EPOXIDISED NATURAL RUBBER AS A REINFORCEMENT MODIFIER FOR SILICA FILLED NATURAL RUBBER AND ACRYLONITRILE BUTADIENE RUBBER

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BY

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Dedicated to my parents

भारतीय रबड़ गवेषण संस्थान
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The Rubber Research Institute of India
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Ref. No. 9/DR/RES/2005 Date 06/06/05

CERTIFICATE

This is to certify that the thesis entitled **'Epoxidised natural rubber as a reinforcement modifier for silica filled natural rubber and acrylonitrile butadiene rubber'**, is a *bona fide* record of the research work carried out by **Mr. Jacob K. Varkey** under my 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 the Mahatma Gandhi University, Kottayam. No part of the work presented in this thesis has not been submitted for the award of any other degree or diploma. It is also certified that **Mr. Jacob K. Varkey** has fulfilled the course requirements and passed the qualifying examination for the Ph.D degree of the Mahatma Gandhi University.

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DECLARATION

I hereby declare that the thesis entitled **'Epoxidised natural rubber as a reinforcement modifier for silica filled natural rubber and acrylonitrile butadiene rubber'** is an authentic record of the research work carried out by me under the supervision of **Dr. N. M. Mathew**, Director, Rubber Research Institute of India, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma.

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6th June 2005

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Preface

Particulate fillers are used as reinforcing agents in rubber, among which carbon black and silica are the most efficient. Carbon black is the largest tonnage filler being used in rubber as a reinforcing agent. On thermodynamic ground also it is the preferred filler for general purpose rubbers. However, due to ecological reasons and the requirements of the products such as high performance tyres, where low rolling resistance is of prime importance, use of silica as a filler in rubber, either for complete or partial substitution of carbon black, is on the increase. The polar surface of silica results in poor rubber-filler interaction and higher filler-filler interaction. In comparison with a carbon black filled rubber, the higher surface polarity of silica also causes poor processability, cure retardation and inferior vulcanizate properties. For effective reinforcement with silica, filler surface modifier or coupling agent is to be used. Silane coupling agents are the most efficient ones. However, the high cost of silanes is a limitation for the widespread use of silica/ silane technology. The present thesis reports the use of epoxidised natural rubber (ENR) as a reinforcement modifier for silica filled rubbers in comparison with silane modified and carbon black filled systems. The reinforcement modification of silica filled rubbers with ENR was made by substituting a portion of the base rubber with ENR, which has a better affinity to silica than the conventional rubbers.

The thesis is presented in nine chapters. The first chapter discusses the basic concepts of reinforcement of rubbers. A review of the developments in the field of particulate filler reinforcement of rubbers, with special reference to carbon black and silica fillers was made. Scope and objectives of the study are also discussed. The experimental techniques and details of the equipment used for the study are described in chapter two. Chapter three to seven describes the use of ENR as a reinforcement modifier in silica filled natural rubber (NR) in comparison with corresponding silane modified and carbon black filled NR with respect to its impact on processibility, filler dispersion, technological and dynamic mechanical properties. Also the effects of filler loading and cure systems in various silica filled systems are reported. Chapter eight discusses the use of ENR as a reinforcement modifier in silica filled nitrile rubber (NBR) in comparison with the corresponding silane modified and carbon black filled. Chapter nine gives a summary of the findings, scope for future studies and conclusions.

ABBREVIATIONS AND SYMBOLS

ACN - Acrylonitrile
ASTM - American Society for Testing and Materials
AFM - Atomic force microscopy
BET - Brunauer, Emmett and Teller
BIS - Bureau of Indian Standards
BR - Polybutadiene rubber
CBS - N-Cyclohexyl 2-benzothiazole sulphenamide
CR - Chloroprene rubber
CRI - Cure rate index
CSDP - Carbon-silica dual phase
CTAB - Cetyl trimethyl ammonium bromide
DBP - Dibutyl phthalate
DCP - Dicumyl peroxide
DEG - Diethylene glycol
DOP - Dioctyl phthalate
DMA - Dynamic mechanical analyser
DMTA - Dynamic mechanical thermal analyser
DOTG - Di ortho tolyl guanidine
DPG - Diphenyl guanidine
DSC - Differential scanning calorimetry
DTDM - Dithiodimorpholine
EPDM - Ethylene propylene diene rubber
ETES - Ethyl triethoxy silane
ENR - Epoxidised natural rubber
FEF - Fast extrusion furnace
FTIR - Fourier transform infrared spectrophotometer
GPF - General purpose furnace
HAF - High abrasion furnace
HD - Highly dispersible
HDTES - Hexadecyl triethoxy silane
HMT - Hexamethylene tetramine
HREELS - High resolution electron energy loss spectroscopy
ISAF - Intermediate super abrasion furnace
IIR - Isobutylene-Isoprene rubber
IGC - Inverse gas chromatography

ISNR - Indian standard natural rubber
MBTS - Mercaptobenzthiazole disulphide
MPS - γ- Mercapto propyl trimethoxy silane
MTMO - Mercapto propyl trimethoxy silane
NBR - Acrylonitrile butadiene rubber (Nitrile rubber)
NMR - Nuclear magnetic resonance
NR - Natural rubber
OCT - Optimum cure time
OTES - Octyl triethoxy silane
PDMS - Polydimethyl siloxane
PEG - Polyethylene glycol
phr - Parts per hundred rubber
PRI - Plasticity retention index
PTES - Poly triethoxy silane
ppm - Parts per million
RS - Raman spectroscopy
SAF - Super abrasion furnace
SBR - Styrene butadiene rubber
SEM - Scanning electron microscopy
SIMS - Secondary ion mass spectroscopy
Si 69 - Bis- (triethoxy silyl propyl) tetrasulphide
STM - Scanning tunnelling microscopy
TEA - Triethanolamine
TESPT - Bis- (triethoxy silyl propyl) tetrasulphide
TESPD - Bis (triethoxy silyl propyl) disulphide
TESPM - Bis (triethoxy silyl propyl) monosulphide
TMTD - Tetramethylthiuramdisulphide
TGA - Thermo gravimetric analyser
UTM - Universal testing machine
XPS - X-ray photoelectron spectroscopy
ZnO - Zinc oxide
% - Per cent
ρ - Density
δ - Delta
F - Force
P_0 - Initial plasticity
R_B - Bound rubber

η Viscosity

γ - Shear rate

τ - Shear stress

σ Tensile stress

T_0 - Threshold tearing energy

T - Temperature

°C - Degree celcius

dN.m - Deci Newton meter

E - Young’s modulus

E’ - Elastic modulus

E” - Loss modulus

g - Gram

G - Shear modulus

G* - Complex shear modulus

h - Hour

H_z - Hertz

k - Boltzman constant

m - meter

cm - centimeter

M_H - Maximum torque

M_L - Minimum torque

MPa - Mega Pascal

Tg - Glass transition temperature

Vr - Volume fraction of rubber

nm - Nano meter

ml - Milli liter

µm - Micro meter

γ_s - Surface energy

°A - Angstrom

CHAPTER 1

INTRODUCTION

1. Reinforcement

Fillers are widely used to enhance the performance related properties of rubbers and other polymeric materials. Rubbers produced by crosslinking of amorphous elastomers are soft and weak. Reinforcement of rubbers with fillers or "hard domains" can increase stiffness and resistance to fracture[1]. Reinforcements are discrete inclusions used to improve the performance characteristics of a material. They can be continuous (fibre, filament or tape) or discontinuous in form (whisker, flake or particle). In addition to the modification of mechanical properties such as stiffness and resistance to fracture, a filler can also modify the electrical, thermal and fatigue properties as well as cost of elastomeric materials[2].

1.1 Reinforcement of rubbers with particulate fillers

In thermoset rubber technology the most important class of reinforcing hard domains are the particulate fillers whereas with thermoplastic elastomers, self reinforcement is provided by thermodynamic phase separation of hard domains. Particulate fillers can increase the strength of vulcanized rubbers. The elastomers reinforced with particulate fillers can maintain almost the same flexibility as that of the unfilled. The improvement in modulus and other physical properties achieved for elastomeric vulcanizates through particulate fillers is more pronounced with non-crystallizing rubbers [3].

The basic parameters of the filler particles, responsible for reinforcement, are particle size, surface area, specific surface activity/chemical composition and structure/porosity.

1.1.1 Particle size / surface area

Filler particle size is the most important property which influences reinforcement [4]. The principal requirement for rubber reinforcement is sufficiently small domain size, less than about 1 µm. Sufficiently small filler can give good reinforcement, even when matrix/domain bonding is poor. (eg graphitised or fluorinated carbon black)[5-6]. However, if domain size is greater than about a micron, reinforcement is absent or minimal regardless of domain shape, and even if bonding between the matrix and domain is quite strong. The most important single factor which determines the degree of reinforcement is the development of a large polymer-filler interface. It can be provided only by particles of colloidal dimensions. Spherical particles of 1 µm in diameter have a specific surface area of $6 m^2/cm^3$. This constitutes approximately the lower limit for significant reinforcement. The upper limit of useful specific surface area is of the order of 300-400 m^2/cm^3 and it is decided based on considerations of dispersibility and processability of the unvulcanized mix and serious loss of rubbery characteristics of the composite[3]. Many effects of filler in rubber are surface area dependent.

The surface area of particulate solid is related to its particle size. If all the particles are considered spheres of the same size, the surface area **As**, per gram of a filler is given by Equation 1.1

$$\mathbf{As = 6/d\rho} \qquad \textbf{Eq.1.1}$$

where d is the diameter and ρ the density of the filler particle.

In reality particles have a distribution of size and are usually far from being spherical. Different fillers of the same particle size may not impart the same reinforcement., eg: carbon black and silica. The shape of particle also may be different for different fillers; viz; spheroidal, cubic/prismatic, tubular, flaky or elongated. Non-spherical particles can impart better reinforcement [7, 8].

1.1.2 Specific surface activity / chemical composition

The nature of the filler surface may be varying in a chemical sense, having different chemical groups, eg: hydroxyl or metal oxide in white fillers and carbonyl, quinone, lactone etc. in carbon black [8]. In a physical sense they may be different in adsorptive capacity and in energy of adsorption, eg: polar rubbers showing dipole interaction with filler surface groups.

Chemical surface groups on fillers play an important role in their effect on rate of cure, with many vulcanizing systems. Physical adsorption activity of the filler surface is of greater importance than its chemical nature. Carbon black which loses the active sites on heat treatment exhibits poor mechanical properties. Strong chemical bonding between filler and polymer does not lead to desirable vulcanizate strength properties, but causes high moduli.

1.1.3 Structure and aggregation/porosity

'Structure' is a measure of aggregation of primary particles resulting in deviation from the spherical shape leading to lower packing density and higher void volume. Aggregates can be of different shape such as (a) spherical (b) ellipsoidal (c) linear and (d) branched [9]. High structure carbon exhibits high oil absorption.

In the case of inorganic or mineral fillers, differences in particle geometry depending on the crystal form of each mineral can be observed. Crystals with almost identical dimensions in the three directions will result in isometric particles. Higher anisometry as in the case of platelets, rod shape etc when used in rubber results in high modulus.

Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loading, leading to chain-like filler structure or cluster, generally termed as 'secondary structure' or filler network. Such a network has a significant effect on the properties of filled rubber. Filler networking is determined by the attractive potential 'S_f' between the aggregates in rubber as well as by their distance. Wang et al[10] studied the effect of distance between filler aggregates on the dynamic mechanical properties of vulcanizates, using fillers of different 'S_f' values. Morphological characterization of fillers was made by many workers [11,12]. Tables 1.1 and 1.2 show the various effects of filler particle size and structure on rubber compound processing and vulcanizate properties [13].

Table 1.1 Effect of particle size and structure on processing characteristics

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

Table 1.2 Effect of particle size and structure on vulcanizate properties

Vulcanizate properties	***Decreasing particle size***	***Increasing structure***
Rate of cure	Decreases	Little effect
Tensile strength	Increases	Decreases
Modulus	Increases to maximum and then decreases	Increases
Hardness	Increases	"
Elongation	Decreases to minimum and then increases	Decreases
Abrasion resistance	Increases	Increases
Tear resistance	"	Little effect
Cut growth resistance	"	Decreases
Flex resistance	"	"
Resilience	Decreases	Little effect
Heat build- up	Increases	Increases slightly
Compression set	Little effect	Little effect
Electrical conductivity	Increases	Little effect

For effective reinforcement, specific surface activity and structure are necessary. High structure without surface activity does not result in high reinforcement [8].

Porosity can be seen with many particulate fillers. Filler porosity can affect the vulcanizate properties. However, its effect on reinforcement is secondary. In the case of carbon black, porosity results in higher viscosity and higher electrical conductivity [8].

1.2 Particulate fillers

Particulate fillers used in rubber industry in general can be classified as "Black" and "Non black", depending on their origin, the former being mostly produced from petroleum feed stock and the latter from mineral sources. The most important particulate fillers being used in rubber industry are carbon black and silica. Silicates, clays, whiting (calcium carbonate) and other mineral fillers are used extensively where a high degree of reinforcement is not essential [3].

1.2.1 Carbon black

Carbon black was introduced as a reinforcing filler in elastomers during 1917-1929. It is a colloidal form of elemental carbon. It owes its reinforcing character to its colloidal morphology (the size and shape of the ultimate units) and to its surface properties. The primary units of carbon black are aggregates. Carbon blacks are prepared by incomplete combustion of hydrocarbons or by thermal cracking. Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black depending on their method of manufacture. The major types of rubber reinforcing carbon blacks are manufactured by the furnace process. The predominant purpose of furnace type carbon blacks in elastomers, is the reinforcement they impart to the vulcanizates [3, 4, 8, 14-16].

Carbon black is characterized based on its surface area, particle size, structure and tinting strength. Surface area is usually determined by iodine adsorption, nitrogen adsorption or cetyl trimethyl ammonium bromide (CTAB) adsorption. Structure refers to the bulkiness of the carbon black aggregate. Bulkiness is associated with large average number of particles per aggregate. Structure is measured by dibutyl phthalate (DBP) absorption (ASTM D-2414) method. Tinting strength is a measure of the amount of carbon per aggregate and is measured by optical means [17-20]. Elastomer reinforcement of carbon black is dependent on these properties. Dispersion of carbon black in the elastomer also influences the extent of reinforcement. A typical range of specifications of the four different carbon blacks are given in Table 1.3.

Table 1.3 Specifications of different carbon blacks

Characteristics	**Lamp**	**Channel**	**Furnace**	**Thermal**
Average particle size (nm)	100-150	1-3	14-80	240-320
Surface area (N_2) (m^2/g)	20-95	100-1125	27-145	7-11
Oil absorption (ml/g)	1.05-1.65	1.0-6.0	0.67-1.55	0.32-0.47
Volatile matter (%)	0.4-0.9	3.5-16.0	0.3-2.8	0.1-1.0
Ash (%)	0 – 0.16	0-0.1	0.1-1.0	0.2-0.5
Sulphur, ppm	-	0-0.1	0.5-1.5	10
pH	3-7	3-6	5.0-9.5	7-9

Table 1. 4 Properties of furnace blacks

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

Carbon blacks have reactive organic groups on the surface that cause affinity to rubber[21]. Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall technological properties. Details of a range of furnace blacks generally used for rubber reinforcement are given in Table 1.4.

1.2.2 Non-black fillers

Non –black fillers include a range of inorganic materials with a variety of particle shapes and sizes. It is available in a broad range of sizes from about 10 to 0.015 microns. These fillers can broadly be classified as

a) Fillers used to reduce cost

b) Semi- reinforcing filler

c) Reinforcing filler

Earlier non –black fillers used were mainly naturally occurring minerals or by – products of manufacturing such as clay, whiting, barytes, zinc oxide, zinc sulphide, blanc-fixe, mica, asbestos, kieselguhr, magnesium carbonate, iron oxide, litharge etc. They were used in rubber to reduce tack, increase hardness, improve durability and reduce cost [3,8,22]. Other important non-black fillers being used in the elastomer industry are aluminium hydrate, aluminium oxide and titanium dioxide.

The need for more reinforcing non-black fillers in many rubber applications led to the introduction of calcium carbonate, calcium silicates, hydrated silicas and fumed silicas between 1940 and 1960. These were characterized by very small particle size much smaller than the natural products and similar to the reinforcing carbon blacks. Since then a lot of developments and refinements in hydrated silicas and fumed silicas have taken place resulting in a number of grades for specific applications [23].

1.2.2.1 Silica

Different forms of silica are commercially available for various industrial applications. Important natural varieties are silica (amorphous), silica (crystalline), silica diatomaceous (fossil origin) and silica (microcrystalline). Types of synthetic silica are precipitated, pyrogenic, aerogels and hydrogels. Of these varieties, precipitated silica and pyrogenic (fumed) silica are being used for elastomer reinforcement [24].

a) Production and Characterization

Precipitated silica is produced by acidification of alkalisilicate solutions under controlled conditions. Colloidal pyrogenic silica is produced by reaction of silicon tetrachloride at high temperatures with water.

$$SiCl_4 + H_2O \rightarrow SiO_2 + 4HCl$$

The reaction products are quenched immediately after coming out of the burner. Pyrogenic silca is too active and expensive [21]. Precipitated silicas are silicon dioxide containing about 10-14% water, with particle size in the range 1-40 nm. They are reinforcing fillers giving composites of high tensile strength, tear resistance, abrasion resistance and hardness. It is being used in the manufacture of translucent and coloured products, shoe soling, tyres and other mechanical rubber goods. Fumed or pyrogenic silica is silicon dioxide containing less than 2% combined water. These silicas are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance and abrasion resistance particularly to silicone rubbers [8].

Characterization of silica filler is also based on particle size and specific surface area. Surface area measurement is usually done by nitrogen adsorption (BET) method. Also pH, chemical composition and oil absorption are specified. The smallest physically observable primary particle for precipitated silica is about 15-20 μm and for fumed silica it is about 15μm in size. The surface forces of the small primary particles are so high that many particles conglomerate to form the so-called secondary particles. Usually the shear forces generated during rubber mixing is not sufficient enough to disperse primary filler particles in the rubber [21].

The secondary particles of silica fillers form further agglomerates. They form chain-like structures, the so-called tertiary structures. Though the tertiary structures are also relatively stable, they get more or less shattered by the shear forces during mixing. The higher the shear force, the better the dispersion [21].

b) Chemistry of silica[3]

(1) Silica which is amorphous, consists of silicon and oxygen arranged in a tetrahedral structure. Particle size usually ranges from 1-30 nm and the surface area from 20-300 m^2/g.

(2) Surface silanol concentration (silanol groups – Si-O-H) influence the degree of hydration. Water content can affect processing and vulcanization. Absorbed water can decrease cure time, tensile strength and also abrasion resistance[25].

(3) Silanol types fall into three categories – isolated, geminal (two-OH groups on the same silicon atom), and vicinal (-OH on adjacent silicon atoms). Isolated hydroxyls exist predominantly on dehydrated silicas, pyrogenic silica and to a lesser extent on precipitated silica. Vicinal hydroxyls are stronger adsorption sites and hence, have stronger reinforcement effect than the isolated hydroxyls.

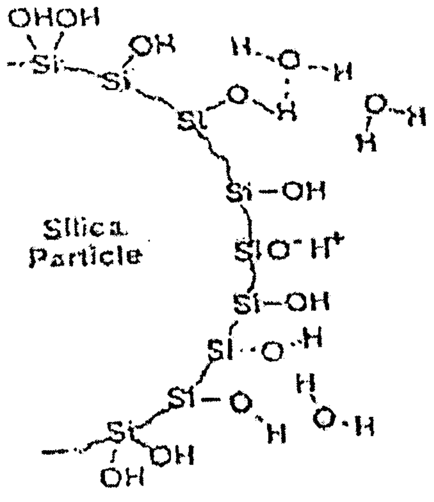


Fig.1. 1. Adsorptive nature of silica filler

(4) Surface acidity is controlled by the hydroxyl groups on the surface of the silica and is intermediate between those of P-OH and B-OH. This intrinsic acidity can

influence vulcanization. The rubber filler interaction is affected by these sites. A general silica structure is depicted in Fig.1.1

Silicas have strongly polar surface groups, mostly hydroxyl groups bound to silicon. The reactivity of the surface causes foreign substances to be adsorbed on the filler surface. With increasing water content the dispersion time of colloidal silica into the rubber gets prolonged.

The filler also adsorbs organic compounds, particularly basic ones: eg diphenyl guanidine(DPG), diortho tolyl guanidine(DOTG). Therefore, a larger amount of the same has to be added to compensate for the loss due to adsorption by silica. Accelerator adsorption by the filler will be lower, if it already contains water.

c) *Activators for silica fillers*

Silica fillers can, not only interact with water and accelerators, but also with polymers. With increasing filler content and consequent increasing filler activity the viscosity of the compound increases, thus making processing difficult. To the extent that filler-polymer interaction is reduced, compound viscosity can be reduced. Materials that get adsorbed stronger on the filler than the rubber, can soften the mixtures and could be processed more easily. Additives of this type are DPG, DOTG, hydroxyl containing compounds like glycols, glycerol etc. and materials with basic nitrogen like triethanolamine and secondary amines. Such additives are technically termed as 'filler-activators' since they act not only to improve processing, but also to reduce accelerator adsorption. In addition to this the glycols, triethanolamine etc. also cause breakdown of the 'tertiary filler structure' thus making dispersion more effective. With highly active silicas by the addition of small amounts of activators an increased viscosity may be observed because of better filler dispersion, and lower viscosity could be achieved with further addition of activator, after passing through a viscosity maximum.

Carbon blacks have reactive organic groups on its surface that cause affinity to rubber [21]. These reactive sites are missing in light coloured fillers. There are other group of filler activators such as silanes [26-36], titanates and zirconates [37-39] and others which can make the filler more reactive.

In general, silicas produce relatively greater reinforcement in more polar elastomers such as acrylonitrile – butadiene rubber (NBR) and polychloroprene rubber (CR) than in non-polar polymers such as styrene butadiene rubber (SBR) and natural rubber (NR). The lack of reinforcement properties of silica in NR and SBR can be corrected through the use of silane coupling agents. An essential prerequisite for a coupling agent is that the molecule is bifunctional, ie., capable of reacting chemically with both silica and either directly or indirectly with the polymer via participation in the vulcanization reaction or sulphur crosslinking process [3].

1.3 Filler surface activity

The surface activity is related to different chemical groups on the surface of fillers such as carboxyl, quinone, phenol and lactone in the case of carbon black and hydroxyl, metal oxide etc in the case of silica. The surface chemical groups play an important role in their reinforcing ability for elastomers [21]. Surface energy of filler particles play much greater role with regard to the mechanical properties of the filled elastomers. The surface free energy γ_s, of a solid has two components viz; dispersive component (London or non-specific) γ_s^d and specific component (including polar, acid–base, hydrogen bonding etc.) γ_s^{sp}, which can be expressed as,

$$\gamma_s = \gamma_s^d + \gamma_s^{sp}$$

Rubber-filler interaction depends on the surface energies of the two. It is the two components of the surface energy of the filler which describes its distribution in the rubber. γ_s^d is high for carbon black, while γ_s^{sp} is high for silica. This implies that the former can disperse easily in rubber, the latter leads to high filler-filler interaction which in turn will lead to filler agglomeration and therefore poor dispersion in the rubber matrix. To overcome these difficulties, filler surface is to be modified. Surface energies of a series of carbon blacks and the interaction between carbon black and elastomers were estimated by Wang and Wolff [40]. Inverse gas chromatography (IGC) is one of the important tools for the investigation of filler surface energies [41,42].

1.4 Filler surface modification

The surface activity of a filler has influence on the reinforcement of rubber. Several methods are being used to modify the filler surface.

1.4.1 Carbon black – surface modification and characterization

1.4.1.1 Modifications

a) Heat treatment

Heat treatment in an inert atmosphere alters the physico-chemical characteristics of carbon black. The chemical nature of surface is modified at a temperature below 1000°C, whereas the physical nature of the surface gets modified around 1000-1500°C[43-46]. A drastic change in surface energy [40] and a change in the crystalline property [47] are the major physical changes of heat treatment. Heat treatment or graphitisation leads to a major reduction in both dispersive component (γ_s^d) and specific component (γ_s^{sp}) of the surface energy [40].

b) Surface grafting

Surface grafting of various organic molecules including polymers on to carbon black surface has been studied extensively [48]. Several techniques are being adopted for the grafting of polymers on to carbon black, of which the important ones are

- Grafting on to carbon by chain termination / or chain transfer of a growing polymer radical [49-51]. Polymer grafted to carbon is only less than 10%.

- Grafting through copolymerisation of the small molecules already grafted on the black [49,50]; most favourable process.
- Grafting by direct reaction of the carbon black surface and functionalised polymer [49, 52,53].

Dannenberg [54] observed that elastomer grafted carbon black did not improve the reinforcing property of the vulcanizate. However, Papier [55] and Wolff et al [56], observed superior reinforcing properties in the case of polyisoprene grafted channel black and silane modified carbon black. The result of grafting on to carbon black surface caused surface deactivation hence, filler-filler interaction decreased drastically [57,58].

c) Plasma treatment

Plasma treatment is an effective means to modify carbon black surface[59-61] and the modification is fairly uniform over the whole surface. Wang[62,63] reported that significant changes in surface chemistry occurred on air and ammonia plasma treatment of graphitised black. Air plasma treatment results in the formation of oxygen containing groups[64] and ammonia plasma treatment results in nitrogen containing groups[65].

d) Surface oxidation

Donnet and Voet[66] reviewed the processes of surface oxidation of carbon blacks and categorized two important methods of oxidation depending on the nature of the oxidizing agent, gas phase and liquid phase. Oxygen, ozone, air or oxides of nitrogen are basically the gas phase oxidants[67-69], whereas nitric acid, aqueous potassium permanganate and bromine water are the liquid phase oxidants[70-72]. Donnet and Papirer [73] reported that increase in the duration of oxidation increases the oxide content on the carbon black surface and consequently the hydrophilicity of the black. The effect of surface oxidation on specific area has been extensively studied[74, 75]. Pores are created on the surface of carbon black during oxidation.

Oxidation of carbon black in liquid phase is characterized by formation of carbon dioxide and oxidised groups on the surface, such as carbonyl, hydroxyl, carboxyl[76,77] etc..

1.4.1.2 Characterization

Considerable efforts have been devoted to the instrumental analysis of carbon black surface. Infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), atomic force microscopy (AFM), secondary ion mass spectroscopy (SIMS), high resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM) are widely used to investigate the physico-chemical properties of carbon black surface. IR, XPS and STM provide the most useful information.

1.4.2 Silica – surface modification and characterization

The surface of silica is less complex than carbon black. Wagner[25] has made an extensive review on different aspects of silica and silicates. Silica consists of silicon and oxygen, tetrahedrally bound in an imperfect three dimensional structure. The imperfections in the lattice structure leave free silanol groups on the surface. The number of silanols, their distribution and also the conformation of the surface siloxanes depend on the method of preparation and thermal treatment. The distribution and also the close proximity of the hydroxyl groups have an influence on the adsorption and reinforcing properties[78]. Three types of surface silanol groups have been identified; isolated, vicinal and geminal adjacent silicon atoms (two hydroxyls on same silicon atom)[78,79]. In IR spectra, the isolated hydroxyls give a strong band at 3750 cm^{-1}, while the vicinal hydroxyls and the geminal hydroxyl show peaks at 3600 $cm^{-1}$and 3500 cm^{-1} respectively[80,81]. The –OH concentration may vary between 4.5 to 12.5 per nm^2.

Various modifications have been done to improve the reinforcing ability of the silica which includes heat treatment, polymer grafting on silica surface and chemical modification by heat treatment with modifiers like silane coupling agent.

Heat treatment is the simplest way of modifying the silica surface. The surface hydroxyl groups remain constant up to a temperature of 300^0C. At this temperature the adsorbed water molecules are removed and then thermal condensation begins. At temperatures beyond $600\text{-}700^0$C, only 1.5 –OH per nm^2 is left over[82]. Linger et al[83,84] had used IGC for characterizing the heat treated silica surface. At infinite dilution, IGC is an ideal tool to characterize the changes in the surface of the silica due to heat treatment.

Silica surface modification by grafting of alkyl chains through esterification has been reported by several workers. Esterification of silica surface by methanol, ethanol and butanol was reported[85-87]. Donnet et al[88-90] have reported the characterization of alkyl grafted silica surface using IGC. Grafting of methyl and hexadecyl chains on the surface of silica has been found to decrease the thermodynamic parameters. Esterification results in the reduction of the dispersive component γ_s^d of the surface energy. By esterification, the surface heterogeneity of the unmodified silica reduces and hence the filler- filler inter-aggregation diminishes.

1.4.2.1 Silanes as silica surface modifier

Varieties of silanes are being used by the polymer industry for improving the interfacial adhesion or bonding of silica with the polymers. Plueddmann[91] gives a detailed account of the use 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.

In silica filled rubber systems, silane modification improves the interfacial adhesion between the two. Silane modified silicas reduces the specific component of surface energy γ_s^{sp} and hence improves its compatibility with rubbers[92]. A series of silane coupling agents are available with general formula $YRSiX_3$, in which Y is the organofunctional radical, R represents the alkyl group and X the silico functional group such as chloro, alkoxy or acetoxy which on hydrolysis get attached to the silica surface groups. Silanes generally are of three categories viz; Monofunctional silanes, bifunctional silanes and non-sulphur bearing silanes[93].

Hydrophobation through silanization of silica with a monofunctional silane reduces the filler network, thereby makes the silica more compatible with the rubber matrix. The extent of network reduction depends not only on the degree of hydrophobation(amount of silane) but also on the kind of silane. Alkyl chain length is a factor in determining the reduction of filler network. Examples of few commercially important monosilanes are

1. PTES - Propyl triethoxy silane
2. ETES- Ethyl triethoxy silane
3. OTES- Octyl triethoxy silane
4. HDTES – Hexa decyl triethoxy silane

Considerable reduction in filler networking could be achieved with HDTES treatment.

Bifunctional silanes are used as coupling agent, which chemically binds silica with rubber. The silicofunctional group reacts with the filler surface groups and the organofunctional group with the rubber resulting in rubber-silica bonding, thus results *in* improved reinforcement. Several silanes with appropriate functionality such as alkoxyl silyl groups have been successfully used as coupling agents[94-96]. Some of the bifunctional silanes of commercial importance are the following.

1. TESPT - Bis (triethoxy silylpropyl) tetrasulphide (Si 69)
2. TESPD - Bis (triethoxy silylpropyl) disulphide
3. TESPM- Bis (triethoxy silylpropyl) monosulphide
4. MTMO-Mercapto propyl trimethoxy silane (A 189)
5. Bis (triethoxysilyl ethyl tolylene) polysulphide (Y9194)

It has also been reported that bis (disisopropyl) thiophosphoryl disulphide, a new group of chemical can also be used as coupling agents to bond silica and rubber.

Wang et.al[97] have showed that silane modified silica increases its compatibility with hydrocarbon elastomers, thereby improving filler dispersion, compound processability and vulcanizate technological properties.

1.5 Rubber reinforcement

1.5.1 Reinforcement mechanism

Addition of fillers to rubber has a strong impact on its static and dynamic behavior. Surface interaction between fillers and rubber molecules involves a range of bond energies from relatively weak to very strong. In general, physical adsorption of polymers on filler surface occurs to varying degrees depending on the filler surface and the nature of the polymer segments. In the case of carbon black, the level of physical interaction is high[98]. Although chemical interaction between carbon black and rubber is taking place, it occurs only to a minor extent and is not a necessary condition for reinforcement. Filler, above a critical concentration in rubber matrix, can cause filler-filler interaction, extent of which is determined by both physical or chemical interaction and the distance between filler aggregates in the rubber compound.

When rigid spherical particles are dispersed into a fluid, an increase in viscosity takes places in the case of liquids or a modulus enhancement in the case of polymers, which is known to be due to the hydrodynamic effect[99].

According to Payne the enhancement of mechanical properties due to the presence of a filler in rubber compounds can be attributed to the additive effects of polymer network, hydrodynamic effect, in-rubber structure and the filler-filler interaction. The dynamic modulus, G*, of a reinforced rubber hence depends both on strain independent parameters such as crosslinking of the matrix, hydrodynamic effect, filler to rubber interaction (in-rubber structure) and the strain dependent filler-filler interaction. The phenomena of stress softening of a filled rubber with strain known as

"**Payne effect**" arises from filler-filler interaction[100,101]. A comparison of the reinforcement behavior due to the above 4 factors of carbon black and silica is given in figure.1.2.

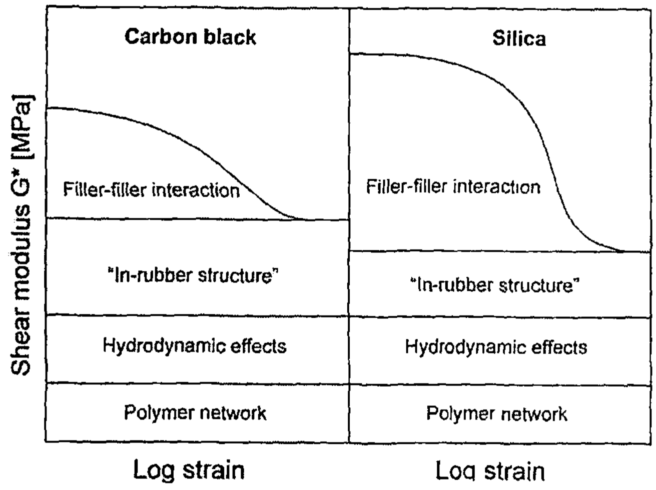


Fig.1. 2 Payne effect- carbon black , silica comparison

a) Polymer network

The first component of the 'additive factors' of reinforcement is the strain independent polymer network which results from the proportionality of the modulus (Go) to that of the crosslink density and can be represented using Equation 1.2 as

$$\mathbf{Go = \nu kT} \qquad \textbf{Eq.1.2}$$

where v= number of moles of elastically effective network chains per unit volume as a result of vulcanization.

k= Boltzmann constant

T = Temperature (K)

b) Hydrodynamic effect

When rigid spherical particles are dispersed into a fluid, whether it be a liquid or an elastomer, an increase in viscosity takes place in the case of the liquid or of the modulus in the case of a polymer. This is generally designated as hydrodynamic effect. The viscosity or modulus increase due to filler addition in liquids and elastomers respectively due to hydrodynamic effect can be represented by the equations proposed by the Guth-Gold[102] and Smallwood[103].

Guth-Gold equation (Equation 1.3) for viscosity[102]

$$\eta = \eta_o \left(1+2.5\phi + 14.1\phi^2\right) \qquad \textbf{Eq.1.3}$$

where η and η_o are the viscosities of the filled and unfilled system, ϕ is the volume fraction of the filler.

Smallwood[103] showed that for an elastic material filled with rigid spherical particles the equation for modulus enhancement can be represented as in Equation 1. 4.

$$G = G_0\left(1+2.5\phi + 14.1\phi^2\right) \qquad \textbf{Eq.1.4}$$

where G and G_0 are the shear moduli of the filled and unfilled system respectively and ϕ is the volume fraction of the filler. The value of G_0 is obtained from equation 1.2. The shear modulus can also be replaced by tension elasticity modulus without much change of the equation.

For non spherical particles, Guth introduced a shape factor, f (the ratio of the longest dimension of the particle to the shortest) and proposed the following equation [104]

$$G = G_0 \left(1+ 0.67\, f\phi + 1.62\, f^2\phi^2 \right) \qquad \textbf{Eq. 1.5}$$

The equations were derived on the assumption that the medium wets the filler particles, but does not chemically react with the filler surface. The modulus as given in equation 1.4 and 1.5 is independent of applied strain.

c) *In-rubber structure*

The in-rubber structure can be understood as a combination of the structure of the filler in the in-rubber state and the extent of filler–polymer interaction. The in-rubber structure is, amongst others, a measure for the occluded rubber, which is shielded from deformation and therefore increases the effective filler content leading to a strain-independent contribution to the modulus. The filler-polymer interaction can be attributed to physical (Van der Waals) as well as chemical linkages or both. In the case of silica-coupling agent system, this interaction is formed by chemical linkages[105-108].

d) Filler-filler interaction

Elastic modulus of a filled rubber is strongly dependent on deformation and decreases substantially at higher strains ('**Payne effect**'). This is attributed to the presence and breakdown of the filler network during dynamic deformation. The sigmoidal decline of the storage modulus at zero amplitude (G_0') to a high amplitude plateau G_∞' was interpreted by Payne as due to the breakage of physical (London and Van der Waals) bonds between filler particles. It was also noted that the value G_0' is mostly recoverable upon return to smaller amplitudes and showed that the phenomenon is independent of the polymer, provided enough time is allowed for recovery. When using silica as a reinforcing filler, a high level of elastic modulus and the drop of elastic modulus at higher strain amplitudes prove the existence of a stable filler network formed by silica as is represented in Fig.1.2[101, 108-111].

A quantitative model of the Payne effect, based on filler agglomeration and deagglomeration was proposed by Kraus[112].

1.5.2 Physical and chemical interactions at the filler surface

Whether reinforcement requires the formation of chemisorptive or primary valence bonds, anchoring polymer chains to the filler surface is a subject of controversy. Some of the experimental evidences indicate that

1) Chemical bonding at the filler- rubber interface is not a necessary condition for reinforcement.
2) Chemical bonding leads to the unique combination of mechanical properties associated with carbon black reinforcement.

Studies with carbon black shows the existence of chemical bonds or chemisorptive linkages of higher energy than physical adsorption[3,113].

Graft formation of polymer with carbon black was reported, through reaction of the functional group of carbon black with rubber during processing and vulcanization[114]. Such reactions are chemisorption of olefin on carbon black at the vulcanization temperature[115], combining with shear induced polymeric free radicals generated during mixing[116] and by free radical inhibition through quinonic group of carbon black[117]. When carbon black is heat treated at 2700^0C or higher in an inert atmosphere, all surface functional groups are removed, but the morphology remains more or less the same. Heat treated black exhibits lower bound rubber, modulus and abrasion resistance, while keeping the tensile strength almost intact [118].

Colloidal silica is a good reinforcing agent, imparting high tensile strength and excellent resistance to tearing[25], however in comparison to carbon black, silica is deficient in modulus and resistance to abrasion. By the use of coupling agents with silica, performance enhancement closer to that with carbon black could be achieved. Esterification of silica can deactivate its surface, giving a stress-strain behaviour similar to graphitised carbon black[119].

The surface interaction between fillers and rubber molecules involves a range of bond energies from relatively weak Van der Waals force to very strong chemical bonds[120]. The number of each kind of interaction is difficult to characterize[121]. In all cases physical adsorption occurs to varying degrees depending on the particular surface and molecular segments. Evidence for chemical bonding at the interface is also conclusively found in certain systems[122]. The relative contributions of physical and chemical interactions to reinforcement, differ both with the nature of the filler and the elastomer. When physical interaction is high, such as that for carbon black in hydrocarbon rubbers, there is little contribution to reinforcement from chemical bonding, although this may contribute to other desirable properties. Chemical interaction improves wetting and adhesion, improves dispersion and prevents reflocculation of dispersed particles. Chemical interaction may result in actual bridging of the particle surface to the elastomeric network[123, 124].

Adsorption of polymer segments on the filler surface leads to some loss of mobility of the chains. Studies of proton magnetic resonance in carbon black- reinforced rubbers have shown that there is a loss in segmental mobility, but severe restriction of motion is confined to a layer of 5^0A thick at the surface ie., a distance of few carbon lengths along the polymer chain[125]. However, the chains of bound rubber may extent far into the polymer matrix where they freely intermix with unadsorbed rubber molecules. During vulcanization, they become part of the network and becomes undistinguishable from free rubber.

1.5.3 State of the filler in the rubber mix

When carbon black is mixed into rubber, the first step is the penetration of the rubber into the void space. If at this stage considerable rubber-filler interaction occurs, subsequent dispersion is rendered difficult, as bound rubber cements many primary aggregates together. For this reason low-structure, high surface area blacks are difficult to get dispersed uniformly, though incorporation takes place rapidly. High structure blacks are slowly incorporated but easily attain uniform dispersion.

1.5.4 State of rubber in the filled composite

Adsorption of polymer segments on the filler surface must lead to loss of mobility of the chains. Any loss of mobility will affect the physical properties of the rubber. Degree of immobilization is of fundamental importance. Severe restriction of motion is confined to a layer of about 5 A^0 (a few carbon bond length) thick at the surface[125]. For a black with about 80 m^2/g specific surface area, a surface coating of $5A^0$ thick roughly represents 2% of the total rubber. Mobility gradually increases outward from the filler surface so that a thicker layer estimated at 30 A^0 finds itself under the influence of the surface layer[126]. Thus the glass transition temperature (Tg) of carbon black filled rubbers is raised by about 2-3°C[110, 127]. Substantial immobilization, if occurs, would cause a much larger change[128]. Somewhat larger changes have been reported for polymers with polar groups along the chain, reinforced with inorganic fillers[126]. Immobilized rubber and bound rubber are different. The rubber that finds itself in the void space of the filler structure aggregates is called the occluded rubber[109,129].

1.5.5 Rubber- filler interaction

Bound rubber

It has been generally accepted that bound rubber provides a valuable information regarding rubber-filler interaction. Several reviews have been published on this topic[55,130-133].

The mechanism of formation of bound rubber is not very clear[134]. Whether bound rubber can be taken as a measure of the surface activity of filler is also not well established[55, 135, 136]. Free radical reaction between carbon black and rubber is proposed as a mechanism for chemisorptive adsorption[137]. Watson et.al[138,139] proposed free radical mechanism for bound rubber formation, based on the fact that common free radical scavengers like thiophenol can reduce bound rubber formation. However Donnet et.al could not find any correlation between free electron and reinforcement in carbon black filled natural rubber[140-142].

Oxygen containing functional groups on the carbon black surface lowers rubber-filler interaction for unsaturated rubbers[143]; Gessler[144] proposed a cationic interaction between polymer double bond and carbon black. Ban et al[145] attributed physical adsorption for bound rubber formation. Wolff et al [146] observed that, on high temperature extraction, the extent of insolubilized rubber was low and therefore concluded that the rubber-filler interaction involved in bound- rubber formation is essentially physical in nature. Gessler holds the view that carbon black aggregates breakdown on milling and the active filler surface thus formed will react with rubber chains which gets activated by mechanical breakdown[147].

Rubber -filler interaction also results in the formation of an immobilized layer or rubber shell around the filler. This arises due to the restriction of the molecular mobility of the rubber in the vicinity of the filler surface. Though bound rubber and rubber shell arise from rubber-filler interaction, basic concept for the two are different. Bound rubber refers to the whole molecule in which one or more segments are in contact with filler, whereas in shell rubber, segments rather than molecules are affected by the force field of the filler. Westlinning[148] and Schoon et.al[149] reported the formation of about 3-5 nm of rubber layer around the filler surface. Smit et al[150] proposed a shell thickness of 2-5 nm on carbon black surface. The studies were elucidated further by NMR[151], DSC and DMTA[152].

1.5.6 Effect of filler on processability of rubber compounds

The flow characteristics of filled rubber compounds is of prime technological importance. The melt viscosity of rubber mixes increases with decreasing filler particle size and increasing structure. The viscosity of the unfilled polymers is strongly dependant on their molecular weight distribution and chain branching[153]. The enhancement in viscosity on incorporation of carbon black in rubber is attributed to occlusion of rubber within and between the carbon aggregates[154] and immobilization of a layer of elastomer at the filler surface[155]. Changes in the viscosity of rubbers with filler addition for a series of SBR and NR compounds, have been attributed to entanglement or bound rubber formation[156,157].

Physical properties of silicas were reported to affect the viscosity of rubbers. Hewitt reported that compound viscosity is directly related to the surface area of silica[158]. Highly developed filler networks of silicas can give rise to compounds of high viscosities[159]. Silicas and silicates generally cause higher Mooney viscosity in rubber mixes than other fillers of comparable particle size. The difference between types of filler became less pronounced as the average filler particle size is increased[160]. At about 20 nm size silica produces significantly higher viscosity than carbon black of comparable size[161]. However, at about 40 nm size silica and black filled compounds exhibit almost similar viscosity[160].

Viscosity modification studies of rubbers filled with smaller particle size silica was reported by Dunnom[162]. Use of silane coupling agent in silica filled rubbers is an effective means of reducing viscosity of the compounds[163]. Generally, with rare exceptions, viscosity of high molecular weight rubbers is shear rate dependent. The increase in viscosity caused by the fillers is more prominent at low shear rates. The viscosity of filled rubber compounds at very low shear rates becomes effectively infinite. This phenomenon is due to the secondary filler agglomeration, resulting in the formation of a weak filler network held together by Van der Waals forces. At higher shear rates, the difference between types of fillers get reduced[164-166], so that the difference between silica and carbon black get reduced at high shear rates.

1.5.7 Effect of filler on cure behavior and crosslink formation

Fillers (surface groups on fillers) generally tend to accelerate or retard cure. Carbon black can influence the total concentration of chemical crosslinks and the proportion of mono, di and polysulphidic crosslinks and these factors, in turn, can affect the vulcanizate properties[167,168]. Janacek[169] has reported that for a carbon black filled natural rubber system, crosslink density increased proportionally with the concentration of the carbon black by volume. Studies by Cotton[170] revealed that the chemistry of carbon black surface plays an important part in the preceding steps of vulcanization and the rate of vulcanization. Maximum torque in a rheograph (M_H) can indicate the characteristic effects of the filler.

Bhowmick et al[171] have studied the effect of addition of HAF black on the kinetics of vulcanization and the changes in the network structure of natural rubber cured with DTDM. Addition of HAF black enhanced the polysulphidic crosslinks as well as total crosslinks. Bhowmick et al[171] and Porter[172] have reported that HAF black influenced the chemistry of sulphuration of sulphur cure systems of NR. The observation of Bhowmick et al[171] indicate that filler surface may catalyze the sulphuration process and the observed increase in crosslink density may be due to increase in covalent crosslinks and merely not due to polymer-filler attachment. Duchacek[173] reported that HAF black does not alter the mechanism of TMTD accelerated sulphur vulcanization of NR.

Silica / silicates contain substantial amounts of combined oxygen in the form of silanol (Si-OH) and siloxane (Si–O–Si) which retard sulphur vulcanization [174]. The silanol groups can interact with elastomers, curatives and can also form hydrogen bonding. Effect of these interactions can affect compound properties such as viscosity, scorch time, cure rate and cure efficiency and also the vulcanizate properties. Retardation of vulcanization was earlier attributed to the adsorption of curatives by the silica surface[175]. Later studies claim that retardation is due to a deactivation mechanism involving interaction of the filler with the zinc-accelerator- sulphur complex[43]. Addition of activators such as triethanolamine (TEA), diethylene glycol (DEG) and polyethylene glycol are used to reduce the adverse effects of silanol groups[174].

1.5.8 Effect of filler on vulcanizate properties

1.5.8.1 Failure properties

Strong rubber-filler bonding improves modulus at high elongation, tensile strength, tear strength and hysteresis. Strong rubber-filler bonding permits bridging of infinite number of rubber chain through carbon black and is the main reason for improvement of the physical properties of vulcanizates. Development of high strength is on account of the ability of the rubber to dissipate strain energy near the tip of the growing crack by viscoelastic processes. Addition of a filler introduces additional mechanisms by which strain energy is dissipated. Inclusion of particles in a viscoelastic medium increases hysteresis[176]. Loss of segmental mobility in the polymer matrix resulting from interaction with the filler will increase hysteresis. Motions of filler particles, chain slippage or breakage and dewetting at high strains can also enhance hysteresis. The dispersed filler particles in addition to providing energy dissipation, also serve to deflect or arrest growing cracks, thereby delaying the onset of catastrophic failure[3].

The increase in tearing energy for carbon black filled rubbers is due to the increases in the threshold tearing energy (T_o), which may be due to micro deviations in tear[177-179]. Tear deviation in carbon black reinforced systems may be due to creation of barriers in the tear path.

Tensile strength has a positive dependence on surface area of carbon black. The effect of structure and loading have been studied by Kraus[180]. With reinforcing blacks, in tensile strength measurements the effective loading of filler, that is the carbon black plus the occluded rubber is taken in to account. In accordance with Kraus's observation, at a fixed loading a low structure black gives a higher tensile strength and higher elongation than a high structure black of the same surface area[181], as at this loading low-structure blacks are near the maximum of both properties and high-structure blacks are to the right of the maximum. The loading at which the tensile strength is a maximum, increases somewhat with increasing particle size[3], likely to be due to the lower effectiveness of the occluded rubber.

The increase in ultimate properties with increased effective loading up to the maximum is likely to be due to increased tear deviation. To be effective, tear deviation must take place during the initial stages of the growth of the random flaws[3]. Cut growth and fatigue are two important failure properties which occur on cyclic deformation. The fatigue life increases with structure level and decreases with specific surface area[182].

Natural rubber and other strain crystallizing elastomers display more complex behavior in their response to filler reinforcement[183]. When crystallinity develops as a result of deformation, the crystallites assume the role of reinforcing fillers and the gum vulcanizates exhibit good tensile strength. In real practical applications, such as in tires the strain rate and temperature encountered are such that crystallization cannot occur. Hence, reinforcement is important in NR just like that is required for SBR or SBR-BR blends[3].

Wear or abrasion are important properties which gets modified by reinforcement. Wear rate is related to filler surface area and structure. Colloidal silicas, even when compounded with bonding agents do not equal carbon black in wear reinforcing capability[184]. For off the road tires, blends of silica and carbon black provide improved cut growth resistance[185].

1.5.8.2 Dynamic mechanical properties

a) Dynamic mechanical behavior of rubbers

Rubber is a viscoelastic material: as it deforms, a fraction of the energy is stored elastically, and the remainder is dissipated as heat in a hysteric manner. This behavior can be mathematically expressed as given below.

When a linear viscoelastic material is subjected to a sinusoidal shear deformation γ of angular frequency ω, can be related by equation,

$$\gamma(t) = \gamma o \sin(\omega t) \qquad \textbf{Eq. 1.6}$$

Where γo is maximum strain and 't' is time; the shear stress response σ is also sinusoidal, but out of phase with the strain

$$\sigma(t) = \sigma o \sin(\omega t+\delta) \qquad \textbf{Eq.1.7}$$

where σo is the maximum stress. The strain lags behind the stress by a phase angle δ. A vector method of representing the dependence of γ and σ on ωt is shown in Fig.1.3.

Equation for shear stress can be written as

$$\sigma(t) = (\sigma o \cos\delta)\sin\omega t + (\sigma o \sin\delta)\cos\omega t. \qquad \textbf{Eq 1.8}$$

Shear stress consists of two components ; one in phase with the strain ($\sigma o \cos\delta$); the other 90° out of phase ($\sigma o \sin\delta$).

The relation between stress and strain can be put into a form

$$\sigma(t) = \gamma o\, [G' \sin\omega t + G'' \cos\omega t] \qquad \textbf{Eq. 1.9}$$

in which

$$G' = \sigma o/\gamma o\, (\cos\delta) \qquad \textbf{Eq. 1.10}$$

$$G'' = \sigma o\, /\gamma o\, (\sin\delta) \qquad \textbf{Eq. 1.11}$$

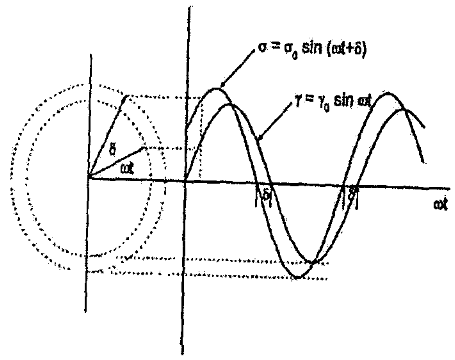


Fig.1. 3 Plot of sinusoidal deformation – viscoelastic material

The component of the stress G'γo is in phase with the oscillatory strain; the component G''γo is 90° out of phase.

A complex representation of the shear modulus (G*) can be written as follows.

$$G^* = G' + iG'' \qquad \textbf{Eq.1.12}$$

where G' is called the real part of the shear modulus and G'' the imaginary part or loss modulus. Thus when a rubber sample is subjected to dynamic mechanical analysis, the G' (storage modulus) is the measure of energy (elastic) stored and recovered in cyclic deformation, G'' (loss modulus) is a measure of energy dissipated as heat. The tangent of the phase angle (loss tangent) is the ratio of G'' to G',

$$\tan \delta = G''/G' \qquad \textbf{Eq. 1.13}$$

G' and G'' are frequency and temperature dependent. A typical frequency-dependence of the dynamic moduli (storage, G' and loss, G'') for a viscoelastic material like rubber is shown in Fig. 1.4. The variations of the modulus with frequency can be

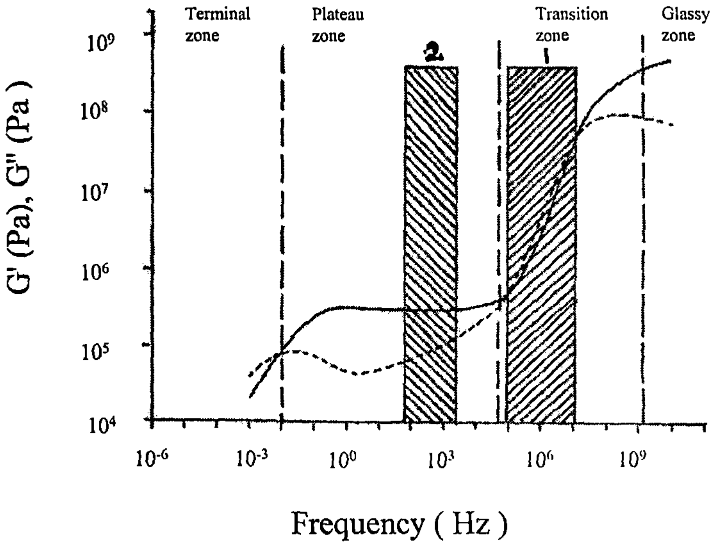


Fig. 1. 4 Typical variation of G' (——) and G'' (- - - -) with frequency of unvulcanized viscoelastic material

explained on the basis of segmental and chain movements in the rubber molecule. At low frequencies of deformation, all changes of the molecular conformation are possible with in one cycle of deformation and there is almost no loss of energy. This part of the frequency- modulus plot is termed as the 'terminal zone'. The next zone corresponding to the variation of the modulus with immediate higher frequency is the rubber zone (plateau zone). At this zone with one cycle of deformation the entanglements cannot straighten out and therefore acts as 'time dependent' cross links. G' reaches a plateau, which can be related to the entanglement density. All other movements are still possible and elastic behaviour takes place at these frequencies. In the rubber plateau region there is a minimum in G". After the rubber plateau, at still higher frequencies there is another transition called glass transition where both G' and G" are increasing. Chain segments between the entanglements are not able to follow the applied deformation any further. This causes another phase shift resulting in the glassy zone. The frequency is so high that only local chain movements can occur. The value of G' equals the glass modulus, while G" decreases slightly. At every transition zone energy is dissipated which causes a peak in G".[186]

b) Dynamic mechanical properties of filled rubbers

Enhancement of mechanical properties due to the presence of a filler in rubber compounds can be attributed due to various factors such as polymer network, hydrodynamic effect of filler in rubber, in-rubber structure and filler-filler interaction. The ultimate properties exhibited by the reinforced rubber hence will be resultant of the combined effects of these aspects. The extent of these effects vary from filler to filler and their characteristics.

Dynamic mechanical properties of carbon black filled rubbers has been reported by many researchers[187-190] and reviwed by Medalia[110]. The general observations made from the earlier studies are that the incorporation of carbon black in different types of rubbers results in an increase in storage and loss modului, G' and G" and an increase in hysteresis, tan δ . Dynamic storage modulus of filled rubbers is strain dependent. This is due to filler networking. At a lower strain, filler secondary agglomeration remains intact and the large modulus is caused by the elastic response of this network[191]. As the amplitude of deformation is increased, disruption of the agglomeration network causes the G' to fall ("Payne effect") until a new plateau value is approached, where the network gets disrupted. A sigmoidal drop of modulus occur with strain as is shown in Fig. 1.2. The second plateau value (modulus) has been explained satisfactorily with Equation 1.14 with a correction of filler concentration for the occluded rubber[192]. Dynamic modulus at moderate strain amplitude is a function of primary filler structure. Modulus of the secondary agglomeration network must increase with density of filler- to- filler contacts.

Silica filled rubber exhibit specific differences in its dynamic mechanical properties with that of carbon black, because of the specific characteristics of silica. Blume has reported that the amount of silanol groups on the silica surface has an influence on the dynamic stiffness, G^* at 60 °C [23]. Silanol groups will also leads to filler network. Silica filled rubber exhibits larger Payne effect or strain dependent drop in modulus than the carbon black filled.

The effect of temperature dependence of tan δ for reinforced rubber compounds is the result of the characteristics of reinforcing fillers to form a filler network. A comparison of the tan δ values at different temperatures for silica filled and carbon black filled rubber is given in Fig.1.5 [193-195] . Silica filled exhibited lower tan δ at lower

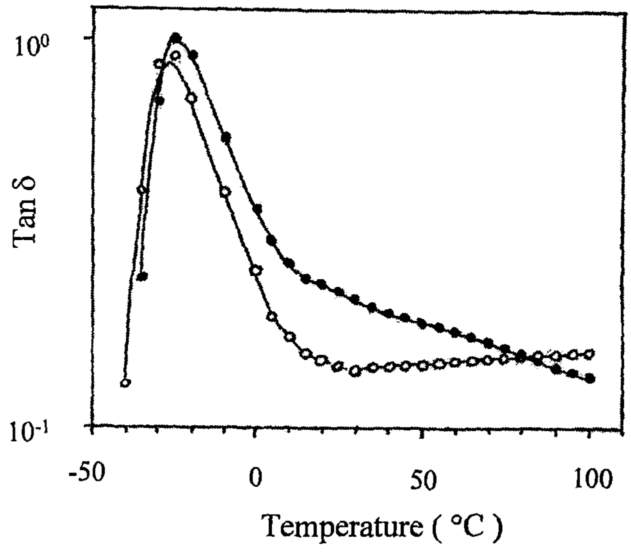


Fig. 1. 5 Typical variations of tan δ with temperature for a silica (o) and carbon black (•) filled rubber

temperatures. In the rubbery state at temperatures beyond 20 °C, the tan δ and hysteresis is still higher for carbon black. Replacement of carbon black with silica in tyre compounds, therefore results in a decrease of tan δ at higher temperatures and thereby results in a reduction of rolling resistance. The use of silica also does not adversely affect the ice and wet grip, as the tan δ values at very low temperatures of both are comparable [196,197].

By increasing the average distance of separation of the aggregates from each other the value of ΔG' (drop in modulus with strain) and tan δ (thus hysteresis) can be reduced. This can be achieved by prolonged or a two stage mixing technique, or by use of coupling agents as is often done with silicas and mineral fillers. Heat treatment of the mix can also be used to promote carbon black-rubber interaction (eg.butyl rubber). Special varieties of SBR and BR with molecules terminated by reactive end groups have also been found to increase the distance between aggregates[198,199]. If rubber compounds are compared at the same strain, their hysteresis is proportional to their values of G" or G' tan δ. If they are compared at the same stress, the hysteresis is proportional to tan δ/G', whereas at constant energy input, hysteresis is proportional to tan δ itself. G' increases with increasing structure, while tan δ remains constant.

c) Relevance of dynamic mechanical analysis in tyre compounds

Dynamic mechanical properties of a rubber compound could be used for predicting its performance properties in tyres. Abrasion resistance, low temperature flexibility, wet traction, rolling resistance and heat build-up are some of the important properties most relevant for tyre tread compounds. Rolling resistance, is predominantly related to the loss tangent of the bulk polymer at comparatively low frequencies in the plateau region of the storage modulus (region 2 in Fig.1.4). This low frequency region is in the order of the angular velocity of the rolling tyres. Tan δ in the glass transition region can give an indication of the wet skid resistance[200]. Higher the Tg, higher the wet

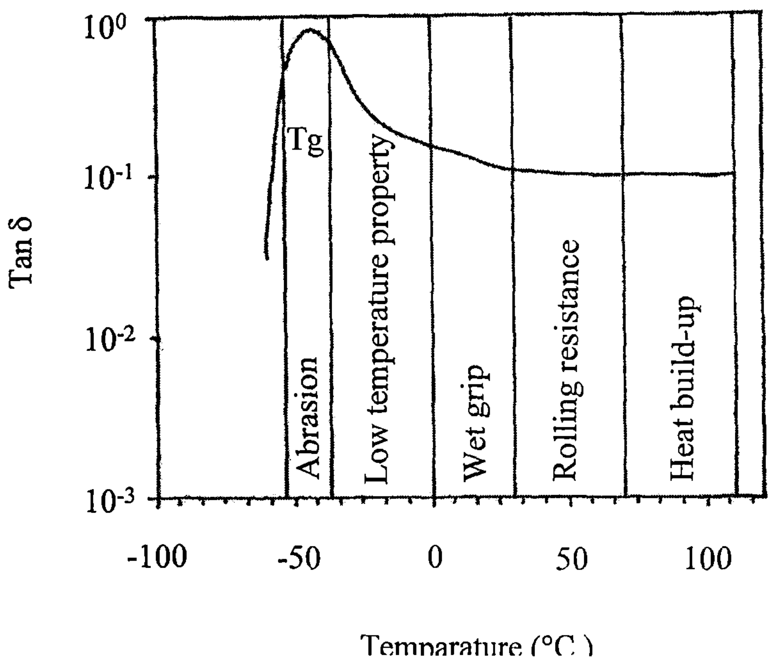


Fig. 1. 6 Typical tan δ curve with temperature for a vulcanized tyre tread compound

skid resistance [201]. Nordsiek related the tan δ values at various temperature to a number of tyre tread properties as given in Fig.1.6 [202]. Abrasion resistance also shows a relation to the glass transition temperature. Temperatures of about +30 to +70° C is the usual running temperature of a tyre. Under these temperature conditions the tan δ essentially determines the degree of rolling resistance. Tan δ above 70° C indicates the heat build-up. Thus the choice of the rubber with optimum glass transition temperature (Tg) is an important factor in achieving a compromise between many tyre requirements.[202,203]

d) Large deformation behaviour of rubber

For viscoelastic materials, stress is not only a function of strain, but also of time. Stress relaxation occurs throughout the experiment. For different strain rates, the stresses attained at any given extension will be higher for higher strain rate. Hysteresis, which is related to stress softening, is more pronounced with filled rubbers. The initial slope of the stress-stain curve of a reinforced vulcanizate will be higher than that of the corresponding gum. Once the effects of secondary agglomeration are overcome, several mechanisms remain which will keep the stress rising faster than the unfilled. Various mechanisms will contribute to this, of which 'strain amplification' is an important phenomenon. Rigid filler do not share in the deformation[204] and hence inclusion of a rigid filler in a soft matrix will cause the average local strain in the matrix to exceed the macroscopic strain. Thus the rubber in the filled vulcanizate finds itself more highly strained and responds with a higher stress. The quantity in parenthesis in the equation 1.4 is in fact a strain amplification factor[205] which in turn depends on the filler concentration and structure. At higher strains occluded rubber tends to be pulled out of the interstices of the aggregate, diminishing the strain amplification effect. These process causes high elongation at break[206].

Consideration of rubber on a molecular scale, provides insight into the stress-raising mechanisms. The retractive force 'F' of a rubbery network is proportional to the network chain density, v

$F \alpha v RT$

Adsorption of polymer segments at several sites of a filler particle effectively introduces multifunctional crosslinks into the system, thus enhancing the network chain density [207].

Several mechanisms have been proposed for stress relaxation of a filled system. On stretching a filled vulcanizate some of the polymer chains linked to the filler particles will get broken thus giving rise to stress-relaxation[208]. Also at large strains there occurs "dewetting" from the filler surface, which also causes stress relaxation[209]. Dewetting is delayed to higher elongations as specific surface area and structure of carbon black increases. Hess et al[209] observed dewetting stresses of 10 MPa for a furnace black of surface area 30 m^2/g, while only 1-2 Mpa for graphitised black. Molecular slippage also causes stress relaxation[206].

Stress softening[210] is another important property associated with filler reinforcement. When a filled rubber is extended to a certain strain, then returned to zero strain and stretched again, the second stress-strain curve lies below the first one, which is resultant of a stress-softening. This phenomenon is known as '**Mullins effect**'. Several mechanisms are proposed for stress softening, viz; incomplete elastic recovery[210], progressive breaking or detachment of network chains attached to the filler particles [207] and chain slippage of attached polymer segments along the surface[206] would have a similar effect.

With carbon black and silicas, the contribution of the filler to the modulus can be described by equation 1. 4, ($E = E_0 (1 + 2.5\phi + 14.1\phi^2)$), in which φ is replaced by "$f\phi$"

where “f” is an experimentally determined function of strain, temperature and filler surface activity[211]. The stiffness of rubber vulcanizates is usually expressed as modulus at 300% extension (σ_{300}), the strain in the region where secondary agglomeration effects have almost disappeared and dewetting has not initiated.

1.5.8.3 Swelling behavior

Uncrosslinked rubber gets dissolved in a good solvent, but a vulcanized or cross-linked sample can only swell. Solvent swelling of rubber is affected by incorporation of filler. In the case of a reinforcing filler, strong rubber- filler interaction will have some effect on the apparent crosslink density of the system. Ratio of the restriction of swelling of the filled rubber vulcanizate to that of the gum rubber is used as a means for evaluating the reinforcing ability of a filler in rubber. Kraus[212] developed the following expression relating volume fraction of filled rubber in the swollen gel, Vr_f and volume fraction of gum or unfilled system in swollen gel, Vr_0 as,

$$\frac{Vr_0}{Vr_f} = 1 - \frac{m\phi}{1-\phi} \qquad \textbf{Eq.1.15}$$

where m = 3C (1-Vr_0)+ Vr_0 –1, ϕ is the volume fraction of the filler and ‘C’ the characteristic parameter of the filler related to the rubber –filler interaction [213].

Cunneen-Russell equation (Eq.1.16), which is based on vulcanizate swelling parameters, is also used for reinforcement characterization [214].

$$\mathbf{Vr_0/Vr_f = ae^{-z} + b} \qquad \textbf{Eq.1.16}$$

where Vr_0 and Vr_f are the volume fractions of the rubber in the unfilled and filled vulcanizates respectively after swelling in a solvent to equilibrium, z is the weight fraction of filler in the polymer and a and b are two constants which depend on the filler activity. High value of 'a' and low value of 'b' indicates polymer-filler attachment. $Vr_0/Vr_f < 1$ indicates reinforcement.

Paauw et al[215] and Gajewski et al[216] reported that chemically modified carbon black increases the apparent crosslink density of the filled rubber vulcanizates. The strong secondary inter-aggregates formed in the case of silica filled vulcanizates play an important role in reducing solvent swelling[217].

1.6 Silica reinforcement of rubbers

Maximum reinforcement effect of a filler can be achieved through good dispersion and better chemical or physical interaction with the rubber.

1.6.1 Silica as a filler in rubber – compounding aspects

Compounding with precipitated silica is quite different from compounding with carbon black; silica has a more reactive surface than carbon black. Carbon black has good affinity with non-polar rubbers, while silica being hydrophilic is incompatible. Silica-to-silica interaction is high, resulting in the formation of large aggregates ultimately impeding the compound flow character. In the case of both carbon black and silica with lower surface area (bigger particle size), viscosity is lower and dynamic properties are better[218]. Fine particle silica though could reinforce rubber, silica filled compounds exhibits higher viscosity and slower cure.

Some softeners could effectively reduce the viscosity. Natural softeners of vegetable origin, such as tall oil and hydrogenated rosin are effective in reducing viscosity, though its mechanism is not fully understood. Petroleum based aromatic resins are effective in giving smooth extrusion, better tensile strength, tear strength and abrasion resistance. Considerable reduction in viscosity is obtained only with additives that de-agglomerate the silica. Additives such as soluble zinc compounds (eg. zinc octoate), hexamethylene tetramine (HMT), magnesium Oxide etc. are reported to reduce compound stiffness. Activators such as diethylene glycol (DEG), polyethylene glycol(PEG) and triethanolamine(TEA) are used in compounding, which reduces the cure time, compression set and heat build-up and enhances the tensile strength.

Use of silane coupling agents in silica compounding is an important development. Coupling agent bridges the silica filler and rubber, thus enhancing the rubber- filler interaction. Silane coupling agent in silica filled rubbers, could reduce the compound viscosity and enhance the modulus, tensile strength and abrasion resistance.

1.6.2 Silane modification in silica filled rubbers

Organofunctional silanes are being widely used to enhance the bonding properties of glass fibers with various polymers and also to modify siliceous filler surface in rubber and other hydrocarbon polymers. Silane modified silica in elastomers can produce considerable improvement in its failure poperties. Use of silane coupling agent as a silica surface modifier has been reviewed by Wagner[25] and Plueddeman[219]. Hewitt[220] describes the reinforcement modification achieved with the use of silane coupling agent in SBR. In NR, with silica/silane combination, properties equivalent to that of carbon black of similar surface area as that of silica could be achieved[221]. By silane modification viscosity reduction of the compound and improvement in tensile strength, modulus, set, heat build-up and abrasion resistance could be achieved[222-224]. Improved filler dispersion occurs on silane modification. Many researchers have suggested that improved dispersion results in reduced viscosity[100, 225-227] of rubber matrix. Dannenberg and Cotton[228] reviewed the mechanism for the improved silica reinforcement with silanes and suggested a molecular slippage mechanism. Harwood et al[229] proposed a mechanism based on shell rubber which could account for most of the reinforcement phenomena.

The silanes which are effective in enhancing the reinforcement have functional groups which can chemically react with both silica and rubber, thus forming a bridge between the two. Many researchers have made studies on the reaction between silanes and silica filler [230-232]. Mercaptan, vinyl and methacrylic based silanes were found to be effective in crosslinking with rubber. Wagner reported that silanes are also effective in the case of carbon black filled matrices [225]. Xue et.al have made studies on the kinetics of the reaction between epoxy group of an epoxy based silane with silanol and alcoholic groups[233]. Blackshaw have reported that silane can also function as a vulcanizing agent[234]. Silica filled tyre compounds modified with TESPT exhibited improved technological properties [235].

Of the several bifunctional silane coupling agents, a few have attained commercial significance in the rubber industry. TESPT was introduced as a coupling

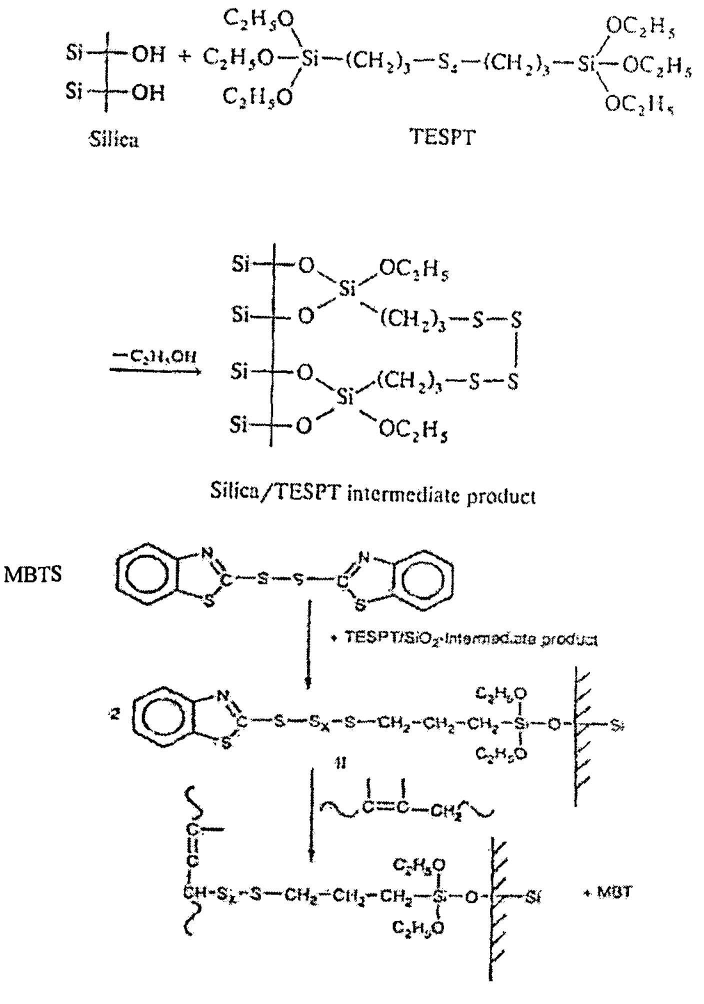


Fig. 1. 7 Reaction mechanism of TESPT with silica and rubber

agent in 1970's. The coupling agent TESPT has been covered more extensively in the literature than the other silane coupling agents [3].

The mechanism of silane coupling agent reinforcement comprises two phases.

(i) Silanization reacion in which the coupling agent reacts with silica and

(ii) Formation of crosslinks between the modified silica and the polymer.

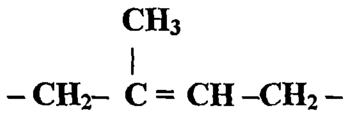
Probable reaction mechanism of TESPT with silanol groups of silica and rubber through accelarator such as mercaptobenzthiazole disulphide (MBTS) is given in Fig.1.7. Silanization of the silica surface can occur quite readily, though with TESPT systems, the reaction is generally carried out *in- situ* between 150 and 160°C in an internal mixer. Though excess silanol groups are present on the silica surface and reaction rates are fast, high temperature is generally used because of the steric hindrance around the silyl propyl group in TESPT.

1.6.3 Silica reinforcement of non-polar rubbers

Carbon black is the ideal filler for reinforcing hydrocarbon rubbers. Since both are hydrophobic substances, mixing and reinforcement problems do not usually arise when those two are mixed. Precipitated silica, which is of mineral origin, is one of the most promising alternatives to carbon black. However, due to the difference in surface energy, when silica is mixed with the commonly used non-polar olefinic hydrocarbon rubbers, occurrence of filler-filler interaction leads to mixing and reinforcement problems[236]. For overcoming the technical difficulties associated with silica reinforcement of hydrocarbon rubbers bifunctional organosilanes are generally used.

1.6.3.1 Natural rubber and its reinforcement

Cis-polyisoprene, the hydrocarbon component of NR, the structure of which is given below, is fairly wide spread in nature, having been identified in about 2000 plant species [237].



$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-$$

Only the species *Hevea brasiliensis* is of any commercial significance. From the tree the rubber is collected in the form of latex by tapping. Rubber is separated from the latex by coagulation usually by acidification. The resultant coagulum is then processed into different marketable forms of NR such as sheet rubber, technically specified rubber and crepe rubber. Most of the natural rubber based products are made from any of these forms. Also certain products are made from concentrated latex [238].

The rubber separated from latex contains more than 90% of the hydrocarbon, cis-1,4 – polyisoprene in admixture with naturally occurring resins, proteins, sugars etc. The polyisoprene is having a broader molecular weight distribution with a number average molecular weight of about $5x10^5$. [239, 240]

Most of the latex rubber products can be made from NR latex including medical products. Apart from the conventional rubber products made from dry natural rubber, it finds a few specialized applications. Natural rubber is a versatile and adaptable material which has been successfully used for transport and engineering applications such automobile tyres, aero tyres, off-shore and aerospace industries, civil engineering, railways, vibration engineering etc. Though natural rubber exhibits very good strength even without reinforcement by filler, excepting a few latex products, most of the rubber products require reinforcement [241]. The discovery of reinforcement of natural rubber by particulate fillers, is almost a century old.

1.6.4 Silica reinforcement of polar elastomers

Generally, silicas produce relatively greater reinforcement in polar elastomers such as NBR and CR than in non-polar elastomers such SBR and NR[3]. Reinforcement studies of silica in acrylonitrile butadiene rubber of varying acrylonitrile content (NBR) was made by Tan et al [242] using a series of silica in comparison with carbon black. The study showed that the changes in viscoelastic properties of the silica-filled compounds can be attributed to improved polymer-filler interaction relative to those of the carbon black filled ones.

Studies conducted by Wang et al[42] using model compounds revealed that aromatic hydrocarbons exhibit stronger interaction with silica surface than olefins, which may be attributed to the high electron density associated with the conjugated π bond system. They have also found that nitriles exhibited the highest interaction with silica probably through the hydrogen bond interaction between the –CN group and silanol groups. Based on their study they have proposed the order of interaction of elastomers with silica as NBR> SBR> NR ≥ BR> High vinyl-BR> EPR> IIR. Thus as the polarity of the elastomer increases the silica-polymer interaction increases and consequently the filler networking get reduced.

Reinforcement behavior of fumed silica on the reinforcement properties of silicone rubber was studied by Cochrane et al [243]. In the silica filled silicone rubbers both silica-silica and silica-polymer-silica networking can occur. Increasing the silica loading, surface area and structure increases the level of interactions and hence also the networking. Wang et al [244] have studied the reinforcement characteristics of *in-situ* precipitated silica in polydimethyl siloxane (PDMS) elastomers and found that good mechanical properties could be achieved.

1.6.4.1 Acrylonitrile – butadiene rubbers –relevance of reinforcement

Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene. Konrade and co-workers [245] first prepared the polymer. It, when vulcanized, had excellent resistance to oil and petrol. Its commercial production in Germany started in 1937.

Nitrile rubbers are manufactured by emulsion co-polymerisation of butadiene with acrylonitrile. Commercially available nitrile rubbers differ from one another in three respects; acrylonitrile content, polymerization temperature and Mooney viscosity.

Acrylonitrile content has the most profound effect on the properties of a vulcanized nitrile rubber, most important of which is the oil and fuel resistance. NBR possesses generally better heat resistance than polychloroprene rubber. But like NR its ozone resistance is poor. Nitrile rubbers, suitably compounded, have a service temperature range of –50 to +120^{0}C.

Unfilled nirile rubber vulcanisates have very low tensile strength. Carbon black and non-black fillers are used for reinforcement. Silicas or clays are used where non-black compounds are required, but compression set performance is not so good as a black reinforced compound, unless silane-treated silicas are used.

1.7 Epoxidised natural rubber

1.7.1 Preparation and properties

Epoxidised natural rubber (ENR) is a chemically modified form of natural rubber(NR). In the 1930's German chemists have prepared rubbers with epoxide groups, by reacting peracids with natural rubber in solution. The reaction resulted in a range of secondary products caused by epoxide ring opening reactions. Gelling et al [246, 247] later optimized the conditions for the preparation of ENR with different levels of epoxidation and to avoid ring opened products. ENR is industrially produced through the latex stage epoxidation of natural rubber using performic acid generated *in situ* from formic acid-hydrogen peroxide combination [248]. Epoxidised natural rubber has improved oil resistance, gas impermeability and higher damping over NR. In addition to this ENR possesses strain crystallization [247] behavior and hence necessary tensile strength required for many applications. Commercial production of ENR started in Malaysia in 1987. Initially it was thought that ENR, due to its improved oil resistance and air impermeability, could compete with synthetic rubbers such as nitrile, butyl and polychloroprene. However, in reality it could not penetrate much into those areas. Other applications proposed are in vibration damping and in adhesives.

1.7.2 Silica reinforcement of ENR

An important feature imparted to NR by epoxidation is inherent reinforcement with silica even without coupling agent. It has been reported that both 25 and 50 mol percent epoxidised natural rubber exhibit the same properties, when reinforced with silica as with a highly reinforcing black [249]. A comparison of properties of the black and silica reinforced ENR vulcanizates is given in Table 1.5.

Table : 1.5 Comparison of Black and Silica- Reinforced ENR Vulcanizates

	ENR -25		ENR -50	
	Black*	**Silica***	**Black***	**Silica***
Hardness, IRHD	69	67	73	68
Modulus at 300%, Mpa	12.4	12.8	13.5	12.6
Tensile strength, MPa	25.4	21.0	24.5	22.4
Elongation at break, Mpa	435	405	500	435
DIN abrasion loss, mm^3	272	250	278	289
Goodrich heat buildup from 100^0C, ^0C	7	7	23	19

* 50 phr black (N330) or 50 phr silica (HiSil 233).

ENR based tread compounds when reinforced with silica have improved wet grip and reduced rolling resistance, a combination of properties not observed in other general purpose rubbers.

1.7.3 Blending of ENR with other elastomers

Blending or mixing of elastomers is generally undertaken for three main reasons; improvement of the technical properties of the base elastomer, achievement of better processing behavior and lowering of compound cost. Elastomer blends are one class of composite materials which are made by macroscale mixing of high molecular weight elastomers. Unlike many organic liquids, which are fully or partially miscible with each other at room temperature, polymers by virtue of their chain length, are not easily miscible. Walters et.al [250] first demonstrated that elastomer blends are never truly homogenous and showed discrete areas of each elastomer varying in size from 0.5µm upward, depending on mixing methods, elastomer viscosity etc.

The most widely used method for preparing elastomer blends in industrial operations is mechanical mixing. It was realised that [251] although two high molecular weight polymers may be mutually insoluble, blends can be made with macroscopic homogeneity and useful properties, provided that mechanical mixing is sufficiently intense and that the viscosities after mixing are sufficiently high to prevent gross phase separation. While blending of elastomers it is desirable that the components have similar viscosities for ease of dispersion.

The mutual solution of two materials demands that the free energy of mixing be negative, a situation brought about by exothermic mixing and/or a large entropy of mixing. The mixing of polymers is in general endothermic [252]. Thus for chemically dissimilar polymers, incompatibility is the rule.

Important tools being used for elastomer blend characterisation are microscopy (optical, electron, atomic force), thermal and thermo mechanical devices such as differential scanning calorimetry and dynamic mechanical analysis and spectroscopy (IR, NMR).

Other important aspects determining thermoset elastomer blend properties are curative diffusion [253] and filler migration [254] between component phases. Maiti et. al. [255] have reported on silica distribution studies in NR/ENR blends.

Blending of ENR with rubbers for achieving specific requirements such as with NR for improved adhesion [256], for air impermeability [257, 258], in elastic garments for oil resistance [259] and in tyre tread compounds for improved rolling resistance and wet grip [260] are reported.

1.8 Carbon black and silica / silane in the tyre industry

The general concept of "reinforcement with carbon black" is well accepted by the rubber and especially the tyre industry. The newer tailor-made carbon blacks with wide variations in surface area, surface energy and structure can be produced using the furnace production process. Due to its performance, flexibility and cost carbon black has been the dominating filler in the tyre industry. This situation began to change with the introduction of "green tyre" or an eco-friendly tyre. Carbon black offers good abrasion resistance to tyres whereas silica offers better rolling resistance and wet grip. Development of highly dispersible (HD) silica is an advancement in silica production technology, which may lead to its wider use in tyre industry [261]

The most important requirements of high performance tyres are lower rolling resistance, less tread wear and better wet grip. These properties are popularly represented with a 'Magic triangle'. Fig.1.8 gives a pictorial representation of the same for the performance comparison of ASTM carbon black and HD-silica in tyre compounds.

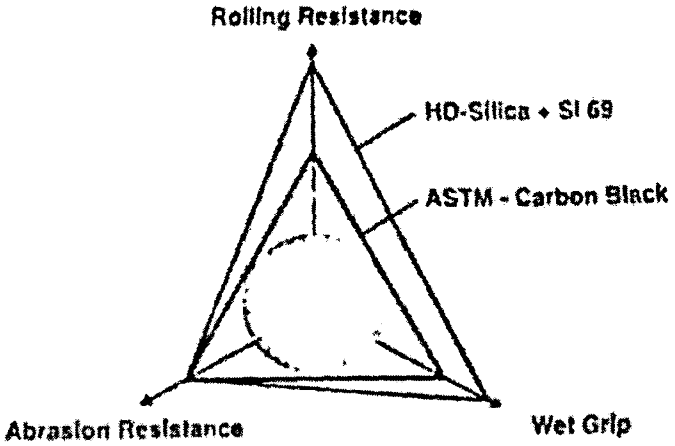


Fig. 1. 8 Magic Triangle – comparison of carbon black and silane modified HD – Silica

However, use of silica / silane by the tire industry though is growing, still have many problems which need to be overcome. Some important limitations are given below.

- Difficult processing
- Poor filler dispersion
- Longer vulcanization time
- Lower abrasion resistance
- Static electricity build-up
- High cost of silane

1.9 Carbon-silica dual phase filler for tyre industry

An ideal filler for tyre tread compounds are those which possess high polymer-filler and low filler-filler interactions. The former ensures higher abrasion resistance and the latter is necessary for lower hysteresis or lower rolling resistance. Based on this objective a new class of filler material 'carbon-silica dual phase (CSDP)' filler has been commercialized under the trade name "ECOBLACK" which claims best balance of these properties. These fillers are produced using a special co-fuming technology developed by Cabot Corporation. Instead of containing the typical 90-99 % elemental carbon as in traditional carbon black, the new filler consists of silica phase finely distributed in the carbon phase(about 5% silicon). The main features claimed for the new material are high polymer-filler and low filler-filler interactions .[262, 263]

1.10 Objective and scope of the present work

Annual global industrial rubber consumption, including both natural and synthetic is about 19.5 million tonnes. A major share of this is by the tyre sector [264]. Rubbers mostly used for tyre manufacture are hydrocarbon based. Carbon black is the ideal filler for reinforcing such rubbers. However, compared to carbon black, precipitated silica in tyres can provide lower rolling resistance and therefore reduced fuel consumption [265]. Hence, use of precipitated silica as a filler in tyre sector is on the increase either for complete substitution or partial substitution of carbon black. Silica reinforcement has great potential in footwear and other non- tyre sectors also [266].

Automobile sector aims at tyres with higher wear resistance and lower rolling resistance. This can be achieved mainly through two aspects viz; tyre design and compound design. Development of radial tyres is an advancement in the tyre design for achieving the said goal. With regard to compounding, selection of filler and polymer are important. Silica is known to contribute to lower rolling resistance. Radialization of tyres has led to the usage of larger proportion of NR. In a cross ply tyre the usage of NR is about 40 to 90 %, while for a radial tyre it is about 98 to 100 %. This has led to a situation where silica reinforcement of NR has become more relevant [262].

The surface activity and surface energy of the filler play an important role in the reinforcement of polar rubbers such as NBR and CR[267-269]. Polar elastomers, unlike hydrocarbon elastomers, provide comparatively better rubber-silica interaction and therefore results in improved filler dispersion [25]. In general the vulcanizate properties of silica filled polar rubbers are better than non-polar rubbers. However, the properties of the silica filled polar elastomers could further be enhanced with the use of silane coupling agents. Acrylonitrile butadiene rubber is a typical example of polar elastomer which exhibits comparatively better reinforcement with silica than the hydrocarbon rubbers. It is also reported that when the polymer to be reinforced contains a reactive group, capable of interacting with fillers, the same could modify reinforcement [270]. Polymers such as SBR and NBR when partially functionalized with epoxy functionality, exhibited improved reinforcement with silica [271,272]. Carbon black and silica also contain functional groups capable of interacting with rubbers.

Coupling agents are known to greatly influence filler dispersion, compound processing properties and failure properties of rubber [273-275]. Large varieties of coupling agents are being used [276,277]. Silane coupling agents usually used with rubber are bifunctional. It generally will have silanol reactive groups (ethoxy, methoxy etc.) and a rubber reactive group. For most of the hydrocarbon rubbers sulphide group of the silane will be the rubber reacting entity. With certain other rubbers, silanes having any of the rubber reactive functionality such as chloro, amino, vinyl, methacryl or epoxy group are also used [273]. Typical rubber- silica reaction product through the silane-coupling agent, TESPT can be illustrated as in Fig. 1.9.

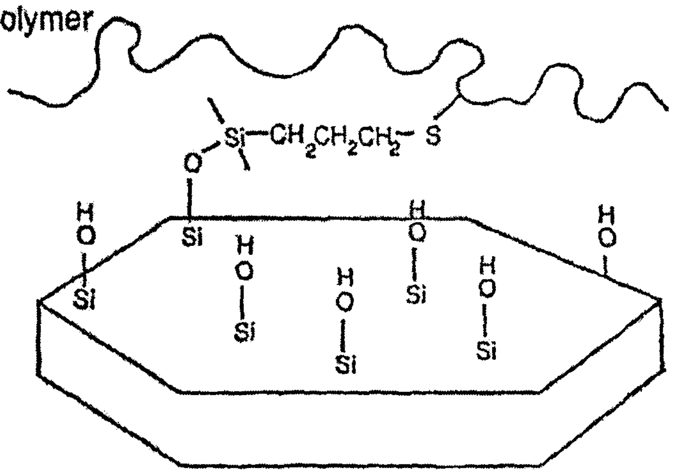


Fig. 1. 9 Rubber- Silica reaction

Viable alternative methods or materials for overcoming the problems associated with the silica reinforcement of rubbers is therefore a current research priority [278-285]. Recently Varkey et.al have reported the feasibility of using epoxidised natural rubber (ENR) as a reinforcement modifier for silica filled rubbers [286]. The present thesis describes a detailed study of various aspects of using ENR as reinforcement modifier in silica filled natural rubber and nitrile rubber.

Epoxidised natural rubber, can be considered a bifunctional polymer as it contains two functionalities; viz the epoxy and the double bond. It is already reported that the epoxy group can interact with the silanol groups [271]. It is also known that the unsaturation in NR can serve as a site for sulphur crosslinking [287]. The bifunctional structure of ENR is given in Fig.1.10. Moreover ENR is more polar than NR as it contains the epoxy functionality and therefore may get preferentially adsorbed on the silica surface. Therefore, it is likely to function as an interface modifier between rubber and silica or as a silica dispersion modifier. The acid-base interaction between epoxy group and silanol or hydrogen bonding between the two can lead to better rubber-silica interaction. It is reported that ENR can effectively be reinforced with silica even without silane coupling agent [249]. ENR when used in tyres offer better wet grip and low rolling resistance [249]. Silane coupling agents being expensive, their widespread use in silica reinforced products of rubber especially in tyres is limited [261].

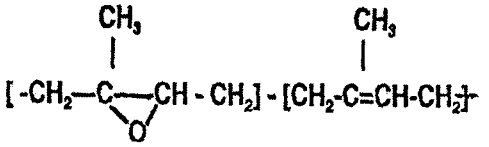


Fig.1. 10. Structure of ENR

The objective of the present work is to study the effect of using ENR as a silica reinforcement modifier in NR and NBR on its processability and technological properties. These composites were also compared with the corresponding silane modified silica filled and the carbon black filled systems.

To achieve the said objectives the following studies were carried out.

1. NR/ENR blends containing 0-20% ENR were prepared and mixed with silica. The epoxy content of the ENR used was varied from 10 to 60 mole %. Sulphur vulcanized samples of these composites were compared with the corresponding silica

filled silane modified and carbon black filled NR. Cure characteristics and compound properties were determined. Vulcanizates were characterized for crosslink density, stress-strain, technological properties and ageing resistance. Scanning electron microscopy was used for characterizing the silica distribution in various systems.

2. Dynamic mechanical analysis of the sulphur vulcanized silica filled NR modified with ENR of varying epoxy content was made in comparison with that of silane modified and carbon black filled vulcanizates. Variations in storage modulus, loss modulus and tanδ were determined in the temperature range of -80 to +100°C.
3. Mixing characteristics and rheological behavior of NR/silica, NR/ENR/silica, NR/silane/silica and NR/carbon black composites were studied using 'Haake Rheocord' and 'Zwick Capillary Rheometer' respectively. Mixing parameters such as mixing torque, mixing energy and temperature developed were measured using Haake Rheocord. Processability characteristics such as viscosity variations with temperature and shear rate, at different modifier concentrations in the composites were compared using the capillary rheometer.
4. Peroxide cured vulcanizates of silica filled NR and its ENR and silane modified compounds were compared for property variations. Effect of filler loading in those systems were studied. Compound viscosity and vulcanizate properties were determined. Reinforcement characterization of the vulcanizates was made by swelling studies. Selected samples (at 50 phr filler loading) from each series were studied using dynamic mechanical analyzer for the viscoelastic properties and scanning electron microscopy for filler distribution.
5. Effect of filler loading in sulphur cured vulcanizates of silica filled NR and its ENR and silane modified systems were studied. Compound and vulcanizate properties were determined. Reinforcement characterization of those systems was made by swelling studies. Comparison of the selected vulcanizates from each of the series was

made with respect to stress relaxation, thermogravimetry, differential scanning calorimetry, strain dependent dynamic mechanical analysis and scanning electron microscopy.

6. Sulphur cured silica filled nitrile rubber (NBR) of medium acrylonitrile content and the same modified with ENR50 and silane were compared with carbon black filled. Compounds were tested for cure characteristics and the vulcanizates for technological properties, ageing, swelling resistance and dynamic mechanical properties.

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CHAPTER 2

EXPERIMENTAL

This chapter deals with details of materials and experimental techniques.

2.1 Materials

2.1.1 Rubbers

a) Natural rubber

The natural rubber used was block rubber, ISNR-5 as obtained from the Pilot Crumb Rubber Factory, Rubber Research Institute of India, Kottayam. The Bureau of Indian Standards specifications for the grade of rubber are given in Table 2.1[1].

Table 2.1 BIS specifications of ISNR 5

Sl. No.	Parameters	Limit
1	Dirt content, % by mass, max	0.05
2	Volatile matter, % by mass, max	0.8
3	Nitrogen, % by mass, max	0.6
4	Ash, % by mass, max	0.6
5	Initial plasticity, Po, Min	30
6	Plasticity retention index (PRI), min	60

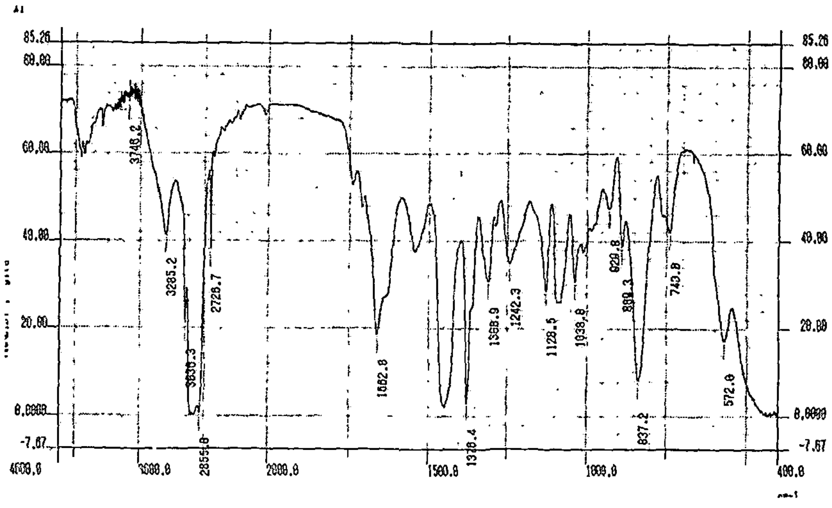

Fig. 2.1 FTIR spectrum of natural rubber

Since it is known that the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variation, season, use of yield stimulants and method of preparation, rubber from the same lot has been used for the experiment[2]. Fourier Transform Infrared (FTIR) spectrum of natural rubber is given in Fig.2.1

b) Epoxidised natural rubber (ENR)

Epoxidised natural rubber, ENR10, ENR 25, ENR 50 and ENR 60 containing 10, 25, 50 and 60 mole percent of oxirane rings, were prepared in the pilot plant facility of the Rubber Research Institute of India [3]. All the ENR samples used for the experiment were prepared from the same lot of centrifuged natural rubber latex using performic acid

Table 2.2

Ingredient	Concentration (m/l)
Rubber hydrocarbon	2.9
Formic acid	0.5 to 0.7
Hydrogen peroxide	0.7 to 2
Non-ionic stabiliser	*

*3 phr

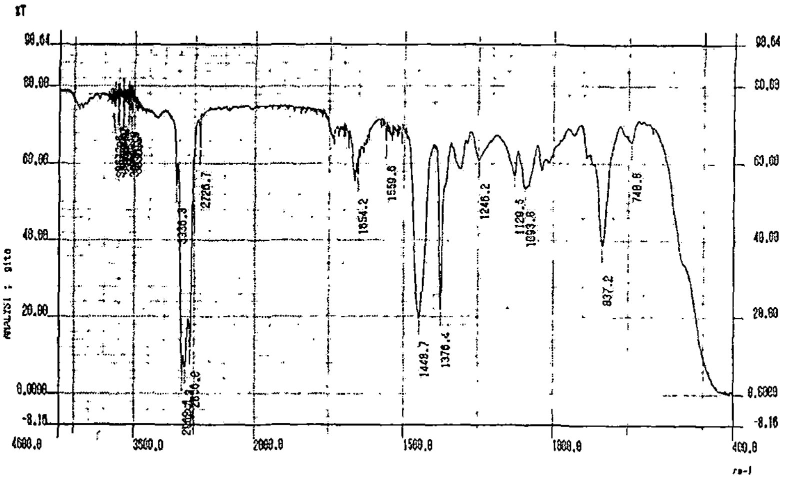

Fig. 2. 2 FTIR spectrum of ENR 10

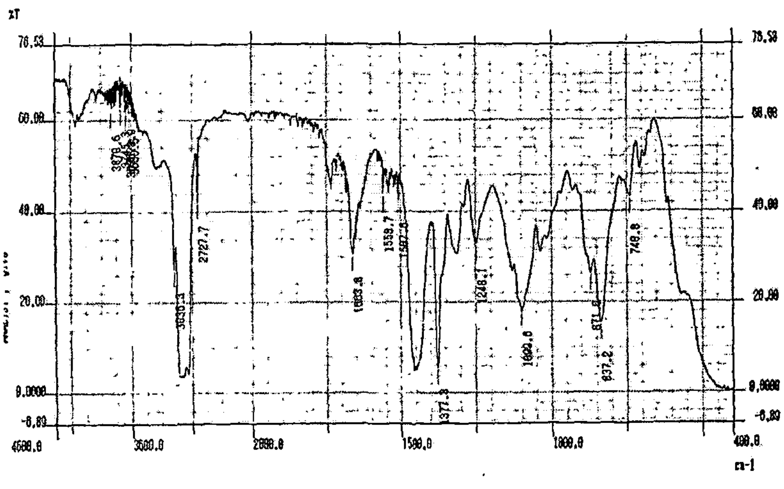

Fig. 2.3 FTIR spectrum of ENR 25

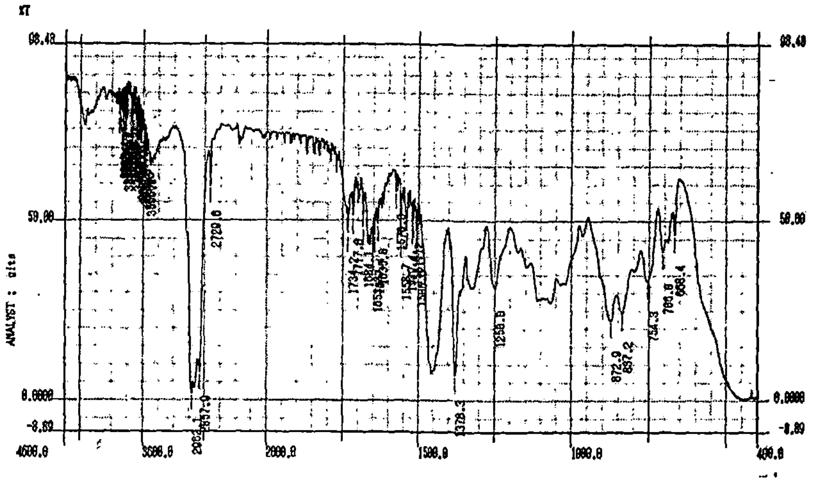

Fig. 2.4 FTIR spectrum of ENR 50

generated *in situ*. A typical formulation of essential ingredients is given in Table 2.2. The reaction was carried out at 60^0C. Time of reaction varied from 25 to 30h. Epoxy concentration of the ENR produced could be varied by varying the reagent concentration and time of reaction. Various ENR samples were characterized using FTIR spectroscopy. The spectra are given in Figs. 2.2, 2.3, 2.4 and 2.5. As the epoxidation progresses the intensity of C-H deformation peak of cis -C = C -H at 837 cm^{-1} get reduced and a new peak at 872 cm^{-1} due to oxirane ring is formed. The intensity of the latter peak increases with the increase in extent of epoxidation[3].

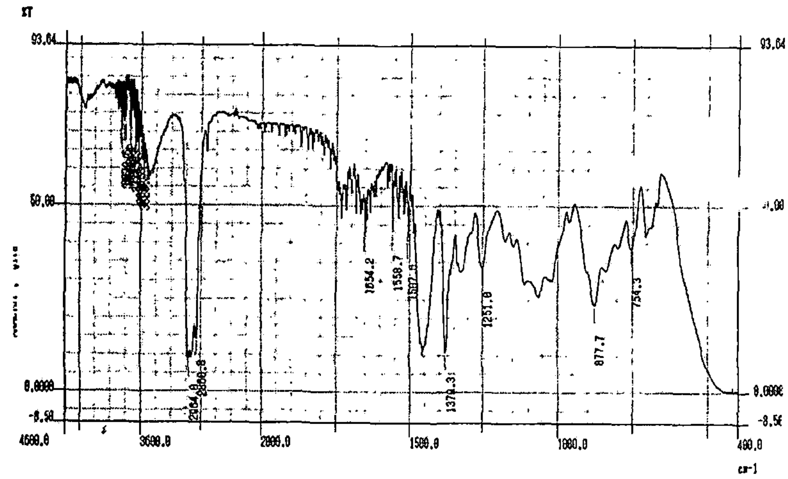

Fig. 2. 5 FTIR spectrum of ENR 60

c) Acrylonitrile butadiene rubber (NBR)

Aparene 423 NS, a product of Gujarat Apar Polymers Ltd., India was used for the study. It is a medium acrylonitrile content (33% by weight) rubber.

2.1.2 Fillers

a) Silica

Precipitated silica was Ultrasil VN3, a product of Degussa AG, Germany. Specifications of the same are given in Table 2.3[4].

Table 2.3 Ultrasil VN3 specifications

Specific surface area (N_2), m^2/g	175
Heating loss, %	5.5
pH	6.2
Tapped density, g/l	220
SiO_2, content %	98
Appearance	white powder

b) Carbon black

ISAF black, a product of Phillips Carbon Black Ltd, India was used.

2.1.3 Coupling Agent

The coupling agent used was Si69, a product of Degussa AG, Germany. Chemically the product is bis (triethoxysilyl propyl) tetrasulphide. The specifications of the product are given in Table 2.4[5].

Table 2.4 Specifications of Si 69

Sulphur content, %	22.7
Volatiles, %	$\leq$4.0
Average sulphur chain length	3.75
Average molecular weight, g/mol	532
Density, g/cm^3	1.1
Appearance	clear yellow liquid

2.1.4 Solvent

Toluene used in the present investigation was of analytical grade.

2.1.5 Other chemicals

CBS (N–Cyclohexyl benzthiazyl sulphenamide) –'Vulcacit CZ' and DPG (Diphenyl guanidine) – 'Vulcacit D' commercial grade products of Bayer (India) Ltd were used. Dicumyl peroxide (DCP), commercial grade product of 'Geo Peroxides' was used. Zinc oxide (ZnO)-specific gravity 5.5, Stearic acid-specific gravity 0.82, Sulphur - specific gravity 1.9, Zinc stearate, Naphthenic oil and Dioctyl phthalate of commercial rubber grade were used.

2.2 Processing

2.2.1 Mastication / Blending

Mastication and blending of rubbers were done in a laboratory model two-roll mixing mill at a friction ratio of 1:1.25. Mixing time and temperature were controlled.

2.2.2 Mixing of rubber compounds

Compounds for various studies were prepared in a laboratory model intermix KO, MK3 of Francis Shaw, Manchester, England. Rotor speed, mixing time and temperature were controlled during mixing. Mastication/ pre-blending of rubbers for compound preparation and the final homogenization of various compounds were done in a laboratory model two-roll mixing mill.

2.2.3 Mixing in Rheocord

Rubber – filler mixing studies and the mixes used for the rheological studies were prepared in a torque - rheometer, Rheocord 90 of Haake, Germany. It is a torque rheometer in which mixing energy and mix viscosity could be continuously measured.

2.3 Moulding and testing

2.3.1 Mooney viscosity

Mooney viscosity of raw rubbers and compounds was determined using a Shimadzu Mooney Viscometer, model SMV 202.

2.3.2 Bound rubber

For the measurement of bound rubber content of various filled rubber composites, a technique described by Wolff et.al. [6] was followed. Samples of known weight (about 0.2 g) cut into small pieces were placed in a weighed stainless steel cage of 150 mesh and immersed in 25 ml of toluene at room temperature(28 ± 1°C). The solvent was renewed after 3 days. After 7 days the steel cages with swollen samples were removed from the solvent, dried in air for 24 h. and subsequently dried to constant weight in an oven at 105°C. The bound rubber (R_B) was calculated using the following equation.

$$R_B = W_{fg} - W\,[m_f / (m_f + m_p)] \,/\, W\,[m_p / (m_f + m_p)] \; * 100 \qquad \text{Eq. 2.1}$$

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

Also for selected compounds, bound rubber in ammonia atmosphere was determined to assess the nature of rubber – filler and filler-filler interactions.

2.3.3 Vulcanization

Vulcanization of various test samples was carried out in a single daylight electrically heated hydraulic press having 45 cm x 45 cm platen at 150 /160^{0}C at a pressure of 45 kg/cm^2 on the mould up to optimum cure times. Moulded samples were conditioned for 24h. before testing.

2.3.4 Cure characteristics

a) Time of optimum cure

Cure characteristics were determined as per ASTM D 2084 -1995. Optimum cure times at 150/160^{0}C were determined using Monsanto rheometer, R-100. The optimum cure time corresponds to the time to achieve 90 percent (t_{90}) of the cure calculated using the Equation 2.2[7].

$$\textbf{Optimum cure} = 0.9\,(M_H - M_L) + M_L \qquad \textbf{Eq. 2.2}$$

where M_H and M_L are the maximum and minimum torques respectively.

b) Cure rate index

Cure rate index was calculated from the rheographs of the respective mixes using Equation 2.3.

$$\textbf{Cure rate index} = 100/\, t_{90} - t_2 \qquad \textbf{Eq. 2.3}$$

where t_{90} and t_2 are the times corresponding to the optimum cure and two units above minimum torque respectively.

2.3.5 Physical testing

a) Modulus, tensile strength and elongation at break (stress – strain properties)

These tests were carried out according to ASTM D 412-1998, using dumbbell specimens[7]. Test specimens were punched out from the moulded sheets using the c-type die, along the mill grain direction. All the above tests were carried out using a Zwick 1474 universal testing machine (UTM) at 28 ±1^{0}C and at a crosshead speed of 500mm per minute.

b) Tear resistance

Tear resistance of the samples was tested as per as ASTM D 624-1998, using unnicked 90^0 angle test specimens that were punched out from the moulded sheets, along the mill grain direction. The test was carried out using a Zwick 1474 UTM, at a crosshead speed of 500mm per minute. The tear strength was reported in N/mm.

c) Hardness

The testing was done as per ASTM D 2240-1997 using Shore A type Durometer[7]. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens.

d) Rebound resilience

Dunlop Tripsometer (BS 903, part A8, 1995)[8] was used to measure rebound resilience. The sample was held in position by suction. It was conditioned by striking with the indentor six times. The test was carried out at $28\underline{+}1^0$C. Rebound resilience was calculated using Equation 2.4.

$$\text{Rebound resilience (\%)} = \frac{(1 - Cos\theta_2)*100}{(1 - Cos\theta_1)} \qquad \textbf{Eq. 2.4}$$

where $\theta 1$ and $\theta 2$ are the initial and rebound angles respectively. $\theta 1$ was 45^0 in all the tests.

e) Abrasion resistance

Abrasion resistance of the samples was tested as per DIN 53516. It consisted of a drum on to which a standard abrasive cloth is fixed. The drum is rotated at a speed of $40\underline{+}1$ rpm and the total abrasion length is 42 meters. A sample having a diameter of $16\underline{+}0.2$ mm and a thickness of 6 to 10 mm is kept on a rotating samples holder. A load of 10N was applied on the sample. Initially a pre run was given for the sample and then its weight taken. The weight after the test run was also noted. The difference in weight is the abrasion loss. The abrasion loss was calculated using Equation 2. 4.

$$V = \frac{\Delta m}{\rho}$$ **Eq. 2.5**

where Δm = mass loss, ρ = density and V = abrasion loss.

f) Compression set

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate compressed to a constant deflection (25%) were kept in an air oven at 70^0C for 22h (ASTM D 395-1998 method B)[7]. The samples were taken out, cooled to room temperature for half an hour and the final thickness measured. The compression set was calculated using Equation 2.5.

$$\text{Compression set (\%)} = \frac{t_0 - t_1 * 100}{t_0 - ts}$$ **Eq. 2.6**

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.

g) Heat build up

The Goodrich flexometer conforming to ASTM D 623-1999 was used for measuring heat build-up[7]. A cylindrical sample of 2.5 cm in height and 1.9 cm in diameter was used for the test. The oven temperature was maintained at 50^0C. The sample preconditioned in the oven for 20 minutes was subjected to a flexing stroke of 4.45 mm under a load of 10.9 kg. The temperature rise ($\Delta T^0 C$) at the end of 20 minutes was taken as the heat build-up.

h) Flex cracking

Flex cracking was determined using a De Mattia flexing machine according to ASTM D 430-1995[7]. Standard specimens 15 cm x 2.5 cm x 0.6 cm having a semi-circular groove moulded transversely in the centre of the strip were used. Samples fixed on the machine were subjected to flexing at a frequency of 300 cycles per minute. The number of cycles required to produce different levels of cracking was noted.

i) Ageing studies

Tests were carried out as per ASTM D 573-1999[7]. Specimens of vulcanized rubber were exposed to the deteriorating influence of air at specified elevated temperature in an air oven, for known periods of time, after which their physical properties determined. These were compared with the properties determined on the original specimens and the changes noted.

j) Scanning electron microscopy (SEM)

In SEM, the electron beam incident on the specimen surface causes various phenomena of which the emission of secondary electrons is used for the surface analysis. Emitted electron strikes the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. There is a one- to- one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the screen and thus an image of the surface is progressively built up on the screen.

Scanning electron microscopic studies of the various silica filled samples were carried out in order to find out the variations in filler dispersion with and without modifiers. The microscopic examinations were carried out on the freshly cut surface in a Hitachi SE Microscope (model H 6010). The sample surface was gold coated prior to the examination.

k) Rheological properties

The rheological properties of the rubber, rubber blends and rubber-filler mixes were studied using a capillary rheometer attached to a ZWICK 1474 universal testing machine as per ASTM D 5099-1998[7]. The barrel was heated using a three zone temperature control system to the required test temperature. The moving crosshead of the UTM runs the plunger in the barrel at a constant speed irrespective of the load on the melt, maintaining a constant volumetric flow rate through the capillary. The crosshead speed was varied from 0.5 to 500 mm per minute giving shear rates ranging from 8.54 S^{-1} to 854 S^{-1} for a capillary of L/D = 30. Forces corresponding to specific plunger speeds were recorded. The values were converted to shear stresses.

The sample for testing was placed inside the barrel, maintained at the test temperature and was forced down the capillary using a plunger attached to the crosshead. After a warming up period of 3 minutes the melt was extruded through the capillary at pre selected speeds of the crosshead. The machine was operated at varying plunger speeds so as to generate different shear rates on the melt. Stabilized forces corresponding to specific plunger speeds were recorded. The force and crosshead speed were converted to apparent shear stress (Γ) and shear rate (γ) at the wall using Equation 2.6 and 2. 7, involving the geometry of the capillary and the plunger.

$$\Gamma w = \frac{F}{Ap(lc / dc)} \qquad \textbf{Eq. 2.7}$$

$$\gamma_{wa} = \left(\frac{3n^1 + 1}{4n^1} \right) * \frac{32Q}{\pi dc^3} \qquad \textbf{Eq. 2.8}$$

where,

F = force applied at a particular shear rate

Ap = Crosssectional area of the plunger

lc = Length of the capillary

dc = Diameter of the capillary

Q = Volumetric flow rate

n^1 = Flow behaviour index defined by d (log Γw)/d (log γ_{wa})

Γw = Apparent shear stress at the wall

γ_{wa} = Actual shear rate at the wall

n^1 was determined by regression analysis of the values of Tw and γ wa obtained from the experimental data. The shear viscosity η was calculated as

$$\eta = \Gamma / \gamma_{wa} \qquad \text{Eq. 2.9}$$

For higher L/D ratio, it is assumed that the Bagley's shear stress correction factor is negligible.

l) Extrudate swell

Extrudate swell was expressed as the ratio of the diameter of the extrudate to that of the capillary used. The diameter of the extrudate after conditioning for a period of 24 h at ambient temperature was measured using a stereomicroscope. The extrudate swell at different shear rates was expressed as (D_e/D_c) where D_e is the diameter of the extrudate and D_c that of the capillary.

m) Thermal analysis

Thermal analysis was carried out using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA).

1) Differential scanning calorimeter

Calorimeter measurements and characterization of various samples were made using a Du Pont differential scanning calorimeter in a temperature range of -60^{0}C to 100^{0}C. Samples of known weight encapsulated in standard aluminium pans placed in the sample holder were subjected to the analysis. While testing, sample holders were purged using dry nitrogen gas of 99.99% purity. The scanning rate was 2^{0}C / minute. The energy changes associated with transitions were recorded.

2) Thermogravimetry

A Shimadzu thermogravimetric analyzer model TGA-50 was used for the studies. It is computer-controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature. The sample placed in a temperature-programmed furnace is subjected to temperatures in the ranges 30^{0}C to 800^{0}C with a heating rate of 10°C/minute and the corresponding weight changes were noted with the help of a ultra sensitive microbalance. Air and nitrogen were used as purge gases.

n) Dynamic mechanical analysis

Viscoeleastic properties of the samples were carried out using a dynamic mechanical analyzer model DMA 2980 of TA Instruments at a frequency of 1 Hz at a strain of 0.1% in the temperature range of -80^0 C to $+100^0$C.The rate of heating was 2^0C/min. The sample dimension was 35 mm x12.5 mm x 2mm.

The strain dependent dynamic properties (isothermal) were also measured in the same instrument at 60^0C at a frequency of 1 Hz. The variation in the strain given was in the range of 0.01 to 5%.

o) Stress relaxation

Stress relaxation measurements were carried out with dumb-bell shaped test specimens as per ASTM D 412- die C, using a ZWICK universal testing machine at 100% strain, given a strain rate of 100mm/min. Decay of stress or stress relaxation as a function of time was recorded[9]. Stress relaxation was plotted as a ratio of σ_t/σ_0 versus time, where σ_0 and σ_t are the initial stress and stress at time 't' respectively.

p) Fourier Transformation Infrared (FTIR) Spectroscopy

Characterization of various ENR samples was made using FTIR spectra. Spectra of various ENR samples were taken using cast films from a solution of chloroform using a Shimadzu spectrophotometer model FTIR-8101M.

q) Swelling studies

Contribution to the reinforcement effect arises from molecular interaction between the rubber and the filler. This interaction leads to an increase in the effective degree of crosslinking and can be evaluated by equilibrium swelling. The equilibrium swelling analysis of rubber vulcanizate is known to indicate the number of effective network chains per unit volume of rubber. For a filled vulcanizate it should reflect not only the effect of chemical linkages but also the density of polymer-filler attachments.

Degree of swelling usually is expressed as V_r and is defined as

V_r = Volume of rubber / Volume of swollen rubber-solvent gel

V_r is dependent on the swelling power of the solvent (high swelling power means low V_r) and the crosslink density. Higher crosslink density results in restraint on the network, which results in lower swelling. V_r of the unfilled vulcanizate is usually denoted as V_{ro} and that of the filled vulcanizate as V_{rf}.

V_{rf} = Volume of rubber(filled) / Volume of swollen rubber-solvent gel (filled)

where the numerator refers to total volume minus the filler volume and the denominator refers to the total swollen volume minus the filler volume.

The ratio of V_{ro}/V_{rf} is used to characterize the filler reinforcement at different loadings. In the present study, the extent of reinforcement was determined using swelling studies of the filled and unfilled vulcanizates in toluene. Swelling experiments were carried out with the moulded samples by immersing them in toluene at 28 ± 1^0C for 72 h. to achieve equilibrium swelling. Volume fraction of rubber in the swollen vulcanizate was determined using the method suggested by Ellis and Welding[10] using the equation

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o.\rho_s^{-1}} \qquad \textbf{Eq. 2.10}$$

where T= weight of test specimen, D = deswollen weight of the specimen, F= weight fraction of insoluble components, A_0= weight of the absorbed solvent, ρ_r and ρ_s are the densities of the rubber and solvent respectively. Volume fraction measurements could also be used for calculating the crosslink density using Flory- Rehner equation[11].

The ratio of the volume fraction of the unfilled to filled was determined and was applied in Cunneen- Russell equation and Kraus equation [12, 13] for determining the extent of reinforcement.

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CHAPTER 3

ENR AS A REINFORCEMENT MODIFIER FOR SILICA FILLED NR

3.1 Introduction

In hydrocarbon rubbers carbon black provides high strength, wear resistance and durability. Though silica in rubber offers high strength, it is accompanied by processing problems such as high viscosity, cure retardation, compound stiffness and lower wear resistance. On comparison with carbon black filled rubber, technological properties such as tear strength, adhesion and heat resistance are higher for silica filled rubber, while abrasion resistance is lower[1]. For a colloidal filler to be effective in rubber as a reinforcing agent, it has to be well dispersed and should also create large polymer-filler interface and the interfacial adhesion between rubber and filler has to be of high level. Filler dispersion depends on the balance between two main opposing interactions. On the one hand, the filler-filler interaction that tends to keep filler particles in agglomerate or aggregate form and on the other hand the filler-matrix interaction, which in turn, depends on the surface energies of the two which decides distribution of filler in rubber [2]. Chemical compatibility has been identified as a factor in the dispersion of filler in rubber[3].

Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction [4]. Reactive silanol groups on the silica surface offers a means for attaching organic groups on it. Esterification or alkylation of silica improve its compatibility, wetting and dispersion of filler in hydrocarbon rubbers and improved technological properties could be achieved [4,5]. Addition of glycols, amines or guanidines to silica compounds could overcome its cure retarding effect [6]. Silane modification is the most widely practised technique for improving silica – rubber bonding [6,7].

Chemical nature of the rubber can also determine the level of filler reinforcement. Reinforcement by a filler generally is achieved by the immobilization of polymer segments on the filler surface [8]. Silica produces greater reinforcement in polar elastomers such as NBR, CR etc.[6]. In acrylonitrile butadiene rubber, strong specific interaction of the acrylonitrile group (ACN) with the silica surface groups result in increased polymer-filler interaction and less filler networking as compared to silica in NR [9]. Silica exhibits better rubber-filler binding in polydimethyl siloxane due to the interaction between silanol and siloxane groups [10]. In a copolymer of vinylpyridine butadiene rubber, silica exhibits good dispersion and reinforcement, which is attributed to the rubber-filler linkages either through complex formation, acid-base interaction and, or pyridine-silanol interactions [6]. Polar rubbers like nitrile rubber exhibits stronger interaction with carbon black as compared to the non-polar olefinic rubbers [11]. Hydroxy functionalised SBR and epoxy functionalised NBR exhibited improved reinforcement with silica over the unmodified [12,13]. Silica is reported to have better binding with rubber in chlorosulfonated polyethylene through the interaction between silanol groups and sulphonyl chloride groups [14]. Silica exhibits good reinforcement in carboxylated nitrile rubber through the carboxyl and silanol entities[15]. Wang et.al using model compound studies found that silica exhibits better affinity with aromatic hydrocarbons and nitriles than olefins [16]. Silyl modified EPDM and SBR are also reported to exhibit good silica reinforcement [6].

Natural rubber (NR) modified with N-(3-triethoxy silyl propyl) carbamoyl azoformate, exhibit improved silica reinforcement [12,17]. Unlike NR, epoxidised natural rubber (ENR) can be reinforced with silica without silane coupling agent [18]. High strength, comparable to that achieved with carbon black could be obtained [19]. Chemical interaction or chemical crosslinks between the epoxy group and silanol groups has been proposed to be the reason for the unusual reinforcement [20]. Xue et al reports that the silanol groups could ring open the epoxy groups [21]. The proposed mechanism of interaction between epoxy and silanol groups is shown in Fig.3.1.

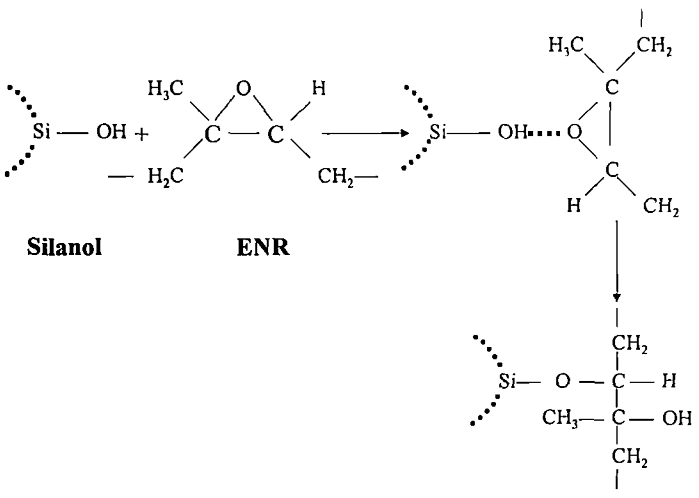


Fig .3.1 Proposed mechanism for epoxy- silanol interaction

This chapter discusses the viability of the use of ENR as a reinforcement modifier in silica filled NR and to compare the same with that of silane modified silica filled and carbon black filled NR. NR was partially substituted with ENR to function as base polymer-cum- silica reinforcement modifier.

3.2 Experimental

3.2.1 Materials

Natural rubber (ISNR-5) and epoxidised natural rubber, having epoxy content 10, 25, 50, and 60 mole percent, were used. Silane coupling agent , ‘Si69’ and Silica, ‘Ultrasil VN3’of Degussa A.G., Germany and carbon black (ISAF) of Phillips Carbon Black were used. The other chemicals used were of rubber chemical grade.

3.2.2 Mixing of rubber compounds

Compounds made for the study can be classified into two series based on the systems of cure used, viz; CBS and CBS-DPG for the first and second series

Table 3.1 Formulation of mixes (S/CBS system)

Ingredient	Mix number							
	A	B	C	D	E	F	G	H
Natural rubber	100	95	90	85	80	-	100	100
ENR50	-	5	10	15	20	100	-	-
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Naphthenic oil	5	5	5	5	5	5	5	5
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	2	2	2	2	2	2	2	2
Ultrasil VN3	50	50	50	50	50	50	50	-
ISAF	-	-	-	-	-	-	-	50
Si-69	-	-	-	-	-	-	4	-

Table 3.2(a) Formulation of mixes (S/CBS/DPG system)

Ingredients*	Mix number								
	AA0	AE1	AE2	AE3	AE4	BE1	BE2	BE3	BE4
NR	100	95	90	85	80	95	90	85	80
ENR10	-	5	10	15	20	-	-	-	-
ENR25	-	-	-	-	-	5	10	15	20

* Mixes also contains the ingredients ZnO 5, Stearic acid 2, Ultrasil VN3 50, CBS 1.5, DPG 2, Naphthenic oil 5 and Sulphur 2.

Table 3.2(b) Formulation of mixes (S/CBS/DPG system)

Ingredients*	Mix number							
	CE1	CE2	CE3	CE4	DE1	DE2	DE3	DE4
NR	95	90	85	80	95	90	85	80
ENR50	5	10	15	20	-	-	-	-
ENR60	-	-	-	-	5	10	15	20

* Mixes also contains the ingredients ZnO 5, Stearic acid 2, Ultrasil VN3 50, CBS 1.5, DPG 2, Naphthenic oil 5 and Sulphur 2.

Table 3.3 Formulation of mixes

Ingredients	Mix number				
	CA1	CA2	CA3	CA4	EE
NR	100	100	100	100	-
ENR-50	-	-	-	-	100
ZnO	5	5	5	5	5
St.acid	2	2	2	2	2
Ultrasil VN3	50	50	50	50	50
CBS	1.5	1.5	1.5	1.5	1.5
DPG	2	2	2	2	2
Naphthenic oil	5	5	5	5	5
Sulphur	2	2	2	2	2
Si 69	1	2	3	4	-

Table 3.4 Mixing sequence-Stage 1

Time seconds	Ingredients
0	Rubber/rubber blend
30	Silica / carbon black (1/3) + coupling agent(1/3) + process oil(1/3)
120	Silica / carbon black (1/3) + coupling agent(1/3) + process oil(1/3)
210	Silica / carbon black (1/3) + coupling agent(1/3) + process oil(1/3)
360	Dump

Table 3.5 Mixing sequence-Stage 2

Time seconds	Ingredients
0	Masterbatch (Mix from stage 1)
30	Zinc oxide + Stearic acid
120	Accelarator + Sulphur
270	Dump

respectively. ENR50 was used as the reinforcement modifier for the first series and was compared with silane modified and carbon black filled NR. For the second series, ENR samples of different epoxy content were used as reinforcement modifier and compared with those of the silane modified.The recipes of the various mixes are given in Tables 3.1, 3.2 (a) and (b) and 3.3.

NR and ENR having Mooney viscosity of 70±2 were premasticated or blended to a Mooney viscosity of 55±2 and used for further mixing. Compounds were made in the laboratory model intermix, Francis Shaw, KO, MK_3 with a two stage mixing schedule as given in Tables 3.4 and 3.5.

For both stages, the initial mixing temperature was 40°C. The final mix obtained from the intermix was homogenized in the two roll mill for 2 minutes.

3.2.3 Testing

Cure characteristic of the compounds were determined using a Monsanto Rheometer R-100 at 150^0C. Test samples for various tests were prepared by vulcanizing the compound at 150^0C up to their respective optimum cure time (t_{90}) in an electrically heated hydraulic press. Physical properties such as modulus, tensile strength, elongation at break, tear strength, hardness, heat build-up, compression set, flex resistance and ageing resistance were determined as per the respective ASTM Standards. Abrasion loss was determined as per DIN 53516. Volume fraction of rubber was determined by swelling studies. Scanning electron microscopy was used for studying the distribution of silica in various samples.

3.3 Results and Discussion

3.3.1 ENR 50 as reinforcement modifier (CBS system)

ENR which is more polar than NR was tried as a base polymer-cum-reinforcement modifier for silica filled NR compounds using ENR50. In carbon black filled NR, sulphur- CBS combination gives satisfactory cure characteristics and technological properties, whereas in silica filled NR the same system exhibits cure retardation and poor technological properties. Therefore, the efficacy of ENR, also as a cure modifier for silica filled NR with the said cure system was evaluated. Silica filled NR compound was modified with ENR in such a way that increasing proportions of NR were substituted with ENR50 up to a weight ratio of 80:20. These compounds were evaluated in comparison with silane modified silica filled NR, silica filled ENR and carbon black filled NR. Formulation of the mixes are given in Table 3.1.

a) Cure characteristics

Silica reinforced rubbers exhibit lower rate and extent of cure than those containing carbon black as reinforcing filler. The polar nature of the silica surface which adsorbs

Table 3.6 Cure characteristics (S/CBS system)

Property	Mix number							
	A	B	C	D	E	F	G	H
Minimum torque, dN.m	18	15	16	16	17	14	12	9
Maximum torque, dN.m	37	51	59	55	56	81	68	80
Δ, Torque, (Max.-Min.) , dN.m	19	36	41	39	39	67	56	71
Scorch time,(ts_2),minutes-150 °C	5.5	8	8	8.5	8.5	8	5	3
Optimum cure time (t_{90}), minutes-150 °C	34	20	15	17.5	18.5	16	15	6
Cure rate index ($100/t_{90}-t_2$)	3.5	8.3	11.7	11.1	10	12.5	10	36

part of the curatives and or a silica-zinc ion interaction leads to slowing down of the curing reaction[6]. Table 3.6 and Fig. 3.2 give the cure characteristics of the mixes given in Table 3.1.

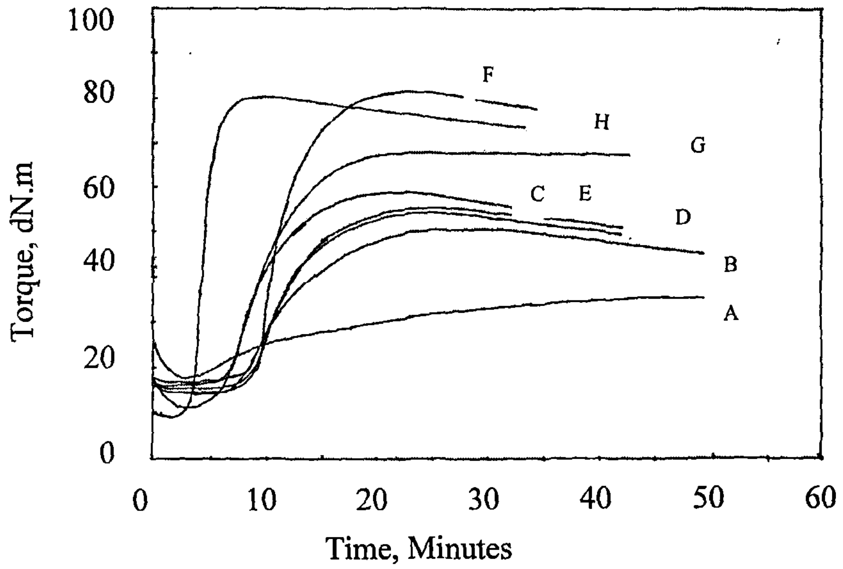


Fig. 3.2 Rheographs(A to H)

On incorporation of ENR or silane into the silica filled NR, improvements in cure behavior was observed as can be seen from the rheographs. Compounds containing ENR50 and Si69 as modifiers were compared with an ISAF filled NR compound. The ENR modified compounds exhibited higher rate and extent of cure over that of silica filled NR control compound. Scorch time was found increased and cure time reduced with ENR incorporation. With an optimum concentration of ENR, cure time and cure rate index are comparable with that of the compound containing silane coupling agent. Addition of silane lowered the minimum torque. However, the carbon black filled mix exhibited the lowest minimum torque, the highest cure rate and the lowest cure time compared to those of the ENR and silane modified mixes. Maximum torque of carbon black filled NR and silica filled ENR were in close range. Improvements noted in the cure behavior of the ENR modified system might have resulted from the preferential interaction of the epoxy group with the silanol groups [21]. This, in turn, may have reduced the chances of interaction of the silanol group with either the accelerator or other compounding ingredients, thus making its availability higher for curing. The increased cure torque (Δ, rheomotric torque) observed for the silica filled NR/ENR blends over NR also support this view.

b) Vulcanizate properties

The vulcanizate properties are given in Table 3.7. Variations in modulus and strength properties of the ENR modified samples are given in Fig. 3.3. Modulus showed a regular increase with concentration of ENR, which is likely to be due to the increasing rubber-filler bonding through its epoxy-silanol interaction. Tensile strength showed optimum in the range of 10-15 parts, and with still higher concentration a decline was noted. Strength variations with concentration of ENR, might have resulted from the changes in crosslink density in the NR and ENR phases of the blend [22]. Silane

Table 3.7 Vulcanizate properties

Property	Sample number							
	A	B	C	D	E	F	G	H
300 % modulus, N/mm^2	5	5.8	7.5	8.1	8.5	13.1	10.6	15.2
Tensile strength, N/mm^2	16.5	16.3	21.3	21	19.2	19.6	25.5	24.3
Elongation at break,%	560	547	529	517	458	340	560	420
Tear strength, N/mm	33	81	89	92	92	47	107	115
Abrasion loss,mm^3	310	255	200	195	173	185	136	97
Heat build-up, °C	91	87.5	83	76	71	34	25	31
Compression set,%	42	38.5	37	36.3	34.7	32	25	25
Resilience,%	49	47	43	42	41	39	59	49
Hardness, Shore A	65	62	62	63	65	66	63	64

modification considerably improved the modulus, as can be seen from the data in Table 3.7. Coupling agent, being a crosslinking agent as well, might have contributed to a higher crosslink density and hence higher modulus [6]. The ENR modified composites exhibited a decrease in elongation at break with concentration of ENR as given in Table 3.7. For effective reinforcement rubber-filler interaction contributes to a considerable extent. The enhanced tensile strength and decreased elongation at break with ENR incorporation might be a consequence of the better rubber-silica interaction and the higher level of crosslinking achieved through ENR.

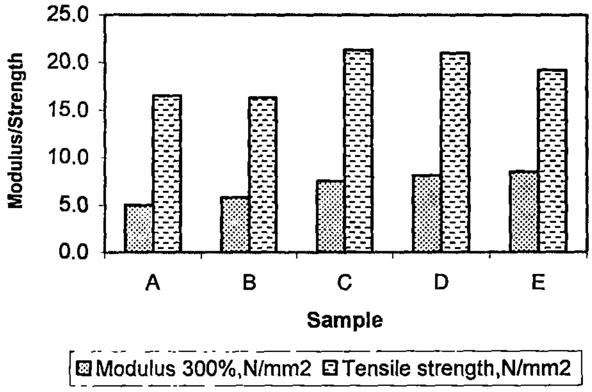


Fig. 3. 3 Variations of strength properties with ENR incorporation

Modulus and strength properties of various silica filled NR compounds are compared with that of ISAF filled NR and silica filled ENR in Table 3.7. Silica filled ENR exhibited a comparatively higher modulus than the other silica filled composites, considered to be due to the higher extent of rubber-filler bonding. Comparison of the stress-strain properties of the selected vulcanizates are given in Fig. 3.4. The ENR modified samples showed improvements in strength properties over the unmodified. However, silane modified and carbon black filled samples exhibited higher strength properties over the other systems. The strength values observed are in the order NR-

ISAF> NR-Si69 –silica> NR-ENR-silica> ENR-silica>NR-silica. The higher extent of rubber- filler coupling of silica filled ENR might have partially affected the stress induced crystallization of ENR thus resulting in lower strength.

ENR incorporation improved the tear strength and abrasion resistance of silica filled NR as can be seen from Figs.3.5 and 3.6. Improved tear strength and abrasion resistance are considered measure of enhanced filler reinforcement [23]. ENR and silane modified composites exhibited higher tear strength than the corresponding NR or ENR. Interface modification of the silica filled NR by ENR and improved crosslinking might

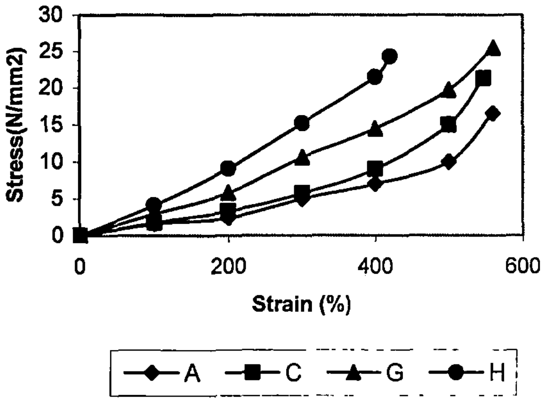


Figure 3.4 Comparison of stress-strain property

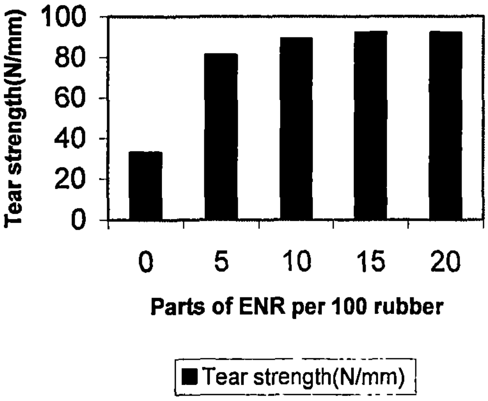


Figure 3.5 Variation of tear strength with ENR incorporation

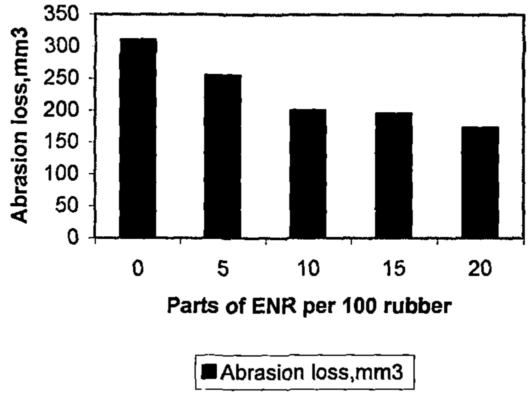


Fig.3. 6 Variation of Abrasion losswith ENR incorporation

have contributed to the higher tear strength. Tear strength values for the silane modified sample was higher than that of the ENR modified, which is likely to be due to the rubber-filler covalent bonding achieved through sulphur bridges. While tearing, intermittent deviation in the direction of tear path was observed for the samples containing ENR and coupling agent as modifiers. The deviation in the tear path, normal to the direction of tear, also known as 'knotty tear' is associated with improved rubber-filler interaction and reinforcement [23]. Incorporation of coupling agent has considerably improved the abrasion resistance of silica reinforced NR. Though the modulus and strength properties of silica filled ENR are higher, their abrasion resistance is inferior, likely to be due to the higher glass transition temperature of ENR. Variations in heat build-up and compression set of NR-silica composites modified with ENR are depicted in Fig.3.7.

Reduction in heat build-up and compression set was noted with the incorporation of ENR in small quantities. The higher crosslink density due to the presence of ENR, might have resulted in lower heat build-up and compression set. Silane modified composites exhibited lower heat build-up and compression set, which also can be attributed to the higher network density. A reduction in resilience with increased concentration of ENR was noted (Table 3.7). This can be attributed to the higher glass transition temperature and lower resilience of ENR depending on its concentration [24]. Slight lowering of hardness also was noted with the incorporation of ENR at lower concentration.

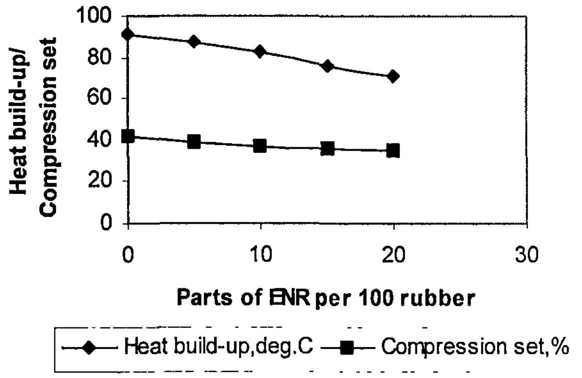


Fig.3. 7 Variation of Heat build up and compression set with ENR content

3.3.2 Effect of varying epoxy concentration (CBS/DPG system)

Silica reinforced systems generally use a binary acceleration system to compensate for the cure problems due to silica. Comparative evaluation of ENR and silane as reinforcement modifier in NR was made with a binary accelerator system viz; CBS-DPG combination in a sulphur cure system. ENR having epoxy levels of 10, 25, 50 and 60 mole percent were used for the study. Modification of silica filled NR with ENR was made by substituting NR with ENR of varying epoxy content up to a maximum blend ratio of NR:ENR of 80:20. Also silane at 2, 4, 6 and 8 percent by weight of filler was used as modifier in silica reinforced NR for comparison. Silica filled ENR also was studied. The formulations of the compounds are given in Tables 3.2 and 3.3.

a) Cure characteristics

The cure characteristics of the ENR modified samples are given in Table 3.8(a) and (b). From the data it is observed that with increasing content of ENR as well as with increase in % epoxidation, rheometric minimum torque (M_L) showed a rising trend. The observed increase in minimum torque of the ENR modified samples could be attributed to the rubber- filler network formed directly or through some complex formation with any of the other compounding ingredients. Maximum torque (M_H) also showed higher values with increasing epoxy concentration. The enhancement in maximum torque might have resulted from the enhanced network formed through cure

Table 3.8 (a)Cure chararacteristics

Property	Mix number								
	AA0	AE1	AE2	AE3	AE4	BE1	BE2	BE3	BE4
Min. torque, dN.m	11.5	12	13	13	13.5	11.6	12.8	14.7	14.8
Max. torque, dN.m	82	83	85	84	85	85	85	85.8	87
Scorch time (t_{s2}), min.	2	2	2.5	2.6	2.5	3	3	3	2.7
Opt. cure time (t_{90}), min.	5.6	5.7	5.9	5.7	5.7	6.3	6	5.5	5.5
Cure rate index ($100/t_{90}$-t_2)	28	27	29	32	31	30	33	40	36
Δ torque (Max.- min.) dN.m	70.5	71	72	71	70.5	73	72	71	72

Table 3.8 (b)Cure chararacteristics

Property	Mix number							
	CE1	CE2	CE3	CE4	DE1	DE2	DE3	DE4
Min. torque, dN.m	13.8	15	16	16.1	11.5	13.5	16	16.5
Max. torque, dN.m	86.7	87.1	87.8	89	85.8	86	86	88
Scorch time (t_{s2}), min.	3.5	3.5	3.1	3.1	3.5	3.2	3.2	3.1
Opt. cure time (t_{90}), min.	6.7	6.7	7	7	7	6.7	7.2	7.5
Cure rate index ($100/t_{90}$-t_2)	31	31	26	26	29	29	25	23
Δ torque (Max.- min.) dN.m	73	72	72	73	74.3	73	69	71

activation or rubber–filler bonding. However, with binary accelerator system the differences in scorch time, cure time, cure rate index and residual torque (M_H-M_L) among samples thin out.

Cure characteristics of the silane modified and silica filled ENR are given in Table 3.9. With progressive addition of silane, minimum rheometric torque continuously decreased and maximum torque and residual torque (M_H-M_L) increased. Lowering of minimum torque is of advantage in terms of easier processing and might be a consequence of the plasticizing effect of low molecular weight silane and the reduction in filler-filler interaction. Enhanced maximum torque with higher concentration of silane might have resulted from the larger extent of coupling bonds formed between silica and rubber through the silane. Scorch time for the silane modified compound was comparatively lower than those of the ENR modified. Processing safety, hence, is better for the ENR modified composites. Cure time showed an increase and cure rate slightly lowered with the addition of silane. Silica filled ENR also showed comparatively higher minimum torque than those of silane modified. However the maximum torque, scorch time, cure time, cure rate index and the differential torque were closer to those with silane of high loading.

Table 3.9 Cure characteristics

Property	Mix number				
	CA1	CA2	CA3	CA4	EE
Min. torque, dN.m	12	10	9	6	13
Max. torque, dN.m	92	94	94	100	99
Scorch time(ts_2),min.	1.6	1.7	2.2	2.6	2.5
Opt.cure time(t_{90}),min.	4.5	5.7	7	6.5	7
Cure rate index(100/t_{90}-t_2)	34	25	21	25.6	22.2
Δ torque,(max.-min.) dN.m	80	84	85	94	86

b) Vulcanizate properties

Vulcanizate properties of the ENR modified samples are given in Table 3.10 (a)

Table 3.10 (a) Vulcanizate technological properties

Property	Mix number								
	AA0	AE1	AE2	AE3	AE4	BE1	BE2	BE3	BE4
Mod.100%, N/mm^2	2.1	2.3	2.4	2.4	2.4	2.4	2.4	2.7	2.7
Mod.200%, N/mm^2	3.9	4.1	4.4	4.4	4.4	4.5	4.6	5	5.1
Mod.300%, N/mm^2	6.5	6.9	7.5	7.6	7.6	8.1	8.2	8.9	9
Tens.strength, N/mm^2	27	27.5	30	28	29	29.5	30.5	30.5	30
Elongation at break,%	625	640	650	650	650	665	670	670	650
Tear strength, N/mm	110	110	120	121	115	115	115	120	115
Heat build-up,°C	20	22	23	23	23	25	26	26	26
Resilience, %	63	62	62	62	62	63	62	62	62
Compression set (%)	39.5	41.4	41	41	41	39.5	40	40	40
Hardness, Shore A	62	64	64	64	65	67	69	70	71
Abrasion loss, mm^3	173	157	152	162	163	156	157	162	164
Demattia-Flex-initiation (k.cycles)	25.5	19	18	16	16	18.8	18.8	17.5	17.5
Demattia-Flex-failure (k.cycles)	42.5	36.8	30.5	28.5	29	35.4	33.5	32.5	32

Table 3.10 (b) Vulcanizate technological properties

Property	Mix number							
	CE1	CE2	CE3	CE4	DE1	DE2	DE3	DE4
Mod.100%, N/mm^2	2.8	2.8	3.2	3.4	2.7	2.8	3.1	3.2
Mod.200%, N/mm^2	5.2	5.3	6.1	6.4	5.2	5.3	6.1	6.2
Mod.300%, N/mm^2	9	9.1	10.1	11.3	9.2	9.2	10.1	10.3
Tens.strength, N/mm^2	29.5	30.5	29	28.2	28.3	28	28	27
Elongation.at break,%	640	650	620	605	620	620	625	610
Tear strength, N/mm	120	120	115	115	120	122	116	116
Heat build-up,°C	25	26	26	27	27	28	29	30
Resilience, %	60	54	52	49	57	51	47	40
Compression set (%)	40	40	40	41	41	41	41	40
Hardness, Shore A	70	72	74	75	72	72	73	75
Abrasion loss,mm^3	153	151	158	168	154	154	162	168
Demattia-Flex-initiation (k.cycles)	18	12.8	11.5	10.2	11.5	10.4	11	8.9
Demattia-Flex-failure (k.cycles)	35	28.9	24.7	20.3	30.9	27.5	24.2	17.5

Table 3.11 Vulcanizate technological properties

Property	Mix number				
	CA1	CA2	CA3	CA4	EE
Mod.100% N/mm^2	3.1	4.1	4.4	4.2	3.7
Mod.300% N/mm^2	10.5	14.8	15.4	15.3	14.5
Tens.strength,N/mm^2	27	28	28.4	27.5	24.1
Elongn.at break,%	530	490	480	470	520
Tear strength,N/mm	111	111	113	110	82
Heat build-up,°C	22	20	21	24	40
Resilience,%	61	63	62	58.4	38
Compression set,%	23	23	23.5	26	41
Hardness, Shore A	65	66	67	74	75
Abrasion loss,mm^3	144	126	121	111	168
Demattia- flex.-Init.(k.cycles.)	12.5	9	7.7	7.6	7.1
Demattia-flex.-failure.(k.cycles.)	27	24.7	24	23.2	21

and (b) and that of silane modified and silica filled ENR in Table 3.11. Fig.3.8 gives a comparison of the change in modulus with various modifiers at different concentrations (in the figure the data point 0 stands for control and 1, 2, 3, 4 stands for 5, 10, 15 and 20 parts of ENR and 1, 2, 3 and 4 phr of silane respectively). For the ENR modified, modulus in general, increases in a regular manner with the concentration of epoxy content and the extent of epoxidation. This clearly indicates the role of epoxy functionality in modulus enhancement, resultant of rubber-silica bonding. Silane modified compounds exhibited higher rate of modulus enhancement than the ENR modified with concentration of silane. For the silane modified compounds, the modulus enhancement is attributed to the rubber-filler coupling through silane. With binary accelerator system, the cure discrepancies due to the polarity of silica is not significant and the modulus improvements noticed in both the cases might have originated from better rubber-filler bonding either through ENR or silane. Strength variations of different modified composites are plotted in Fig.3.9. Tensile strength improved with the incorporation of ENR and exhibited optimum at about 10-15 parts of ENR at varying levels of epoxidation. Composites modified with optimum ENR exhibited better strength over silane modified compounds. Silane also exhibited improvement in strength beyond about four percent by weight of filler. On modification with ENR 10 and 25, elongation at break showed an increase over the unmodified, while with ENR 50 and 60 up to 15 parts, it remained almost similar and at higher loading slight reduction occurred. Better

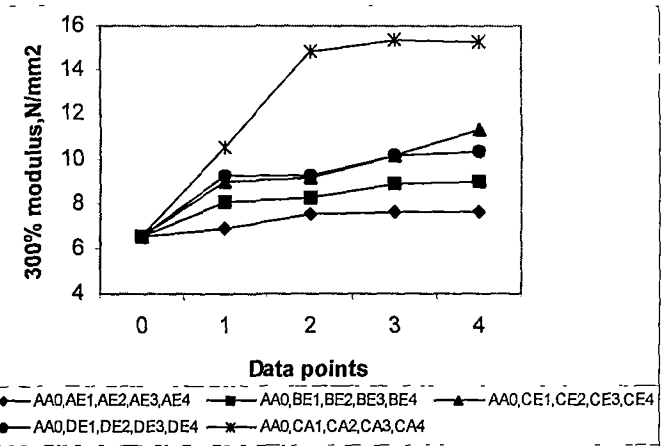


Fig. 3.8 Variation of modulus with concentration of ENR and silane

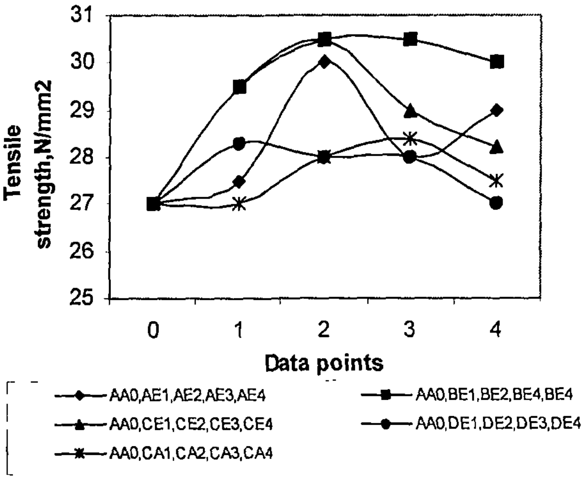


Fig. 3.9 Variation of tensile strength with concentration of ENR and silane

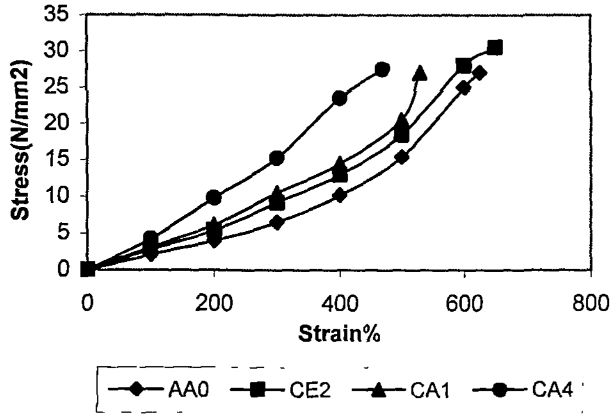


Fig.3. 10 Comparison of stress-strain property

filler distribution is reported to contribute to higher elongation; whereas higher the extent of rubber-filler interaction, reduces it. Larger extent of rubber-filler interaction at higher levels and concentrations of epoxy content might have caused the reduced elongation. For the silane modified, compounds comparatively larger drop in elongation is observed due to the larger cross link density realized from rubber-rubber and rubber-filler bonds. Stress-strain properties of selected samples viz; unmodified (AA0), ENR50 (10 parts, CE2) and silane modified (2 and 8 percentage, CA1 and CA4) are compared in Fig.3.10. On modification with about 10 parts of ENR strength properties closer to that of about 2 percent silane treatment could be achieved. Variations in tear strength and abrasion loss are plotted in Figs.3.11 and 3.12. Tear strength and abrasion resistance, measures of reinforcement, were found improved and passed through a maximum with ENR modification. Compression set and heat build-up, resultant of the viscous component of the silica filled ENR modified system was slightly higher than the unmodified and exhibited an increasing trend with increasing levels of epoxy concentration. Resilience, a measure of the elastic component, was found decreased with ENR incorporation. Changes in compression set, heat build-up and resilience could be attributed to the lower molecular mobility or lower elasticity of the ENR. Presence of ENR, a polymer having higher Tg and lower mobility, might have caused this. However, with silane, lower set and, heat build-up and higher resilience were noted, which can be attributed to the enhancement in the elastic component achieved through silane induced crosslinking. Hardness, a measure of the low strain elastic modulus, was found to be higher for the ENR modified samples and the level of enhancement was

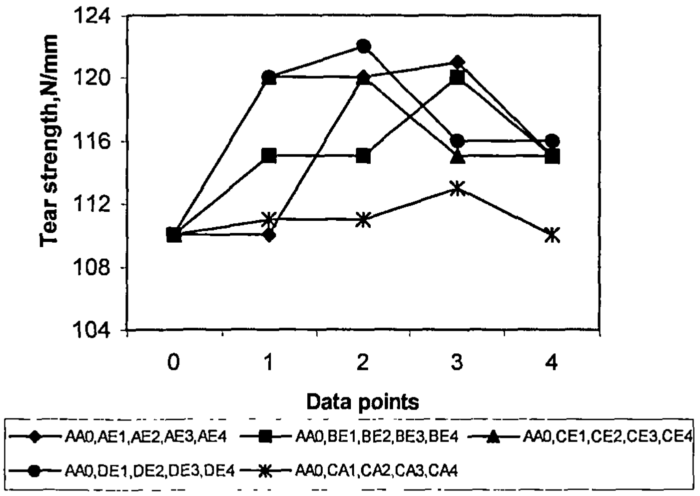


Fig. 3.11 Variation of tear strength with concentration of ENR and silane

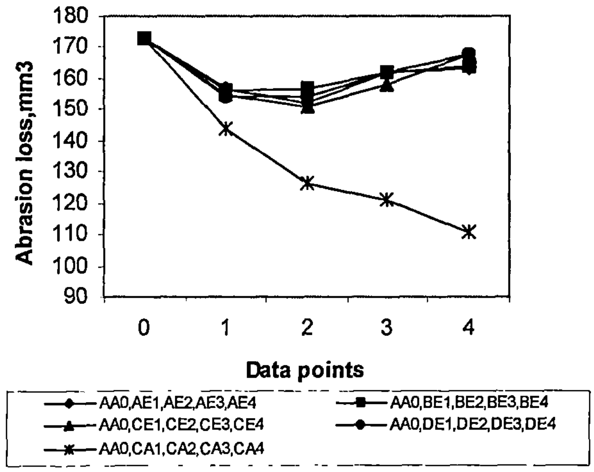


Fig. 3.12 Variation of abrasion loss with concentration of ENR and silane

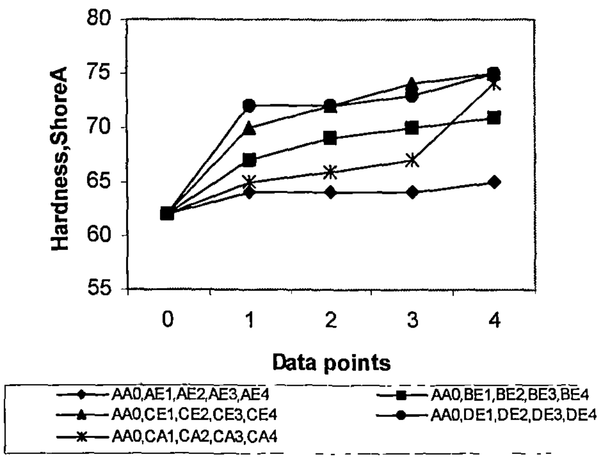


Fig.3.13 Variation of hardness with concentration of ENR and silane

proportional to the extent of epoxidation. Variations in hardness of different modified samples are compared in Fig.3.13. Higher levels of rubber-filler interaction resulting in a closely packed densifiedcomposite might have raised the low strain modulus. Silane modified compound also exhibited progressive concentration dependant enhancement in modulus. Higher composite packing density due to rubber-filler bonding and higher crosslink density might be the reason for it. Demattia flexing an important measure of the flex resistance, especially for tyre applications, also was evaluated for the experimental samples. The number of flex cycles required for crack initiation and final failure was higher for the silica filled NR over that of the ENR or silane modified. This might be resultant of the lower modulus of the unmodified composite. From the data given in Tables 3.8, a decline in the number of cycles required for crack initiation and failure with the level of epoxy content and concentration was noted. Higher hardness and modulus of the samples modified with high epoxy content might have reduced the flex life. Flex life of silane modified samples were comparable to that of those modified with high epoxy content ENR (Table 3.9).

For the silane modified systems modulus and hardness increased and elongation at break decreased with increase in concentration of silane. Higher levels of crosslinking, as observed from the rheograph, also supports this. Improvement in tensile strength could also be achieved with incorporation of silane. Abrasion resistance showed considerable enhancement with silane modification and is concentration dependant, whereas tear strength improvement was only marginal. Minor drop in heat build-up and increase in resilience was observed on addition of coupling agent. Silane modified samples generally exhibited higher flex resistance. However, the same dropped with the concentration of modifier, which is likely to be due to the higher modulus. Though silica filled ENR exhibited modulus values closer to those of the silane modified, its abrasion resistance is inferior. Abrasion resistance of a polymer is dependent on its glass transition temperature. Higher glass transition temperature of ENR over NR might have caused the lower abrasion resistance of silica reinforced ENR.

c) Volume fraction

For a comparative evaluation, selected samples were subjected to swelling study in toluene. Volume fraction of rubber was determined. The data are given in Table3.12.

Table 3.12 Volume fraction of rubber

Property	**Sample number**		
	AA0	**CE2**	**CA2**
Volume fraction of rubber,Vr	0.138	0.153	0.17

ENR and silane modified compounds samples showed higher volume fraction of rubber. Compared to the ENR modified, the silane modified exhibited comparatively higher volume fraction of rubber. The observed trend in modulus values are in agreement with the V_r values which is an indirect measure of crosslink density of the filled matrix.

d) Ageing resistance

The data on ageing resistance of selected ENR modified, silane modified and carbon black filled samples are given in Table 3.13. Ageing of various samples was carried out at 100^0C for 24 and 48 h. It is observed that the ENR modified exhibited initial enhancement in modulus followed by a decline. The likely reasons for modulus enhancement of a filled vulcanizate are further crosslinking or filler reagglomeration at higher temperature. As the epoxy content increases chances for the extent of rubber-filler interaction, crosslinking will be higher and the chances for filler reagglomeration get reduced with increasing polarity of ENR. The silane modified and carbon black filled samples also, after 24 h. of ageing, exhibited modulus enhancement. However, on further ageing, modulus showed a declining tendency. The silane modified sample exhibited higher extent of strength retention on ageing than the ENR modified; after 24 and 48 hours of ageing, the silane modified retained about 83 and 73 percent respectively. Corresponding strength retention of various ENR modified samples was in the range of 71-75 and 63-65 percent and that of carbon black filled was 78 and 58 percent respectively. Elongation at break of all the experimental vulcanizates decreased on ageing. Modulus enhancement on ageing might have resulted in a drop in elongation. Retention of EB for various ENR modified samples was in the range of 76-84 and 69-73 after 24 and 48 h. of ageing respectively. The corresponding values for the silane modified samples are 87 and 85 respectively, while that of carbon black filled was 76

Table 3.13 Ageing resistance

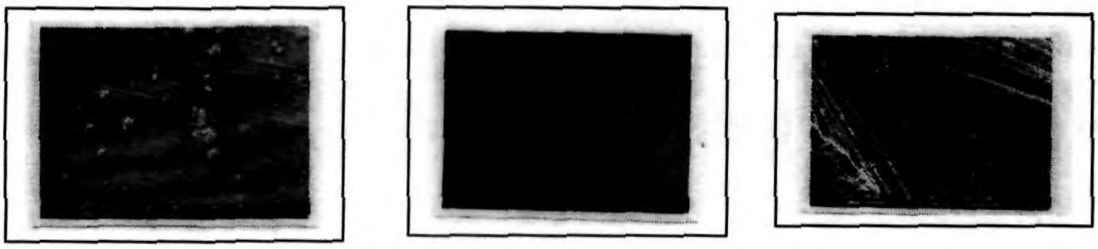
Property	Sample number						
	AA0	AE2	BE2	CE2	DE2	CA4	H
300% modulus [a]	138	128	117	111	102	101	105
300% modulus [b]	130	124	102	101	103	95	90
Tensile strength [a]	71.5	74	75	73	71	84	78
Tensile strength [b]	61	65	64	64	63	73	58
Elongation at break,% [a]	77	84	81	76	77	87	76
Elongation at break,% [b]	67	73	72	74	69	85	61

[a] % Retention after 24 h. of ageing, [b] % Retention of property after 48 h. of ageing

and 61 respectively. The studies indicate that the inherent ageing resistance of ENR modified silica filled NR is in between that of the silane modified and carbon black filled NR. The ENR modified sample exhibited better resistance to ageing than the silica filled NR which can be attributed to better silica-rubber interaction..

e) Scanning electron microscopy

Coupling agents not only contributes to an improvement in filler-rubber bonding, but also facilitates a better dispersion of the filler in the rubber matrix [6,25]. The SEM micrographs of the silica filled NR and those of ENR and silane modified compound are shown in Fig. 3.14 a, b and c.



a) NR/silica(AA0) b) NR/ENR/silica (CE2) c) NR/silane/silica (CA4)

Fig. 3.14 SEM Photographs

It is seen that filler agglomerates in the silica composites modified with Si69 and ENR is smaller in size and less in number than those in the unmodified samples. This indicates that ENR in small quantities added to silica filled NR is effective in controlling the size and distribution of silica which might have contributed to the improved technological properties.

3.4 Conclusions

Evaluation of ENR as a reinforcement modifier in silica filled NR was made in comparison with silane modified and carbon black filled NR. The cure retarding tendency of silica got reduced with the incorporation of small quantities of ENR. Technological properties also got improved with ENR modification. However, the silane modified samples exhibited superior technological properties. For the carbon black filled

NR, CBS cure gave satisfactory technological properties, while the silica filled required a secondary accelerator. Modification with ENR of varying epoxy content, revealed that the extent of property improvement is dependent on the extent of epoxidation and the concentration of the modifier. Optimum performance properties were achieved for a concentration of 10-15 parts of ENR. ENR-50 exhibited comparatively better performance. Technological properties of the silane modified samples were also concentration dependent. Microscopic studies revealed that both ENR and silane could improve the distribution of silica in NR. Silica filled ENR, though exhibited strength properties comparable to that of silane and cabon black filled NR, the other important performance properties were adversely affected. Partial substitution on NR with ENR up to an optimum concentration provided better reinforcement properties for silica filled NR.

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CHAPTER 4

DYNAMIC MECHANICAL PROPERTIES OF SILICA FILLED NATURAL RUBBER MODIFIED WITH EPOXIDISED NATURAL RUBBER

4.1 Introduction

Rubber is frequently used for applications in which it undergoes rapid cyclic deformations at varying frequencies. Dynamic mechanical properties describe the response of materials to periodically varying strain or stress and are usually measured as functions of frequency or temperature. Under cyclic deformation the energy dissipated as heat is measured as loss modulus and the energy stored and recovered is measured as storage modulus. The ratio of loss modulus to storage modulus gives the loss tangent ($\tan\delta$) which indicates the damping characteristics of the material[1]. Dynamic measurements are important for rubber products which undergo cyclic deformations while in use such as engine mounts and tyres. Heat generation or fatigue life is important for the former and heat generation and skid or rolling resistance are important for the latter. Rolling resistance is related to the movement of the whole tyre corresponding to deformation at a frequency of about 10 to 100 Hz and a temperature of about 50 to 80^{0}C. The frequency of the movement corresponding to skid or wet grip is very high of the order of 10^4 to 10^7 Hz at room temperature. However, due to the difficulties in measurement of these properties at high frequencies, the frequency is reduced to a measurable level, usually at 1 Hz and at lower temperature by applying the frequency-temperature equivalence principle based on WLF equation [2-5]. High performance tyre should exhibit a low $\tan\delta$ at 50-80^{0}C for lower rolling resistance and high $\tan\delta$ at about 0^{0}C for high skid resistance and wet grip [6,7].

Incorporation of filler in polymer or blending of polymers are known to cause changes in dynamic properties. The viscoelastic properties of filled systems depend on several factors such as filler-filler, polymer-filler and polymer-polymer interactions[8-10]. For the polymer blends, the compatibility among the blend components, the selective adsorption of polymer by the filler due to polymer-filler interaction, blend composition and morphology and the filler distribution in the blend components are important. Dynamic mechanical analysis gives valuable information on the morphology of blend systems, filler-filler and polymer-filler interactions and could also be used for the measurement of rolling resistance and wet traction of tyre composites [11-13].

Unlike carbon black, silica provides lower rolling resistance to tyres. However, silica has the disadvantages of poor polymer-filler interaction and strong filler-filler interaction. Silane modification of silica filled systems is reported to reduce the filler-filler interaction and improve its polymer-filler interaction resulting in improved dynamic mechanical characteristics [14]. Epoxidised natural rubber is reported to have better interaction with silica. Use of ENR in tyre tread compositions could enhance their wet grip [15,16].

The present chapter discusses the effect of blending small quantities of ENR of varying epoxy content with silica filled natural rubber on its viscoelastic properties in a range of temperature. ENR is presumed to promote better rubber-silica interaction in silica filled natural rubber and therefore better reinforcement. ENR modified systems are compared with silane modified silica filled NR and carbon black filled NR.

4.2 Experimental

4.2.1 Materials

Natural rubber- ISNR-5, was obtained from the Pilot Crumb Rubber Factory, Rubber Research Institute of India (RRII). Epoxidised natural rubber (ENR10, ENR25, ENR50 and ENR60) were prepared in the pilot plant of RRII. Ultrasil VN3 (BET surface area 175 m^2/g) and the silane coupling agent (Si69) were products of Degussa AG, Germany. Carbon black (ISAF) was the product of Phillips Carbon Black Ltd., India. The other ingredients were of rubber grade.

4.2.2 Testing

The viscoelastic properties of the vulcanizate samples were determined using a dynamic mechanical analyzer model DMA-2980 of TA Instruments Ltd, USA using a dual cantilever device. Rectangular vulcanizate samples of dimension 35mm x12.5mmx2 mm were used. The tests were carried out at a frequency of 1 Hz at 0.1% strain in a temperature range of –80 to +100^{0}C with a heating rate of 2^{0}C /minute. Liquid nitrogen was used as the coolant.

4.3 Results and Discussion

4.3.1 Viscoelastic properties

Viscoelastic properties of the rubber composites depend on the molecular motion of the elastomers, which in turn, depends on temperature. Decrease of temperature causes resistance to molecular motion and hence will lead to higher storage modulus. At sufficiently low temperature $\tan\delta$ value is very low, because the viscosity of rubber is so high and the free volume of the polymer is so small that the movement of the polymer segments hardly take place in the normal conditions of the dynamic experiment. This will result in low energy dissipation and hence low hysteresis. Under this condition the polymer is stated to be in the glassy state with very high elastic modulus (G'). With increase in temperature the movement of the polymer segments increases. When the temperature reaches a certain level, the free volume of the polymer increases more rapidly than the volume expansion of the molecules, facilitating segmental motion. The temperature at which this occurs is known as the glass transition temperature, Tg. From the Tg point, the viscosity of the polymer decreases very rapidly and molecular adjustment take place easily resulting in the drop of elastic modulus and a consequent rise in energy dissipation (loss modulus, G'') or hysteresis. However, on further heating up to a sufficiently high temperature, the Brownian motion is very rapid resulting in low viscosity and the polymer molecule exhibits segmental motion or low resistance to strain and is said to be in the rubbery state with low modulus and low energy dissipation. Between the glassy and rubbery region is the transition zone where the elastic modulus drops monotonically by several orders of magnitude and loss modulus (G'') and loss tangent (tan δ) pass through a maximum [1,8].

4.3.2 Viscoelastic properties of silica filled NR and its modified forms

Viscoelastic properties of silica filled NR and that modified with ENR and silane coupling agent, carbon black filled NR and silica filled ENR50 were studied. The variations of viscoelastic properties of silica filled NR on incorporation of ENR of varying epoxy content at different dosages in a temperature range of –80 to +100^{0}C were examined. ENR of epoxy content 10, 25, 50 and 60 mole percent were incorporated into silica filled NR by substituting 5, 10, 15 and 20 parts of NR per hundred rubber by weight with corresponding ENR. ENR modified systems were compared with silane modified silica filled NR and carbon black filled NR. Silica filled NR modified with

Table 4.1(a) Formulation of mixes

Ingredients*	***Mix number***								
	AA0	**AE1**	**AE2**	**AE3**	**AE4**	**BE1**	**BE2**	**BE3**	**BE4**
NR	100	95	90	85	80	95	90	85	80
ENR 10	-	5	10	15	20	-	-	-	-
ENR 25	-	-	-	-	-	5	10	15	20

* Also contains ZnO 5, Stearic acid 2, Ultrasil VN3 50, CBS 1.5, DPG 2, Naphthenic oil 5 and Sulphur 2

Table 4.1(b) Formulation of mixes

Ingredients*	Mix number							
	CE1	CE2	CE3	CE4	DE1	DE2	DE3	DE4
NR	95	90	85	80	95	90	85	80
ENR 50	5	10	15	20	-	-	-	-
ENR 60	-	-	-	-	5	10	15	20

* Also contains ZnO 5, Stearic acid 2, Ultrasil VN3 50, CBS 1.5, DPG 2, Naphthenic oil 5 and Sulphur 2

Table 4.2 Formulation of mixes

Ingredients	Mix number				
	CA1	CA2	CA3	H	EE
NR	100	100	100	100	-
ENR 50	-	-	-	-	100
ZnO	5	5	5	5	5
St.acid	2	2	2	2	2
Ultrasil VN3	50	50	50	-	50
CBS	1.5	1.5	1.5	1.5	1.5
DPG	2	2	2	-	2
Naphthenic oil	5	5	5	5	5
Sulphur	2	2	2	2	2
Si 69	1	2	3	-	-
ISAF	-	-	-	50	-

silane at concentrations of 2, 4 and 6 percent by weight of silica filler were studied. The selected mixes from Chapter 3 were used for DMA analysis and their formulations are given in Tables 4.1 (a) and (b) and 4.2. Samples were prepared by curing the mixes at 150°C to optimum cure time (t_{90}) and were subjected to dynamic mechanical analysis. Storage modulus, loss modulus and tan δ variations with temperature were examined.

a) Storage modulus

Dynamic modulus of elastomers is temperature dependent. Modulus of filled systems are also dependent on factors such as filler- filler and polymer-filler interactions. With decreasing temperature, filler-filler and polymer–filler interaction increase [1]. Elastic modulus in general increases with filler loading[17,18]. Filler networking will result in 'occluded rubber' which, normally at low strain, will not exhibit rubbery behavior and hence is considered a part of filler, thereby raising the 'effective filler volume' and hence exhibits high modulus[19]. However, at high strain the filler network will be broken releasing the 'occluded rubber' resulting in a lower filler fraction and low modulus. Physi-sorption or chemi-sorption of polymer molecules on the filler surface due to the polymer-filler interaction results in the restriction of mobility of those adsorbed molecules hence affecting their viscoelastic behavior[20,21]. Adsorbed polymer molecules on the filler surface act as a rubber shell. The concept of rubber shell can explain the reduction in "storage modulus" with increasing temperature. Absorbed polymer causes a broader relaxation spectrum. Raising temperature reverses the molecular immobilization of the adsorbed molecules and hence will result in a decrease in modulus[8,22,23]. Surface modification of silica with materials like di-ethylene glycol (DEG) reduces the dynamic modulus. Modification with mono functional silanes, though improves the filler dispersion, could not enhance polymer-filler interaction and therefore, result in lower static modulus and poor failure properties. Bifunctional silanes cause polymer-filler linkages through covalent bonds. Silane treatment reduces 'Payne effect' and improves dynamic properties[24-27].

Storage modulus variations with temperature of silica filled NR modified with ENR10, 25, 50 and 60 each at 4 different concentrations were compared with silane modified and carbon black filled NR in Figs.4.1 to 4.5 and in Table 4.3. Peak transition temperatures are given in Table 4.4.

Comparison of the variations of storage modulus of ENR10 modified, (AE1 to AE4) with that of silica filled NR (AA0) is given in Fig.4.1 and Table 4.3. Fig. 4.1 shows that the modulus below -70°C can be treated as glassy modulus. With incorporation of ENR10 up to 15 parts showed a drop in glassy modulus from 2450 MPa to 2119 MPa. The transition from glassy state starts at about –70°C. With rise in temperature the ENR modified mix exhibited a broadened relaxation than the silica filled

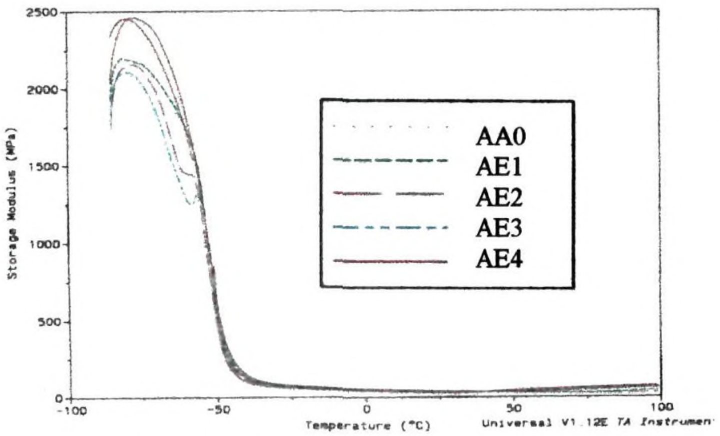

Fig.4.1 Comparison of storage modulus of ENR 10 modified silica filled NR

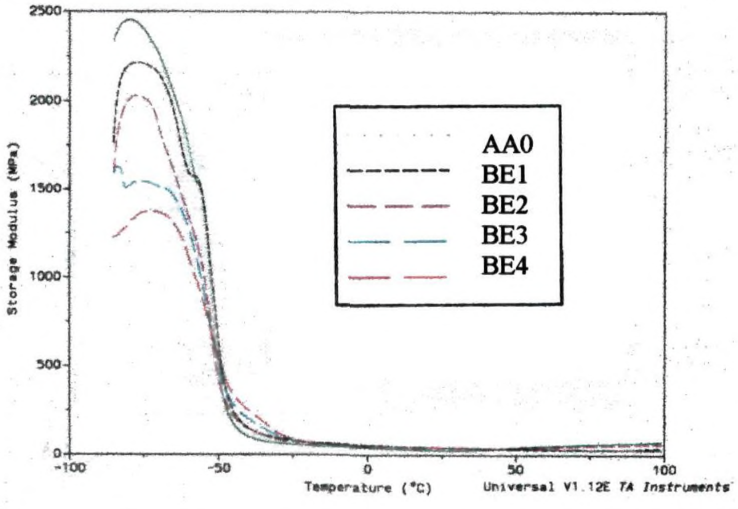

Fig.4.2 Comparison of storage modulus of ENR 25 modified silica filled NR

NR. The glassy modulus can be resultant of filler-filler, polymer-filler and polymer–polymer interactions. The relaxation spectra of storage modulus at about - 45^{0}C showed minor progressive positive temperature shift or a shoulder formation towards the end of the transition due to NR with incorporation of ENR10, which is likely to be due to the

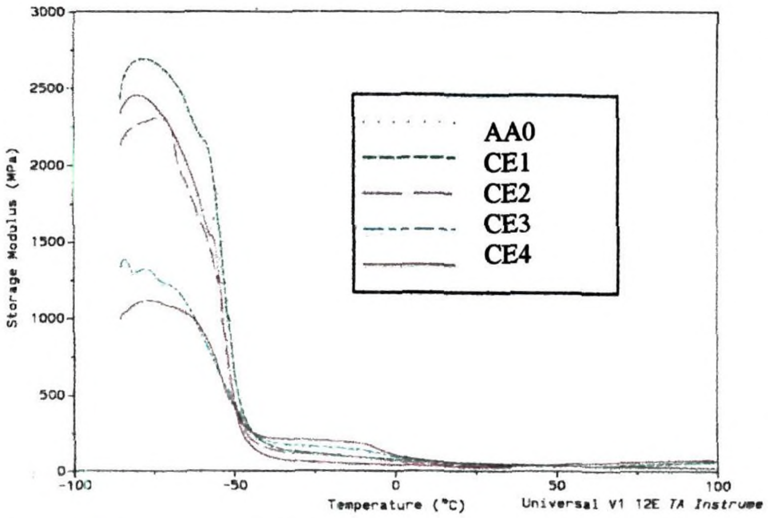

Fig.4. 3 Comparison of storage modulus of ENR 50 modified silica filled NR

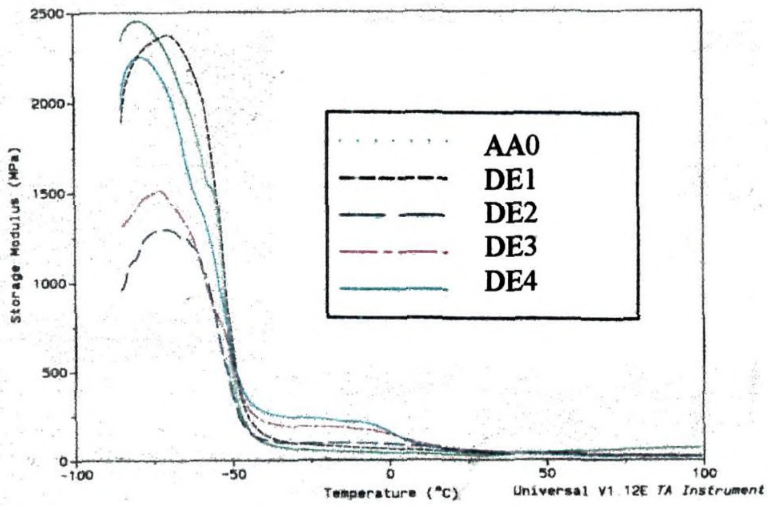

Fig.4.4 Comparison of storage modulus of ENR 60 modified silica filled NR

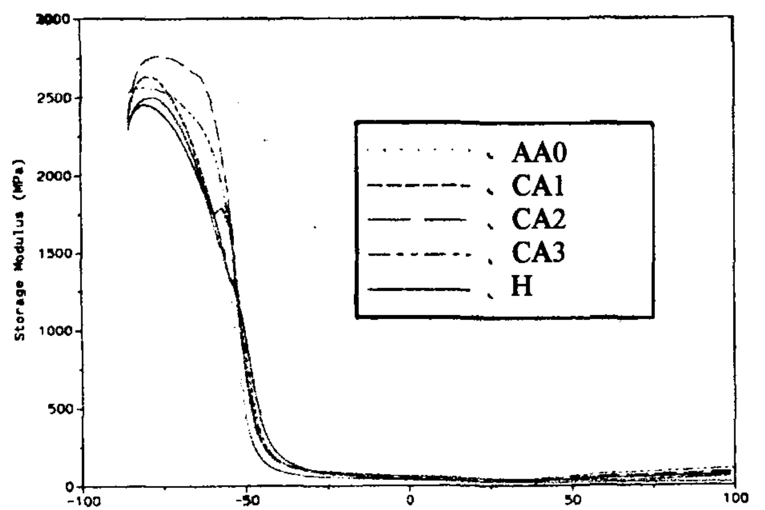

Fig.4. 5 Comparison of storage modulus of Silane modified silica filled NR and carbon black filled NR

Table 4. 3 Comparison of Storage modulus (G')

Sample	**Storage modulus (MPa)**							
	-70°C	**-45°C**	**-40°C**	**-25°C**	**-12.5°C**	**0°C**	**50°C**	**80°C**
AA0	2450	124	-	-	-	-	45	65
AE1	2202	149	-	-	-	-	31	10
AE2	2169	148	-	-	-	-	30	25
AE3	2119	155	-	-	-	-	34	56
AE4	2450	182	-	-	-	-	35	51
BE1	2218	-	132	-	-	-	34	31
BE2	2036	-	132	-	-	-	48	50
BE3	1540	-	182	-	-	-	37	33
BE4	1375	-	248	-	-	-	37	30
CE1	2701	-	-	100	-	-	29	49
CE2	2314	-	-	100	-	-	42	57
CE3	1350	-	-	159	-	-	36	20
CE4	1132	-	-	209	-	-	34	14
DE1	2367	-	-	99	-	-	30	22
DE2	1291	-	-	99	-	-	39	29
DE3	1507	-	-	199	-	-	39	29
DE4	2230	-	-	248	-	-	39	21
CA1	2632	149	-	-	-	-	36	46
CA2	2761	150	-	-	-	-	50	75
CA3	2562	150	-	-	-	-	59	95
H	2503	198	-	-	-	-	22	23
EE	2741	2443	2403	2026	227	198	40	40

broadening of the relaxation due to the ENR. Temperature region of –70 to -30°C can be treated as the transition region. Also the dynamic storage modulus in the temperature range of – 50^0C to 30^0C was slightly higher for the ENR modified mix and is in the range of 124 to 182 MPa. Higher modulus is probably due to the ENR phase which remains in association with the silica filler. The temperature region of –25 to 100°C can be treated as rubbery region. The dynamic modulus in the rubbery region of 40 to 100^0C showed a decrease with ENR incorporation likely to be due to the reduction in filler-filler interaction.

Variations of the storage modulus of the ENR25 modified (BE1 to BE4) systems are given in Fig. 4.2 and Table 4.3. On substitution with ENR25, the glassy modulus is

Table 4. 4 Comparison of transition temperature

Sample	Peak Transition Temperature, °C			
	Loss peak, 1[a]	Loss peak, 2[b]	Tan δ peak, 1[a]	Tan δ peak, 2[b]
AA0	-52	-	-49	-
AE1	-51	-	-49	-
AE2	-51	-	-48	-
AE3	-49	-	-47	-
AE4	-50	-	-48.5	-
BE1	-48	-	-47	-25
BE2	-51	-32	-48.5	-29
BE3	-51	-32	-48.5	-29
BE4	-51	-32	-48.2	-29
CE1	-50	-6	-48	0
CE2	-51	-6	-48.5	-2
CE3	-50	-6	-48	-2
CE4	-51	-6	-48	-2
DE1	-50	1	-49	13
DE2	-48.5	1	-48	10
DE3	-49	1	-48.3	6.6
DE4	-48.5	1	-50.4	3.9
CA1	-52.5	-	-47.4	-
CA2	-51.5	-	-47.4	-
CA3	-50.5	-	-46.4	-
H	-49	-	-44.8	-
EE	-	-9.4	-	-6.1

a – Transition peak due to NR, b - Transition peak due to ENR seen at about –70^{0}C. With addition of ENR25, a progressive drop in glassy modulus from 2450 MPa to 1375 MPa was noted. Glass transition took place in the temperature range of –70 to -25°C. Silica filled NR, immediately after transition of the NR phase showed the lowest modulus at about –45^{0}C, whereas the ENR25 modified system showed a modulus crossover with the unmodified at about –50^{0}C giving a shoulder peak towards the end of NR transition exhibiting progressively higher modulus in the temperature region of –45^{0}C to -25^{0}C. Peak modulus values at –40°C varied from about 132 to 248 MPa probably due to the transition of ENR phase. Broadening of transition is associated with the filler-matrix interaction[28]. Rubbery modulus in the temperature region 45 to 100^{0}C showed a decrease with ENR incorporation likely to be due to lesser filler-filler interaction in the modified system.

Changes in storage modulus of ENR50 modified (CE1 to CE4) systems are given in Fig. 4.3 and Table 4.3. These systems showed the glassy modulus at about –75^{0}C and with temperature enhancement the onset of transition occurs. Compared to the silica filled NR, with 5 parts of ENR50 a minor increase in glassy modulus and a positive temperature shift in transition were noted. Small quantities of ENR function as a cure activator in silica filled rubber[29]. Higher network density in the presence of ENR and the enhanced rubber-filler interaction might have resulted in higher modulus and shift in transition. With 10 parts of ENR onwards a drop in glassy modulus was noted. With 15 and 20 parts considerable reduction in glassy modulus was observed. Modulus values dropped from 2450 to 1132 MPa. With higher concentrations of ENR a stepwise and broadened transition was seen. The storage modulus in the temperature range of –45 to +30^{0}C was higher for the ENR modified and was proportionate with ENR concentration. Values varied in the range of 100 to 209 MPa. Rubbery modulus in the temperature range of 50 to 100^{0}C was lower for the ENR modified. With 15 and 20 parts a progressive reduction was noted. This might be due to the reduction in filler-filler bonds.

Dynamic modulus of the ENR60 modified (DE1 to DE4) systems are given in Fig. 4.4 and Table 4.3. On substitution with 5 parts of ENR60 a minor positive shift in transition temperature was noted likely to be due to improved rubber-filler interaction and enhanced network density resulting from cure activation. With incorporation of ENR glassy modulus showed considerable reduction. Modulus dropped from 2450 MPa to 1291 MPa. However, the storage modulus in the temperature range of –45 to 0^0C showed a progressive increase with ENR concentration, which corresponds to the transition of ENR. The values varied from 99 MPa to 248 MPa. The higher the concentration of ENR, the broader the transition. In the temperature range of 50 to 100^0C with ENR modification considerable reduction in storage modulus was observed with rise in temperature which can be attributed to the reduction in filler networking with temperature.

A comparison of the variations in storage modulus of carbon black filled (H) and the silane modified systems (CA1 to CA3) are given in Fig.4.5 and Table 4.3. The carbon black filled and the unmodified silica filled mixes showed glassy modulus values in a closer range at about –75°C. The silane modified system in general exhibited higher glassy modulus than the carbon black filled and the unmodified systems. Values varied in the range of 2503 to 2761 MPa. The higher glassy modulus of the silane modified mix might be a resultant of the covalent bonds formed between silica and the polymer matrix through the silane. Phase transition as shown by modulus drop showed a positive temperature shift with silane modification and carbon black loading. Compared to the silica filled mix, the carbon black filled NR exhibited positive temperature shift in transition towards the extreme end. The silane modified mix also showed a similar trend but to a lesser extent. For the unmodified and carbon black filled mixes, modulus transition begins at about –75^0C while that in the silane modified system is at about

–70 to –65^{0}C. In the temperature range of –45 to 10^{0}C, the storage modulus was higher for the silane modified and the black filled which is likely to be due to better rubber-filler interaction. Silane at 2 percent concentration exhibited lower storage modulus than the unmodified mix in the temperature range of 50-100°C. However, modulus gets enhanced over the unmodified mix with higher concentrations of silane. Temperature dependant filler flocculation or the silica-silane bonding might have enhanced the modulus at high temperature ^{30}. Corresponding dynamic modulus of the carbon black filled mix was the lowest and exhibited only a minor enhancement at higher temperatures. The lower modulus of the carbon black filled mix may be due to lower level of filler-filler networking.

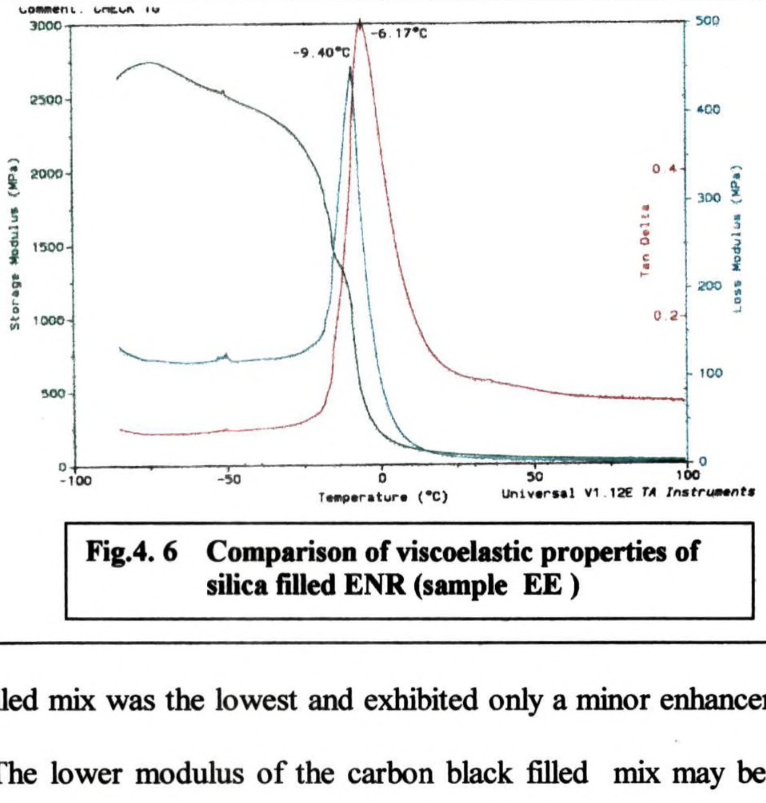

Fig.4. 6 Comparison of viscoelastic properties of silica filled ENR (sample EE)

Viscoelastic properties of silica filled ENR50 (EE) is given in Fig. 4.6 and Table 4.3. Glassy modulus value of silica filled ENR50 is similar to that of the silane modified mix and is about 2741 MPa. Transition took place in a broader temperature range of -75°C to 0°C. Unlike silica or carbon black filled NR, major transition and consequent drop in modulus of the silica filled ENR50 occur at about -6°C. Beyond 0°C, modulus showed a decreasing tendency indicating drop in filler-filler or polymer–filler interaction with temperature.

Transition behavior due to the NR phase of the carbon black filled mix is similar to that of the ENR10 and ENR25 modified silica filled system. With ENR modification of silica filled NR, the general drop in glassy modulus seen at about -70°C may be attributed to any of the factors such as reduction in filler-filler interaction due to the plasticizing effect of ENR or the hindrance to crystallization of the NR phase due to the ENR-silica interaction or due to the enhanced 'effective filler volume' due to the intercalation of ENR into the silica network[5,31]. The drop in modulus in general was dependent on the polarity of ENR; the higher the polarity of ENR, the higher the drop in glassy modulus. With ENR incorporation modulus transition get broadened dependent on the polarity of ENR and the widening of ENR transition could be attributed to the ENR-silica interaction. Also with ENR of higher polarity the storage modulus in the rubbery region (40 to 100 °C) exhibited a linear decrease, which could be attributed to the reduction in filler-filler interaction.

b) Loss modulus

Loss modulus or hysteresis of an elastomer is a measure of its energy dissipation capacity. Gum rubber gives relatively low hysteresis at high temperature. However, at the transition zone it is the elastomer which dissipates energy. Increased polymer-filler interaction will lead to rubber shell formation over the filler surface and will result in enhanced effective filler volume. High 'effective filler volume' increases hysteresis. Polymer-filler network also determines a critical role in its dynamic properties. Rubber shell formation over the filler surface explains the reduction in loss modulus with temperature. Hysteresis also depends on filler morphology. Hysteresis of silica filled rubber increases with temperature due to the clustered network. Silane treatment improves dynamic hysteresis. Breakdown and reformation of filler network and filler-polymer network causes additional energy dissipation and therefore results in high hysteresis in the rubbery state. In the transition region the hysteresis is due to the polymer[1,8].

Variations of loss modulus with temperature on incorporation of ENR10 is given in Fig. 4.7. Peak value of loss modulus due to the NR phase transition showed a decrease with progressive incorporation of ENR from 584 to 489 MPa. Transition peak due to the loss component of silica filled NR is seen at about -52°C. On incorporation of ENR10, peak loss modulus values showed a decrease with addition of up to 15 parts of ENR. However, with 20 parts a minor increase was noted. Peak narrowing and a minor positive peak shift with addition of ENR10 is observed. Maximum peak shift occurred from –52°C to -49°C. Blending of ENR10 with silica filled NR did not exhibit a two phase system as only one loss peak is observed. Reduction in peak height and narrowing of peak indicate lesser energy dissipation in the transition region of NR. At the transition temperature of NR, ENR10 which may remain preferentially adhered to the filler will

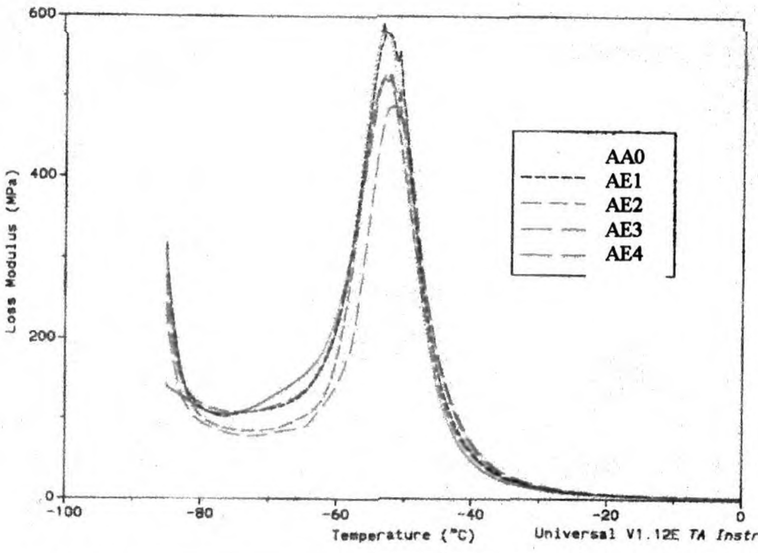

Fig. 4. 7 Comparison of loss modulus of ENR 10 modified silica filled NR

remain in the glassy state and is not capable of dissipating energy. Positive shift of peak transition temperature can be attributed to improved rubber-filler interaction, higher network density and the transition of ENR phase at high temperature in continuity to the NR phase[15]. With the incorporation of ENR, at about –40°C progressively higher loss modulus dependent on its concentration was noted. This could be attributed to the transition of ENR phase. Loss modulus of the ENR10 modified mix in the rubbery region of 40 to 100°C was lower than that of the unmodified mix, which could be attributed to lower filler-filler interaction.

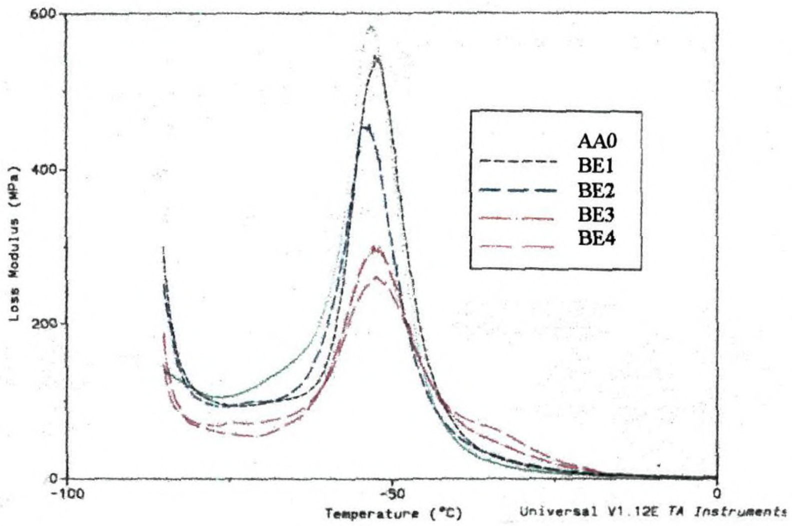

Fig.4. 8 Comparison of loss modulus of ENR 25 modified silica filled NR

Variations of loss modulus with temperature for the ENR25 modified systems are compared in Fig.4.8 and Table 4.5. Modification with ENR25 resulted in large disproportionate decrease in the loss peak height due to the transition of the NR phase, which occurred at about –51°C. Values dropped from 584 MPa to 261 MPa. Presence of ENR25 probably associated with silica filler might have affected the mobility of the

Table 4. 5 Comparison of loss modulus (G'')

Sample	Loss modulus (MPa)									
	-52°C	-47°C	-35°C	-25°C	-12°C	-5°C	0°C	10°C	50°C	80°C
AA0	584	-	-	-	-	-	-	-	3.7	5.5
AE1	584	-	-	-	-	-	-	-	2.5	2.8
AE2	525	-	-	-	-	-	-	-	2.4	2.5
AE3	489	-	-	-	-	-	-	-	2.9	4.4
AE4	525	-	-	-	-	-	-	-	3.2	4.4
BE1	545	-	20	-	-	-	-	-	2.5	2.5
BE2	454	-	32	-	-	-	-	-	3.2	4.4
BE3	296	-	43	-	-	-	-	-	2.6	2.5
BE4	261	-	59	-	-	-	-	-	2.4	2.2
CE1	678	-	-	-	-	5.2	-	-	3.1	3.6
CE2	495	-	-	-	-	10.5	-	-	4.4	5.3
CE3	216	-	-	-	-	16	-	-	3.1	2.4
CE4	210	-	-	-	-	32	-	-	3.1	2.4
DE1	572	-	-	-	-	-	3.9	-	2.9	2.3
DE2	268	-	-	-	-	-	7.9	-	3.1	2.5
DE3	300	-	-	-	-	-	17.8	-	3.1	2.6
DE4	399	-	-	-	-	-	31.6	-	3.4	2.6
CA1	616	-	47.3	-	-	-	-	-	2.8	3.8
CA2	679	-	47.3	-	-	-	-	-	3.7	5.4
CA3	579	-	58	-	-	-	-	-	4.5	6.7
H	-	474	74	-	-	-	-	-	3.7	3.8
EE	118	-	-	12.5	437	-	82	23	3	3

NR phase and also enhanced the 'effective filler volume' due to the intercalation of ENR into the silica networking. Hence the reduced energy dissipation result in reduced loss factor. Also a new loss peak appeared at about –35^{0}C due to the ENR phase and the peak value enhanced from 20 MPa to 59 MPa. With increasing concentration of ENR25, progressive enhancement in loss peak has occurred. Broadening of the peak width might be a consequence of the interaction of ENR with silica. The loss modulus of the ENR modified mix in the rubbery region (40-100^{0}C) was lower than that of the unmodified. At 80^{0}C the values dropped from 5.5 to 2.2 MPa. Hysteresis of the silica filled rubber in the rubbery region increases with temperature due to the clustered network. Lower filler networking in the presence of ENR might have led to lower loss modulus in the rubbery region.

Loss modulus variation of ENR50 modified systems are compared in Fig. 4.9 and Table 4.5. Loss component due to NR transition got modified with ENR50 incorporation. With 5 parts substitution, peak loss modulus showed an increase, while with higher concentrations a progressive decrease was noted. Peak values dropped from 678 to 210 MPa. Decrease in loss component is likely to be due to the mobility restriction of the NR phase and the enhanced 'effective filler volume' due to ENR-silica interaction. A corresponding increase in loss modulus was noted in the temperature region -10^{0}C to $+10^{0}$C which can be attributed due to the transition of ENR component. At -5^{0}C the values enhanced from 5.2 MPa to 32 MPa. Beyond this region, transition of ENR50 occurs to the rubbery phase. The decrease in loss peak due to the NR transition is not in proportion to the increase in loss modulus due to ENR. This is likely to be due

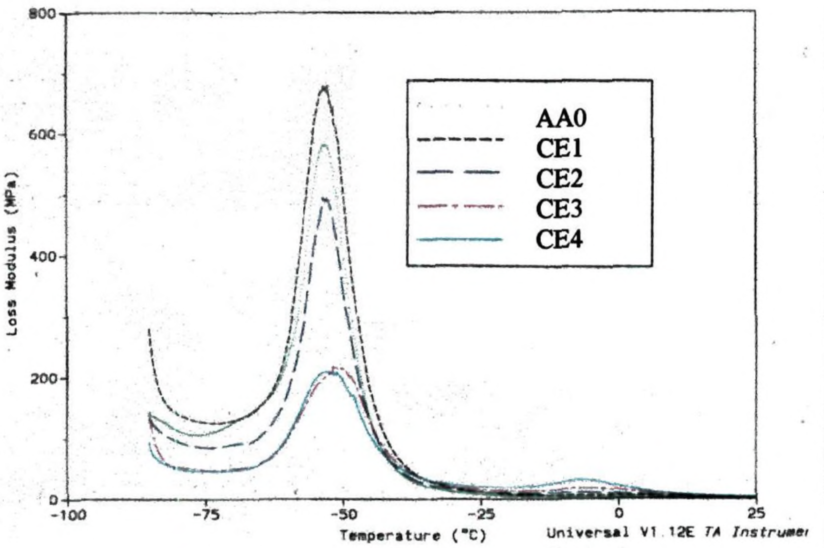

Fig.4. 9 **Comparison of loss modulus of ENR 50 modified silica filled NR**

to the restriction of damping capability of NR due to the presence of ENR in association with silica particles. With ENR50 modification, the loss modulus in the rubbery region between 40 to 100^{0}C showed only minor variation with temperature.

Variation of loss modulus with ENR60 modification is given in Fig.4.10 and Table 4.5. Like ENR50, on incorporation of ENR60, loss peak due to the NR transition showed a declining trend, probably due to the restriction of mobility of NR phase and the larger 'effective filler volume'. Values varied in the range of 572 MPa to 268 MPa. Also a corresponding enhancement of the loss peak was observed in the temperature range of –20 to +20^{0}C due to the transition of ENR phase. Loss peak corresponding to the ENR transition is seen at about 0^{0}C, and the values varied from 3.9 to 31.6 MPa. In the rubbery region of 40 to 100^{0}C loss modulus showed a linear decrease with ENR modification, whereas the unmodified mix showed an increasing tendency. With the unmodified mix, the filler networking might have caused the formation of occluded rubber, thereby raising the 'effective filler volume'. Also the bonding-debonding

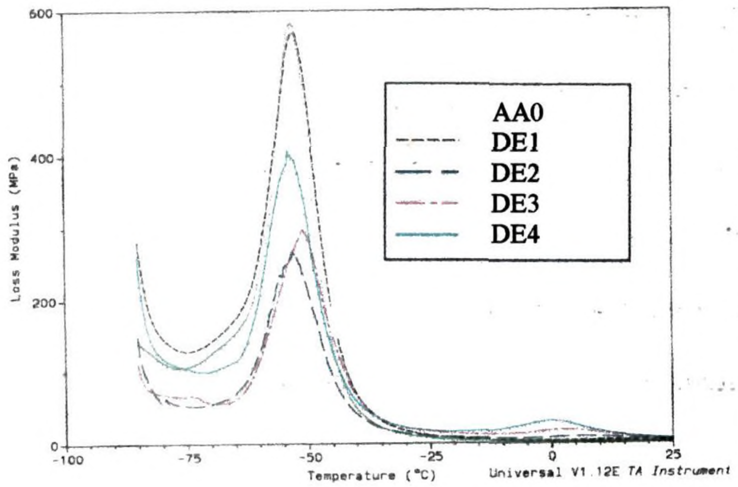

Fig.4. 10 Comparison of loss modulus of ENR 60 modified silica filled NR

mechanism might have led to higher hysteresis. ENR60 being more polar might have considerably reduced the silica networking through rubber-filler bonding thereby reducing the energy dissipation.

Loss modulus variations of carbon black filled and silane modified mixes are compared in Fig.4.11 and Table 4.5. Loss modulus due to the transition of NR phase of the silane modified mix at about -50^0C showed only a small variation with that of the unmodified mix and is in the range of 579 to 679 MPa. Also a minor positive peak shift in the temperature scale was noted. Silane modification might have reduced the polar interaction of NR with silica thereby enhancing its mobility and the hysteretic efficiency thereby resulting in a minor rise in loss modulus. For the carbon black filled mix the peak height decreased to 474 MPa. Also a peak shift of about 3^0C was noted for the carbon black filled mix. The peak shift and the reduction in peak height for the carbon black filled mix is considered to be due to the rubber-filler bonding or interaction.

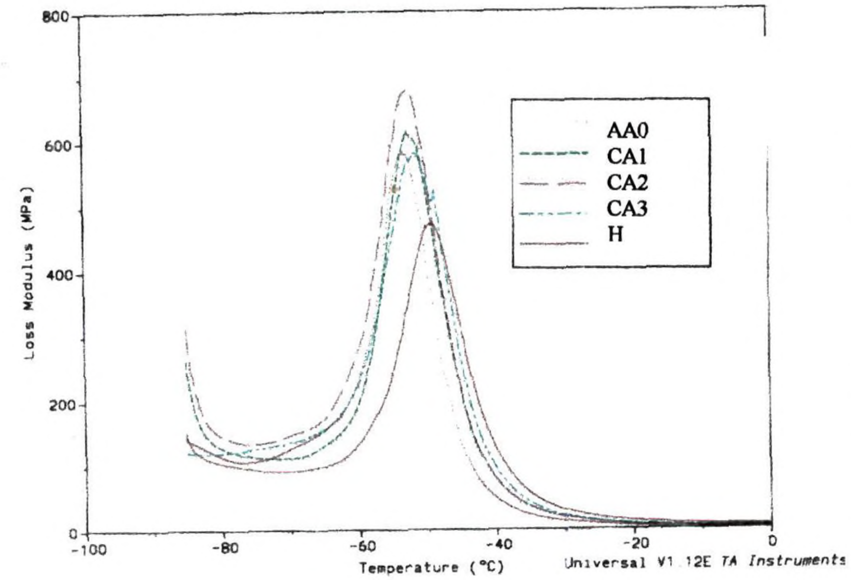

Fig.4. 11 Comparison of loss modulus of silane modified silica filled NR and carbon black filled NR

Loss modulus variation of silica filled ENR50 is given in Fig. 4.6 and Table 4.5. Unlike silica filled NR, the loss peak of ENR is seen at about -9.4^0C due to the higher Tg of ENR. Loss peak at the transition point is about 437 MPa. In the rubbery zone the loss modulus showed a steady decrease similar to that of carbon black filled which could be attributed to the drop in filler-filler and polymer-filler interaction with temperature.

c) Loss tangent (Tan δ)

Gum rubber gives relatively low hysteresis or tan δ in the rubbery zone, whereas it increases with filler loading and passes through a maximum with strain amplitude. In the transition zone damping is mainly due to the polymer component and therefore with filler loading tan δ get reduced. Filler incorporation leads to reduction of polymer fraction which results in lowering of tan δ in the transition zone. In the rubbery region, tan δ increases with filler surface area and in the transition zone it is the reverse. Silica network causes temperature dependence of $\tan\delta$. Beyond 20^0C, $\tan\delta$ is higher for the carbon black filled mix and it decreases with temperature primarily due to the reduction of filler-filler and polymer-filler interaction. Hysteresis of silica filled rubber increases with temperature due to the clustered network. Matrix–filler bonding significantly reduces $\tan\delta$ [32]. Modification with silane reduces $\tan\delta$ in the rubbery region. Polymer-filler interaction results in the reduction of chain mobility which can be assessed from the broadening of the half width of Tg peak[33]. Polymer-filler interaction or polymer modification may result in the shifting of Tg[34]. Carbon black at 50 phr loading shifts Tg by about 3°C. ENR exhibits higher Tg than NR due to the reduction in chain mobility of the former. For tyres, high hysteresis or $\tan\delta$ at low temperature (about 0°C) and low hysteresis at high temperature (about 60°C) are preferred for high wet grip and low rolling resistance respectively.

Variations in loss tangent of the ENR10 modified samples are given in Fig. 4.12 and Table 4.6. With the addition of ENR10 in silica filled NR a linear drop in peak tan δ

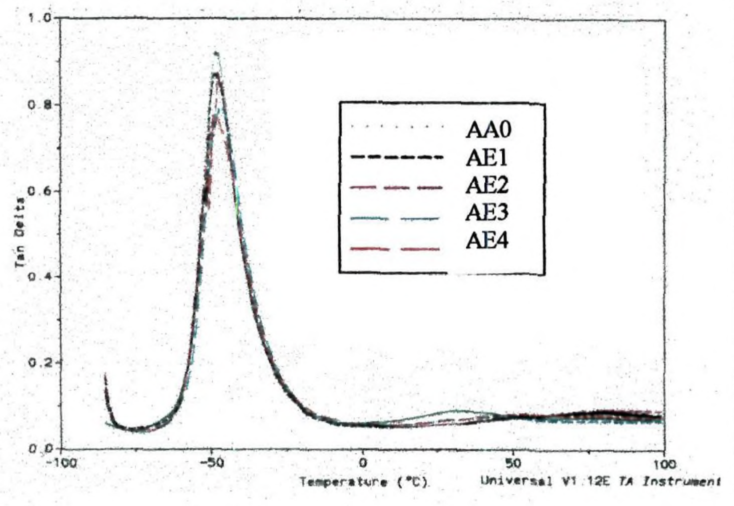

Fig.4. 12 Comparison of loss tangent of ENR10 modified silica filled NR

value due to the transition of NR phase was noted. Tan δ peak values decreased from 0.92 to 0.79. Similarly a hike in tan δ value at -40^0C from 0.45 to 0.51 has occurred due to the transition of ENR phase. A minor positive shift in tan δ peak temperature due to the NR phase also was observed with ENR addition (Table 4.4), which is likely to be due to better rubber-filler bonding. Tan δ peak temperature for the unmodified mix was -49^0C, while that of the 15 parts ENR modified mix was shifted to -47^0C indicating that ENR10 could enhance rubber-filler bonding or the total matrix network density. Also a minor relaxation peak was observed for the silica filled NR at about 30^0C which is likely to be due to the filler bound polymer. Similar observations were reported for rubber swollen layered silicates which exhibit relaxation peak at 30-60^0C[32]. Presence of ENR was effective in shifting the relaxation peak of silica filled NR to a higher temperature indicating better matrix-filler bonding. Tan δ values of ENR10 modified in the rubbery region of 30 to 80^0C were closer to that of the silane modified mix.

Variation in tan δ for the ENR25 modified mixes are given in Fig. 4.13 and Table 4.6. On incorporation of ENR25, with increasing concentration a progressive reduction

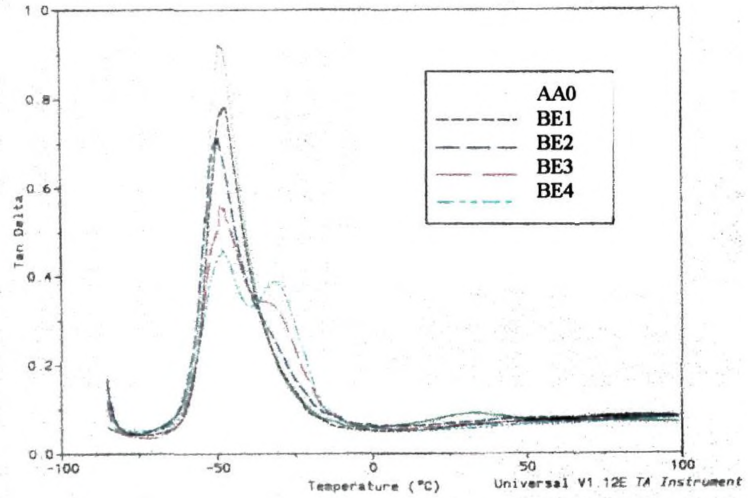

Fig.4. 13 Comparison of loss tangent of ENR 25 modified silica filled NR

in tanδ peak value from 0.78 to 0.46 was observed at about –49°C. Also a corresponding peak was formed at about –30°C, which could be attributed to the ENR phase transition. The peak height, peak width and the area increased on increasing the concentration of ENR. Peak widening is an indication of the reduction in chain mobility of the ENR due to its interaction with silica[33]. On substitution of up to 20 parts of ENR25 only a marginal shift in Tg due to NR phase is seen. With ENR25 modification the peaks due to NR and ENR shows a merging trend, with chances for inter-phase formation[34]. On incorporation of ENR25 the relaxation peak at 30°C for the silica filled NR got shifted to higher temperatures indicating that the filler-rubber bonding of the modified mix involves higher energy. In the rubbery region of 40 to 80°C tan δ values of the ENR25 modified mix were similar to that of the unmodified.

Variations of tan δ for the ENR50 modified system are given in Fig.4.14 and Table 4.6. A gradual reduction of tan δ peak value due to the NR phase from 0.92 to 0.47

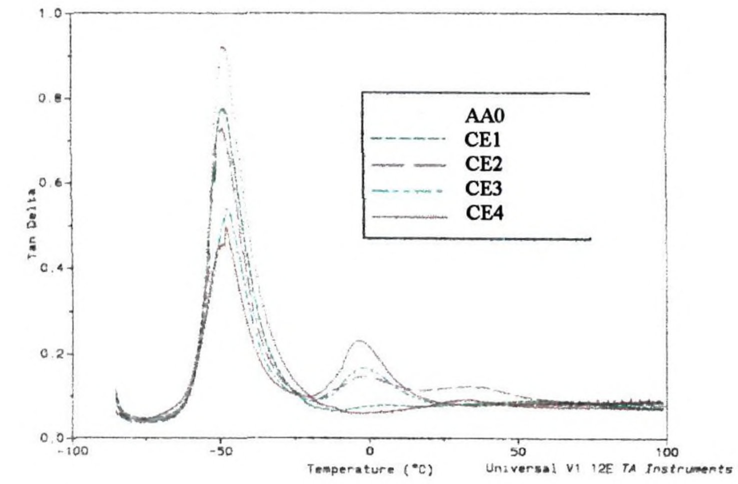

Fig.4. 14 Comparison of loss tangent of ENR50 modified silica filled NR

has occurred with incorporation of ENR50 depending on its concentration. Maximum positive tan δ peak shift occurred in the temperature scale for the NR phase was only about 1^0C. A corresponding loss tangent peak has occurred at about -3^0C due to the ENR phase. Tan δ peak value has increased from 0.07 to 0.23 depending on ENR concentration. Unlike ENR10 or 25, ENR50 exhibited two independent Tg peaks indicating that it forms a two phase system. The phase transition due to ENR occurs in the temperature range of –15 to +15^0C. High damping at this temperature range is much desired for tyres requiring good ice or wet grip[6,7]. Hence, ENR50 modification is also ideal for imparting ice or wet grip in tyre compositions. Tan δ in the rubbery region of 40 to 100^0C was slightly higher than the unmodified mix. This is likely to be due to the enhanced chances of bonding and debonding that occur between filler-filler and rubber and filler which is dependent on the extent of interaction between them. ENR50 which is more polar might have favored larger extent of interaction. Tan δ values in the rubbery region of the ENR50 modified mix were closer to those of the silane modified mix.

Table 4.6 Comparison of loss tangent (Tan δ)

Sample	Loss tangent(Tan δ)-peak height							
	-49°C	-40°C	-30°C	-3°C	5°C	30°C	50°C	80°C
AA0	0.92	0.45	-	-	-	0.09	0.05	0.04
AE1	0.87	0.45	-	-	-	0.06	0.07	0.07
AE2	0.87	0.46	-	-	-	0.06	0.07	0.09
AE3	0.79	0.51	-	-	-	0.07	0.08	0.08
AE4	0.78	0.49	-	-	-	0.07	0.07	0.06
BE1	0.78	-	0.19	-	-	0.02	0.04	0.06
BE2	0.71	-	0.24	-	-	0.04	0.06	0.06
BE3	0.57	-	0.32	-	-	0.03	0.04	0.05
BE4	0.46	-	0.39	-	-	0.01	0.03	0.05
CE1	0.78	-	-	0.07	-	0.08	0.09	0.08
CE2	0.72	-	-	0.14	-	0.12	0.1	0.08
CE3	0.54	-	-	0.17	-	0.08	0.08	0.08
CE4	0.47	-	-	0.23	-	0.08	0.08	0.08
DE1	0.82	-	-	-	0.07	0.09	0.09	0.1
DE2	0.65	-	-	-	0.1	0.08	0.08	0.08
DE3	0.58	-	-	-	0.15	0.09	0.09	0.09
DE4	0.53	-	-	-	0.22	0.12	0.12	0.12
CA1	0.78	0.28	0.18	-	0.05	0.06	0.08	0.08
CA2	0.82	0.3	0.19	-	0.06	0.07	0.07	0.07
CA3	0.83	0.35	0.22	-	0.08	0.1	0.07	0.07
H	0.73	0.59	0.26	-	0.12	0.14	0.16	0.15
EE	0.04	0.04	0.05	0.55	0.3	0.16	0.14	0.12

Modification with ENR60 also affected loss tangent. Corresponding tan δ variations are given in Fig.4.15 and Table 4.6. Progressive reduction in tan δ value from 0.82 to 0.53 due to the NR transition has occurred, depending on ENR concentration. Modification with up to 15 parts of ENR60 has resulted in a minor positive temperature shift of about 1^0C in Tg. However, with 20 parts, a minor negative temperature shift was noted. The negative shift of tan δ, above a critical concentration of ENR, is believed to be due to the silica-ENR bonding thereby making the NR phase more mobile resulting in transition at a lower temperature. Also with progressive addition of ENR60, tan δ peak due to the ENR phase has appeared in the temperature range of 0 to 20^{0}C. Peak tan δ values due to ENR transition increased from 0.07 to 0.22. Like ENR50, blending of NR with ENR60 exhibits two independent transition peaks indicating a two-phase system. With higher concentration of ENR60, the ENR relaxation peak get shifted to the lower temperature. This indicates that as the concentration of ENR increases only a part of the polymer is being used for bonding with the filler surface groups and the non-bonded ENR get relaxed at a lower temperature. It is also interesting to note that the relaxation peak observed at 30°C due to the filler bound rubber in the unmodified system seems to have merged with the ENR relaxation peak of the ENR60 modified system. In the rubbery region of 40 to 100^{0}C, the ENR modified systems, in general, showed higher tan δ than the silica filled NR. Higher tan δ might have resulted from the higher loss factor, which could be attributed to dynamic bonding- debonding mechanism of filler-filler and

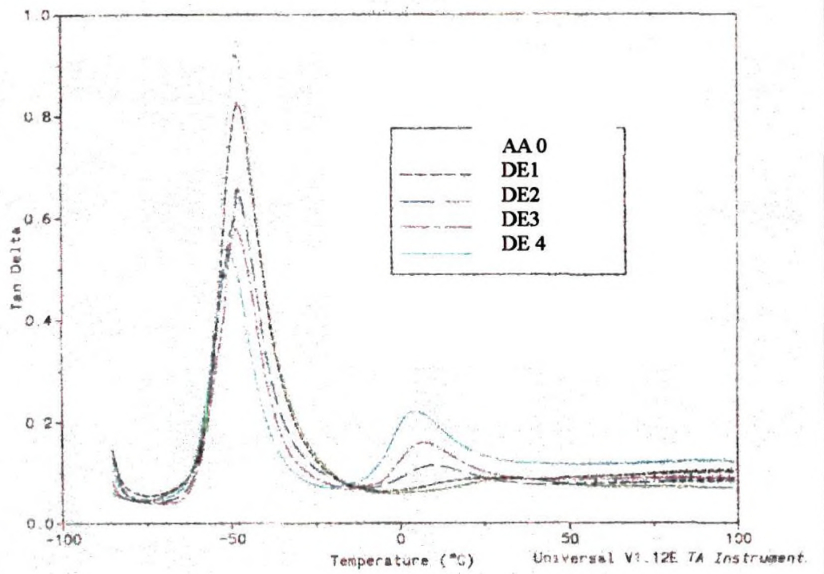

Fig. 4.15 Comparison of loss tangent of ENR 60 modified silica filled NR

polymer-filler interactions and also due to the higher 'effective filler volume' resulting from the intercalation of ENR into the silica networking. For the ENR modified mix the chances for the same is high due to the epoxy-silica interactions and hence the higher tan δ values. On substitution with 20 parts of ENR60 considerably high tan δ was observed in the rubbery region. However, the values were still lower than those observed for the carbon black filled.

Comparison of loss tangent of silane modified and carbon black filled mixes with that of the unmodified silica filled NR is given in Fig. 4.16 and Table 4.6. Tan δ peak height values for the silane modified mix due to the transition of NR phase was lower than that of the unmodified mix. However, unlike ENR modification, with silane modification the tan δ peak height values showed a minor increase from 0.78 to 0.83, when the silane concentration was increased from 1 phr to 3 phr. The carbon black filled mix exhibited tan δ peak value of 0.73. Reduction in tan δ peak can be attributed to better rubber- filler interaction. Both the silane modified and carbon black filled mixes exhibited positive temperature shift in tan δ, which is likely to be due to larger rubber-filler networking. The carbon black filled mix exhibited a larger shift of about 4°C while the silane modified mix exhibited a shift of about 1 to 2.4°C. This can be attributed to the differences in the nature of bonding of silane modified silica and carbon black with rubber. With silane, bonding is through the flexible silane moiety whereas that of black is rather direct. Tan δ in the rubbery region of transition, a measure of energy dissipation or heat build up is much higher for the carbon black filled mix than the silica filled NR and that of the silane and ENR modified mixes. The tan δ values in the rubbery region of ENR10 and ENR25 modified systems are similar to those of the silane modified, whereas with ENR 50 and 60 a slightly higher tan δ was observed.

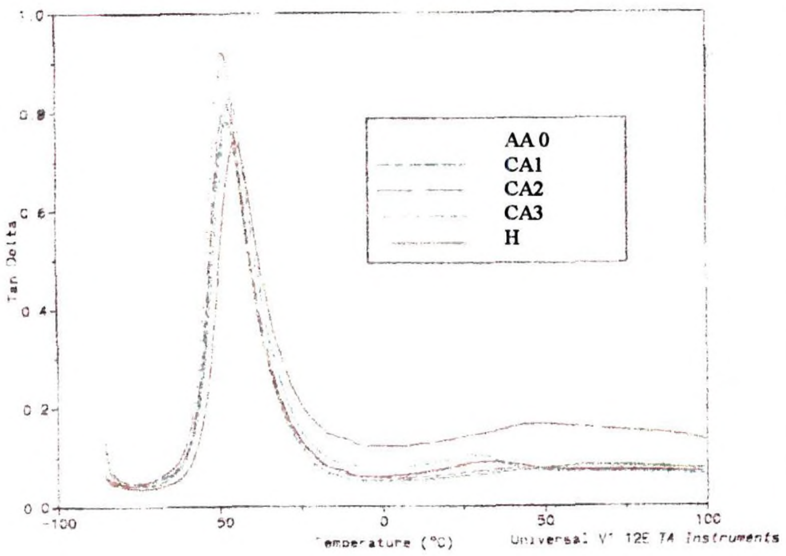

Fig.4. 16 Comparison of loss tangent of silane modified silica filled NR and carbon black filled NR

Variations in tan δ peak height values of the silica filled ENR50 with temperature is given in Fig. 4.6 and Table 4.6. Peak loss tangent appeared at about –6.1°C and exhibited a value of about 0.55. The corresponding value for the silica filled NR at the transition temperature was 0.92. The decrease in tan δ for the silica reinforced ENR could be attributed to silica-ENR interaction. Compared to NR the transition occurred at the higher temperature can be attributed to the lower chain mobility of ENR[15]. Tan δ peak height values of the silica filled ENR in the rubbery region of 30 to 80°C were closer to that of the carbon black filled mix. Higher tan δ at –6.1°C is ideal for good ice and wet grip for tyres.

4.3.3 Miscibility of NR/ENR blends

Rubber blends can be characterized through dynamic mechanical analysis. Glass transition temperature of blend components depends on the mobility of polymer molecules with temperature. If the components are immiscible or exists in a two phase morphology, separate damping peaks are observed for the blend components[12]. Silane modification for silica reinforcement does not pose the problem of multiphase system.

ENR modification for silica reinforcement has also to consider the miscibility factor. However, this may not be a critical factor since the ENR used is only a minor fraction. Absence of a separate tan δ peak for ENR10 indicates its miscibility with NR. However, for ENR25,50 and 60 separate damping peaks are seen. The miscibility reduces as the polarity of ENR increases. Shift in Tg observed with either ENR or silane indicates better rubber – filler bonding or higher network density.

4.4 Conclusions

In the present study ENR of varying epoxy content at different concentrations was used as modifier for silica filled natural rubber. Dynamic mechanical properties of the ENR modified mixes were compared with those of the silane modified silica filled NR and carbon black filled NR. Variations in the storage modulus, loss modulus and tan δ in the temperature range of –80 to 100°C and the miscibility of NR/ENR blends were analyzed. With incorporation of ENR in silica filled NR, drop in glassy modulus was seen dependent on the concentration of ENR and its epoxy content. Also the glass to rubber transition got broadened and minor shifts in transition peaks were observed with ENR modification. Lowering of loss modulus and tan δ peak height values due to the transition of NR phase, has occurred on incorporation of ENR which could also be considered an indication of rubber–filler interaction. ENR10 was found miscible with NR, whereas ENR25, 50 and 60 exhibited independent Tg peaks indicating immiscibility. Silane modified and carbon black filled NR, though exhibited Tg shift, did not exhibit any drop in glassy modulus. The higher tan δ peak height value observed for the ENR50 modified system at about 0°C is expected to provide good wet grip to tyre tread compositions. Similar to the carbon black filled mix, lowering of tan δ with temperature in the rubbery zone for those modified with ENR of higher polarity is an indication of the reduction in filler-filler networking. ENR modified silica filled NR exhibited lower tan δ than the carbon black filled mix in the rubbery region.

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CHAPTER 5

MIXING, BOUND RUBBER AND RHEOLOGICAL CHARACTERIZATION OF NR-SILICA COMPOSITES

5.1 Introduction

Manufacturing of rubber products involves mixing of various ingredients into rubber usually followed by a few further processing operations such as extrusion, calendering etc. and the final curing. Mixing involves energy consumption. The production sector always looks for energy efficient processing operations. Mixing and processability of rubber compounds are hence important for a product manufacturer. Processability of rubber compounds, especially filled compounds, generally depends upon their rheological properties[1]. Carbon black and silica are the two important reinforcing fillers being used by the rubber industry. Unlike carbon black, silica has many mixing and processing problems due to its surface polarity and the resulting filler-filler networking which ultimately results in stiff and viscous rubber compounds which are difficult to handle[2]. To overcome the problems with silica and to bridge the technological gap between silica and carbon black, conventionally silane coupling agents are used in silica compounds[3].

In the present chapter a processability study of silica in NR in the presence of different modifiers such as silane and ENR was conducted in comparison with carbon black. The composites thus produced were also evaluated for bound rubber.

5.2 Experimental

5.2.1 Materials

Natural rubber (ISNR-5) and epoxidised natural rubber(ENR50) were obtained from the Rubber Research Institute of India. Silica (Ultrasil VN3) and silane coupling agent (bis (3-triethoxysilyl propyl) tetrasulphide (TESPT) “Si 69”) were products of Degussa A.G. Germany, and carbon black (ISAF-N220) of Phillips Carbon Black Ltd., India.

5.2.2 Mixing of rubber-filler composites

Various composites of rubber with silica or carbon black were prepared in a Haake Rheocord (Model, Rheocord 90). Natural rubber alone or in combination with ENR50 having similar viscosity ($M_L(1 + 4)$, 73)was either premasticated or blended in the Rheocord at 40 °C ,60 rpm for 5 minutes. The resultant rubber was used for further mixing with silica and carbon black. The conditions of premastication/blending and the respective data generated are given in Table 5.1.

Table 5.1 Mastication/Blending data (Rheocord)

Sample	Blending parameters				Final Mooney viscosity, $M_L(1+4)$, 100°C
	Init. temp. °C	Final temp. °C	Final mixing torque (Nm)	Totalized torque (Nm.min.)	
NR(100)	40	143	96.1	1100	58.4
NR/ENR(95/5)	40	141	95.5	1075	57.6
NR/ENR(90/10)	40	140	97.6	1080	59.3
NR/ENR(85/15)	40	139	96.3	1083	58.5

The rubber or rubber blend thus made was used further for making the rubber-filler composites. The formulations of the rubber-filler composites made, mixing conditions and mixing data generated are given in Table 5.2.

Table 5. 2 Filler mixing studies (Rheocord)

Sample	Mixing parameters				Final Moone viscosity, $M_L(1+4)$, 100° C
	Temp. (initial) °C	Temp. (final) °C	Final mixing torque (Nm)	Totalized Torque (Nm.min.)	
NR/Silica (100/50)	40	130	53	577	>100
NR/Silane/Silica(100/1/50)	40	126	50.3	580	98
NR/Silane/Silica(100/2/50)	40	122	46.5	568	95
NR/Silane/Silica(100/3/50)	40	114	48.3	564	92
NR/ENR/Silica(95/5/50)	40	111	43.1	514	80
NR/ENR/Silica(90/10/50)	40	112	41.3	506	81
NR/ENR/Silica(85/15/50)	40	109	41.2	514	78
NR/ISAF(100/50)	40	116	53.3	514	60

5.2.3 Testing of samples

Mastication/blending of the gum rubber and mixing of the rubber-filler composites were made in the Haake Rheocord. The viscosity of the masticated/blended gum rubber and the composites made from it was determined using a Mooney viscometer model Shimadsu SMV 202. Rheological characterization of the gum rubber and filled composites was made using a capillary rheometer attached to a Universal Testing Machine model Zwick 1474. Rubber – filler composites were also evaluated for bound rubber by swelling in toluene.

5.3 Results and Discussion

5.3.1 Mixing

5.3.1.1 Mixing of filler in rubber

Compared to carbon black, silica causes many mixing problems. Silica aggregates are comparable to those of carbon blacks, but have a relatively higher structure. This structure accounts for a higher reinforcing power than carbon black. Because of its high specific component of surface energy (γ_s^{sp}), silica has a stronger tendency to agglomerate, and is difficult to disperse in rubber and rapidly reagglomarates after mixing [4,5]. To obtain a high dispersion with silica, higher shear stress is required. High shear stress can be obtained when the viscosity of the mass is high, which can be achieved by high filler loading and by use of high viscosity polymers and lower mixing temperature[6]. Silica possess very strong filler-filler interaction. When no coupling agent is used, the compounds show very high viscosity. The handling of such silica-filled compounds is very difficult. When hydrophobing occurs, the surfaces of the silica particles are covered with the coupling agents and filler-filler interactions get reduced, thus leading to low viscosity [7]. High viscosity, generates high shear stresses and consequent excessive energy dissipation in the compound, which will lead to substantial rise in compound temperature. Boonstra and Medalia [8] suggested that the total filled volume should include not only the filler but also the rubber that is occluded within the agglomerates. During the dispersive mixing stage, these agglomerates are broken down, the amount of occluded rubber decreases, and thus the filled volume decreases, leading to lower viscosity [9-12]. The bound rubber molecules on the silica surface have more freedom of movement. As a result, hysteresis and heat build-up of silica filled vulcanizates are lower than the corresponding carbon black filled vulcanizates [5].

A plot of mixing torque versus mixing time shows normally an exponential drop, after the addition of the last ingredients, to some limiting value P_∞. Such data can be fitted by the following equation. [10,13].

$$\ln\frac{P_t - P_\infty}{P_0 - P_\infty} = -Kt \qquad \textbf{Eq. 5.1}$$

where P_o, P_t and P_∞, represent the torque values just after the addition of the last ingredients, at time t and the limiting torque after infinitely long mixing. The total change in torque ($Po-P_\infty$) can be taken as a measure of the initial volume of occluded rubber and P_t-P_∞ is proportional to the volume of occluded rubber at time 't'. The constant 'K' represents the rate at which the filler is dispersed. The above equation represents a process obeying first order kinetics.

5.3.1.2 Mixing in Haake Rheocord

Mixing studies were conducted using the Haake Rheocord. It is a computer controlled torque rheometer that can be used for mixing and extrusion. The mixing device fitted with banbury type rotors was used for the present study. In this equipment temperature and rotor speed can be varied. It can measure torque and melt temperature. This device has been used for studying processing characteristics such as viscosity, energy consumption etc. Objective of the study was to understand the mixing behavior of silica in natural rubber with and without ENR/silane as modifier and to compare with carbon black. Premastication of rubber or rubber blends and the mixing of rubber-filler composites were done in the Rheocord. The filled mixes made were NR/Silica, NR/ENR/Silica and NR/Silane/Silica (Three different concentrations each of ENR and silane) and NR/ISAF. Data for premastication/blending of gum rubbers and their viscosities are given in Table 5.1. The rubber-filler composites made, conditions of mixing, mixing data and the composite viscosities are given in Table 5.2. The rheograms of mixing for the rubber-filler composites are displayed in Figs. 5.1 to 5.8

From the data it is observed that the order of temperature development at the end of the mixing was NR/Silica>NR/Silane/Silica> NR/ENR/Silica. NR/ISAF shows mix temperature in between that of the silane and ENR modified mixes. The temperature developed during mixing and the final mixing torque value can be taken as a measure of the viscosity of the mix [7]. With the addition of ENR and silane, temperature development and viscosity were lower and the former exhibited the lowest value. The final mixing temperatures developed with the ENR modified systems were comparable to that of the carbon black filled and that of the mix with silane at higher concentration. Also the totalized torque value, which can be taken as a measure of the energy consumed for mixing, was the lowest for the ENR modified mix. The highest value of final torque, totalized torque and the temperature developed for the unmodified NR/Silica mix might have resulted from the high viscosity of the mix caused by filler-filler networking. The efficiency of mixing of the filler in rubber was evaluated from the rheograms using Equation 5.1. The mixing efficiency, as given by the slope (-K), is given in Table 5.3. Slope values indicate that in the presence of ENR, efficiency of mixing silica in natural rubber has increased considerably and is in similar trend as that of carbon black in rubber. Though silane at higher concentration also has improved the mixing efficiency, it is not as high as that for the ENR modified mix. The epoxy-silanol interaction or the

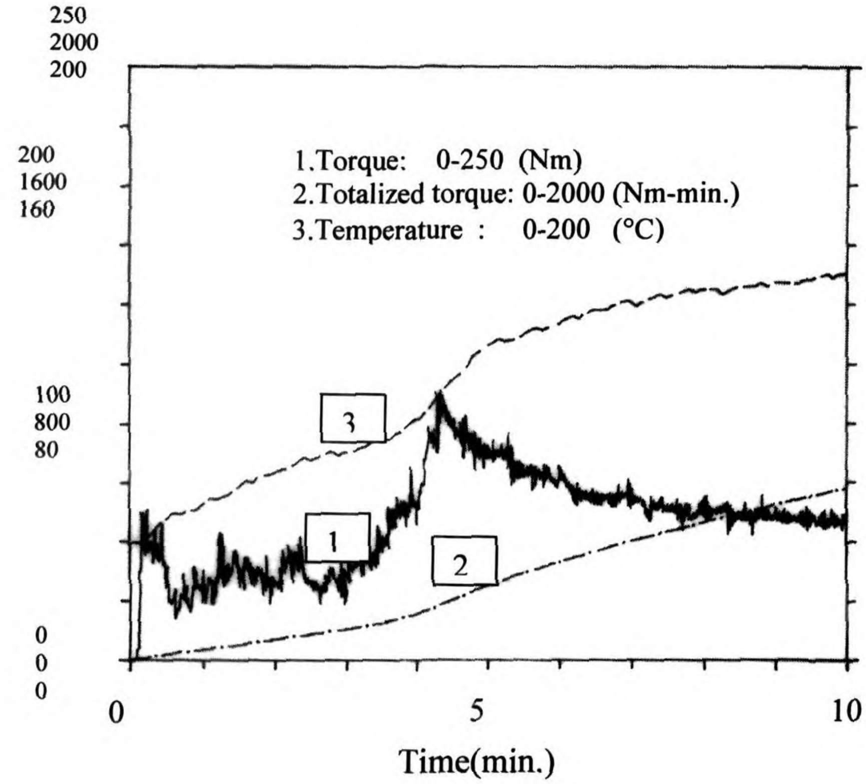

Fig. 5.1 Mixing curve -NR/Silica(100/50)

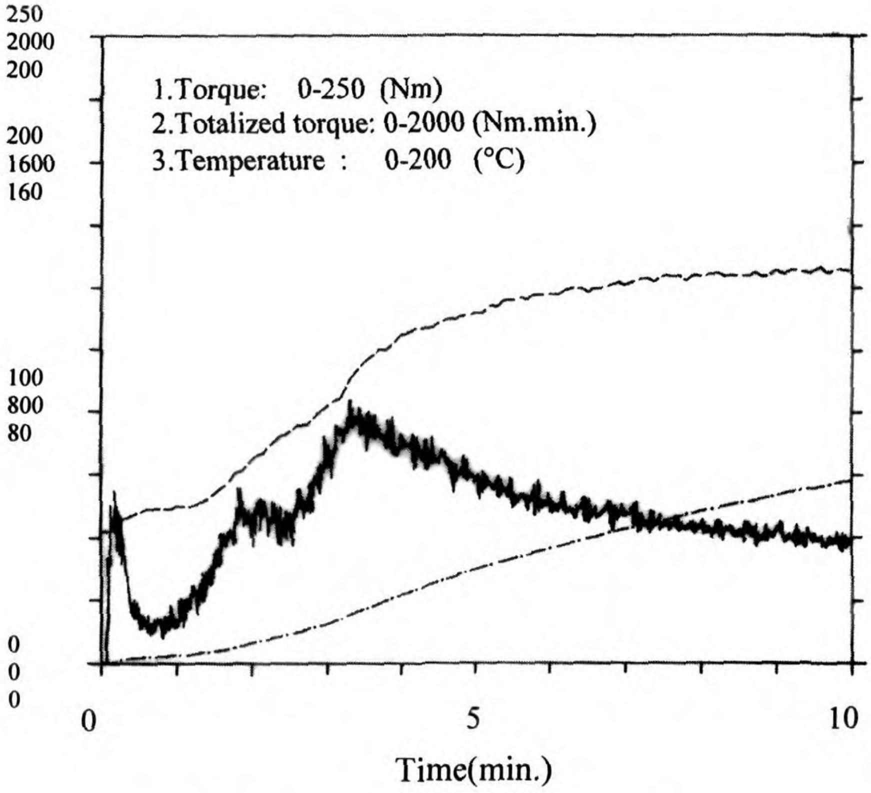

Fig. 5.2 Mixing curve –NR/Silane/Silica(100/1/50)

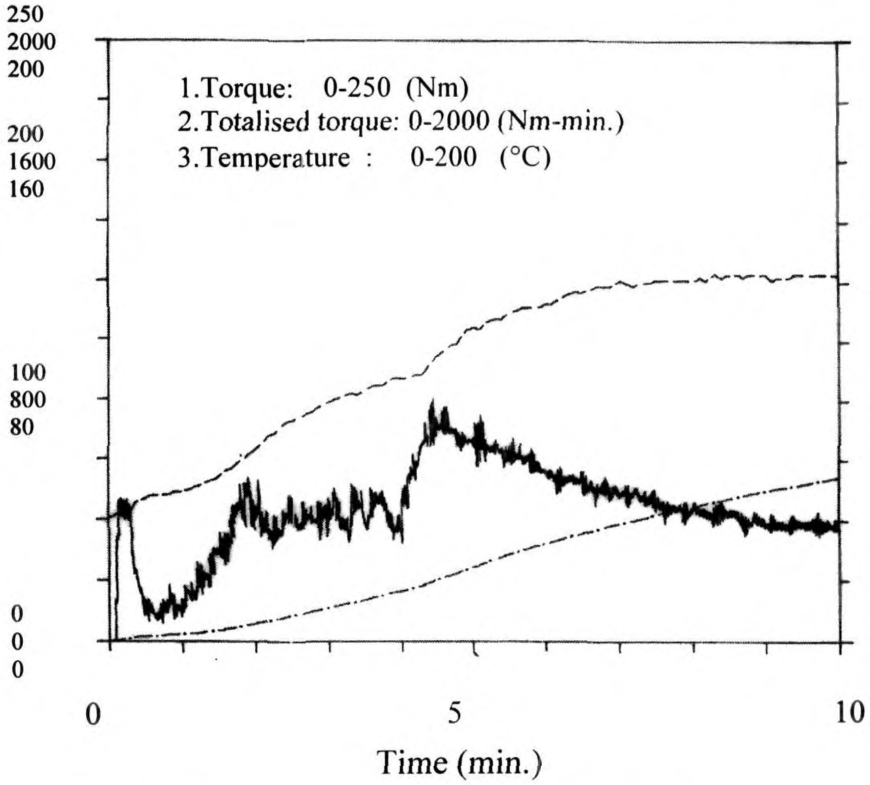

Fig. 5.3 Mixing curve –NR/Silane/Silica(100/2/50)

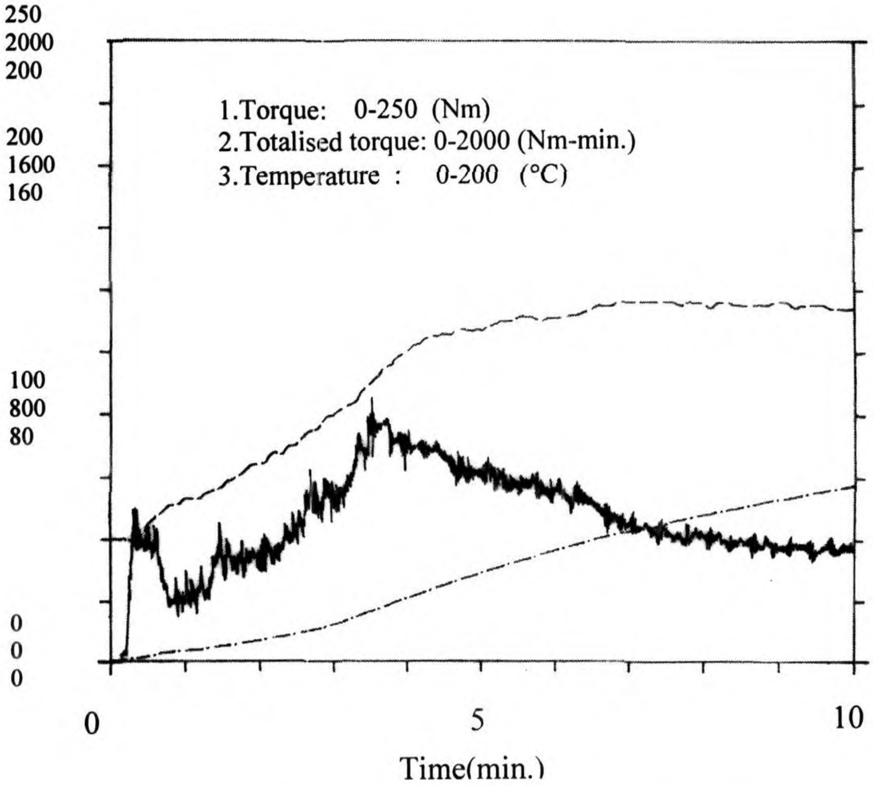

Fig. 5.4 Mixing curve –NR/Silane/Silica(100/3/50)

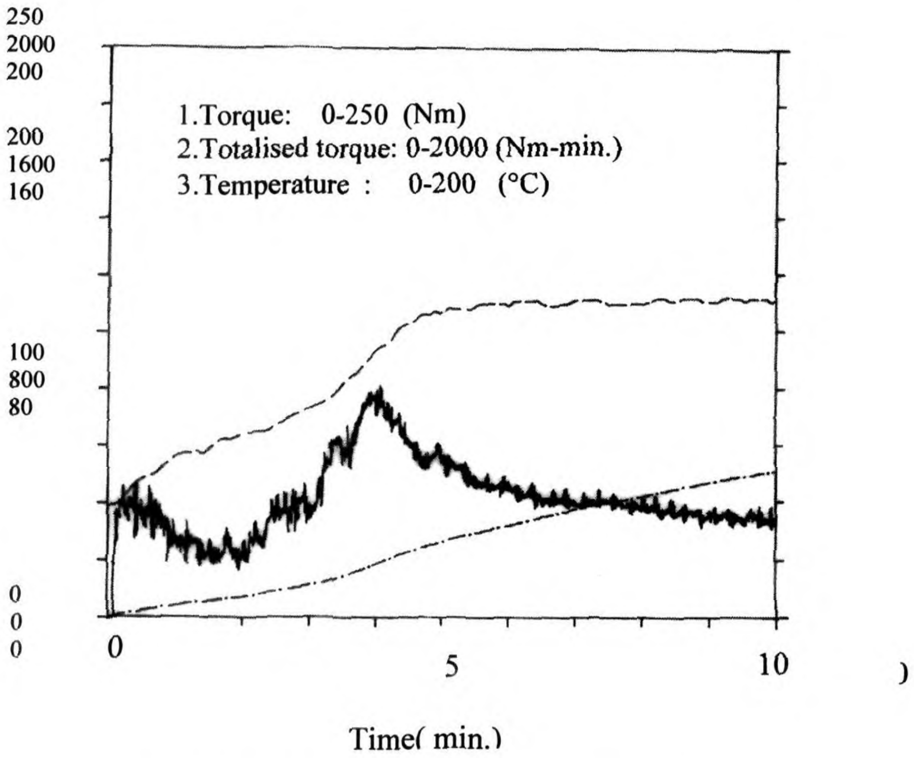

Fig. 5. 5 Mixing curve –NR/ENR/Silica(95/5/50)

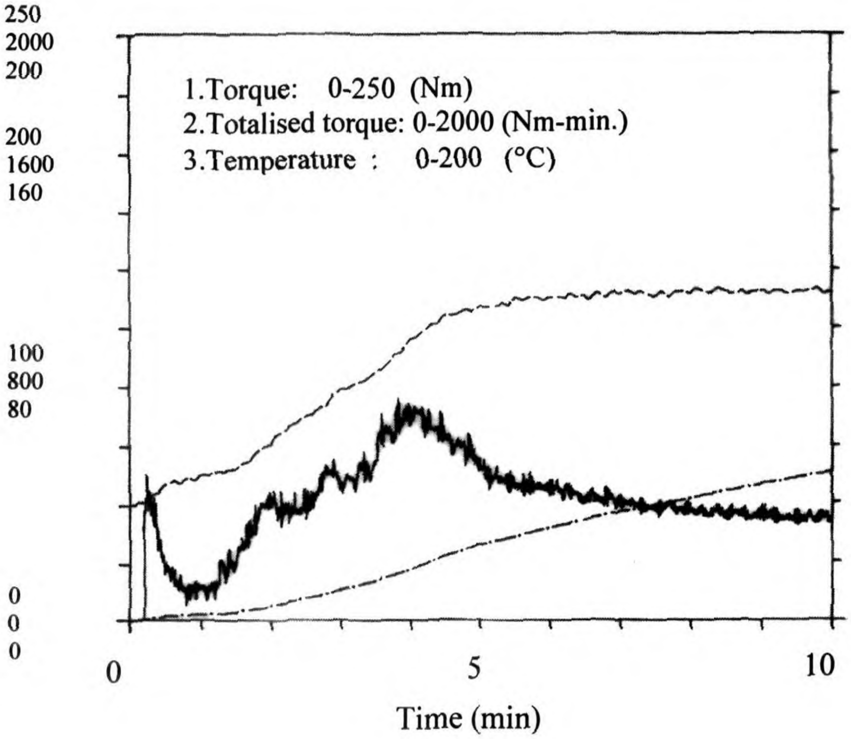

Fig. 5. 6 Mixing curve –NR/ENR/Silica(90/10/50)

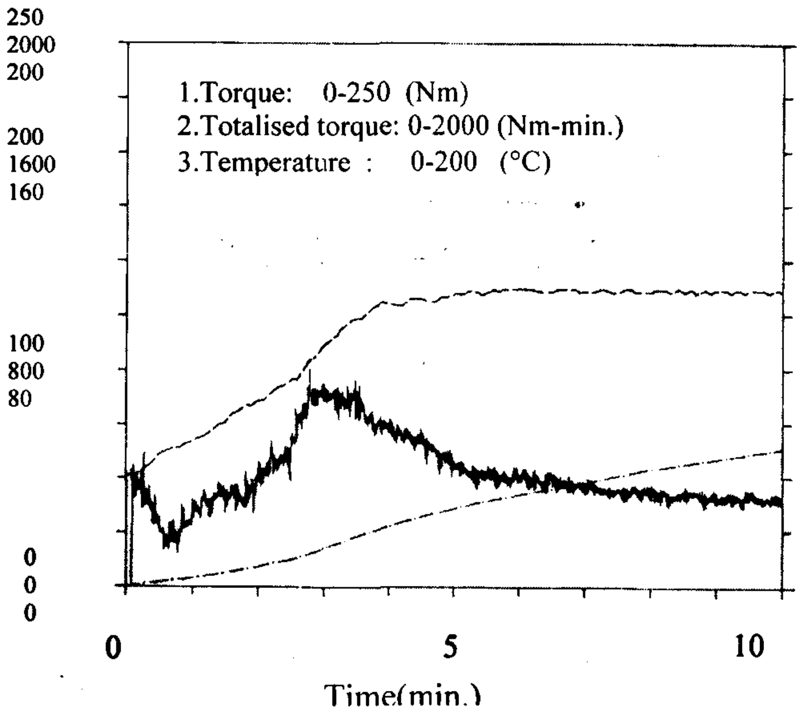

Fig. 5.7 Mixing curve -NR/ENR/Silica(90/15/50)

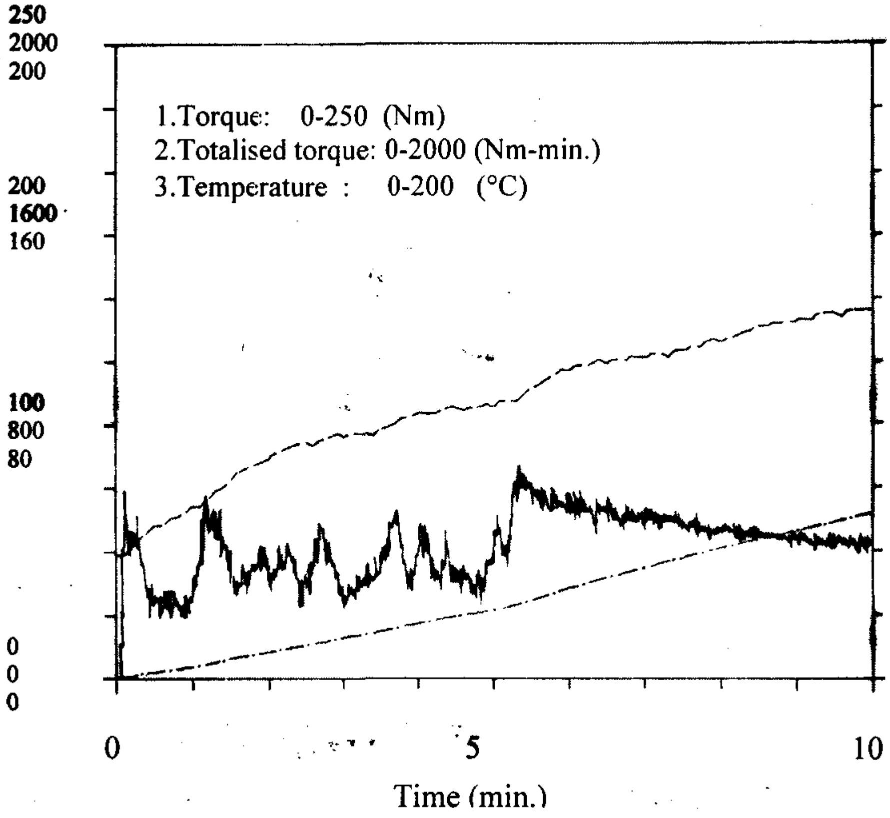

Fig. 5. 8 Mixing curve -NR/ISAF (100//50)

hydrogen bonding between the two, might have contributed to improved filler dispersion and lower filler-filler interaction resulting in lower Mooney viscosity and better mixing efficiency.

Table 5.3 Rheocord mixing-Comparison of dispersion efficiency

Mix	Slope (K)
NR/Silica(100/50)	-0.471
NR/Silane/Silica(100/1/50)	-0.389
NR/Silane/Silica(100/2/50)	-0.482
NR/Silane/Silica(100/3/50)	-0.498
NR/ENR/Silica(95/5/50)	-0.6182
NR/ENR/Silica(90/10/50)	-0.59
NR/ENR/Silica(85/15/50)	-0.696
NR/ISAF(100/50)	-0.627

5.3.2 Bound Rubber

5.3.2.1 Bound rubber and rubber-filler interaction

Bound rubber is essentially the gel formed in a filler-rubber mix and its estimation is considered to be a practical means of assessing rubber-filler interaction in the uncured state. The gel formed due to polymer-polymer crosslinking is not considered as bound rubber. Bound rubber is generally determined by swelling measurements.

Physical as well as chemical interactions are believed to involve in bound rubber formation. In the case of carbon black, free radical interaction between the filler surface groups and the polymer is proposed as a mechanism for bound rubber formation. Bound rubber is also related to filler surface area and surface activity [14]. High structure black generally exhibits larger rubber- filler interaction. Freshly formed filler surfaces have great adsorption capacity[15]. In the polymer matrix, above a critical concentration ($C_{crit.}$) filler transforms from a disperse to a coherent gel and $C_{crit.}$ decreases with increasing surface area[16]. The filler-filler aggregates, which get broken down during mixing with the elastomers may get reformed during the post-mixing period. The trapped rubber in such aggregates can also cause bound rubber [17]. Comparatively higher bound rubber exhibited by black filled NR and SBR can be attributed to the high dispersive component (γ_s^d) of the surface energy of carbon black. High bound rubber exhibited by these rubbers is attributed to physical phenomena [18]. Graphitised carbon black (surface groups are lost) exhibits lower bound rubber. Chemical interaction of a filler particle with elastomer can affect the properties of both the uncured mix and the vulcanizate. Covalent bonds between rubber and carbon black contribute to reinforcement, while it is not a necessary condition for bound rubber formation. The bound rubber retained at higher temperature ($>100^0$C) is likely to be due to rubber-filler covalent bonds[16]. Polarity of the polymer also contributes to enhanced bound rubber. Polarization of the unsaturated polymers in the presence of polar fillers also contribute to polymer-filler interaction[19]. Bound rubber can be formed even when effective reinforcement is not there as in the case of silica in hydrocarbon rubbers. Important reinforcement properties are considered to be resultant of rubber- filler interaction [20]. Silica exhibits comparatively higher bound rubber with polar polymers like nitrile rubber [21].

5.3.2.2 Bound rubber in ammonia atmosphere

Bound rubber in ammonia atmosphere is usually determined to assess the extent of rubber-filler physical bonding. Ammonia is known to cleave physical linkages between silica and rubber. Silica-ammonia interaction is stronger than silica-rubber interaction. For the carbon black filled rubbers, especially with hydrocarbon rubbers stronger interaction with filler occurs, which cannot be easily broken down by ammonia and consequently the reduction in bound rubber in ammonia atmosphere is not very high [22]. In the case of silica filled systems considerable reduction in bound rubber occurs, in ammonia atmosphere and it can be attributed to the weak silica-polymer interaction. Moreover, the swelling of silica filled vulcanizates in ammonia atmosphere was found larger than those of the carbon black filled vulcanizates, which also indicates the weakening of silica – rubber interaction [22].

5.3.2.3 Observations on bound rubber

The eight rubber-filler composites given in Table 5.2 were analyzed for bound rubber. Bound rubber values for all the three series of silica filled compounds viz; NR/Silica, NR/ENR/Silica and NR/Silane/Silica (with 3 different ENR and silane concentrations) and NR/ISAF are given in Table 5.4.

Table 5.4 Bound rubber data (Rubber–Filler mix)

Sample	Bound rubber(%)	Bound rubber(%) (ammonia atmosphere)
NR/Silica(100/50)	33.1	9.01
NR/Silica/Silane (100/50/1)	35.98	20.9
NR/Silica/Silane (100/50/2)	36.07	19.38
NR/Silica/Silane (100/50/3)	34.38	22.19
NR/ENR/Silica (95/5/50)	28.52	21.59
NR/ENR/Silica (90/10/50)	32.93	25.18
NR/ENR/Silica (85/15/50)	32.62	25.74
NR/ISAF (100/50)	33.55	27.7

The values are found to be in the range of 28 to 36%. Bound rubber in a limited range shows that both the silica filled and carbon black filled mixes give almost the same level of networking either due to filler-filler or filler-rubber interaction. The polar surface groups on silica can interact with NR through dipole-dipole interaction[23]. Bound rubber values of the corresponding samples measured in ammonia atmosphere were interesting. The lowest bound rubber value retained was for the NR/Silica system. This clearly shows that the bound rubber originated from the rubber–filler interaction in the NR/Silica system could be weakened by ammonia, whereas in the case of NR/ISAF the bonding is stronger, and was not much affected by ammonia. Both ENR and silane modified systems retained high bound rubber values even in the ammonia medium. The silane modified system exhibited a bound rubber in the range of about 20 to 22%

whereas with the ENR modified system it was in the range of about 22 to 25.7. The better interaction of silica with rubber in the silane modified mix can be due to the silanol-ethoxy interaction which provided the silica with a hydrocarbon entity which then might have interacted with the polymer chains through better dispersion entanglement or through its sulphur entity. In the case of ENR modified systems, during mixing, a preferential adsorption of ENR over the silica surface might have taken place through the epoxy-silanol interaction and/or hydrogen bonding. The ENR modified silica, would have dispersed well in the rest of the hydrocarbon matrix thus giving the possibility of better rubber–filler binding. The silanol-epoxy interaction might be stronger than the silanol-ammonia interaction thus giving better retention of bound rubber in the ammonia modified swelling for the ENR containing samples.

5.3.3 Rheological Studies

5.3.3.1 Rheology of rubber-filler composites

The rheological properties of polymers in the presence of filler depend largely on polymer filler interaction. Guth and Gold [24] utilized Einstein's [25] hydrodynamic concept to explain the increase in viscosity for the filled elastomers over the gum and proposed the following equation.

$$\frac{\eta_f}{\eta_g} = 1 + 2.5\phi + 16.1\phi^2 \qquad \textbf{Eq. 5.2}$$

where η_f and η_g are the viscosities of the filled and gum elastomers respectively and 'ϕ' is the volume fraction of filler.

The shear viscosity of polymers is reported to increase significantly with incorporation of carbon black[26-28]. However, the increase in viscosity is dependent largely on the surface area, structure and surface activity of the filler [29-31]. Silica, being a highly polar material[32], the rheological behavior of rubbers filled with it, obviously varies from those filled with carbon black. Many investigations on the rheological behaviour of carbon black filled [33-38] and silica filled [1,2,39-41] elastomers have been reported.

5.3.3.2 Flow behavior of polymeric materials

Viscosity models (Power law model)

The equation derived by Newton for expressing the viscosity of liquid is given by

$$\tau = \eta\gamma \qquad \text{Eq.5.3}$$

where τ = shear stress

γ = shear rate

η = proportionality constant known as viscosity

The liquids which follow the above equation are called 'Newtonian liquids'. Polymeric materials deviate considerably from Newtonian behavior and their behaviour is usually represented by the Power law equation given below[42].

$$\tau = k\,\gamma^{n} \qquad \text{Eq. 5.4}$$

where k = constant

n = Power law index which is generally <1 for polymers

Average apparent viscosity 'η_a' is defined as

$$\eta_a = \tau / \gamma \qquad \text{Eq. 5. 5}$$

where γ = average shear rate over the capillary diameter

$$\eta_a = \tau/\gamma \;= k\gamma^n/\gamma \;= k\,\gamma^{n-1} \qquad \text{Eq. 5.6}$$

$$\ln \eta_a = \ln k + (n-1) \ln \gamma \qquad \text{Eq. 5.7}$$

The above equation indicates that apparent viscosity of liquids which follows the Power law equation having n<1, decreases with increasing shear rate. Such materials are known as 'Pseudoplastic'.

5.3.3.3 Rheological measurements

Processability of NR, NR/ENR blends and its filled composites were characterized by rheological means. Masticated rubber/rubber blends (4 samples) as given in Table 5.1 and rubber-filler composites (8 samples) as given in Table 5.2, made in the Haake Rheocord, were subjected to rheological studies.

The shear stress, shear viscosity and extrudate swell of various experimental composites at different shear rates and temperatures were determined using a capillary rheometer attached to a UTM, model ZWICK 1474. The capillary used was made of tungsten carbide and has an l/d ratio of 30 and an angle of entry of 180^0. The sample for testing was placed inside the barrel of the extrusion assembly and forced down the capillary with a plunger attached to the moving crosshead. After a warming up period of 3 minutes the mix was extruded through the capillary at preselected speeds of the crosshead, which varied from 0.5 to 500 $mm.min^{-1}$. The forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate (γ_w) at the wall respectively, using the following equations involving the geometry of the capillary and the plunger.

$$\tau_w = F/4A_p(l_c/d_c) \qquad \textbf{Eq. 5.8}$$

$$\gamma_w=(3n'+1)/4n'*32Q/\pi d_c^3 \qquad \textbf{Eq. 5.9}$$

where F is the force applied at a particular shear rate, Ap is the crosssectional area of the plunger, lc is the length of the capillary, and dc is the diameter of the capillary, Q is the volume flow rate and n' the flow behaviour index. Volume flow rate is calculated from the velocity of the crosshead and the diameter of the plunger. The flow behavior index n' is defined by

$$n'=d\ (\log \tau_w)\ /\ d\ (\log \gamma_{wa}) \qquad \textbf{Eq. 5.8}$$

The parameter n' is determined by regression analysis of the values of τ_w and γ_{wa} obtained from the experimental data. γ_{wa} is the apparent wall shear rate calculated as $32Q/\pi d_c^3$.

The shear viscosity η was calculated as

$$\eta = \tau_w / \gamma_w \qquad \textbf{Eq.5.9}$$

Various experimental composites extruded through the capillary were analyzed for shear stress, shear viscosity and extrudate swell.

5.3.3.4 Rheological characterisation of the experimental samples

The four premasticated gum rubber/rubber blends given in Table 5.1 and the eight filled composites given in Table 5.2 were subjected to rheological measurements. Each sample, having the same volume of material loaded into the capillary rheometer, was extruded through the capillary at selected shear rates. From the shear force required for each stabilised extrusion at different shear rates, shear stress was calculated. From the shear stress and shear rate data shear viscosity was calculated. The extrudates at different shear rates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured using a binocular stereo microscope. The die swell is expressed as the ratio of the diameter of extrudate to that of the capillary (D_e/D_c).

a) Shear viscosity

Processing of most of the rubbers are in the 'non-Newtonian' flow regime. For many polymers the flow is non-Newtonian even at the lowest shear rates attainable [43]. Rheological properties of the compounds under study are discussed. A comparison of the plot of log viscosity vs log shear rate of the outcome of the rheological experiments of NR and NR/ENR blends given in Table 5.1, carried out at 90°C and 120°C are given in Figs. 5.9 and 5.10. Similar behavior was observed at 100°C and 110°C. All the samples exhibited pseudoplastic behavior, that is, the viscosity decreased with shear rate. The flow pattern of NR did not change much with substitution of NR with ENR 50 in small quantities upto 15 parts per hundred rubber.

Viscosity of filled rubbers in general increases with decreasing filler particle size and increasing 'structure'. Bound rubber also in certain cases leads to increased viscosity[43].

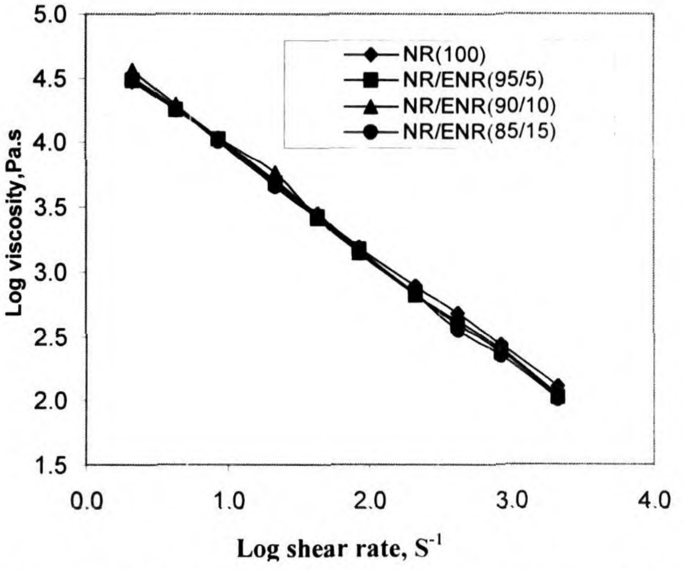

Fig.5.9 NR/ENR gum blend (Viscosity vs Shear rate) -90 deg.C

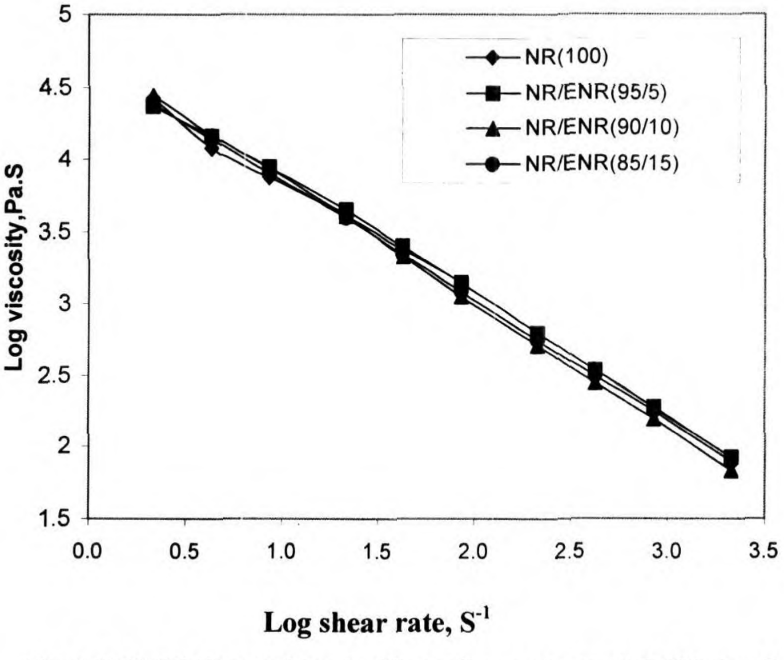

Fig.5.10 NR/ENR gum blends-(Viscosity vs shear rate)-120 deg.C

Silica filled rubbers generally exhibit high viscosity and therefore their processability is poor as compared to the black filled rubbers[44]. Derringer [42] reported that silica filled SBR exhibits higher viscosity, compared to the corresponding ISAF filled, especially at lower shear rates, while at higher shear rates the viscosity margin get reduced. Time and temperature of storage enhances the viscosity of silica filled composites, which is attributed to the formation of filler network or bound rubber[2]. With annealing, the filler network get stiffened. Schaal et al [41] reported that ingredients such as CBS or DPG and moisture could reduce the viscosity of silica filled composites. Compared to gum EPDM, silica incorporation considerably raises the compound viscosity especially at lower shear rates[1].

Studies on viscosity change with shear rate conducted at 4 different temperatures viz; 90,100,110 and 120°C for composites of NR/Silica and the same modified with silane or ENR 50 at 3 different concentrations each, as given in Table 5.3, were made. Results are compared in Figs.5.11 to 5.18. Filled samples also exhibited pseudoplastic behavior. Unmodified silica filled NR exhibited a slight non-linearity in viscosity drop especially at medium to high shear rates which is likely to be due to some filler networking at higher shear rates. Similar observations were noted for silica filled EPDM [1]. As compared to the unmodified silica composites, a general decrease in viscosity was noted with incorporation of silane and ENR at all ranges of shear rates. The viscosity was found to get reduced to a larger extent with ENR incorporation than with silane. With silane incorporation, the margin of viscosity decrease with that of the unmodified mix got reduced with increase of temperature. This is likely to be due to filler reagglomeration at higher temperatures [2]. With ENR modification considerable viscosity difference with that of

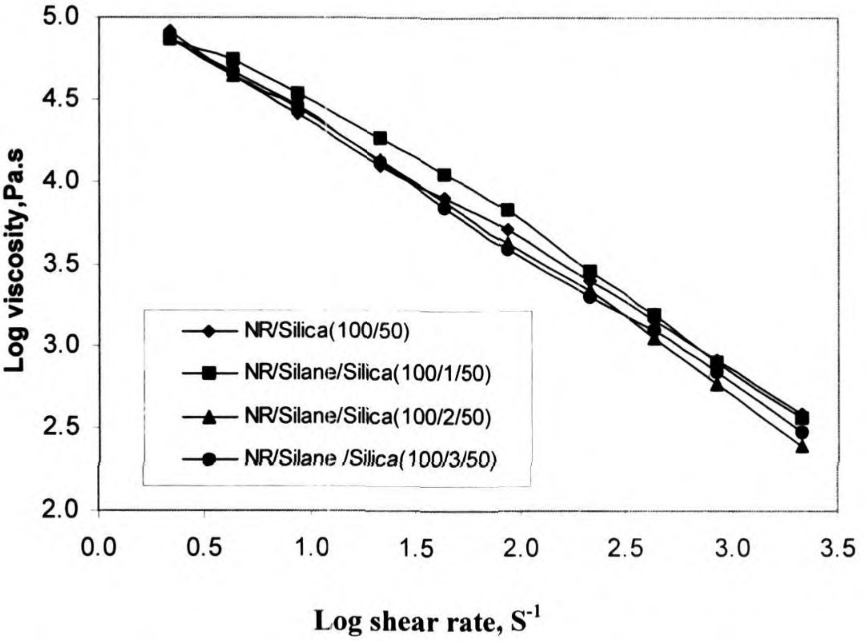

Fig.5.11 NR/Silica -Effect of silane (Viscosity vs Shear rate-90 deg.C)

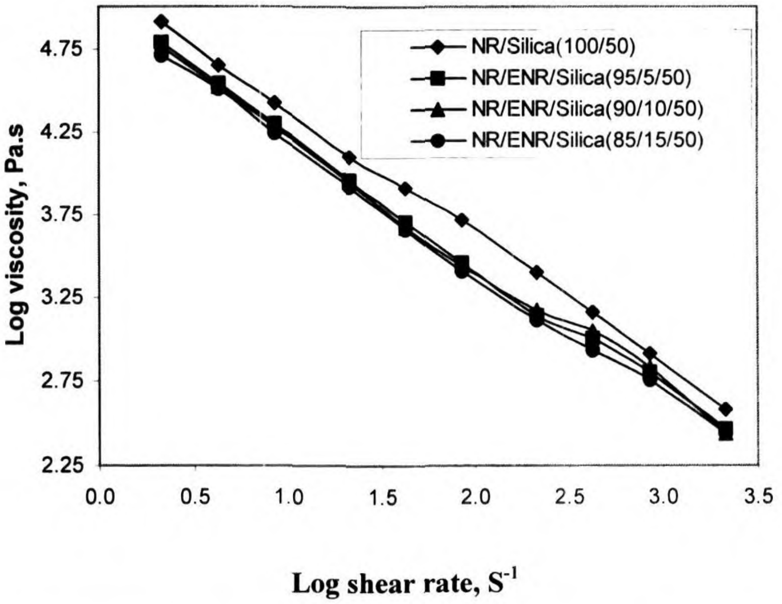

Fig. 5.12 NR/Silica-Effect of ENR (Viscosity vs Shear rate-90 deg.C)

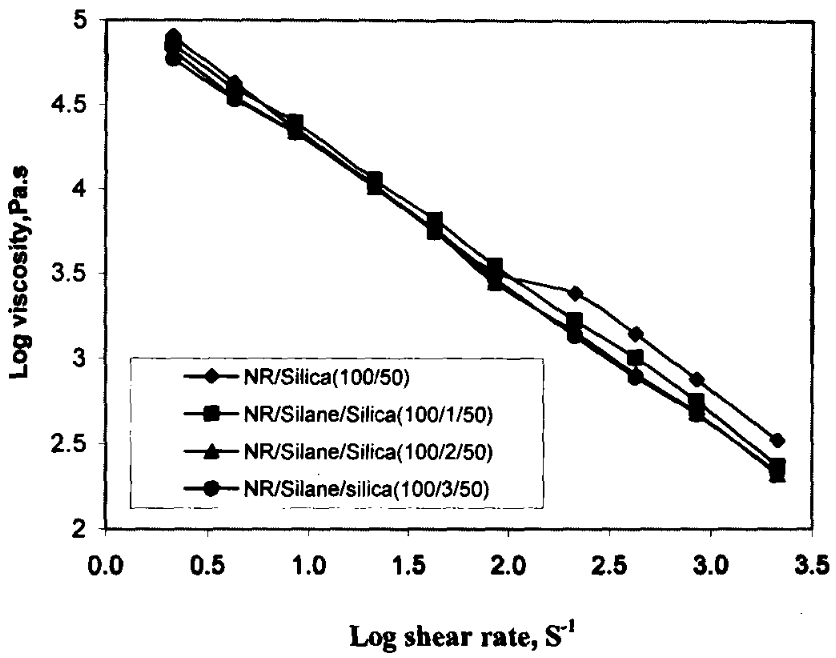

Fig. 5.13 NR/Silica-Effect of silane(Viscosity vs shear rate) 100 deg.C

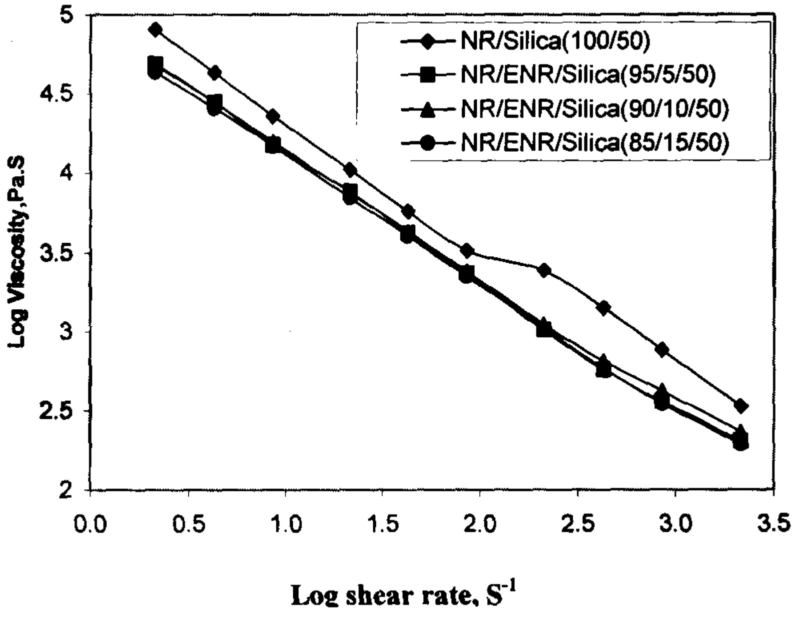

Fig. 5.14 NR/Silica-Effect of ENR(Viscosity vs shear rate)-100 deg.C

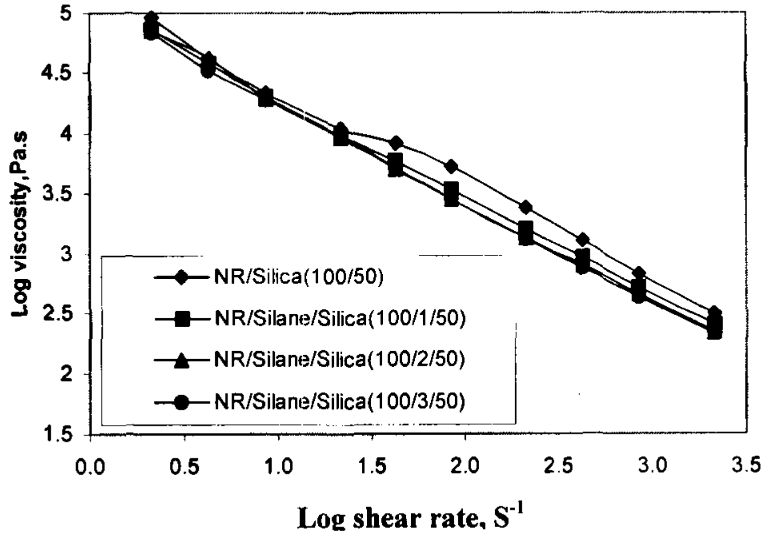

Fig. 5.15 NR/Silica-Effect of silane(Viscosity vs Shear rate)-110 deg.C

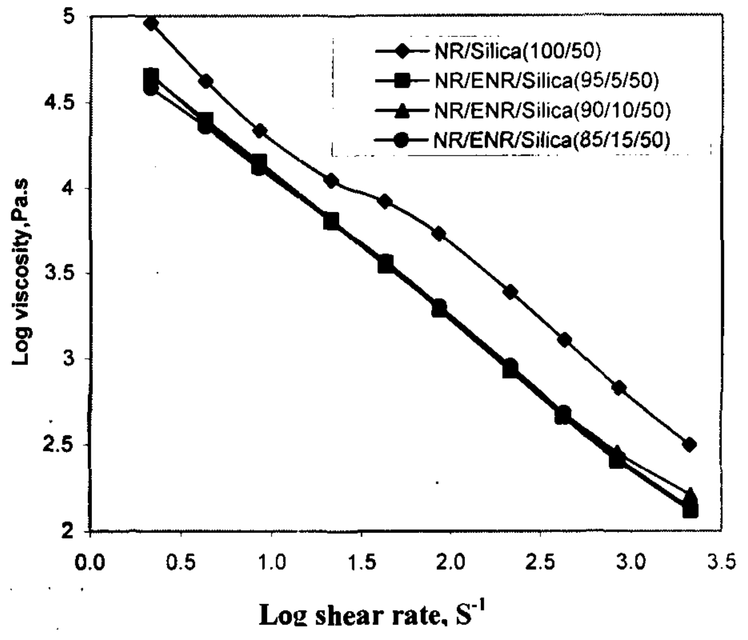

Fig. 5.16 NR/Silica-Effect of ENR(Viscosity vs shear rate)-110 deg.C

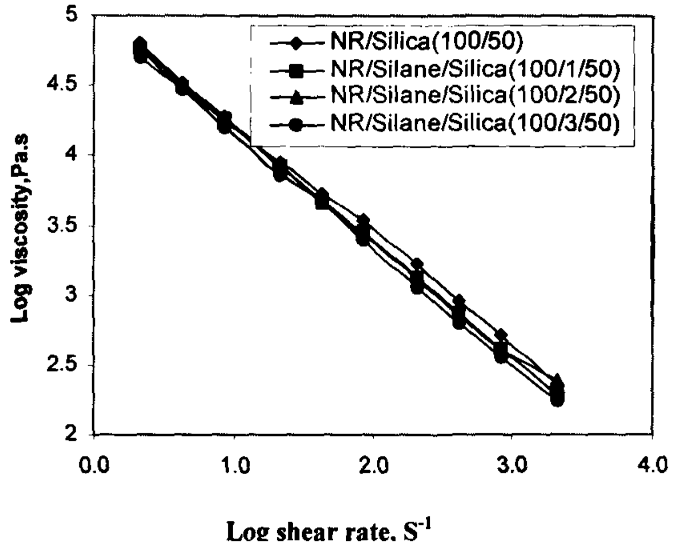

Fig. 5. 17 NR/Silica -Effect of Silane(Viscosity vs shear rate)-120 deg.C

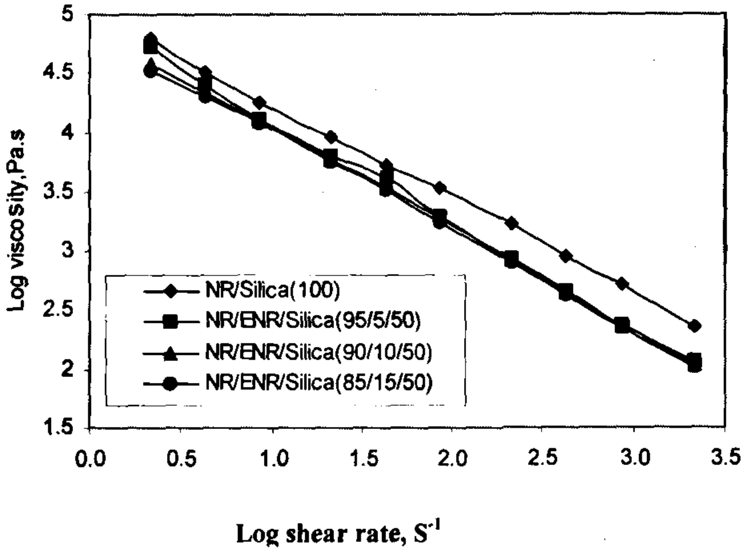

Fig. 5.18 NR/Silica-Effect of ENR(Viscosity vs shear rate)-120 deg.C

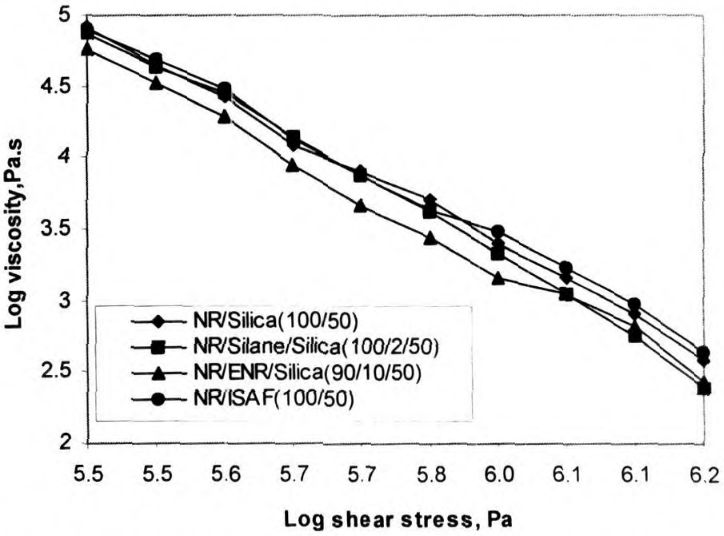

Fig. 5.19 Comparison of Viscosity variation with Shear stress(90 deg. C)

the unmodified was retained even at higher temperatures. This indicates that ENR could function also as a process aid for the silica filled NR. Earlier workers have reported that addition of certain ingredients such as glycols [44] and curatives such as CBS, DPG and moisture could reduce the viscosity of silica filled rubbers [1]. Composites filled with stearic acid treated inorganic fillers exhibits lower viscosity [1]. This is attributed to the hydrogen bonding ability of these materials. The tendency for viscosity increase at higher shear rates, also get considerably reduced with ENR incorporation and the viscosity drop became almost linear.

A comparison of the viscosity variation with shear rate for NR/Silica and its silane and ENR modified systems at particular concentrations with that of carbon black filled at 90 and 120°C are given in Figs.5.19 to 5.20. It can be observed that among the filled samples, the ENR modified system exhibited the lowest viscosity at different shear rates and temperatures.

b) Shear viscosity- Effect of temperature

A comparison of the variation of viscosity with temperature for the silica filled NR, silane modified, ENR modified and carbon black filled systems are compared in Figs. 5.21 to 5.24. The silica filled NR showed a non-linear viscosity relation with temperature, whereas silane modification reduces viscosity linearly with temperature. ENR modified silica filled and black filled NR exhibited a steady viscosity drop with temperature at all shear rates. This indicates that the processability of silica filled NR got considerably improved with ENR addition and is similar to that of the carbon black filled. The dependence of viscosity of various composites on temperature at a shear rate of 854 S^{-1} is shown in Fig. 5.25, in semi logarithmic Arrhenius plots of η vs 1/T . In the Arrhenius equation η is related to absolute temperature(T) by the relation,

$$\eta = A.e^{-E/RT} \qquad \textbf{Eq. 5.10}$$

where A, is a constant characteristic of the polymers, E, is the activation energy of flow, T, is the absolute temperature and R, the universal gas constant.

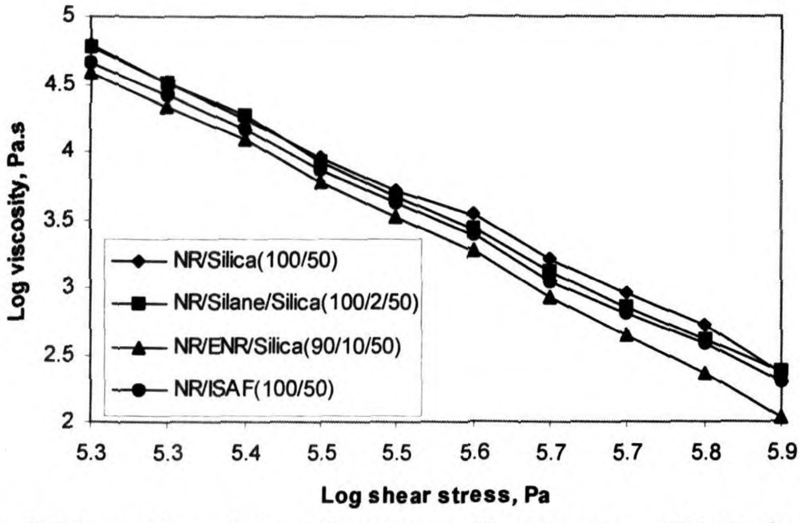

Fig. 5.20 Comparison of viscosity variation with shear stress (120 deg.C)

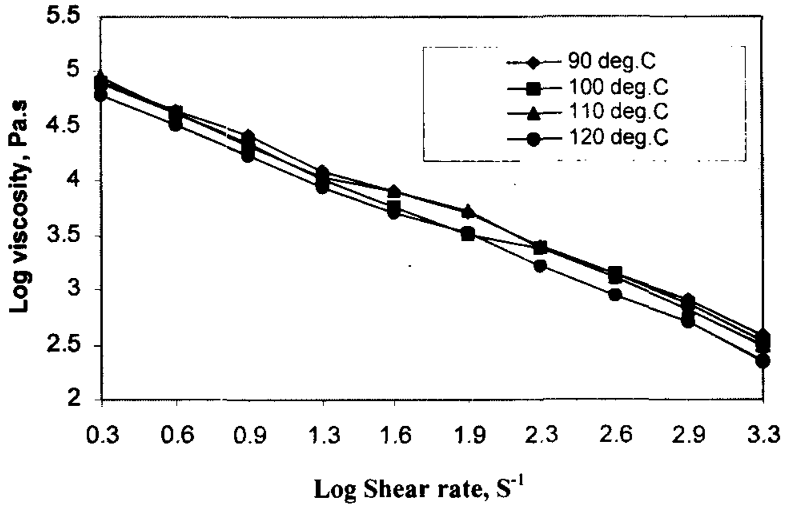

Fig. 5. 21 Effect of temparature on variation of viscosity with shear rate (NR/Silica)

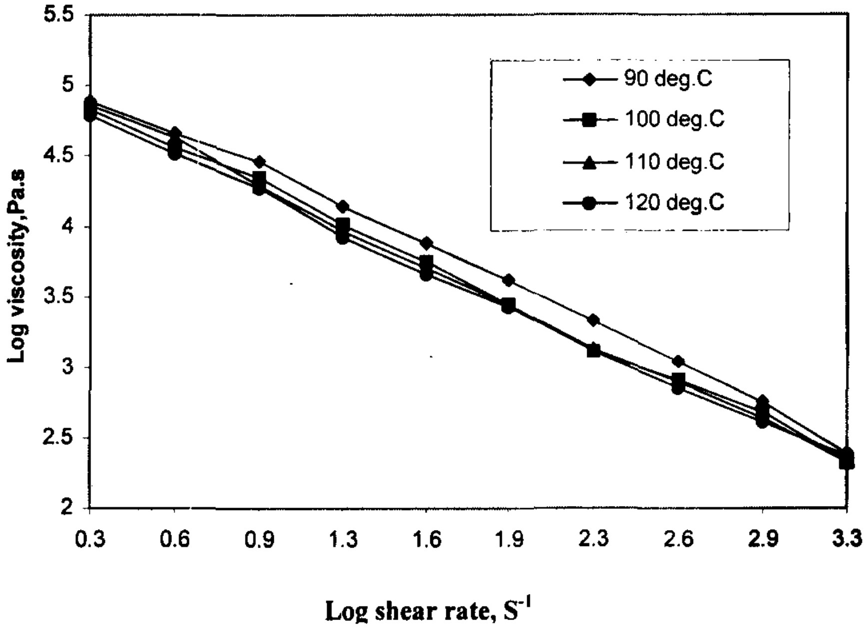

Fig. 5.22 Effect of temparature on viscosity (NR/Silane/Silica,100/2/50)

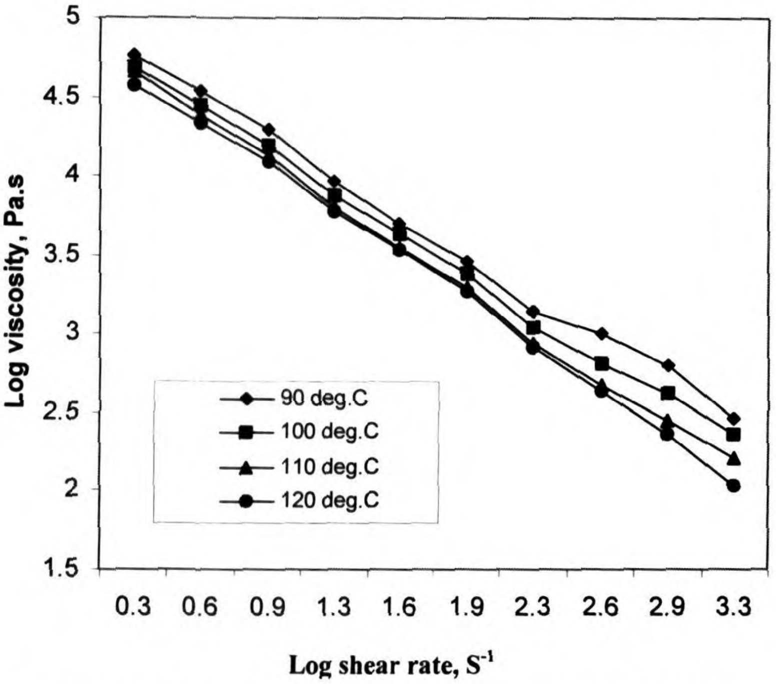

Fig. 5.23 Effect of temparature on viscosity (NR/ENR/Silica,90/10/50)

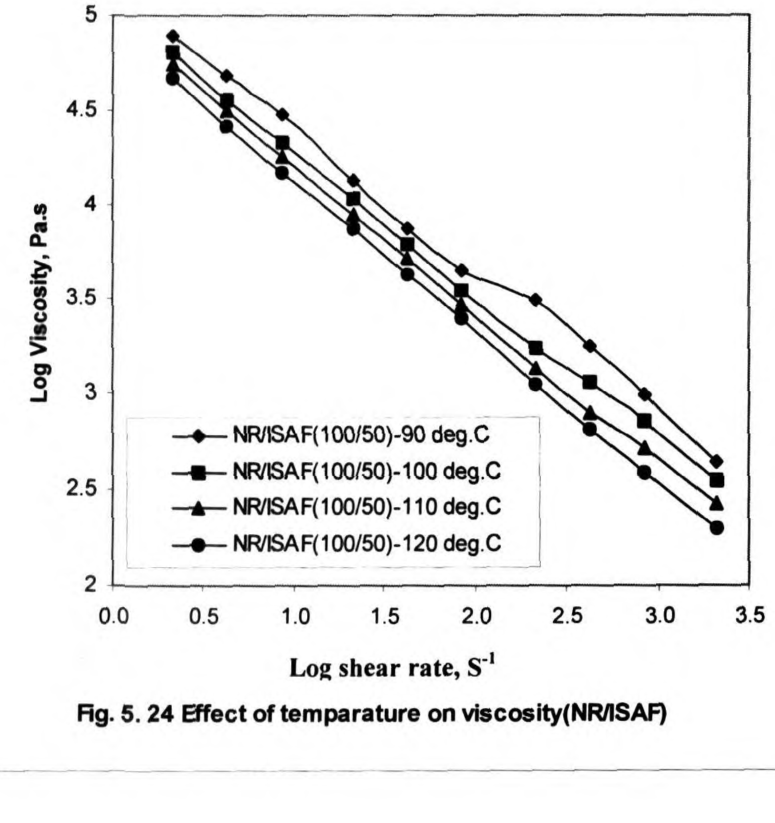

Fig. 5. 24 Effect of temparature on viscosity(NR/ISAF)

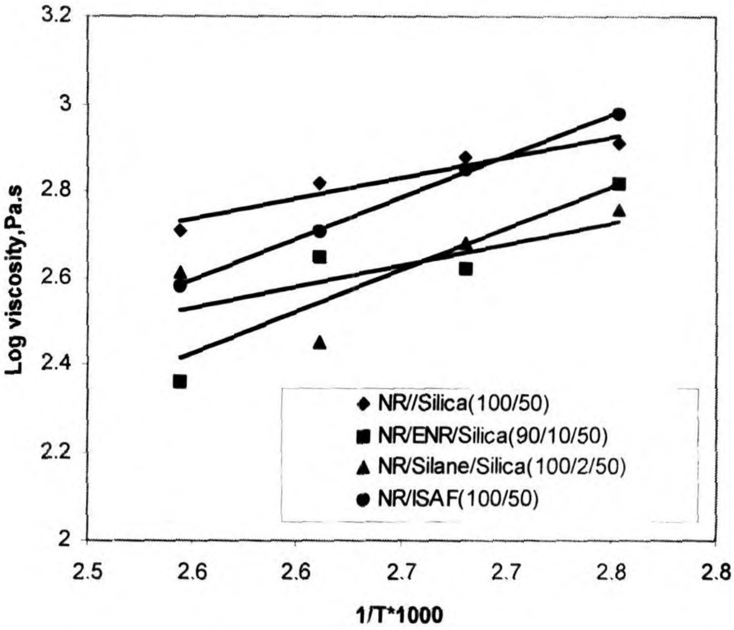

Fig. 5.25 Arrhenius plot (Shear rate 854 S^{-1})

Table 5. 5 Activation energy of flow (E)

Sample	**(E), Cal.mole^{-1}deg.$^{-1}$ at 854 S^{-1}**
NR/Silica (100/50)	1.86
NR/ENR/Silica (90/10/50)	3.81
NR/Silane/Silica (100/2/50)	1.96
NR/ ISAF (100/50)	3.8

Table 5. 6 Flow behavior index (n')

Sample	**n' Values**			
	90 °C	**100 °C**	**110 °C**	**120 °C**
NR/Silica (100/50)	0.239	0.236	0.215	**0.208**
NR/ENR/Silica (90/10/50)	0.245	0.212	0.169	**0.147**
NR/Silane/Silica (100/2/50)	0.1748	0.1718	0.161	**0.187**
NR/ISAF (100/50)	0.262	0.246	0.217	**0.205**

From the slope of the curves, E, the activation energy values were calculated. A comparison of the activation energy of flow for different composites is given in Table 5.5.

Variation of flow behavior with temperature for ENR modified and carbon black filled systems is almost similar. Arrhenius plots and the activation energy values indicate that with temperature rise, considerable viscosity reduction has occurred for the ENR modified and the carbon black filled systems, whereas significant change could not be seen for the silica filled NR and its silane modified. Flow behavior index values for selected composites given in Table 5.6 also indicate that for the ENR modified and the carbon black filled systems pseudoplasticity or reduction in viscosity with shear rate has occurred with temperature rise.

c) Shear stress

Filled composites generally exhibit yield stress for flow to occur. Yield stress generally increases with particle concentration and decreasing particle size. Yield stress usually is attributed to the filler particle network. Dominant networking factors are filler-filler and filler-polymer interactions. Processing aids could lower the yield stress [38,45].

For a better understanding of the flow behavior of various experimental composites, the plots of log shear stress versus log shear rate were compared. The plots

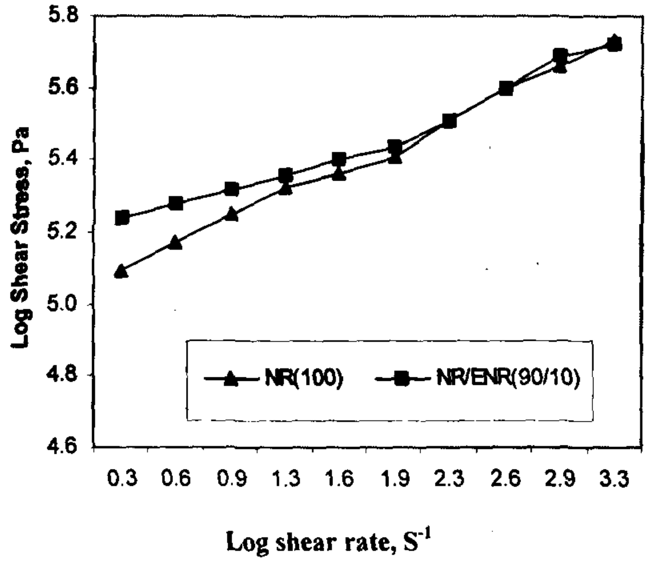

Fig. 5. 26 Variation of shear stress with shear rate-90 deg.C

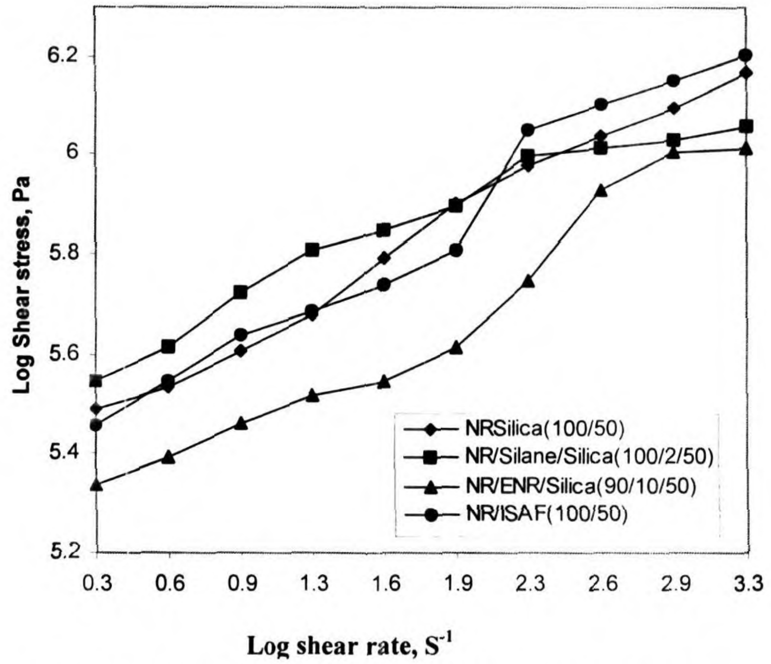

Fig. 5. 27 Variation of shear stress with shear rate(90 deg .C)

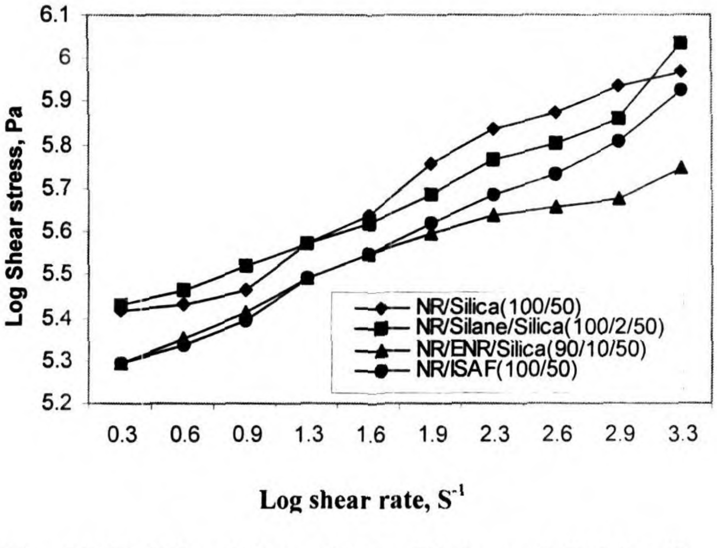

Fig . 5.28 Variation of shear stress with shear rate(120 deg.C)

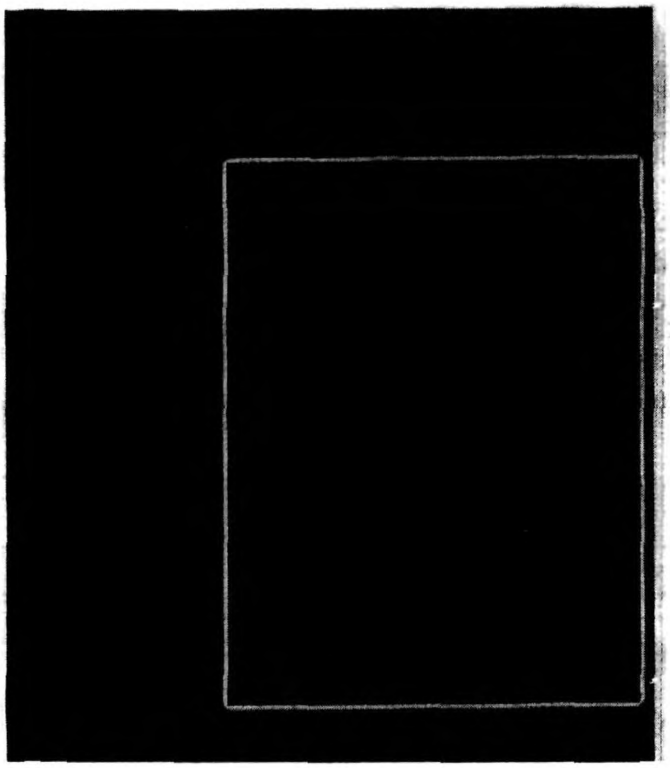

Fig. 5.29 Die swell characteristics (90° C)

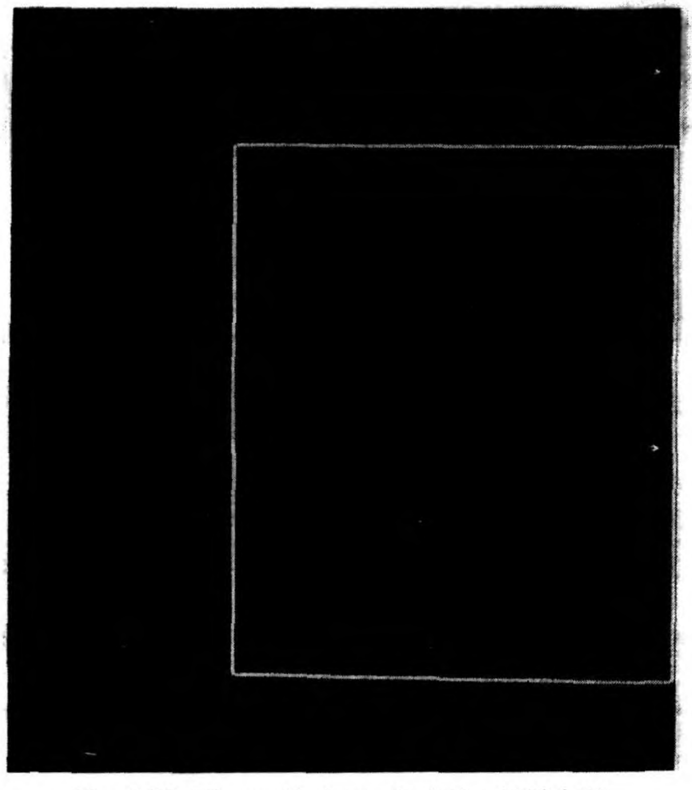

Fig. 5.30 Die swell characteristics (120 ° C)

Table: 5.7 Die swell data (Extrudate), 90 °C

Sample	De/Dc (90°C)		
	$8.54\ S^{-1}$	$85.4\ S^{-1}$	$854\ S^{-1}$
NR	1.41	1.88	2.6
NR/ENR50 (95/5)	1.21	1.62	2.12
NR/ENR50 (90/10)	1.17	1.62	2.11
NR/ENR50 (85/15)	1.22	1.74	2.36
NR/Silica (100/50)	1.12	1.07	1.06
NR/Silica/Silane (100/50/1)	1.15	1.12	1.1
NR/Silica/Silane (100/50/2)	1.21	1.16	1.09
NR/Silica/Silane (100/50/3)	1.38	1.3	1.18
NR/ENR/Silica (95/5/50)	1.03	1.09	1.12
NR/ENR/Silica (90/10/50)	1.06	1.12	1.12
NR/ENR/Silica (85/15/50)	1.03	1.12	1.12
NR/ISAF (100/50)	1.18	1.2	1.19

for gum NR and NR/ENR (90/10) blend are compared in Fig. 5.26. It can be observed that ENR blended NR exhibited slightly higher shear stress than NR alone at lower shear rate and became almost identical at higher shear rates. Similar plots of the selected silica filled and carbon black filled composites at 90 and 120°C are given in Figs. 5.27 and 5.28. ENR modified silica filled composites exhibited lower shear stress, compared to other composites. It is reported that filled systems containing process aids could lower the shear stress indicating better processability [38,46]. Processing promoters generally improve filler dispersion, flow properties and scorch safety and reduce the energy for processing [46]. It could be presumed that ENR might have acted also as a processing aid in getting silica better dispersed in NR. At 90°C, black filled composites exhibited higher shear stress, while the corresponding NR/ENR/Silica composite exhibited the lowest shear stress at all shear rates. Under the same temperature condition, incorporation of silane in silica filled NR could not reduce shear stress at lower shear rate, while at higher shear rate, the stress get closer to that of the ENR modified system. At 120°C and at higher shear rates, variations in shear stress among the composites were found to be in the order NR/Silica> NR/Silane/Silica> NR/Black> NR/ENR/Silica.

Table 5.8 Die swell data (Extrudate), 120 °C

Sample	**De/Dc (120°C)**		
	8.54 S^{-1}	**85.4 S^{-1}**	**854 S^{-1}**
NR	1.47	1.38	1.77
NR/ENR50 (95/5)	1.41	1.36	1.83
NR/ENR50 (90/10)	1.3	1.33	1.88
NR/ENR50 (85/15)	1.36	1.24	1.77
NR/Silica (100/50)	1.04	1.13	1.13
NR/Silica/Silane (100/50/1)	1.16	1.17	1.24
NR/Silica/Silane (100/50/2)	1.21	1.24	1.25
NR/Silica/Silane (100/50/3)	1.24	1.27	1.38
NR/ENR/Silica (95/5/50)	1.0	1.07	1.15
NR/ENR/Silica (90/10/50)	1.0	1.09	1.13
NR/ENR/Silica (85/15/50)	1.0	1.06	1.11
NR/ISAF (100/50)	1.15	1.2	1.3

d) Die swell:

Unfilled elastomers generally exhibit higher melt elasticity or higher die swell. Higher molecular weight and broader molecular weight distribution enhances die swell. Decrease in filler particle size and increase in structure reduce die swell [43].

A comparison of the die swell (D_e/D_c) of various extrudates under study at different shear rates at 90°C and 120°C are given in Tables 5.7 and 5.8 respectively and their photographs are given as Fig. 5.29 and 5.30. Unfilled elastomers exhibited the highest swell. Extrudates of gum NR and NR/ENR blends have not shown significant difference.

Among the filled composites, the unmodified and ENR incorporated compounds in general, exhibited lower die swell. Black filled and silane modified silica filled composites exhibited die swell in a narrow range, slightly higher than the other two silica filled systems, most likely to be due to a networking of rubber and filler and the resultant elasticity.

5.4 Conclusions

A comparative processability study of NR/Silica and ENR and silane modified composites was made with that of NR/Carbon black mixes. Mixing behavior of NR/Silica composites improved on incorporation of ENR in limited quantities. Energy requirements for mixing of silica in NR in the presence of ENR was found comparable to that for carbon black. Viscosity values of ENR modified silica filled and carbon black filled systems are almost close. Higher bound rubber values for the ENR modified system indicated better rubber-filler interaction. Larger retention of bound rubber in ammonia medium for the ENR modified system indicates, stronger rubber-filler interaction. Rheological studies showed improved processability of NR/Silica composites with ENR incorporation. ENR modified system exhibited lower die swell as well.

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CHAPTER 6

STUDIES ON PEROXIDE VULCANIZATION OF SILICA-FILLED NATURAL RUBBER AND ITS MODIFIED SYSTEMS - EFFECT OF FILLER LOADING

6.1 Introduction

Elastomers derived from isoprene and butadiene are readily crosslinked by peroxide, but many of the vulcanizate properties are inferior to those of accelerated sulphur vulcanizates. However, peroxide vulcanizates may be desirable in applications where improved thermal ageing and low compression set are required. Peroxide vulcanization occurs through a free radical mechanism [1]. A review of the peroxide crosslinking of elastomers has been made by Class [2].

Properties of filled rubber compounds and vulcanizates are largely the result of the combined influence of filler-polymer bonds and the type and number of crosslinks. These two factors determine the balance between the elastic and viscous responses to deforming stresses. Carbon black reinforcement mainly operates through rubber-filler bonding in which the influence of the filler on crosslinking is relatively less. Unlike carbon black, precipitated silica has a considerable influence on sulphur crosslinking and therefore it is difficult to assess its true reinforcing effect [3]. Due to the silanol-zinc oxide interaction in silica-filled systems, zinc activated sulphur vulcanization gets decelerated. In peroxide cure system, unlike sulphur crosslinks, carbon-to-carbon crosslinks are produced [3,4]. The study of peroxide curing of silica-filled elastomer compounds provides an opportunity to explore silica reinforcement mechanism free from the constraints and ambiguities present in zinc oxide activated sulphur cure system. Such studies have been reported by Wolff et.al [5,6].

The present chapter deals with the studies on peroxide vulcanization of silica-filled natural rubber modified with ENR and silane, with special reference to its reinforcement characterization.

6.2 Experimental

6.2.1 Materials

Materials used and the source of supply are given below.

Material	**Source of supply**
Natural rubber (ISNR-5)	Rubber Research Institute of India
Epoxidised natural rubber (ENR 50)	,,
Precipitated silica (Ultrasil VN3)	Degussa A.G. Germany
Silane coupling agent (Si 69)	,,
Dicumyl peroxide (DCP)	Geo Peroxides

6.2.2 Mix recipes

Formulation of the mixes are given in Table 6.1. The mixes can be broadly classified into three groups. viz; NR/Silica, NR/ENR/Silica and NR/Silane/Silica.

Table 6. 1 Formulation of mixes

Ingredients	**Mix designation**		
	A	**B**	**C**
NR	100	90	100
ENR50	-	10	-
Ultrasil VN_3	0-60	0-60	0-60
Zinc stearate	0.5	0.5	0.5
DCP(40% active)	3	3	3
Si-69	-	-	*

*4% based on weight of filler

6.2.3 Mixing of compounds and moulding

Rubbers used for compounding were having an initial Mooney viscosity of 70 ± 1. It was then masticated /blended in a laboratory two roll mill for 5 minutes. The resultant rubber was used for further compounding. Compounds were prepared in a laboratory model internal mixer (FRANCIS SHAW, K0, MK3) with a fill factor of 0.7. The mixing sequence is given in Table 6.2. A second stage mixing of the compounds from the internal mixer was done in the laboratory model two roll mixing mill for three minutes under identical conditions for finer homogenization. The mixes are designated as A_0 to A_{60} (NR/Silica) B_0 to B_{60} (NR/ENR/Silica) and C_0 to C_{60} (NR/Silane/Silica) as is given in Table 6.3.

Table 6.2 Mixing sequence

Ingredient	**Time of addition (sec)**
Rubber	0
Zinc stearate	30
Silica (1/2)	60
Silica (1/2)	120
DCP	300
Dump	480

Table 6.3 Mix identification

Compound	**Filler loading(phr)**						
	0	**10**	**20**	**30**	**40**	**50**	**60**
NR/Silica	A_0	A_{10}	A_{20}	A_{30}	A_{40}	A_{50}	A_{60}
NR/ENR/Silica	B_0	B_{10}	B_{20}	B_{30}	B_{40}	B_{50}	B_{60}
NR/Silane/Silica	C_0	C_{10}	C_{20}	C_{30}	C_{40}	C_{50}	C_{60}

Moulding of various test samples was done in a hydraulic press fitted with electrically heated platens by compression moulding technique at 160°C.

6.2.4 Testing of samples

Mooney viscosity of the various mixes was determined using Mooney viscometer Model SHIMADSU SMV 202 and the curing characteristics using Monsanto Rheometer-R_{100}.

Mechanical properties of the vulcanizates viz; stress-strain properties, tear strength, hardness and heat build-up were tested as per the respective ASTM standards, resilience as per BS 903, part A8 and abrasion loss as per DIN 53516. Reinforcement characterization was done by equilibrium swelling studies. Viscoelastic characterization of the vulcanizates in a range of temperature (-80 to +100°C) was done using DMA analyzer (DMA 2980) of TA Instruments, USA. Filler distribution studies of selected vulcanizates were done using Hitachi scanning electron microscope (Model H 6010 A).

6.3 Results and Discussion

6.3.1 Mixing temperature and compound viscosity

Silica filled rubbers in general show higher viscosity, especially at low shear rate, higher filler loading and with finer particle size [7,8]. Silica possesses very strong filler-filler interaction and hence the high viscosity. On silane treatment hydrophobation of the silica surface occurs and the filler-filler interaction and thus the viscosity are dramatically reduced [9]. High viscosities generate high shear stresses and the consequent excessive energy dissipation in the compound, will result in high mix temperature. Activators such as glycols, triethanolamine etc. are known to reduce viscosity. The viscosity reduction mechanism of these materials is attributed to the hydrogen bonding capability of these materials with silica [10]. Mooney viscosity (low shear rate) values have been used as a measure of compound viscosity.

Temperature rise of the experimental compounds at the time of dumping is given in Table 6.4. Temperature rise is mostly viscosity and rubber-filler interaction dependent.

Table 6.4 Temperature rise during mixing, ^{0}C (Initial temperature, 40^{0}C)

Compound	Filler Loading(phr)						
	0	**10**	**20**	**30**	**40**	**50**	**60**
A	91.4	88.4	88.6	82.6	87.6	88.6	90
B	101.4	85.4	83.4	84.6	88.4	84.1	91.6
C	91.4	91.4	83.4	83.6	85.4	85.1	90

Mooney viscosity measurements of the experimental compounds are given in Table 6.5. Up to 50 phr loading, Mooney viscosity was found to be slightly lower for the

ENR containing samples than the unmodified. Up to 30 phr silica loading Mooney viscosity of ENR and silane modified mixes are almost within a range. Above this level all the samples exhibited higher Mooney viscosities. Order of viscosity increase was NR/Silica> NR/Silane/Silica> NR/ENR/Silica. The slight lowering of viscosity with addition of ENR is likely to be due to the interaction between epoxy group and the silanol groups, which might have contributed to better filler dispersion and rubber-filler interaction and the lowering of filler-filler interaction. However, at higher filler concentrations the high viscosity exhibited may be due to the higher filler-filler interaction resulting from the high filler-filler proximity. Since ENR is prone to degradation at higher temperatures, the maximum dump temperature for all the compounds was kept below 100^{0}C.

Table 6. 5 Mooney viscosity of the mixes

Property	Compound	Filler loading(phr)						
		0	10	20	30	40	50	60
Mooney viscosity, $M_L(1+4)$, 100^o C	A	34.7	52.2	59.2	74	100.3	-	-
	B	35.9	45.7	57.4	61.3	65.9	70.2	-
	C	34.7	51.4	56.2	63.7	73.8	118.2	-

6.3.2 Cure characteristics

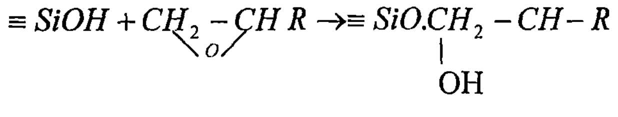
Results of the rheometric studies are given in Table 6.6. The minimum torque obtained with a Monsanto Oscillating Disc Rheometer is also a measure of the compound viscosity. For all the three systems studied, minimum torque showed a regular increase with filler loading. The trend observed was as in the case of Mooney viscosity. Up to 40 phr, the viscosity values of ENR and silane modified systems were lower than that of the unmodified mix. Lower viscosity might have resulted from a reduction in filler-filler interaction due to the epoxy-silanol interaction and the silane modification of the silica.

Table 6. 6 Rheometric values

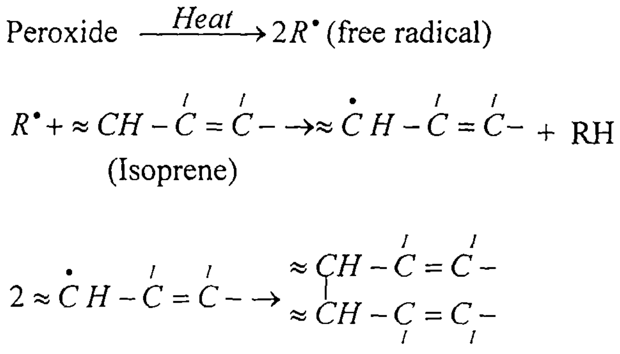
Property	Compound	Filler loading, phr						
		0	**10**	**20**	**30**	**40**	**50**	**60**
Minimum torque, dN.m	A	13	14	16	19	23	30	37
	B	10	11	14	16	17	28	40
	C	13	12	14	15	17	21	24
Maximum torque,dN.m	A	42	51	59	67	75	81	87
	B	41	50	61	70	79.5	87	89
	C	42	47	53	59	63	66	68
Optimum cure time (t_{90}), min.	A	30	25	23.5	19	17.5	16	15.5
	B	26.5	25.5	28	22	21	17.5	15
	C	30	22	27	24	19	18	16.5
Cure rate index, $100/(t_{90}-t_2)$	A	3.6	4.2	4.5	5.4	6	6.7	6.7
	B	4	4.2	3.8	4.9	5	6	7.1
	C	3.6	4.7	3.9	4.4	5.7	6	6.4

For all the three systems, maximum rheometric torque also was found increased with filler loading. Of the three systems, maximum torque was the highest for the ENR modified system. The relatively higher torque observed for the ENR modified system might have resulted from the known silanol- epoxy reaction. In general, with the sulphur cured systems, addition of TESPT is known to increase the torque due to filler-rubber bonding achieved through silanol-alkoxy and rubber-sulphide linkage. For the peroxide-cured system vinyl silanes are generally used. For the present experiment TESPT was used only for a comparative evaluation.

The probable rubber-filler bonding that might have occurred for the ENR modified peroxide cure system is given below[1].



$$\equiv SiOH + \underset{\diagdown O \diagup}{CH_2 - CH}\,R \rightarrow \equiv SiO.\underset{\overset{|}{OH}}{CH_2} - CH - R$$



Peroxide $\xrightarrow{Heat} 2R^{\bullet}$ (free radical)

$$R^{\bullet} + \approx CH-\overset{/}{C}=\overset{/}{C}- \rightarrow \approx \overset{\bullet}{C}H-\overset{/}{C}=\overset{/}{C}- + \mathrm{RH}$$

(Isoprene)

$$2\approx \overset{\bullet}{C}H-\overset{/}{C}=\overset{/}{C}- \rightarrow \begin{array}{l}\approx CH-\overset{/}{C}=\overset{/}{C}-\\ \approx CH-\underset{/}{C}=\underset{/}{C}-\end{array}$$

Hence ENR can interact with both silica and with the bulk of the rubber through peroxide induced crosslinking, hence the functional similarity with the silane. Unlike sulphur-cured systems, peroxide curing of silica-filled systems is unaffected by the presence of silica [11,12]. For all the three systems progressive incorporation of silica was found to have reduced the cure time. Cure rate index variation among the three series is only very narrow indicating that the rate of cure of peroxide system is not much affected by the introduction of modifiers.

When a filler is incorporated into a compound, the maximum torque increases during vulcanization. The ratio between the torque increase of the loaded compound and that of the gum was found to be directly proportional to filler loading. The slope of the linear plot showing the relative torque increase is a function of filler loading as defined by Wolff [13,14] as α_f.

$$\frac{D\max,f - D\min,f}{D\max,g - D\min,g} - 1 = \alpha_f . \frac{m_f}{m_p} \qquad \textbf{Eq. 6.1}$$

where, $D\max,_f - D\min,_f$ = Maximum change in torque during vulcanization for filled rubber, $D\max,_g$ - $D\min,_g$ = maximum change in torque during vulcanization for gum, m_p = mass of polymer in the compound, m_f = mass of filler in the compound and α_f = proportionality constant, which has been used to characterize the filler structure existing in the vulcanizates.

The differential torque (Dmax-Dmin), with filler loading for the three systems, are compared in Fig. 6.1. For all the three systems, differential torque increases with filler loading. The rate of increase is the highest for the ENR containing samples up to about 40 phr loading. This indicates that the presence of ENR might have caused some extra networking in the silica filled system. The silane modified compound gave the lowest torque enhancement. As there is no chance for filler rubber bonding through sulphur bridges in the peroxide cure system, the TESPT, being a low molecular weight material, might have lowered the effective torque.

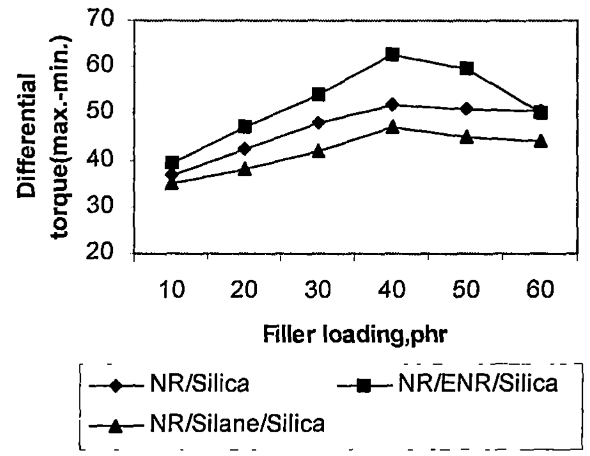


Fig. 6. 1 Variation of differential rheometric torque with filler loading

$\frac{D\max,_f - D\min,_f}{D^0\max,_g - D^0\min,_g} - 1$ is plotted against m_f/m_p in Fig.6.2. The slope of this curve, α_f gives an indication of the filler structure or the added network formed due to the silica-rubber interaction. The α_f values calculated for 0-40 phr filler loading, up to which the trend is linear, is given in Table 6.7. The ENR modified systems exhibited the highest α_f values, indicating added network structure in them than the NR/Silica composites, which is likely to be due to ENR- silica interaction.

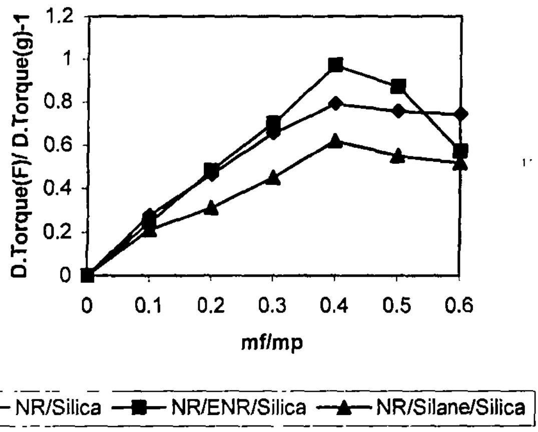


Fig. 6. 2 Variation of (DLf/DLg-1) with mf/mp

Table 6.7 αf values of mixes

Sample	α_f
NR/Silica	1.74
NR/ENR/Silica	2.39
NR/Silane/Silica	1.4

6.3.3 Vulcanizate properties

Vulcanizates made from each of the compounds cured to its optimum cure time (t_{90}) of the three series were tested for stress-strain and other mechanical properties.

6.3.3.1 Stress –strain properties

Modulus, tensile strength and elongation at break

Silicas in general are known for the relatively low modulus imparted to rubber, compared to that of the carbon black-filled. However, generally tensile strength values are of similar magnitude for the two types of fillers of comparable particle size. Accompanying the lower modulus and equal tensile strength is higher elongation at break. Modulus and tensile strength are dependent on the state of cure, the former increasing linearly with crosslinking and the latter passing through a. maximum.

Elastomers such as SBR, NBR and CR with silica filler, are known to exhibit lower modulus, higher elongation and equal tensile strength [15,16]. However, exceptions like vinylpyridine- butadiene rubber, are reported to exhibit good reinforcement with silica due to the specific strong interaction with the elastomer molecules. Increased modulus and abrasion resistance, concurrent with maximum tensile strength, can be achieved only through increased silica – rubber interaction [17].

Table 6.8 Stress- strain properties

Sample	Property	Filler loading, phr						
		0	10	20	30	40	50	60
A	Mod. 100%, MPa	0.41	0.53	0.7	0.89	1.15	1.38	1.85
	Mod. 200%, MPa	0.75	1.01	1.27	1.55	1.91	2.36	3.22
	Mod. 300%, MPa	0.90	1.24	1.58	1.94	2.42	3.01	4.14
	Tensile strength, N/mm^2	8.72	11.18	14.67	21.58	22.19	21.77	21.11
	Elongation at break, %	859	838	926	945	733	739	662
B	Mod. 100%, MPa	0.42	0,58	0.85	1.07	1.43	1.65	2.17
	Mod. 200%, MPa	0.42	1.17	1.79	2.27	3.03	3.24	3.87
	Mod. 300%, MPa	0.93	1.48	2.35	3.03	4.06	4.32	4.98
	Tensile strength, N/mm^2	4.36	10.97	16.7	21.3	23.7	24.93	26.1
	Elongation at break, %	826	690	664	603	637	646	627
C	Mod. 100%, Mpa	0.41	0.52	0.66	0.78	0.92	1.08	1.6
	Mod. 200%, Mpa	0.75	0.96	1.25	1.43	1.68	2.08	2.46
	Mod. 300%, Mpa	0.9	1.18	1.55	1.88	2.29	2.83	3.47
	Tensile strength, N/mm^2	8.72	8.73	15.57	21.9	23.7	26.6	27
	Elongation at break, %	859	674	747	956	812	840	865

A comparison of the modulus, tensile strength and elongation at break for the vulcanizates of the three systems at different filler loadings, is given in Table 6.8. The general observations that can be made are that modulus and tensile strength showed an increasing trend with filler loading. However, of the three systems, the ENR modified system exhibited comparatively higher modulus than the other two. A comparatively better tensile strength was also observed for the ENR modified system over the other two. The increase in modulus and tensile strength and the decrease in elongation at break

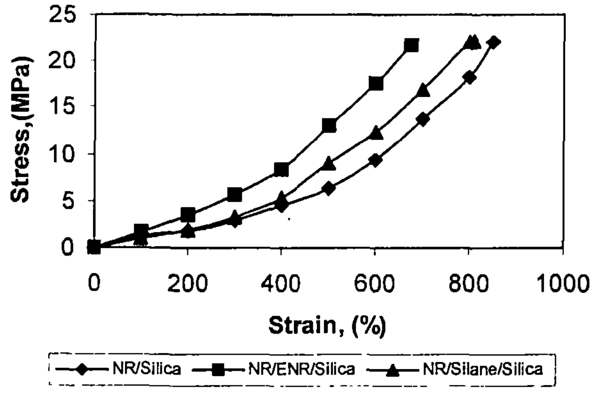


Fig. 6. 3 Stress- strain curve-30 phr filler loading

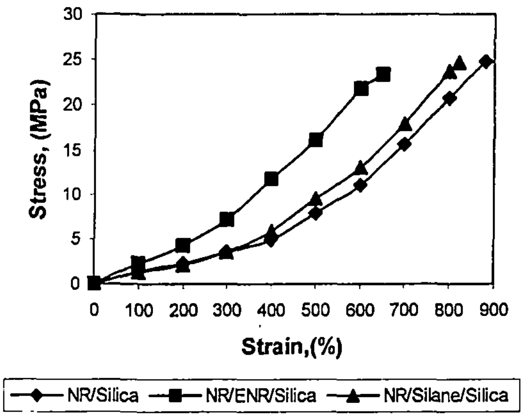


Fig. 6. 4 Stress-strain curve -40 phr filler loading

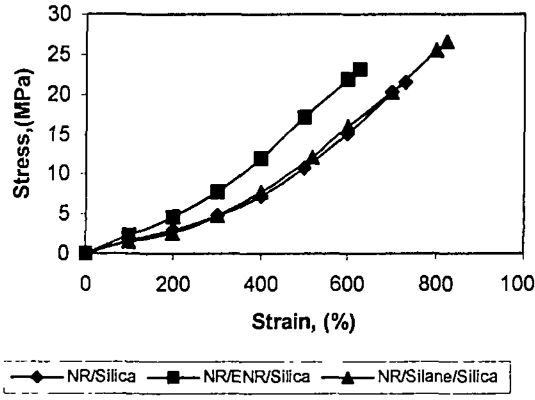


Fig. 6.5 Stress-strain curve-50 phr filler loading

with filler loading for the ENR modified systems can be considered as an indication of the better rubber-filler bonding.

Stress-strain behaviour of the three different systems at 30, 40 and 50 phr filler loading is compared in Figs. 6. 3, 6.4 and 6.5. The deformation behaviour of the various systems of vulcanizates are clear from the curves. The ENR modified system requires higher energy for deformation. The silane modified system also exhibited a slightly higher energy curve over the unmodified. Enhanced rubber-silica interaction achieved with ENR and silane might have caused the higher modulus and deformation energy.

6.3.3.2 Mechanical properties

A few important technological properties influenced by reinforcement viz. tear strength, abrasion loss, rebound resilience and hardness are given in Table 6.9.

Tear strength of a finished rubber product is an important factor influencing its failure behavior. Therefore, considerable importance is given to the tear resistance of rubbers. The development of high tear strength in a rubber is owing, to its ability to dissipate energy near the tip of a growing crack. Addition of filler introduces additional mechanisms by which strain energy is dissipated. Tear strength of the three different systems are compared in Fig.6.6. With the addition of filler, tear strength was found to

Table 6. 9 Technological properties

Property	Sample	Filler loading (phr)						
		0	10	20	30	40	50	60
Tear strength, N/mm	A	18.1	21.6	29.4	32.7	35.4	57.4	60.5
	B	17.4	24.6	36.1	38.8	44.6	58	59
	C	18.1	26.8	33.4	47.7	57.7	65.6	79.1
Hardness, Shore A	A	26	28	35	42	60	68	80
	B	28	30	43	52	61	66	80
	C	26	30	38	44	48	54	59
Abrasion loss, mm^3	A	-	-	257	222	187	168	135
	B	-	-	85	76.7	70.5	64.4	61.8
	C	-	-	197	130	111	91.5	71.3
Rebound resilience, %	A	61.8	58.4	54.9	54.9	51.9	50.1	50.2
	B	51.4	61.8	58.3	54.9	51.8	50.1	48.8
	C	61.8	58.4	58.4	58.4	58.4	54.9	51.8

have increased in an almost linear manner. ENR and silane modified systems showed comparatively higher tear strength than the unmodified, possibly owing to the improved wetting and interaction of the filler with the rubber.

Another important property relevant to reinforcement is the abrasion or wear resistance of rubber. Abrasion loss of the experimental systems are depicted in Fig.6.7. It is seen that the lowest abrasion loss or the highest abrasion resistance is exhibited by

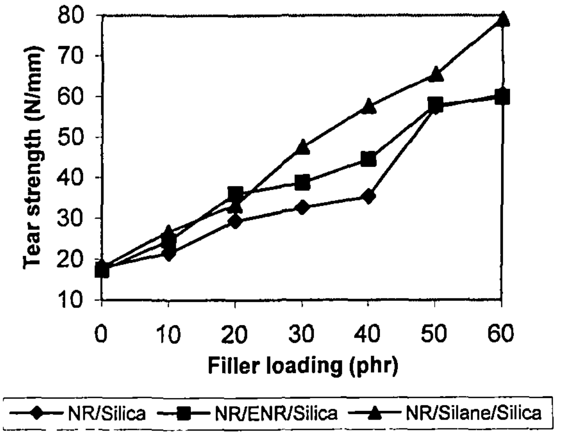


Fig. 6. 6 Variation of tear strength with filler loading

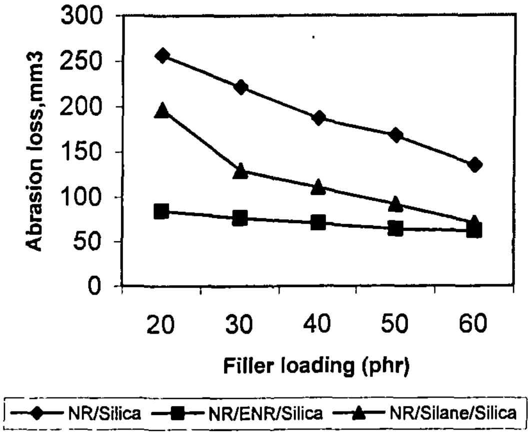


Fig .6. 7 Variation of abrasion loss with filler loading

the ENR modified system. As the general factors determining abrasion resistance remain the same for all the systems, the improvement shown by the modified system especially that with ENR might be due to the improved rubber-filler interaction and the filler structure in the rubber matrix. Hardness is considered a measure of the elastic modulus of rubber. The changes in hardness for the experimental filled vulcanizates are given in Fig.6.8. The three systems exhibited higher hardness with filler loading. The higher elastic modulus or hardness for the ENR modified system over the other two might be due to the epoxy group-silica networking and the resultant immobilization of the polymer molecules. Variations of resilience for the three series of vulcanizates are

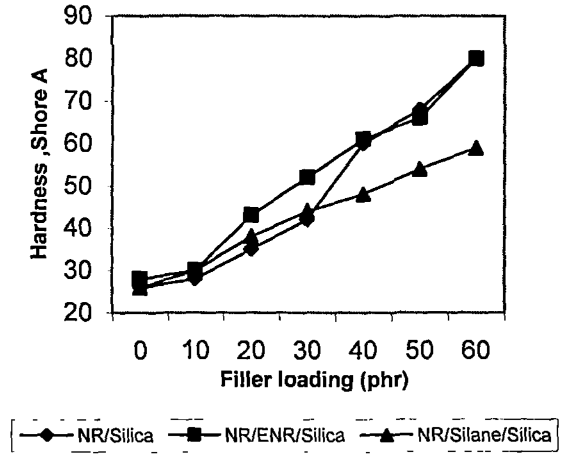


Fig.6. 8 Variation of hardness with filler content

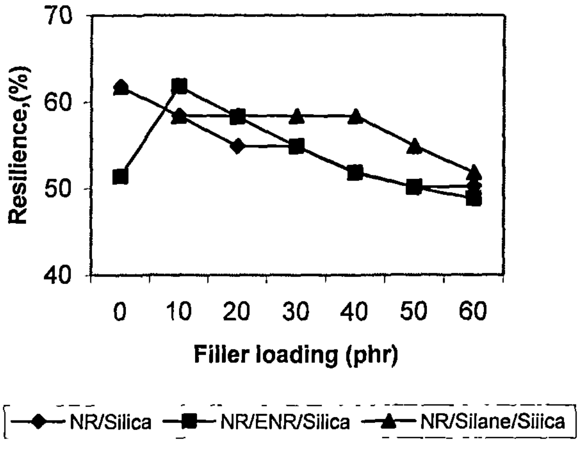


Fig. 6. 9 Variation of resilience with filler loading

presented in Fig. 6. 9. Drop in resilience was observed with filler loading. The ENR modified series showed lower resilience at moderate filler loading which is likely to be due to the inherent damping character of ENR and the restriction of the polymer segmental mobility by rubber-filler boding.

6.3.4 Equilibrium swelling studies

Equilibrium swelling of a filled vulcanizate can be used to characterize the extent of rubber-filler interaction. For peroxide vulcanization of natural rubber, Hummel [12] and Wolff [18] have shown that the crosslink density of the rubber matrix is not affected by fillers.

Cunneen-Russell [19] proposed an equation which is a variant of the Lorenz – Parks model [20] for characterizing reinforcement using equilibrium swelling of vulcanizates.

$$\frac{V_{ro}}{V_{rf}} = \mathbf{a.e^{-z} + b} \qquad \textbf{Eq. 6.2}$$

where Vr_o and Vr_f are the volume fraction of the rubber in unfilled and filled vulcanizates, respectively, after swelling in a solvent. The ratio of Vr_o to Vr_f is a measure of the polymer – filler interaction in the system. 'z' is the weight fraction of

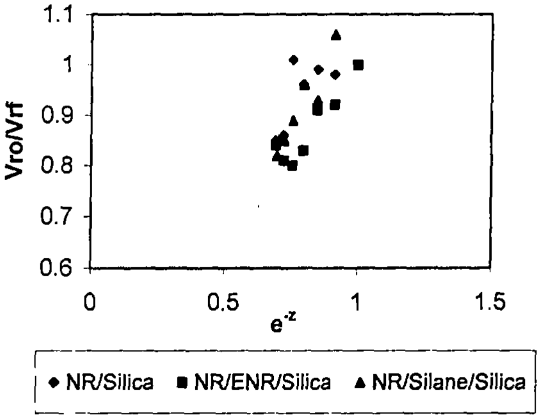


Fig.6.10 Reinforcement characterisation - Swelling studies (Cunneen- Russell)

filler in the polymer, a and b are constants which depend on the filler activity. High value of 'a' and low value of 'b' indicate strong polymer – filler attachment [19]. $V_{r0}/V_{rf} \leq 1$ indicates reinforcement. The data obtained from equilibrium swelling studies for the three series of vulcanizates as per the Cunneen-Russell equation are plotted in Fig.6.10. The slope of the curves is given in Table 6.10. The higher slope for the modified systems over the unmodified indicates better reinforcement.

Table 6. 10 Slope of V_{ro} / V_{rf} Vs e^{-z}

Sample	Slope
NR/Silica	0.42
NR/ENR/Silica	0.61
NR/Silane/Silica	0.665

From the equilibrium swelling studies of filled and gum vulcanizates, Kraus [21] derived the following expression to characterize rubber-filler interaction.

$$\frac{V_{ro}}{V_{rf}} = 1 - m\frac{\phi}{1-\phi} \qquad \textbf{Eq. 6.3}$$

where Vr_0 and Vr_f are the volume fraction of rubber in the swollen gum and filled vulcanizates respectively.

$$m = 3C\,(1-Vr_0^{1/3}) + Vr_0 - 1$$

where 'C' is a parameter characteristic of the filler and is related to filler-polymer interaction and the filler structure. For fillers having the same structure, a higher value of 'C' suggests higher rubber-filler interaction. The parameter 'm', obtained from the slope of the plot Vr_0/Vr_f versus $\phi/(1-\phi)$ is a means to quantify the extent of swelling restriction by polymer-filler interaction. For the three series of experimental vulcanizates, the swelling data are plotted as Vr_0/Vr_f vs $\phi/(1-\phi)$ and are given in Fig. 6.11. The

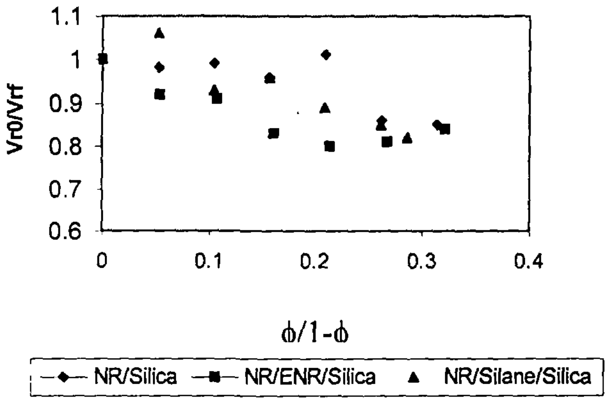


Fig. 6. 11 Reinforcement characterisation(Kraus)

slopes for the three series, obtained through regression analysis, are given in Table 6.11. The higher negative slope values for ENR and the silane modified systems indicate higher rubber-filler interaction.

Table 6. 11 Slope of V_{ro}/V_{rf} vs $\phi/1-\phi$

Sample	Slope
NR/Silica	-0.456
NR/ENR/Silica	-0.54
NR/Silane/Silica	-0.57

6.3.5 Dynamic mechanical analysis

Rubber being a viscoelastic material, is known to be temperature sensitive and its filled systems also exhibit the basic elastomeric property. However, incorporation of filler can alter the dynamic mechanical behaviour of filled systems. Dynamic mechanical properties of the three experimental vulcanizates at 50 phr silica loading for a temperature range of –100° C to +100° C at a frequency of 1 Hz, are compared for their storage modulus and tan δ in Figs. 6.12 and 6.13 respectively.

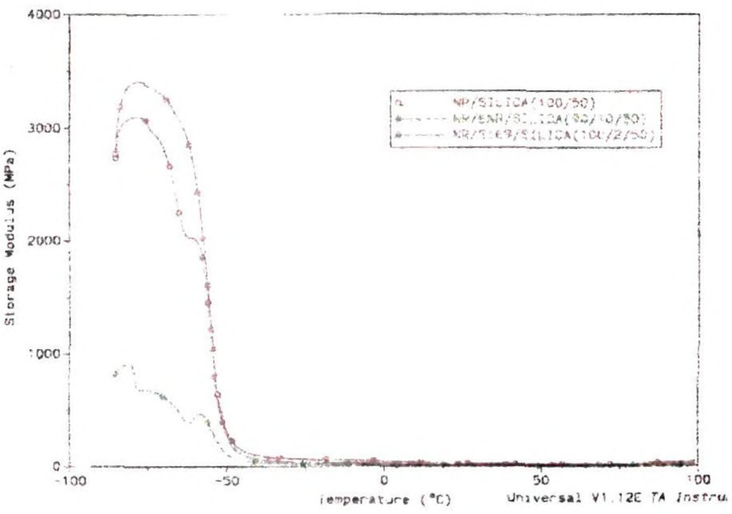


Fig. 6.12 Comparison of storage modulus

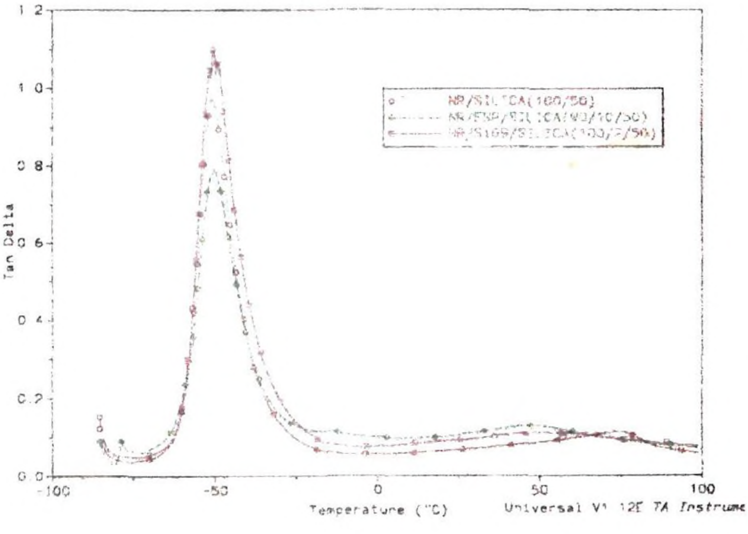


Fig. 6.13 Comparison of loss tangent

The striking features noted from the DMA analysis are;

i) Considerable reduction in storage modulus at temperatures below the glass transition temperature of the component rubbers was observed.

b) Reduction in tan δ peak height and broadening of the peak

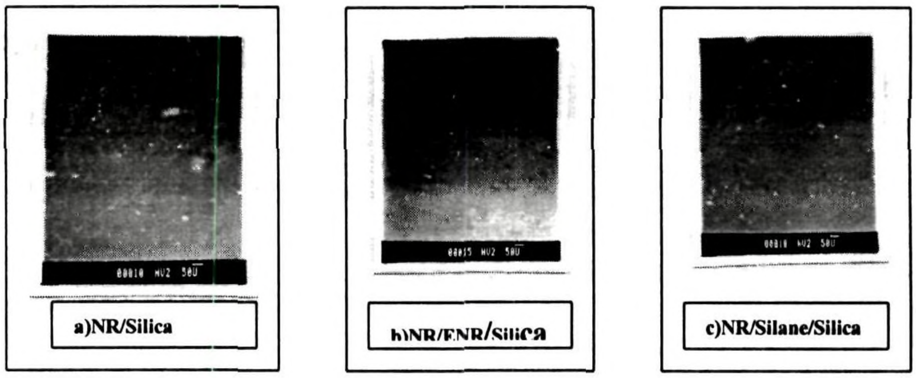
c) Higher tan δ for the ENR modified system at 0^0C.

d) No separate tan δ peak for NR and ENR.

Decrease in storage modulus at low temperature for the ENR containing system is likely to be due to either the hampering of the crystallization of the NR phase at lower temperature because of the ENR- silica networking or a reduction in filler-filler networking. Reduction in tan L peak height and its broadening with the introduction of ENR is probably due to the enhanced rubber-filler interaction. ENR modified systems exhibited higher tan L at 0^0C, which is considered an index for the wet grip property for tyres. Absence of separate tan L peak for NR and ENR points to the fact that both the polymers might have co-crosslinked in the presence of peroxides to form a single phase system.

6.3.6 Scanning electron microscopy (SEM)

Scanning electron microscopy can be used as a tool to characterize the filler distribution in the rubber matrix. SEM Photomicrographs of the cut surfaces of the three experimental vulcanizates viz: NR/Silica, NR/ENR/Silica and NR/Silane/Silica at 40 phr filler loading, are given in Fig. 6.14 a, b and c respectively. From the micrographs it can


a)NR/Silica

b)NR/ENR/Silica

c)NR/Silane/Silica

Fig. 6. 14 SEM Photographs of silica filled NR and its modified forms

be inferred that ENR and silane modification provides comparatively better filler distribution with less number of agglomerates.

6.4 Conclusions

Peroxide cured silica filled NR systems modified with ENR and silane were compared at varying filler loading. Modification of silica filled NR with ENR was found effective in reducing the viscosity of the resulting mixes. Cure characteristics showed that the ENR modified systems exhibited higher differential torque than the other two, likely to be due to improved rubber-filler bonding. Cure time and rate was not much affected due to the presence of modifiers. ENR modified system exhibited comparatively higher vulcanizate modulus than the other two. For the filled systems above 20 phr silica loading, ENR and silane modified systems exhibited higher tensile strength than the unmodified. Stress-strain behaviour showed that the ENR modified system exhibited higher energy for deformation than the other two. ENR and silane modified systems exhibited higher tear strength than the unmodified. Higher hardness and abrasion resistance were observed for the ENR modified system. ENR modified systems exhibited higher swelling resistance likely to be due to better rubber-filler bonding. ENR modified system exhibited lower modulus below the glass transition temperature. SEM studies also indicate better filler distribution in ENR modified composites.

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CHAPTER 7

REINFORCEMENT CHARACTERIZATION OF SULPHUR VULCANIZED SILICA FILLED NATURAL RUBBER -ROLE OF MODIFIERS

7.1 Introduction

Majority of rubber products are filler reinforced and sulphur vulcanized. Use of silica as a filler in rubber products either alone or in combination with carbon black or other fillers has been on the increase [1-3]. Natural rubber exhibits good strength even without fillers, due to its inherent strain crystallizing behaviour. However, most of the tonnage rubbers such as SBR, BR and EPDM require reinforcement for achieving strength. Properties other than strength such as modulus, elongation, hardness, compression set, resilience and wear resistance are also influenced by filler characteristics and loading. Reinforcement generally can be assessed based on the improvement in strength, modulus and other failure properties [4]. Energy at rupture (area under the stress-strain curve) a numerical measure for reinforcement generally passes through a maximum with filler loading [4]. Swelling restriction is another measure used to characterize rubber-filler interaction [5]. Better rubber- filler interaction could lead to reduced filler-filler interaction. Filler-filler or rubber-filler interaction could be assessed using stress-relaxation studies[6] and dynamic mechanical analysis [5]. Although considerable research efforts have been dedicated to the understanding of the mechanism of silica reinforcement in rubbers, several questions still remain unanswered [7]. Thermal analytical techniques such as thermogravimetry (TGA) and differential scanning calorimetry also could be used for characterizing filled vulcanizates [8]. Assesment of filler dispersion can be made using microscopic techniques [9].

The present chapter discusses the effect of filler loading in silica filled natural rubber with those of the same modified with ENR and silane coupling agent. Reinforcement characterization of these systems were carried out by physical testing, dynamic mechanical analysis, stress relaxation, thermal analysis, SEM and swelling studies.

7.2 Experimental

7.2.1 Materials

Raw materials used for the study and their source of supply is given below.

Material	**Source of supply**
Natural rubber (ISNR-5)	Rubber Research Institute of India
Epoxidised natural rubber (ENR 50)	”
Precipitated silica (Ultrasil VN3)	Degussa A.G. Germany
Silane coupling agent (Si 69)	”

All the other materials used for compound preparation were of rubber grade.

7.2.2 Compound recipes

The formulation of the compounds are given in Table 7.1. The compounds can be broadly classified into three groups viz; NR/Silica, NR/ENR/Silica and NR/Silane/Silica.

Table 7. 1 Formulation of mixes

Ingredients	**Compound designation**		
	A	**B**	**C**
NR	100	90	100
ENR-50	-	10	-
ZnO	5	5	5
St.acid	2	2	2
CBS	1.5	1.5	1.5
DPG	2	2	2
Sulphur	2	2	2
Silica (Ultrsil VN_3)	0-60	0-60	0-60
Si 69	-	-	*

* 4% of filler weight.

7.2.3 Mixing of compounds and moulding

The rubber or rubber blends used for making the compounds were premasticated to a Mooney viscosity of 50 ($M_{L(1+4)}$, 100 °C) in a laboratory model mixing mill. Further compounding was done in a laboratory model internal mixer (FRANCIS SHAW, KO MK3) with a fill factor of 0.7. Mixing was done in two stages. The sequences are given in Table 7.2. For both stages the initial temperature of mixing was set at 40 °C. Dump temperature of the composites after the first stage of mixing varied between 90 and 100 °C and that of the second stage between 82 and 90 °C. A final mixing of the compounds, after the mixing in the internal mixer, was done in the two- roll mixing mill for three minutes for a finer homogenization. The compounds are designated as A_0 to A_{60} (NR/Silica), B_0 to B_{60} (NR/ENR/Silica) and C_0 to C_{60} (NR/Silane/Silica) respectively depending on the filler loading as is given in Table 7.3.

Table 7.2 Mixing sequence

Time of addition	Ingredient	
	Stage 1	Stage 2
0	Rubber	Rubber-Silica
30	1/3 Silica	ZnO + Stearic acid
90	-	Accelarator + Sulphur
120	1/3 Silica	
210	1/3 Silica	
240	-	Dump
420	Dump	

Table 7. 3 Mix designation

Compound	Silica loading(phr)						
	0	10	20	30	40	50	60
NR/Silica (100/50)	A_0	A_{10}	A_{20}	A_{30}	A_{40}	A_{50}	A_{60}
NR/ENR-50/Silica(90/10/50)	B_0	B_{10}	B_{20}	B_{30}	B_{40}	B_{50}	B_{60}
NR/Silane/Silica (100/2/50)	C_0	C_{10}	C_{20}	C_{30}	C_{40}	C_{50}	C_{60}

Moulding of various test specimens was done by compression moulding technique in an electrically heated hydraulic press at 150^{0}C.

7.2.4 Testing of samples

Means and method of testing followed are given below.

Compound testing	Means/Method
Mooney viscosity	Mooney viscometer (SHIMADZU SMV 202)
Cure characteristics	Monsanto Rheometer (R-100)

Vulcanizate testing	Means/Method
Stress-strain, tear strength, hardness and heat buildup	ASTM D 412, D 624, D2240 and D 623 respectively
Resilience	BS 903
Abrasion loss	DIN 53516
Reinforcement characterization	Swelling study (in toluene)
Thermal degradation	Thermogravimetry
Thermal characterization	Differential scanning calorimetry
Filler-filler and rubber-filler interaction	Dynamic mechanical analysis
Filler distribution	Scanning electron microscopy

7.3 Results and Discussion

7.3.1 Compound viscosity

Silicas and silcates generally cause higher Mooney (low shear rate) viscosity in rubber mixes than other fillers of comparable particle size. The differences among types of filler become less pronounced as the average filler particle size is increased. At a fine particle size of approximately 20nm, silica causes a significantly higher viscosity than carbon black of comparable size, whereas at a larger particle size of approximately 40nm both cause similar viscosities [10,11]. Typical activators such as zinc oxide and glycols could result in significant viscosity changes with silica-filled SBR. Time of incorporation of zinc oxide in the compound could also alter its viscosity, an early addition favoring low viscosity and late addition in high viscosity, which is likely to be due to the silanol-zinc ion interaction [12]. The structure responsible for high Mooney viscosity is found to be temperature sensitive. A temperature difference in testing also is reported to affect the viscosity [13]. At higher shear rates both silica and black produce comparable and low viscosities which is likely to be due to reduced filler-filler and filler-polymer interactions at higher shear rates [14]. The use of silane coupling agents such as alkoxy silanes is also an effective means of reducing viscosity of silica-filled elastomers such as NR, SBR, EPDM and their blends [13,15]. In chloroprene rubber, reactive silanes such as mercaptosilanes were found to increase the viscosity, while less reactive silanes reduce the viscosity [13].

Viscosity of the experimental compounds at various filler loading was assessed using Mooney viscometer at 100°C and from the minimum rheometric torque at 150^{0}C. The results are given in Tables 7.4 and 7.5. The Mooney viscosity and minimum rheometric torque of the unfilled ENR containing mix was slightly lower than the other two systems. For all the three systems a linear increase in viscosity was noted with filler loading. With progressive addition of silica the ENR containing mix showed slightly higher viscosity than the unmodified and the silane modified mix. This might have resulted from better polymer-filler interaction through epoxy-silanol groups or from a complex zinc ion-silanol-epoxy interaction. At higher filler loadings silane modified mixes gave lower viscosity among the three, and the ENR modified mixes exhibited the highest. This might have resulted from both filler-filler and filler-polymer interactions at higher loadings.

Table 7. 4 Mooney viscosity, $M_L(1+4)$,100^0 C

Compound	Filler loading (phr)						
	0	10	20	30	40	50	60
A	28.2	35.8	45.6	48.7	52.8	60.9	84.1
B	25.8	40.2	50.6	57.1	58.8	73.9	109
C	28.2	38.2	45.1	53.5	54.8	58.4	63.1

7.3.2 Cure characteristics

Silica filler in rubber compounds is known to retard cure with certain accelerator combinations. Special considerations need to be given in the choice of accelerators for silica- filled systems. In the present study a typical accelerator combination recommended for silica-filled systems viz; sulphenamide-guanidine combination, is used. With the use of secondary accelerators the general retarding effect of silica gets nullified. The cure retarding effect of silica is considered to be due to the zinc ion interaction with the sulphur cross- linking reaction [16]. Silanes can alter scorch and cure times [17,18].

Table 7. 5 Cure characteristics

Property	Compound	Filler loading (phr)						
		0	10	20	30	40	50	60
Minimum torque, dN.m	A	7.5	11	12.5	11.5	11.5	13	19
	B	9	11	14	14	15	17	22
	C	7.5	10.5	11.5	11.5	12	12	14
Maximum torque, dN.m	A	62	73	82	83	86	91.5	100
	B	62.5	73	82	82	87	94	100
	C	62	77	87	92	96	109	116
Optimum cure time, t_{90},minutes	A	11.5	7	6.5	7	7	7	7
	B	6	6	5.5	6	6	6.5	7.5
	C	11.5	7.5	8	9.5	9.5	9.5	9.5
Cure rate index $(100/t_{90}-t_2)$	A	1.83	1.61	1.44	1.4	1.34	1.27	1.23
	B	1.87	1.61	1.47	1.47	1.39	1.3	1.28
	C	1.83	1.5	1.32	1.24	1.19	1.03	0.98

Cure characteristics of the compounds are given in Table 7.5. Minimum and maximum torque are found to have increased with filler loading. Maximum torque was the highest for the silane modified samples. The differential torque ($D_{max,f}-D_{min,f}$) is given in Fig.7.1. The higher differential torque for the silane modified mixes might have resulted from the rubber –filler bonding achieved through the coupling reaction. No significant difference in maximum torque was observed for those samples with and without ENR. ENR containing compounds exhibited comparatively lower cure time and faster cure rate. This might have occurred owing to the preferential interaction of the epoxy group with the silanol group, consequently reducing the cure retardation tendency of the silica surface groups.

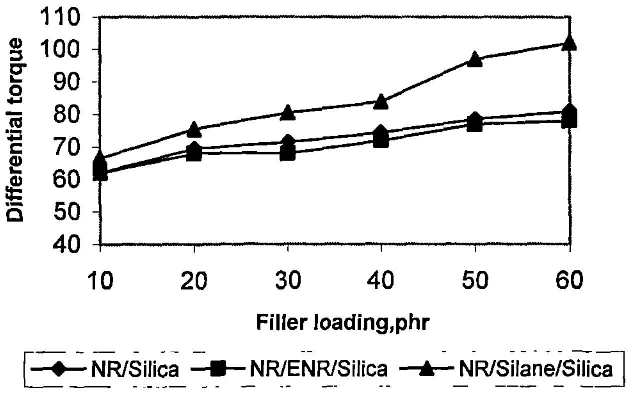


Fig.7.1 Variation of differential torque with filler loading

7.3.3 Vulcanizate properties

Vulcanizates made from the three series of compounds (Table 7.1) cured to optimum cure (t_{90}) were tested for stress-strain and other technological properties.

7.3.3.1 Stress-strain properties

Reinforcement characterization of the three series of silica-filled compounds viz; NR/Silica, NR/ENR/Silica and NR/Silane/Silica with varying filler loadings was carried out. In the ENR containing series, the ratio of NR to ENR was kept constant at 90:10. Owing to the epoxy-silanol interaction, enhanced reinforcement was expected.

Comparison of the modulus, tensile strength and elongation at break of the experimental vulcanizates is given in Table 7.6 and in Figs. 7.2, 7.3 and 7.4. The silane modified system exhibited progressive and almost linear increase in modulus with filler loading. NR/Silica and its ENR modified system also exhibited a linear modulus enhancement with filler loading. Though ENR containing samples exhibited higher modulus than the corresponding unmodified mixes, it remained almost steady above 40 phr of filler loading. Modulus and its rate of enhancement with filler loading especially above 20 phr was the highest for the silane modified mixes. Considerable improvement

Table 7.6 Stress-strain properties

Sample	Property	Filler loading(phr)						
		0	10	20	30	40	50	60
A	Modulus,100%, N/mm^2	1.2	1.65	1.9	2.01	2.21	2.35	2.5
	Modulus,200%, N/mm^2	2.04	3.1	3.6	3.7	4.0	4.3	4.6
	Modulus,300%, N/mm^2	3.5	4.6	6.2	6.5	7.3	7.75	8.2
	Tensile strength,N/mm^2	15.8	6.0	12.5	17.5	24	23	21.5
	Elongation at break,%	495	310	390	450	520	540	525
B	Modulus,100%, N/mm^2	1.15	1.52	2.15	2.4	2.6	2.6	3.0
	Modulus,200%, N/mm^2	1.95	2.8	4.0	4.5	4.8	4.6	5.35
	Modulus,300%, N/mm^2	3.3	4.75	7.2	8.1	8.2	8.1	9.0
	Tensile strength, N/mm^2	19	21.5	31.5	33.5	31	23	27.5
	Elongation at break,%	530	530	580	620	625	580	620
C	Modulus,100%, N/mm^2	1.2	1.7	2.1	3.3	3.75	4.9	5.4
	Modulus,200%, N/mm^2	2.04	3.6	4.8	7.8	8.6	11.1	12.4
	Modulus,300%, N/mm^2	3.5	6.3	9.2	14.3	15.2	18.1	20
	Tensile strength,N/mm^2	15.8	18.6	23	23	31	29	28.3
	Elongation at break,%	495	455	410	400	490	450	420

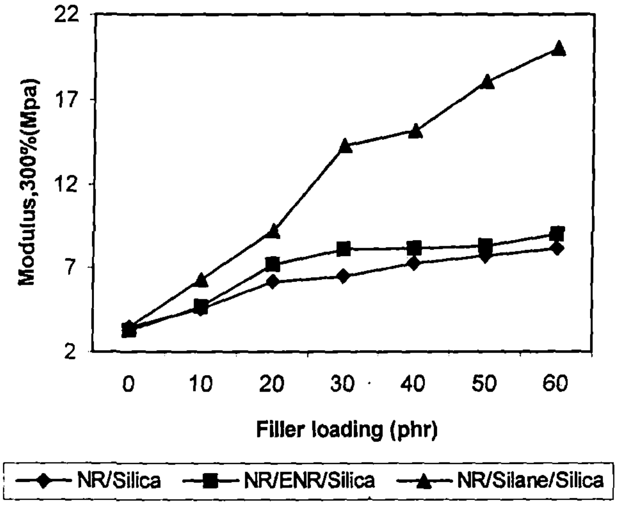


Fig. 7. 2 Variation of modulus with filler loading

in tensile strength was noted for the ENR modified mix over the unmodified and silane modified mixes upto 30 phr silica loading. Above 40 phr loading, silane and ENR modified mixes were almost in a close range and was higher than that of the unmodified mix. Unlike the silane modified and silica-filled NR, ENR modified mixes exhibited

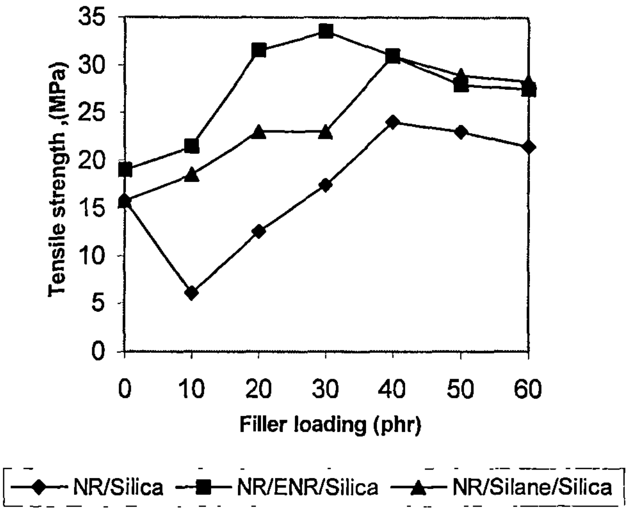


Fig. 7.3 Variation of Tensile strength with filler loading

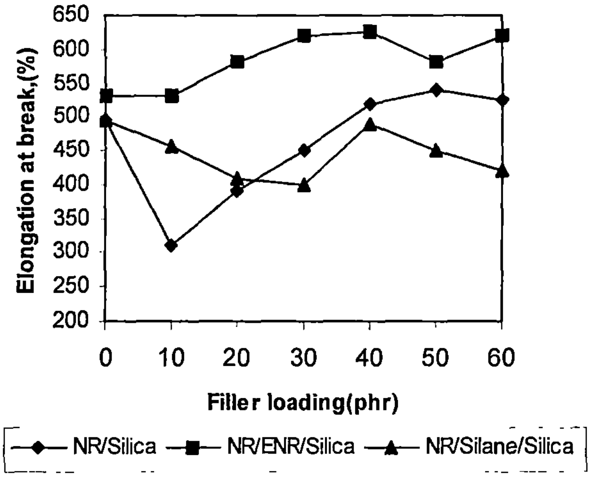


Fig.7.4 Variation of elongation at break with filler loading

comparatively higher elongation. All the three systems exhibited comparatively higher elongation above 40 phr silica loading. The highest elongation shown by the ENR modification might have resulted from better filler dispersion and reduced filler-filler

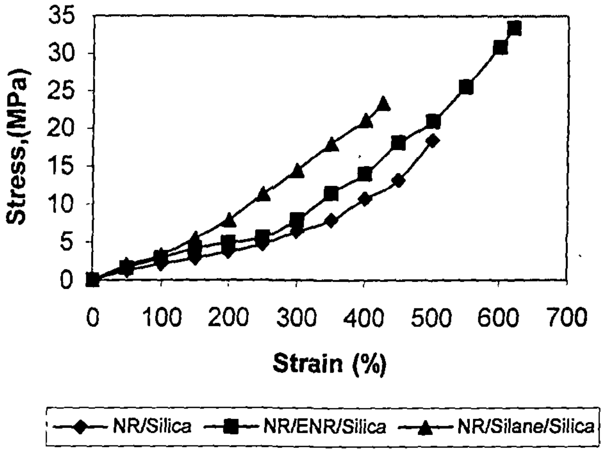


Fig.7.5 Stress-strain curve(30 phr filler loading)

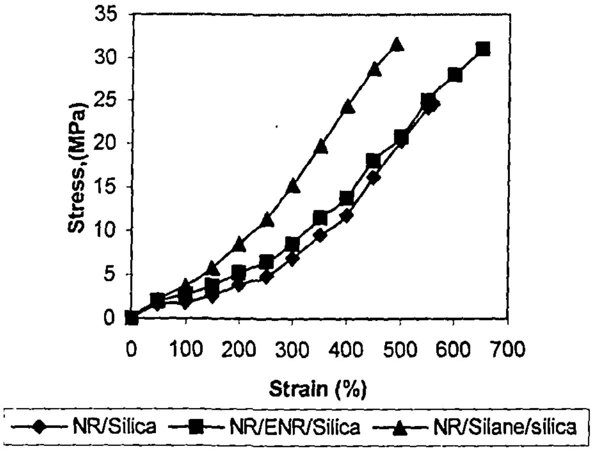


Fig.7.6 Stress-strain curve (40 phr filler loading)

interaction. Comparison of the stress-strain properties for the three systems at three different filler loadings are given in Figs. 7.5, 7.6 and 7.7. At 30 phr filler loading the energy at rupture was found to be the highest for the ENR modified mix followed by the silane modified and the least for the unmodified mix. The superiority of the ENR modified mix in rupture energy is decreased with filler loading while correspondingly that of the silane modified mix increased. At 50 phr filler loading the highest rupture energy was shown by the silane modified mix, followed by ENR modified and the least for the unmodified mix.

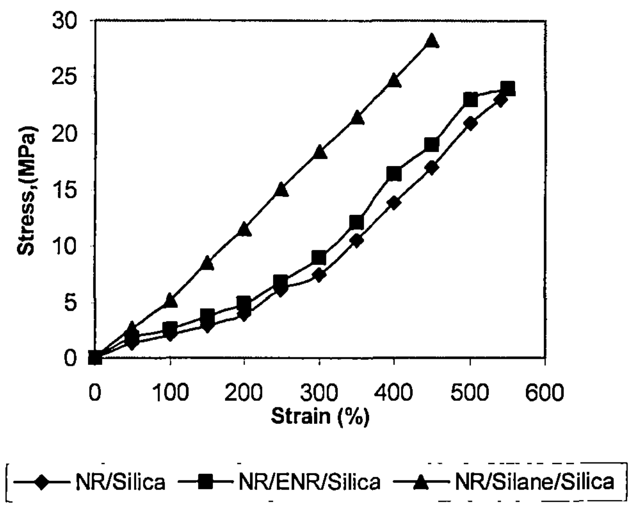


Fig.7.7 Stress-strain curve (50phr filler loading)

7.3.3.2 Technological properties

Development of high strength in elastomers depends on the ability of rubber to dissipate strain energy near the tip of the growing cracks. Strain crystallizable polymers exhibit high strength even in the amorphous state, while non-crystalizable ones may not. The addition of a filler introduces additional mechanisms by which strain energy is dissipated[19]. Carbon black incorporation leads to tear deviation presumably by creating barriers in the path of the tear. The increase in ultimate properties with increased effective loading upto the optimum is due presumably to increased tear deviation. Colloidal silicas even when compounded with coupling agents do not equal carbon black in wear resistance.

Some of the important technological properties relevant to the reinforcement of elastomers viz; tear strength, abrasion loss, rebound resilience, hardness and compression set are given in Table 7.7. For all the three stystems tear strength is found to have increased with filler loading. The ENR modified system exhibited the highest tear strength. Abrasion loss is found reduced initially with filler loading and then increased after a critical loading of about 30 phr. Resistance to abrasion was the highest for the silane modified, followed by the one with ENR. For all the three systems, hardness increased with filler loadings. ENR and silane modified systems exhibited higher hardness than the unmodified. Heat build-up and compression set were found increased with filler loading for all the three systems and in general the ENR modified system exhibited the highest and the silane modified the lowest. Silanol groups and the adsorbed water on the silica particles are known to produce lower modulus and higher abrasion

Table 7.7 Technological properties

Properties	**Sample**	**Filler loading(phr)**						
		0	**10**	**20**	**30**	**40**	**50**	**60**
Tear strength, N/mm	A	27	38	55	72	92	94	100
	B	42	52	59	79	93	123	128
	C	27	51	56	76	96	101	120
Hardness, Shore A	A	41	47	51.5	56	59	62	69
	B	40	48	51	57	63	67	77
	C	41	48	52	60.5	63.5	70	75
Abrsion loss,mm^3	A	191	146	149	153	161	182	185
	B	172	161	152	144	152	165	178
	C	191	152	135	129	129	136	141
Heat build-up, °C	A	3	5	8	10	14	19	27
	B	3	6	11	14	21	24	28
	C	3	5	7	9	14	19	23
Compression set, %	A	13	26	27	32	35	35	39
	B	18	24	30	33	33	37	41
	C	13	25	26	24	27	23	24

loss. Silane modification can improve modulus, and abrasion resistance and reduce the heat build-up and compression set. Silanes can modify the reinforcing ability of silica to a level comparable to that of carbon black. Higher hardness, of the ENR or silane containing samples can be attributed to the better rubber-filler interaction achieved through the silica surface groups and that of either ENR or silane. Higher tear strength and abrasion resistance shown by the ENR and silane modified systems might also be due to the better rubber-filler interaction. Carbon black filled compounds generally exhibit higher heat build-up due to dynamic flexing. Comparatively higher heat build-up exhibited by the ENR containing samples might also be due to the higher modulus and the making and breaking of bonds between the functional groups of filler and the polymer during dynamic flexing. The comparatively higher compression set exhibited by the ENR containing samples might be due to the high damping character of ENR and due to the breakage of temperature sensitive bonds between the rubber and the filler.

7.3.4 Equilibrium swelling studies

The equilibrium swelling analysis of rubber vulcanizates is known to indicate the number of effective network chains per unit volume of rubber. For a filled vulcanizate it

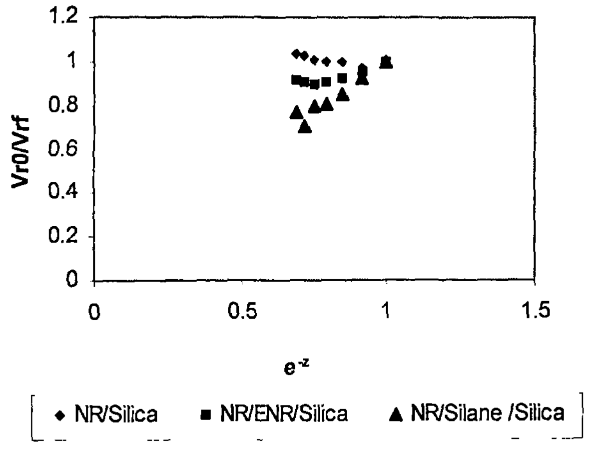


Fig. 7.8 Reinforcement characterization (Cunneen - Russell equation)

should reflect not only the effect of chemical linkages between the polymer molecules, but also the density of polymer-filler attachments. In the present study equilibrium swelling of the three series of vulcanizates viz; NR/Silica, NR/ENR/Silica and NR/Silane/Silica in toluene was made at room temperature and the volume fraction of rubber at different loadings were determined. The ratio of Vr_o/Vr_f is used to characterize the filler reinforcement at different loadings.

Table 7. 8 Swelling data (Cunneen-Russell)

Sample	**Slope**
NR/Silica	-0.1227
NR/ENR/Silica	0.2965
NR/Silane/Silica	0.8694

The data obtained from swelling studies for the three series of vulcanizates were plotted as per the Cunneen-Russell[20] equation in Fig. 7.8. The slope of the experimental points for the three series of vulcanizates is given in Table 7.8. The higher slope for the ENR modified and silane modified mixes is an indication for better reinforcement.

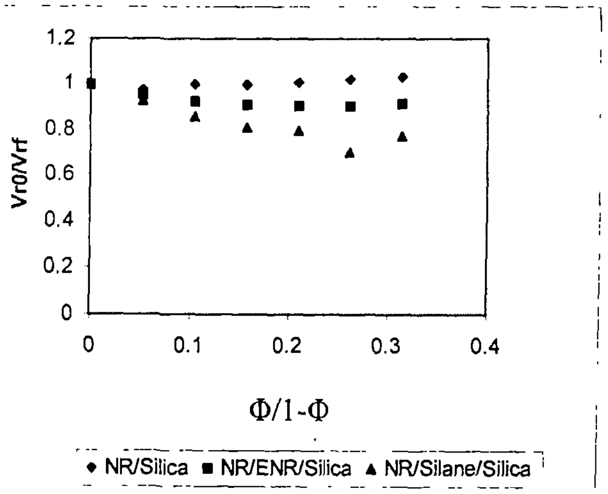


Fig. 7.9 Reinforcement characterization (Kraus)

Gradation of reinforcement based on the slope values is in the order Silane modified> ENR modified>Unmodified.

Swelling data for the three series was also plotted as per the Kraus[21] equation in Fig.7.9. The slope for the three series obtained through regression analysis is given in Table 7.9. The higher slope values obtained for the ENR and the silane modified systems indicate higher rubber-filler interaction and the order of reinforcement is similar to that obtained for the Cunneen-Russell equation.

Table 7.9 Swelling data (Kraus)

Sample	Slope
NR/Silica	0.134
NR/ENR/Silica	-0.261
NR/Silane/Silica	-0.817

7.3.5 Dynamic mechanical analysis

Incorporation of filler can alter the static and dynamic mechanical behaviour of elastomers. Modulus of filled elastomers can be a resultant of the contributions from polymer network, hydrodynamic effects, in-rubber structure which are strain independent and the filler-filler interaction which is strain dependent [22]. The stress softening at small deformations, is known as Payne effect [23]. The modulus drop with strain amplitude ($\Delta G=G_0'-G_\alpha'$) in a non-linear pattern represents the Payne effect. Go', low strain modulus represents combined effects of polymer network, hydrodynamic effects, in –rubber structure and the filler-filler interaction, while G_α' represents the first three aspects [24].

Three selected vulcanizates of NR/Silica and the ENR and silane modified systems at 50 phr filler loading were subjected to a strain-dependent dynamic mechanical analysis at a frequency of 1 Hz. at an isothermal condition of 60°C. The influence of filler-filler and filler-polymer networks on dynamic properties is characterized with the changes in dynamic modulus with dynamic strain. Vulcanizates containing silica as a reinforcing filler exhibit higher G' and low strains. The breakdown and reformation of the network linkages during dynamic deformation consumes energy (hysteresis loss), which is reflected in the variation of tan δ with increasing dynamic strain [25]. The results of the dynamic testing of the experimental vulcanizates is given in Fig.7.10. From the figure it can be seen that at very low strain the silane modified system exhibited a lower modulus than the ENR modified and the unmodified ones. G_0 and G_α values are given in Table 7.10. G_α values were in the order ENR modified > unmodified > silane modified. The highest G_α values for the ENR modified system might have resulted from the enhanced network caused by the ENR-silica interaction. G_0 values were almost closer for NR/Silica and the ENR modified systems while it was lower for the silane modified system. The plasticizing effect of the silane and the lower filler-filler interaction might

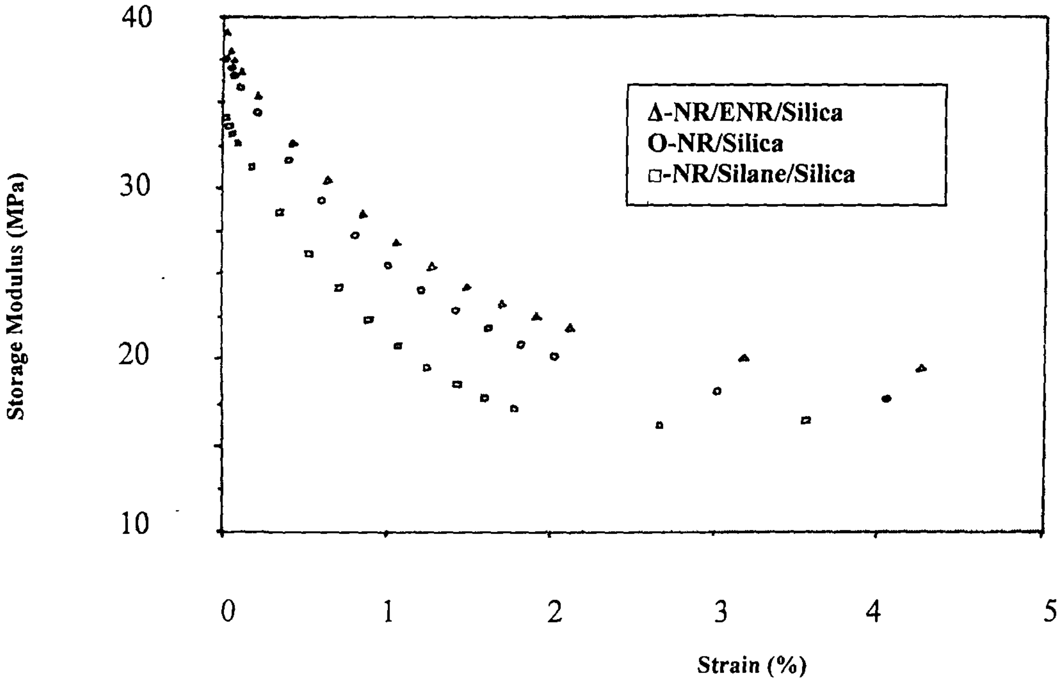


Fig. 7. 10 Modulus variations with strain

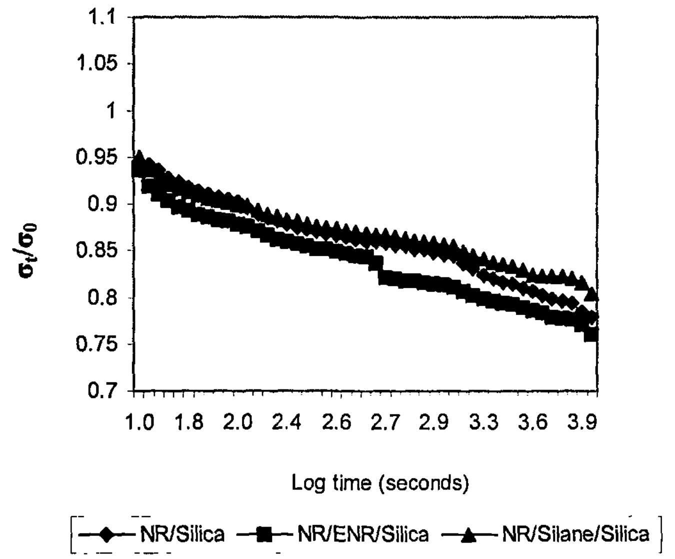
have caused the lower G_0 value. For the ENR modified, the epoxy-silanol interaction also might have contributed to the comparatively higher G_0 values.

Table 7.10 Dynamic modulus-Effect of strain

Sample	Low strain modulus (G_0),MPa	High strain modulus (G_α),MPa
NR/Silica	37.5	18
NR/ENR/Silica	38.5	20.5
NR/Silane/Silica	34.5	17

7.3.6 Stress relaxation studies

Direct measurement of filler-polymer interactions in the vulcanizate is virtually impossible. One important phenomenon associated with filler reinforced rubber is the "Mullins effect" [26]. A filled rubber vulcanizate becomes less stiff when stretched a second time, but the original stiffness can be substantially recovered with time. Rubbers containing reinforcing fillers exhibit "Mullins effect" or stress softening. Unfilled rubbers and those containing non-reinforcing fillers exhibit less stress softening. Stress softening involve the rupture of filler-polymer attachments [13]. Softening behaviour of



Fg. 7.11 Stress relaxation studies (30 phr silica)

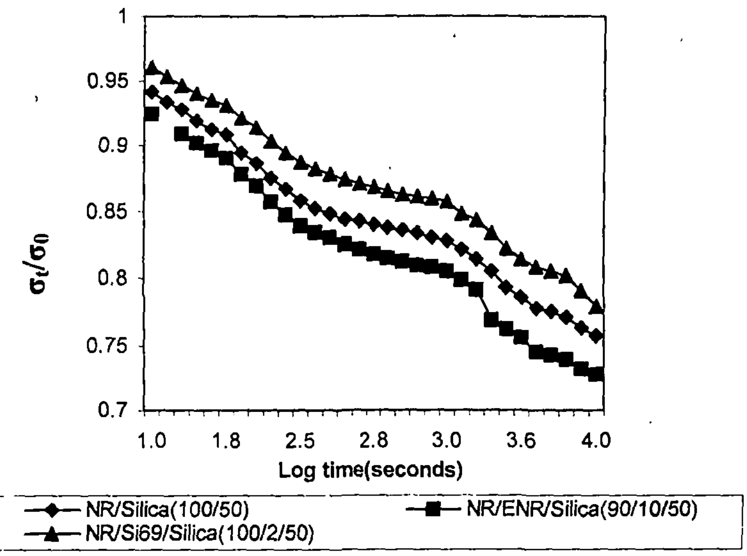


Fig.7.12 Stress relaxation studies (50 phr silica)

Table 7. 11 Comparison of the slope of stress relaxation

Sample	Slope	
	30 phr silica	50 phr silica
NR/Silica	-0.059	-0.063
NR/ENR/Silica	-0.061	-0.068
NR/Silane/Silica	-0.048	-0.058

silica and carbon black-filled rubbers differ [27]. Important causes attributed to stress softening are slippage of elastomer chains at the filler surface and rupture of filler aggregates, filler-polymer network and filler-structure [28, 29].

Results of the stress relaxation studies of the three series of experimental vulcanizates at two different silica loadings viz; 30 and 50 phr, are given in Table 7.11 and Fig 7.11 and 7.12. For both filler loadings the slope of the relaxation curve was the highest for the ENR modified system indicating higher relaxation resulting from polymer-filler interactions. The lowest slope for the silane modified system might have resulted from the added strong chemical linkages between rubber and filler through the coupling agent.

7.3.7 Thermogravimetric analysis

Thermogravimetry (TG) is being used as an analytical tool for characterizing the chemically complex mixtures of elastomer compounds or vulcanizates. TG curve gives

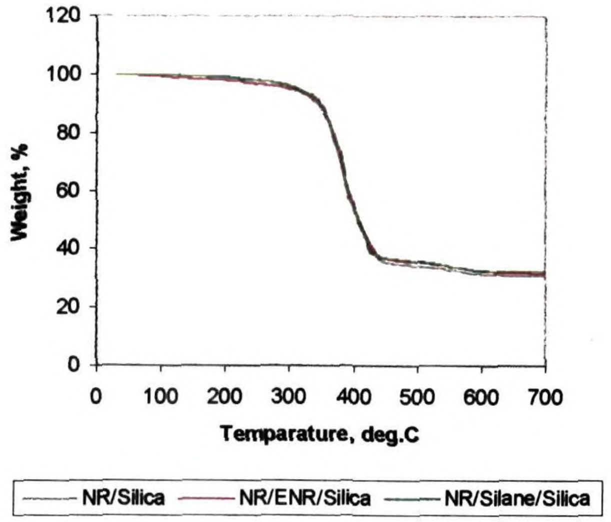


Fig. 7.13 Thermal degradation studiex (Thermogravimetry-nitrogen medum)

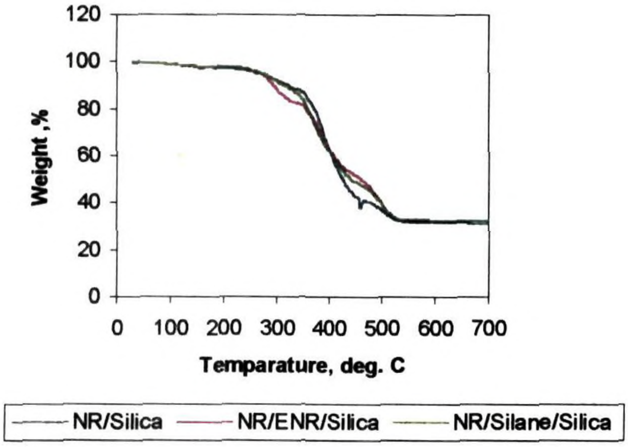


Fig. 7.14 Thermal degradation studies (Thermogravimetry- Air medium)

primary weight loss changes with temperature. Differential thermograms (DTG) could also be constructed from TG curves, in which the weight loss events could be well separated on the temperature scale. TG curve provides information on the carbon black and inorganic filler content. Surrounding atmosphere, oxidative or inert, affect the stability and the subsequent course of the degradation reactions. Most organic elastomers when heated in nitrogen undergo thermal degradation above 300 ^{0}C which is usually complete by about 500°C. It was reported that from the TG degradation pattern, natural rubber and synthetic polyisoprene could be differentiated [30]. Thermal stability of polymers also could be differentiated with TG curves. TG could also be used to characterize the type of carbon black from its rate of oxidation. Natural rubber is known to degrade at 373°C in nitrogen atmosphere.. Silicas have high thermal stability[31].

In the present thermogravimetric experiment, vulcanizates of NR/silica and the same modified with ENR and silane at 50 phr filler loading, compared in nitrogen and air medium, are plotted in Fig 7.13 and 7.14 respectively. Under nitrogen atmosphere no significant difference among samples was noted, whereas in air medium the degradation has occurred in steps at different temperatures. The fraction of the sample undergoing high temperature degradation was higher for the ENR and silane modified systems. This is likely to be due to the polymer fragment which gets modified with silica either through ENR or silane.

7.3.8 Differential scanning calorimetry (DSC)

DSC measures the temperature and heat flow associated with transition in materials. Such measurements provide qualitative information about physical and chemical changes that involve endothermic or exothermic processes. Most of the heat changes associated with physical or chemical transition of elastomers such as glass transition, vulcanization and degradation could be detected by this technique [8].

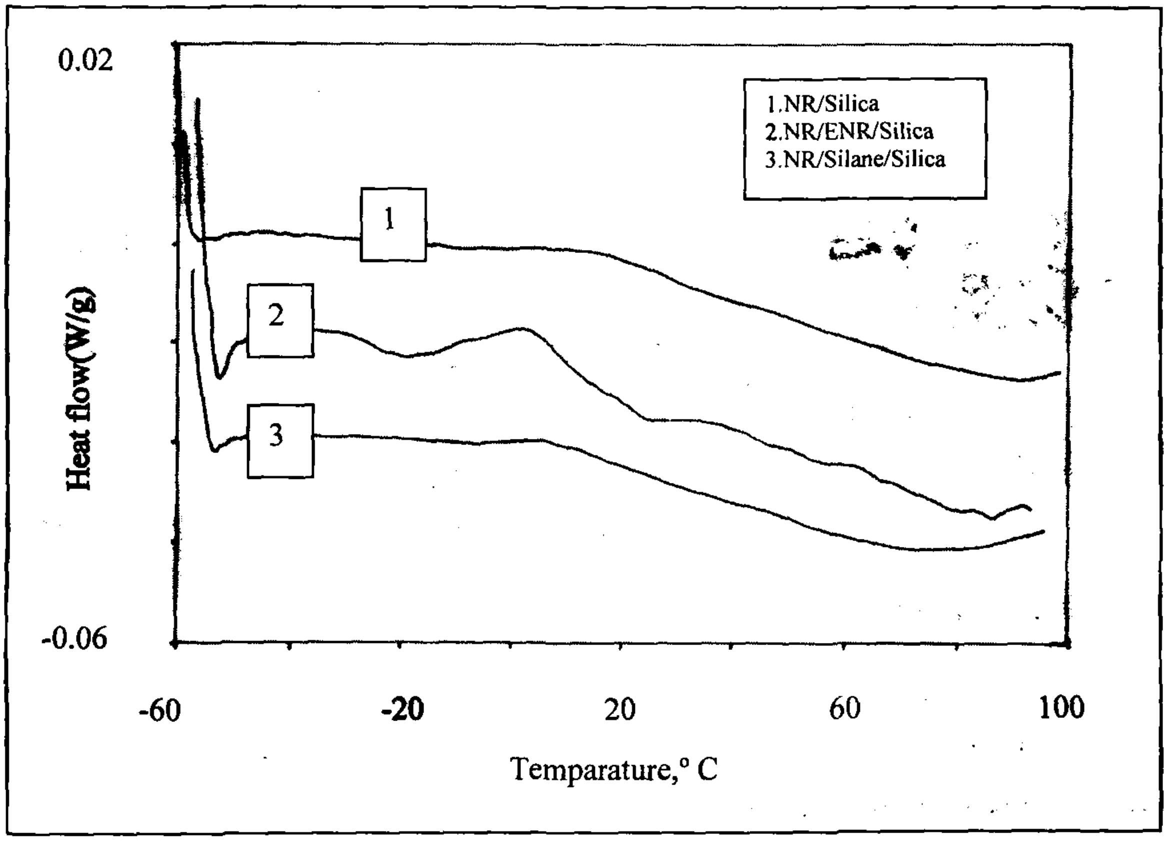


Fig. 7. 15 DSC thermogram

In the present experiment vulcanizates of NR/Silica NR/ENR/Silica and NR/Silane/Silica at 50 phr filler loading were subjected to DSC analysis. Due to the constraints of the equipment the tests could be carried out only within the temperature range of –60 to +100^{0}C. DSC thermogram is given in the Fig.7.15. From the thermograms it could be found that the ENR modified sample exhibited a transition at about 0^{0}C which corresponds to the glass transition of epoxidised natural rubber present in the composite.

7.3.9 Scanning electron microscopy(SEM)

Scanning electron microscopy is being widely used to characterize the filler distribution and dispersion characteristics [7,31,32]. In the present experiment, vulcanizates of NR/Silica and its ENR and silane modified samples at 30 phr silica loading which exhibited considerable difference in physical properties among the samples were examined using a scanning electron microscope. SEM micrographs of NR/Silica, NR/ENR/Silica and NR/Silane/Silica are shown as Fig.7.16 a, b and c respectively. From

a)NR/Silica b)NR/ENR/Silica c)NR/Silale/Silica

Fig.7.16 SEM photomicrographs (30 phr silica)

the photographs it can be seen that ENR and silane modified systems exhibit better silica distribution than the unmodified system.

7.4 Conclusions

Like silane coupling agent, ENR could modify many of the important processing and technological properties of silica-filled natural rubber. Compound viscosity in general increased with filler loading. Viscosity modification with ENR and silane mostly depend on loading level. Stress-strain and other technological properties are also found dependent on filler loading. Swelling studies revealed that ENR and silane served as reinforcement modifiers to varying levels. Dynamic mechanical analysis showed that in ENR modified system, the filler-rubber interaction is higher as is evident from the higher G_{α} values. Silanes could lower the low strain modulus of silica filled natural rubber probably due to the lower filler-filler interaction and the plasticizing action of silane. Stress relaxation studies revealed that ENR causes more number of filler-rubber bonds that might have undergone bonding –debonding mechanism, ultimately resulting in larger stress relaxation. Thermogravimetric studies revealed that unlike silica filled natural rubber, ENR and silane modified systems exhibited a two stage degradation likely to be due to better rubber-filler interaction. Differential scanning calorimetry could be used for characterizing ENR containing mixes. SEM observations showed that ENR and silane modification improved the distribution of silica in natural rubber.

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CHAPTER 8

EPOXIDISED NATURAL RUBBER AS A REINFORCEMENT MODIFIER FOR SILICA FILLED NITRILE RUBBER

8.1 Introduction

Nitrile rubber (NBR) is generally considered a special purpose rubber and is being used for applications requiring oil and solvent resistance. Presence of acrylonitrile makes the rubber polar and provides special features to the polymer. Nitrile rubber which remains amorphous even under strain, requires reinforcing filler for use in the manufacture of products[1]. Carbon black and silica are the common fillers used for reinforcement . Unlike hydrocarbon rubbers such as NR, SBR and the like, nitrile rubber exhibits comparatively better reinforcement with silica because of its improved dispersion[1]. However, for achieving optimum reinforcement, silane coupling agents are being used [2].

Butadiene copolymerised with vinyl pyridine show improved reinforcement by silica, due to the interaction between silanol and pyridine groups [3]. Attempts have been made to improve silica reinforcement of NBR by functionalising it with pendant epoxy groups[4]. ENR used alone or added in small quantities to NR, can provide improved silica reinforcement than NR[5,6]. Since NBR and ENR can form blends with good compatibility due to their polar nature, a better performance in silica reinforcement is expected in the blend[7]. The present study examines the possibility of the use of ENR as a reinforcement modifier in silica filled nitrile rubber in comparison with silane modified silica filled and carbon black filled NBR.

8.2 Experimental

8.2.1 Materials

Nitrile rubber;	Aparene N 423-NS, manufactured by Gujarat Apar Polymers (India), having an acrylonitrile content of 33 per cent.
ENR 50 ;	Epoxidised natural rubber (50 mole per cent epoxy content), prepared in the pilot plant facility of the Rubber Research Institute of India [8].
Hydrated silica ;	Ultrasil VN3, a product of Degussa AG (Germany)
Coupling agent ;	Si-69, [bis (3-triethoxy propyl) silyl tetrasulphide] – product of Degussa AG (Germany).

The other ingredients used were of commercial (rubber) grade.

8.2.2 Preparation of compounds

The formulations of the compounds are given in Tables 8.1 and 8.2. The rubbers in different proportions were blended in a two-roll laboratory mixing mill for 5 minutes and the blend was used for making the compounds. A two stage mixing procedure was followed. The first stage was done in a laboratory model internal mixer (SHAW INTERMIX-MK3, size KO) whereby the polymer, filler and process aids were mixed. The initial mixing temperature and rotor speed were 40°C and 60 rpm respectively. The batch was dumped after 10 min. The curatives were incorporated in the second stage of mixing in a two- roll mill.

To assess the inter-polymer interaction of NBR and ENR at the vulcanization temperature, a separate experiment was conducted. The rubbers in different proportions as given in Table 8.3 (compounds 20-25), were blended in a laboratory model two-roll mixing mill for 5 min. Rheographs of the mixes at 150°C were taken and were used to quantify the polymer-polymer interaction resulting in crosslinks. To evaluate the added

Table 8.1 Formulation of compounds (CBS cure)

Ingredient	Mix number									
	1	2	3	4	5	6	7	8	9	10
Nitrile rubber	100	97.5	95	90	85	80	75	100	100	100
ENR50	-	2.5	5.0	10	15	20	25	-	-	-
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ultrasil VN_3	50	50	50	50	50	50	50	50	50	-
DOP[a]	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CBS[b]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Si 69	-	-	-	-	-	-	-	1.0	4.0	-
ISAF	-	-	-	-	-	-	-	-	-	50

[a] Dioctyl phthalate [b] N-Cyclohexyl-2-benzthiazyl sulphenamide

Table 8. 2 Formulation of compounds (CBS-DPG cure)

Ingredient	Mix number								
	11	12	13	14	15	16	17	18	19
Nitrile rubber	100	97.5	95	90	85	80	75	100	100
ENR 50	-	2.5	5.0	10	15	20	25	-	-
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ultrasil VN_3	50	50	50	50	50	50	50	50	50
DOP	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
DPG[a]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Si 69	-	-	-	-	-	-	-	1.0	4.0

[a] Diphenyl guanidine

interaction of silica in the blend it was mixed with filler as per the formulation given in Table 8.3 (compounds 26-30), in a laboratory model internal mixer at a mixing temperature of 40°C and at 60 rpm for 10 min. Rheographs of these mixes at 150°C were also taken.

Table 8. 3 Formulation of mixes

Ingredient	Mix number										
	20	21	22	23	24	25	26	27	28	29	30
Nitrile rubber	100	90	85	80	75	50	100	90	85	80	75
ENR 50	-	10	15	20	25	50	-	10	15	20	25
Ultrasil VN_3	-	-	-	-	-	-	50	50	50	50	50

8.2.3 Testing

a) Bound rubber content

For the measurement of bound rubber content, samples of rubber compound were placed in a stainless steel cage of 150 mesh size, and immersed in toluene at room temperature. The solvent was renewed after three days. After seven days, the steel cage with the swollen sample was removed from the solvent. The samples were dried in air for 24 h. and subsequently dried to constant weight in an oven at 105 ^{0}C. The bound rubber (R_B) was then calculated as described by Wolff *et.al*[9].

b) Physical testing

Cure characteristics of the compounds were determined using a Monsanto R-100 Rheometer at 150^{0}C. Test samples were moulded using an electrically heated hydraulic press to their respective optimum cure times. Stress-strain, tear strength, hardness, resilience, compression set, heat build- up and ageing resistance of the vulcanizates were tested as per the respective ASTM standards. Abrasion resistance was tested as per DIN 53516.

c) Dynamic mechanical analysis

The viscoelastic properties of the vulcanizates were determined using a dynamic mechanical analyzer model DMA-2980 of TA Instruments Ltd, USA using a dual cantilever device. The tests were carried out at a frequency of 1Hz at 0.1% strain in a temperature range of –70 to 60°C with a heating rate of 2°C/minute. Liquid nitrogen was used as the coolant.

8.3 Results and Discussion

8.3.1 Cure characteristics

The cure characteristics of the two sets of compounds with N-cyclohexyl-2-benzthiazyl sulphenamide (CBS) and CBS- diphenyl guanidine (DPG) combination, are given in Tables 8.4 and 8.5 respectively. Silica filled nitrile rubber compounds, containing different concentrations of ENR and Si-69 as reinforcement modifiers, were compared with an Intermediate Super Abrasion Furnace (ISAF) black filled nitrile rubber compound and an unmodified control compound. Cure characteristics of silica filled compounds were found modified with the incorporation of the modifiers. Maximum torque and differential torque were found to have increased with the incorporation of

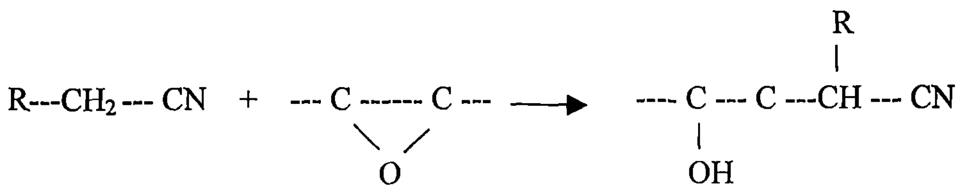
Table 8. 4 Cure characteristics (CBS cure)

Parameter	Mix number									
	1	2	3	4	5	6	7	8	9	10
Minimum torque, dN.m	9.0	10	12	26	26	20	21	18	8	12
Maximum torque, dN.m	39	38	42	74	84	78	83	80	87	52
Δ, Rheometric torque, dN.m (Max. –Min.)	30	28	30	48	58	58	62	62	79	40
Optimum cure time (t_{90}) at 150°C, min	74	63	52	52	50	49	49	58	56	16
Scorch time (ts_2) at 150°C, min	20.5	18.5	15.0	14.0	12.0	11.5	11.5	14.0	13.5	5.5
Cure rate index [$100/(t_{90}-ts_2)$]	1.87	2.25	2.70	2.63	2.63	2.67	2.67	2.27	2.35	9.5

Table 8. 5 Cure characteristics (CBS-DPG cure)

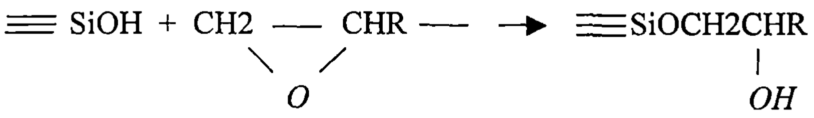
Parameter	Mix number								
	11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Minimum torque, dN.m	21	26	26	26	26	27	26	17	14
Maximum torque,dN.m	98	98	98	102	105	106	106	100	114
Δ, Rheometric torque, dN.m(Max.-Min.)	77	72	72	76	79	79	80	83	100
Optimum cure time (t_{90}) at 150°C, min	49.5	32.0	32.0	30.5	27.5	25.5	26	39	34
Scorch time (ts_2) at 150°C, min	8.0	6.0	6.0	5.5	5.0	4.0	4.5	5.5	4.5
Cure rate index [$100/(t_{90}-ts_2)$]	2.3	3.9	3.9	4.0	4.5	4.7	4.7	3.0	3.4

ENR, indicating the likely formation of additional crosslinks by polymer-polymer and polymer-filler interactions. The polymer-polymer interaction resulting in chemical crosslinks was assessed through the rheometric study of compounds 20-25 of Table 8.3. The respective rheographs are given in Fig. 8.1. For mixes 20-25, a gradual increase in torque was noted with increasing concentration of ENR. The increased torque might have resulted from NBR-ENR interaction. It was reported that acetonitriles can open the epoxy ring by the following mechanism [10].



$$R{-}{-}{-}CH_2{-}{-}{-}CN \; + \; {-}{-}{-}\underset{\diagdown\;O\;\diagup}{C{-}{-}{-}{-}{-}{-}C}{-}{-}{-} \longrightarrow {-}{-}{-}{-}\underset{OH}{\underset{|}{C}}{-}{-}{-}C{-}{-}{-}\overset{R}{\overset{|}{CH}}{-}{-}{-}CN \qquad (I)$$

A similar interaction might have occurred in the case of NBR-ENR blends resulting in crosslinked structures, as evidenced from the rheometric study. Earlier investigators [4] reported that the epoxy group of ENR can also react with the hydroxyl group of silica as



$$\equiv \mathrm{SiOH} + \mathrm{CH2} \underset{\mathrm{O}}{\underset{\diagdown\ \diagup}{—}} \mathrm{CHR} \longrightarrow \equiv \mathrm{SiOCH2}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CHR}}} \tag{II}$$

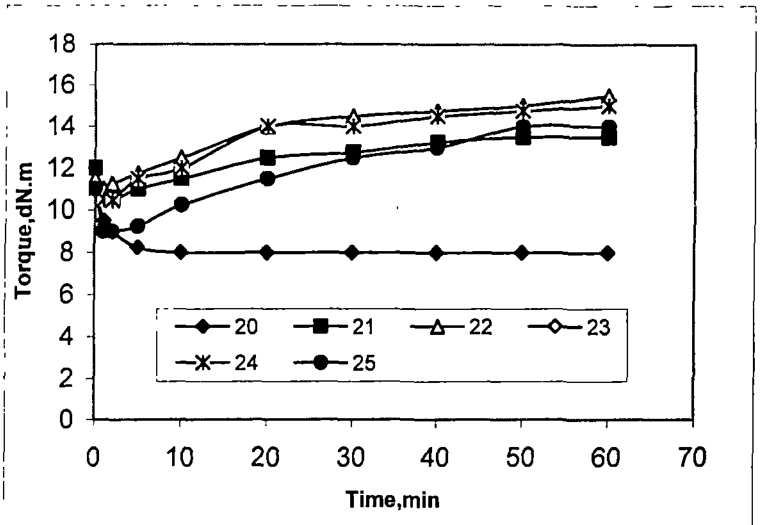


Fig. 8.1 Rheograph of the gum compounds

The contribution of rubber-silica interaction achieved through the incorporation of ENR was evaluated by rheometric study of compounds 26-30. The rheographs are given in Fig.8.2. The observed torque enhancement with ENR addition was higher in the filled mixes than that in the corresponding gum mixes. A comparison of the differential torque obtained from the rheographs of gum and filled mixes is shown in Table 8.6. The increase in differential torque observed for the filled mix over the gum is taken as a measure of polymer – filler interaction . Enhanced differential torque with increased concentration of ENR showed a progressive improvement in rubber-filler interaction. Maximum torque and differential torque were found increased with incorporation of coupling agent in a pattern similar to that obtained for compounds containing ENR as modifier.

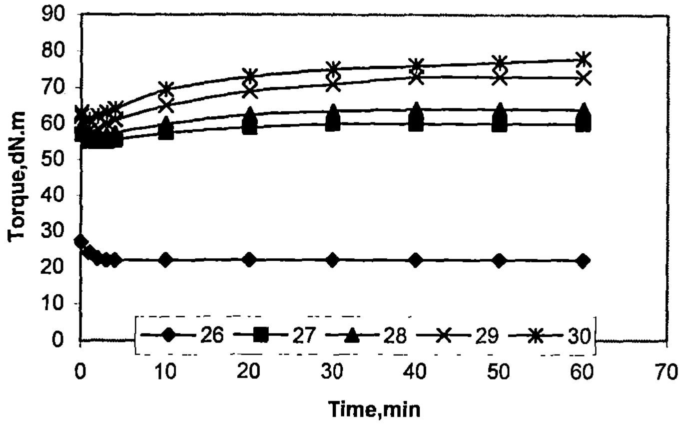


Fig.8.2 Rheograph of the filled compounds

Table 8. 6 Rheometric data

Mix No./Identification	Differential torque, dN.m (Max - Min)	Increase in differential torque, dN.m (Filled – Gum)
21 (gum)	3	
27 (filled)	5	2
22 (gum)	3.5	
28 (filled)	8	4.5
23 (gum)	5	
29 (filled)	15	10
24 (gum)	5.25	
30 (filled)	17	11.75

The rheometric study of compounds given in Table 8.3 showed that ENR can serve as a coupling agent in a pattern similar to that of silane coupling agent, given that it can interact with both NBR and silica. ENR can interact with NBR through the crosslinks formed by the mechanism given in (I) and also through sulphur crosslinks, whereas silica interacts with the rubber through the mechanism given in (II). The NBR-ISAF composite exhibited higher values of maximum and differential torque than NBR-silica composites but lower compared to those containing modifiers. With increased concentration of ENR, an increase in the minimum rheometric torque, an indication of compound viscosity was noted. The observed higher compound viscosity, in general, can be attributed to polymer-polymer and polymer-filler interaction. The optimum cure time (t_{90}) and scorch time (ts_2) were found decreased and the cure rate index (CRI) increased with increased concentration of ENR, the values of which were closer to those of mixes containing a coupling agent. However, in carbon black filled mixes, lower t_{90} and ts_2 and higher CRI were observed.

8.3.2 Bound rubber

Bound rubber (R_B) measurement is conventionally being done to assess the rubber-filler interaction; the higher the bound rubber, the higher the polymer- filler interaction [11]. In the present experiment, the bound rubber content of a few selected NBR-Silica mixes with and without modifiers and that in NBR-ISAF mix were measured. The results are given in Table 8.7.

Table 8.7 Bound rubber

Mix No./Identification	Bound rubber(R_B), %
11 (NBR-Silica)	27.16
14(NBR-10ENR-Silica)	40.44
15(NBR-15ENR-Silica)	41.59
18 (NBR-2%Si 69)	29.12
19 (NBR-8%Si 69)	31.36
10 (NBR-ISAF)	34.81

Silica- filled mixes containing modifiers and the NBR-ISAF mix showed higher R_B values than those of the unmodified samples. With an increase in the concentration of the silane coupling agent, an increase in bound rubber was noted. ENR modified samples gave much higher R_B values than the samples modified with coupling agent and than the NBR – ISAF mix. With increased concentration of ENR, an increase in R_B

value was noted. The unusually high values might have resulted from the combined effect of polymer-filler interaction and the gel content resulting from the NBR-ENR interaction mentioned earlier. Tan *et al.,*[11] reported that, the gel content resulting from polymer – polymer network can contribute to higher values of bound rubber. The higher R_B value in NBR-ISAF mix over that of the NBR-Silica mix is attributed to the larger polymer-filler interaction for carbon blacks in NBR[11].

8.3.3 Vulcanizate properties

The technological properties of selected samples from the mixes given in Tables 8.1 and 8.2 are shown in Tables 8.8 and 8.9, respectively, and in Figs. 8.3 to 8.12.

8.3.3.1 Stress-strain properties

Stress-strain properties of selected samples from the mixes given in Tables 8.1 and 8.2 with two systems of cure are represented in Figs. 8.3 and 8.4 respectively. It is observed that the stress-strain properties were modified with the incorporation of ENR and are comparable to those of composites modified with silane coupling agent and the one containing ISAF.

a) Modulus

Variations in tensile modulus of ENR-modified composites for the two systems of cure are given in Fig.8.5 and in Tables 8.8 and 8.9. For both cure systems, an increase in modulus was observed with increased concentration of ENR. The higher crosslink density resulting from polymer–polymer and polymer-filler interactions might have contributed to the modulus enhancement. Silane modified systems also showed modulus enhancement dependent on silane concentration as can be seen from Tables 8.8 and 8.9. The modulus values for NBR/ENR blend containing 15 parts of ENR were higher than those observed with coupling agent. The silane coupling agent, which is itself a crosslinking agent, increases the crosslink density of the composites, thereby enhancing

Table 8.8 Technological properties (CBS cure)

Parameter	Mix No./Identification					
	1 (NBR-Silica)	4 (NBR-10ENR-Silica)	5 (NBR-15ENR-Silica)	8 (NBR-2% Si69-Silica)	9 (NBR-8% Si69-Silica)	10 (NBR-ISAF)
Modulus at 100% elongation, MPa	1.2	2.9	3.7	2.3	2.6	3.1
Modulus at 300% elongation, MPa	1.9	8.3	12.2	7.2	10.3	13.6
Tensile strength, MPa	14.7	20.4	21.8	23.2	23.6	23.4
Elongation at break, %	928	583	537	707	535	458
Tear strength, N/mm	41.4	63.6	65.3	66.2	65.4	64.7
Abrasion loss, mm^3	108.4	85.6	84.5	82.7	81.4	77.2
Resilience ,%	45.7	36.5	34.1	41.6	42.7	37.7
Hardness, Shore A	58	73	74	66	68	64
Compression set, %	55.2	36.6	35.9	34.1	31.3	32.5

Table 8.9 Technological properties (CBS- DPG cure)

Parameter	Mix No./Identification				
	11 (NBR-Silica)	14 (NBR-10 ENR - Silica)	15 (NBR-15ENR-Silica)	18 (NBR-2% Si69-Silica)	19 (NBR-8% Si69-Silica)
Modulus at 100% elongation, MPa	1.8	3.7	3.8	2.4	3.3
Modulus at 300% elongation, MPa	4.4	12.7	13.6	9.6	12.8
Tensile strength, MPa	19.5	21.5	23.7	23.8	23.9
Elongation at break, %	677	507	456	557	446
Tear strength, N/mm	55.9	65.3	66.0	67.5	64.7
Abrasion loss, mm^3	106.3	85.2	84.0	82.0	78.5
Resilience, %	43.4	41.8	42.8	42.8	43.9
Hardness, Shore A	70	74	74	72	72
Heat build-up, ΔT°C	71	61	59	65	61
Compression set, %	41.2	34.5	34.0	33.4	31.0

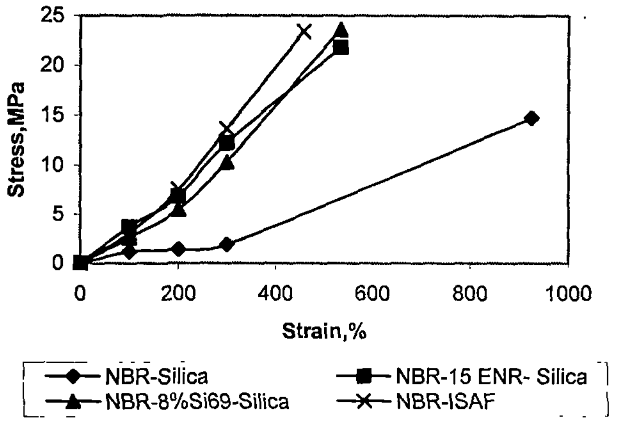


Fig. 8.3 Comparison of the stress-strain property(CBS cure)

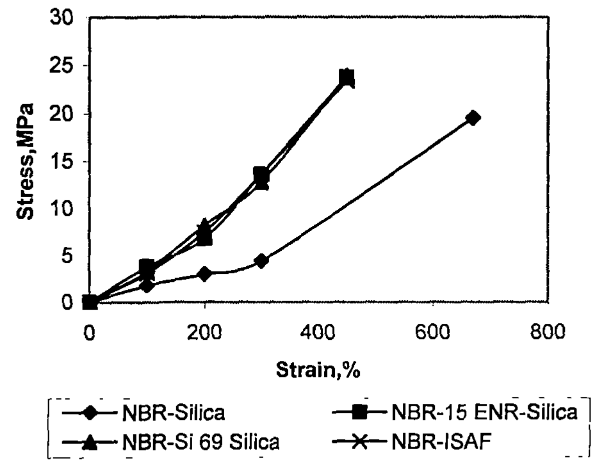


Fig. 8. 4 Comparison of the stress-strain property(CBS-DPG cure)

the modulus[12]. For the CBS accelerated composite the modulus increase was more pronounced with higher concentrations of ENR and the value obtained with 15 parts of ENR was even higher than that obtained for the composites containing 8% Si-69. The secondary accelerator system improved the modulus in all cases. For this system also, the modulus achieved for silica filled NBR, modified with 15 parts of ENR, was found to be higher than that of the same modified with Si-69 and the value was closer to that of the NBR-ISAF composite.

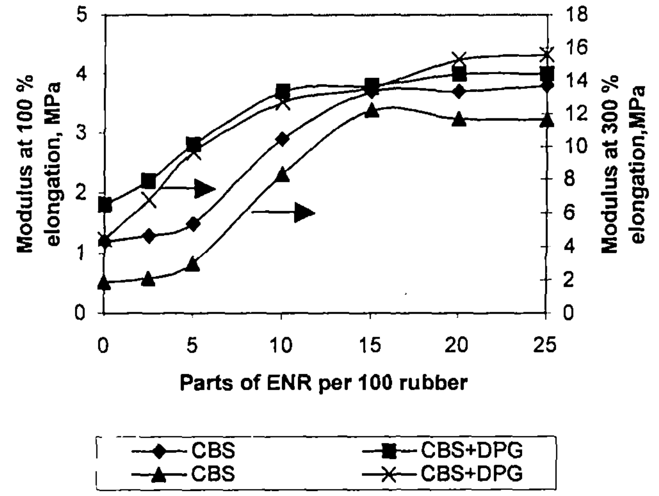


Fig. 8.5 Variation in modulus with ENR incorporation

b) Tensile strength and elongation at break

Improved tensile strength and reduced elongation at break (EB) are considered criteria for higher filler reinforcement [13]. Fig. 8.6 shows the variation in tensile strength and EB of ENR- modified composites with the two cure systems. These two properties are also related to the nature and number of crosslinks. For the CBS cure system, tensile strength showed an increase up to 15 parts of ENR and then decreased, whereas EB showed a continuous decrease with increased ENR concentration. The changes were not very marked up to 5 parts of ENR, beyond which a sharp difference in both cases was noticed. Increased tensile strength and reduced EB with increased concentration of ENR can be attributed to increased interaction between the polymers and that between the polymer and the filler. Improved tensile strength and reduced EB achieved with ENR addition for the CBS based cure systems were found further enhanced by the incorporation of a secondary accelerator. Here also tensile strength showed an increase up to 15 parts of ENR and then decreased, whereas EB showed a continuous decrease with increase in the concentration of ENR. Higher concentrations of coupling agent could not impart any further enhancement in tensile strength while EB decreases. From

Tables 8.8 and 8.9 it was observed that 15 parts of ENR incorporation was sufficient for obtaining tensile strength values comparable to those of Si-69 modified and NBR-ISAF composites. EB values obtained with 15 parts of ENR were closer to those of NBR modified with 8% coupling agent and NBR-ISAF composite.

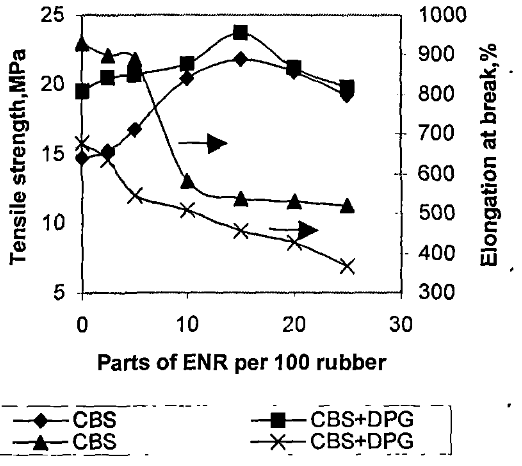


Fig. 8. 6 Variation in tensile strength and elongation at break with ENR incorporation

8.3.3.2 Technological properties

a) Tear strength and abrasion resistance

Variations in tear strength and abrasion loss for different compositions of silica filled NBR/ENR blends for the two cure systems are given in Fig. 8.7. Improvements in tear strength and abrasion resistance are measures of enhanced filler reinforcement[14]. For both cure systems, tear strength showed an increase up to 15 parts of ENR and then showed a decrease. With the CBS cure system, beyond 5 parts of ENR incorporation, the increase in tear strength was sharp. Improved tear strength observed for composites modified with a coupling agent and with ISAF black could also be achieved for NBR-silica composite, modified with a limited concentration of ENR as can be observed from the data given in Tables 8.8 and 8.9.

Substitution of NBR with ENR and incorporation of a coupling agent in NBR-Silica composites improved their abrasion resistance to a greater extent than that of the unmodified mix for both the cure systems. With the binary accelerated system, the improvement in abrasion resistance observed over the CBS system was only marginal. NBR-ISAF and NBR- Silica mixes containing a coupling agent showed the maximum resistance. However, the NBR-Silica composite modified with 15 parts of ENR and cured with both the systems exhibited comparable values, as can be seen from Tables 8.8 and 8.9. Improved tear strength and abrasion resistance observed for the ENR-modified composites can be attributed to the enhanced polymer–polymer and polymer–filler interactions achieved through ENR.

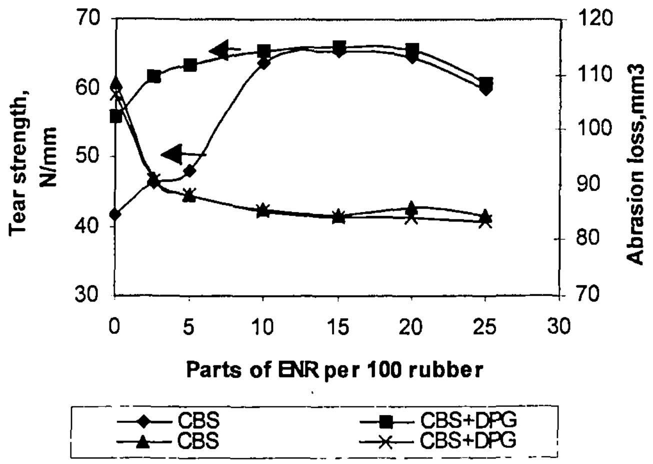


Fig. 8. 7 Variation in tear strength and abrasion loss with ENR incorporation

b) Resilience and hardness

Figure 8.8 shows the variation in resilience and hardness of NBR-silica composites modified with varying proportions of ENR for both the cure systems. With the CBS cure system, resilience showed a continuous decrease, whereas hardness showed an increase and then remained almost steady with increased concentration of ENR. For the CBS cured system the changes were not very marked up to 5 parts of ENR, beyond which a sharp fall in resilience and an increase in hardness were noted. For the CBS-DPG combination, no marked difference in resilience was noticed with ENR

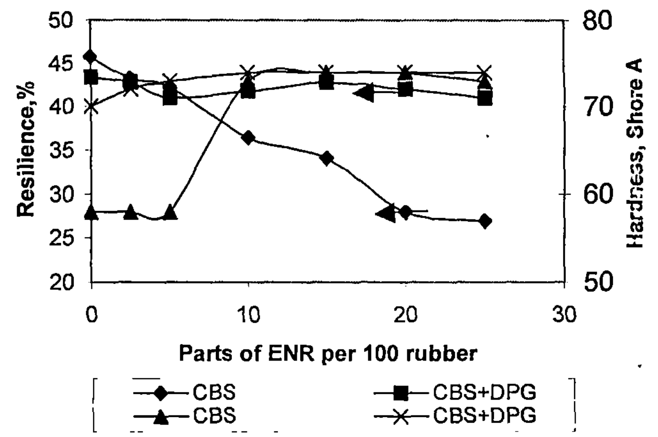


Fig.8. 8 Variation in resilience and hardness with ENR incorporation

incorporation. For both the cure systems, beyond 10 parts of ENR, hardness remained very close, whereas lower resilience values were noted for the CBS system. This discrepancy may be the result of the difference in the nature of crosslinks formed. For the CBS cure system, the optimum cure times of the mixes were higher than those for the corresponding binary system. This might have produced more NBR-ENR crosslinks, resulting in reduced polymer mobility and hence reduced resilience.

From Tables 8.8 and 8.9 it was observed that the resilience value obtained for the composite modified with 15 parts of ENR for the binary cure system was closer to that of those modified with the silane coupling agent. The resilience of the unmodified silica filled compound was marginally altered with the change in cure system. The resilience value observed (Table 8.8) for the carbon black-based composite was closer to that of the silica filled composite modified with ENR. The hardness values obtained for the composites modified with a limiting concentration of ENR for both the cure systems were higher than those modified with Si-69 and NBR-ISAF composite. This may be attributable to increased crosslink density resulting from ENR incorporation.

c) Compression set and heat buildup

Variations in compression set and heat buildup for different compositions of silica-filled NBR/ENR blends for the two systems of cure are given in Fig.8.9. For both the cure systems, a reduction in compression set with incorporation of ENR was noted, which can be attributed to the increased crosslink density achieved through it. With increased concentration of coupling agent a reduction in compression set was noted. The set values obtained for NBR-Silica composites modified with an optimum concentration of ENR was close to that obtained for the coupling agent as is seen from Tables 8.8 and 8.9. With the dual accelerator system, there was a reduction in heat build up to 15 parts of ENR, after which there was a slight increase with increased ENR concentration.

Reduction in heat build up observed with ENR incorporation can be attributed to the increased crosslinks resulting from the interaction between the polymers and between the polymer and filler. Higher concentrations of coupling agent can allow a considerable reduction in heat build up. With 15 parts of ENR, the heat development was lower than that achieved for NBR-Si-69-silica and NBR-ISAF, as observed from Table 8.9.

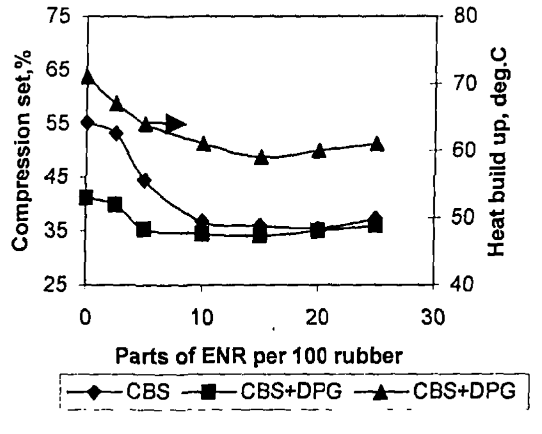
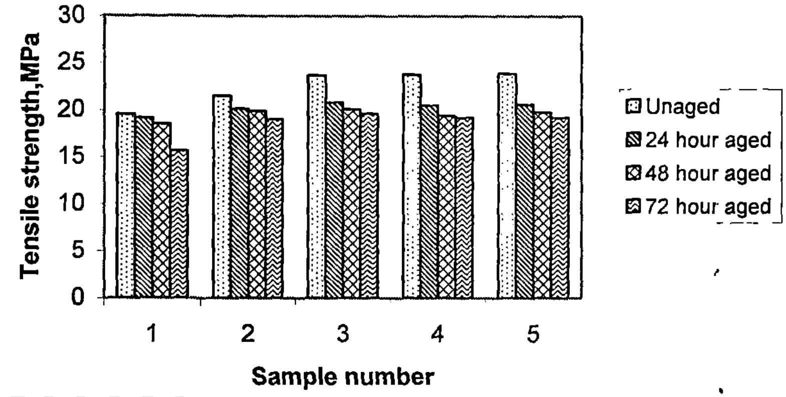
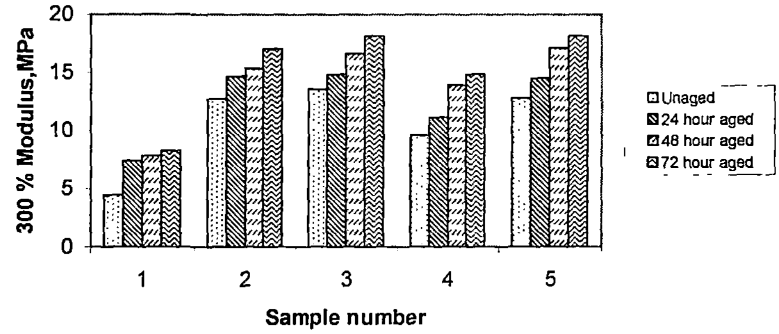


Fig. 8.9 Variation in compression set and heat buildup with ENR incorporation



Sample identification
1.NBR-Silica 2.NBR-10ENR-Silica 3.NBR-15 ENR-Silica 4.NBR-2% Si69-Silica 5.NBR-8%Si69 -Silica

Fig.8.10 Effect of ageing on tensile strength

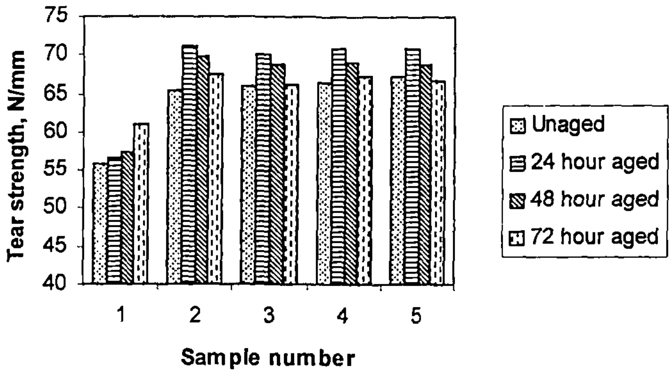


Sample identification
1.NBR-Silica 2.NBR-10ENR-Silica 3.NBR-15 ENR-Silica
4.NBR-2% Si69-Silica 5.NBR-8%Si69 -Silica

Fig.8.11 Effect of ageing on 300 % modulus

d) Ageing resistance

The ageing resistance of the vulcanizates was assessed by determining tensile properties before and after ageing. Figs 8.10 and 8.11 show the ageing resistance in terms of retention of tensile strength and modulus, for the dual accelerator system of a few selected samples, that is, NBR-Silica, NBR-ENR-Silica and NBR-Si 69-Silica after ageing at 100°C for 24, 48 and 72 h. Retention of strength and modulus for the ENR-substituted samples was better than those of the unmodified sample and was comparable with those of the Si-69- modified sample. Tear strength values for the binary accelerator



Sample identification
1.NBR-Silica 2.NBR-10ENR-Silica 3.NBR-15 ENR-Silica
4.NBR-2% Si69-Silica 5.NBR-8%Si69 -Silica

Fig.8.12 Effect of ageing on tear strength

system, after ageing for 24, 48 and 72 h. are given in Fig. 8.12. Retention of tear strength was greater for the ENR-substituted composites than that of the unmodified samples and was close to that of the mix modified with the coupling agent.

8.3.4 Dynamic mechanical analysis

Results of the DMA analysis are given in Table 8.10 and in Figs.8.13 to 8.16. Silica filled (samples 11,15 and 19) and carbon black filled (sample 10) NBR were subjected to dynamic mechanical analysis. Storage modulus, loss modulus and tan δ were determined in a temperature range of –60°C to +60°C. Unmodified and ENR modified silica filled composites showed a glassy modulus of about 1836 and 1665 MPa respectively. Corresponding value of the silane modified mix was only 1289 MPa. Lower glassy modulus values observed for the modified systems might have resulted from either of the factors such as reduction in filler agglomerates, plasticizing action of either silane or ENR or the improved filler dispersion. The carbon black filled mix exhibited glassy modulus of 980 MPa. Transition of storage modulus for the unmodified, silane modified and carbon black filled mixes occurs in the temperature range of about -30°C to -5°C, whereas that of ENR modified mix exhibited a broader transition in the range of -30°C to +5°C. Table 8.10 shows that the ENR modified mix exhibited a higher storage modulus at 0°C indicating incomplete transition.

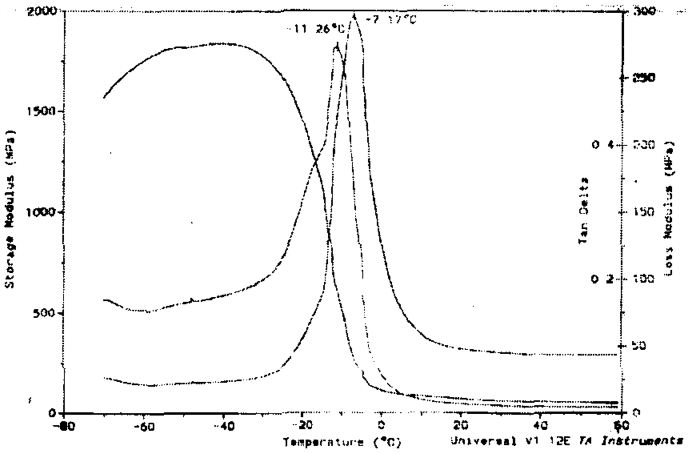


Fig. 8. 13 Variations in viscoelastic properties of silica filled NBR

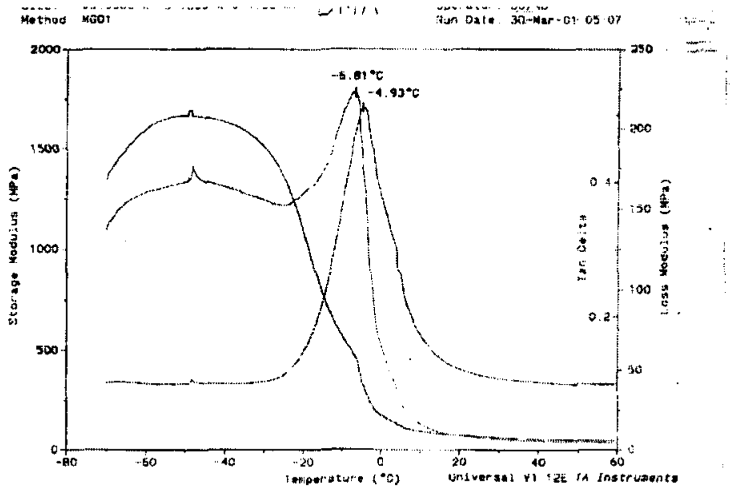


Fig. 8. 14 Variations in viscoelastic properties of ENR modified silica filled NBR

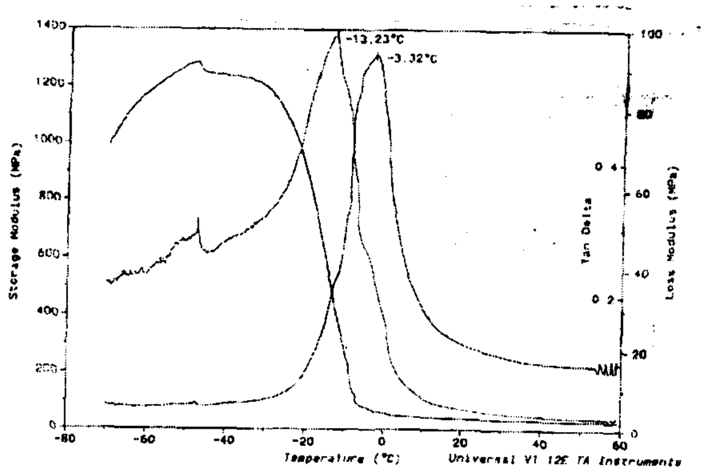


Fig. 8. 15 Variations in viscoelastic properties of silane modified silica filled NBR

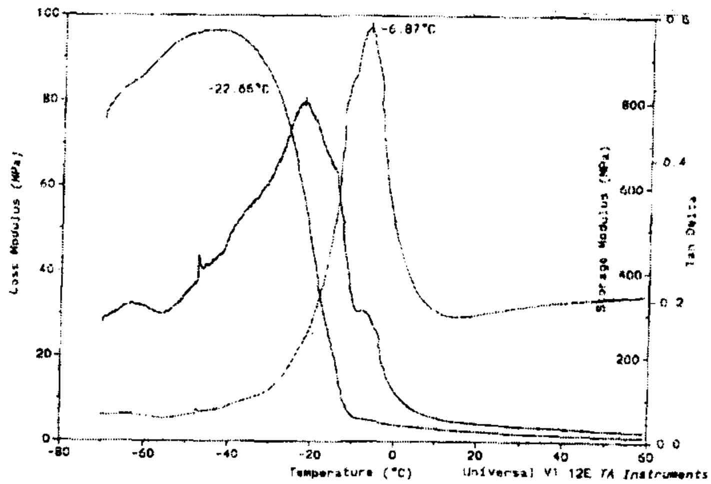


Fig. 8.16 Variations in viscoelastic properties of carbon black filled NBR

Extended transition can be considered to be due to the presence of the ENR ase. The modified system exhibited comparatively lower modulus at 5°C. Loss dulus values at -50°C for the unmodified, ENR modified, silane modified and carbon ck filled mixes were 81, 161, 46 and 86 MPa respectively. The highest modulus erved for the ENR modified mix may be the resultant of the interpolymer cosslinked

Table 8.10 Dynamic mechanical characteristics

Sample No.	Storage modulus(G'), MPa			Loss modulus(G''), MPa		Loss modulus peak value (MPa)	Peak loss modulus temperature, °C	Tan δ peak value	Tan δ peak temperature, °C
	-50°C	0°C	50°C	-50°C	50°C				
11	1836	118	65	81	4.9	272	-11.3	0.59	-7.2
15	1665	203	53	161	4.9	222	-6.8	0.5	-4.9
19	1289	64	32	46	3.2	98	-13.2	0.56	-3.3
10	967	32	13	36	3.8	80	-22.6	0.58	-6.9

structures. However, at 50°C difference in loss modulus could not be observed among the unmodified and ENR modified mixes, whereas the silane modified and carbon black filled mixes exhibited a slightly lower values. Corresponding peak loss modulus values were 272, 222, 98 and 86 MPa respectively. However, after transition, the modulus values were in a narrow range. The highest tan δ peak value was seen for the silica filled NBR; whereas lower values were observed for ENR and silane modified and carbon black filled mixes. Comparatively broader tan δ peaks were observed for ENR and silane modified NBR and carbon black filled NBR. Tan δ transition showed a positive temperature shift for the ENR and silane modified mixes over the unmodified indicating higher network density for the former. Lower tan δ peak values together with shifting and broadening of tan δ peak shows that these systems benefit from better rubber-filler interaction.

8.4 Conclusions

ENR could serve as coupling agent between silica and nitrile rubber. NBR and ENR can form self-crosslinked structures and ENR could also link with silica particles at the vulcanisation temperature. Observations from bound rubber and rheometric studies support this view. These composites were also compared with those of silica filled NBR modified with silane coupling agent and that filled with carbon black. Incorporation of an optimum concentration of ENR in NBR-silica composites gave technological properties comparable to those containing a coupling agent and NBR-ISAF composites. Both single and binary accelerator systems showed improvements in properties with ENR addition. ENR-substituted composites exhibited ageing resistance comparable with that of those modified with a silane coupling agent. Vulcanizates were also characterized using DMA. Broadening of tan δ peak, reduction in peak height and positive shift of the peak on the temperature scale for the ENR modified system indicates better rubber-filler interaction. Higher loss modulus below the transition temperature for the ENR modified mix may be due to the NBR-ENR interaction. The overall property enhancement indicates that ENR can serve as a reinforcement modifier for silica-filled nitrile rubber.

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CHAPTER 9

SUMMARY AND CONCLUSIONS

9.1 Introduction

Unlike carbon black, silica reinforcement of rubbers, especially hydrocarbon rubbers, poses technical difficulties such as poor processability and technological properties, due to the differences in surface energy of the two with that of rubber. Carbon black, which is non-polar, exhibits good rubber-filler interaction, whereas silica which is polar, exhibits higher filler-filler interaction and therefore, results in poor rubber-filler interaction. Several techniques are being used to overcome the problems associated with the use of silica as a filler in rubber, of which silane modification is the most accepted one. However, the high cost of silane is a limitation to its widespread adoption. Several alternatives to silanes are being attempted. The present study describes the use of epoxidised natural rubber (ENR) as a reinforcement modifier in silica filled natural rubber and acrylonitrile butadiene rubber in comparison with the corresponding silane modified and carbon black filled systems.

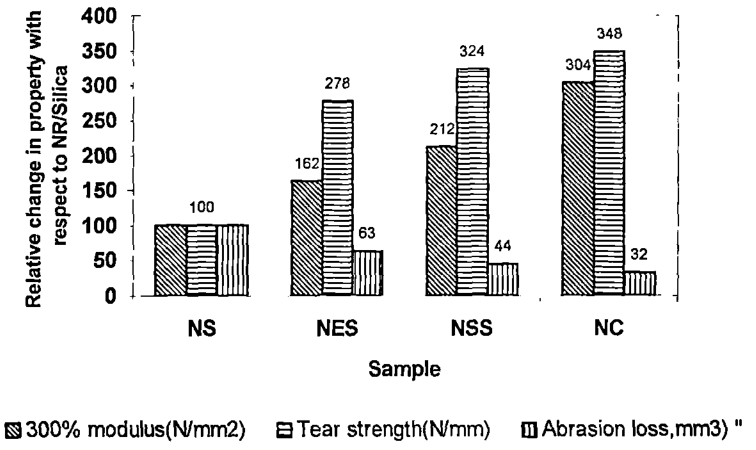
9.2 ENR as a silica reinforcement modifier in rubbers

The focus of the work is to utilize the bifunctionality of ENR, the oxirane and the unsaturation and its polarity to improve the rubber-filler interaction of silica with rubbers.

9.3 ENR as a reinforcement modifier in silica filled natural rubber

With the objective of improving the reinforcement of silica-filled NR, ENR which is more polar than NR was introduced into the matrix as a modifier with the assumption that it will act at the interface of silica and rubber thus enhancing the rubber-filler interaction. ENR modification was made by substituting NR with ENR up to 20 % by weight.

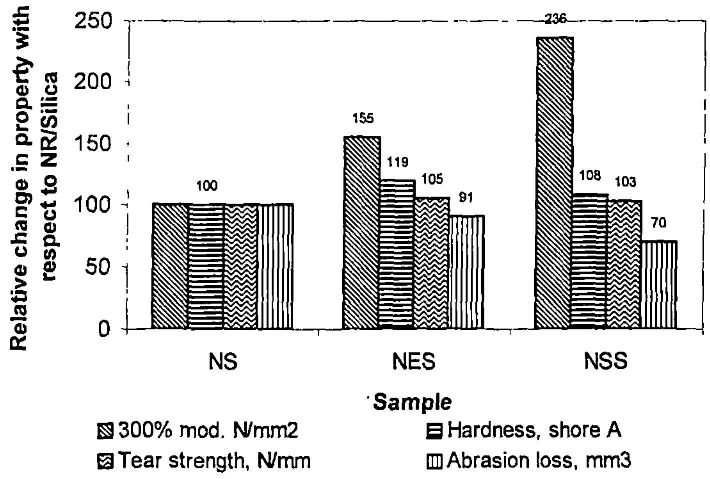
In carbon black reinforced NR, S/CBS cure system gives satisfactory cure characteristics and vulcanizate properties, whereas silica filled NR with the same cure system exhibits cure retardation and poor vulcanizate properties. ENR50, added in limited quantity, was found to function as a cure activator-cum- reinforcement modifier in silica filled NR systems containing S/CBS system. Modifications were carried out by substituting NR with ENR 50 up to 20 percent by weight of the total rubber. Properties such as modulus, tensile strength, tear strength and abrasion resistance are considerably improved. Comparison of a few properties is given in Fig.9.1 Though considerable improvement in reinforcement could be achieved, properties attained were not up to the level observed for the corresponding carbon black filled or silane modified system. Silica filled ENR50 (based on 100% ENR 50), however, showed modulus and elongation at break closer to those of the carbon black filled system, while its abrasion resistance and tear strength were inferior.



NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50), NSS = NR/Silane/ Silica (100/3/50), NC = NR/ISAF (100/50)

Fig.9.1 Relative change in properties(S/CBS)

Modification of silica filled NR with ENR of varying epoxy content was carried out with a conventional binary accelerated cure system for silica compounds consisting of S/CBS/DPG. ENR of varying epoxy content at 10, 25, 50 and 60 mole % were incorporated as modifier. Modification was done by substituting NR with ENR of a particular epoxy content at 5,10,15 and 20 % of the total rubber by weight. The variations in properties observed were dependent on the extent of epoxidation and its concentration. These systems were also compared with those containing 1 to 4 phr of silane. For the ENR modified systems with binary accelerated system, marked effect on



NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50), NSS = NR/Silane/ Silica (100/3/50)

Fig. 9.2 Relative change in properties (S/CBS/DPG)

cure activation could not be seen. However, for the ENR modified systems, scorch and cure time showed an increase with the increase of epoxy content of ENR. Silane modification resulted in a decrease in scorch time and a minor increase in cure time. Modification with ENR improved the vulcanizate properties of the NR/Silica system. Modulus, tensile strength, tear strength and hardness showed increase with ENR concentration and epoxy content. A comparison of the selected properties of ENR50 and silane modified NR/ Silica systems relative to that of the unmodified system is given in Fig.9.2. Abrasion loss passes through a minimum at 10-15 parts of ENR 50. Ageing resistance of the ENR modified system was comparable to that of the silane modified.

Though silica filled ENR 50 (based on 100 % ENR50) exhibited modulus values closer to those of the silane modified, its abrasion resistance is inferior.

ENR and silane modified systems showed higher V_r values than the unmodified. SEM analysis revealed that both ENR and silane could improve the distribution of silica in NR. Improved technological properties observed for the ENR modified system is supported by the higher V_r values and SEM micrographs.

9.4 Dynamic mechanical properties of silica filled NR modified with ENR

Dynamic mechanical properties of silica filled NR, and those modified with ENR of varying epoxy content at different concentrations were compared with those of the silane modified silica filled and carbon black filled NR and silica filled ENR50. Addition of filler in rubber or blending of polymers can cause variations in dynamic properties. In blend systems visco-elastic properties give information on their morphology. In filled systems such properties give informations on filler-filler, polymer-filler and polymer-polymer interactions. In tyre compositions tan δ measurement at 0°C and 70°C gives information on wet grip and rolling resistance respectively. High performance tyres should exhibit a low tanδ at 50-80°C for lower rolling resistance and high tan δ at about 0°C for high skid resistance and wet grip. Variations in the storage modulus, loss modulus and tan δ of the experimental vulcanizates in the temperature range of –80 to 100°C and the miscibility of NR/ENR blends were analyzed.

a) Storage modulus

With incorporation of ENR in silica filled NR, drop in glassy modulus was seen dependent on the concentration of ENR and its epoxy content. Silica filled NR showed a glassy modulus of 2450 MPa. On modification of the same with ENR of varying epoxy content at 15% by weight, the corresponding modulus values are ENR10 (2119 MPa), ENR25 (1375 MPa), ENR50 (1132 MPa) and with ENR60 (1507 MPa) respectively.

ENR modified samples exhibited a broadened glass transition extending to a higher temperature than the silica filled NR dependent on the epoxy content. Thus with silica filled NR the glass-rubber transition took place in the temperature range of –70 to -40 °C and with ENR 60 in the range of -70 to 20 °C and the other ENR modified samples in between these temperature ranges.. Broadening of transition is likely to be associated with the relaxation of ENR phase and the filler-matrix interaction.

Silane modified composites in general exhibited higher glassy modulus than the carbon black filled ones. The carbon black filled and silane modified samples exhibited a minor positive temperature shift in glass transition. Modulus in the temperature range of –45 to 10°C was higher for the black filled and silane modified composites, likely to be due to better rubber-filler interaction. Silica filled ENR50 exhibited a transition in the temperature range of –75 to 0°C.

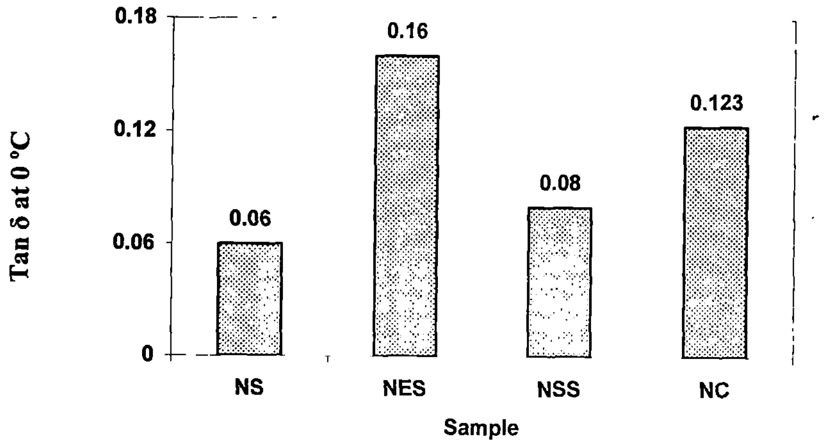
b) Loss modulus

Loss modulus or hysteresis of an elastomer is a measure of its energy dissipation capacity. Variations in loss modulus of silica filled NR with the incorporation of ENR of varying epoxy content were studied. Silica filled NR exhibited a peak loss modulus value of 584 MPa. With the incorporation of ENR, peak value of loss modulus due to the NR transition in general showed a decrease dependent on the epoxy content of ENR. Thus the resultant loss (peak) values for selected ENR modified (with 15% by weight of rubber) systems are ENR10 (489 MPa), ENR25 (296 MPa), ENR 50 (216 MPa) and ENR 60 (300 MPa) respectively. Blending of ENR10 in NR did not exhibit a two phase system as only one loss peak is observed. For the ENR 25, 50 and 60 modification has caused additional loss peaks at about –35°C, -5°C and 0 °C respectively. The lowering of loss modulus peak values (due to the transition of NR phase), on incorporation of ENR, could be considered an indication of enhanced rubber–filler interaction.

Compared to the unmodified silica filled NR, minor increase in peak loss modulus for the silane modified and a decrease for the carbon black filled composites due to the NR transition were noted. Transition temperature due to the NR phase of the carbon black filled composites exhibited a minor positive shift over the silica filled NR.

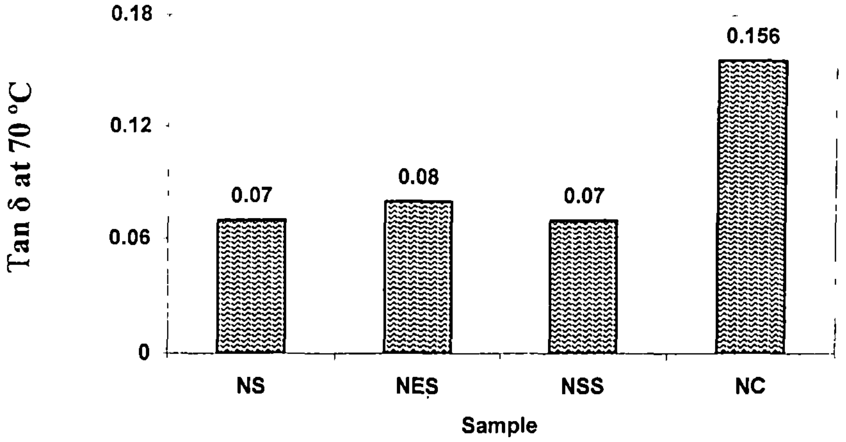
c) Loss tangent (Tan δ)

For rubbers, loss tangent is a measure of damping or hysteresis and for rubber blends it could be used for assessing the miscibility of the components. Loss tangent analysis indicates that ENR10 is miscible with NR as no independent tan δ peak was seen for the two. However, blends of NR with ENR25, 50 and 60 exhibited independent Tg peaks, a measure of immiscibility. ENR10 modification also exhibited minor positive shift in Tg and broadening of the relaxation spectrum of NR phase. Blending of ENR25, 50 and 60 with silica filled NR has resulted in a progressive reduction of tan δ peak value due to the transition of NR, dependent on the concentration of ENR in the blend.



NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50),
NSS = NR/Silane/ Silica (100/3/50), NC = NR/ISAF (100/50)

Fig.9.3 Variations of tan δ at 0 °C



NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50),
NSS = NR/Silane/ Silica (100/3/50), NC = NR/ISAF (100/50)

Fig. 9. 4 Variations in tan δ at 70 °C

Modification with ENR25 showed a merging of tan δ peaks due to NR and ENR indicating chances for inter-phase formation. ENR50 modified composites exhibited higher tan δ values over the unmodified ones in the temperature range of 40 to 100°C. The higher tan δ value observed for the ENR50 and ENR60 modified systems in the temperature range of −15 to +15°C is expected to provide good wet grip to tyre tread compositions. A comparison of the tan δ at 0 °C, a measure of wet grip of NR/Silica, NR/ENR/Silica , NR/Silane/Silica and NR/ISAF is given in Fig. 9.3. The order of wet grip thus can be NR/ENR/Silica > NR/ISAF > NR/Silane/Silica > NR/Silica. Similarly tan δ at 70 °C can be considered a measure of rolling resistance for tyre composites. Tan δ at 70 °C of selected experimental samples are given in Fig. 9.4. The highest rolling resistance as indicated by the tan δ at 70 °C was shown by the carbon black filled system. ENR modified system gave a slightly higher tan δ at 70 °C than the unmodified or silane modified systems.

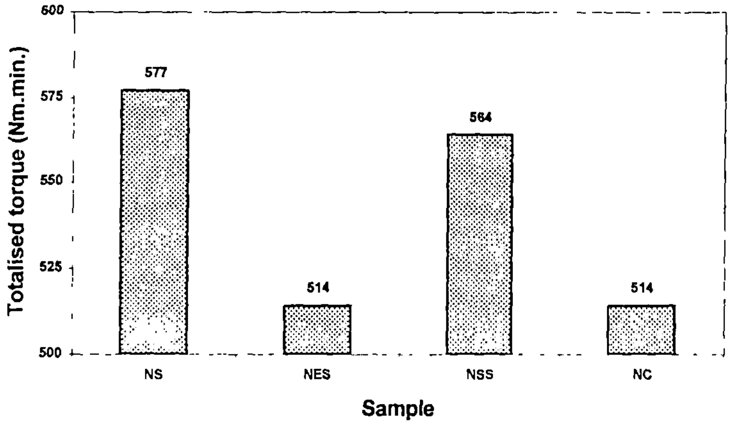
Silane modified and carbon black filled NR, exhibited minor positive shift in glass transition temperature (Tg), an indication of better rubber- filler interaction. Tan δ peak values of the silane modified composite (due to the transition of NR phase) was lower than that of the unmodified and was slightly higher than that of the carbon black filled systems. Lowering of tan δ with temperature in the rubbery zone observed for carbon black filled and silica filled NR modified with ENR of higher polarity is an indication of the reduction in filler-filler networking. The ENR modified silica filled NR in general exhibited lower tan δ than the carbon black filled mix in the rubbery region.

9.5 Mixing, bound rubber and rheological characterization of NR-Silica composites

Mixing studies of silica in natural rubber with and without silane coupling agent or ENR as modifier were carried out in comparison with that of carbon black in NR. The composites thus made were analyzed for bound rubber and processability. For all the filled mixes, filler loading given was 50 phr. Modification of silica filled NR with ENR50 was carried out by substituting 5,10 and 15 percent by weight of NR with it. For the silane modified compounds, silane at 2, 4 and 6 % by weight of the filler were used.

a) Mixing

Mixing studies were carried out in a laboratory model internal mixer (Haake Rheocord 90). Initial mixing temperature for all the experimental mixes was 40°C. Mixing parameters such as mixing torque, mixing energy and temperature developed during mixing were determined. Final mixing torque was taken as a measure of compound viscosity. With the incorporation of ENR or silane in silica filled NR, final mixing torque and temperature developed during mixing were lower than the unmodified mix. The ENR modified compound exhibited the lowest value. Final mixing temperature observed for the ENR modified systems were comparable to that of the carbon black



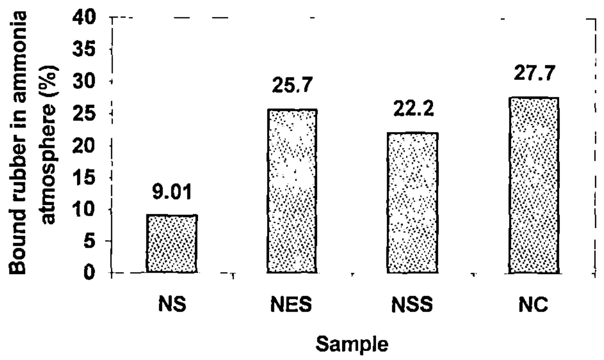
NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50),
NSS = NR/Silane/ Silica (100/3/50), NC = NR/ISAF (100/50)

Fig. 9.5 Comparison of mixing energy

filled compound and that of the mix with silane at higher concentration. Temperature developed during mixing was in the order unmodified > silane modified > ENR modified. Comparison of the totalized torque, a measure of the mixing energy for different systems are given in Fig.9.5. It shows that, the energy for mixing silica in NR in the presence of ENR becomes comparable to that for carbon black in NR and is less than that for the silane modified composites. Thus the mixing efficiency of silica in NR composites got improved, with the incorporation of ENR. Epoxy-silanol interaction or the hydrogen bonding between the two might have contributed to improved filler dispersion.

b) Bound rubber

Bound rubber is a measure of rubber-filler interaction. Silica filled NR and the corresponding ENR and silane modified composites were compared with the carbon black filled NR for bound rubber. Bound rubber for different samples varied in a narrow range of 28 to 36 %. Closer values of bound rubber for the ENR modified silica filled and carbon black filled NR indicate similar rubber-filler networking status for both.



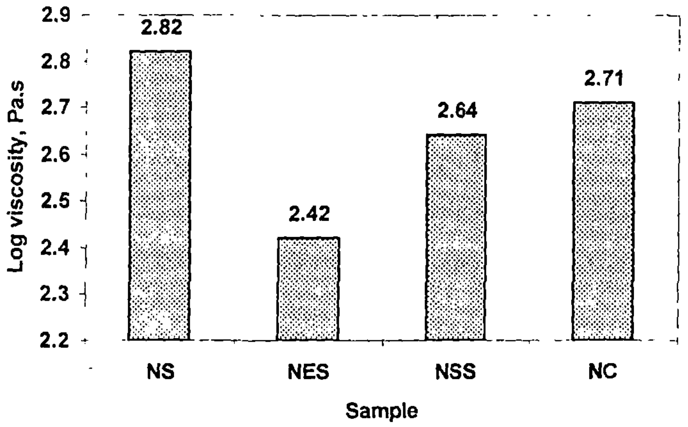
NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50), NSS = NR/Silane/ Silica (100/3/50), NC = NR/ISAF (100/50)

Fig.9.6 Comparison of bound rubber in ammonia atmosphere

Bound rubber in ammonia atmosphere was determined to characterize the nature and extent of rubber-filler bonding. Results of selected samples are given in Fig.9.6. Ammonia is known to cleave the weak linkages between silica and rubber. In ammonia atmosphere, the NR/Silica composite exhibited the lowest bound rubber of about 9%, whereas the silane modified, ENR modified and carbon black filled compounds exhibited about 21 to 28 %. Bound rubber in ammonia medium for the ENR modified system is comparable to that of the silane modified silica filled NR and carbon black filled NR. This indicates stronger rubber-filler interaction for the ENR modified compounds.

c) Processability

Processability study of the mixes of NR/Silica, NR/ENR/Silica, NR/Silane/Silica and NR/Carbon black was carried out in a capillary rheometer. The modified mixes containing silane or ENR50, each at 3 different concentrations as stated earlier were made. Corresponding NR and NR/ENR gum blends which were used for filler incorporation studies were also compared for their processability. Variations in shear stress, viscosity and die swell with varying shear rate, modifier concentration and temperature



NS = NR/Silica (100/50), NES = NR/ENR50/Silica (85/15/ 50),
NSS = NR/Silane/ Silica (100/3/50), NC = NR/ISAF (100/50)

Fig.9.7 Comparison of viscosity at 854 s^{-1} (110 ^{0}C)

were determined. Studies on viscosity changes with shear rate were conducted at 4 different temperatures (90,100,110 and 120°C) for the composites of NR/Silica and the modified systems and carbon black filled NR. Both the gum and filled samples exhibited pseudoplastic behavior. Processability of NR/Silica composites improved with ENR or silane modification as indicated by the lowering of viscosity at all shear rates. Comparison of the viscosity variations of the selected samples of NR/Silica, NR/ENR/Silica, NR/Silane/Silica and NR/ISAF at a shear rate of 854 s^{-1} is given in Fig.9.7. ENR incorporated samples exhibited larger viscosity reduction.

Effect of temperature on flow behaviour of various composites was also studied. Silica filled NR showed a non-linear viscosity variation with temperature. Silane and ENR modified silica filled NR and the corresponding black filled composite exhibited a steady viscosity drop with temperature. Activation energy of flow indicates that ENR modified silica filled NR and carbon black filled NR show similar flow characteristics.

Filled composites generally exhibit yield stress for flow to occur. Yield stress generally increases with particle concentration and decreasing particle size. Process aids which could reduce filler networking could lower the shear stress thereby enhancing the processability. From the plots of shear stress versus shear rate of selected experimental composites viz; NR/Silica, NR/ENR/Silica, NR/Silane/Silica and NR/ISAF, it was observed that the ENR modified composite exhibited lower shear stress compared to the other composites. Silane modified composites exhibited higher shear stress at lower shear rates, while at higher shear rates the stress get closer to that of the ENR modified system. Variations in shear stress among the composites were found to be in the order NR/Silica> NR/Silane/Silica>NR/Black>NR/ENR/Silica.

Various systems were also compared for die swell. ENR modified silica filled composites in general exhibited the lower die swell.

9.6 Peroxide vulcanization of silica-filled natural rubber and its modified systems – Effect of filler loading

Studies on peroxide curing of silica-filled NR compounds were carried out to asses the modification of reinforcement of such systems on addition of ENR or silane, free from the constraints of sulphur cure systems such as cure retardation. Peroxide vulcanized samples of NR/Silica, NR/ENR/Silica and NR/Silane/Silica were compared with special reference to their reinforcement characterization. Silica loading was varied from 0 to 60 phr. For the silane modified systems, silane coupling agent at a concentration of 4% on filler weight and for the ENR modified systems, 10 parts of NR substituted with ENR50 were used.

a) Processability and cure characteristics

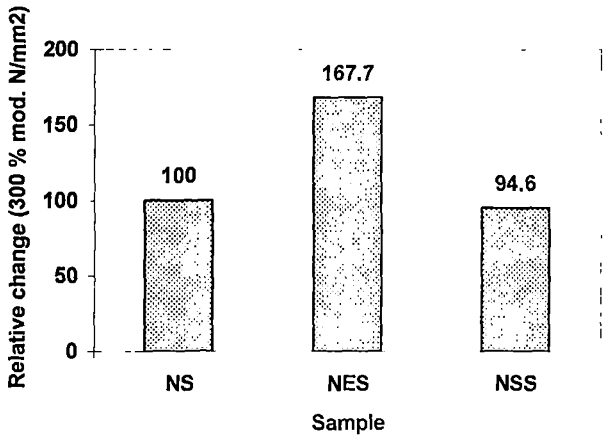
Mooney viscosity values of the modified systems were lower than those of the unmodified system at equal filler loading. Among the modified systems, the ENR modified system showed the lowest Mooney viscosity, which indicates that ENR is more efficient in reducing compound stiffness than the silane coupling agent.

Cure characteristics of the compounds were determined. For all the three series, the minimum(M_L) and maximum torque(M_H) increased with filler loading. Of the three series the highest M_H was observed for the ENR modified mix, likely to be the result of the combined effects of the interaction of ENR with silica and the crosslinking of ENR with the rest of the of rubber through peroxide. With regard to optimum cure time and cure rate index, marked differences among the three series could not be observed. Among the three series, the maximum differential torque(M_H - M_L) and the highest relative torque(differential torque of the filled/differential torque of the gum) observed were higher for the ENR modified.

b) Vulcanizate properties

The stress-strain behaviour of the vulcanizates made from each of the three systems showed differences. The modulus and tensile strength increased with filler loading. For the NR/Silica series, modulus at 300% elongation varied from 0.9 to 4.14 MPa, when the silica loading was varied from 0 to 60 phr. The corresponding values for the ENR modified systems varied from 0.93 to 4.98 MPa, while for the silane modified system the variation was between 0.9 and 3.47 MPa. At equal silica loading, the ENR modified system exhibited comparatively higher modulus than the other two. Comparison of modulus variations with respect to NR/Silica is given in Fig.9.8. The ENR modified system exhibited comparatively higher modulus. At 20 to 60 parts of filler loading, ENR and silane modified samples exhibited comparatively higher tensile strength over the unmodified. Among the three, the ENR modified system exhibited lowest EB values. Stress - strain plots of the three systems at 30, 40 and 50 phr silica loading showed that the ENR modified system required higher energy for deformation than the other two.

Variations in tear strength, abrasion loss, hardness and rebound resilience with filler loading for NR/Silica and its ENR and silane modified versions were compared. For all the three systems, with increase in filler loading, tear strength and hardness improved in an almost linear manner. ENR and silane modified systems showed comparatively higher tear strength than the unmodified system. Up to 40 phr filler loading, the ENR modified composites exhibited higher hardness than the other two. Abrasion loss for the three systems at 20 to 60 phr filler loading were compared. Among the three series, the ENR modified system exhibited the highest abrasion resistance.



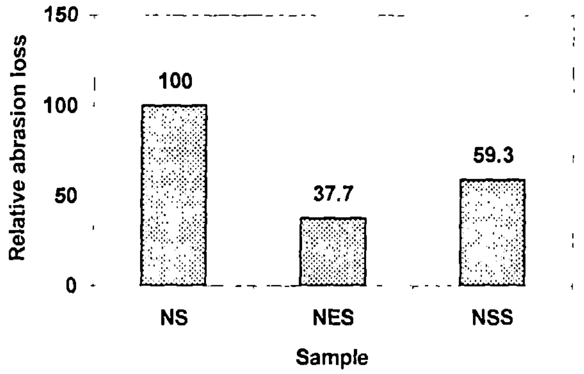
NS = NR/Silica (100/40), NES = NR/ENR50/Silica (90/10/ 40),
NSS = NR/Silane/ Silica (100/1.6/40)

Fig.9.8 Comparison of relative modulus variations with respect to NR/Silica

Comparison of relative abrasion loss, with respect to NR/Silica is given in Fig.9.9. Rebound resilience, in general, got reduced with filler loading. Among the three systems no marked difference in resilience was noted.

c) Swelling studies

The three series of vulcanizates were subjected to swelling studies. Using the swelling data, Kraus and Cunneen-Russell plots were made. From the plots it was observed that ENR and the silane modified samples exhibited higher swelling restriction resulting from higher rubber-filler interaction than the silica filled NR.



NS = NR/Silica (100/40), NES = NR/ENR50/Silica (90/10/ 40),
NSS = NR/Silane/ Silica (100/1.6/40)

Fig.9.9 Comparison of variations of relative abrasion resistance with respect to NR/Silica

c) **Dynamic mechanicl analysis**

Dynamic mechanical analysis of the selected experimental vulcanizates, one from each of the three series, at 50 phr silica loading in a temperature range of -80°C to + 100°C and at a frequency of 1Hz was carried out. The important features noted are;

1. Storage modulus values below the glass transition temperature for the unmodified, silane modified and ENR modified systems are 3450, 3050 and 975 MPa respectively.
2. Tan δ peak heights due to NR transition for the unmodified, silane modified and ENR modified systems are 1.13, 0.98 and 0.79 respectively. The ENR modified system showed comparatively higher tan δ at 0^0C than the other two. Though no separate peak for ENR could be seen for the ENR modified system, the peak due to NR showed a broadened transition.

e) Scanning electron microscopy

From the SEM micrographs of sample from each of the three series, at 40 phr silica loading it was inferred that ENR and silane modification provide comparatively better filler distribution with less number of agglomerates.

9.7 Reinforcement characterization of sulphur vulcanized silica filled natural rubber – Role of modifiers

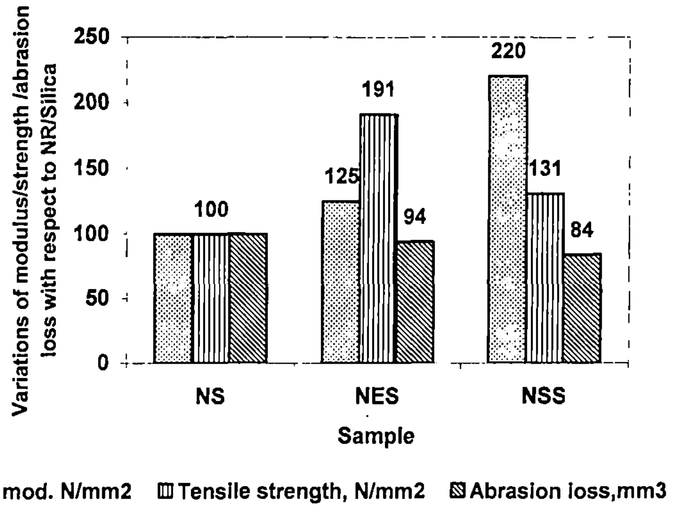
Modification of silica filled NR with ENR and silane was carried out with a sulphur cure system at different filler loadings for improving its reinforcement. For the ENR modified systems, 10 parts of NR was substituted with ENR50 and for the silane modified ones, silane at 4% concentration on filler weight was used. Filler loading was varied from 0 to 60 phr in each of the three series.

a) Processability and cure characteristics

Unlike the peroxide system, in sulphur based compounds, the ENR modified series in general exhibited higher Mooney viscosity. The higher Mooney values for the ENR modified system may be due to the complex interaction between ENR, silica and the other ingredients such as zinc oxide. For all the three systems, minimum and maximum torque increased with filler loading. Minimum torque(M_L) was the lowest for the silane modified and the highest for the ENR modified systems. Maximum torque (M_H) and maximum differential torque(M_H-M_L) were higher for the silane modified system. Mixes containing ENR exhibited comparatively shorter cure time and faster cure rate.

b) Vulcanizate properties

Vulcanizates made from the three series were tested for stress-strain and other technological properties. Modulus showed a regular increase with filler loading. At equal filler loading, modulus enhancement observed was in the order silane modified > ENR modified> unmodified. Tensile strength, in general, passes through a maximum with filler loading and the optimum loading varied among the series. ENR modified systems, in general, showed higher tensile strength and elongation at break (EB) than the unmodified and the silane modified systems. Tear strength and hardness progressively increased with filler loading. Comparatively higher tear strength and hardness were shown by the ENR and silane modified systems. Abrasion loss passes through a minimum with filler loading. Abrasion resistance was in the order silane modified > ENR modified >unmodified. Fig.9.10 gives a comparison of the relative changes in modulus, tensile strength and abrasion loss with respect to NR/Silica at 30 phr silica loading. From the stress- strain data it was observed that, at 30 phr filler loading the energy at rupture was the highest for the ENR modified system. Heat build-up and compression set showed an increase with filler loading. Among the three series, the ENR modified system exhibited higher heat build-up and compression set.



NS = NR/Silica (100/30), NES = NR/ENR50/Silica (90/10/ 30),
NSS = NR/Silane/ Silica (100/1.2/30)

Fig. 9.10 Comparison of relative variations of modulus, tensile strength and abrasion loss

c) Swelling studies

Reinforcement characterization of the three series was carried out by swelling studies. Higher negative slope values obtained in the Kraus plots and higher positive slope values for the Cunneen- Russell plots for the ENR and silane modified systems indicate their higher reinforcement potential.

d) Dynamic mechanical analysis

Dynamic mechanical analysis was used to characterize rubber-filler and filler-filler interactions by measuring the modulus response to varying strain. Three selected vulcanizates of NR/Silica and the ENR and silane modified systems at 50 phr filler loading were subjected to a strain–dependent isothermal dynamic mechanical analysis at a frequency of 1Hz at 60°C. Silanes could lower the low strain modulus of silica filled NR probably due to the lower filler-filler interaction and the plasticizing action of the silane. Larger high strain modulus(G_α) for the ENR modified systems indicates the presence of strain independent filler-rubber linkages.

e) Stress relaxation

Stress relaxation studies were carried out to assess the stress decay with time for the three series of vulcanizates at 30 and 50 phr filler loading. The higher rate of stress decay with time for the ENR modified systems indicates the presence of filler-rubber linkages which can undergo bonding-debonding processes under strain.

f) Thermal analysis

Thermogravimetric analysis (TGA) in nitrogen and air medium of the three series of silica filled NR samples (modified and unmodified) at 50 phr silica loading in the temperature range of 30 to 700°C was carried out. Under nitrogen atmosphere, no significant difference among the samples was noted, whereas in air medium degradation has occurred in steps at different temperatures. The fraction of the sample undergoing high temperature degradation was higher for the ENR and silane modified systems. This is likely to be due to the polymer fragment which gets modified with silica either through ENR or silane.

g) Scanning electron microscopy

SEM studies showed that ENR and silane modified systems exhibited better filler distribution.

9.8 ENR as a reinforcement modifier for silica filled nitrile rubber

The effects of incorporation of ENR in sulphur vulcanized silica filled nitrile rubber(NBR) are discussed. NBR compounds containing 50 phr silica were modified with ENR50 at different concentrations. NBR was substituted with 2.5, 5, 10, 15, 20 and 25 parts of ENR50 per hundred rubber. These systems were compared with silane modified silica filled and carbon black filled NBR. Two systems of cure , S/CBS(1.5/1 phr) and S/CBS/DPG(1.5/1/1.5 phr) were used.

a) Cure characteristics

With both cure systems changes in cure behavior was noticed with the incorporation of the modifiers. On modification with ENR, minimum torque(M_L), maximum torque(M_H) and differential torque(M_H - M_L) increased, cure time and scorch time reduced while the cure rate increased.

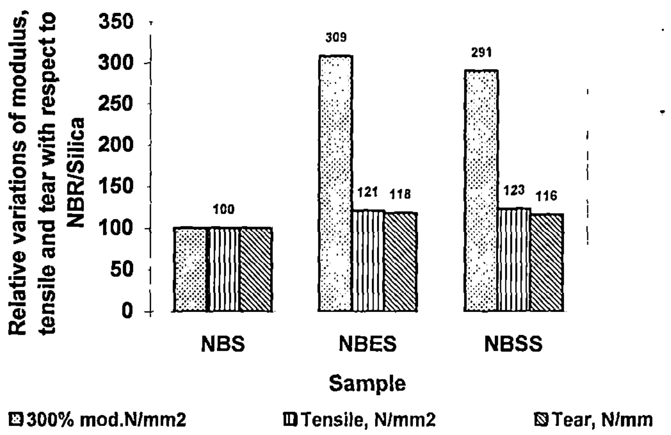
Polymer-polymer interactions resulting in chemical crosslinks were assessed through rheometric study of the gum blends of NBR and ENR50 at 150°C. The corresponding silica filled systems were also analyzed. On increasing the ENR content in the blend, a gradual increase in torque was noted, for both the gum and filled compounds. The increased torque might have resulted from NBR-ENR crosslinking through the epoxy and cyano (-CN) groups. Thus it could be presumed that, ENR would function as a coupling agent between silica and NBR.

b) Bound rubber

Selected compounds of NBR/Silica, NBR/ENR/Silica, NBR/Silane/Silica and NBR/ISAF were subjected to bound rubber analysis. The higher bound rubber observed for the ENR modified, silane modified and carbon black filled systems over the unmodified silica filled NBR indicates better rubber-filler interaction in the former cases.

c) Vulcanizate properties

Stress-strain plots of the CBS and CBS/DPG cured systems of selected samples of NBR/Silica and its modified systems and carbon black filled NBR were compared. For both systems, modulus of the silica filled NBR was found enhanced with ENR modification. Enhanced crosslink density of the ENR modified system might have improved the modulus. Tensile strength improved on modification with ENR and passed through a maximum with optimum concentration. Strength values comparable to those of the silane modified and black filled systems could be achieved . Elongation at break decreased with ENR incorporation and was also found comparable to that of the silane modified and carbon black filled systems. ENR modified systems exhibited stress-strain behaviour closer to that of the silane modified and carbon black filled systems. Tear strength and abrasion resistance of silica filled NBR improved on modification with ENR. Fig.9.11 gives a comparison of the modulus, tensile and tear strength of the modified NBR/Silica system with respect to the unmodified. Hardness increased and compression set decreased with ENR modification. The properties observed for the ENR



NBS = NBR/Silica (100/50), NBES = NBR/ENR50/Silica (85/15/50), NBSS = NBR/Silane/ Silica (100/4/50)

Fig.9.11 Comparison of modulus, tensile and tear strength with respect to NR/Silica modified system were comparable to those of the silane modified and carbon black filled systems. ENR substituted composites also exhibited ageing resistance comparable with that of those modified with a coupling agent.

d) Dynamic mechanical analysis

Vulcanizates of silica filled NBR, its modified systems and carbon black filled NBR were characterized using dynamic mechanical analysis. Storage modulus, loss modulus and tanδ were determined in a temperature range of -60°C to +60°C . The unmodified silica filled NBR exhibited a glassy modulus of 1836 MPa, while the modified systems and carbon black filled systems exhibited lower values. Unlike the other composites, the ENR modified system exhibited extended glass-rubber transition and the highest loss modulus at -50°C. Broadening of the tanδ peak, reduction in peak height and a positive shift of the peak on the temperature scale for the ENR modified system indicate better rubber-filler interaction. The overall property enhancement indicates that ENR can serve as a reinforcement modifier for silica-filled nitrile rubber.

9.9 Scope for future work

The observations of the present study may find applications in the tyre and non-tyre industry. Therefore the studies on the use of ENR as a reinforcement modifier in silica filled rubbers shall be explored further for the following aspects.

- Optimisation of cure system.
- Optimisation of ENR characteristics.
- Effect of temparature of processing
- Silane/ENR combined system.
- Silica reinforcement modification of other general and special purpose rubbers and rubber blends
- Effect of ENR in mixed filler (carbon/silica)reinforced rubbers.

9.10 Conclusions

ENR could be used as a silica reinforcement modifier in NR and NBR, the two rubbers which vary in their chemical nature and polarity.. These systems were also compared with the corresponding silane modified and carbon black filled systems. Extent of improvement in reinforcement achieved was found dependent on the polarity of the base polymer and its ability to interact with ENR. Incorporation of ENR modified the processability, cure characteristics and technological properties. Characterization of various samples was made by physical methods, swelling studies, dynamic mechanical analysis and scanning electron microscopy. This technique of using ENR as a silica reinforcement modifier is expected to function in other rubber-silica systems as well. The level of improvement may be dependent on the chemical nature and polarity of the base polymer. Use of ENR as a reinforcement modifier in various silica filled rubbers is a new concept and needs to be explored further.

APPENDIX

List of publications

1) Indian patent application No. 1109 /MAS / 99-98 / RQ / CHE /04 – for 'Rubber Silica Composites with Epoxidised Natural Rubber as a Reinforcement Modifier' on behalf of Rubber Research Institute of India; Inventors – Jacob K. Varkey, Susamma Joseph and K. Mariamma George.

2) Jacob K. Varkey, Susamma Joseph, K.T. Thomas and N.M. Mathew, 'Epoxidised Natural Rubber- An Interface Modifier for Natural Rubber- Silica composites, Proceedings of International Rubber Conference (IRCO '98) December 7-9, 1998, Chennai, India, Vol.1, P.123

3) Jacob K. Varkey, K.Mariamma George, Susamma Joseph, K.T. Thomas and N.M. Mathew, Silica filled Rubbers- Epoxidised Natural Rubber as a Reinforcement Modifier in comparison with a silane' Proceedings of the International Conference and Exhibition on Rubber and Allied Materials (Asia RubTech Expo 2002) November 28-30, 2002, New Delhi, India, T2-B/iv, P.189.

4) K.Mariamma George, Jacob K. Varkey, K.T. Thomas and N.M. Mathew, 'Epoxidised Natural Rubber as a Reinforcement Modifier for Silica Filled Nitrile Rubber', Jl. Appl. Polym. Sci., Vol.58, P292, 2002.

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