted).
10. Properties of SBR-Aluminium Powder Composites in Presence of Bonding Agents, V. S. Vinod, Siby Varghese and Baby Kuriakose, *J. Appl. Polym. Sci.*, (Submitted).

Presentations

1. Effect of Aluminium Powder on Filled Natural Rubber Composites, V. S. Vinod , Siby Varghese and Baby Kuriakose . Eleventh Kerala Science Congress, Kasaragod, February 27 to March 1, 1997.
2. Properties of Aluminium Powder Filled Natural Rubber Vulcanizates, V. S. Vinod, Siby Varghese and Baby Kuriakose, UGC sponserd seminar held at Nirmala College, Muvattupuzha, November 5, 1999.
3. Uniform Curing and Reduction in Vulcanization Time of Thick Rubber Articles Using Aluminium Powder, V. S. Vinod, Siby Varghese and Baby Kuriakose, Twelfth Kerala Science Congress, Kumily, January 27-29, 2000.
4. Effect of Bonding Agents on the Properties of Natural Rubber-Aluminium Powder Composites, V. S. Vinod, Siby Varghese and Baby Kuriakose, Indian Science Congress, Pune, 87th Session, January 3-7, 2000.
5. Use of Aluminium Powder in Thick Rubber Articles for Uniform Curing and Reducing Cure Time, V. S. Vinod, Siby Varghese and Baby Kuriakose, IRMRA 18th Rubber Conference, Mumbai, January 20-21,2000.