PHOSPHORYLATED CASHEW NUT SHELL LIQUID AS A MULTIFUNCTIONAL ADDITIVE IN NATURAL RUBBER

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PHOSPHORYLATED CASHEW NUT SHELL LIQUID AS A MULTIFUNCTIONAL ADDITIVE IN NATURAL RUBBER

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dedicated to
all those who have contributed in making me
what I am

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In my opinion, the thesis fulfills all the requirements according to the regulations laid down by the Institute for the award of the Ph.D. degree. The results embodied in this thesis has not been submitted for any other degree or diploma.

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This is to certify that the thesis entitled "**Phosphorylated Cashew Nut Shell Liquid as a multifunctional additive in Natural Rubber**" is an authentic record of the research work carried out by **Mr.A.R.Ravindra natha Menon,** BSc., BTech., under our supervision in partial fulfilment of the requirements for the degree of **Doctor of Philosophy** of the Indian Institute of Technology, Kharagpur and further that no part thereof has been presented before for any other degree.In our opinion, this thesis has reached the standard specified for the award of the degree. Eight papers from this thesis have been published in various international journals.

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TABLE OF CONTENTS

Abstract i
Preface ii
List of Abbrevations iv
List of Symbols vi

CHAPTER - I

INTRODUCTION 1 - 21

I.1 Natural Rubber - Significance 3
I.2 Modification of NR 4
I.3 NR compounding 4
I.4 Multifunctional additives 5
I.5 Requirements for multifunctional additives 6
I.6 Cashew Nut Shell Liquid 6
i. Cardanol - Structural features and composition 7
ii. Polymerization characteristics of CNSL 9
iii. Applications of CNSL and CNSL based products 9
(a) Rubber compositions 9
I.7 Scope of the present work 11
i. Phosphorylated Cashew Nut Shell Liquid 11
I.8 Objectives of the present work 14

References 16

CHAPTER - II

EXPERIMENTAL 22 - 28

II.1 Materials 22
II.2 Methods 22
i Processability characteristics 22
(a) Mixing 22
(b) Plasticity 22
(c) Melt-rheology 23
(d) Cure characteristics 23
(e) Dispersion of filler 23
(f) Self-adhesion strength 23
ii Physico-mechanical properties of the vulcanizates 24
(a) Preparation of test samples 24
(b) Physico-mechanical properties 24
(c) Flammability 25
(d) Aging characteristics 25
(e) Dielectric properties 26
(f) Fracture morphology by SEM 26
(g) Thermal analysis 26
(h) Chemical crosslink density of the vulcanizates 27

(i) Determination of type of crosslinks 27
(j) WAXS study 27
(k) IR spectroscopy 27

References 28

CHAPTER - III

PCNSL AS A PLASTICIZER 29 - 62

III.1 Introduction 29
III.2 Mill mixing characteristics 33
III.3 Processing characteristics of NR modified with PCNSL in a Monsanto Processability Tester - (Rheological characteristics). 35
i. Melt-flow characteristics 35
(a) Melt-viscosity 35
(b) Pseudo-plasticity index and consistency index 42
(c) Activation energy of melt flow 45
ii Melt elasticity 46
(a) Die swell ratio 46
(b) Principal normal stress difference 48
III.4 Glass-transition 51
III.5 Mixing characteristics of PCNSL modified NR in a Brabender Plasticorder 53

References 59

CHAPTER - IV

PCNSL AS A TACKIFIER 63 - 71

IV.1 Introduction 63
IV.2 Self adhesion strength 64
i Effect of variations in the dosage of PCNSL. 65
ii Effect of variation in contact time 66
iii. Effect of variation in contact pressure 66
iv Effect of variation in storage time before testing 68
v. Effect of variation in dosage of PCNSL in the substrates 68

References 71

CHAPTER - V

PCNSL AS A CO-AGENT FOR VULCANIZATION AND A MODIFIER OF PHYSICO-MECHANICAL PROPERTIES 72 -133

V.1 Introduction 72

V.2 Cure characteristics of the mixes 72
i Effect of PCNSL on NR in different vulcanization systems 73
ii Effect of different accelerator types and doses 76
iii Effect of PCNSL content 78
iv Effect of increase in the dosage of ZnO 80
v Kinetics of cure 82
(a) Cure characteristics 82
(b) Kinetic parameters 82
V.3 Physico-mechanical properties 85
i. Variation in the vulcanization system 85
ii Variation in dosage of PCNSL in the SEV system 86
iii Optimisation of the dose of ZnO 87
iv. Physico-mechanical properties of PCNSL modified NR vulcanizates at PCNSL/ZnO ratio of 1:1 88
v. Fracture behaviour of the vulcanizates from Scanning Electron Microscopy studies 93
(a) Tensile fracture surface 94
(b) Tear failure surface 101
(c) Tensile fatigue failure surface 102
vi Stress-relaxation characteristics 102
(a) Effect of dosage of plasticizer 103
(b) Effect of strain rate and strain level 105
vii Dynamic Mechanical Analysis 109
V.4. Chemical Analysis of PCNSL modified NR vulcanizates 114
i. Crosslink density and network structure 114
ii Effect of dosage of PCNSL on CLD of the vulcanizates 119
iii. Effect of thermo-oxidative aging on the CLD of PCNSL modified NR vulcanizates 124
iv. Effect of dose of ZnO on CLD of PCNSL modified NR 124
v Effect of PCNSL on the network structure of the NR vulcanizates 125

References 128

CHAPTER - VI

THERMAL ANALYSIS OF NR MODIFIED WITH PCNSL 134-149

VI.1 Introduction 134
VI.2 Thermal decomposition and thermal stability of the vulcanizates 136
VI.3 Decomposition residue (char yield) 144
VI.4 Kinetics of thermal degradation of the vulcanizates 144
VI.5 Resistance to thermo-oxidative decomposition (Antioxidant activity) 145

References 148

CHAPTER - VII

COMPARISON OF PCNSL WITH COMMERCIAL PLASTICIZERS 150-167

VII.1 Introduction 150
VII.2 Comparison of PCNSL with a phosphatic plasticizer (2-ethyl hexyl diphenyl phosphate) in NR 150
i Cure characteristics 151
ii Compatibility of the plasticizer with rubber 153
iii. Physico-mechanical properties of the vulcanizates 153
iv Flame retardancy 154
v Resistance to thermo-oxidative aging and decomposition 154
(a) Thermo-oxidative aging 154
(b) Thermo-oxidative decomposition 155
VII.3 Comparison of PCNSL with a conventional plasticizer (Spindle oil) 160
i Cure characteristics 160
ii. Physico-mechanical properties of vulcanizates 161
iii Retention in mechanical properties after aging 163
iv Resistance to thermo-oxidative decomposition 164

References 167

CHAPTER - VIII

EFFECT OF FILLERS ON PHYSICO-MECHANICAL PROPERTIES OF PCNSL MODIFIED NR 168-185

VIII.1 Introduction 168
VIII.2 Cure characteristics 168
VIII.3 Physico-mechanical properties 170
i. Reinforcement index 171
ii. Dispersion of filler in PCNSL modified NR 172
iii Mechanical properties of the vulcanizates 174
(a) Hardness 174
(b) Tensile properties 174
(c) Tear strength 179
iv Resistance to aging 179
v Thermal stability and thermo-oxidative decomposition characterisics 179

References 185

CHAPTER -IX

SUMMARY AND CONCLUSION 186-190

LIST OF PUBLICATIONS 191

ABSTRACT

The role of Phosphorylated Cashew Nut Shell Liquid (PCNSL) prepolymer as a 'multifunctional additive'(MFA) in Natural Rubber (NR) has been studied with special reference to processability characteristics of the mixes and physico-mechanical properties of the vulcanizates. Studies in a Brabender Plasticorder and a Monsanto Processability Tester have shown considerable plasticizing effect of PCNSL in NR in the concentration range of 10 to 20 phr. The improvement in the self adhesion strength (tack strength) of PCNSL modified NR measured by the 180° peel test has been attributed to the enhanced interfacial diffusion of NR in presence of PCNSL. NR vulcanizates containing 10 phr of PCNSL vulcanized by semi-efficient vulcanization (SEV) system showed higher physico-mechanical properties, resistance to fatigue failure and thermo-oxidative decomposition as compared to the conventional (CV) and efficient (EV) vulcanization systems at an optimal ZnO/PCNSL ratio of 1 and compared to vulcanizates without PCNSL. Elucidation of the network structure of PCNSL modified NR vulcanizates using the determination of chemical crosslink density (CLD) by equilibrium swelling method and chemical probes indicated a complex network structure with extra-network materials. The probable formation of entanglements between the aliphatic side chain of PCNSL and the NR chains is thought to account for the improved tensile and elongation properties despite a reduction in the total CLD.Thermal analysis of the PCNSL modified NR vulcanizates using TGA, DSC and DTA showed improved resistance to thermal and thermo-oxidative decomposition of the vulcanizates in air, in presence of 10 phr of PCNSL.

Key Words:- Phosphorylated Cashew Nut Shell Liquid, Multifunctional additive, Natural Rubber, Processability, Physico-mechanical properties, Self adhesion strength, Network structure, Thermo-oxidative decomposition

PREFACE

The system of 'compounding of elastomers' widely practised in the industry often employs a variety of additives, each with a specific functional requirement either during processing or in the final product. As functional requirements increased, the number of additives also increased, thereby complicating the compounding procedure. Apart from the problems of high cost, limited availability and in certain cases poor processability, the use of a number of additives is found to affect the vulcanizate properties as well. This has necessitated the need to search for additives with multiple functions. Although a number of chemicals emerged with more than one function, their applicability was limited by the lack of 'true multifunctional' behaviour *ie.* a number of properties being exhibited by one compound with all the requirement for being an additive. A search for low cost naturally occuring monomers having the reqiured structural features for the synthesis of an MFA led to the identification of long chain hydrocarbon phenols found in Cashew Nut Shell Liquid (CNSL), a natural product obtained from the cashew tree *Anacardium occidentale L.* as an ideal candidate. A phosphorylated derivative of CNSL (Phosphorylated CNSL prepolymer, PCNSL) was found to have a unique combination of excellent flame-retardancy, plasticizing effect, antioxidant action and thermal stability in various polymers. Preliminary results in natural rubber (NR) indicated the improvements in processability, flame-retardancy, tensile properties and resistance to thermo-oxidative decomposition of NR in presence of low concentrations of PCNSL. This necessitated a detailed study on the processability characteristics and physico-mechanical properties of PCNSL modified NR with the objective of cultivating and establishing the concept of 'PCNSL as a multifunctional additive in NR'

The present investigation is mainly concerned with the study of the processability characteristics and physico-mechanical properties of PCNSL modified NR carried out with a view to establishing its multifunctional behaviour. Chapter I of this thesis gives an out-line of the concept of MFA along with an introduction to the status of rubber technology and the scope and objectives of the present work.

The materials used for the present study and the different methods of processing and testing the various processability characteristics and rheological parameters of the mixes and physico-mechanical properties of their vulcanizates are described in chapterII

Chapter III deals with the processability characteristics and melt-rheology of PCNSL modified NR in a Monsanto Processability Tester and Brabender Plasticorder.

Chapter IV deals with the self adhesion characteristics of PCNSL modified NR. The self-adhesion strength ('tack-strength') of NR compounds was studied with respect to variations in contact time, contact pressure, storage time and concentration of PCNSL

Chapter V describes the cure characteristics of PCNSL modifed NR compounds and the physico-mechanical properties of their vulcanizates in comparison with unmodified NR compounds. Results on the elucidation of the chemical crosslink density (CLD) and network structure of PCNSL modified NR vulcanizates of various vulcanization systems (conventional, semi efficient and efficient) have also been presented to enable the interpretation of the observed results on cure characteristics and physico-mechanical properties

Chapter VI describes the results of the studies on thermal and thermo-oxidative decomposition characteristics of PCNSL modified NR vulcanizates carried out using various thermal analysis methods such as thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)

Chapter VII deals with a comparative study of PCNSL, 2-ethyl hexyl diphenyl phosphate (*Santicizer 141*) and an aromatic oil with respect to the processability characteristics of the mixes and physico-mechanical properties of their vulcanizates

Chapter VIII presents the results on the cure characteristics and physico-mechanical properties of PCNSL modified NR containing different fillers such as carbon black, silica and china clay.

The summary and conclusions of the present study are given in chapter IX. The present data amply illustrate the 'multifunctional role' of PCNSL in NR compounding as a plasticizer ('crosslinkable'), as an aid for filler dispersion, as a tackifier, as a processing aid and softening agent and as an improver of physico-mechanical properties such as tensile strength, elongation at break, toughness, tear strength, fatigue resistance, thermal stability and resistance to thermo-oxidative decomposition. The property profile of PCNSL modified NR indicates possibilities for its utilization for the design and development of 'high-performance products' having specific application requirements.

List of abbreviations

ABS	-	Acrylonitrile butadiene styrene
BI	-	Breakdown Index
BR	-	Butadiene Rubber
BrPCNSL	-	Brominated Phosphorylated Cashew Shell Liquid
CBS	-	Cyclohexyl benzothiazole sulphenamide
CLD	-	Chemical crosslink density
CNSL	-	Cashew Nut Shell Liquid
CRI	-	Cure Rate Index
CV	-	Conventional Vulcanization
DBP	-	Dibutyl phthalate
DMTA	-	Dynamic Mechanical Thermal Analysis
DOP	-	Dioctyl phthalate
DSC	-	Differential Scannning Calorimetry
DT	-	Decomposition Temperature
DTA	-	Differential Thermal Analysis
DTG	-	Derivative Thermo-Gram
ENR	-	Epoxidized Natural Rubber
EPDM	-	Ethylene Propylene Diene Monomer
EV	-	Efficient Vulcanization
HAF	-	High Abrasion Furnace black
IIR	-	Isoprene Isobutylene Rubber
IPDT	-	Integral Procedural Decomposition Temperature
IR	-	Infrared
ISNR	-	Indian Standard Natural Rubber
LCP	-	Liquid Crystalline Polymer
L/D	-	Length / Diameter ratio
LDPE	-	Low Density PolyEthylene
LNR	-	Liquid Natural Rubber
LOI	-	Limiting Oxygen Index
MBI	-	Mercaptobenzimidazole
MBT	-	Mercaptobenzthiazole
MBTS	-	Dibenzthiazyldisulphide
MFA	-	Multifunctional additive
MOZ	-	Morpholinobenzthiazyl sulphenamide
MPT	-	Monsanto Processability Tester
NBR	-	Nitrile Butadiene Rubber
NR	-	Natural Rubber
ODR	-	Oscillating Disk Rheometer
PCNSL	-	Phosphorylated Cashew Nut Shell Liquid
PCP	-	Phosphorylated Cardanol Prepolymer
PE	-	Polyethylene
phr	-	Parts per hundred rubber

List of Symbols

η – Melt viscosity, Intrinsic viscosity

$\dot{\gamma}$ – Shear rate

n - Flow behavior index, Order of decomposition reaction

$E\gamma$ –Activation energy of melt flow at constant shear rate

B - Die-swell ratio

T - Temperature in absolute scale, Weight of specimen

η_a - Apparent melt viscosity

R - Universal gas constant

S_R- Recoverable shear strain

T_2- Brabender torque at 2 min

T_{10}-Brabender torque at 10 min

K -Consistency index, Rate constant of cure

E- Energy input in Plasticorder, Sulphur inefficiency parameter, Activation energy of cure, Tensile rupture energy per unit volume

M- Torque output of Plasticorder, Molecular weight before crosslinking

C(n)- A function of flow behavior index

S - Rotor speed of Plasticorder

E_a- Activation energy of melt flow, Activatio energy of thermal decomposition

P - Power consumption during mixing in Plasticorder

k - Consistency index, Specific rate constant of thermal decomposition

N, $(\tau_{11} - \tau_{22})$ - Principal normal stress difference

G - Shear modulus

τ_a - Apparent shear stress

γ_a - Apparent shear rate

A - Pre-exponential factor

G_c - Self adhesion strength

D_e - Diameter of extrudate

D_0- Diameter of die orifice

F - Force of separation (T-peel test), Weight-fraction of insoluble components in vulcanizate

w - Width of sample

t_5 , t_2 - Scorch time

t_{90} - Optimum cure time

L_f - Maximum cure

M_L- Minimum torque

M_H- Maximum torque

σ - Surface resistivity

ρ - Volume resistivity, Density of polymer

R_s - Surface resistance

R_v - Volume resistance

t - specimen thickness

P_0 - Plasticity (initial)

E^* - Dynamic modulus

E' - Storage modulus

E'' - Loss modulus

δ - Phase angle
$\tan \delta$ - Loss tangent
ΔH - Enthalpy of oxidation
T_g - Glass transition temperature
V_r - Volume fraction of rubber in swollen gel
D - Deswollen weight of vulcanizate
A_0 - Weight of absorbed solvent, Cross sectional area of undeformed specimen
ρ_r - Density of rubber
ρ_s - Density of solvent
$(2M_{c\cdot chem})^{-1}$ - Chemical crosslink density
M_n - Number average molecular weight
S_c - Combined sulphur
U_b - Energy input per unit volume to break a vulcanizate
H_b - Energy dissipated in deformation prior to break
E_b - Strain at break
T_c - Tear strength
d - Diameter of tear tip
T_i - Initial decomposition temperature
T_{50} - Temperature at 50% decomposition
ΔT - Difference between sample temperature and reference temperature in DTA
C_p - Specific heat capacity of the sample in DSC
L_{max} - Maximum change in torque during vulcanization
α - Filler reinforcement index
$M_{c(phys)}$ - Number average molecular weight between physically effective crosslinks
v - Elastically effective network chain density
c - Crosslink density
ε - Entanglement density
v - Chemical crosslink density
V_s - Molar volume of solvent for swelling
ζ - Polymer - solvent interaction parameter
f - Force in tensile test
A - Equilibrium extension ratio
C_1, C_2 - Mooney - Rivlin constants
n - Order of decomposition reaction
$(w_r = w_c - w)$
w_c - Maximum mass-loss in TGA
w - Total mass-loss upto time t
T_{max} - Temperature at which rate of mass-change is a maximum
T_f - Final decomposition temperature
X - Amount of sample undergoing decomposition reaction
A_0 - Cross sectional area of undeformed polymer.

CHAPTER - I

INTRODUCTION

The history of the developments of rubber science and technology since the rediscovery of NR by Christopher Columbus in 1496 (1) to the present day, has been an amazing one - the pace of which has been marked with important milestones Simultaneously, developments in the fields of processing technology, compounding ingredients and methods of polymer characterization have advanced our knowledge in the field of elastomer science and technology One of the earlier reports on the natives of Haiti playing games with 'bouncing balls' made from the gum of a tree called 'cau-uchu' (weeping - wood) throws light upon the advancement of Mayan civilization in the eleventh century (1) The use of rubber for water proofing of garments was noted by Pizarro in 1540 (2) There is documentary evidence that in 1615 the Spanish troops in Mexico wore rubber-coated clothes to guard themselves from rain (1). Charles de la Condamine, a French-man first described *'Hevea brasiliensis'* tree in 1751 as the source of NR The name 'rubber' was coined by Joseph Priestly in 1770 based on its use as an eraser of pencil marks The use of rubber for water-proofing of fabrics was made a commercial proposition in 1823 by Charles Macintosh. Thomas Hancock made many remarkable observations and inventions from 1819 which established a real base for the rubber industry, particularly in the area of 'rubber compounding' (3). The 'masticator' fabricated by Hancock and the mixing mill and calender developed by Chaffee in 1836 are landmarks in the history of rubber industry. Charles Goodyear spent his whole life and money on improving the properties of rubber, whose persistent works led to the discovery of 'vulcanization' in 1839 that revolutionized the whole rubber industry. The process of vulcanization was patented by Charles Goodyear in 1841. Though the first pneumatic tire was invented by Thomson as early as in 1845, it was the re-invention of pneumatic tire by J B.Dunlop, a veterinary surgeon of Belfast in 1888 that has come to the lime light bringing the tire industries of the world to this stage. The invention of pneumatic tire was a milestone in the history of rubber industry since the tire sector revolutionised the automobile industry and stands as the biggest consumer of rubber today. Since then, the advances in the fields of processing and manufacture of elastomers such as mixing (eg. Banbury, transfer-mixing (4) etc.), extrusion (eg. co-extrusion (5), profile extrusion / multiplex extrusion (6) etc.), injection molding (eg. reaction injection molding (7), injection blow molding (8) etc), vulcanization / curing (eg. continuous vulcanization, microwave (9) / radiation curing (10) etc) and specific manufacturing techniques for products such as tires, cables, hoses etc , have resulted in remarkable developments in the rubber manufacturing sector.

The developments in the fields of elastomers and compounding ingredients throughout the years have also been equally impressive.

The use of metallic oxides such as those of zinc, calcium, magnesium and lead as 'inorganic accelerators' for vulcanization was practised until after the World War I (11). The discovery of mercapto benzothiazole (MBT) - an organic accelerator for vulcanization was one of the landmarks, followed by the use of zinc oxide as an activator and stearic acid as a co-activator. The subsequent discoveries of a wide variety of accelerators, antioxidants, antiozonants, black and non-black fillers, platicizers and other special purpose additives enabled the design of elastomer formulations to meet the exact service requirements for any specific application (12,13) It was later found that rubbers, both natural and synthetic could be vulcanized by means of peroxides, but the practical application is confined mostly to certain synthetic rubbers (13). Recently, heat resistant NR vulcanizates with improved reversion - resistance and aging stability have been obtained by crosslinking with dithioalkane(14). Other sulfur-less curing agents have also been introduced, including polymerisable oligomers (15) and diurethanes viz., 'Novor cure systems'(16). However, the popularity of the sulfur cure even today is evident from the widespread use of various vulcanization systems of the 'conventional', 'semi-efficient' and 'efficient' types(17-19).

The direct use of NR latex containing 30% solids and preserved with ammonia had been known since 1791. Concentration of latex to 60% by creaming, centrifuging, evaporation and electro-decantation resulted in its widespread use since 1925 for various applications such as gloves, adhesives, carpet-backing, foam rubber and so on. The subsequent developments in latex compounding technology including the use of a variety of additives such as fillers, curatives, antioxidants, stabilizers, etc., and the introduction of various manufacturing techniques such as dipping, coating, extrusion, slush molding, rotational moulding and foaming (Dunlop process, 1929 and Talalay process, 1946), contributed significantly to the progress in the manufacture of latex based products (11,20). Also, since the World War II, most of the widely used synthetic rubbers such as styrene-butadiene, chloroprene, butyl and nitrile rubber have become available in the latex form(21) followed by the introduction of various special purpose elastomers such as silicone rubber, fluorocarbon elastomers, polysulfide rubber, poly phosphazenes (22), hydrogenated nitrile rubber (23) etc., specially designed for higher performance requirements such as high temperature stability, resistance to flame, chemicals, solvents, oils, etc. Recent advances in polymer synthesis led to the birth of a new generation of polymers such as thermoplastic elastomers (24,25), ionomers (26), liquid crystalline elastomers (27,28) such as nematic monodomain elastomers (29), segmented liquid crystalline polyurethane elastomers (30) and ferroelectric liquid crystal elastomers (31), bi-modal elastomers (eg. polydimethyl siloxane networks) (28) and conducting rubbers (32) apart from a variety of blends (33, 34) and alloys, adding to the range of 'high-performance elastomers'. The recent innovations in the field of 'reactive fillers' (35), reinforcing fillers precipitated *in-situ* in polymer network structures (eg.silica by hydrolysis of organo-silicates) (28, 36), immobilization of stabilizers in polymer matrix (37, 38), special- purpose rubber chemicals (eg.for reversion resistance) (39), nitrosamine-free crosslinking systems (40), hybrid cords (41) and novel reinforcing fibers for composites (eg.polyethylene naphthalate (42) etc., provide the polymer scientists and technologists with sufficient materials to experiment with and to generate new products with unique combination of properties. Thus, the present availability of a wide range of elastomers (both natural and synthetic), compounding ingredients (43), advanced processing and characterization techniques (44), manufacturing methods and knowledge on the science and technology of elastomers, inevitably lead to a wider adoption of the 'compounding technology'(4,45) for the present day service requirements of various rubber products.There have been many attempts to reduce the number of ever increasing additives by the use of single additive having more than one function (46-56). But no concerted efforts have been reported in this area so far. In this respect, the study and development of 'multifunctional additives' (MFA) may prove to be of immense help in designing formulations to meet specific service requirements.

1.1. Natural Rubber - Significance

Natural rubber (NR) is a material that has attracted the curiosity of common people ever since the Mayan civilization of the 11th century (57) and has remained till date as the material of strategic importance with regard to its commercial, technological and industrial applications. This is mainly due to its unique combination of properties that has elevated its covetus position as an engineering polymer(58) from that of an ordinary commodity polymer. These include an excellent combination of physico-mechanical properties (59 - 60) such as tensile and tear strength, good abrasion and fatigue resistance, elasticity, low heat build-up and good tack strength that are responsible for a host of properties encompassing wide range applications. For instance, it is used in making inexpensive toy balloons to sophisticated and expensive components such as aircraft and automobile tires (61). NR is also being used successfully as a structural material in the construction of high rise buildings and important bridges in the form of expansion rings, rubber springs, rail pads, bridge bearings and so on(62). NR is abundantly available and is a renewable natural resource of comparatively low cost (compared to synthetic rubbers). The increasing demand for NR is evident from the increasing trend in the production and consumption pattern of NR (63) (Table I.1).

Table I.1. World Production & Consumption of NR (63)

Year	1992	1993	1994	1995	1996
Production , Tonnes	5480	5310	5680	5820	6330
Consumption, Tonnes	5310	5330	5630	5920	6310

According to the forecasts of IIRSP, NR should experience an annual growth rate of 1.8% over the next five year term from1995 (64).

Inspite of many of its remarkable properties, NR is having a variety of inherent short-comings also. Some of these include its poor resistances to thermo-oxidative decomposition, flame, ozone, oil and reversion at high cure temperatures (65). Considering the performance and cost benefits of NR over many of the commercially available synthetic rubbers, there is sufficient scope for improving many of the properties mentioned above to enable it to meet the stringent service requirements of many of its products. With this objective in mind, attempts have been made by various workers to modify NR by various physical and chemical methods(38, 66-73).

1.2. Modification of NR

There has recently been an upsurge in the R&D activities to develop and commercialize new forms of NR such as Epoxidized Natural Rubber (ENR), Thermoplastic Natural Rubber (TPNR), Liquid Natural Rubber (LNR), etc.(66). NR vulcanizates containing diphenyl amine chemically attached to it showed improved aging resistance along with reduced volatility and extractibility of the antioxidant (38). Gelling (67) proposed the chemical modification of NR as a route to renewable resource elastomers. Epoxidation of NR led to products having excellent oil-resistance (68). Chemical modification of NR in the latex stage with trichloro bromo methane resulted in significant improvements in the flame resistance and self-extinguishing characteristics (69). Flame resistant rubbers have been synthesized recently, by incorporating phosphate groups in LNR (70). Production of a truly thermoplastic polymer by the chemical grafting of polystyrene chains on NR molecule has been reported (71). TPNRs having improved processability have also been made by the physical blending of NR with various thermoplastics such as polyethylene (PE), polypropylene (PP) etc. NR has been modified with Cellobond resin, which is having multifunctional role as a tackifier and modifier of physico-mechanical properties (72). Various other derivatives of NR such as rubber hydrochloride, chlorinated rubber, cyclized rubber, oxidized rubber, ebonite, graft copolymer (Hevea plus-MG), etc. have also been reported (73).

Though the different forms of modified NR mentioned above, (especially the chemically modified forms) show excellent improvement in certain specific functional requirement, it is often at the expense of some of the other desirable requirements such as physico-mechanical properties or processability. Besides, the laborious synthetic procedures needed and the accompanying expenses prompt one to resort to the relatively inexpensive compounding route to meet the same standards of functional requirements.

1.3. NR compounding

Compounding of elastomers for specific applications has developed as an 'art and science' over the years, adding newer and newer dimensions with the availability of novel polymers and compounding ingredients (74). However, the present day formulations for specific applications almost always contain around a dozen additives - each with a specific functional requirement. Thus, apart from the polymer, these include additives such as crosslinking agents, accelerators, activators, antioxidants, antiozonants, processing aids / plasticizers, fillers (reinforcing and non-reinforcing types) and special purpose additives such as flame retardants, tackifiers etc. - each with a specific functional requirement. Apart from the high cost of these chemicals (- most of which are based on petrochemical sources), some of the drawbacks of using a number of additives include the difficulty in handling and processing, lack of permanence / durability in service, and variability in vulcanizate properties arising out of improper dispersion of the additives in the polymer matrix. The problems as mentioned above can be eliminated to a great extent, by the use of a 'multifunctional additive' - a single additive that can meet many of the functional requirements simultaneously.

1.4. Multifunctional additives

The concept of a multifunctional additive for rubber compounding (46) is not totally new, though not widely accepted. The bi- and multifunctional nature of quite a few rubber chemicals are known in the literature (46 -56, 75-101) Roy et al. (75) have reported the potential of a quinazolinone derivative as an accelerator and antioxidant in rubber . The accelerator cum antioxidant characteristics of mercapto benzimidazole (MBI) derivatives in rubber vulcanizates has been studied by Khanra et al.(76) A novel class of accelerator cum antioxidant capable of linking with the rubber network during vulcanization has been reported recently (77 -79) . The methods of preparation and evaluation of multifunctional rubber ingredients have been reported by Yehia and Ismail (80) . Pyridazine derivatives have been found to function as antioxidants and secondary accelerators in NR(81). The use of polymeric ingredients having multifunctional role (eg. as antioxidants and antirads) in rubber formulations has been advocated by Bary et al. (82) . Epoxidised oleic acid modified with p-phenylene diamine has been found to be functioning as an antioxidant and plasticizer in natural and synthetic rubber formulations with additional advantages of lower volatility, absence of blooming to the surface and good dispersion characteristics (83, 84) . Multifunctional additives have been synthesized by the reaction of p-substituted anilines with epoxidised linseed oil(85) . The insitu reaction products of epoxidised oleic acid with α and β naphthyl amines were found to be suitable as antioxidants and antirads in NR compounds without the addition of stearic acid (86). The role of oligoamid -phosphate as a crosslinking agent and antioxidant in isoprene rubber has been studied by Vladkova et al. (87) . Hepburn and Mahdi(88) reported the bi-functional role of fatty acid diamine salts as accelerator and processing aid in SBR / NR blends for tire tread mixes . Certain phenolic resins (eg. based on p-octyl phenols) can be used as crosslinking agents and modifier of physico-mechanical properties such as strength and heat resistance in rubbers (89) . The multifunctional role of a variety of plasticizers in elastomers is well known (90) . Thus, methyl, ethyl, propyl and butyl ethers of anacardic materials were shown to act as excellent plasticizers and modifiers of physico-mechanical properties of chloroprene rubber (91) . The multifunctional role of many of the commercially available rubber chemicals in elastomer formulations is well known (92), as given below. N (1,3 - dimethyl butyl) N'- phenyl p- phenylene diamine (Vulcanox 4020) functions as an antioxidant and antiozonant. Wood rosin (FF Wood Rosin) functions as a plasticizer, softener, tackifier and process aid for rubber formulations. Coumarone Indene Resins (Cumar R-12 and R-16) can function as a plasticizer, softener, reinforcer, tackifier and processing aid. The multifunctional role of 2-ethyl hexyl diphenyl phosphate (Santicizer 141) as a plasticizer, softener and flame retardant, is well known. Alkyl phenyl formaldehyde resin of (Para Resin 1753) may be used as a tackifier, plasticizer, processing aid and antioxidant in rubber formulations. Recent investigations have revealed the 'multifunctional role' of a variety of flame retardant additives. Polyphosphates have been reported to function as flame retardants and plasticizers (93, 94) The multifunctional nature of zinc borate (Fire break - ZB), as a flame retardant and suppressant of smoke and after-glow, has been reported (95) . Multifunctional smoke and gas suppressant systems for polyurethane foams have been reported (96) . Antimony trioxide was found to act both as a flame retardant and smoke suppressant in ABS / PVC blends (97) Adhikari et al (46) in a recent review have critically analysed seven categories of multifunctional additives having various combinations of antidegradant, activator, processing aid, accelerator, antioxidant, retarder, curing agent, dispersant and mold release agent functions. Though the review is fairly exhaustive covering upto 1993, the compounds mentioned as multifunctional additives mostly have limited combinations of functional performance and suffer from many drawbacks as outlined below.

Though the proposition of "multifunctional additive" in many of the above mentioned compounds is quite attractive, it is possible that they may possess many of the inherent deficiencies such as (i) difficulties in synthesis, (ii) lack of permanence during service arising out of incompatibility, (iii) affecting processing, (iv) affecting physico-mechanical properties and / or (v) high cost. This brings out the necessity for considering the various requirements for an ideal 'multifunctional additive' before attempting to synthesize one.

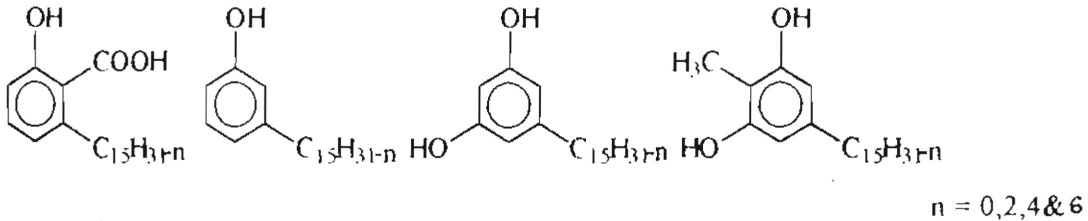
1.5. Requirements for Multifunctional additives

Some of the structural requirements expected for a molecule to function as a multifunctional additive are (i) presence of chemically modifiable groups in the base molecule such that the modification can give desirable vulcanizate properties, (ii) structure that leads to compatibility with a wide range of base polymers of both polar and non polar nature, (iii) structural features that improves the processability of the polymer being modified, (iv) presence of groups which can react chemically with the base polymer, leading to durability / permanence of the additive in service (eg: non-leachability in solvents and non-diffusability), (v) a structure that permits an easy and quick synthesis of the MFA by simple chemical reactions and (vi) cost effectiveness, which means that the raw material for the synthesis of the multifunctional additive (MFA) should be readily available in sufficient quantity and quality, at a low cost.

A survey of a number of molecular systems, both synthetic and naturally occuring, pointed to unsaturated hydrocarbon phenols as having desirable properties to act as MFAs. Further search indicated that such molecules are easily available as components of a naturally occuring material commonly known as Cashew Nut Shell Liquid (CNSL) found in the cashew tree *Anacardium occidentale L.* and extracted from the cashewnut shells as a byproduct of the cashew industry.

1.6. Cashew Nut Shell Liquid

Cashew Nut Shell Liquid (CNSL) (102) is an ideal raw material for the synthesis of a MFA, taking into consideration the various factors as mentioned above. Natural CNSL has m-pentadecenyl salicylic acid (*anacardic acid*, 64.93 %) as its major component (103). The composition of CNSL has been studied by various investigators (104 -107). Cold extracted CNSL was found to consist mainly anacardic acid 90% and m-pentadecenyl resorcinol (*cardol* 10%) (108 - 111). Tyman showed that cold extracted CNSL contained 82 ± 1.05% anacardic acid, 13.8 ± 0.17% cardol, 2.6 ± 0.16% 2-methyl cardol and 1.6 ± 0.17% m-pentadecenyl phenol (cardanol), by the use of gas-liquid chromatographic methods (112) the structures of which are shown in Fig.1.1.



Anacardic acid Cardanol Cardol 2-Methyl Cardol

m-pentadecenyl salicylic acid m-pentadecenyl phenol m-pentadecenyl resorcinol 2-methyl m-pentadecenyl resorcinol

Fig.I.1. Structure of components of CNSL

During commercial extraction under hot conditions, the anacardic acid fraction of CNSL gets decarboxylated to cardanol (102). Commercial CNSL contains cardanol (83±0.51%) and cardol (2.7 ± 0.34%) as major constituents. The substituent chain present in anacardic acid, cardol and cardanol was shown to be a mixture of olefins with different degrees of unsaturation (111, 113-116). The physical and chemical characteristics of typical samples of CNSL are given in Table I. 2. (102).

Table I.2. Characteristics of CNSL

	Solvent extracted CNSL	Commercial CNSL
Specific gravity, 30°C	0.9958 - 0.9998	0.92 - 0.98
Viscosity,30°C (cP)	170 - 230	150 - 160
Loss on heating (%)	8 - 12	2
Acid value	104 - 110	8 - 20
Iodine value (wijs) 1 hr	220 - 230	220 - 270
Saponification value	106 - 118	18 - 30

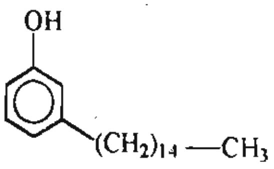
i. Cardanol - Structural features and composition

Murthy et al. (117) obtained pale coloured cardanol in 60 - 70% yield by distillation of CNSL under low pressures. Two grades of cardanol with specifications as given in Table I.3 were obtained (118).

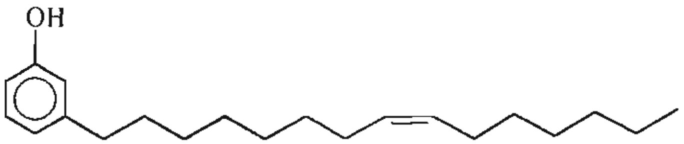
Table I.3. Characteristics of cardanol

	Grade I	Grade II
Empirical formula	$C_{21} H_{32} O$	$C_{21} H_{32} O$
Specific gravity, 30°C	0.9272 - 0.9335	0.9272 - 0.9335
Viscosity, 30°C (cP)	47 - 52	47 - 52
Volatile loss (%)	1	2
Ash content (%)	Negligible	0.5
Iodine value	212 - 228	212 - 228
Acid value	2	5
Hydroxyl value	180 - 200	180 - 200
Colour	Straw pale	Pale brown

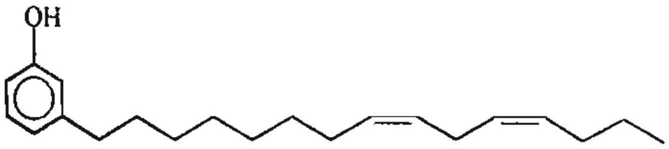
Cardanol was found to be mainly a mixture of four components - the C_{15} unsaturated side chain at the meta position of the phenolic ring being composed of monoene (48.5%), diene (16.8%), triene (29.3%) and fully saturated form (5.4%)$^{(119)}$ as shown in Fig.I.2.



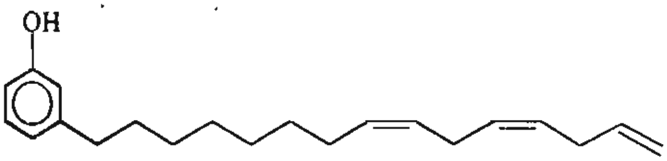
Saturated (5.4%)



Mono olefin (48·5%)



Di olefin (16·8 %)



Tri olefin (29·3 %)

Fig.I.2. Constituents of cardanol

The presence of the non polar C_{15} unsaturated side chain and the polar hydroxyl group in the same molecule makes it amphiphyllic in nature - being compatible with a wide range of polar and non polar polymers(120). Also, it imparts dual functionality. The presence of long alkyl side chain imparts 'internal plasticization' and flexibility to the products containing it(121)

ii. Polymerization characteristics of CNSL

One of the unique features of cardanol is its amenability for chemical modification by a variety of means. It can be used as an excellent source of 'monomer' or starting material for polymer synthesis. Manjula et al.(122, 123) have synthesised cardanol-formaldehyde / poly (methyl methacrylate) semi-interpenetrating polymer networks having enhanced thermal stability. George John et al.(124, 125) have described the synthesis and characterization of a self crosslinkable polymer (poly cardanyl acrylate) from cardanol . Cardanol has been shown to be an ideal raw material for the synthesis of precursors for liquid crystalline polymers (LCP) for potential high performance applications (126). The unsaturation of the side chain of cardanol lends itself for polymer production by a variety of addition or substitution reactions. CNSL can be polymerized by various methods such as oxidation (127), metal-activation (128), heat polymerization (129), addition (130) or condensation (131). Besides, the scope for substitution reactions at the aromatic ring and chemical modification at the hydroxyl group extends the range of possibility (132). This is very well reflected in the wide range of industrial chemicals and polymeric products synthesised from CNSL and cardanol, over the years (133 - 135) and the extensive reviews on the subject (136 - 141) that have been published .

iii. Applications of CNSL and CNSL based products

There exists an enormous number of publications and patents on CNSL and CNSL based products some of which have been mentioned in the earlier section (6.ii). These include a variety of polymeric products and industrial chemicals such as brakelining materials, surface coatings (paints, primers, varnishes , cements and lacquers), adhesives and binder resins, pesticides, emulsifiers, dye-stuffs, plasticizers, ion exchange resins, plastic materials and rubber compositions (133).

(a). Rubber compositions

In the literature a number of references show that CNSL and its derivatives are being used in a variety of ways in rubber compounding in the form of cure accelerators, antioxidants, plasticizers, process-aids and modifiers of physico-mechanical properties independently (142 - 152).

Phenolic sulphide compounds prepared from tetra hydro anacardol were found to be effective antioxidants for NR gum and channel black compounds (91). Synergistic mixtures of CNSL with amine type antioxidants have been reported by Rajapakse et. al. (142, 143).

Ghatge et al ([illegible]) have studied the plasticizing effect of polymerised CNSL in rubber Also, the resins obtained on heating CNSL with acrolein in presence of an acid at 125 °C have been found to be useful as plasticizers for NR, reclaimed rubber and synthetic rubbers (91) Sulphurated CNSL and other CNSL derivatives find use as plasticizers in synthetic rubbers(131-136)

Unsymmetrical thioureas prepared from 4- amino 3-pentadecyl phenol act as secondary accelerators in NR formulations with sulphenamides as primary accelerators(147). 2- Pentadecyl benzoquinone dioxime synthesized from CNSL gave heat resistant vulcanizates from styrene butadiene and butyl rubbers (91,148,149)

The potentiality of CNSL and its derivatives as antioxidants, plasicizers and as processing aids for a wide variety of rubber compounds has been studied by a galaxy of investigators (153 - 160). CNSL is found to enhance the insolubility of NR vulcanizates in petroleum solvents Nitrile rubber (NBR) and styrene butadiene rubber (SBR) latices mixed with CNSL modified phenolic resins, hexamine and suitable fillers have been found to give compositions suitable for moulding or extrusion (91). Modified novolac resin from cardanol and paraformaldehyde on isocyanate modification gave higher values of tensile strength, modulus and hardness in NR vulcanizates (91). Cardanol, when used as a plasticizer in NR, improved its tear strength, solvent resistance and aging properties (91). The low temperature properties of SBR plasticized with cardiolite - 625, the ethyl ester of mono phenolic component of CNSL, were superior to those of similar compounds containing naphthene based plasticizers (91) Polymerised CNSL was found to be equivalent to DBP or DOP, as a plasticizer for NBR, except for the low temperature properties (146).

Ghatge and Shinde (161) reported the synthesis of isocyanate modified novolac resins for use in natural and synthetic rubbers. The antioxidant effectiveness of derivatives of CNSL in gum NR has been reported by Ghatge and Gokhale (165). Alkoxy and poly sulphide silane coupling agents synthesised from cardanol were found to improve the physical properties of NR (163)

Cellular rubber compositions have been developed from CNSL - phenol - aldehyde - nitrile rubber mixes (135) Blends of CNSL resin with SBR were used to produce rail - road brake shoes (147). Compositions suitable as 'bead fillers' for tires have been developed by compounding NR with CNSL modified novolac cured with hexamethylene tetramine (164).

Banerjee (165) observed that CNSL can be used as a tackifier for nitrile rubber (NBR). Extensive studies have been carried out on the compounding of natural and styrene butadiene rubber with cardphenol, styrenated cardphenol and polymerised cashew nut shell liquid (CNSL-1000) in the presence and absence of black and non black fillers (166). Ghosh et al.(161) reported improvements in tensile strength, abrasion resistance and elongation at break of calcium carbonate filled SBR vulcanizates containing 5 to 7 phr of cardphenol.

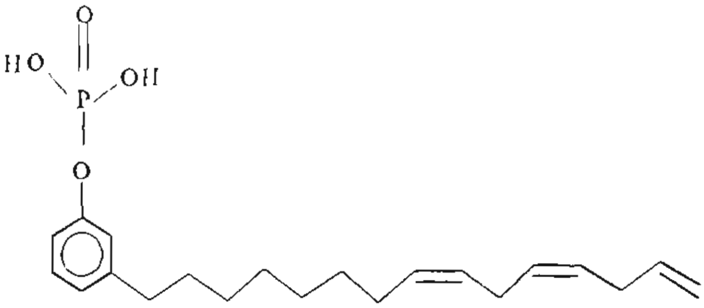
I.7.Scope of the present work

The foregoing discussion amply illustrates the versatility of CNSL for diverse applications Literature on the previous works shows that CNSL and its derivatives may be used as 'special purpose additives' for rubber compounding in the form of plasticizers, antioxidants, accelerators or physical property modifiers Many of the above mentioned products are interesting and useful with respect to their unique combination of properties enabling the modification of elastomers. However, it should be noted that in most of these cases, CNSL or its derivatives have been used with a specific functional objective and not as a multifunctional additive It is readily apparent from the plethora of patents and publications on the subject that systematic attempts to synthesise a 'multifunctional additive' from CNSL, making use of its peculiar structural features, are rather scanty. Further, the fact that CNSL is a 'renewable natural resource', abundantly available at a low cost, adds to the scope of such an endeavour The synthesis of Phosphorylated Cashew Nut Shell Liquid (PCNSL) at Regional Research Laboratory (CSIR), Trivandrum, is an attempt in this direction

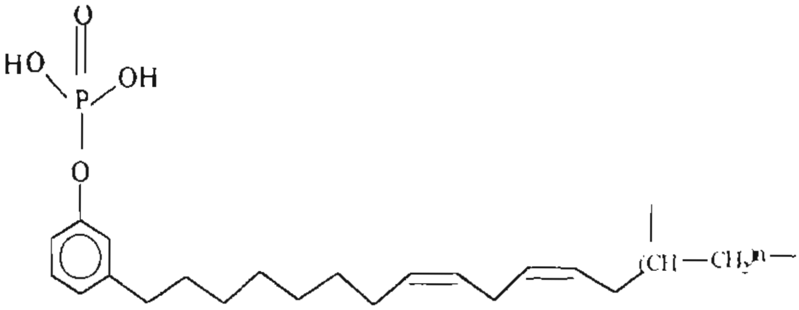
i. Phosphorylated Cashew Nut Shell liquid

Manjula et al. (168) studied the kinetics and mechanism of oligomerisation of cardanol in presence of acidic catalysts such as sulphuric acid and phosphoric acid . Pillai and co-workers (169 - 171) observed that phosphorylation of CNSL with o-phosphoric acid at 175 ± 5°C, resulted in the simultaneous esterification at the hydroxyl group and oligomerization at the unsaturated side chain of cardanol leading to a resinous material having an interesting combination of properties . The introduction of a phosphate group into the CNSL improves bonding characteristics with various substrates, reduces flammability and enhances hydrolytic and thermal stabilities over that of conventional CNSL - formaldehyde resins (170) . It is found to be suitable for applications such as friction dust and resin for brake linings, flame retardant additive for plastics and elastomers, flame retardant matrix resin for composites and adhesives

Phosphorylated Cashew Nut Shell Liquid (PCNSL) prepolymer has been found to be a mixture of oligomers - mainly consisting of dimer, trimer and tetramer and a small amount of higher oligomers (171) as shown in Fig.I.3 (a & b). PCNSL is a light brown liquid resin soluble in most of the common organic solvents and insoluble in water. The chemical and physical characteristics of PCNSL are given in Table I. 5



(a) Triene component of the monomer of PCNSL



(b). Pre polymer of PCNSL (n = 4 to 5)

Fig.1.3. Monomer and pre polymer of PCNSL, (a) monomer, (b) prepolymer

Similarly, diene and monoene components of PCNSL are also present.

Table I. 5. Chemical and physical characteristics of PCNSL

Property	Value
Colour	Light brown
Moisture content (%)	0.05 - 0.065
Specific gravity at 29 C	1.0590
Viscosity at 30 C (cps)	350,000 - 450,000
Hydroxyl number, mg of KOH	4 - 10
Iodine value, g/100 g of resin	90 - 100
Unreacted phosphoric acid content(%)	0.01 - 0.009
Phosphorus content (%)	7.9

PCNSL is insoluble in water and soluble in acetone, CCl_4 and it is found to be highly reactive with aldehydes, amines and isocyanates (17). It shows higher thermal stability of more than 500°C. Crosslinked PCNSL is highly resistant to water. Completly cured PCNSL do not propagate fire and do not show any after-glow and has a Limiting Oxygen Index (LOI) of 35. The unusually high bulk viscosity of PCNSL at room temperature has been ascribed to the presence of hydrogen bonds between the phosphate groups of adjacent molecules of PCNSL.(172)

The superior flame retardancy of PCNSL and its bromo derivative is indicated by their higher values of Limiting Oxygen Index (LOI) as given in Table 1.6.

Table 1.6. LOI of PCNSL resins (173).

Resin	LOI
PCNSL	38
PCNSL (para formaldehyde cured)	33
Brominated PCNSL	42 / 44

The presence of both hydrophilic and hydrophobic groups in the same molecule makes PCNSL an ideal candidate for 'wide spectrum polymeric flame retardants' (173). Previous studies carried out at the Regional Research Laboratory, Trivandrum shows that PCNSL may be used for a variety of applications such as brake linings, adhesives and as a foundry core-binder. Asbestos short fibre filled brake lining formulations reinforced with PCNSL shows improved wear resistance, friction coefficient and better retention in friction coefficient after repeated application of brake, compared to some of the commercially available automobile brake linings (174,175). PCNSL has been used in foundry sand core binder formulations (176). Superior molding properties such as strength and permeability and casting characteristics such as surface quality of castings, core collapsability and anti damping behaviour have been observed for the PCNSL based binder, compared to other systems of binders such as sodium silicate (176). Adhesives based on PCNSL for bonding wood to wood, showed a five fold increase in adhesion strength over that based on CNSL formaldehyde resins (177). Modification of low density polyethylene (LDPE) with upto 15% of PCNSL was found to improve its flame retardant properties and processablity, without deterioration in mechanical and aging properties (178).

Preliminary works on modification of NR with PCNSL (179 - 181) and its bromo derivative (182 -184), threw light upon their 'multifunctional role' in NR as flame retardant, antioxidant and improver of tensile properties and processability. NR gum vulcanizates modified with small amounts of PCNSL showed improvements in tensile strength, elongation at break and LOI (179). PCNSL was also found to act as a plasticizer and softening agent for NR. At lower concentrations (2 to 4 phr), the antioxidant activity of PCNSL in NR was reported to be much better than that of styrenated phenol, as evidenced by the superior resistance to thermal aging of the former (180). Ozone aging studies with NR vulcanizates containing PCNSL showed that at 2 phr level, the crack initiation time increased by 2 hours (181). The mixing and cure characteristics of NR formulations modified with PCNSL have been studied over a wide range of temperature and shear rate on a Brabender

Plasticorder (180) The PCNSL modified samples showed higher degree of plasticization along with lower rates of cure and cure reversion compared to the unmodified sample Cure retardation at higher concentrations of PCNSL and cure restoration with subsequent increase in concentration of ZnO, have also been observed (181)

It has been found that formulations having very good self extinction property in vertical burning tests, high LOI (28) and improved tensile characteristics, could be made by modifying it with upto 30 phr of BrPCNSL (182) Synergistic improvements in self extinction property was observed for NR formulations modified with BrPCNSL and antimony trioxide (183) The effect of compositional variables, temperature and shear rate on the mixing and cure characteristics of fire retardant NR formulations containing BrPCNSL has been studied on a Brabender Plasticorder (184) The lower power consumption and better 'scorch - safety' of the BrPCNSL modified formulations indicated their 'superior processability' compared to that of the unmodified sample

I. 8. Objectives of the present work.

The need for improving many of the 'processability characteristics' and 'vulcanizate properties' of NR to enable it to meet the challenging demands of the present time culminated in developing multifunctional additives such as PCNSL. The advantages and attractiveness of this multifunctional additive in the compounding of NR has been outlined in preceeding sections

The high cost and limited availability of many of the compounding ingredients (most of which are based on petrochemical sources that are depleting rapidly), with many of their accompanying demerits such as - (i) limited functional value, (ii) adverse effects on many of the desirable physico-mechanical properties, (iii) processing difficulties arising out of incompatibility with the base polymer and (iv) non-permanence during service, alongwith the multi-faceted advantages of developing new low cost multifunctional additive for rubber compounding, necessitated to start the present work Further, the preliminary observations that chemically modified CNSL such as PCNSL and BrPCNSL can function as multifunctional additives in NR provided tremendous impetus for carrying out a serious study on the compounding behaviour of NR with PCNSL, such as the processability of the compounds and physico-mechanical properties of the vulcanizates. This study is thus expected to fillup the lacuna as far as the role of MFA in NR is concerned

The objectives of the present work are the following -

(a) To study the processability characteristics (mixing, extrusion, melt-rheology and filler dispersion) of NR modified with PCNSL.

(b) To study the self adhesion characteristics of NR containing different dosages of PCNSL under various test conditions

(c) To study the cure characteristics and vulcanizate properties (tensile, tear, fatigue, thermal stability, dynamic mechanical properties at various frequencies and temperatures, stress relaxation characteristics, electrical properties, hysteresis behaviour in compression and tension modes, abrasion resistance, compression set etc.) of NR modified with PCNSL (d)To evaluate the properties of the MFA - NR system with reference to a few commercially available additives.

(e) Elucidation of the structure of the PCNSL modified NR vulcanizates by chemical crosslink density measurements and other physical and chemical test methods , to get an insight into the mechanism of chemical modification and to facilitate the interpretation of the observed mechanical properties. , and

(f) To study the thermal and thermo-oxidative decomposition characteristics of the PCNSL modified NR vulcanizate by various thermo-analytical methods.

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CHAPTER - II

EXPERIMENTAL

II.1. Materials

Natural Rubber (NR) conforming to the Indian Standard Natural Rubber specification (grade - ISNR-5) was obtained from the Rubber Research Institute of India, Kottayam

Technical grade CNSL of Indian Standard specification IS: 840 (1964) was obtained from Kerala State Cashew Development Corporation, Quilon. PCNSL was synthesized at the Regional Research Laboratory (CSIR), Trivandrum, by the phosphorylation of CNSL with o-phosphoric acid at 175±5°C, according to a patented process (1). The chemical and physical characteristics of PCNSL are given in Table I. 5, in chapter I.

The chemicals for vulcanization such as ZnO, stearic acid, sulphur, MBT, TMT, MBTS, CBS, MOZ, ZDC, ethylene glycol and the fillers such as carbon black (HAF-N330), silica (HiSil) and china clay (soft) were of the commercially available grades.

The aromatic oil used as a process-oil was also of commercially available grade (*Spindle oil*). 2-ethyl hexyl diphenyl phosphate (*Santicizer - 141*) was obtained from Monsanto Chemical Co., USA.

II.2. Methods

i. Processability characteristics

(a). Mixing

The mixing of NR with PCNSL and other additives was carried out on a two roll open mixing mill (300mm X 150mm) (Model-Schwabenthan) at a friction ratio 1:1.12 as per ASTM D-3182-74 at room temperature and for 10 minutes. The mastication of NR was carried out on the roll mill for 2-3 minutes followed by the addition of curatives and then PCNSL. The uniformly mixed batch was homogenised by passing through the nip 6 times prior to sheeting out. Mill shrinkage of the NR and PCNSL modified NR was studied on the same two roll mixing mill.

The mixing behaviour of unmodified and PCNSL modified NR under dynamic conditions was studied using a Brabender Plasticorder (model - PLE 651) fitted with a cam type mixer - measuring head (N-50) at rotor speed ranging from 30 to 90 rpm and temperature ranging from 80 to 140 °C

(b). Plasticity

The initial plasticity (P_0) and Plasticity Retention Index (PRI) of NR before and after modification with PCNSL and spindle oil were measured on a Wallace rapid plastimeter as per ASTM D-3194-73

Mooney viscosity [ML(1+4)100°C] and Mooney scorch time (t_s) were determined *as per ASTM D-1646-81* using a Mooney shearing disc viscometer (model - Negretti-MKIII).

(c). Melt - rheology

The melt-rheology of NR, oil modified NR and PCNSL modified NR was studied using a Monsanto Processability Tester at various temperatures ranging from 100°C to 160°C and apparent shear rates ranging from 18.08 s^{-1} to 991.6 s^{-1}. The samples were prepared by mastication of NR on the roll mill, followed by mixing with PCNSL and/or carbon black for 8 minutes. The total time of mixing on mill was kept costant (10 min.). The extrusion characteristics were measured using a circular die (diameter 1.5mm and L/D ratio 20/1).

The viscosity of PCNSL at room temperature was measured using Brookfield Synchro Lectric viscometer (model- HBT) with spindle no. 7 at speeds ranging from 0.5 to 100 rpm. The variation of viscosity of PCNSL with temperature (ranging from 60°C to 160° C) was measured using spindle no. 21 on the same instrument connected to a temperature controller (model 74R).

(d). Cure characteristics

The cure characteristics of the NR formulations with and without PCNSL such as optimum cure time and cure rate index were measured using Oscillating Disk Rheometers (model - Monsanto R-100 & R-100S) according to the standard ASTM D-2084-81.

(e). Dispersion of filler

The dispersion of carbon black in NR matrix in presence and absence of PCNSL was measured by using dark field reflected light microscopy with the help of a polaroid optical microscope (Polaroid -Reichert Jung) fitted with Polaroid MP4 land camera. The vulcanizate was cut and placed below the microscope. The quality of the dispersion was assessed as per the numerical rating proposed by Stumpe and Railsback (2) ranging from 1 to 10.

(f). Self-adhesion strength

The self adhesion strength ('tack-strength') of the unmodified and PCNSL modified NR formulations were measured as per the standard 180 ° peel test (ASTM D - 903-49 (1978)). The formulations were mixed on a two roll mixing mill (150mm X 300mm) at a friction ration of 1.1.12 for 10 to 12 minutes. An uncured sheet of each mix (3mm thick) was compression molded between cotton fabric and aluminium (Al) foil on both sides at a pressure of 6.38 N/mm^2 at room temperature for 60 s. Strips of width 20 mm was cut out from the pressed sheet. After partly removing the Al foil, two such strips were brought into contact with each other (contact length 80 mm) under a specified contact pressure and time in a hydraulic press (Labo-press, model - Toyo Baldwin) at room temperature The two tabs of the test specimen were fixed to the grips of the tensile tester (ZWICK - UTM model - 1435) and separated at an angle of 180 ° and at a crosshead speed of 50 mm/min Figure II.1 shows the geometry of the T-peel test specimen

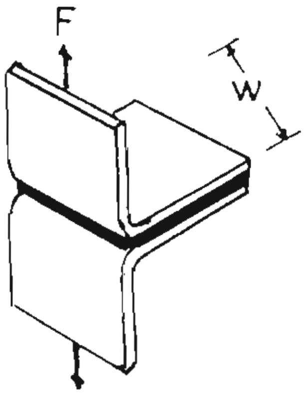

Figure II.1 T-peel test specimen

The self adhesion strength G_c was calculated from the mean force of separation F and the width of the sample w using the relation $G_c = 2F/w$ The effects of variation in contact time (from 15 to 120 s), contact pressure from 0.2 to 0.55 N/mm^2 and storage time prior to testing (from 3 to 7 days) on the self adhesion strength were studied.

ii. Physico-mechanical properties of the vulcanizates

(a). Preparation of test samples:

Test specimens for different tests were molded in an electrically heated hydraulic press (model - David Bridge Rochdale) at 150 °C and 6.38 N/mm^2 pressure, for the respective optimum cure times as measured by the oscillating disk rheometer

(b). Physico-mechanical properties

The tensile properties of the vulcanizates were measured in a universal tensile testing machine (model - Zwick 1435) using dumbell test specimens punched from tensile sheets, at a crosshead speed of 500 mm/min., as per ASTM D-412-87 (method -A)

Tear strength of the samples was also measured in a UTM (Zwick - 1435), as per ASTM D- 624-86, using unnicked test specimens (Die-C) and at a crosshead speed of 500 mm/min

Hardness of the vulcanizates was measured as per ASTM D-2240-86, using an indentation hardness tester (type - Shore A)

The heat- buildup of the vulcanized samples under compressive deformation cycles, was measured using a Goodrich flexometer as per ASTM D-623-83 (method A) at a load of 24 lb and a stroke length of 4.45 mm. The ambient temperature was 50 °C

The hysteresis characteristics of the samples under tensile deformation cycles were measured on a tensile tester (model - Zwick 1465) using dumb-bell test specimens at 100% extension and at a crosshead speed of 500 mm/min.

The rebound resilience of the samples was measured with the help of a Dunlop tripsometer as per BS . 903, Part A-8, 1963 (method A).

The compression set of the vulcanizates at constant strain was determined as per ASTM D-395-85 (method B), after subjecting them to 25% compressive deformation at 70°C for 22 hours

The abrasion resistance of the samples was measured using the Du Pont abrasion tester, as per BS : 903, Part A-9, 1957 (method A).

The fatigue resistance of the vulcanizates to tensile deformation cycles (as shown by the 'crack-initiation time' and 'cycles to total failure') was measured using a Monsanto fatigue- to- failure tester, at an extension ratio of 1.61.

The dynamic flex fatigue resistance of the vulcanizates was studied using a De Mattia flexing machine as per ASTM D-430-73 (Method B) under a strain of 20% .

The storage modulus (E'), loss modulus (E'') and the loss tangent (tan δ) of the vulcanizates over the temperature range from -100 °C to 50°C, were determined using a micro-processor controlled Dynamic Mechanical Thermal Analyzer (model - PL-DMTA), in tensile deformation mode, at frequencies of 3 Hz, 10Hz and 30 Hz and at a rate of heating of 2 °C / minute.

The stress-relaxation characteristics of NR vulcanizates containing 0, 10 and 20 phr were measured on the UTM (Zwick - 1435), in tension mode, at room temperature and at different initial strain levels (50%, 100% and 150%) and strain rates of 0.0208 s^{-1},0.1042s^{-1} and 0.2083 s^{-1}

(c). Flammability

The Limiting Oxygen Index (LOI) of the vulcanizates (as a measurement of flame retardancy) was measured using a flammability tester (Stanton - Redcroft ; FTA) as per ASTM D-2863-77

(d). Aging characteristics

Thermal aging and air aging of the specimens at 70°C for 24 and 48 hours was carried out in a multi-cell test tube aging oven and a circulating hot-air oven respectively

The retention of the properties in percentage was measured and reported as per ASTM D-865-81.

(e). Dielectric properties

The surface and volume resistivity of the vulcanizates were measured using a high resistance meter (Hewlett - Packard, model - 4329 A) at an applied voltage of 100 V (DC), after a charging period of 1 minute. The size of the specimens was 10 cm X 10 cm. Surface resistivity (σ) and volume resistivity (ρ) were calculated from the measured values of surface resistance (R_s) and volume resistance (R_v) respectively, using the following relations $\sigma = 18.8\,R_s$ and ρ $(19.6 \text{ X } R_v) / t$, where t is the thickness of the specimen.

(f). Fracture morphology by SEM

The topography of the fracture surfaces of the samples after tensile, tear and fatigue *failures were studied* under a scanning electron microscope (Philips ; model- Cam Scan Series - II). The fracture zones of the samples were taken out carefully without touching the surface, fixed on stubs, sputter-coated with gold in vacuum within 24 hours after testing and observed under SEM at 0 ° tilt-angle.

(g). Thermal analysis

The thermogravimetric analysis of the unmodified and PCNSL modified NR vulcanizates in air and nitrogen atmospheres was carried out on a thermal analyzer ('Du Pont - 951') coupled with a data- processor (Thermal Analyst - 2000), at a heating rate of 20 °C / min and at temperatures ranging from 25 °C to 700 °C, and the kinetic parameters for degradation were determined by the method of Freeman and Carroll(3).

The differential thermal analysis of the test specimens was carried out on a thermal analyzer (Schimadzu DTA - 50 H), at the temperature range from 30 °C to 600 °C, in both air and nitrogen atmospheres at a heating rate of 20 °C / min.

The enthalpy of oxidation of the vulcanizates (ΔH) was estimated from the area under the exotherm plots obtained from differential scanning calorimetry (DSC) carried out with the Du Pont 900 thermal analyzer in oxygen atmosphere, at a heating rate of 10 °C / in, over the temperature range from 50 to 550 ° C

The glass transition temperatures (T_g) of the NR vulcanizates containing 0 to 20 phr of PCNSL was measured using a DSC in the temperature range from -100°C to 25 °C in nitrogen atmosphere at a heating rate of 10°C/min The abrupt changes in the slope of the heat flow curves *ie.* the transition at temperatures below -60°C was recorded

(h). Chemical crosslink density of the vulcanizates

The chemical crosslink density (CLD) of the vulcanizates was determined by following the procedure of 'equilibrium swelling' in benzene at room temperature, using circular test specimens (diameter 10 mm) in duplicate The volume fraction of the rubber was calculated from the swollen and de-swollen weights, using the relation -

$V_r = ((D - FT)\rho_r) / ((D-FT)/\rho_r) + (A_0/\rho_s))$, where T is the weight of the specimen, D is the de-swollen weight, F is the weight-fraction of the insoluble components, A_0 is the weight of the absorbed solvent and ρ_r and ρ_s are the densities of the rubber and the solvent respectively

The CLD expressed as $(2 M_{c\,chem})^{-1}$ was calculated using the Flory - Rehner equation$^{(4)}$. The number average molecular weight of NR was determined from the intrinsic viscosity data using the relation , $\eta = 2.29 \times 10^{-7} M_n^{1.33}$.

(i). Determination of type of crosslinks

The proportions of mono, di- and polysulphidic crosslinks in the network structure of the vulcanizates were determined by measuring the CLD after treatment with thiol-amine reagents. For the selective cleavage of the polysulphidic crosslinks, the specimens were treated with a mixture of propane - 2 - thiol and piperidine, under nitrogen atmosphere, for 2 hours, as per the method reported by Campbell and Saville (5). To cleave both di- and polysulphidic crosslinks, leaving monosulphidic crosslinks intact, the vulcanizates were treated with a solution of 1- hexane thiol in piperidine, under nitrogen atmosphere for 48 hours, according to the method of Campbell and Saville.

The amount of sulphur combined with the polymer network (S_c) was determined by estimating the zinc-sulphide sulphur and free sulphur of the vulcanizates as follows. The free sulphur of the vulcanizate was determined by following the procedure given in ASTM D-297-72 A. The sulphur present as ZnS was estimated iodimetrically, after converting it to Cd S by reaction with HCl and absorption of the liberated H_2S in $CdCl_2$, as per the standard BS . 903 . Part B (1958). The sulphur inefficiency parameter E was calculated as, $E = (S_c) / (2 M_{c\,chem})^{-1}$.

(j). WAXS study

Wide angle X-ray diffraction studies of unmodified and PCNSL modified NR vulcanizates was carried out with the help of a XRD spectrometer, model - 'Philips A-1710' using a Cu-K α source at 35 kV, 15 mA in the angular range from $2\theta=10°$ to $2\theta=50°$.

(k). IR spectroscopy

The IR spectra of PCNSL and the NR / ZnO, NR / PCNSL and NR / PCNSL / ZnO systems were studied by casting thin films of the samples (from a solution in chloroform) on KBr plates, by an IR spectro-photometer (model - 'Perkin-Elmer 843'). The possible interaction between NR and PCNSL has been examined

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CHAPTER III

PCNSL AS A PLASTICIZER

III.1. Introduction

The ease in processability of an elastomer compound in the conventional processing equipment is often an essential requirement for many of the applications, apart from the specified physico-mechanical properties of the finished product. Normally, the processing of an elastomer compound involves various unit operations such as mixing, forming (extrusion, calendering or assembling) and curing or vulcanization, each under the desired conditions of temperature and shear rates. The ease in processability of an elastomer compound under these conditions is decided essentially by its rheological characteristics , which inturn is dependent on various factors such as the nature and type of elastomer, compounding ingredients used (eg:- fillers, plasticizers, processing aids, crosslinking agents etc)(1) apart from a combination of temperature and shear-rates employed.

Bristow et al.(2) have given an account of the parameters indicative of the processability of rubbers . Some of the factors determining processability of raw or compounded rubber on a micro-molecular scale include (1) molecular weight, (2)molecular weight distribution, (3) type and extent of branching, (4) gel content and (5) non-rubber content. Other factors determining the processability on a macro scale include (a)visco-elasticity in shear and elongation, (b) thixotropy, (c) stress-hardening (crystallisation) and (d) molecular breakdown as functions of temperature and strain rate, apart from filler dispersion and filler wetting(2) . The Mooney viscosity (3), Plasticity (P_0) and Plasticity Retention Index (PRI) determine the mixing and break-down characteristics of a polymer on the roll mill. The particle size, structure and dosage of fillers (4) and the nature and type of process aids (5) or plasticizers (6) used generally affects the mixing characteristics, flow properties, tack and pigment dispersion.

Today, scientists and technologists employ a number of rheological parameters to study and monitor the processability characteristics of polymers. Parameters such as flow behaviour index (n), consistency index (k) and viscosity (η) have a key role to play on the mixing and flow characteristics of molten polymers at various shear rates and temperatures(7) . Rheological parameters such as activation energy of melt flow, zero shear rate viscosity, principal normal stress difference ($\tau_{11} - \tau_{22}$),their dependence on shear rate and relevance with respect to polymer melt flow have been illustrated by Brydson (8) .

The relationship between melt-viscosity, shear rate (γ) and flow behaviour index has been described in terms of a power law fluid model (9-11) The activation energy of melt- flow at constant shear rate (E_γ) may be determined from the dependence of melt viscosiy on temperature, as given by the Arrhenius - Frenkel - Eyring equation (12,13) , $\log\eta_a = B\, e^{(E\ RT)}$, where η_a is the apparent viscosity, R is the universal gas constant, T is the temperature in absolute scale and B is a constant.

The occurence of normal stresses and shear stresses in polymer melt-flow and the significance of parameters such as shear-viscosity, primary and secondary normal stress coefficients etc., have been described by Pearson (14) Wissbrun and Dealy(15) have dealt with the significance of normal stresses in blow-moulding of thermoplastics Tanner (16) observed that the die swell of polymer fluids during extrusion through a capillary could be expressed as a function of its recoverable strain (S_R) which is a measure of the melt-elasticity The recoverable strain has been found to be related to the principal normal stress difference (17,18) The miscibility between polymeric constituents may be enhanced by specific ion-ion, ion-dipole or dipole-dipole interactions, hydrogen bonding or physical entanglements(19) Han and Yang (20, 21) studied the rheological behaviour of blends of polymethyl methacrylate (PMMA) with ABS and styrene acrylonitrile (SAN) with polycaprolactam . Good compatibility between PMMA and ABS is shown by a regular decrease in the principal normal stress difference with an increase in the content of PMMA in the blend (20) . Chuang and Han(22) showed that in a truly compatible blend system, a composition independent correlation can be obtained when principal normal stress difference is plotted against apparent shear stress .

An account of the historical background of the developments in the study of rheological properties and processing of elastomers has been given by White (23) . Innumerable references in the literature on studies on the flow behaviour and fabrication of NR are available (24 - 30). Studies on the deformation and flow of unvulcanized rubber have also been carried out by Marzetti (31), Dillon(32) and Mooney (33 - 35) . The extrusion of rubber through a cylindrical die has been described in terms of the flow of a fluid with a shear rate dependent viscosity (31). The first quantitative data on viscosity- shear rate dependence in rubber and elastic recoil in rubber compounds have been obtained by Mooney (33-35). Studies on the relationship between elastic shear recovery and shrinkage of calendered and extruded components, surface-roughness developed during calendering and extrusion and screw extrusion behaviour as a function of non-Newtonian viscosity have also been carried out Tobolsky and Andrews (36 - 38) studied the stress relaxation characteristics of poly isobutylene extensively and the visco-elastic behaviour of the system was correlated with molecular parameters such as molecular weight and glass transition temperature. Pioneering studies on normal stress and Weissenberg effect, typical of non-linear visco-elastic behaviour of polymers have been carried out in the 1940s and 1950s (39-42). Bernstein, Kearsky and Zapas(43) studied the non-linear visco-elastic properties of poly isobutylene and a tensor constitutive equation was proposed to represent its properties. During the 1960s, White and Tokita(44-48) and Ninomiya et al.(49,50) interpreted various processing characteristics of polymers in terms of the theory of visco-elasticity . The influence of molecular structure on the rheological properties of elastomers was studied by Kraus et. al (51 - 55).

The developments in the field of rheology have led to the development of a wide range of sophisticated instrumentation and processing facilities, with which the rheology of polymers can be studied on a smaller scale, simulating the temperature and shear rate conditions of larger production machines. Thus, for instance, the mixing characteristics of an elastomer compound can be studied on a Brabender Plasticorder under controlled conditions of temperature and shear rates, simulating those of an internal mixer used in the industries(56,57) Also, the melt-flow and extrusion characteristics of compounds can be studied on a capillary rheometer (eg.- Monsanto Processability Tester) at temperatures and shear rates approximating those of commercial extruders

Adequate mixing of compounding ingredients with the elastomer matrix is of paramount importance in the manufacture of any rubber product since many of the vulcanizate properties are governed by the dispersion of the additives in the rubber matrix(58). Die swell is reported to be dependent on parameters such as mixing time and dispersion of carbon black in the rubber matrix (59). The technology of mixing in rubber had its origin more than 150 years ago, consequent to the discovery of vulcanization by Goodyear in 1839 (25). Since then, rapid strides have been made in the science and technology of mixing, leading to fundamental understandings on the nature of mixing and dispersion of the additives in the polymer matrix (60-62). This led to the design and development of a variety of mixing equipments such as roll mills, internal mixers and extruders (58) to cater to the specific needs of the rubber industry. Danckwerts(62) defined the goodness of mixing in terms of the scale and intensity of segregation of particles. Apparent viscosity and effective relaxation time of rubber - carbon black compounds have been used as measures to evaluate the quality of mixing (63).

The mixing behaviour and rheological characteristics of a rubber compound can be studied conveniently in a small scale using a Brabender Plasticorder ([illegible] 56,58), which is a torque rheometer operating under controlled conditions of temperature and shear rate, simulating a larger internal mixer. Mun et al (64) have defined Brabender Breakdown Index (BI) as a quantitative measure of processability of NR. The break-down index is given as, $BI = (T_2 - T_{10}) K / E$, where T_2 and T_{10} are the Brabender torque values after 2 minute and 10 minute of mixing respectively in a 12 minute test run, E is the energy input between this time interval and K is a convenience factor depending on the units adopted for energy. Rheological analysis of Brabender torque rheometer data has given reliable estimates of parameters such as melt viscosity, flow behaviour index, activation energy of melt-flow and power consumption during processing of polymer melts (65-74). Brabender Plasticorder can be used to measure the flow behaviour of elastomers (65). Lee and Purdon(66) observed very good correlation between the flow curves derived from Brabender Plasticorder and Instron capillary rheometer. The flow behaviour index (n) of polymer melts has been obtained from the Brabender flow curves using the relation, $M = C(n)KS^n$, where M is the torque, S is the rotor speed, C(n) is a function depending on the machine geometry and K is a constant (67, 68). The flow behaviour index n and activation energy of melt-flow E obtained from the Plasticorder are found to be identical with that derived from other capillary rheometer methods (67). The *melt viscosity is related to the torque* M *and rotor* speed S as, $\eta = K\,M/S$, where K is a constant depending on the mixer measuring head (69,70). Activation energy of melt flow E_a is known to depend on the viscosity η and temperature T as given by the relation $E_a = Rd(\ln\eta)/d(1/T)$, where R is the gas constant (71). Brabender torque M can be converted to units of power P using the relation $P = 2\pi M S / 60$, which may be used to generate practical process engineering data (69). The thermal processing stability of thermoset materials may be determined from the length of the stable portion of the Brabender torque profile, before the onset of cure (72). The band-width of the torque profile obtained from the plasticorder is a good indicator of the elasticity of polymer melts (7). A lower band-width indicates lower elasticity. The shorter time needed to attain a minimum torque level and steady band-width shows the better processability of a sample. The plasticizing effect of bromo derivative of PCNSL (BrPCNSL) in natural rubber and that of Tetra Bromo Pentadecyl Tribromo Phenol (TBPTP) in polyethylene (73) and ethylene vinyl acetate copolymer (74) have been studied using a Brabender Plasticorder. A higher average torque level is *indicative of the greater amount of energy required for* processing(73,74). There are numerous reports on the use of Brabender Plasticorder to investigate processability of rubber compounds (56,57,75) and to study the effects of reinforcing pigments (57,76,77), *plasticizers, process oils and other ingredients*(76,78) *on their* rheological properties. Dispersion of carbon black in rubber compounds and its effects on physical properties have also been studied using Plasticorder (79).

The mixing behaviour of NR with the additives in the Brabender Plasticorder covers a smaller range of shear rate starting from 10 s^{-1} to 100 s^{-1} only. But many of the subsequent processing operations such as extrusion and injection molding of rubber compounds encompasse a much higher range of shear rate viz., *100* s^{-1} *to 10000* s^{-1} (69). Also, the visco-elastic properties and rheological properties of polymers in general, are highly shear and temperature dependent(80,81). Hence, to make reasonable and valid predictions on the melt-rheology of polymers, it is absolutely essential to carry out the studies under the same shear rate and temperature conditions inorder to simulate the factory conditions. Thus, the results obtained from capillary rheometers (eg: Instron capillary rheometer or Monsanto Processability Tester), under simulated conditions are found to be highly useful in this regard(82-92).

Kumar et al (82) have studied the visco-elastic behaviour of gum and filled NR during processing on a Monsanto Processability Tester (MPT). The various rheological parameters such as die swell, recoverable deformation, principal normal stress difference and activation energy of melt-flow have been evaluated .The use of MPT as an ideal tool for evaluating the processability of rubber compounds in an injection molding machine has been described by Sezna (83). Also, data obtained from MPT correlates well with the observed processing characteristics during injection molding with larger production units (84). Beardsley and Ho(85) used MPT to study the rheological properties of EPDM polymers. They observed that the stress relaxation time of samples having a broader molecular weight distribution increases in difference to that observed for those having narrower molecular weight distribution. The suitability of MPT as an instrument for controlling compound processability has been described by Amsden (86). Sezna (87) used MPT to study the extrusion characteristics of rubber compounds and predicted their die swell behaviour. *Consistency index (k) and flow*-behaviour index (*n*) values obtained from MPT are commonly used to describe the rheological characteristics of rubber/plastic blends. Varughese (88) studied the melt-rheology of blends of plasticized PVC and ENR on a capillary rheometer and evaluated the various melt-elasticity parameters such as principal normal stress difference (N), recoverable shear strain (S_R) and shear modulus (G) . The dependance of principal normal stress difference on die-swell in capillary rheometer was observed by Han (89). Flanagan (90) reported that the higher elasticity of a material is indicated by higher die swell and longer relaxation times in a capillary rheometer. The application of a *capillary rheometer (MPT) to measure the* running and relaxed die swells and stress relaxation time has been described by DiMauro (91). He has also suggested a correlation between die swell obtained from capillary extrusion to that from factory extruders The usefulness of MPT in testing the processability of elastomers, particularly their viscosity at different shear rates along with their elastic responses has been noted by Bittel (92). Melt-viscosity is a parameter of prime importance in processing of polymers The dependence of melt-viscosity on shear rate and temperature are factors of major significance with respect to processing operations such as extrusion (14) Melt-viscosity influences the pressure build-up in the barrel of an extruder and is inversely proportional to the concentration of plasticizer in the polymer system (93) Also, the melt viscosity of a polymer at any specified temperature is often considered to be a measure of the mobility of the polymeric chains relative to each other and is controlled by the flexibility of the chains (94) Some of the factors affecting melt-viscosity of polymers have been described by Kumar (95) as - (i) flow conditions such as shear rate, temperature, pressure etc , and (ii)resin composition as given by chemical structure of polymer, molecular weight distribution of polymer, presence of long chain branches in the polymer and nature and concentration of additives The pseudoplasticity index (flow behaviour index) n and consistency index K of polymer melts can be determined from the power law expression, $\tau_a=K(\eta_a)^n$ of the Ostwald - de Waele model (7, 9,10). These indices indicate the flow behaviour and viscosity of the polymer melt subjected to deformation. The flow behaviour index n describes the non-Newtonian character of the melt (90) Thus, in the case of pseudoplastic or shear-thinning fluids n is less than 1 and for Newtonian fluids n=1(96).

The present work envisages the study of processability characteristics of NR modified with PCNSL in operations such as mixing, extrusion, assembling and curing, with emphasis on their rheological behaviour under various conditions of temperature, shear rate and concentration of PCNSL

III.2. Mill mixing characteristics

The processing characteristics of NR on a two roll mixing mill before and after modification with 5, 10 and 20 phr each of PCNSL and an aromatic oil (Spindle oil) have been studied. The composition of the mixes are given in Table III.1 and the processability parameters in Table III 2

Table III.1 Composition of the mixes

Mix code	U	P_5	P_{10}	P_{20}	O_5	O_{10}	O_{20}
NR	100	100	100	100	100	100	100
PCNSL	-	5	20	20	-	-	-
Spindle oil	-	-	-	-	5	10	20

Generally, the processing of NR on a two roll mill in presence of 5 to 20 phr of PCNSL has been found to be easier mainly due to the softening effect of PCNSL in NR After mastication of NR on the roll mill for two minutes and the formation of a band over the front roll, PCNSL is added. Upon incorporation of PCNSL into the NR matrix, a smooth band is formed on the front roll without any sticking to the rolls within 5 minutes. The softening effect of spindle oil in NR is comparatively higher, particularly at the higher dosage of 20 phr.

Table III.2. Processability parameters of the mixes

Mix code	U	P_5	P_{10}	P_{20}	O_5	O_{10}	O_{20}
Mill shrinkage, (%)	6	2.5	1.5	1.5	3	3	1.5
Initial Plasticity, P_0	87	93	92	99	93	94	100
Plasticity Retention Index, PRI	101	102	102	94	100	100	100
Mooney viscosity, ML(1+4) 100°C	49	33	38	34	32	31	17

The results given in Table III.2 show a considerable reduction in mill shrinkage of NR in presence of 5 and 10 phr of PCNSL as against the unmodified NR and the NR containing 5 and 10 phr of spindle oil. This indicates greater dimensional stability of the uncured PCNSL modified NR compounds during melt-flow and better surface finish . An increase in the dosage of PCNSL from 0 to 20 phr resulted in an increase in the Wallace plasticity number (P_0) from 87 to 99 and a decrease in Mooney viscosity from 49 to 34. This indicates the plasticizing action of PCNSL in NR A comparatively higher value of PRI (102) of NR containing 5 and 10 phr of PCNSL as against that of NR containing the same dosages of spindle oil (100) shows an improved resistance to thermo-oxidative decomposition of PCNSL modified NR

III.3. Processing characteristics of NR modified with PCNSL in a Monsanto Processability Tester - (Rheological characteristics).

It is appropriate at this juncture to study the extrusion characteristics and melt *rheology* of NR before and after modification with PCNSL These studies were carried out on a Monsanto Processability Tester The melt-flow behaviour and die-swell characteristics of the samples have been studied at various shear rates and temperatures Also, the different parameters characterizing their viscoelastic behaviour have been evaluated, the results of which are described below. The melt-flow characteristics studied include apparent viscosity, psuedoplasticity index, consistency index and activation energy of melt-flow. The elasticity parameters represented by die-swell ratio and principal normal stress difference have also been measured

The melt-rheology of raw NR (ISNR-5) masticated for 10 minutes on a roll mill, has been studied in comparison with that of similar samples containing 10 and 20 phr of PCNSL For the purpose of comparison, these studies were also carried out using 10 and 20 phr of an aromatic process oil (*Spindle oil*) The rheological characteristics were measured in a Monsanto Processability Tester with a circular die having a diameter of 1.5 mm and L/D ratio of 20 at the temperatures 100°C , 120 °C and 160°C and four shear rates ranging from 18.08s^{-1} to 991.6 s^{-1}. The viscosity of PCNSL at room temperature was measured with the help of a Brookfield Synchro-Lectric viscometer (model- HBT), with spindle no 7 at speeds ranging from 0.5 rpm to 100 rpm. The variation of viscosity with temperature over the range of 60 °C to 160 °C has been measured in the same equipment coupled with a temperature controller (model- 74R), using spindle no: 21, at the speed range of 0.5 rpm to 100 rpm The apparent shear stress of the polymer melts (τ_a) and the apparent shear rate (γ_a) have been calculated using the following relationships, based on which the rheological parameters have been estimated.

Apparent shear stress (τ_a) = (Gauge pressure) 4 (die length / die diameter)

Apparent shear rate (γ_a) = 32 Volumetric flow rate / π (die diameter)^3

i. Melt flow characteristics

(a). Melt viscosity

The apparent melt-viscosity (η_a) of the samples were calculated using the relation,

Apparent viscosity (η_a) = Apparent shear stress / Apparent shear rate

The variations in the apparent viscosity of the samples with apparent shear rates at the different temperatures are given in Figure III.1 (a-c) It shows a lower melt viscosity of NR in presence of PCNSL and higher rate of reduction in the melt viscosity of NR in presence of 10 and 20 phr of PCNSL as compared to the samples containing the same dosage of spindle oil This is particularly prominent at the lower temperatures of 100°C and 120°C

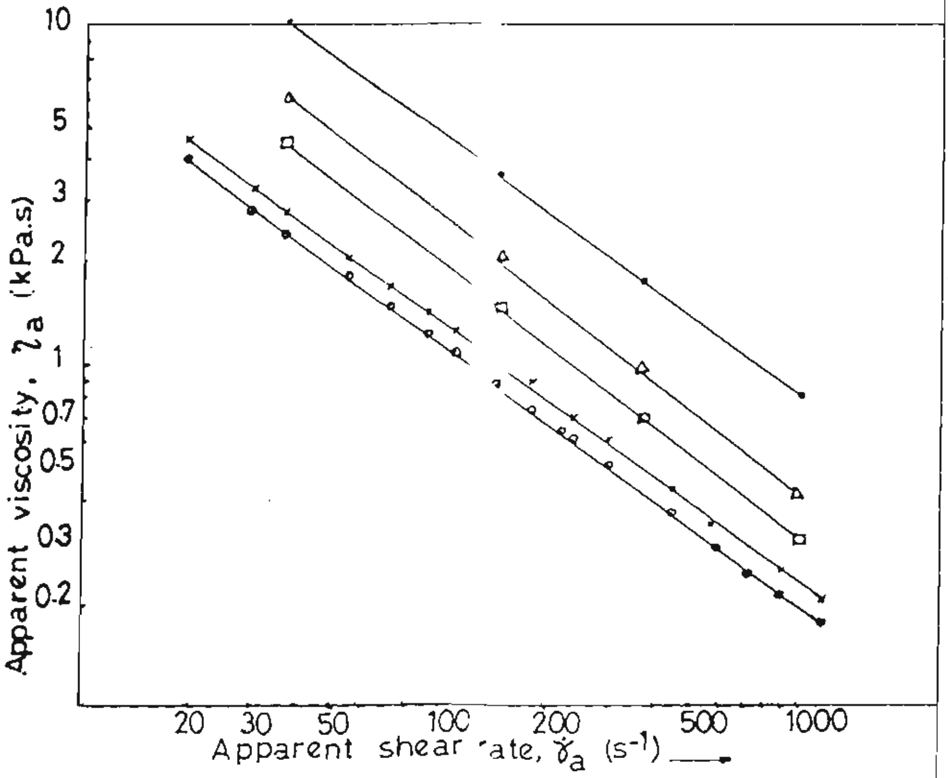

Fig. III.1(a). Variation in apparent viscosity with apparent shear rate of unmodified, PCNSL modified and oil modified NR at 100°C

•—• U △—△ P_{10} □—□ P_{20} ×—× O_{10} ○—● O_{20}

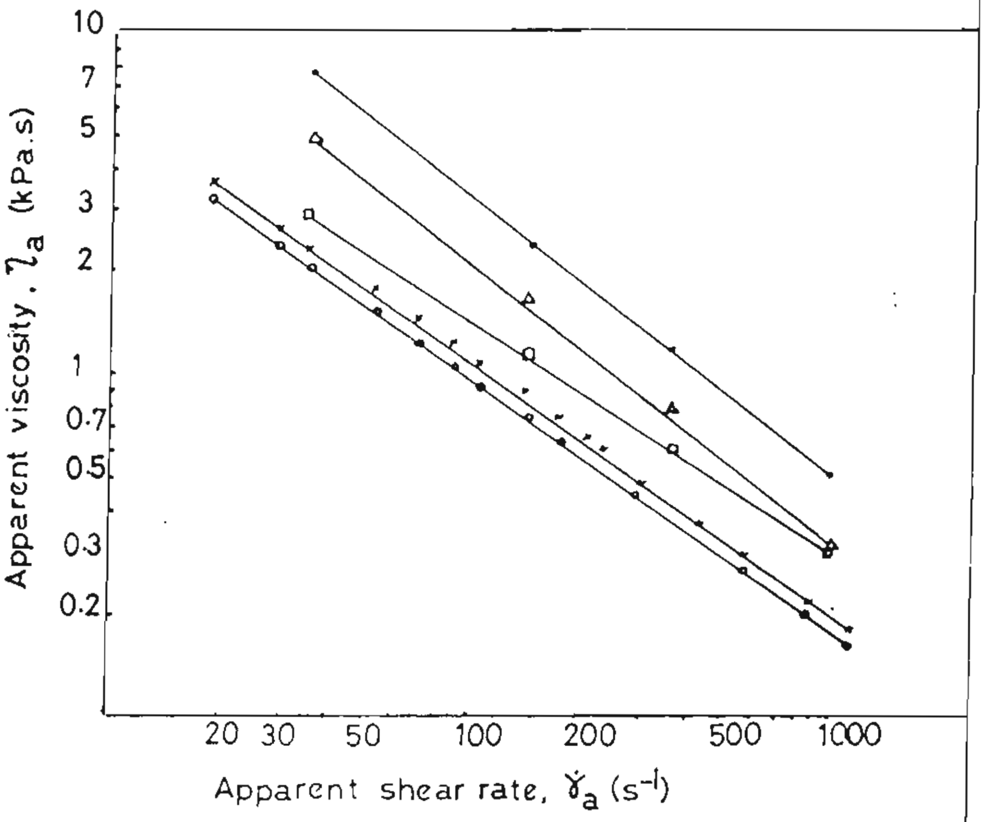

Fig.III.1(b). Variation in apparent viscosity with apparent shear rate of unmodified, PCNSL modified and oil modified NR at 120 °C

•——• U △——△ P_{10} □——□ P_{20} ×——× Q_{10} o——o O_{20}

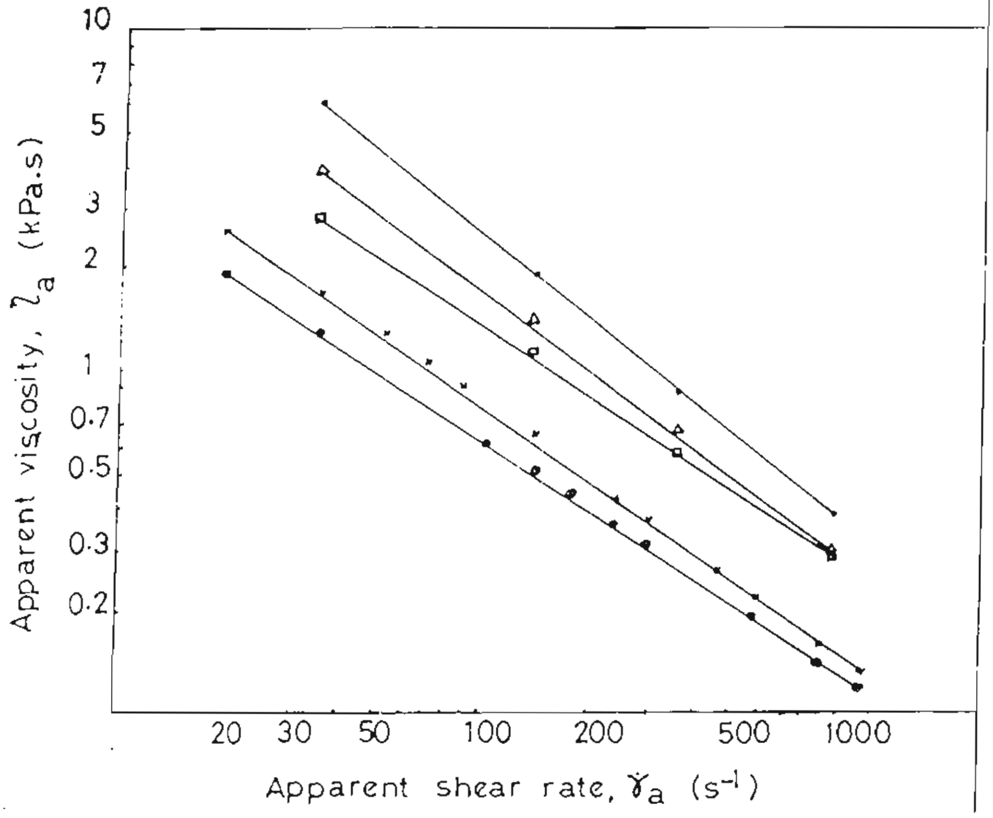

Fig.III.1(c). Variation in apparent viscosity with apparent - shear rate of unmodified, PCNSL modified and oil modified NR at 160°C

—— U △——△ P_{10} □——□ P_{20} ×——× O_{10} ○——○ O_{20}

The variation in apparent viscosity with temperature of the different mixes at constant shear rates is given in Figure III 2(a-d) Table III 3 gives the rate of reduction in apparent viscosity with temperature in the range 100° C - 120 °C

Figure III 2 shows that in all the cases there is a noticeable reduction in the viscosity in the range 100-120° C Further reduction in viscosity with temperature is marginal. This observed for both the PCNSL and oil modified NR compounds as well as at all the shear rates. The reduction in viscosity is particularly prominent at the lower shear rates which indicates the relative advantage of PCNSL over oil in processing operations such as mixing and extrusion The higher rate of reduction in viscosity of the PCNSL modified mixes is due to their higher shear sensitivity (lower n values) as compared to the oil modified systems The results in Table III 3 shows a comparatively higher rate of reduction in viscosity with temperature for PCNSL modified NR as against that of the samples containing the same dosage of oil.

It has been well established that the efficiency of a plasticizer depends considerably on the diffusion rate of its molecules in the polymer matrix and that a lower viscosity leads to better diffusion (97) However, the viscosity of the plasticizer itself is quite often temperature dependent. The unusually high bulk viscosity of PCNSL at ambient temperature and its drastic reduction to a very low value at 150°C, has been reported by George John et al (98) Figure III.3 shows an exponential reduction in the bulk viscosity of PCNSL when the temperature increases from 60°C to 100°C with negligible reduction there-after. This clearly indicates that the decrease in the melt-viscosity of NR modified with PCNSL in the temperature range 100°C to 160°C is not due to a significant reduction in the viscosity of PCNSL, but due to an increase in the plasticizing efficiency of PCNSL. This is in accordance with the generally accepted rule of a plasticizer lowering the melt-viscosity of a polymer (99).

Table III.3 Rate of reduction in apparent viscosity with temperature at different shear rates (Pa.s/°C)

Apparent shear rate (γ_a), s^{-1}	40	100	400	900
Mix code				
U	140	75	30	19
P_{10}	75	35	14	7
P_{20}	80	30	7	2
O_{10}	30	15	5	3
O_{20}	20	12	4	2

Inorder to check the possibility for the occurence of any chemical reaction between PCNSL and NR at high temperatures, mixes of NR with 10 phr of PCNSL were prepared

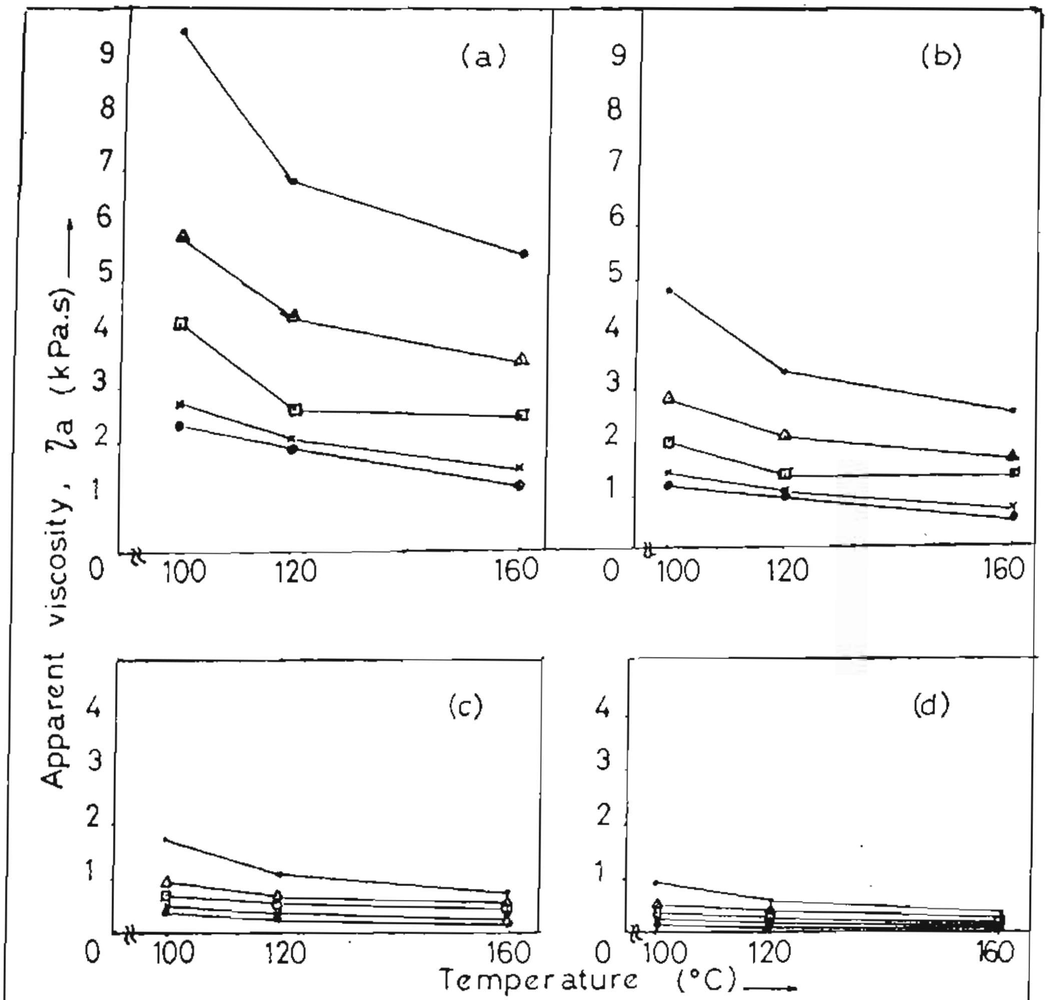

Fig.III.2. Variation in apparent viscosity with temperature of unmodified, PCNSL modified & oil modified NR at constant shear rate, $\dot{\gamma}_a$

U P_{10} P_{20} O_{10} O_{20}

$\dot{\gamma}_a$ - (a) 40 s^{-1} (b) 100 s^{-1} (c) 400 s^{-1} (d) 900 s^{-1}

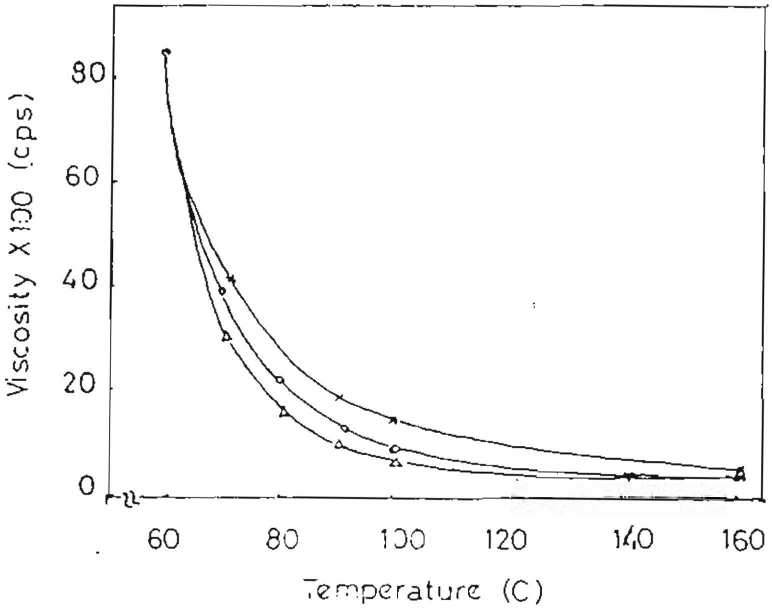

Fig.III.3. Variation in viscosity of PCNSL with temperature - (Brookfield viscometer)

Shear rate ×——× $2.3 s^{-1}$ ○——○ $4.7 s^{-1}$ △——△ $18.6 s^{-1}$

at the higher temperatures of 100°C, 120°C and 160°C and characterized by IR spectroscopy. The spectrograms of the mixes are shown in Fig. III.4 (a-c). It is evident that there is no change in the position of peaks with the increase in temperature of mixing from 100°C to 160°C. This clearly indicates the absence of any chemical interaction between PCNSL and NR at higher temperatures which could influence the melt rheology.

(b). Pseudoplasticity index and consistency index

The flow curves of the unmodified NR and the samples containing 10 and 20 phr each of PCNSL and spindle oil at different temperatures are given in Figure III.5 (a-c), from which the pseudoplasticity index and consistency index were calculated. The results are shown in Table III.4.

Table III.4. Pseudoplasticity index and consistency index of NR before and after modification with PCNSL or Spindle oil at different temperatures. (MPT)

Parameter	Mix code	Temp. (°C) 100	Temp. (°C) 120	Temp. (°C) 160
Pseudoplasticity index, n	U	0.15	0.17	0.18
	P_{10}	0.17	0.19	0.24
	P_{20}	0.23	0.25	0.29
	O_{10}	0.23	0.25	0.28
	O_{20}	0.25	0.27	0.29
Consistency index, K (kPa s^n)	U	360	230	170
	P_{10}	190	143	110
	P_{20}	120	75	65
	O_{10}	76	62	42
	O_{20}	62	51	34

The results given in Table III.4 show a progressive increase in the pseudoplasticity index of NR with an increase in dosage of PCNSL and oil from 0 to 20 phr and with an increase in temperature from 100°C to 160°C. The higher values of flow behaviour index under these conditions show a lower deviation from the Newtonian behaviour. It is known that as the behaviour departs more from Newtonian (with lower values of n), the melt flow becomes more plug-like with high shear rates being concentrated near the surface of the compounding machine leading to a low shear within the main body of the melt (58). In other words, the higher flow behaviour index of the PCNSL modified NR is expected to result in a more uniform distribution of shear rate through-out the bulk of the polymer melt leading to better mixing. The practical significance of pseudoplasticity index with respect to extrusion has been described by Stevens (96). Pseudoplasticity index is important in deriving the relation between viscosity in the screw channel at a low shear rate and in the die at a high shear rate and that in the flight clearance and accordingly in the design of the screw of the extruder.

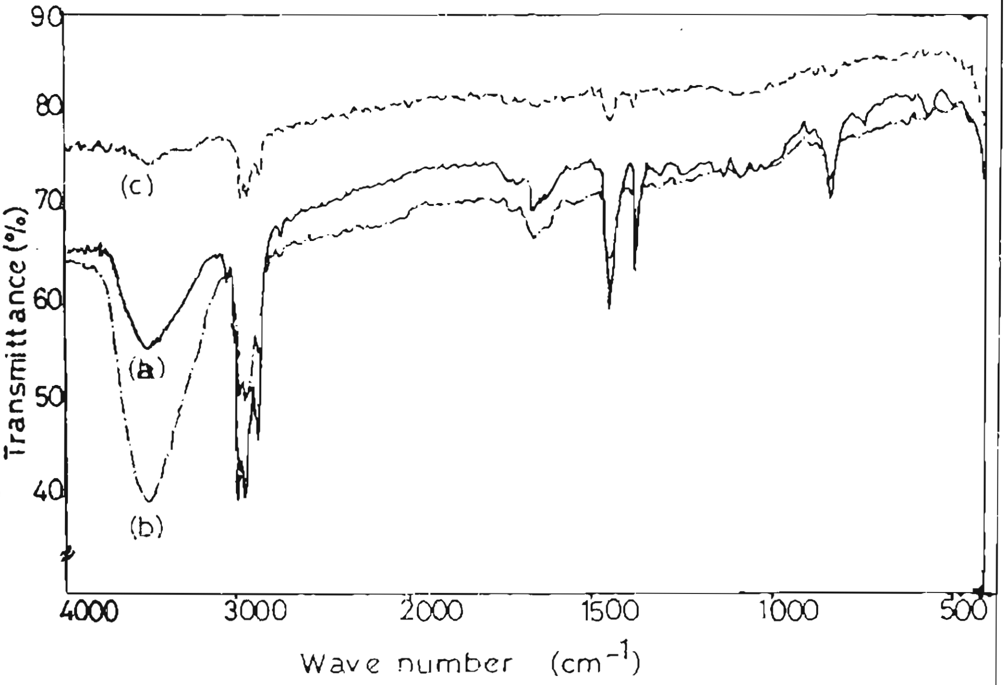

Fig.III.4. IR spectra, of PCNSL modified NR mixed at (a) 100 °C ——— (b) 120 °C —·—· & (c) 160 °C - - - -

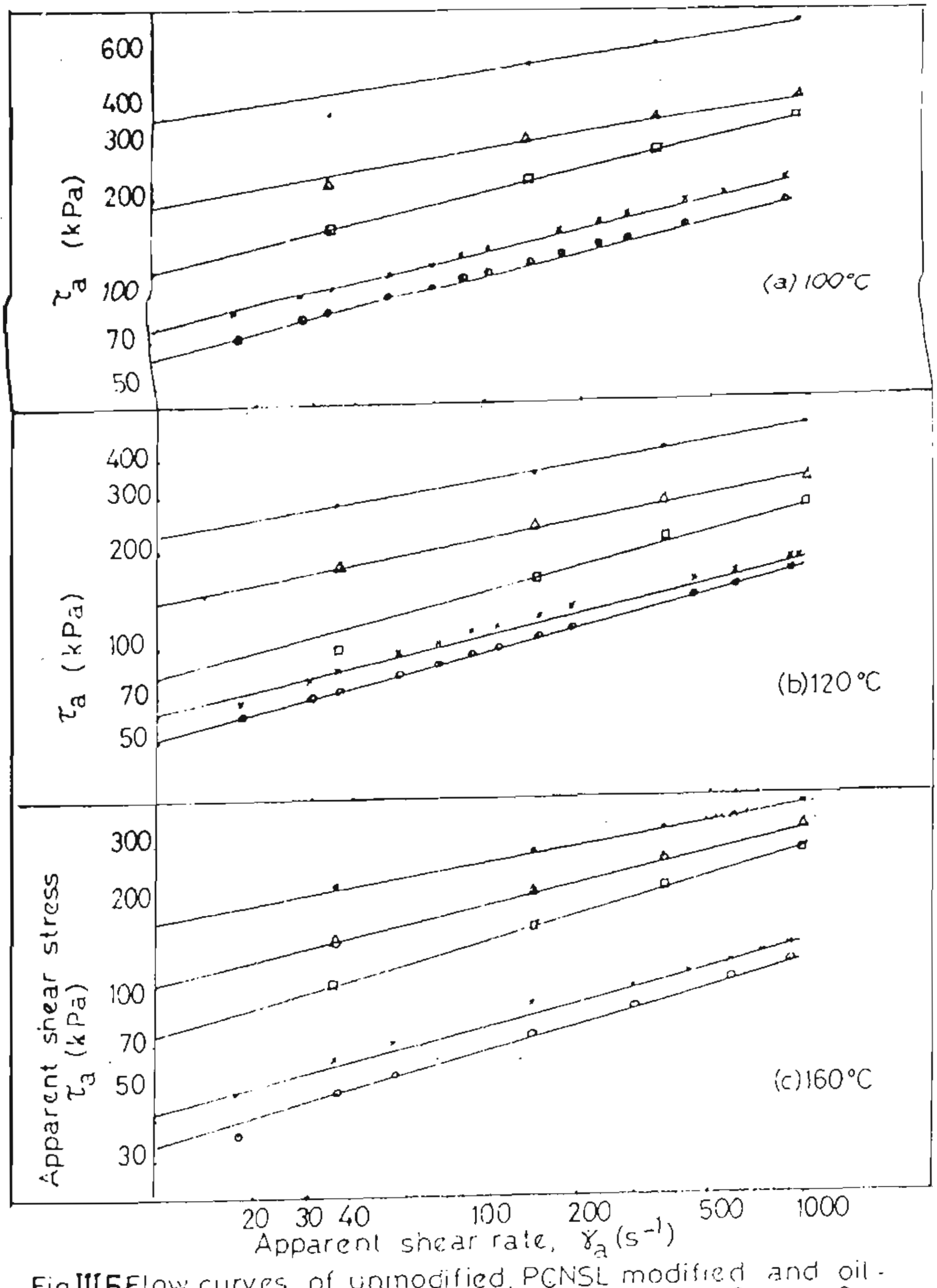

Fig.III.5 Flow curves of unmodified, PCNSL modified and oil-modified NR. U P_{10} P_{20} O_{10} O_{20}

An increase in temperature from 100°C to 160°C results in a decrease in the consistency index of the PCNSL modified NR from 190 to 110 in presence of 10 phr of PCNSL and from 120 to 65 in presence of 20 phr of PCNSL as against the decrease from 360 to 170 for the unmodified sample. The relatively lower values of the consistency index of PCNSL modified NR reflects its lower melt viscosity. The lower melt-viscosity inturn may facilitate a faster extrusion (100)

(c). Activation energy of melt-flow

The activation energy of melt-flow at constant shear rate (E_a) of the samples in the temperature range from 100°C to 160°C has been determined from the viscosity - temperature dependence following the Arrhenius - relationship (8) given as, $\eta_a = A\,e^{(E/RT)}$, where, η_a is the apparent melt viscosity, R is the gas constant and T is the temperature in absolute scale. The activation energy was calculated from the slope of the plots of log η_a vs (1/ T). The results given in Table III.5 show comparatively lower values of activation energy for the PCNSL modified NR. It also shows comparatively higher rate of reduction in the activation energy with an increase in shear rate. The increase in the dosage of PCNSL from 10 to 20 phr also results in a decrease in the activation energy of melt-flow as against the samples containing the same dosage of spindle oil. The decrease in the activation energy for melt-flow in presence of PCNSL shows the efficiency of PCNSL as an effective plasticizer, since it meets the condition for a plasticizer to be one that lowers the activation energy of melt-flow for the plasticized system (97). In this respect, the results in Table III.5 shows comparatively greater lowering of the activation energy of melt-flow of NR in presence of PCNSL as against that containing the same dosage of spindle oil.

Activation energy of melt-flow is often considered to be an indicator of the mobility of macromolecules in polymer melts (101,102). It is expected that the plasticizing effect of PCNSL in NR increases the segmental mobility of the latter, resulting in lowering of the activation energy.

Table III.5. Activation energy of melt-flow at constant shear rate (E_a) of unmodified NR, PCNSL modified NR and oil modified NR (kJ/mol)

Apparent shear rate (γ_a), s^{-1}	40	100	400	900
Mix code				
U	0.517	0.562	0.652	0.719
P_{10}	0.449	0.427	0.360	0.337
P_{20}	0.427	0.315	0.305	0.090
O_{10}	0.494	0.472	0.427	0.449
O_{20}	0.607	0.539	0.449	0.337

Temperature 100°C to 160°C

ii. Melt elasticity

Die swell ratio and principal normal stress difference constitute two important rheological parameters in characterizing the elastic properties of polymer blends (88). These parameters have higher significance also with respect to the processability of polymer blends since they influence the nature and dimensional stability of the extrudates (103-105).

It is reported that during extrusion the elastic strain at the entry of the die is very high which relaxes in the duct and reaches a steady equilibrium value at an L/D ratio of 20 or more (17, 103). Hence the L/D ratio of 20/1 was selected for the determination of these parameters

(a). Die swell ratio

Extrudate swell is presumed to be very much dependent on the phenomenon of elastic recovery (23) and hence is a good measure of the elasticity of polymer melts. Generally, an increase in molecular weight and molecular weight distribution leads to an increase in die-swell of polymer melts (106). The die swell ratio given as $B = D_e / D_o$, where D_e is diameter of the extrudate and D_o is diameter of the die orifice is calculated from MPT as B = (Running die swell (%) /100)+1. The die swell is very rapid and relatively large near the die-tip or die exit and is known as running die-swell (107). At specified extrusion rates and instrument settings, the running die swell depends on the swelling behaviour of the particular test compound (105)

The running die swell of the extrudates have been measured using the MPT. Plots of the die swell ratio against apparent shear rate for the unmodified NR, PCNSL modified NR and oil modified NR at 100°C, 120°C and 160°C are given in Figure III 6. Fig.III.6 shows that the die swell of PCNSL modified NR is very much dependent on temperature and shear rate. Unlike that for NR, the die swell ratio of NR modified with PCNSL stabilizes rapidly to a nearly constant value with increasing shear rates and at lower temperatures (100°C & 120°C). Also, at 100°C and 120°C and at high shear rates, the die swell ratio of NR modified with PCNSL are lower than that of NR alone. This is quite advantageous during processing as these conditions are normally employed in rubber extrusion

The reduced die swell of PCNSL modified NR may be explained on the basis of the molecular interpretation of the die swell behaviour (8). It is expected that at lower temperatures, the shear force within the capillary maintaining molecular orientation predominates over that of the force of Brownian movement of chain segments causing disorientation which results in reduced die swell. It appears that the orientation effect of the shear force is particularly dominant in the PCNSL modified NR at higher shear rates and low temperature (100°C & 120°C) condition aided by the softening effect of PCNSL on NR.

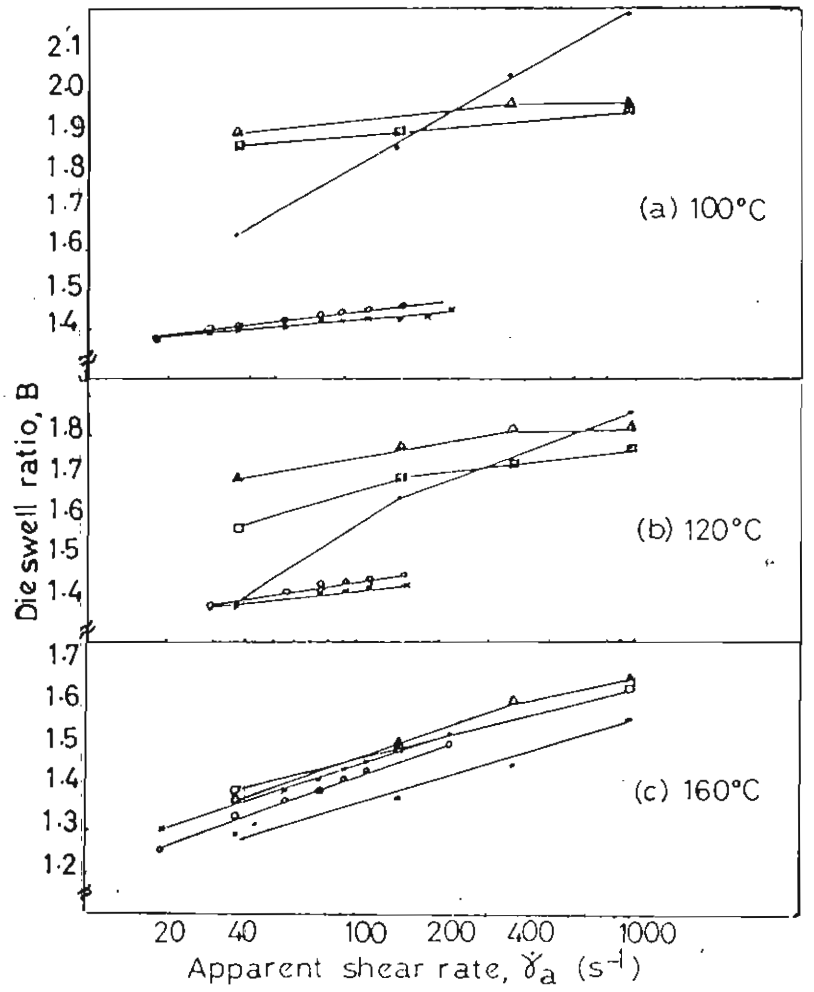

Fig. III.6. Variation in die swell ratio of unmodified, PCNSL modified & oil modified NR

•—• U   △—△ P_{10} □—□ P_{20} ×—× O_{10} ●—● O_{20}

The oil modified samples gave lower die swell as compared to that of the PCNSL modified samples indicating that oil is more effective in reducing the nerve or elasticity of the rubber than PCNSL, particularly at lower temperature. At the higher temperature of 160°C, the die swell of PCNSL modified NR and oil modified NR are found to be higher than that of unmodified NR. In this case, it is possible that the reduced viscosity and enhanced flow may lead to an increase in the force of Brownian motion over the shear force leading to an increase in the die swell as compared to the unmodified NR.

(b). Principal normal stress difference

The die swell and other elastic effects are the consequence of the normal stresses generated during the shear flow of polymer melts and depend on the normal stress difference. The principal normal stress difference is found to be related to the exit pressure of the melt and the shear stress at the wall during extrusion(8)

The principal normal stress difference ($\tau_{11}-\tau_{22}$) of the unmodified NR, PCNSL modified NR and oil modified NR have been estimated using the Tanners equation(16) given as $(\tau_{11}-\tau_{22})=2\tau_a(S_R)$, where τ_a is the apparent shear stress and S_R is the recoverable strain. The variation in the principal normal stress difference with apparent shear stress for the NR samples are given in Table III 6(a&b).

The high degree of compatibility between NR and PCNSL is shown by the regular decrease in the values of principal normal stress difference in presence of PCNSL. Han and Yang(20) have reported similar reduction in principal normal stress difference in compatible blends of poly methyl methacrylate with acrylonitrile butadiene styrene copolymers and in styrene acrylonitrile copolymer with poly caprolactam (21) Chuang and Han (22) have shown a composition independent correlation between the principal normal stress difference and apparent shear stress in blend systems that are compatible at the molecular level. The results in Table III 6(b) also show low values of principal normal stress difference for the spindle oil modified NR mixes and a regular decrease with the decrease in apparent shear stress, at the various temperatures. This also indicates the compatibility between spindle oil and NR

Table III.6(a). Variation in principal normal stress difference (τ_{11}-τ_{22}) (kPa) with apparent shear stress (τ_a)(kPa) for unmodified NR and PCNSL modified NR

Mix code	U	U	P_{10}	P_{10}	P_{20}	P_{20}
Parameter	(τ_a)	(τ_{11}-τ_{22})	(τ_a)	(τ_{11}-τ_{22})	(τ_a)	(τ_{11}-τ_{22})
100°C	373 535 636 741	4528 9616 15388 21917	212 295 346 412	4065 5653 7418 8835	159 217 264 349	2906 4173 5573 7244
120°C	282 349 416 495	2035 4400 6637 8900	179 241 285 316	2437 3781 4789 5312	87 166 223 269	934 2300 3261 4150
160°C	229 286 327 369	1230 1914 2660 3897	148 220 261 293	992 2046 2995 3694	108 166 215 258	763 1795 2465 3139

Table III.6 (b). Variation in principal normal stress difference (τ_{11}-τ_{22}) (kPa) with apparent shear stress (τ_a) (kPa) for spindle oil modified NR

Mix code	O_{10}	O_{10}	O_{20}	O_{20}
Parameter	(τ_a)	(τ_{11}-τ_{22})	(τ_a)	(τ_{11}-τ_{22})
100°C	62	340	55	306
	85	595	72	506
	96	706	82	625
	102	772	87	679
	114	899	97	777
	123	983	106	864
			112	929
			117	987
120°C	48	236	43	236
	66	349	69	471
	79	543	74	524
	85	601	83	651
	97	727	90	710
	104	785	97	767
	111	861	102	821
	117	918		
160°C	33	129	23	70
	48	263	36	169
	64	442	49	298
	74	517	57	373
	81	609	64	454
	91	760	68	510
	99	831	69	549
	103	964	77	675
	109	1058	82	753
	111	1101		

Smooth uniform and glossy extrudates have been obtained for the PCNSL modified NR at temperatures above 120°C

The following conclusions may be drawn from the above mentioned results. The modification of NR with PCNSL results in an increase in the pseudoplasticity index and a decrease in the melt viscosity and activation energy of melt-flow. This indicates the plasticizing action of PCNSL in NR. The lower die swell of PCNSL modified NR at high shear rates and at lower temperatures (100°C & 120°C) shows a reduction in melt elasticity of NR in presence of PCNSL. Also, a decrease in principal normal stress difference of NR in presence of PCNSL indicates good compatibility between NR and PCNSL. These results, thus, show that the processability of NR improves in presence of PCNSL 67/1863

III.4. Glass-transition

At sufficiently low temperatures, polymers often transform from an amorphous rubbery state to a brittle glassy state along-with dramatic changes in the physico-mechanical properties This 'glass transition temperature' denoted as T_g, is often an important criterion for the characterization of polymers and in designing compounds for a variety of applications Thus, for instance, the wear pattern of automobile tire treads is known to be influenced by the T_g of the polymer apart from other factors such as additives in the tread formulation and environmental conditions(108). The T_g of a particular polymer changes with processing conditions, molecular weight and other detailed compositional changes(109). Quite often, a shifting of T_g is observed towards lower temperature in presence of plasticizers(110) and the extent of depression in T_g is considered to be a measure of its plasticizing ability(111) Normally, an increase in the dosage of a soluble plasticizer in a polymer leads to a lowering of the viscosity and also the T_g of the system(112). Approximate values of T_g can be obtained from a large range of methods such as measurements such as measurements of density, linear expansion, dynamic mechanical properties and IR absorption as a function of temperature(108) T_g can also be measured directly from the ΔT vs T plots of DTA and the specific heat (C_p) vs T traces from DSC It is found that on either side of the transition the specific heat content is linear with temperature(108).

Since PCNSL has been found to plasticize NR, it is pertinent to gather information on the low temperature behaviour of PCNSL modified NR from DSC study. Thus, the transition from rubbery to glassy state of NR vulcanizates containing 0 to 20 phr of PCNSL has been determined using DSC The thermograms obtained in an atmosphere of nitrogen at a heating rate of 10 °C/min are given in Figure III-7. The abrupt changes in the slope of the heat-flow curves at temperatures below - 60°C show the glass-rubber transition. The transition temperature (T_g) for NR gum vulcanizate is - 65 °C. The glass transition temperatures for NR containing 10 phr of PCNSL and that for NR containing 20 phr of PCNSL are - 75 °C and - 80 °C respectively. The figure shows a clear and progressive shift in the onset temperature to lower values with the increase in concentration of PCNSL in the vulcanizate, indicating the effectiveness of PCNSL as a plasticizer at low temperatures. The mechanism of action of plasticizers in reducing T_g has been described earlier by Gowariker et al(113) They suggest that the plasticizer molecules penetrate into the polymer matrix and establish polar attractive forces between it and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the 'segmental mobility', thereby reducing the T_g value. Hence, it is expected that the observed shift in T_g of the NR vulcanizates towards lower temperatures is due to the progressive increase in segmental mobility of NR with increase in dosage of PCNSL

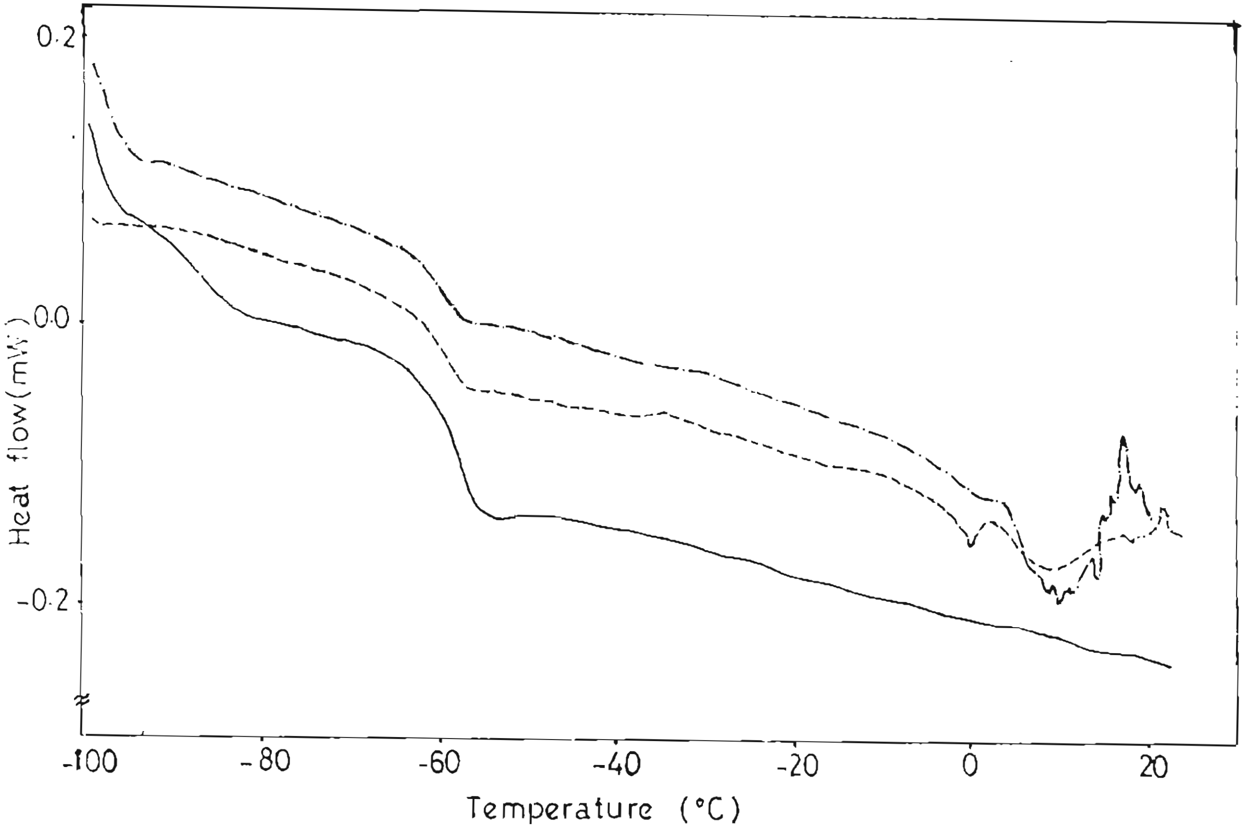

Fig.III.7. DSC thermograms of NR vulcanizates containing PCNSL.

PCNSL content (phr) —— 0 ---- 10 —·— 20

Medium - Nitrogen
Ramp - 10 °C/min

III.5. Mixing characteristics of PCNSL modified NR in a Brabender Plasticorder

The reults described in the previous sections (III.3) show the plasticizing action of PCNSL in NR at high shear rate and temperature conditions. However, it is essential to study the processability characteristics (particularly the mixing behaviour) of PCNSL modified NR at lower shear rates similar to that encountered in an internal mixer such as Brabender Plasticorder. Since NR modified with 10 phr of PCNSL showed better plasticizing action in NR as compared to the same dosage of spindle oil over a wide range of shear rates, the present study has been confined to unmodified NR and that containing 10 phr of PCNSL only.

A preliminary study on the processability of NR formulations modified with PCNSL in a Brabender Plasticorder under various conditions of temperature and rotor speed indicated their improved mixing characteristics as compared to the unmodified sample [114]. The results indicate the plasticizing and softening action of PCNSL in NR and the better scorch safety of the modified formulations. In the present context, the processability of raw NR and a homogeneous mixture of NR with PCNSL (10 phr) has been studied in a Brabender Plasticorder at rotor speeds ranging from 30 to 90 rpm and temperatures ranging from 100°C to 140°C. From the equilibrium values of torque, various parameters such as melt viscosity, melt elasticity and power consumption for mixing have been estimated. The Brabender torque vs time profiles for unmodified NR and PCNSL modified NR obtained at various temperatures and rotor speeds are given in Fig.III.8(a&b respectively). Figure III.9(a) shows plots of torque to rotor speed ratio (an index of melt-viscosity) vs rotor speed. Figure III.9(b) shows plots of band-width (an index of melt-elasticity) vs rotor speed in the temperature range from 100°C to 140°C. The values of equilibrium torque and power consumption during mixing are given in Table III.7

The torque-profiles shown in Fig.III.8 show a steady reduction in the torque values indicating distinct improvement in the processability of NR containing 10% of PCNSL at various rotor speeds and temperatures. The smoothness of the torque-profile in presence of PCNSL, particularly at the higher rotor speeds (60 & 90 rpm) and temperatures (120°C & 140°C), is indicative of superior processability of PCNSL modified NR compared to that of the unmodified NR sample. Quite often, higher values of torque and band-width in a torque-time plot from Brabender Plasticorder are indicative of poor moldability. The higher torque values suggest a higher average molecular weight and the wider band-width reflects a greater degree of elasticity[115]

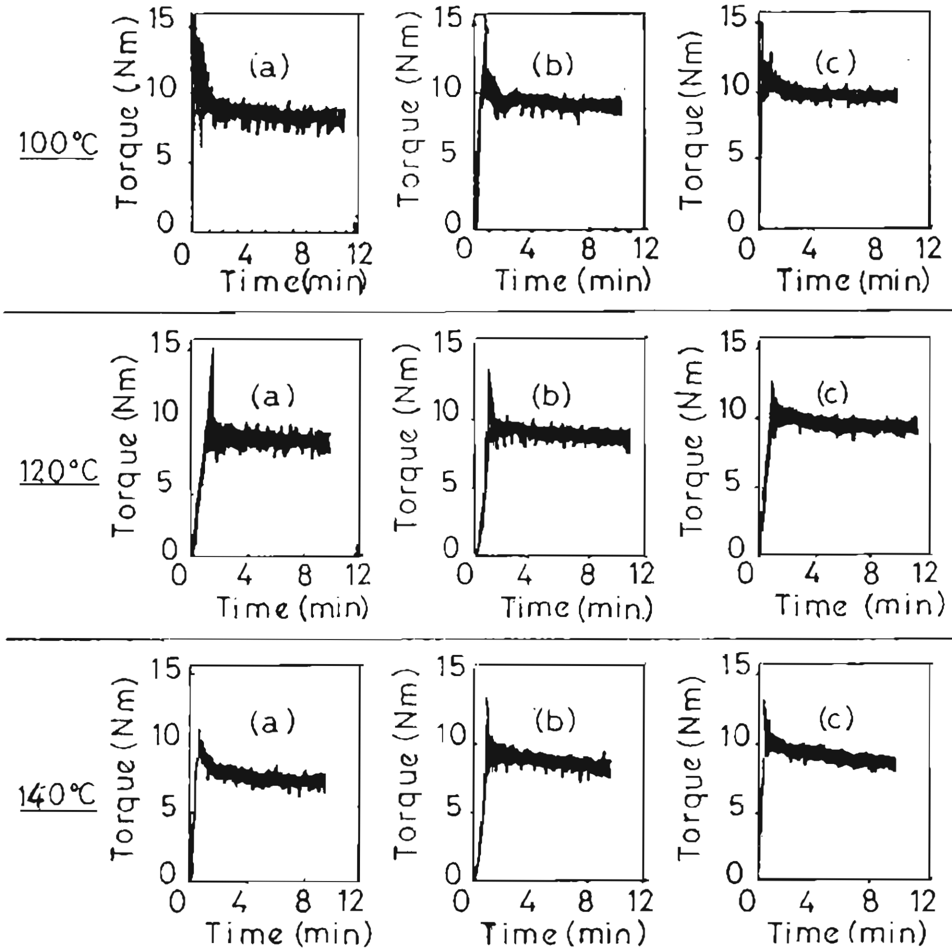

Fig.III.8(a).Brabender torque-profiles of unmodified NR at 100°C, 120°C & 140°C
Rotor speed (rpm) - (a) 30 (b) 60 (c) 90

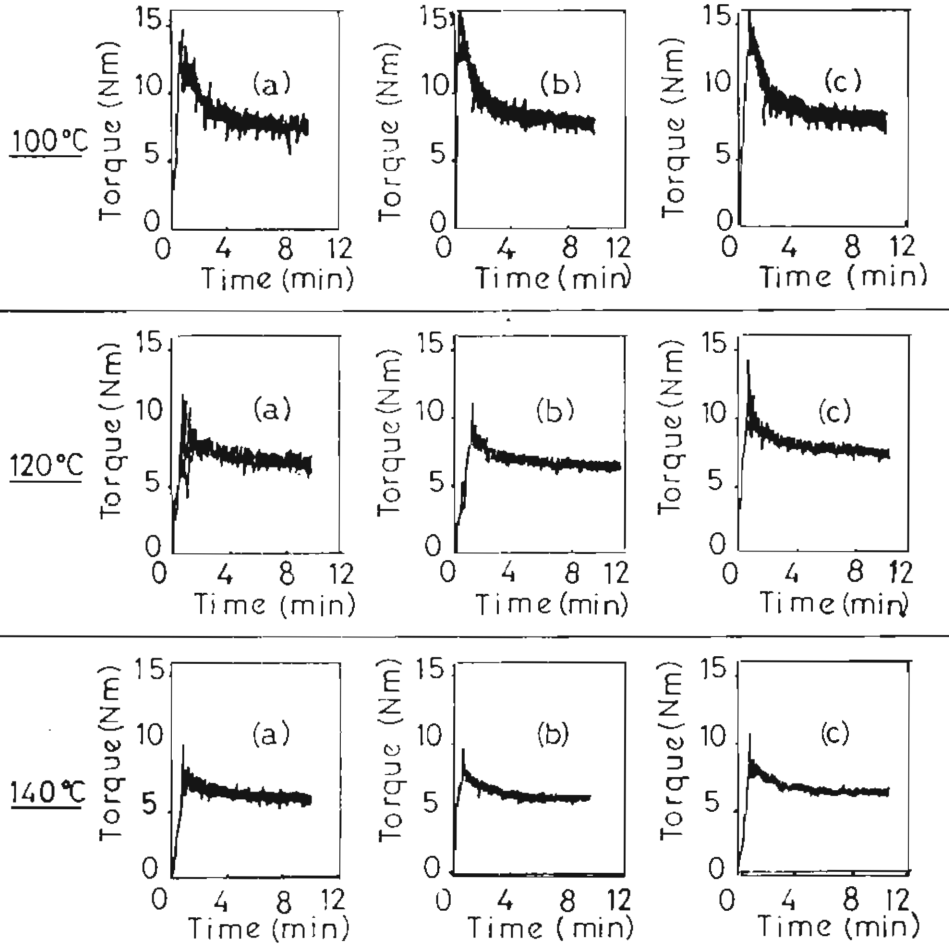

Fig.III8(b) Brabender torque-profiles of PCNSL-modified NR at 100°C,120°C & 140°C

Rotor speed (rpm) - (a) 30 (b) 60 (c) 90

Table III 7 Processability of NR before and after modification with PCNSL in a Brabender Plasticorder at 100°C, 120°C and 140°C

Temp (°C)	Sample	NR			NR+PCNSL(10%)		
	Rotor speed, S (rpm)	30	60	90	30	60	90
	Shear rate, (s^{-1})	34	68	102	34	68	102
100	Equilibrium torque, M (Nm)	9.25	10	10.25	8	8.25	8.5
	Power consumption for mixing, P (W)	29.04	62.80	96.55	25.12	51.81	80.07
120	Equilibrium torque, M (Nm)	9.25	9.75	10	7.5	7.6	7.75
	Power consumption for mixing, P (W)	29.04	61.23	94.20	23.55	43.96	73.00
140	Equilibrium torque, M (Nm)	8	9	9.25	6.5	6	6.75
	Power consumption for mixing, P (W)	25.12	56.52	87.14	20.41	37.68	63.59

The PCNSL modified NR shows lower melt-viscosity and melt-elasticity than the unmodified NR at all rotor speeds and temperatures The melt viscosity index of the samples has been calculated from the ratio of equilibrium torque (M) and rotor speed (S), assuming a Newtonian dependence of shear stress on torque and shear rate on rotor speed(115) . The reduction in melt-viscosity index with the increase in rotor speed (shear rate) and temperature is quite prominent for the PCNSL modified NR compared to the unmodified NR sample as shown in Figure III 8 The shear rate obtained at the rotor speed range of 30 rpm (23 s^{-1}) to 90 rpm (103s^{-1}) includes most of the milling and calendering shear rate range (10 s^{-1} to 100 s^{-1}) The relatively lower band-width of the PCNSL modified NR and its higher rate of decrease with increase in rotor speed and temperature compared to that of the unmodified NR as shown in Fig.III.9(b) clearly indicate a significant reduction in melt-elasticity of the former

The equilibrium values of the Brabender torque at different rotor speeds and temperatures of NR with and without PCNSL are given in Table III 7 The results show that the increase in torque with respect to rotor speed is relatively lower for the PCNSL modified NR as compared to that of the unmodified sample at 100°C,120°C and 140°C Also, with an increase in temperature from 100°C to 140°C, the torque (at the different rotor speeds) decreases considerably for PCNSL modified NR as compared to that for the unmodified sample This is of particular significance with respect to mixing, since a lower value of equilibrium torque leads to lower energy consumption for mixing. Thus, the relatively lower power consumption for the PCNSL modified sample during mixing at various shear rates and temperatures clearly indicates its processing advantage over the unmodified sample. This in turn may be used advantageously to enhance the productivity of NR compounds modified with PCNSL by operating at higher rotor speeds and temperatures.

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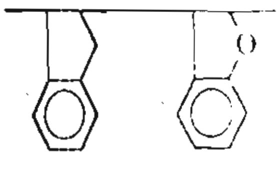
CHAPTER - IV

PCNSL AS A TACKIFIER

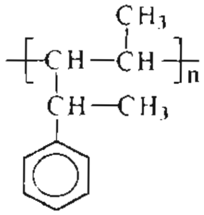
A part of this chapter has been published in the 'Journal of Adhesion Science and Technology', 9(4), 433 (1995).

IV.1. Introduction.

NR is endowed with a high natural tack or self adhesion strength compared to many of the synthetic rubbers such as styrene butadiene rubber (SBR), butadiene rubber (BR), butyl rubber (IIR) and ethylene propylene diene rubber (EPDM) (1). But for many of its applications, it becomes essential to increase the self adhesion strength (tack strength) of NR by modification with suitable tackifiers. The tack strength of the rubber compound used is an essential criterion with respect to the fabrication stage of composite products such as automobile tires, footwears etc (2). Some of the tackifiers used in rubber compounding include (i) coumarone indene resins (I),

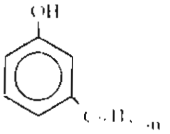


(I) Coumarone indene resin



(II) C_5terpene hydrocarbon resin

(ii) C_5 terpene hydrocarbon resin (II) and (iii) linear and intramolecular p-alkylated phenolic resins (eg. based on p - octyl phenol) (3,4). Tackifiers from alkyl phenols were reported to give improved tack retention under high relative humidity and temperature along with good physico mechanical properties of the vulcanizates (5). Alkyl phenol based poly condensation products of the novolak types are widely used as tackifiers in compounding for tires(6) Polyterpene resins based on beta-pinene and dipentene were found to increase the peel - adhesion strength of NR formulations (7). The use of tackifying additives of a resinuous type such as colophony, cumar or coumarone - indene resins for the maintenance of tack in NR has also been mentioned (2). CNSL ('technical grade', conforming to Indian Standard specification IS 840 (1964)) contains cardanol (meta penta decenyl phenol) (III) as its major component (8).



(III)Cardanol n 0, 2.4.6

Since the only difference of cardanol from p-octyl phenol is that the hydrocarbon side chain of the former is at the meta position of the phenolic ring and that it is unsaturated, the phosphorylated derivative of CNSL (PCNSL) was expected to show the properties of a tackifier in NR.

IV.2. Self adhesion strength

Brown (9) has pointed out the possibility for a high degree of variability in the test results from tack measurements. This is particularly prominent in rapid test methods (10) such as Monsanto tel-tack, loop peel method or Wallace rapid tack test, where the probability of operator error is high Bussemaker and van Beek (11) have reported a method for the tack measurement of rubber plies (with a minimum of standard deviation) involving 180° separation of the substrates, after bringing them into contact. The 180° peel test / T - peel test conforming to the standard ASTM D-903-49 (1978) has been used widely to measure the self adhesion strength of elastomers (12-16).

The factors affecting the tack strength of elastomers has been studied extensively by various investigators (11, 15-24). Bussemaker and van Beek (11) have identified some of the factors affecting tack measurement as surface smoothness, dirt, aging and thickness of the plies and compression conditions such as contact time, contact pressure and temperature. The dependence of tack of elastomers on the rate of measurement and contact time has been described by Hamed and Shieh(15). Gent and Kim (19) observed that autohesion is controlled by intimate molecular contact at the interface of the substrates coming into contact. The dependence of tack strength on molecular properties was studied by Forbes and Mc Leod (20). They proposed an improvement in tack - bond strength with a decrease in molecular weight and a limited increase in temperature, pressure and contact time. Voyutskii (21) reported that the factors favouring diffusion and mutual compatibility between the substrates generally favour an increase in adhesive strength Some of these include increase in contact time, rise of the temperature of contact, increase of flexibility of molecular chains, decreased number and size of branching and so on. Andries and Rhee(22) reported that a maximum tack is obtained at an optimum molecular weight of the polymer and that it will decrease with increasing carbon black level and surface area. They also studied the dependence of tack on the dosage, structure and molecular weight of tackifiers, the amount of processing of the stock, aging of the sample and conditions of measurements such as temperature and humidity. The effect of interfacial bonding on the self adhesion strength of elastomers has been studied by Chang and Gent(23) and Bhowmick and Gent (24) They found that the main factors controlling the threshold adhesion strength were the number and length of molecular chains across the interface.

Though the self adhesion strength of elastomers is dependent on various factors as mentioned above, it was found worthwhile to study the effect of variations in some of the 'technologically important' variables such as contact time, contact pressure, dosage of tackifier and 'storage time' after contact, on the self adhesion strength of NR formulations modified with PCNSL. In a typical SEV system of NR, the dosage of PCNSL was increased from 0 to 20 phr. The formulations are given in Table IV.1.

Table IV.1. Formulations of NR containing different proportions of PCNSL

Mix code	M_0	M_5	M_{10}	M_{15}	M_{20}
PCNSL content (phr)	0	5	10	15	20

Base mix :- NR - 100, ZnO - 10, Stearic acid - 2, Sulphur - 2, MBT - 1.5, TMT - 0.5

The mixes were prepared on a two roll mill and test specimens were prepared from uncured sheets compression molded at room temperature. The self adhesion strength of these mixes was measured with variations in contact time, contact pressure and storage time prior to testing as per the standard 180° peel test, on a tensile tester (ZWICK UTM , model 1435) at a crosshead speed of 50 mm/min. The self adhesion strength G_c was calculated from the mean force of separation F and the width of the sample w , using the relation $G_c = (2F / w)$, as reported by Gent (25).

i. Effect of variations in the dosage of PCNSL

The self adhesion strength of NR formulations containing 0 to 20 phr of PCNSL, is given in Table IV.2.

Table IV.2 .Effect of dosage of PCNSL on the self adhesion strength of unfilled NR formulations.

Mix code	M_0	M_5	M_{10}	M_{15}	M_{20}
Self adhesion strength (kN / m)	2.01	2.26	2.33	1.79	1.75
Standard deviation (kN/m)	0.03	0.05	0.16	0.11	0.20

Contact time = 60 s. Contact pressure = 0.2 N / mm^2

The results show an increase in self adhesion strength with an increase in concentration of PCNSL upto 10 phr and a decrease there after at higher concentrations. Peaks in the tack- force plots are reported to occur at specific resin / rubber ratios in a wide range of polymer - resin mixtures (26). Following the mechanism proposed by Wake (2), it is assumed that at lower concentrations of PCNSL eg. 5 phr, a single NR / PCNSL phase may exist. At higher concentrations eg. at approximately 10 phr, a second dispersed phase may form both in the bulk and at the contacting surfaces leading to a 'liquid-like tack' from a multitude of droplet contacts. This helps in wetting the contacting surfaces and forming an intimate contact between them. It is expected that the plasticizing effect of PCNSL on NR facilitates the interfacial diffusion of macromolecules of NR resulting in higher self adhesion strength upto the concentration of 10 phr of PCNSL in NR. Ansarifar et. al (16) have shown that limited interdiffusion near the interface may lead to strong mutual adhesion in unvulcanized elastomers The significance of viscous flow of polymers followed by interdiffusion in developing self adhesion strength in elastomers has been pointed out by Symes and Oldfield (27) Gent and Tobias (28) suggested the possibility for interlinking by molecular entanglements in such a system The reduction in self adhesion strength at the higher concentrations of PCNSL (15 and 20 phr) may be due to the formation of a weak boundary layer of resin- rich phase on the surface of NR. Due to the low cohesive strength of this phase, cohesive failure in this phase is more likely to take place than the adhesive failure between the substrate and the resin rich phase. Thus, the observed variation in self adhesion strength of PCNSL modified NR is in agreement with the fact that plasticizers can increase tack at lower concentrations and reduce it at higher concentrations (2).

ii. Effect of variation in contact time

The self adhesion strength of the formulations are given in Table IV.1 The contact time was varied from 15s to 120s at a contact pressure of 0.2 N/mm^2 . The variations in self adhesion strength with contact time for different samples at room temperature are shown in Figure IV.1(a). It shows a maximum self adhesion strength for the unmodified NR compound at a contact time of 30 s. The self adhesion strength of the samples containing 5 and 10 phr of PCNSL reaches a maximum (above that of the unmodified sample) at 60s and remains stable there-after upto a contact time of 120s. However, the stabilized values of the self adhesion strength for the samples containing 15 and 20 phr of PCNSL are below that of the unmodified sample.

Generally, an increase in self adhesion strength with an increase in contact time may be due to the interdiffusion of macromolecule chain ends across the interface (29). After a certain time of contact, the contact zone will disappear and the tack-strength will become identical to that of bulk strength ('cohesive strength') of the elastomer (15, 30) . The occurence of an initial time-dependent wetting followed by interdiffusion has been reported by Wool (31) . Gent and Kim (19) studied the effect of contact time on tack and found that autohesion is controlled by the intimate molecular contact at the interface. It is possible that in presence of 5 to 10 phr of PCNSL, a greater degree of interfacial diffusion of chain ends occur (though at a higher contact time), leading to a higher self-adhesion strength.

iii. Effect of variation in contact pressure

Figure IV.1(b) shows the variations in the self adhesion strength of the formulations at various contact pressures The increase in contact pressure from 0.2 N/mm^2 to 0.55 N/mm^2 did not result in an increase in self adhesion strength in any of the PCNSL modified NR formulations . This shows that adequate contact between the surfaces required for a high self adhesion strength is achieved even at the low contact pressure of 0.2 N/mm^2 However, the self adhesion strength of the NR formulation containing 10 phr of PCNSL is higher than that of the unmodified sample at all the contact pressures tested

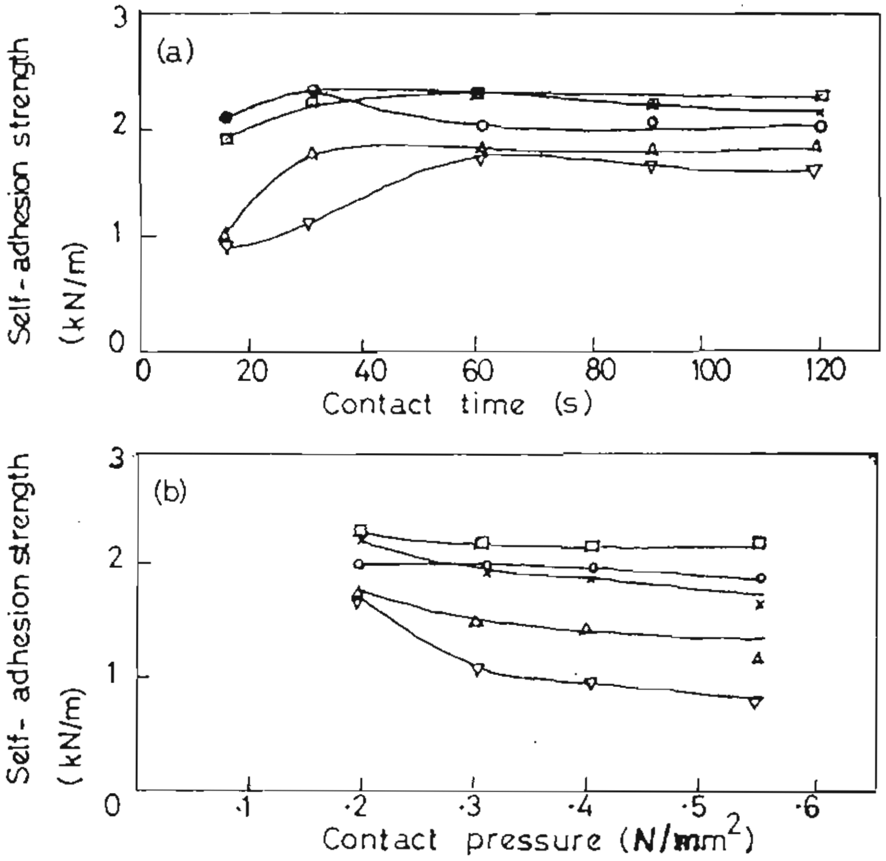


Fig.IV.1. Effect of variations in (a) contact time and (b) contact - pressure on the self-adhesion strength of PCNSL - modified NR formulations

PCNSL (phr) - ○—○ 0 ×—× 5 □—□ 10 △—△ 15

▽—▽ 20

The existence of a 'saturation point' in contact pressure at which maximum molecular contact ('wetting') occurs has been observed by Wool [31]. The above results show that the contact pressure required for maximum self adhesion strength in the PCNSL modified NR formulations is comparatively lower than that of the unmodified sample, implying the ease of wetting of the substrates in presence of PCNSL

iv. Effect of variation in storage time before testing

The 'maturation' during storage of freshly mixed rubber compounds generally affects its processing properties [32]. It is essential that composite products such as tires should maintain their self adhesion strength till curing after assembling and the assembly should remain intact during the storage time between fabrication and final curing. Forbes and Mc Leod [33] observed that the 'relative tack strength' of NR increases from 0.53 to 1, with an increase in storage time from 30 minutes to 4 -5 hours. Figure IV.2 shows that on storing the contacted test specimens at room temperature from 3 to 7 days prior to testing, the self adhesion strength increases above that of the initial value for the unmodified NR formulation and for that containing 5 to 15 phr of PCNSL. This is presumed to be due to better interfacial diffusion occuring during storage, particularly for the samples containing 5 to 15 phr of PCNSL. Also, the failure mode changed gradually from 'interfacial' to 'cohesive' in nature with the increase in storage time showing a higher degree of 'homogenity' in the system

v. Effect of variation in dosage of PCNSL in the substrates

In the manufacture of products such as tires, hoses, footwears, etc., the desired degree of self adhesion strength of the plies may be obtained by the incorporation of 'optimum doses' of tackifying resins in the rubber compounds. In such applications, though the plies coming into contact may have different concentrations of tackifiers or other additives depending on the performance requirement, the product as a whole should have sufficient self adhesion strength and 'compatibility' between the components

Figure IV.3 shows the effect of variation in the dosage of PCNSL in one of the substrates on the self adhesion strength at concentrations of PCNSL ranging from 0 to 20 phr in the other. The figure shows that the self adhesion strength of the assembly increases to a maximum in presence of 5 to 10 phr of PCNSL in the second substrate for the samples containing 0 and 5 phr of PCNSL in the first substrate. This is presumed to be due to the greater extent of interfacial diffusion of NR in presence of low concentrations of PCNSL. Also, it was observed that the adhesion strength did not increase when PCNSL was present in only one of the substrates at concentrations above 15 phr. In the former case, the failure in peel adhesion test was found to be 'cohesive' in nature in the phase containing the higher concentration of PCNSL. This is expected, since the lower cohesive strength of the phase containing the higher concentration of PCNSL facilitates failure along this path. In the latter case, when both the substrates contain PCNSL above 15 phr, lower cohesive strength of the assembly as a whole leads to an early 'cohesive failure'.

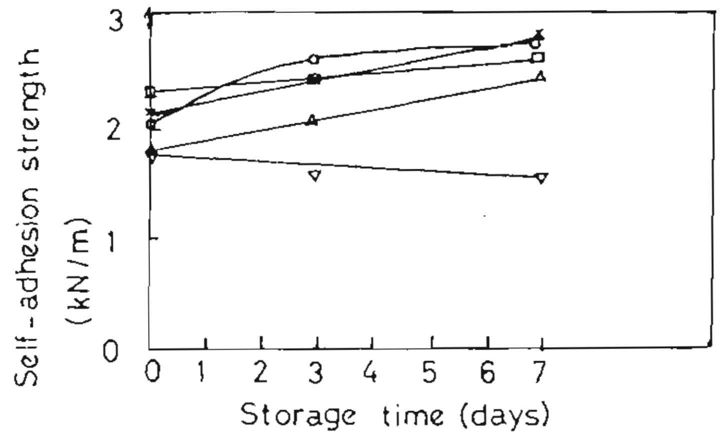


Fig.IV.2. Effect of storage time on self-adhesion strength of PCNSL modified NR formulations

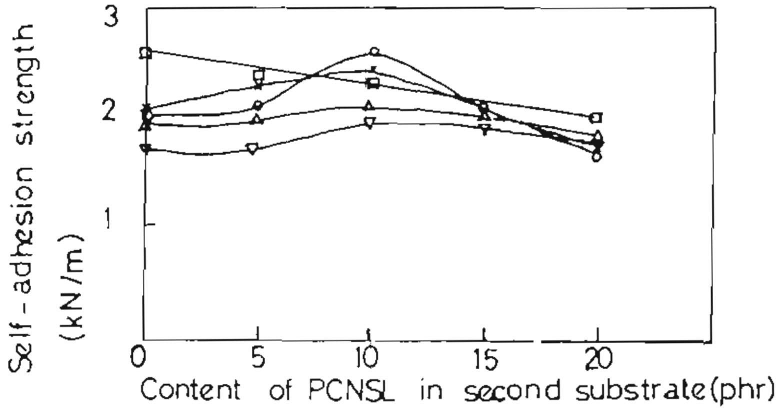


Fig.IV.3. Effect of variation in the content of PCNSL in second substrate on the self-adhesion strength

PCNSL(phr) ○—○ 0 ×—× 5 □—□ 10 △—△ 15 ▽—▽ 20

The foregoing discussion shows the improvement in self adhesion strength of gum NR, obtainable by compounding it with 5 to 10 phr of PCNSL which is assumed to be partly due to a higher extent of 'interfacial diffusion' of the molecules of NR, presumably resulting from the enhanced mobility of the molecules of NR in presence of PCNSL. However, the higher extent of softening of NR in presence of 15 to 20 phr of PCNSL leads to a reduction in the self adhesion strength, possibly due to the reduction in the 'green strength' of the NR matrix. The progressive increase in self adhesion strength of PCNSL modified NR with storage time prior to testing indicates the possibility of 'time-dependent interfacial diffusion' of NR in these samples.

Thus, the above results all-together establishes the role of PCNSL as a 'tackifier' in NR at lower concentrations of 5 to 10 phr (34).

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V.1. Introduction

Some of the prime requirements of a 'high performance elastomer' as observed by Mark and Erman (1) consists of higher values of modulus at rupture (tensile strength), elongation at rupture (maximum extensibility) and energy at rupture (toughness), maintenance of rubber- like elasticity at low temperatures (a low value of T_g) besides high temperature stability, resistance to chemical agents, solvents, etc., some of these features being mutually exclusive(2,3). It is essential that the modification of elastomers or the additives used for compounding should not adversely affect the physico-mechanical properties of the vulcanizate; rather they should improve them. The multifunctional role of PCNSL in NR as a plasticizer, processing aid, softening agent and tackifier leading to improvements in processability have been described in Chapters III and IV. It is equally important that upon modification of NR with PCNSL, the composition should have the desirable cure characteristics and the final product in the vulcanized form should have an acceptable combination of physico-mechanical properties suitable for a variety of applications. This necessitated a detailed study on the cure characteristics and physico-mechanical properties of PCNSL modified NR in gum and filled vulcanizates. The cure characteristics of these formulations were determined essentially by (i) the nature of vulcanization system (eg. CV, SEV and EV), (ii) the dosage of PCNSL and (iii) the dosage of cure activator (ZnO) which is particularly important in this case of PCNSL modified stocks as it bears a direct relationship with cure .

V.2. Cure characteristics of the mixes.

Generally, the cure characteristics of an elastomeric compound is of foremost importance as it dictates the processing conditions and the properties of the final product for any specific end use and vice-versa Though there exists a variety of methods for crosslinking of elastomers such as 'resin-cure' (4-8) , curing with quinone derivatives and maleimides, 'metal oxide cure' (8), 'peroxide-cure' (8,9), micro-wave / radiation curing (10,11) apart from sulphur cure, sulphur has maintained an enviable status of an 'ideal crosslinking agent' for most of the applications (12) for more than a century ever since the discovery of vulcanization in 1839 (13,14) The continuing popularity of sulphur as a crosslinking agent has been attributed to a variety of reasons such as low cost, ease of availability, fast vulcanization, minimal interference with other compounding ingredients and the excellent balance of properties in the final product (12). Some of the factors determining the choice of vulcanizing agents have been identified to be (i) processing safety, (ii) cure rate and state of cure, (iii) reversion resistance (iv) vulcanizate properties and (v) cost (12). Thus, in an ideal case the compounding ingredients used should not cause premature cure (scorching) during processing , should provide adequate rate and state of cure during crosslinking; should have considerable resistance to deterioration in the vulcanizate properties on over-cure, should give an optimal combination of end use properties in the final product and preferably should provide all of the above at an affordable cost. This necessitates an indepth study of the physico chemical changes taking place during the processing in rubber involving interactions between polymer and additives such as filler, plasticizer, activators, curatives and so on This results in a characteristic change in physico-mechanical properties

Some of the fillers such as carbon blacks are known to increase the rate of cure (15) while some of the non-black fillers such as silica may cause 'cure-retardation' by interactions with the cure-accelerators present in the system (16) Besides, plasticizers and other additives having acidic character may reduce the rate of cure(17). Hence, it is essential to have a proper understanding of the cure characteristics of the formulations designed for specific applications Thanks to the availability of a variety of 'rubber - compounding ingredients', along with a fairly good knowledge of their behaviour in rubber compounds, today it is possible to design formulations to meet the specific service requirements of the customer. The versatility of the compounding technique is clear from the fact that minute changes in the processing parameters can have profound influence on the ultimate properties of the finished product(18) . Thus, small changes in the accelerator / sulphur ratio in the compounding formulations can lead either to 'conventional'(<1), 'semi-efficient' (=1) or efficient' (>1) vulcanization systems with widely varying physico-mechanical properties (12 Similarly, the vulcanization characteristics of elastomer formulations are considerably affected by the nature and dosage of cure - activators and accelerators.

Rapid and direct measurements of the cure characteristics of rubber compounds can be made on a series of instruments called 'cure-meters' (20,21) among which those measurements that are carried out in an Oscillating Disc Rheometer (ODR) are widely accepted (22) . The torque registered by this instrument is directly proportional to the crosslinks formed within the rubber compound during vulcanization. This torque is an indication of the modulus of the compound (20). The Brabender Plasticorder can also be used as a sensitive tool to monitor the crosslinking of elastomers(23) . The slope of the torque profile at the termination of a steady state gives a measure of the rate of cure. The crosslinking starts at this stage Also, the bandwidth increases as crosslinking takes place in the material with resultant increase in the elasticity.

In the present work, the effects of compositional variables on the cure characteristics of NR in presence and absence of PCNSL and other additives have been studied

i. Effect of PCNSL on NR in different vulcanization systems

The conventional vulcanization (CV) system of elastomers obtained with a high sulphur / accelerator ratio (>1) generally have a higher proportion of polysulphidic crosslinks in the vulcanizates, possess superior physico-mechanical properties and poor thermal stability, whereas the efficiently vulcanized (EV) systems with the lowest sulphur / accelerator ratio impart excellent thermal stability but at the expense of strength properties to the vulcanizates In many cases, the 'semi-efficient vulcanization' (SEV) systems are found to strike an optimal balance between the two. The SEV systems usually have an accelerator / sulphur ratio of 1:1. (24) They may find applications in volume - market for tire treads (12) Also, in the automotive suspension components SEV systems give longer life than those using CV and EV systems (25).

The effect of CV, SEV and EV systems on the cure characteristics of gum NR formulations modified with PCNSL has been studied. The dosage of PCNSL was varied from 0 phr to 20 phr in all the systems. The formulations are given in TableV.1(a). The rheographs of the compounds obtained from the Oscillating Disk Rheometer at 150°C are shown in Figure V.1. The cure characteristics at 150°C of the mixes are given in in Table V.1(b).

Table V.1(a) Formulations of the NR gum mixes by varying the cure systems and dosage of PCNSL.

Vulcn system*	CV	CV	CV	SEV	SEV	SEV	EV	EV	EV
Mix code#	C_0	C_{10}	C_{20}	S_0	S_{10}	S_{20}	E_0	E_{10}	E_{20}
Sulphur	2.5	2.5	2.5	2.0	2.0	2.0	0.5	0.5	0.5
MBT	0.6	0.6	0.6	1.5	1.5	1.5	2.5	2.5	2.5
TMT	0.2	0.2	0.2	0.5	0.5	0.5	0.5	0.5	0.5
PCNSL	0	10	20	0	10	20	0	10	20

* - Base mix (phr) :- NR 100, ZnO 15, Stearic acid 2

Subscript indicates the dosage of PCNSL in the mix

V.1.(b) Effect of different vulcanization systems on the cure characteristics at 150°C of NR formulations containing different dosages of PCNSL.

Vulcn. system	CV	CV	CV	SEV	SEV	SEV	EV	EV	EV
Mix code	C_0	C_{10}	C_{20}	S_0	S_{10}	S_{20}	E_0	E_{10}	E_{20}
Scorch time t_2 (s)	143	150	173	100	112	120	140	160	160
Optimum cure time t_{90} (s)	270	600	1170	210	240	315	375	450	465
Maximum cure L_f (dNm)	42	33.3	27.8	70	40	35.5	34.5	25	18.5
Cure rate (s^{-1})	0.78	0.22	0.10	0.85	0.78	0.51	0.41	0.34	0.33

Fom the results given in Figure V.1 and Table V.1 (b) it is clear that the SEV systems give a relatively higher 'rate of cure' as well as the highest state of cure as compared to the CV and EV systems. However, the increase in dosage of PCNSL results in a progressive decrease in the torque values in all the vulcanization systems. Also, it is noteworthy that the SEV systems attain a maximum state of cure in less time in the unmodified and PCNSL modified NR formulations as compared to that observed for CV and EV systems. Also, the ' plateau effect ' is very significant for the SEV systems over a longer period of time leading to the conclusion that there is less tendency for 'cure - reversion'. In addition, the data indicates a higher degree of 'scorch - safety' for the

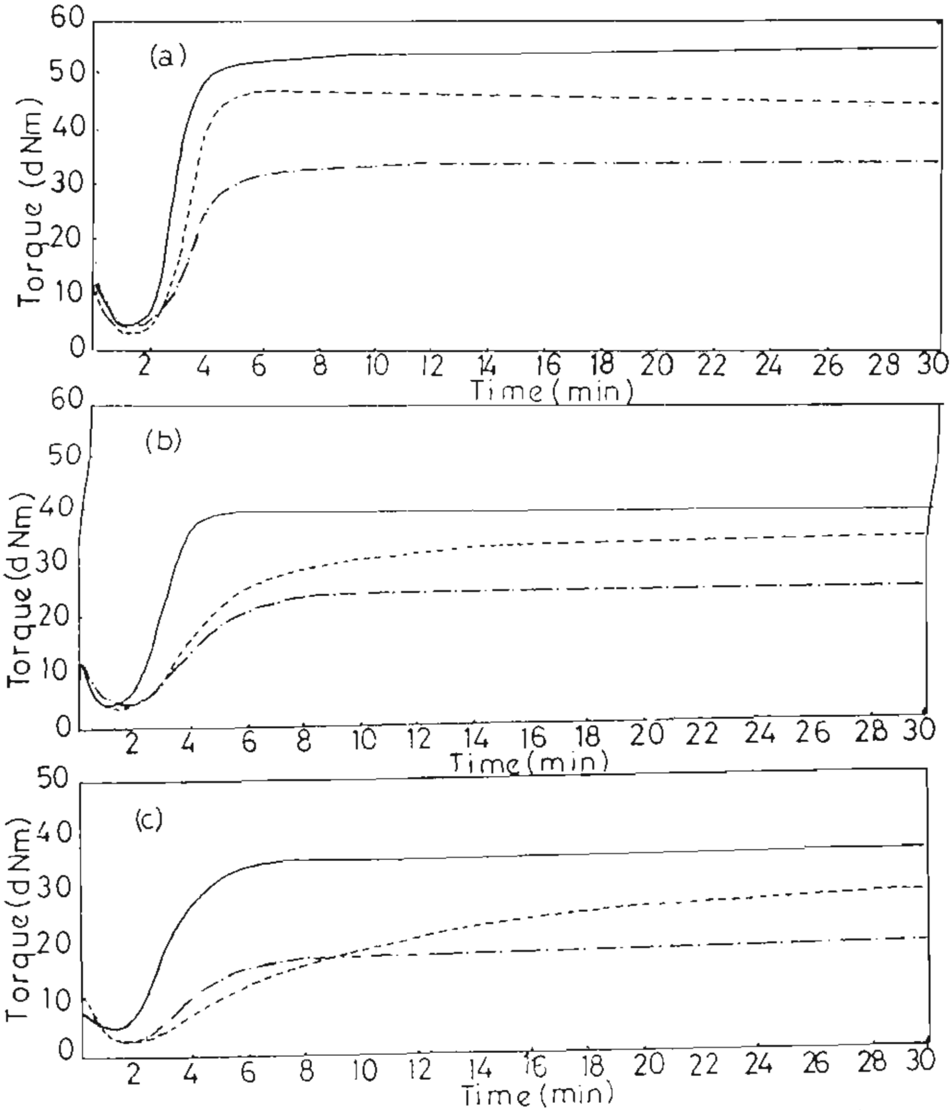


Fig.V.1. Rheographs of NR formulations containing (a) 0, (b)10 and (c) 20 phr of PCNSL.

—— SEV ---- CV —·—·EV

PCNSL modified NR formulations vulcanized by conventional and efficient vulcanization systems However, the optimum cure time goes on increasing rapidly with the incorporation of PCNSL in the mixes.

ii. Effect of different accelerator types and doses

The results mentioned in the preceding section indicates the superiority of SEV systems of PCNSL modified NR formulations over those of the CV and EV systems with respect to cure characteristics such as high rate and state of cure and reversion resistance. Hence, an SEV system was selected for further studies. However, the cure characteristics are determined to a great extent by the nature and type of accelerator or accelerator combinations used and their proportions.

The effect of different types of accelerators, either alone or in combination with other accelerators on the cure characteristics and physico-mechanical properties of NR modified with PCNSL has been studied The vulcanization system chosen was SEV only. The formulations are given in Table V 2 (a). The cure characteristics at 150°C of these formulations are given in Table V.2 (b). It shows that the mix S6 containing 1.5 phr of MBT and 0.5 phr of TMT exhibits the maximum state of cure (35 5 dNm), higher scorch time (120 s) and a high cure rate index ($0.51s^{-1}$). Hence, this accelerator combination has been selected for detailed studies.

Table V.2. (a) Formulations* of the mixes based on NR by varying the accelerator type and dosage in a SEV system.

Mix No:	S1	S2	S3	S4	S5	S6	S7	S8
Accelerators (phr)								
MBTS	2	1.5	-	-	-	-	-	-
TMT	-	0 5	0.5	0.5	-	0.5	-	0.5
CBS	-	-	1 5	-	-	-	-	-
MOZ	-	-	-	1.5	-	-	-	-
MBT	-	-	-	-	2	1.5	-	-
ZDC	-	-	-	-	-	-	2	1.5

* Base formulation - NR 100, ZnO 15, Stearic acid 2, Sulphur 2, PCNSL 20

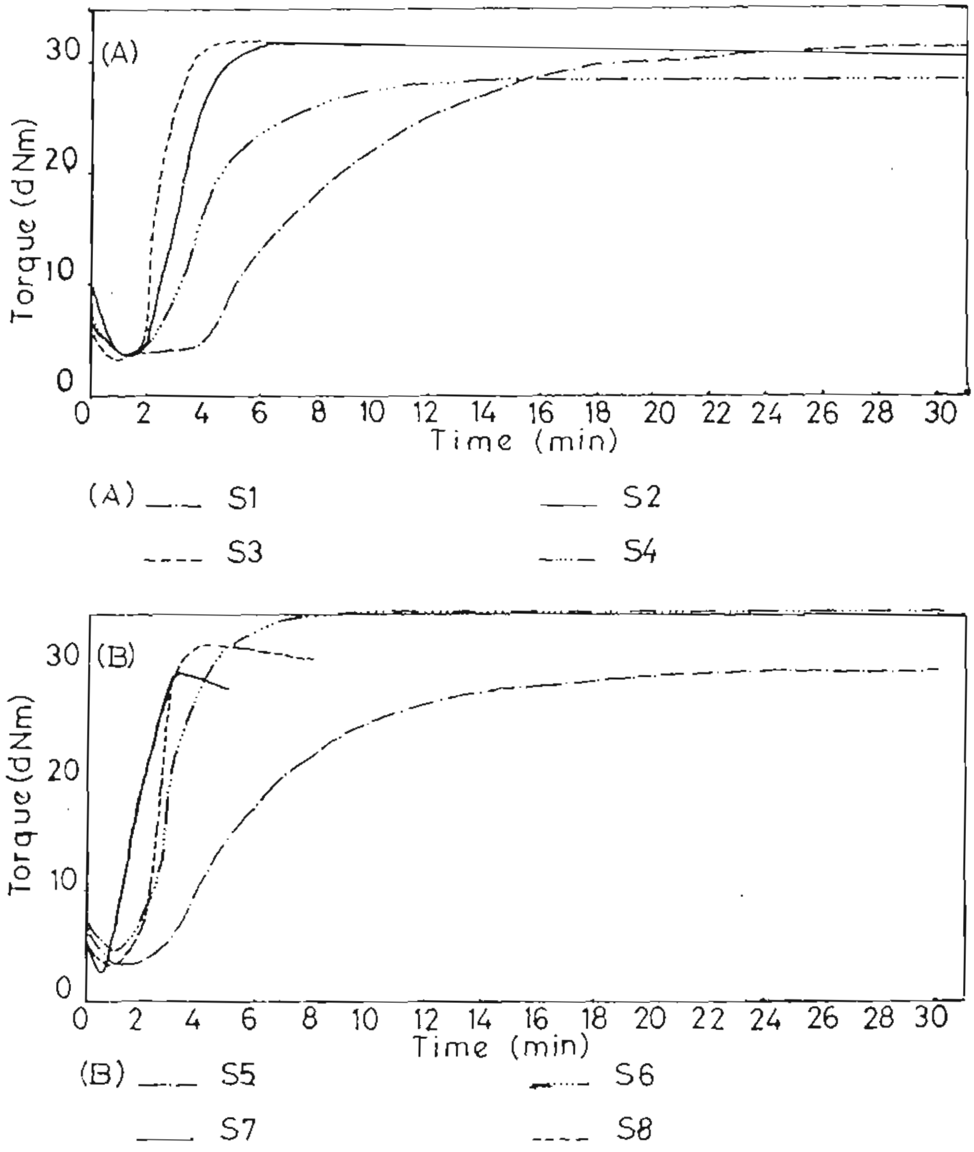


Fig.V2 Rheographs at 150°C of PCNSL modified NR formulations containing different accelerators. (PCNSL -20 phr)

Table V.2 (b). Cure characteristics at 150°C of PCNSL modified NR formulations containing various accelerators. (ODR- 100S)

Mix No.	S1	S2	S3	S4	S5	S6	S7	S8
Parameter								
Scorchtime, t_2 (s)	210	150	110	165	150	120	75	105
Maximum cure, L_f (dNm)	31.5	32	32	28.8	30	35.5	30	32.5
Optimum *cure time*, t_{90} *(s)*	1080	270	210	480	750	315	150	195
Cure rate,$(100/(t_{90} - t_2))(s^{-1})$	0.12	0.83	1	0.32	0.17	0.51	1.33	1.11

The rheographs at 150 °C of the above formulations are given in Figure V.2. The **higher** degree of torque- stability of the sample containing MBT and TMT probably **indicates** its superior reversion resistance.

iii. Effect of PCNSL content.

It has been reported earlier that modification of NR formulations with increasing **dosages** of PCNSL resulted in relatively 'softer' vulcanizates having a lower state of **cure**[36]. The effect of increase in dosage of PCNSL on the cure characteristics of a SEV **system** of NR has also been studied using an Oscillating Disk Rheometer (ODR) at 150°C. **The** cure parameters such as scorch time, optimum cure time, cure rate index and **maximum** state of cure of these samples are given in Table V.3. The rheographs of the **formulations** containing 0, 10 and 20 phr of PCNSL are shown in Figure V.3.

Table V.3. Effect of PCNSL content on the cure characteristics of NR gum at 150°C.

Dosage of PCNSL (phr)	0	10	20
Scorch time, t_2 (s)	105	150	150
Optimum cure time, t_{90} (s)	218	270	480
Cure rate, (s^{-1})	0.89	0.83	0.30
Maximum cure, L_f (dNm)	73	38.8	26.3

†**Base mix** :- NR - 100, ZnO - 10, Stearic acid - 2, Sulphur - 2, MBT - 1.5, TMT - 0.5

The above results show a progressive reduction in the 'ultimate state of cure' with **an** increase in the dosage of PCNSL. Also, an increase in concentration of PCNSL above **10 phr** resulted in a considerable reduction in the cure rate index. Besides, the scorch time **of the** NR compound increased from 105 s to 150 s in presence of 10 to 20 phr of **PCNSL**. The results obtained from the ODR are analogous to that obtained in an earlier study carried out under more dynamic conditions in a Brabender Plasticorder (37). Chemical analysis of the vulcanizates containing different doses of PCNSL showing comparatively lower chemical crosslink density (CLD) in presence of PCNSL(38) are shown subsequently

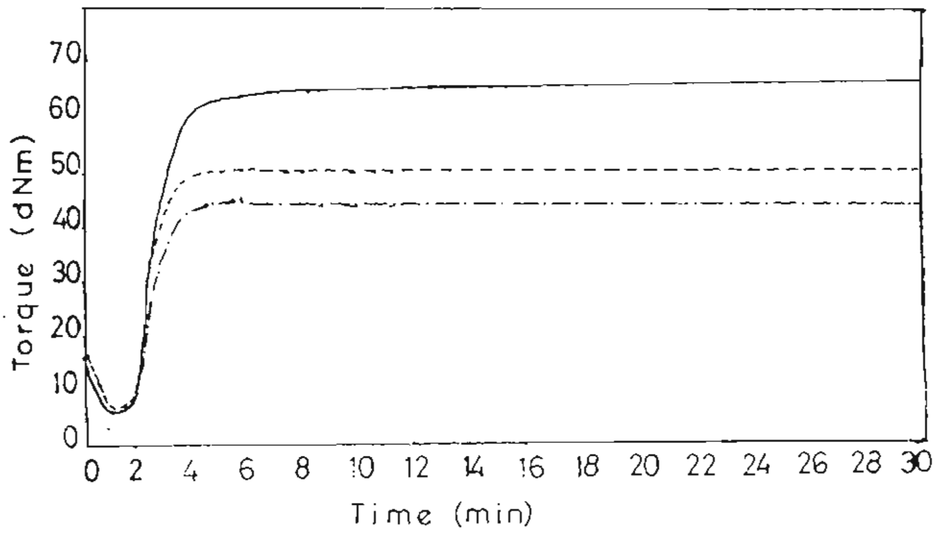


Fig.V.3. Rheographs at 150 °C of NR formulations containing various dosages of PCNSL

PCNSL (phr) ——— 0 - - - - 10 —·— 20

in section V 4 of this chapter. The lower rate and state of cure of the PCNSL modified NR, particularly at the higher concentration of 20 phr may be ascribed to two factors. It may be partially due to the 'residual acidity' of PCNSL present as acidic materials, in general, are known to have a retarding effect on cure(21). Secondly, the interaction between Zn^{++} ions of the cure activator (ZnO) and the phosphate group of PCNSL may result in the 'cure - retardation' (28) because the Zn^{++} ions are no more available for the thiazole accelerated vulcanization of NR.

iv.Effect of increase in the dosage of ZnO.

It has been shown earlier (26,27) that an increase in concentration of PCNSL above 10 phr in the compositions of NR containing lower doses of ZnO (5 to 10 phr) results in significant 'cure-retardation' and a reduction in ultimate state of cure. Therefore, the effect of variation in ZnO dosage on the cure characteristics of NR modified with a definite proportion of PCNSL has been studied. It has been found that an increase in concentration of ZnO resulted in restoration of cure in PCNSL modified NR processed in a Brabender Plasticorder, especially at higher dosages of PCNSL (27). Similar studies have also been carried out on mixes prepared on a mixing mill. Thus, in a typical SEV system of NR containing 20 phr of PCNSL, the concentration of ZnO has been varied from the conventional 5phr to 25 phr and the cure characteristics have been determined. The results are given in Table V.4.

The rheographs obtained at 150°C of these compounds are given in Figure V.4. The above results show a distinct increase in the rate of cure and state of cure, with an increase in dosage of ZnO. Interestingly, it has been observed that a maximum state of cure is obtained at a ZnO / PCNSL ratio of 1:1. Correspondingly, optimum physico-mechanical properties also have been observed at this ZnO / PCNSL ratio. Hence, it is concluded that for obtaining optimum physico-mechanical properties of the compositions containing PCNSL, the PCNSL/ ZnO ratio should be 1:1.

Table V.4. Effect of dosage of ZnO on the cure characteristics of PCNSL modified with 20 phr NR at 150°C.

Dosage of ZnO (phr)	5 (+)	7.5(+)	10	12.5	20	25
Scorch time, t_2 (s)	-	-	143	53	110	98
Optimumcure time, t_{90}(s)	-	-	585	180	220	195
Cure rate, (s^{-1})	-	-	0.23	0.79	0.91	1.03
Maximum cure L_f(dNm)	<2	4	21.5	30	44	40

(+) Sample not cured

Base mix :- NR - 100, Stearic acid - 2, Sulphur - 2, MBT - 1.5, TMT - 0.5, PCNSL - 20

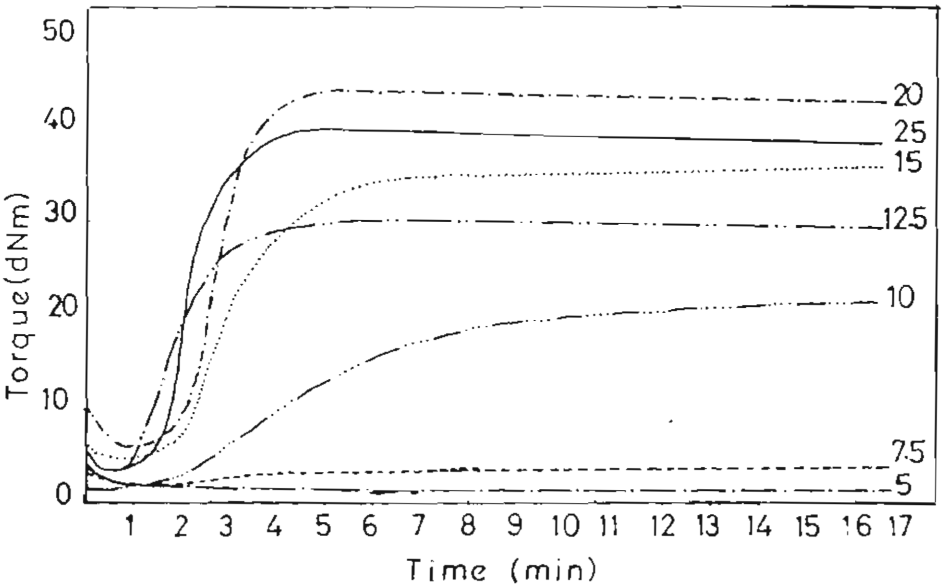


Fig. V.4. Rheographs at 150°C of PCNSL modified NR formulations containing various dosages of ZnO (PCNSL - 20 phr)

V. Kinetics of cure.

(a). Cure characteristics

The cure characteristics of a typical SEV system of NR before and after modification with 10 phr of PCNSL have been determined at temperatures ranging from 150°C to 180°C. The rheographs obtained from the ODR are given in Figure V.5. and the cure characteristics in Table V 5(a)

Table V.5(a). Cure characteristics of unmodified and PCNSL modified NR formulations at different temperatures

Temp: (°C)		150	160	170	180
Mix code*	Parameter				
U	Scorch time, t_2 (s)	115	83	58	47
	Optimum cure time, t_{90} (s)	203	143	96	79
	Minimum torque, M_L (dNm)	3.3	3.0	3.5	3.5
	Maximum torque, M_H (dNm)	60	58.5	55	54
P	Scorch time, t_2 (s)	109	82	68	53
	Optimum cure time, t_{90} (s)	185	135	105	83
	Minimum torque, M_L (dNm)	4	4.3	4.5	4.5
	Maximum torque, M_H (dNm)	45.5	46	45.3	43.8

* U - Unmodified NR ; P - PCNSL (10phr) modified NR

Base mix .- NR - 100, ZnO - 10, Stearic acid - 2, Sulphur - 2, MBT - 1.5, TMT - 0.5

The results given in Table V.5 (a) show that with the increase in temperature from 150°C to 180°C, the rate of reduction in scorch time of the PCNSL modified NR formulation is comparatively lower than that of the unmodified formulation. Also, the relatively higher scorch time of the PCNSL modified NR formulation at 170°C and 180°C indicates its potential 'scorch safety' at elevated temperatures. Further, with an increase in temperature from 150° C to 180°C, the ultimate state of cure represented by the maximum rheometric torque decreases at a higher rate (from 60 dNm to 54 dNm) for the unmodified formulation compared to that of the sample containing 10 phr of PCNSL (from 45.5 dNm to 43.8 dNm). In other words, the high degree of 'cure - stability' and freedom from reversion of the PCNSL modified NR formulation is shown by the almost stable values of maximum torque at the different cure temperatures.

(b). Kinetic parameters

Smith(29) has reported four 'kinetically distinct' regions of the vulcanization reactions in thiazole accelerated sulphur vulcanization of NR. These are (i) a chemical induction period, (ii) first order crosslinking reaction, (iii) a network degradation reaction of limited extent and (iv) a slow crosslinking reaction observed only at long times of cure. The results

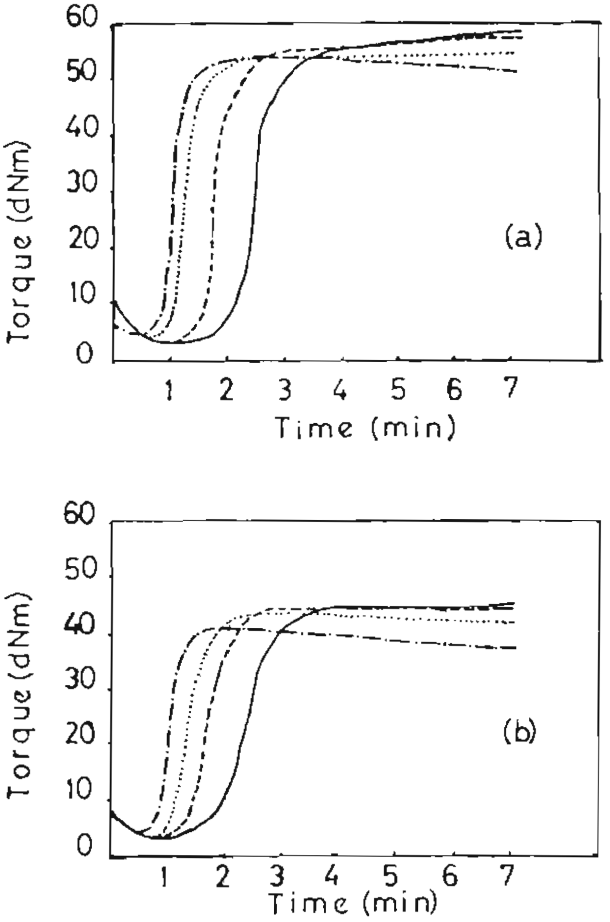


Fig.V.5. Rheographs of (a) un-modified & (b) PCNSL (10phr) modified NR formulations at different temperatures

—— 150 °C ---- 160 °C .... 170 °C _._._ 180°C discussed in section V 2 5i showed a general increase in the induction period prior to crosslinking of the PCNSL modified NR formulation. However, it is essential to have an idea of the kinetic parameters for the cure of PCNSL modified NR formulations as curing constitutes an inevitable stage in the formation of any finished product.

Various methods such as isothermal differential calorimetry (30), Oscillating Disk Rheometry(31, 32) and chemical and physical methods (33) are reported for studying the kinetics of vulcanization of elastomers. Yehia and Stoll (32) reported a simple procedure for the determination of kinetic parameters such as 'cure rate index' and 'rate constant' for the vulcanization of NBR. Thus, Cure Rate Index, CRI = 100 / (t_{90} - t_2) where, t_{90} is the optimum cure time and t_2 is the scorch time and the rate constant K is given as K = (dM/dt) / (M_H - M_L) where, M is obtained as (M_H+M_L)/2 from the rheometer curve corresponding to the time t for 50 % of the cure, M_H is the maximum modulus and M_L is the minimum modulus obtained directly from the rheograph. The activation energy of cure E was determined assuming the dependence of the optimum cure time (t_{90}) on the cure temperature (T) in absolute scale, as per the Arrhenius equation, - $t_{90} = A e^{(E\ RT)}$ where, A is the pre-exponential factor and R is the universal gas constant. The Arrhenius type of dependence of optimum cure time on temperature has been reported by Haifa et al.(31). The kinetic parameters for the cure of the unmodified and PCNSL modified NR formulations are given in Table V.5 (b)

Table V.5(b).Cure parameters of PCNSL modified NR formulations at different temperatures

Temp: (C)		150	160	170	180
Mix code*	Parameter				
U	Rate constant 100K (min $^{-1}$)	78.9	85.6	92.2	100
	Cure Rate Index CRI (min $^{-1}$)	68.4	100.2	157.8	187.8
	Activation energy (kCal/mol)	<----	--6.587--	----------	----->
P	Rate constant 100K (min $^{-1}$)	88	88	89	86
	Cure Rate Index CRI (min $^{-1}$)	79.2	113.4	162	199.8
	Activation energy (kCal/mol)	<----	--4.714--	--------	---->

*U - Unmodified NR, P - PCNSL modified NR

The crosslinking reaction of NR at high temperatures is generally considered to be of apparent first order (34). The results given in Table V.5 (b) show that the rate constant for the cure of unmodified NR increases at a higher rate with an increase in temperature, compared to that of the PCNSL modified NR formulation. The lower rate of rise in the rate constant with temperature for the PCNSL modified NR formulation may possibly be due to reduced mobility of the C_{15} - unsaturated side chain of PCNSL which is thought to partake in the cure reaction with NR (28). It has been shown by Gee and Morrell (35) that the reciprocal of the rate constant is a valuable measure of the vulcanization time required. However, the cure rate index determined from the scorch time and optimum cure time is found to be comparatively higher for the PCNSL modified NR formulation at different temperatures. This means that, once the cure starts, it proceeds at a relatively higher rate in the NR formulation containing 10 phr of PCNSL, as against that in the unmodified formulation. Also, the lower value of the activation energy for crosslinking of PCNSL modified NR formulation (4.714 kCal / mol) as against that of the unmodified sample (6.587 kCal/mol) clearly indicates the ease of crosslinking of NR in presence of 10 phr of PCNSL. This is in contrast to the report of Kumaran et al.(36) that additives such as lignin do not play an active role in the overall vulcanization reaction of NR.

V.3.Physico-mechanical properties

Apart from the effect on cure characteristics, changes in the composition of elastomer formulations as mentioned above have a profound effect on the vulcanizate properties also, due to the dependence of the latter on structural parameters such as crosslink density, type of crosslinks etc.(37). Hence, the effect of variations in vulcanization systems and dosages of PCNSL and ZnO on the physico-mechanical properties of gum NR vulcanizates have been studied, the results of which are enumerated below:-

i.Variation in the vulcanization system.

Elastomer formulations are often designed with the aim of getting the desired rate and state of cure and a balance in the vulcanizate properties for any specific application(3) Developments in the science and technology of vulcanization have lead to different vulcanization systems including the conventional (CV), semi-efficient (SEV) and efficient (EV) systems(38) as discussed earlier, each having its own advantages / disadvantages with respect to vulcanizate properties such as strength, thermal stability, flexibility etc. Plasticizers in general and particularly 'reactive plasticizers' such as PCNSL can alter the vulcanization mechanism and affect the physico-mechanical properties of the vulcanizates depending on their type and dosage in the formulations. Hence, the dosage of PCNSL is varied from 0 to 20 phr in typical CV, SEV and EV systems of NR as per the formulations given in Table V.1(a). The mechanical properties of the vulcanizates are reported in Table V.6 .

The cure characteristics of the formulations have been described in the previous section. Among all the systems and at all the concentrations of PCNSL studied, the SEV system showed higher state of cure within a short time and stable rheometric torques on prolonged cure (cure-plateau) This indicates better reversion resistance of PCNSL modified NR in the SEV system.

Table V.6. Effect of different vulcanization systems on the mechanical properties of PCNSLmodified NR vulcanizates

Mix code	C_0	C_{10}	C_{20}	E_0	E_{10}	E_{20}	S_0	S_{10}	S_{20}
Modulus-300%(MPa)	2.0	1.5	1.2	1.1	0.6	0.7	2.1	1.9	1.7
Tensile strength(MPa)	24	17	12	16	10	7	13	22	21
Elongation at break (%)	1170	1190	1160	1250	1300	1150	920	1140	1250
Tear strength (kN/m)	34	29	24	22	20	16	26	34	30

The results in Table V.6 show that the tensile strength decreases on increasing the PCNSL content in CV and EV systems, whereas in SEV system, it increases reaching a maximum at 10 phr of PCNSL. The tear strength of the vulcanizates also show a similar trend. In CV and EV systems, the elongation at break increases initially with an increase in concentration of PCNSL (upto 10 phr), followed by a decrease, where-as in the SEV system the increase is steady with the increase in concentration of PCNSL from 0 to 20 phr The tensile modulus decreases with the increase in content of PCNSL in all the three systems, showing the softening effect of PCNSL in NR vulcanizates.

ii. Variation in dosage of PCNSL in the SEV system.

A gum NR formulation of SEV system was modified with different concentrations of PCNSL viz., 0, 5, 10, 15 and 20 phr as shown in Table V.1(a). Above 10 phr of PCNSL 'cure - retardation' is observed as reflected by the reduction in the rate and state of cure. The results in Table V.7 show a steady decrease in the tensile moduli and hardness and increase in the elongation at break, with an increase in the dosage of PCNSL from 0 to 20 phr in the gum NR vulcanizate. This indicates the softening effect of PCNSL in NR

Table V.7. Effect of variation in the dosage of PCNSL on physico-mechanical properties of the NR gum vulcanizates in the SEV system.

Mix code*	S_0	S_5	S_{10}	S_{15}	S_{20}
Properties					
100% Modulus-(MPa)	0.8	0.7	0.7	0.7	0.6
200% Modulus-(MPa)	1.4	1.3	1.3	1.3	1.2
300% Modulus-(MPa)	2.1	2	1.9	1.9	1.7
Tensile strength (MPa)	13	15	22	19	21
Elongation at break(%)	920	1030	1140	1180	1250
Tear strength (kN/m)	26	31	34	32	30
Hardness (Shore A)	41	37	38	37	37

* - Base mix (phr) :- NR 100, ZnO 15, Stearic acid 2, Sulphur 2,MBT 1.5 & TMT 0.5
Subscript indicates the dosage of PCNSL

However, at lower concentrations of PCNSL, the tensile and tear strengths of the vulcanizates increase, reaches a maximum at 10 phr of PCNSL and then remains almost constant

iii. Optimisation of the dose of ZnO

It was observed earlier that the rate of cure of PCNSL modified NR formulations reduced significantly with the increase in content of PCNSL above 10 phr. It has been presumed to be either due to the obscuration of the cure sites of NR or to the absorption of cure activator (ZnO) by PCNSL. The primary role of ZnO as the cure activator in thiazole accelerated vulcanization of NR has been established earlier by several investigators (39-49). Therefore, the dose of ZnO in NR formulation was increased from 10 to 25 phr in the SEV system containing 20 phr of PCNSL, as shown in Table V.8. The rate and state of cure of the mixes increased significantly with an increase in concentration of ZnO, as reported in the previous section. The state of cure obtained for the mix containing 20 phr of ZnO was the highest. The mechanical properties of the vulcanizates are given in Table V.9

Table V.8. Formulation of the NR mixes containing PCNSL at various doses of ZnO in the SEV system

Mix code	$S_{20\ 10}$	$S_{20\ 12.5}$	S_{20}	$S_{20\ 20}$	$S_{20\ 25}$
NR	100	100	100	100	100
ZnO	10	12.5	15	20	25
Stearic acid	2	2	2	2	2
Sulphur	2	2	2	2	2
MBT	1.5	1.5	1.5	1.5	1.5
TMT	0.5	0.5	0.5	0.5	0.5
PCNSL	20	20	20	20	20

Table V.9. Effect of variation in dosage of ZnO on the physico-mechanical properties of the vulcanizates.

Mix code	$S_{20\ 10}$	$S_{20\ 12.5}$	$S_{20\ 15}$	$S_{20\ 20}$	$S_{20\ 25}$
Properties					
100% Modulus-(MPa)	0.6	0.6	0.6	0.7	0.7
200% Modulus-(MPa)	1	1.1	1.2	1.3	1.5
300% Modulus-(MPa)	1.4	1.5	1.7	1.9	2.4
Tensile strength(MPa)	16	18	21	22	22
Elongation at break (%)	1270	1240	1250	1190	1080
Tear strength (kN/m)	22	29	30	33	35

An increase in the tensile modulus and a decrease in the elongation at break with an increase in the dosage of ZnO indicated the probable formation of a higher degree of crosslinking. The tensile and tear strengths of the vulcanizates increased progressively with the dosage of ZnO, levelling -off at and above 20 phr. This shows that the ratio of PCNSL to ZnO should be minimum 1:1 for achieving optimum properties of the vulcanizates.

iv. Physico-mechanical properties of PCNSL modified NR vulcanizates at PCNSL/ZnO ratio of 1:1.

The formulations of the mixes containing PCNSL and ZnO in the proportion 1:1 are given in Table V.10. The processability characteristics and physico-mechanical properties of these vulcanizates are given in Table V.11.

Table V 10. Formulation of NR mixes with variation in doses of ZnO and PCNSL in SEV system

Mix code	S_{0-10}	S_{10-10}	S_{20-20}
NR	100	100	100
ZnO	10	10	20
Stearic acid	2	2	2
Sulphur	2	2	2
MBT	1.5	1.5	1.5
TMT	0.5	0.5	0.5
PCNSL	-	10	20

The reduction in optimum cure time and higher cure rates of the PCNSL modified NR formulations indicate an effective utilization of ZnO when the proportion of PCNSL and ZnO is maintained at 1:1 The reduction in tensile modulus and hardness and a significant increase in the elongation at break of the vulcanizates indicate the softening effect of PCNSL in NR . The stress - strain curves of the PCNSL modified gum NR vulcanizates containing 0, 10 and 20 phr of PCNSL are given in Figure V.6 . Generally an increase in the area under the stress - strain curve of a polymer indicates an improvement in its toughness (49) . Thus, an increase in the area under the stress - strain curves of the PCNSL modified NR vulcanizates may be considered as a reflection of their enhanced toughness characteristics. Toughness is often considered to be one of the essential and useful properties of a polymer (50) for various damping applications. Toughness or energy input to break is considered to be measure of the strength of a polymer, as it combines both the attributes of stress and strain at break(51,52). The results in Table V.11 show that in presence of 10 phr of PCNSL, the tensile strength of the gum NR vulcanizate increases from 2 MPa to 25 MPa and the tear strength from 32 kN/m to 36 kN/m. The vulcanizate containing 20 phr of PCNSL also shows higher values of tensile strength (22MPa) and elongation at break (1030 %) as compared to the NR gum vulcanizate.

The tensile properties and hardness of the vulcanizates after aging in a hot air oven at 70°C for 24 and 48 hrs are also given in Table V.11. After aging at 70°C for 24 hrs, the tensile strength of the vulcanizate containing 10 phr of PCNSL increases from 25MPa to 28MPa. The corresponding increase in tensile strength for the NR vulcanizate containing 20 phr of PCNSL has been from 22 MPa to 25 MPa. The tensile modulus of the vulcanizates also increased after aging at 70°C for 24 hrs. The above findings indicate that there is a sort of "post - curing" reaction taking place in the PCNSL modified NR vulcanizates. This has been confirmed by an increase in their chemical crosslink density measured subsequently by the equilibrium swelling technique (28). However, after aging at 70°C for 48 hrs the tensile strength decreased for all the vulcanizates, the reduction being comparatively lower for the mix containing 20 phr of PCNSL.

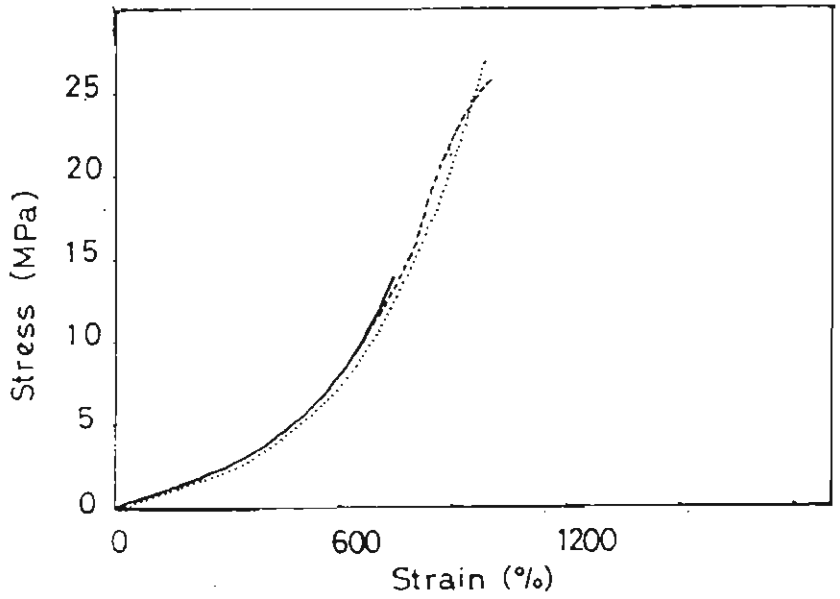


Fig-V.6. Stress - strain plots of PCNSL modified gum NR vulcanizates

—— M_0 ----- M_{10} ········ M_{20}

PCNSL (phr) - M_0 - 0, M_{10} - 10, M_{20} - 20

Table V.11. Physico-mechanical properties of PCNSL modified NR vulcanizates at PCNSL/ZnO ratio of 1:1.

Mix code	$S_{0\ 10}$	$S_{10\ 10}$	$S_{20\ 20}$
Properties			
Mooney viscosity, ML(1+4) 120°C	13	15	17
Mooney scorch time, t_5 (min)	6.75	6	4.75
Optimum cure time at 150°C, t_{90} (min)	4	3.25	3.75
Cure rate (s^{-1})	0.83	1.11	0.91
200% Modulus- (MPa)	1.5	1.4	1.4
Tensile strength (MPa)	2	25	22
Elongation at break (%)	290	1090	1030
Hardness (Shore A)	41	38	39
Tear strength (kN/m)	32	36	32
Goodrich heat-buildup after 20min (°C)	3	6	9
Rebound resilience (%)	84	80	72
Compression set at 70C/22h (%)	2	5	3
Abrasion loss (cm^3/1000rev)	0.600	0.765	0.964
Electrical properties			
Surface resistivity (X 10^{14} ohm)	376	9.4	0.00072
Volume resistivity (X 10^{12} ohm.cm)	120.2	10.7	1.8
Monsanto fatigue-to-failure (kC)	74	125	147
Properties after aging at 70 °C for 24hrs.			
Modulus-200% (MPa)	2	1.8	1.6
Tensile strength (MPa)	2	28	25
Elongation at break (%)	210	1020	1030
Hardness (Shore A)	41	35	35
Properties after aging at 70 °C for 48hrs			
Modulus-200% (MPa)	-	1.7	1.9
Tensile strength (MPa)	2	20	20
Elongation at break (%)	170	920	900
Hardness (Shore A)	42	34	34

The retention in tensile strength after aging at 70 °C for 48 hrs has been 75% for the unmodified NR vulcanizate, 80% for the vulcanizate containing 10 phr of PCNSL and 90% for the vulcanizate containing 20 phr of PCNSL. Also, the retention in elongation at break under the same condition was 59% for the unmodified NR vulcanizate, 84% for the sample containing 10 phr of PCNSL and 87% in presence of 20 phr of PCNSL. Also, the aging at 70°C for 24 and 48 hrs resulted in steady decreases in the hardness of the PCNSL modified NR vulcanizates as against the increase for the unmodified sample. Thus, the above results clearly indicate that there is an improvement in the resistance to thermo-oxidative degradation of the PCNSL modified NR gum vulcanizates as compared to that for the unmodified NR gum vulcanizate.

The heat buildup of the vulcanizates under compressive deformation cycles, measured on a Goodrich flexometer at 50 °C are also shown in Table V.11. The results show a 3 °C rise of temperature for every 10 phr increase in concentration of PCNSL in the NR vulcanizate. Also, the rebound resilience of the vulcanizates measured by a Dunlop Tripsometer decreases steadily from 84% to 72% with an increase in concentration of PCNSL from 0 to 20 phr. As reported in the succeeding section, the unmodified gum NR vulcanizate has a higher chemical crosslink density than the PCNSL modified NR gum vulcanizates(28). It is reported that presence of more crosslinks reduce the deformation arising from the impact of the indentor and as the energy loss is due to the internal friction in the rubber, a reduction in the deformation will lead to an increase in resilience (53). The results mentioned above show the tendency of PCNSL modified NR vulcanizates to dissipate a higher proportion of the incident energy via. non-recoverable deformation modes leading to an increase in the heat-buidup. This has been further confirmed from the results given in Table V.12, showing the hysteretic dissipation of energy of PCNSL modified gum NR vulcanizates.

Table V.12. Hysteretic dissipation of energy of PCNSL modified gum NR vulcanizates

Mix code	S_0	S_{10}	S_{15}	S_{20}
Work done in three cycles *X 10^{4} (J/mm^2)	7	30	32	61

* - at 100% extension

It shows that the work done in three cycles of tensile extension and retraction (calculated from the area of the hysteresis loops) increases from 7 X 10^{4} J/mm^2 to 61 J/mm^2 with an increase in dosage of PCNSL from 0 to 20 phr in the NR vulcanizate. 'Stress-softening' resulting from previous deformation is known to be a frequent and wide-spread phenomenon, reflecting the configurational changes within the fine structure of the material, which permits the subsequent deformation to take place more readily (54). It is possible that the presence of higher proportions of pendant side-chains of PCNSLmodified NR vulcanizates may facilitate the ease of deformation and may dissipate a major proportion of the input energy irrecoverably, leading to higher hysteresis losses.

Compression set is still the most commonly used test to measure the elasticity of rubber products (55) as it measures the elastic recovery after a compressive loading. The more elastic the material the lower is the set. The results in Table V.11 show that the compression set at 70°C for the NR vulcanizates, measured at constant strain of 25% increases in presence of 10 and 20 phr of PCNSL. Thomas (56) used permanent set to investigate the labile nature of crosslinks. He found that the vulcanizates having polysulphidic crosslinks showed higher set compared to those having monosulphidic linkages. The higher set of the former was attributed to the mechanically labile nature of the polysulphidic crosslinks which break and form continuously during a stress - strain cycle unlike that for the monosulphidic linkages. Hence, the higher set for the PCNSL modified NR vulcanizates is expected to be due to their higher proportions of polysulphidic linkages in the network structure (28)

The results in Table V 11 show progressive decrease in the abrasion resistance of the vulcanizates with an increase in dosage of PCNSL. It is reported that abrasion loss in polymers may be due to abrasive wear, frictional wear or wear due to roll formation (57). In polymers such as cis-polyisoprene, under mild abrasion conditions, the particles of wear-debris are often sticky, which agglutinate to form larger particles and develop a tarry liquid surface (58). At at a higher concentration of PCNSL *ie.* 20 phr, the PCNSL modified NR vulcanizate also showed a sticky surface.

The surface and volume resistivities of the NR vulcanizate decreased exponentially in presence of 10 and 20 phr of PCNSL. It is seen that the incorporation of PCNSL in NR increases the polarity of the elastomer matrix probably due to the presence of the phosphate group in PCNSL

Modification of NR with 10 and 20 phr of PCNSL resulted in significant improvements in the resistance to tensile fatigue failure. This is basically due to an increase in the flexibility of the vulcanizates because of plasticization action of PCNSL and also due to a decrease in crosslink density(28). Thus, in the Monsanto fatigue- to- failure test, the frequency for complete failure increased from 74 kC to 147 kC, with the increase in dosage of PCNSL from 0 to 20 phr Also, the crack initiation frequency was increased from 70 kC to 105 kC in presence of 10 phr of PCNSL.

v. Fracture behaviour of the vulcanizates from Scanning Electron Microscopy studies

The morphology of the fracture surfaces of polymer specimens resulting from different modes of failures such as tension, tear, abrasion, cyclic fatigue, etc. as revealed by Scanning Electron Microscopy (SEM) gives valuable insight into the mechanism of failure, thereby facilitating structure - property correlations. SEM has been used widely as a tool to study the fracture surfaces of rubber vulcanizates (57,59-69). Mathew et al.(59) used SEM to study the tear fracture behaviour of NR vulcanizates in the unfilled and HAF black filled states. The tensile rupture characteristics of NR and SBR vulcanized by sulphur and peroxide systems with and without fillers has also been studied by SEM (60). Mathew and De (61) used SEM to study the effect of thermo-oxidative aging on the fracture modes of NR vulcanizates and to correlate strength of the rubber with its fracture surface - topography. Bhowmick et al.(62) studied the fracture surfaces of nitrile rubber vulcanizates from tensile and tear failures using SEM. SEM has also been used in studying the changes in fracture surfaces of gum and filled NR vulcanizates containing lignin, with variations in network structure of the rubber (63). The surfaces of BR and SBR subjected to different degrees of abrasion have also been studied by SEM (64) Datta and Tripathy (67) reported

SEM studies on the tear and tensile failure of plasticized bromobutyl rubber vulcanizates

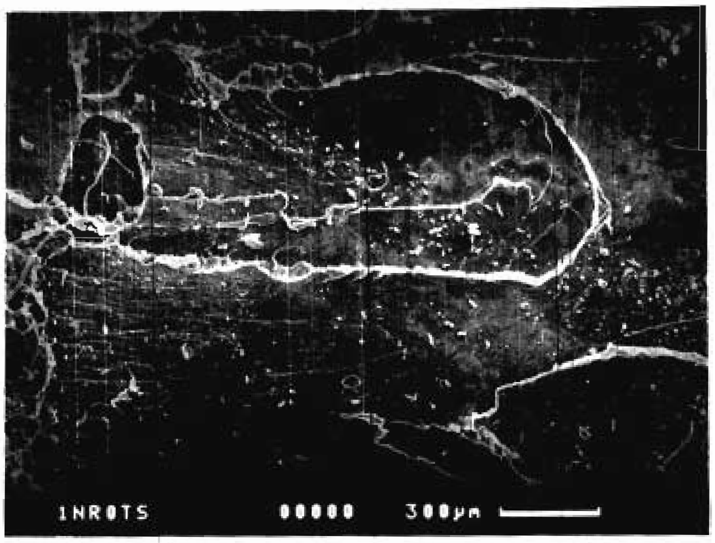
In the present work, NR vulcanizates containing 0 to 20 phr of PCNSL were fractured under different failure modes such as tension, tear and tensile fatigue and the morphology of the fracture surfaces has been studied using scanning electron microscopy. The improvements in tensile and tear strengths and resistance to fatigue failure as reported earlier in the previous section may be explained in terms of the topography of the fracture surfaces of the vulcanizates after testing . The physico-mechanical properties of the vulcanizates containing 0 to 20 phr of PCNSL are given in Tables V.7, V.11 and V.12. The scanning electron microphotographs of the unmodified and PCNSL modified gum NR vulcanizates under the different fracture modes are shown in Figure V.7 (1) to (10).

(a).Tensile fracture surface

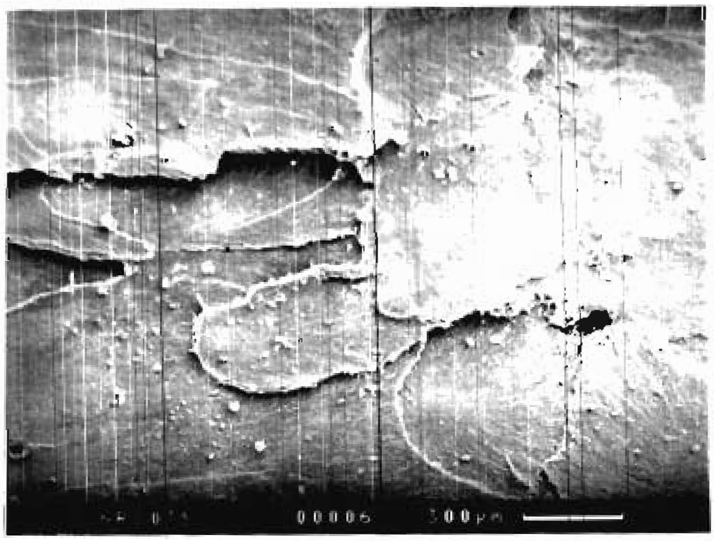
The SEM photomicrographs of the unmodified and PCNSL modified gum NR vulcanizates after tensile failure are given in Figure V.7 (1) to (4).

The unmodified NR gum vulcanizate (Fig.V.7(1)) shows a comparatively smoother fracture surface with less deviation of crack-path and distinct flow-lines across the specimen, accounting for its lower tensile strength . The surface seems to have a brittle failure as observed earlier (59,63) . In contrast, the micrographs of the PCNSL modified NR vulcanizates (Figs.V.7 (2) to (4)) show considerable deviations in the path of crack propagation. This is very much prominent in the samples containing 10 and 15 phr of PCNSL. This change in the fracture morphology of the NR vulcanizate in presence of PCNSL is thought to be a reflection of the enhanced strength of the PCNSL modified NR vulcanizates.

Generally, the tensile strength of elastomers is governed by the extent to which strain energy is dissipated in deforming them (58). A direct relation between tensile rupture energy and hysteretic energy of vulcanizates has been reported by various investigators (70-73) . Thus, the relation between hysteresis and strength is given as $U_b = B\,(H_b\ E_b)^{1\ 2}$ where U_b is the energy input per unit volume to break a vulcanizate (area under the stress-strain curve), H_b is the energy dissipated in the deformation prior to break (area of the hysteresis loop), E_b is the strain at break and B is a constant(72) . The previous results (74) showed a considerable increase in toughness (U_b) of gum NR vulcanizates on modification with PCNSL along with higher values of strain at break (E_b). The results in Tables V.11 and V.12 show considerably high hysteretic dissipation of energy (H_b) in PCNSL modified gum NR vulcanizates subjected to compressive and tensile deformation cycles respectively. The higher energy dissipation characteristic of PCNSL modified NR vulcanizate at ambient temperature was further confirmed from dynamic mechanical analysis of the samples. Dynamic Mechanical Thermal Analysis (DMTA) traces showing the loss tangent of the unmodified and PCNSL modified gum NR vulcanizates at different imposed frequencies of 3, 10 and 30 Hz are shown in Figure V.8. Figures V.8 shows that the loss tangent (Tanδ) of PCNSL modified NR vulcanizate is higher than that of the unmodified sample at the different frequencies viz., 3, 10 and 30 Hz, particularly above 0°C. Thus, these results

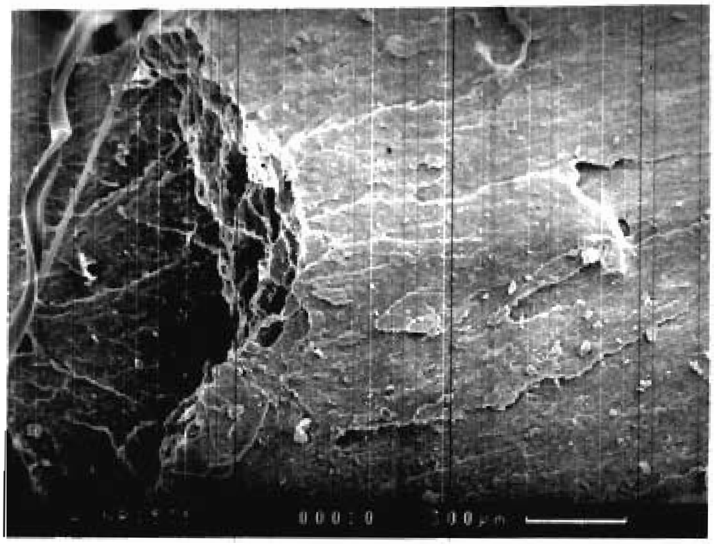


1. SEM photomicrograph of the tensile fracture surface of NR gum vulcanizate - 50X General view ; crystal of NR scattered

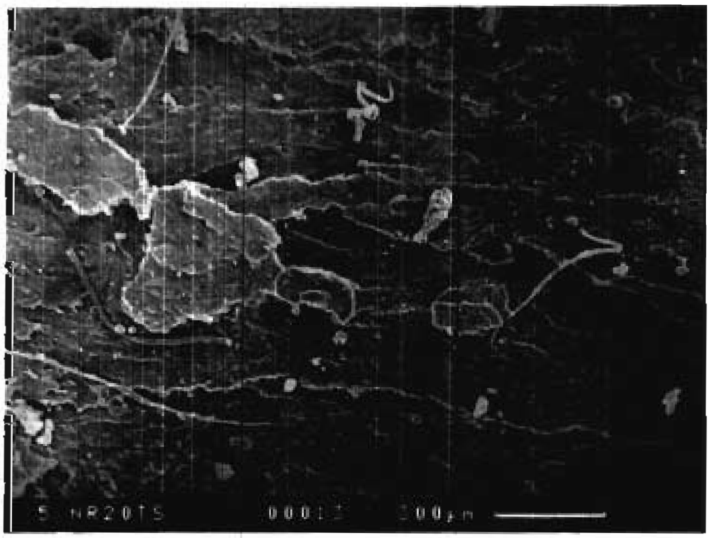


2. SEM photomicrograph of the tensile fracture surface of NR gum vulcanizate containing 10 phr of PCNSL - 50X Crack initiates from right edge ; flow lines.

Fig. V.7. SEM of PCNSL modified NR vulcanizates under different fracture modes

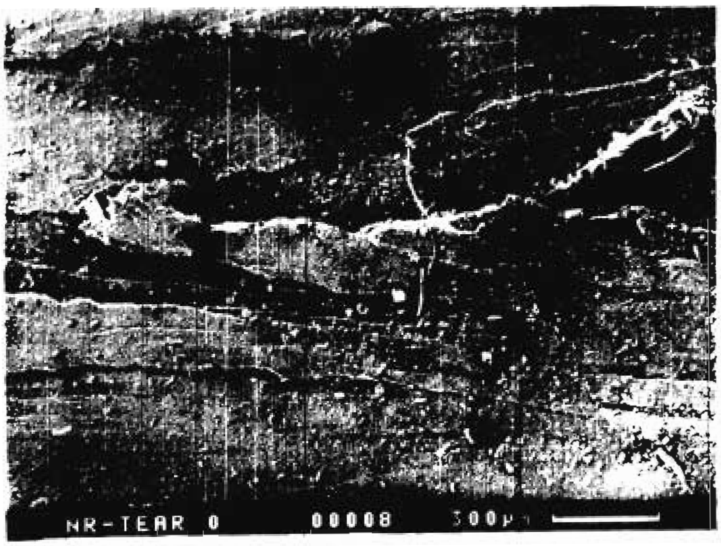


3. SEM photomicrograph of the tensile fracture surface of NR gum vulcanizate containing 15 phr of PCNSL - 50X One edge

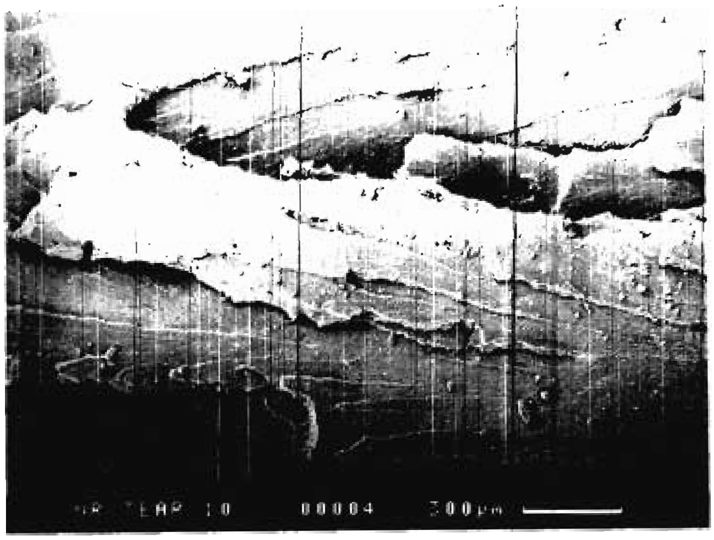


4. SEM photomicrograph of the tensile fracture surface of NR gum vulcanizate containing 20 phr of PCNSL - 50X General view of flow- path ; no crystallite region

Fig. V.7. SEM of PCNSL modified NR vulcanizates under different fracture modes (contd.)

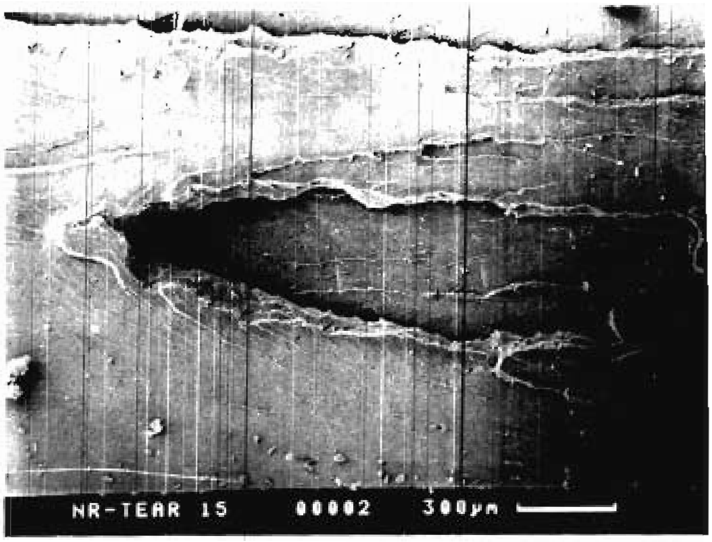


5. SEM photomicrograph of the tear failure surface of NR gum vulcanizate - 50X.Flow lines bifurcated towards the end

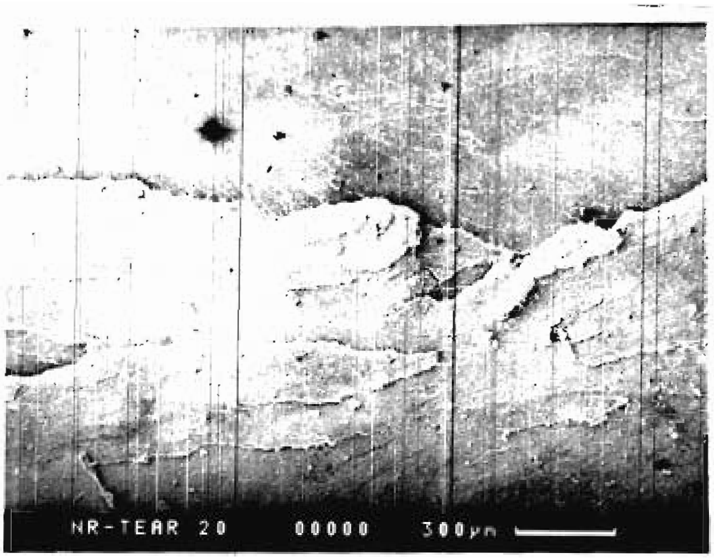


6.SEM photomicrograph of the tear failure surface of NR gum *vulcanizate containing 10 phr of PCNSL - 50X.Flow lines ellipsoidal*

Fig. V.7. SEM of PCNSL modified NR vulcanizates under different fracture modes (contd.)

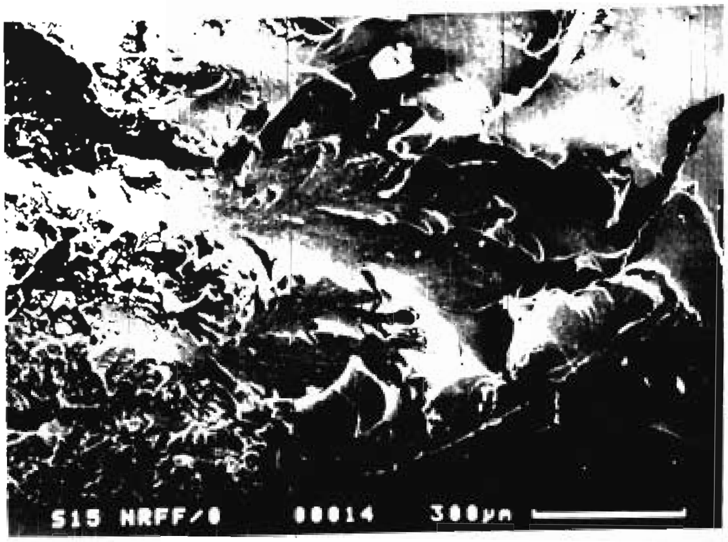


7.SEM photomicrograph of the tear failure surface of NR gum vulcanizate containing 15 phr of PCNSL - 50X General view

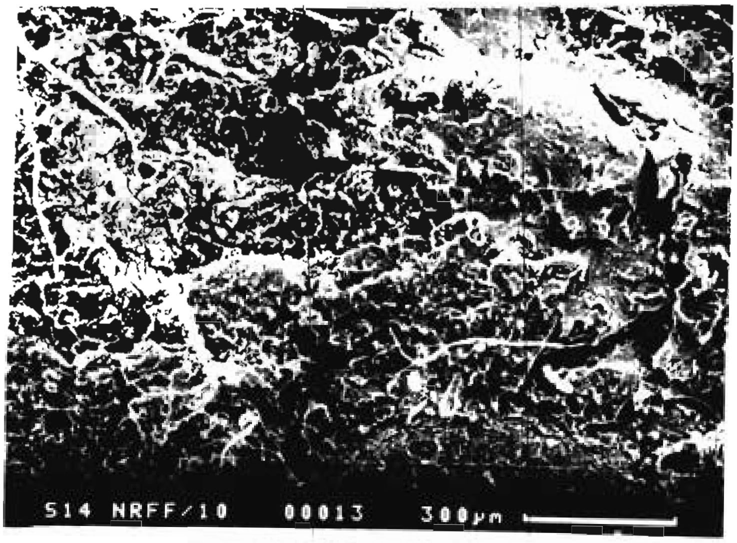


8.SEM photomicrograph of the tear failure surface of NR gum vulcanizate containing 20 phr of PCNSL - 50X General view

Fig. V.7. SEM of PCNSL modified NR vulcanizates under different fracture modes (contd.)



9.SEM photomicrograph of the fatigue failure surface of NR gum vulcanizate - 70X.General view at the edge.



10.SEM photomicrograph of the fatigue failure surface of NR gum vulcanizate containing 10 phr of PCNSL- 70X General view.

Fig. V.7. SEM of PCNSL modified NR vulcanizates under different fracture modes (contd.)

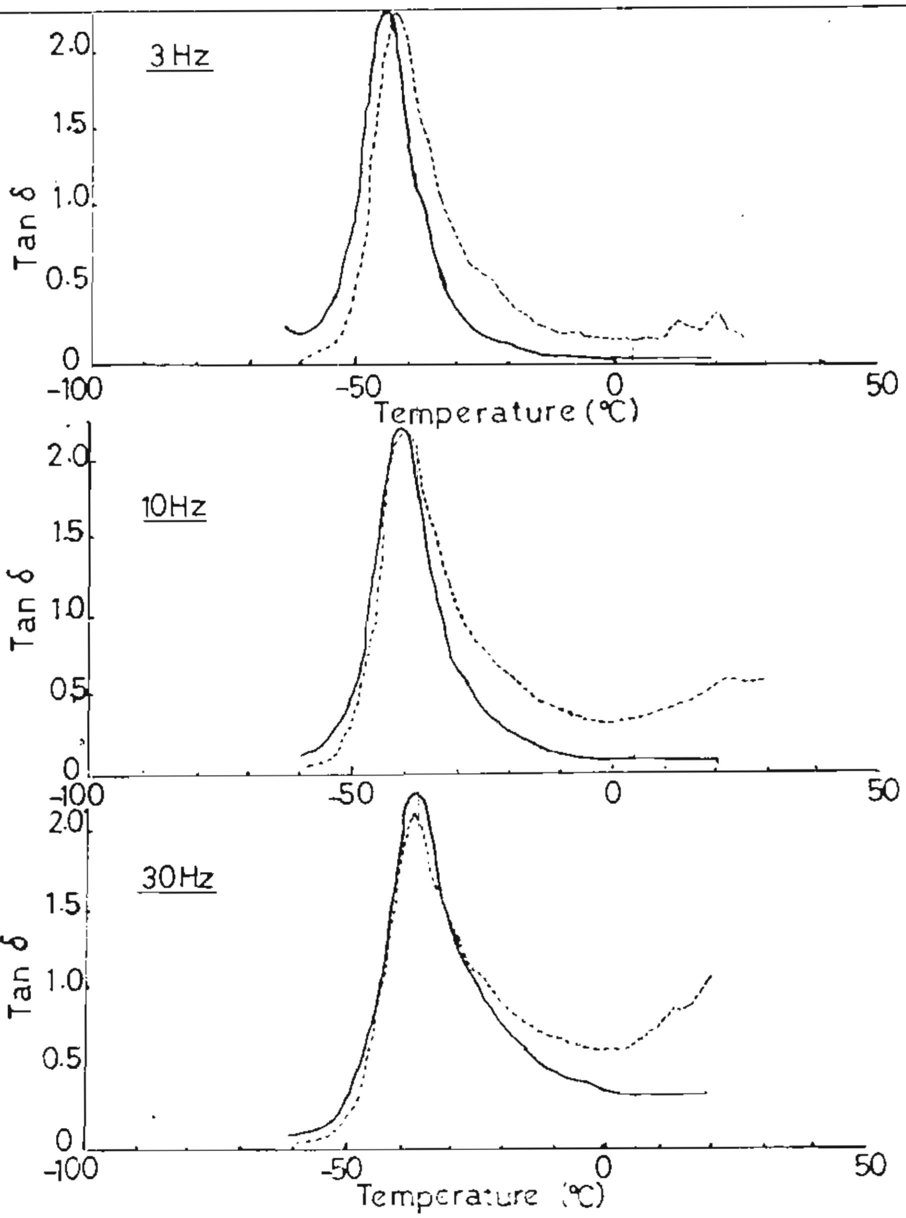


Fig.V.8. **DMTA** of unmodified & PCNSL modified NR vulcanizates

____ Unmodified ------PCNSL (10phr) modified clearly indicate that the higher energy dissipation characteristic of PCNSL modified NR vulcanizate leads to higher strength Apparently, the 'softness' of the NR matrix in presence of PCNSL may also facilitate the observed 'lateral deviation' of crack resulting in higher strength.

Besides, the tensile strength of NR is known to be dependent on the type and degree of crosslinking showing a maximum at an intermediate crosslink density (53). Also, vulcanizates having a higher proportion of polysulphidic linkages are reported to show higher values of tensile strength(2). The comparatively lower chemical crosslink density and higher proportion of polysulphidic crosslinks of the PCNSL modified NR vulcanizates (28) leading to higher tensile strength, amply support the above observations.

(b).Tear failure surface

Figures V.7(5) to (8) show the SEM photo-micrographs of the fracture surfaces of unmodified and PCNSL modified NR gum vulcanizates subjected to tear failure.

The unmodified NR vulcanizate shows a sharp tear-tip with flow lines bifurcating towards the end in a parallel fashion, as shown in Figure V 7 (5). The failure surface is rough may be due to crystallites formed locally during tearing. However, the PCNSL modified NR gum vulcanizates show wider and blunter crack - tips (Fig.V.7 (6) & (7)) and lateral deviation of crack-path (Fig.V.7 (8) - features that hinder the crack-propagation and increase the tear strength

Energy dissipating materials are known to develop low stress concentration at crack-tip leading to slower crack-growth and enhanced tear strength and often a transition from smooth tearing to the characteristic knotty tear pattern (75). The blunter the tear-tip, the greater is the volume of material that undergoes large deformations. This results in the loss of greater amount of energy due to mechanical hysteresis during tearing, resulting in higher tear strength (76). The wider crack-tip and the higher energy dissipation of PCNSL modified NR vulcanizates supports the above view point. The relation between tear strength (T_c), tensile rupture energy per unit volume (E) and effective diameter of the tear tip (d) is given as $T_c = E\ d$ (76,77). Increased crosslink density increases the modulus with consequent lowering of d and the tear strength (76). The higher crosslink density, lower crack-tip diameter and lower tear strength of the unmodified NR vulcanizate support the above view. Lake and Thomas(78) have suggested the dependence of tearing energy and tensile strength on crosslink types in gum NR vulcanizates. The reason for the polysulphidic crosslinks giving higher values of tearing energy is considered to be due to their labile nature under the action of high stresses at the tip of the cut (78). Thus, the higher proportion of polysulphidic linkages of the PCNSL modified NR vulcanizate may also contribute to their higher tear strength.

(c). Tensile fatigue failure surface

The SEM fractographs of the unmodified and PCNSL (10 phr) modified gum NR vulcanizates after tensile fatigue failure test are shown in Figs V 7 (9) & (10) respectively.

The photo-micrographs of the unmodified gum NR vulcanizate (Fig. V.7 (9)) clearly shows the 'severity' of fracture as indicated by the 'localisation' of micro-cracks and their sharpness. In contrast, the NR vulcanizate containing 10 phr of PCNSL shows diffused regions of cracks with a higher degree of deviations in crack-path. This change in fracture - topography is a clear reflection of the superior fatigue resistance of the latter, as shown in Table V.11..

Based on their studies on failure behaviour of NR vulcanizates under cyclic loadings, Lake and Lindley (79) proposed the existence of a minimum tearing energy for mechanical oxidative cut-growth to occur and that it increases as the crosslinking is reduced. Fatigue life depends on the tearing energy since the latter determines the rate of crack-growth (78). Thus, the lower crosslink density of the PCNSL modified NR vulcanizate helps in increasing its fatigue life indirectly. Previously, the improved fatigue life of the NR vulcanizate containing 10 phr of PCNSL has been attributed to its higher content of polysulphidic crosslinks (28). Polysulphidic linkages are known to be capable of relieving rapidly, the localised stresses associated with the growth of a flaw (74). Also, crack-growth is believed to be driven by the chemical degradation due to ozone attack (80) and the tearing energy is influenced by the presence of antioxidants(78). Maret et al.(81) observed improved thermal aging characteristics of gum NR vulcanizates in presence of low concentrations (from 2 to 4 phr) of PCNSL, compared to a formulation containing 2 phr of styrenated phenol as an antioxidant. Also, in a typical ozone - aging test, the crack-initiation time increased from 8 to 10 hrs in presence of 2 phr of PCNSL (81). Hence, the antioxidant and antiozonant effectiveness of PCNSL in NR vulcanizates as mentioned above, may also contribute to the improved fatigue resistance

vi. Stress-relaxation characteristics

Endowed with a unique combination of physico-mechanical properties (82,83), NR has established an enviable position in the industrial market as an excellent 'engineering polymer'(84) In many of its applications as engineering components, long-term dimensional stability under service conditions is an integral requirement, apart from others such as resistance to aging, solvents, chemicals, oils, etc. Mechanical properties of the vulcanizates such as modulus, strength, stiffness, stress-strain characteristics under various deformation modes, stress-relaxation and creep have also been identified to be some of the critical parameters (85) Stress-relaxation characteristics of an elastomer under constant strain and at equilibrium conditions (86) is of paramount importance in products such as oil-seals, gaskets, etc High stress-relaxation is undesirable in gaskets (87) Similarly, a high degree of stress-relaxation in oil-seals may cause dimensional changes during service, leading subsequently to leakages and failure of the assembly Stress-relaxation of a product is found to be dependent on various factors such as composition of the mix including the amount and type of fillers(88-90), plasticizers and antioxidants.(91), nature and type of crosslinks (92,93), crosslink density(92-95), type and quantity of extra-network material arising from vulcanization(96), hysteresis behaviour of the compound (97) etc., apart from the conditions of service or testing such as strain rate, strain level and temperature (98-102).

Since 'physical stress-relaxation' of vulcanizates at normal temperature is important with respect to engineering applications (2) and the PCNSL modified NR vulcanizates showed a good combination of physico-mechanical properties, it was thought worthwhile to study their stress-relaxation characteristics at ambient temperature. So, the stress-relaxation characteristics of NR vulcanizates containing 10 to 20 phr of PCNSL (in tension) have been studied at various strain rates and strain levels, in comparison with that of the Santicizer 141 (a flame retardant plasticizer) modified NR vulcanizates and the unmodified sample.

(a). Effect of dosage of plasticizer

The composition of the mixes are given in Table V.13. The stress-relaxation plots of the different vulcanizates at a strain level of 150% and strain rate of 0.2083 s^{-1} are given in Figure V.9. The extent, time and rate of stress-relaxation at equilibrium conditions are given in Table V.14.

Table V.13. Stress relaxation of NR vulcanizates - Composition of the mixes

Mix code	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
NR	100	100	100	100	100	100	100
ZnO	10	10	10	10	10	10	10
Stearic acid	2	2	2	2	2	2	2
Sulphur	2	2	2	2	2	2	2
MBT	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PCNSL	-	10	15	20	-	-	-
Santicizer 141	-	-	-	-	10	15	20

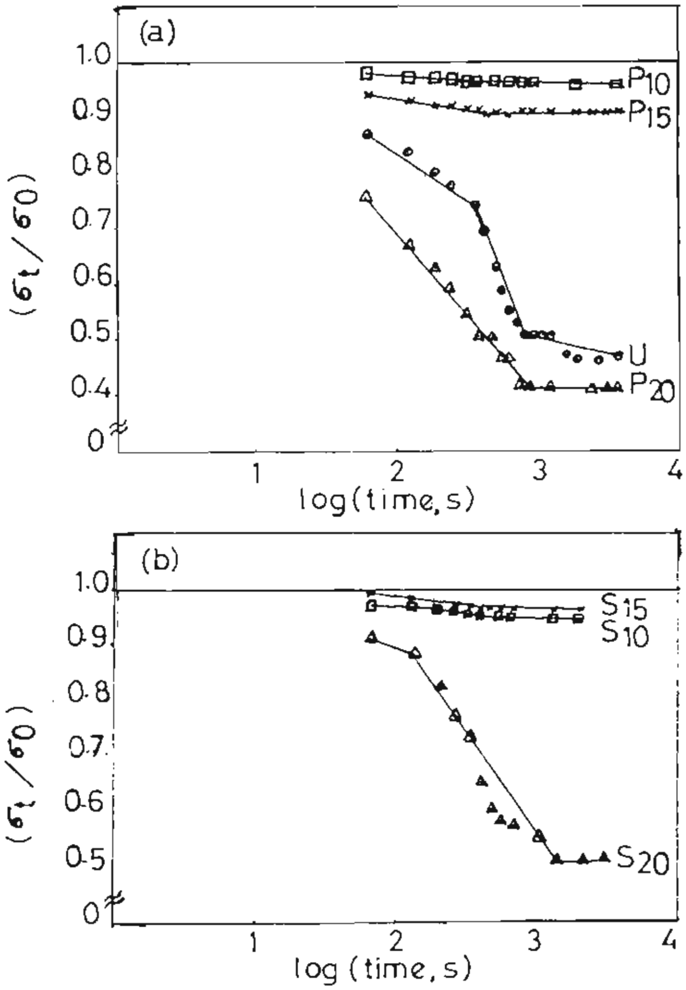


Fig.V.9. Stress relaxation characteristics of NR vulcanizates

(a) Un modified & PCNSL modified

(b) Santicizer modified

Strain rate = 0.2083 s^{-1}, Strain level = 150%

Table V.14 Comparison of PCNSL with 'Santicizer 141' - Stress relaxation characteristics(a) of the vulcanizates

Mix code	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
Stress relaxation time,(s)	1500	1800	300	720	540	360	1200
Stress relaxation (b) (%)	53	5	9	59	6	4	49
Rate of stress-relaxation (%/s)	0.035	0.003	0.030	0.082	0.011	0.011	0.041

(a) - Strain rate = 0.2083 s^{-1} , Strain level = 150 %, (b) - Steady values

These results show comparatively lower degree of stress-relaxation for the vulcanizates containing 10 to 15 phr of either PCNSL or Santicizer. Upon increasing the content of plasticizers to 20 phr, the extent and rate of stress-relaxation increases to considerably higher values, similar to that of the unmodified NR vulcanizate. In unfilled NR vulcanizates at normal temperatures, the rate of stress-relaxation has been shown to be strongly dependent on the degree of crosslinking of the vulcanizates (103). The lower stress-relaxation of the PCNSL modified NR vulcanizates may be explained in terms of the molecular theory for visco-elasticity (104). The reduced crosslink density of the PCNSL modified NR vulcanizates necessitates a greater number of co-ordinated segmental motions of the polymer chains for stress-relaxation. The higher crosslink density of the unmodified NR vulcanizate permits more number of modes of relaxation for its chain segments involving lower degree of co-operation between each, resulting in a higher rate of stress-relaxation. The higher rate of stress-relaxation of the vulcanizates containing 20 phr of the plasticizer may be due to the presence of higher proportions of extra-network materials as a result of lower degree of crosslinking, that may contribute to stress-relaxation as reported earlier (96). The formulations containing 10 to 15 phr of PCNSL or Santicizer may find applications as seals or gaskets which require a high degree of dimensional stability, whereas those containing 20 phr of the plasticizers may be used as sealants for joints. In the application as a sealant, the higher stress-relaxation characteristics reduces the maximum stress in various joint - configurations (105).

(b). Effect of strain-rate and strain-level

The effect of increase in strain rate from 0.0208 s^{-1} to 0.2083 s^{-1} and strain level from 50 to 150% on the stress-relaxation characteristics of the unmodified and PCNSL modified NR vulcanizates are shown in Figures V.10, V.11 & V.12 and Table V.15.

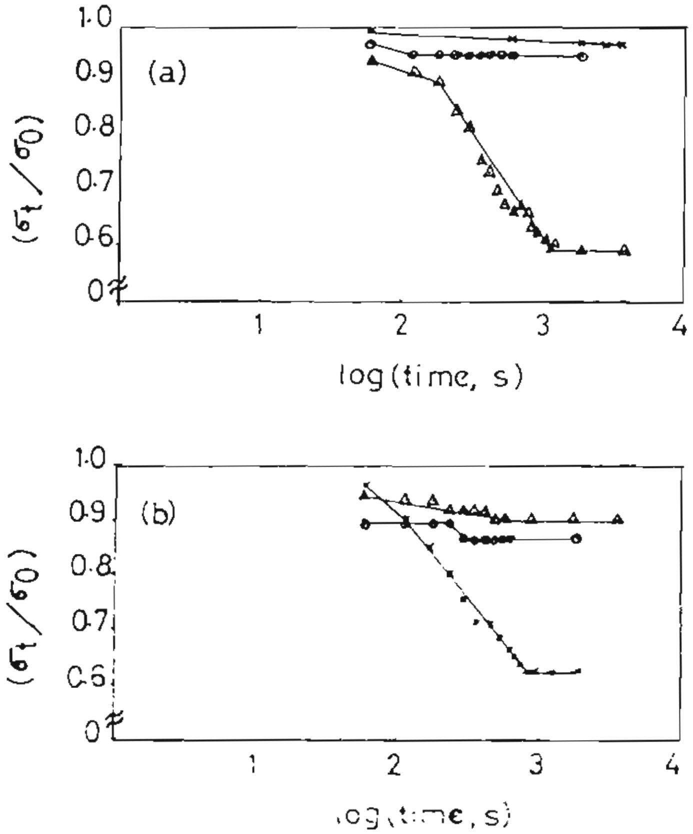


Fig. V.10. Stress relaxation characteristics of NR vulcanizates at strain rate of 0.0208 s^{-1} and at different strain levels

(a) Un modified (b) PCNSL (10 phr) modified

Strain level (%) o—o 50 x—x 100 △—△ 150

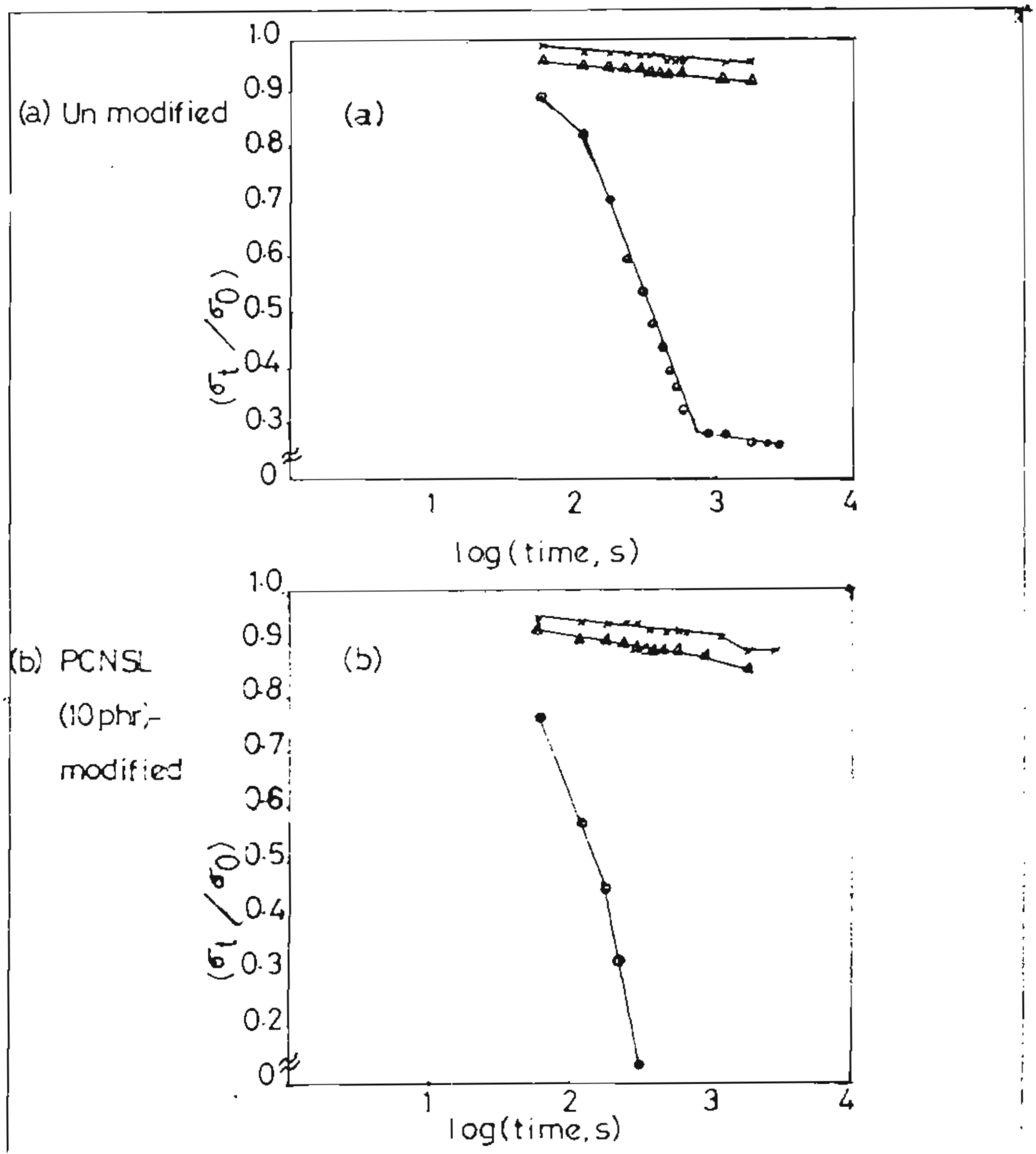


Fig.V.11.Stress relaxation characteristics of NR vulcanizates at strain rate of 0.1042 s^{-1} & at different strain levels.

Strain level (%) ●——● 50 ×——× 100 ▲——▲ 150

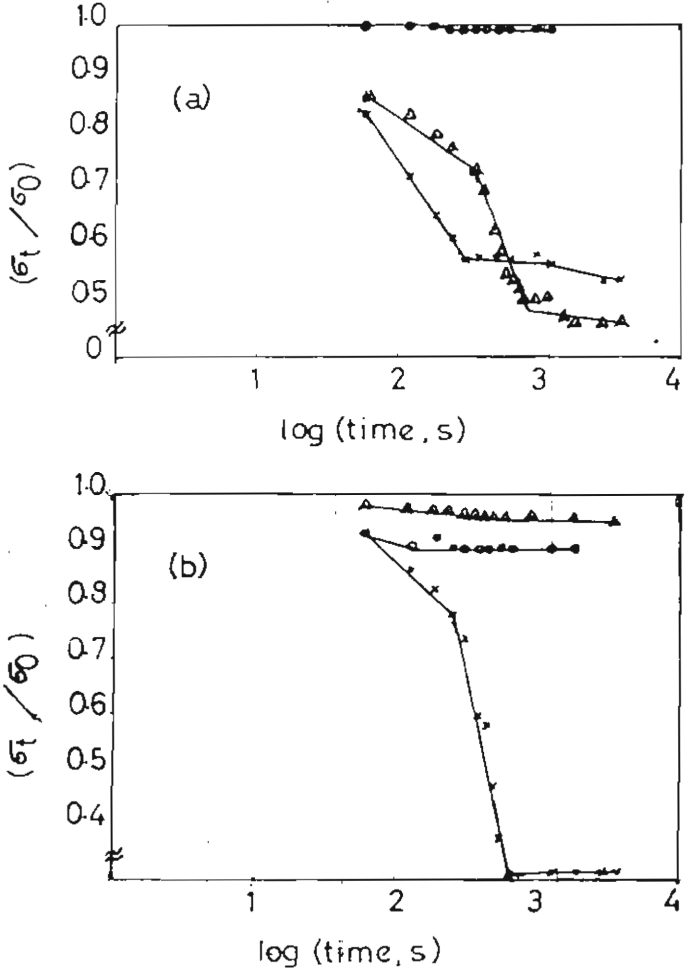


Fig.V.12.Stress relaxation characteristics of NR vulcanizates at strain rate of 0.2083 s^{-1} & at different strain levels
(a) Un modified (b) PCNSL (10phr) modified

Strain level (%) ●—○ 50 ×—× 100 ▲—△ 150

Table V.15. Effect of variations in strain rate and strain level on the stress relaxation of unmodified and PCNSL modified gum NR vulcanizates

Strain rate (s^{-1})	Strain level (%)	Stress relaxation (%)		Rate of stress relaxation (%/s)	
		U	P_{10}	U	P_{10}
0.0208	50	5	13	0.042	0.036
	100	3	37	0.002	0.044
	150	40	10	0.032	0.021
0.1042	50	73	-	0.041	-
	100	4	11	0.008	0.006
	150	8	14	0.004	0.008
0.2083	50	1	10	0.004	0.042
	100	46	68	0.017	0.103
	150	53	5	0.035	0.003

The results show that the extent and rate of stress-relaxation of the vulcanizates are independent of the strain rate and strain levels. This is in accordance with the observation of Gent$^{(106)}$ on the independence of rate of stress-relaxation on the degree of deformation of unfilled NR vulcanizates at extensions below 200%. Chasset et al. $^{(103)}$ also observed that in unfilled NR vulcanizates at normal temperatures, the rate of stress-relaxation was substantially independent of the type and degree of deformation. Table V.15 shows the lower extent and rate of stress-relaxation of the NR vulcanizate containining 10 phr of PCNSL, at various strain rates and strain levels. Thus, at the strain rate of 0.2083 s^{-1} and 150% elongation, the PCNSL modified NR vulcanizate shows 5% stress-relaxation (@ 0.003%/s) as against 53% (@ 0.035%/s) of the unmodified sample. This shows the suitability of NR vulcanizates containing 10 phr of PCNSL for applications requiring dimensional stability at moderate strain levels.

vii. Dynamic Mechanical Analysis

The response of a polymer to a cyclic deformation, usually under forced vibration conditions gives valuable information on its visco-elastic characteristics. The relaxation behaviour of the material can be studied by monitoring the stress-strain relationship with changes in temperature $^{(107)}$. Usually a sinusoidal load gives rise to a sinusoidal deformation with the strain lagging behind the applied stress by a phase angle δ. The dynamic mechanical properties of the material are described in terms of a complex dynamic modulus given as, $E^* = (E'^2 + E''^2)^{1/2} = E' + i E''$, where E' is the storage modulus which is a measure of the recoverable strain energy in the deformed body and E" is the loss modulus which is related to hysteresial energy dissipation $^{(107)}$. The phase angle δ is given by $\tan\delta = E''/E'$. The stiffness and damping properties of the material can be described by any two of the three quantities viz. E', E" and tanδ. The dynamic mechanical properties are of direct significance to rubber engineer as it is applied in many of the engineering products such as sound insulators and vibration dampers (108). Apart from these, the technique is used in characterizing polymers and composites. In characterizing glassy polymers, the storage modulus E' drops abruptly near the rubber - glass transition temperature (107). Snowdon(109) has identified some of the criteria for defining a good resilient vibration isolator as (i) it should possess a large damping factor to provide a low- resonant transmissibility and (ii) it should be free from any major increase in dynamic modulus or damping factor with frequency. NR is a low damping polymer (110). At least 5% damping is required in bearings used for seismic protection of buildings, as earth-quakes have a very broad spectrum of vibrations. Modification of NR with a high viscosity oil is known to give substantial damping characteristics without undue sacrifice of other properties (110).

The dynamic mechanical properties of unmodified and PCNSL modified NR vulcanizates under tensile deformation were measured over the temperature range from -100°C to 50°C at various frequencies viz., 3, 10 and 30 Hz. The DMTA traces of the storage and loss moduli of the vulcanizates at 3, 10 and 30 Hz are given in Figures V.(13-15). Also, Figure V.8 shows the tanδ vs temperature plots of the vulcanizates at all the three frequencies ie. 3, 10 and 30 Hz

Figures V.(13-15) show distinct difference between the unmodified and PCNSL modified NR vulcanizates, particularly at lower temperatures and at all frequencies. The loss modulus (E") of the PCNSL modified NR vulcanizate is considerably lower than that of the unmodified NR vulcanizate at temperatures below - 50 °C implying that PCNSL modified NR vulcanizates will have less loss during dynamic testing. Thus, it can be used for low temperature dampers / isolators. However, above -40°C and upto +50 °C, the loss modulus (E") of the PCNSL modified NR vulcanizate is less or same as that of the unmodified NR vulcanizate.

The storage modulus (E') of the PCNSL modified NR vulcanizate in the temperature range from -100 °C to -50 °C is found to be higher than that of the unmodified NR, implying a higher elasticity at low temperature applications. The dynamic strength of PCNSL modified NR vulcanizate will be higher as compared to unmodified NR vulcanizate at lower temperatures. But at higher temperatures for instance from -25 °C to +50 °C the E' value of PCNSL modified NR vulcanizate is much less than that of unmodified NR vulcanizate at all the three frequencies studied. This implies that at room temperature the elastic property of PCNSL modified NR vulcanizate is much less than that of unmodified NR vulcanizate.

The difference between the loss and storage moduli becomes progressively higher with the increase in temperature from -25 °C to +50 °C and with increase in frequency from 3 to 30 Hz. In the unmodified NR vulcanizate the decrease in loss modulus with respect to storage modulus is comparatively lower. Also, the increase in loss modulus over storage modulus at higher temperatures (above -40 °C) and frequencies is comparatively lower in the unmodified NR vulcanizate. These changes are clearly reflected in the tanδ vs temperature plots of unmodified and PCNSL modified NR vulcanizates at all the three frequencies

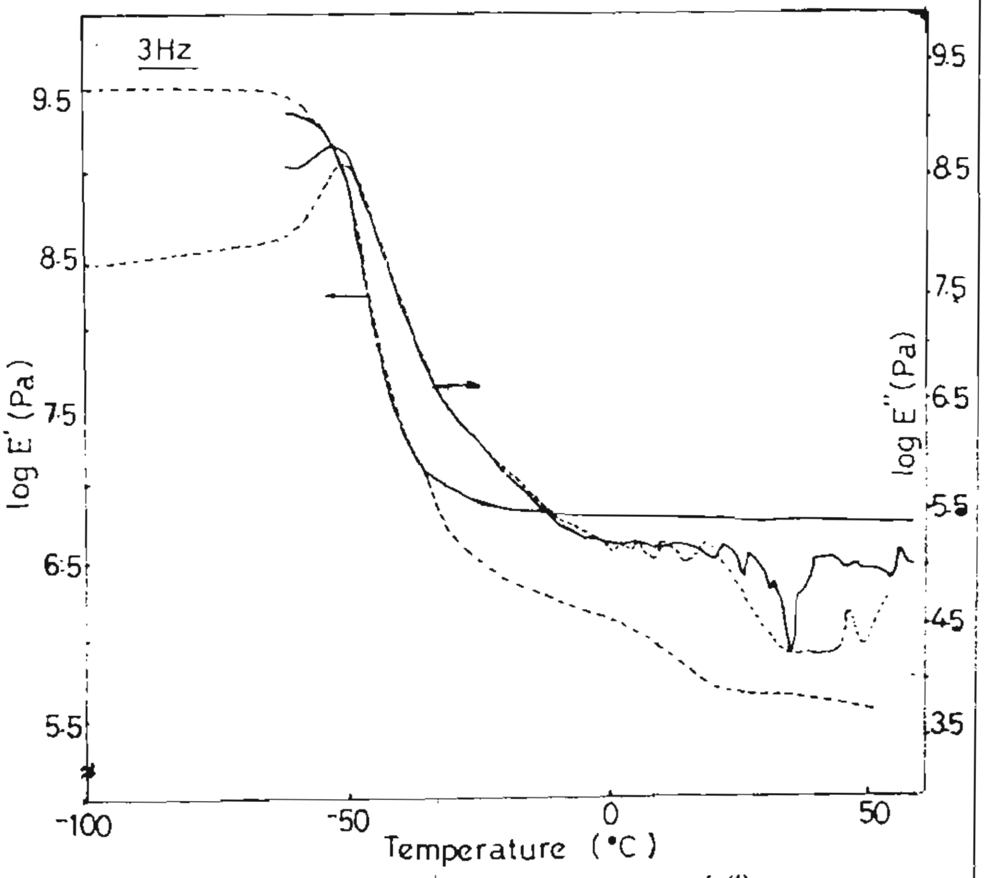


Fig.V.13. Storage modulus (E') and loss modulus (E'') of un modified and PCNSL modified NR vulcanizates (DMTA)

——Un modified ----- PCNSL (10 phr) modified

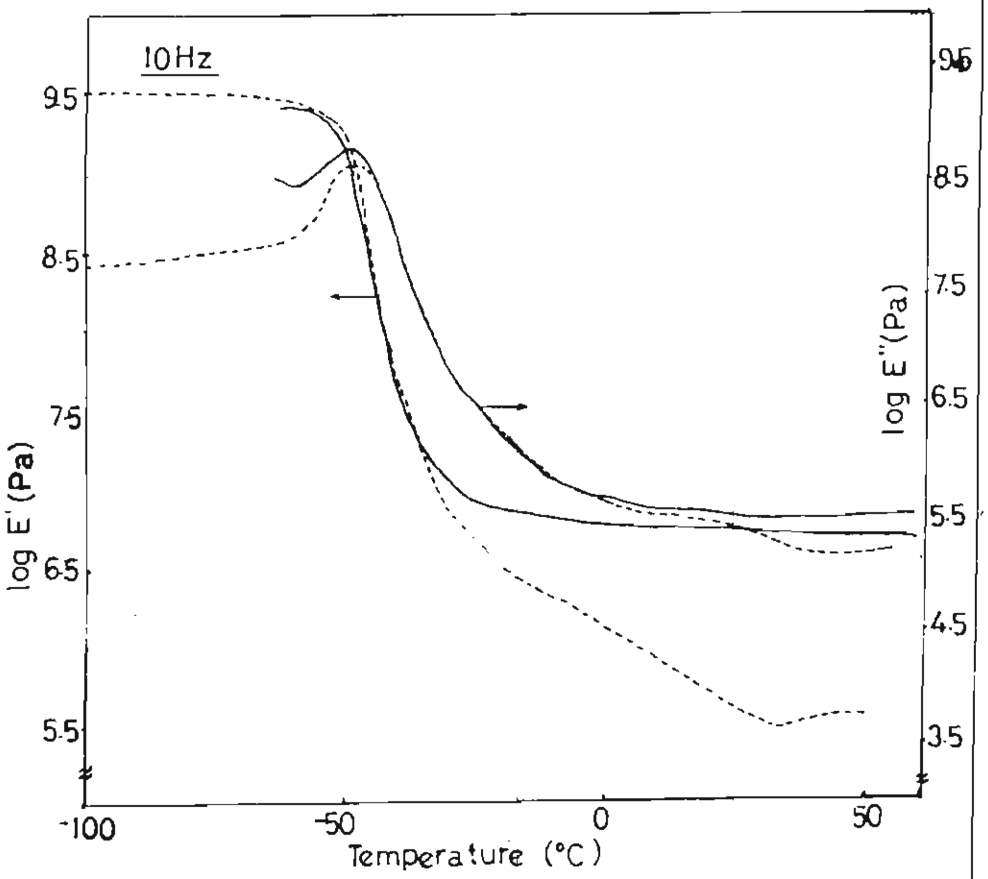


Fig.V.14. Storage modulus (E') & loss modulus (E'') of un modified and PCNSL modified NR vulcanizates. (DMTA)

____ Un modified ..... PCNSL (10 phr) modified

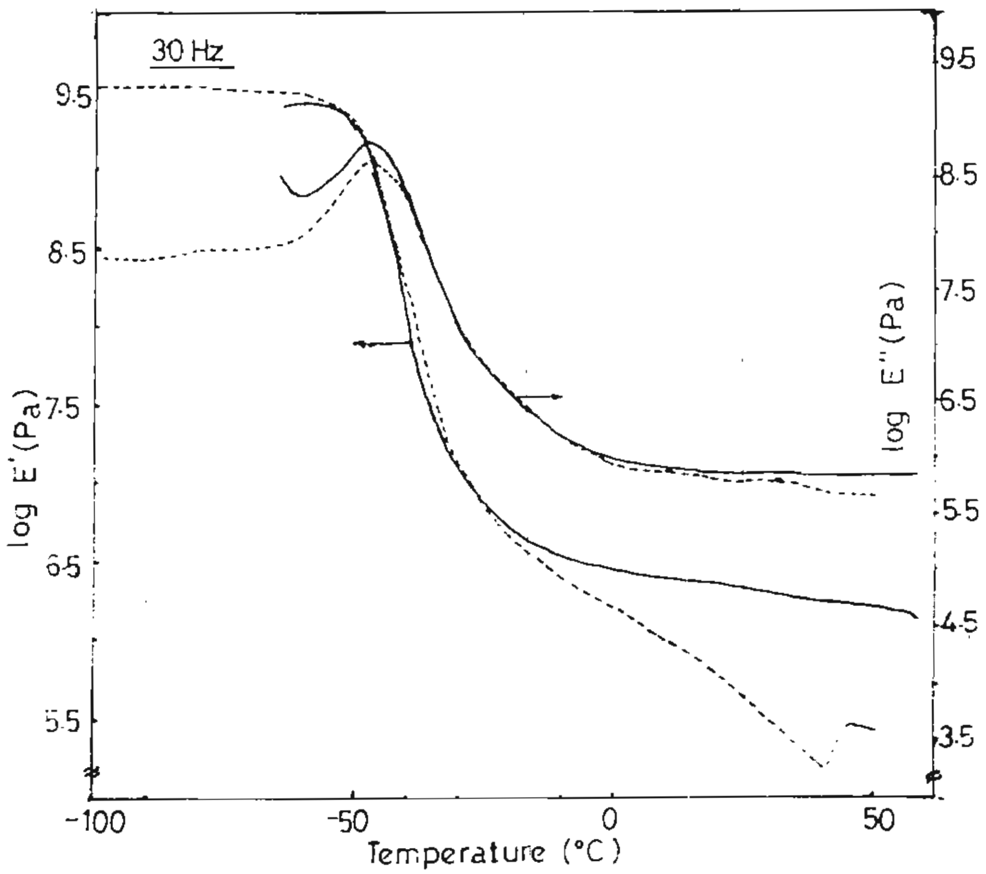


Fig.V.15. Storage modulus (E') & loss modulus(E'') of unmodified and PCNSL modified NR vulcanizates.(DMTA)

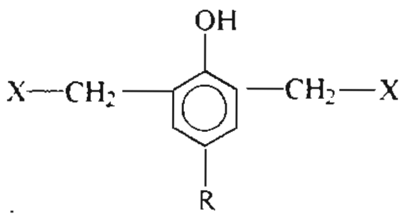
—— Un modified ------ PCNSL (10 phr) modified studied The PCNSL modified NR vulcanizate shows comparatively lower tanδ at temperatures below approximately -40°C as given in Figure V 8. Also, the closeness of the tanδ peaks of the unmodified and PCNSL modified NR vulcanizates at the various frequencies indicates a higher level of compatibility between NR and PCNSL.

The dependence of the dynamic mechanical properties of the vulcanizates on crosslink density has been reported by Rucinski et al. (111) In cis-1,4-polyisoprene vulcanizates, the decrease of loss modulus with increasing degree of vulcanization was related to the decrease in concentration of temporary loop and chain contact nodes (112). The dynamic properties of vulcanized natural rubbers were studied by Rzymski and Jenzsch(113). They found that temporary contacts and entanglement nodes were the basis for damping of the vulcanizates. The reduced damping observed with increasing crosslink density was attributed to a reduction in the concentration of temporary nodes which reduced the friction of the chains. It is expected that the PCNSL modified NR vulcanizate which has a lower crosslink density and a high degree of 'entanglements' (28) may contain a higher concentration of temporary nodes (possibly from the C_{15} hydrocarbon chain of PCNSL) which can contribute to a higher extent of energy dissipation as discussed above.

V.4.Chemical analysis of PCNSL modified NR vulcanizates

i. Crosslink density and network structure

Ever since the discovery of vulcanization of NR (114) by Charles Goodyear in 1839, the science and technology of rubber processing has made an amazing progress with the introduction of a variety of crosslinking methods tailor-made for specific functional requirements of the finished product. Diene rubbers (eg. butyl rubber) are known to be capable of being crosslinked with phenolic resins having the general structure (I)



(I)

where 'X' is -OH or halogen atom giving rise to products having very good resistance to high temperature (39). Different sulphur vulcanization systems of the conventional (CV), semi-efficient (SEV) and efficient (EV) types have evolved (38). Each one is designed for a specific combination of physico-mechanical properties and thermal stability in the vulcanizate Various investigators have observed a high degree of correlation between the vulcanizate properties and the network structure of elastomers (115,116). The dependence of network structure on the flammability and thermal properties of cis-1,4 poly isoprene vulcanizates have been studied by Janowska(117) and Slusarski(118) The physical properties of vulcanizates of diene rubbers are known to be very much dependent on their network structure(119). The nature and type of crosslinks and the crosslink density play a major role in influencing the properties of a vulcanizate(120,121). Hernandez et al. (122) have studied the effects of structure and crosslink distribution on the physical properties of NR networks crosslinked with sulphur, peroxide and benzene 1,3 - disulfonyl azide crosslinking systems. Different vulcanizing systems impart different tensile properties to NR, even at nearly same degree of crosslinking (123,124).

Nasir and Teh (125) studied the effects of various types of crosslinks on the physico-mechanical properties of NR. They found that the tensile strength, modulus and elongation at break of the vulcanizates containing predominantly polysulphidic crosslinks are superior to those of the corresponding vulcanizates containing mainly monosulphidic crosslinks. Brown et al.(126) observed that vulcanizates of NR (of a non-strain crystallizing type) with high polysulphidic crosslinks possess higher tearing energy than those having monosulphidic crosslinks in the network system. The vulcanizates containing higher levels of polysulphidic crosslinks show higher strengths than those containing mono and disulphidic crosslinks, which inturn show higher strengths than vulcanizates containing carbon-carbon crosslinks. This decreasing order of strength properties corresponds to an increase in the bond-strength of the weakest crosslink in the network. Mechanically, weak crosslinks are able to relieve local stresses in the network by breaking and re-forming during deformation(126). Lal and Scott(127) observed a higher strength for gum NR vulcanizates containing higher proportion of polysulphidic crosslinks . The effect of crosslink type on tensile strength of vulcanizates has also been studied (128,129). The effect of crosslink type on the performance of rubber as an engineering material with respect to strength, relaxation processes, energy loss and aging behaviour has been reviewed exhaustively by Southern(130). Mullins(131) found that the tensile strength of vulcanizates are ranked in inverse order to the bond-energies of the crosslinks . While studying the stress relaxation phenomenon of vulcanizates, Farlie (92) observed that the difference between crosslink types is prominent at higher degrees of crosslinking .

In the vulcanization of NR, in addition to sulphur crosslink formation, back-bone modifications such as olefin - isomerization and the formation of polyenes, creation of sulphidic pendent groups and cyclic sulphides also occur, which very much affect the vulcanizate properties(132). Kumaran et al (133) studied the effect of accelerator system and the addition of lignin on the network structure of NR vulcanizates. It has been suggested that lignin increases the structural complexity of the vulcanizates by masking portions of the cure sites of the polymer chains and causing higher modification of the main chain which inhibits strain-induced crystallization. Also, the addition of lignin caused significant reduction in the crosslink density in all vulcanization systems studied (134). It was observed that *the concentration* of crosslinks of *lower sulphidity increases* at *the expense* of polysulphidic crosslinks on changing from conventional to efficient vulcanization systems in *lignin modified NR vulcanizates* (134). *Also, in presence of lignin, the value of* 'sulphur inefficiency parameter' *increased and the crosslink density decreased, leading to a decrease* in technical properties of *the vulcanizate* (131). *Similar reduction in crosslink density has* been reported for SBR vulcanizates modified with cardphenol(135). The physico-mechanical properties of rubber vulcanizates depend very much on their crosslink density. The elongation at which an elastomer chain becomes extended is known to be a distinct function of $M_{c(phys)}$ where $M_{c(phys)}$ is the number average molecular weight between 'physically effective' crosslinks(136). An increase in the crosslink density results in a decrease in the elongation at break and increases in glass transition temperature and rigidity of vulcanizates(137). Saville and Watson(138) made extensive studies on the structural characterization of sulphur vulcanized natural rubber networks employing the data on crosslink density, total combined sulphur (S_c), sulphur inefficiency parameter (E), concentration of polysulphidic linkages and contribution of the network 'entanglements'. Bristow and Tiller(139) found that NR vulcanizates containing different types of crosslinks showed a maximum tensile strength at an intermediate degree of crosslinking. Nando and De(141, 142) studied the changes in the network structure of NR vulcanizates subjected to different physical tests in presence and in absence of lignin. They showed that lignin modified NR vulcanizates have lower crosslink density than the unmodified one. They also observed that the crosslink density of the lignin modified NR vulcanizates increase on aging and also during compression set testing due to the post-vulcanization reactions(140).

Methods for the determination of network combined sulphur (S_c) and sulphur inefficiency parameter (E) have been described by Bhowmick and De(142). The higher values of sulphur inefficiency parameter during vulcanization reactions is suggested to be due to the incorporation of sulphur in the form of long polysulphidic crosslinks, cyclic monosulphides and vicinal sulphidic crosslinks(143).

Bueche(144) has proposed a relation between elastically effective network chain density ν, crosslink density c, entanglement density ϵ and number average molecular weight M_n given as $\nu = 2c - 2\rho/M_n + 2\epsilon(1 - \rho/cM_n)$ where ρ is the density of the polymer. In the rupture of vulcanized rubbers at the elastic region, the force to break is known to depend on the structural features of the vulcanizate such as (i) the density of crosslinks, (ii) bond energy of main chain or breaking energy of the weakest link and (iii) molar volume of a segment(145). Physical crosslinks in a polymer may arise out of H-bonding, ion-dipole interaction and dipole - dipole interaction. IR analysis of sol and gel fractions of NR showed the existence of H-bonding between protein and isoprene chains forming physical crosslinks(146). It is known that satisfactory 'technical materials' are obtained only when the average molecular weight between junction points (M_c) in a polymer network is large and that highly crosslinked polymers of low initial molecular weight are often brittle(147). The concentration of 'elastically effective network chains' in a polymer is given by the Mooney - Rivlin equation(148) as $F/A_0 = (2C_1 + 2C_2\lambda^{-1})(1 - \lambda^{-2})$ where F is the equilibrium force required to maintain extension ratio λ, A_0 is cross section area of the undeformed polymer and C_1 and C_2 are constants. According to the molecular theory, the formation of a network will result in a collection of chain segments of varying lengths connecting various crosslink points, distributed through space in the specimen and perhaps 'dangling' unconnected chain ends or even some entirely linear chains(149). The chain segments will be inter-twined in various ways and some of these ways could present rather permanent entanglements. Chain entanglements contributes to the equilibrium modulus of rubber networks made by crosslinking of long linear chains (150) Physical crosslinks resulting from chain entanglements has been described by Moore and Watson (151). Analysis of the experimental results on 1,2-poly butadiene networks showed that chain entanglements contributed towards 15% of the modulus at elastic equilibrium (152)

The chemical crosslink density of vulcanizates is often determined by following the procedure of equilibrium swelling in benzene (138-155). The chemical crosslink density (CLD) is given by the Flory - Rehner equation (156) as,
$\nu = -(1/V_s)\,(\ln(1-v_r) + v_r + \chi v_r^2)\,/\,(v_r^{1/3} - 0.5\,v_r)$ where, V_s is the molar volume of the solvent, χ is polymer - solvent interaction parameter and v_r is the volume fraction of rubber in the swollen rubber gel (120). The chemical crosslink density represented as, $(2\,M_{c\,chem})^{-1}$ of PCNSL modified NR vulcanizates was determined using the Flory - Rehner equation(28) The number average molecular weight of NR (M_n) was determined from intrinsic viscosity data, with the relation reported by Mullins and Watson (156) as,
$\eta = 2.29 \times 10^{-7} M_n^{1.33}$ The value of χ for NR in benzene at 25 °C was given as 0.44 (157)

The crosslink density can also be estimated from tensile or creep tests by means of the equation, $f = A_0\, RT\nu\, (\lambda - \lambda^{-2})$ where, λ is the equilibrium extension ratio, T is the absolute temperature, R is the universal gas constant, f is the corresponding force and A_0 is the cross-sectional area of the undeformed specimen (120) Estimates of crosslink density from chemical analysis which solely reflects chemical crosslinks will generally be lower than values obtained by stress-strain data, because the latter measurements include the influence of 'permanent entanglements'. An empirical relation between physical and chemical crosslinks including a correction for flaws due to chain ends is given (158) as,
$C_1 = 1/2\rho RTM_{c\,(physical)}^{-1}(1-2.3M_{c\,(chemical)}/M)$ where , $M_{c\,(physical)}$ is the number average molecular weight of the elastically effective chain segments and includes the contribution of all crosslinks both real and virtual such as entanglements, $M_{c\,(chemical)}$ is the molecular weight between the chemical crosslinks , M is the molecular weight before crosslinking (raw rubber) and C_1 is the 'elastic constant' given as $1/2\,\rho\,R\,T\,M_c^{-1}$ where M_c is the average molecular weight between elastically effective crosslinks (159). Other physical test methods can also be used for the study of crosslink density and network structure of vulcanizates (160-164) Gronski et al.(160) used high resolution solid state carbon NMR (C_{13}) to study the crosslink structure in accelerated sulphur vulcanized NR . Simon and Schneider(161) have described non-destructive test methods for the determination of molecular weight between crosslinks (M_c) of elastomers by proton NMR relaxation and deuterium NMR spectroscopy Other methods for the determination of network structure of vulcanizates include FT-NMR spectroscopy (162), moving die-rheometry (163) and studies using Rubber Process Analyzer (164).

The estimation of crosslink types (mono, di and polysulphidic) in the network structure of vulcanizates has been carried out using 'thiol-amine chemical probes'(165,166,28), which help in the selective cleavage of crosslinks prior to the determination of crosslink density Kheraskova et al (167) have reported a procedure for the estimation of 'free - sulphur' in vulcanizates using sodium sulphite The sulphur combined in the form of zinc sulphide is often estimated as per the British Standard BS-903. Part B (1958). The network combined sulphur (S_c) is determined from compounded sulphur available for crosslinks, zinc-sulphide sulphur and free sulphur (133) Also, the sulphur inefficiency parameter (135) (E) is defined as $E = (S_c) / (2 M_{c,chem})^{-1}$.

A knowledge of the chemical constitution of the vulcanizate, particularly the density of crosslink formation and network structure is an essential pre-requisite for the correct interpretation of its physico-mechanical properties and to arrive at reasonable structure - property correlation. The improvements in some of the physico-mechanical properties of PCNSL modified NR vulcanizates such as tensile strength, tear strength, elongation at break and resistances to thermo-oxidative aging and tensile fatigue have been described in the previous section (V.3.iv). The studies on the effect of variations in concentration of the curatives, (especially ZnO) on the rate of cure of PCNSL modified NR formulations strengthened the belief that PCNSL may affect the crosslink density and network structure of NR to a considerable extent This necessitated a detailed analysis of the network structure of PCNSL modified NR vulcanizates, specifically with respect to the chemical crosslink density (CLD) and the nature and extent of different type of crosslinks. Further, this was expected to lead to a better understanding of the role of additives such as PCNSL prepolymer on the vulcanizate structure- property relationship, which may be of use in the design of multifunctional additives for compounding with elastomers. Thus, the effects of variations in the dosages of PCNSL and ZnO and the type of vulcanization systems on the CLD and network structure of gum NR vulcanizates have been studied in the present section Some of the parameters employed in the elucidation of the network structure of the vulcanizates are the total crosslink density, the proportion of mono, di and polysulphidic crosslinks in the network structure. network combined sulphur and sulphur inefficiency parameter Other methods of characterization such as IR spectroscopy and X-ray diffraction have also been utilized to supplement the findings towards a good structure-property relationship

Table V.16 gives the composition of mixes based on conventional, semiefficient and efficient vulcanization systems of NR with variation in the proportion of ZnO and PCNSL.

Table V.16. Effect of PCNSL on chemical crosslink density of NR vulcanizates
Composition of the mixes.

Materials	Vulcn. System^a									
	CV		SEV						EV	
	Mix code		Mix code						Mix code	
	$C_{10\ 0}$	$C_{10\ 10}$	$S_{10\ 0}$	$S_{10\ 10}$	$S_{10\ 20}$	$S_{15\ 20}$	$S_{20\ 20}$	$S_{25\ 20}$	$E_{10\ 0}$	$E_{10\ 10}$
NR	100	100	100	100	100	100	100	100	100	100
ZnO	10	10	10	10	10	15	20	25	10	10
Stearic acid	2	2	2	2	2	2	2	2	2	2
Sulphur	2.5	2.5	2	2	2	2	2	2	0.5	0.5
MBT	0.6	0.6	1.5	1.5	1.5	1.5	1.5	1.5	2.5	2.5
TMT	0.2	0.2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PCNSL	0	10	0	10	20	20	20	20	0	10

^{a}- CV - Conventional, SEV - Semi efficient & EV - Efficient

ii. Effect of dosge of PCNSL on CLD of the vulcanizates

Among the various factors affecting the CLD and the physico-mechanical properties of vulcanizates, the nature of the vulcanization system (123,124) and the type and dose of network modifying agents such as resins (132,133, 3,168) and plasticizers have a major role to play. It has been shown that the CLD and mechanical properties of NR vulcanizates are very much dependent on the nature of the vulcanization system employed (126,134,135). The effect of different accelerator systems and the addition of lignin on the network structure of NR was studied by Kumaran et al.(133) and Nando and De(140,141). It has been found that the CLD of all the systems reduced significantly with the addition of lignin. Another study on the network structure of lignin modified NR vulcanizates showed that the concentration of crosslinks of lower sulphidity increased at the expense of polysulphidic crosslinks on shifting from the conventional to efficient vulcanization system, apart from reduction in CLD and technical properties(134).

The considerably higher tensile properties observed for the PCNSL modified gum NR vulcanizates in the SEV system as against that of the CV and EV systems (74) made it imperative to explore the effect of variation in the dosage of PCNSL on the network structure. The results on the chemical crosslink density of the vulcanizates before and after thermal aging and the distribution of different types of crosslinks are given in Table V.17.

Table V 17 Crosslink density and distribution of different types of crosslinks in PCNSL modified gum NR vulcanizates

Parameters	Vulcn system									
	CV		SEV						EV	
	Mix code		Mix code						Mix code	
	$C_{10\,0}$	$C_{10\,10}$	$S_{10\,0}$	$S_{10\,10}$	$S_{10\,20}$	$S_{15\,20}$	$S_{20\,20}$	$S_{25\,20}$	$E_{10\,0}$	$E_{10\,10}$
Total CLD [a]										
(i). Original	6.78	3.97	7.48	6.56	2.97	6.02	6.81	5.12	4.50	3.26
(ii). After - aging	6.45	4.68	7.10	7.00	3.64	6.07	6.65	5.98	4.67	3.09
Type of crosslinks [a] (Original)										
Polysulphidic	2.48	1.22	1.78	2.00	0.46	1.71	2.67	1.46	0.77	0.66
Disulphidic	0.72	2.75	2.06	1.74	2.51	1.36	1.73	0.89	0.97	0.58
Monosulphidic	3.58	-	3.64	2.82	-	2.95	2.41	2.77	2.76	2.02
Net-work - combined sulphur (S_c)[b]	7.37	7.27	5.90	6.09	5.90	5.85	5.88	5.75	1.30	1.24
Sulphur - inefficiency - parameter (E)[c]	10.9	18.3	7.9	9.3	19.9	9.7	8.6	11.2	2.9	3.8

a - CLD X 10^5 mol / g RH, *b* - S_c X 10^4 mol S /g RH, c - E - atoms / chemical crosslink.

The results in Table V 17 show that the CLD decreases in all the vulcanization systems in presence of PCNSL, the decrease being comparatively lower for the SEV system. Thus, the presence of 10 phr of PCNSL decreased the original (unaged) CLD by 41.45% for the CV, 27.56% for the EV and 12.30% for the SEV system. Also, the results show a progressive decrease in the CLD of the vulcanizates with the increase in dosage of PCNSL from 0 to 20 phr in the SEV system The decrease in CLD is particularly considerable at 20 phr of PCNSL in the vulcanizate containing a lower level (10 phr) of ZnO. As mentioned earlier(131), a similar decrease in CLD of NR vulcanizates has been reported for systems containing lignin

PCNSL is known to contain a mixture of oligomers(169). The structures of the triene component of monomer and prepolymer of PCNSL are shown in chapter I (Figure I.3). Based on these structures, the possible interactions between PCNSL and NR have been envisaged(128) as -

(i) the interactions between the aliphatic segment of PCNSL and NR

(ii) hydrogen bonding between the phosphate groups of PCNSL and (iii) the phosphate - metal (eg. Zn^{++}) interaction, forming a metallic complex / ionic bonds.

It is possible that the above-mentioned interactions may operate simultaneously to varying extent, leading to a network structure of the vulcanizate shown schematically in Figure V.16. John et al.(170) have ascribed the unusually high bulk viscosity of PCNSL to the interactions between the phosphate groups of PCNSL because of hydrogen bond formation. They observed a broadening of the IR spectrum of a neat film of PCNSL in the region 1250 cm^{-1} and a shifting by 10 cm^{-1} of the said peak towards the lower wavelength range in a dilute solution (0.3 molar) of PCNSL in CCl_4. This is an indication of the presence of hydrogen bonds between the phosphate groups of adjacent molecules of PCNSL. Also, there is every possibility of chemical interactions between the unsaturated aliphatic segment of PCNSL and the main chain of NR. Thus, by heating a mixture of NR, PCNSL (10 phr) and sulphur (0 to 8 phr) at 150 °C under pressure cured films of PCNSL have been obtained with reduced solubility in acetone. The results given in Table V.18 indicate probable chemical reactions between PCNSL and NR particularly in presence of higher dosages of sulphur and on prolonged heating. This may be facilitated by an increase in the effectivelength of the oligomer unit of PCNSL through intermolecular hydrogen bonding (28).

Table V.18. Solubility of mixture of NR, PCNSL and sulphur in acetone after heating at 150°C(%)

Time of heating (hrs)	Dosage of sulphur (phr)			
	0	2	4	8
1/2	-	90	80	70
1	-	80	70	70
2	80	60	60	50

The presence of the oligomeric moieties of PCNSL between the unsaturation sites of NR may be responsible for the lower CLD of the PCNSL modified NR vulcanizates. The formation of 'virtual crosslinks' (158) resulting from chain entanglements between NR and PCNSL may also contribute for the higher tensile strength and elongation at break of the PCNSL modified NR vulcanizates. The X-ray diffraction patterns of NR vulcanizates in a SEV system before and after modification with PCNSL have been studied in the unstretched and stretched conditions. The diffractograms are given in Figure V.17. It is seen that intensity of the crystalline peaks for the PCNSL modified NR vulcanizates as compared to that of the unmodified sample reduces, increasing amorphosity of the matrix. The reduced intensity of the peaks for the PCNSL modified NR vulcanizate even after stretching (as shown in Fig. V.17 (a) & (b)) indicates the absence of any strain induced crystallization in the modified matrix. This, along with an increase in the proportion of the amorphosity of the PCNSL modified vulcanizate (because of the presence of a higher

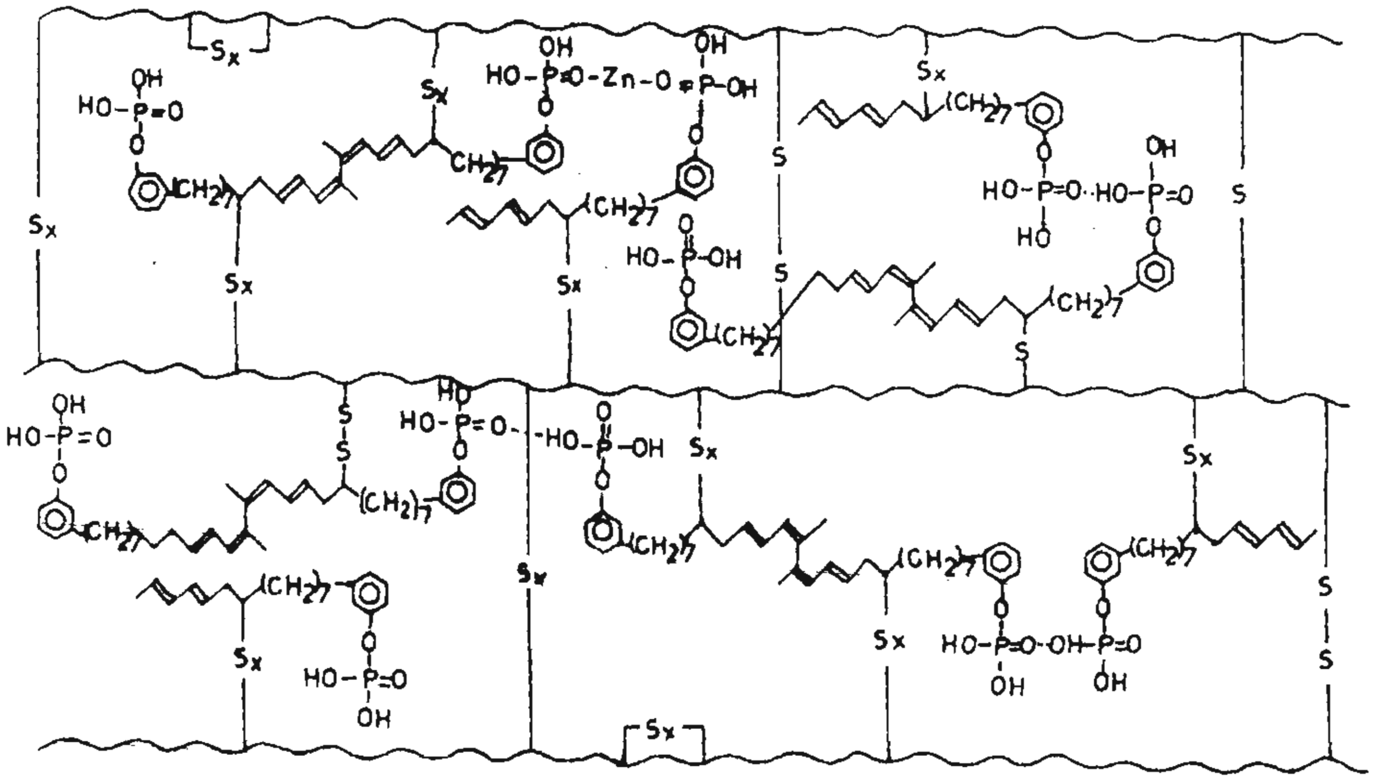


Fig. V.16. A schematic representation of the possible chemical linkages in the network structure of PCNSL modified NR vulcanizates.

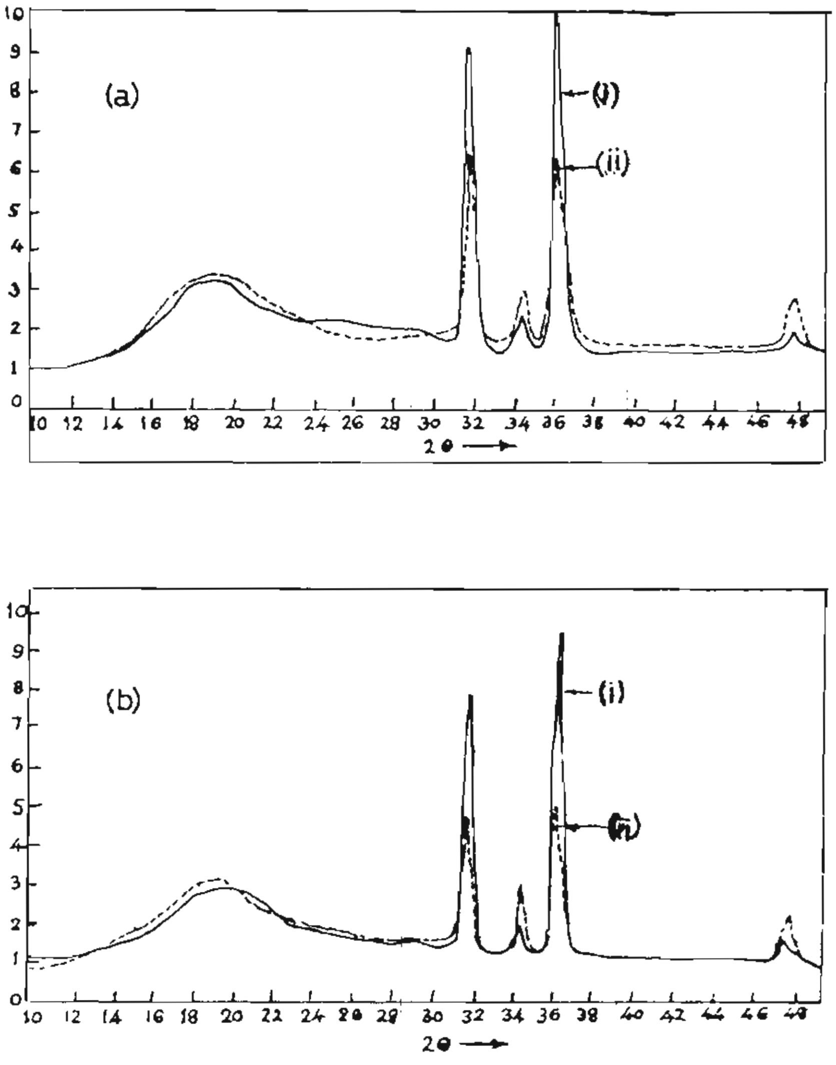


Fig.V.17. X-Ray diffraction patterns of PCNSL modified NR - vulcanizates.(a) unstretched,(b)stretched 300%, 30min. PCNSL (phr) - (i) 0 , (ii) 10 proportion of the entangled network structure) is responsible for hindering any sort of ordering in the matrix

iii. Effect of thermo-oxidative aging on the CLD of PCNSL modified NR vulcanizates.

The results on the CLD of the vulcanizates after aging at 70 °C for 48 hours are also given in Table V.17. It shows that after aging the CLD of the vulcanizate containing 10 phr of PCNSL increases by 18 % in the CV system and by 7 % in the SEV system. This is in contrast to the decrease in CLD of the unmodified NR vulcanizate by 5 % each in the CV and SEV systems. These results support the observation made earlier that an increase in tensile strength of PCNSL modified NR vulcanizates and a decrease in tensile strength of unmodified NR vulcanizate occur after aging(74). The increase in CLD of the PCNSL modified NR vulcanizates after aging is attributed to the formation of additional crosslinks between the unsaturation sites of the side chain of PCNSL and the main chain of NR during aging at elevated temperatures in both the CV and SEV systems. This supports the earlier finding that PCNSL acts as a 'crosslinkable plasticizer' in NR.

iv. Effect of dose of ZnO on CLD of PCNSL modified NR.

A significant retardation in the rate and state of cure of gum NR compounds has been observed earlier (74) in presence of higher concentrations (20 phr and above) of PCNSL with normal dosage (5 phr) of ZnO. However, a restoration in the rate and state of cure of these formulations was achieved by increasing the dosage of ZnO from 5 to 20 phr so that the ratio of PCNSL to ZnO becomes unity. Improvements in the physico-mechanical properties of their vulcanizates has also been observed. This indicated the pivotal role of ZnO in the network structure (including CLD) of NR vulcanizates in presence of higher concentrations of PCNSL and determining its performance properties. Thus, the CLD and the various chemical parameters have been determined for NR containing 20 phr of PCNSL and 10 to 25 phr of ZnO, in a typical SEV system. Table V.17 gives the CLD (before and after aging) and the distribution of different types of crosslinks in the vulcanizates. The results show that the CLD increases significantly with an increase in the concentration of ZnO, reaching a maximum at the 1:1 ratio of ZnO/PCNSL. The above results show that ZnO plays a vital role in the thiazole accelerated vulcanization of NR, particularly in presence of higher concentrations of PCNSL

The crucial role of ZnO in the vulcanization reactions of diene rubbers has been emphasized and critically analyzed by various investigators as mentioned earlier. Extensive studies have been carried out on the role of ZnO in thiuram based vulcanization systems of cis - 1,4 polyisoprene and NR (40-45). It has been reported that the cure accelerator, tetra methyl thiuram disulphide (TMT) reacts with ZnO to form, zinc perthio mercaptide XS_xSZnSX, ($X = Me_2NC(S)$, $x>1$) prior to crosslinking(43). Kinetic studies by Duchacek (44) revealed that the vulcanization rate and crosslink density increased when the amount of ZnO was increased from 0 to 1.5 phr in a NR compound cured with

TMTD The vulcanization time of a NR system containing 8 phr of sulphur was found to have been halved by the addition of 5 phr of ZnO without affecting physical properties such as tensile strength and elongation at break of the vulcanizate (45) Coran (171) has proposed the following mechanism in a thiazole accelerated sulphur vulcanization system of NR *It has been suggested that in this system an increase in the concentration of soluble* Zn ions increases the overall rate of formation of rubber - S_x - A_c within the matrix, where S_x - A_c is the accelerator-terminated polysulphidic moiety This increase in turn increases the extent of crosslink formation due to Zn^{++} ions forming complexes with accelerator and accelerator-polysulphides. The chelated form of the accelerator terminated polysulphidic chain modified rubber has been postulated to be more reactive than the free accelerator -derived polysulphidic moiety, resulting in the formation of a higher extent of crosslinks Because of the zinc-chelation, the S-S bond is most likely to break in the rubber-S_x - A_c complex resulting in monomeric rubber radical that is highly sulphurated (39) and that can recombine to form crosslinks.

The increase in CLD at a higher concentration of ZnO may be explained on the basis of the above-mentioned mechanism At the ZnO / PCNSL ratio of less than 1:1 and at higher concentration of PCNSL, it is most likely that sufficient soluble Zn^{++} ions are not available for the chelate formation due to interaction of Zn^{++} ions with the phosphate groups of PCNSL as shown in Fig V 16. Evidence for such an interaction has been *obtained from the reduced intensity of* IR absorption at 1250 cm^{-1} for the NR sample *containing* 10 phr each of ZnO *and* PCNSL *(Fig. V.18(a)) compared to the one having* 10 phr of PCNSL only *(Fig. V 18 (b)) The reduced availability of* Zn^{++} *ions as a result of the* above interaction, inturn, leads to a reduction in the extent of crosslink formation as per the mechanism of Coran (171) At higher concentrations of ZnO (ZnO/PCNSL ratio 1:1 and above), it is expected that sufficient free Zn^{++} ions are available to influence the vulcanization reactions, even if a part of the ions are not available because of the complex-formation with PCNSL Also, the IR spectrum of the neat film of PCNSL cast from $CHCl_3$ (Fig V 18 (c)) showed higher absorption intensity at 1250 cm^{-1} indicating the presence of a higher extent of hydrogen bonding.

v. Effect of PCNSL on the network structure of the NR vulcanizates

The distribution of different types of crosslinks (mono, di and polysulphidic) with respect to the original CLD of the unmodified and PCNSL modified NR vulcanizates is given in Table V 17 The estimated values of the network combined sulphur (S_c) and sulphur inefficiency parameter (E) of the different vulcanizates are also given in Table V 17

These results show that the PCNSL modified NR vulcanizates of the CV and SEV systems contain a relatively higher proportion of polysulphidic crosslinks (approximately 30%) and network combined sulphur (6 to 7 X 10^{4} mol S / g RH) as against that of the EV system (approximately 20% and 1 2 X 10^{4} mol S / g RH respectively). The higher values of sulphur inefficiency parameter for the PCNSL modified NR vulcanizates of the CV and SEV systems (18 3 and 9 3 respectively) in contrast to that of the EV system (3 8) are indicative of the lesser amount of 'chemically effective' combined sulphur in the former

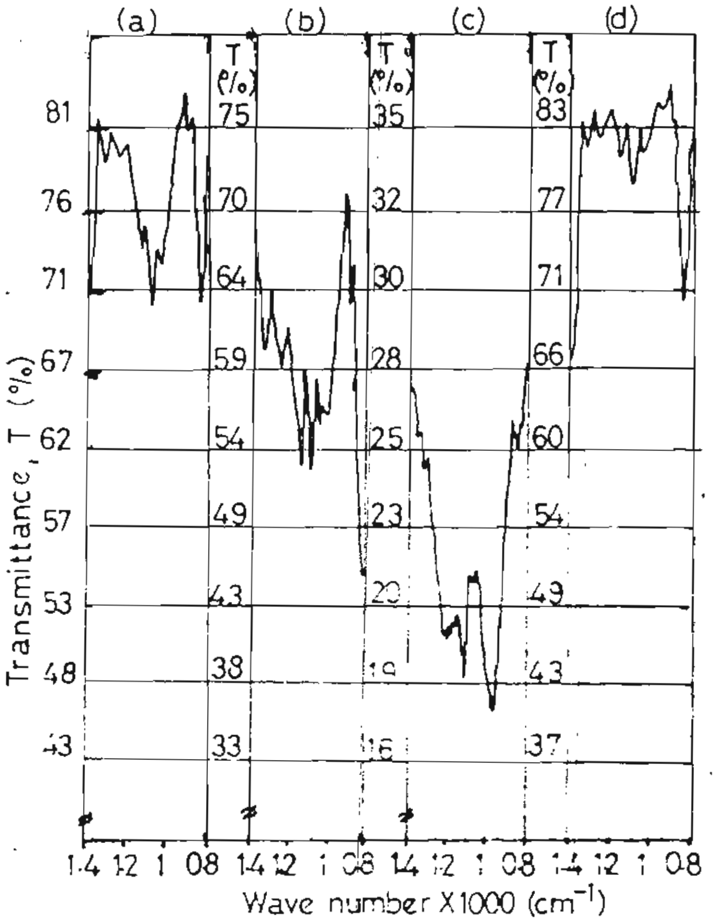


Fig.V-18. IR Spectra of NR containing PCNSL and ZnO.

NR/PCNSL/ZnO - (a) 100/10/10, (b) 100/10/0
(c) 0/100/0, (d) 100/0/10

This is in agreement with the fact that higher concentrations of sulphur yield more polysulphidic crosslinks and more sulphur combined with the rubber chains in cyclic modifications (19). Further, the results show that on changing the system from CV to SEV in presence of PCNSL, there is an overall increase in CLD from 3.97 X 10^5 mol / g RH to 6.56 X 10^5 mol/ gRH. This is expected to be due to the improved efficiency of the SEV system

The superior tensile properties and tear strength of the PCNSL modified NR vulcanizates (vulcanized by SEV system) as compared to that of the CV and EV systems(38) are ascribed partly to the higher proportion of polysulphidic crosslinks of the former, apart from the probable existence of physical entanglements of the aliphatic segment of PCNSL with the isoprene chains of NR. This is in agreement with the findings of Nasir and Teh (125), Brown et al. (126) and Lal and Scott (127) that the tensile properties of vulcanizates with predominantly polysulphidic crosslinks are superior to that of corresponding vulcanizates having crosslinks of lower sulphidity. The improved fatigue life of the PCNSL modified NR vulcanizates in the SEV system (34) may also be attributed to higher content of polysulphidic crosslinks, since polysulphidic crosslinks are known to be capable of relieving rapidly the localized stresses associated with the growth of a flaw (39).

The better retention of tensile properties after aging of the PCNSL modified NR vulcanizates of the SEV system (34) may be explained considering their comparatively high proportion of poly sulphidic linkages, which upon thermal decomposition can reform into more number of crosslinks having lower sulphidity, thereby increasing the CLD.

The results in Table V.17 show that at the high concentration of PCNSL viz. 20 phr, the increase in the dosage of ZnO from 10 to 20 phr results in an increase in the proportion of poly sulphidic crosslinks from 16 % to 39 % along with an increase in CLD from 2.97 X 10^5 mol / g RH to 6.81 X 10^5 mol / g RH and a decrease in sulphur inefficiency parameter from 19.9 to 8.6. It is concluded that a higher proportion of polysulphidic crosslinks and a higher CLD at the ZnO / PCNSL ratio of 1:1 are responsible for the observed improvement in the physico-mechanical properties of the vulcanizates (28).

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CHAPTER - VI

THERMAL ANALYSIS OF NR MODIFIED WITH PCNSL

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VI.1.Introduction

The versatility of the different thermal analytical techniques such as TGA, DTA, DSC, DMTA etc., has made them indispensible tools in the characterization of polymers. Thermal analytical procedures are used to study the oxidative (1) and thermal (2-4) degradation of elastomers and its composites. Effect of compounding variables on heat-release rate of poly chloroprene foam(5), cure characteristics and glass-transition temperature of elastomers (6), thermal stability of vulcanizates (7), identification of natural and synthetic polyisoprene vulcanizates (8), comparison of antioxidants in elastomers (9,10), characterization of the composition of elastomer vulcanizates (11-18), improvement and quality assurance of elastomers (19) and evaluation of the decomposition characteristics of flame retardants in a polymer matrix (20) are all studied with the help of thermal analytical techniques. Matching the degradation curve of a polymer with that of the flame retardants is known to be the key factor in effecting flame retardancy (21). Thermal analytical procedures have been used widely to evaluate the 'oxidation induction time' of polymers (22), particularly in presence of additives such as antioxidants and flame retardants. Bair (23) reported the oxidation induction time (determined using TGA) as a measure of the 'effectiveness' of the flame retardant system. Otey (24) used TGA to monitor the UV degradation of PVC by oxidation induction period analysis. Turi (25) described the use of oxidation induction period analysis to monitor the concentration of antioxidant and to predict the service life of poly ethylene.

The thermal / thermo-oxidative decomposition of polymers is governed by various factors such as the decomposition temperature, mechanism of decomposition including char-yield and the kinetic parameters of decomposition such as specific rate constant (k), order (n) and activation energy for decomposition (E_a) (26). Generally, the Integral Procedural Decomposition Temperature (IPDT) determined from TGA gives a good estimate of the thermal stability of polymers (27). The kinetic parameters of decomposition such as activation energy (E_a), pre-exponential factor (A) and reaction order (n) also give a quantitative measure of the thermal stability (28). Quite often, in dynamic thermogravimetric analysis the activation energy (E_a) and order (n) of degradation reaction are determined conveniently using the Freeman - Carroll equation (29-33) given as -
$-((E_a / 2.303\,R)\,\Delta(1/T)) / \Delta \log w_r = -n + (\Delta \log (dw/dt)) / \Delta \log w_r$ where, $w_r = w_c - w$, in which w_c is the maximum mass-loss and w is the total loss in mass upto time t, R is the gas constant and T is the temperature in absolute scale. Dunn (34) has summarized the information obtainable from derivative thermogram (DTG) curves, as - (i) it helps the quick determination of the temperature at which the rate of mass-change is a maximum (T_{max}), along with extrapolated onset temperature (T_i) and final temperature (T_f), (ii) the area under the DTG curve is directly proportional to the mass-change and (iii) the height of the DTG peak at any temperature gives the rate of mass-change at that temperature. The kinetic parameters (A and E_a) can be determined from the rate of mass-change (dm/dt) using the equation given by Chen (35) as $--(dm/dt) = A\, e^{(-Ea/RT)} f(m)$. The application of DTG curves in thermogravimetry include separation of overlapping reactions, 'fingerprinting' materials, calculation of mass-change in overlapping reactions and quantitative analysis by peak height measurement (11).

The foundation for the calculations of kinetic data from a thermogram is based on the formal kinetic equation $-(dX/dt) = k X^n$ where, X is the amount of sample undergoing reaction, n is the order of reaction and k is the specific rate constant (36). The rate constant k often follows the Arrhenius relation given as, $k = A e^{(-Ea/RT)}$, applying generally to a narrow temperature range (36) Derivative thermogravimetry (DTG) is known to be more reproducible than DTA (37) ; the former permitting an exact quantitative analysis and the division of decomposition stages into parts. The advantages of determining kinetic parameters by dynamic thermogravimetry, rather than by conventional isothermal studies have been described by Coats and Redfern (38). The former requires only a single sample and considerably fewer data for the evaluation of the kinetic parameters Additionally, these parameters can be calculated over an entire temperature range in a continuous manner Also, the results obtained by an isothermal method are often questionable for a sample undergoing considerable reaction on being raised to the required temperature. The explicit advantages of non-isothermal methods over isothermal methods have been explained by Bagchi and Sen(39) also. It is possible to determine the reaction onset temperature (T_i) very precisely by the non-isothermal method, which is almost impossible with the isothermal method

Since thermal / thermo-oxidative decomposition forms the 'critical initial stage' in the pyrolytic decomposition cycle of polymers (40,41) (determining the subsequent combustion and flammability characteristics) which is influenced strongly by the presence of additives such as flame retardant chemicals and plasticizers, it is essential to study the initial stage of decomposition using thermal analysis technique. The importance of this has been recognized by many of the earlier investigators. Cullis (42) has reviewed the role of pyrolysis in polymer combustion and the effect of fire-proofing agents on it Stuetz et al (43) observed that the 'intrinsic combustibility' as determined by the minimum oxygen concentration required for self-sustained combustion was related to the thermo-oxidative stability of the polymer. Nakagawa and Komai (44) have reported the correlations between the results obtained from thermogravimetric analysis and flammability tests on covers of rubber conveyor belts. From the results obtained from TGA and DTA, they compared the LOI of the specimens with the minimum temperature for rapid weight loss in TGA

The discovery of vulcanization (45) that has revolutionized the rubber industry world-wide may be considered as the pioneering step towards the thermal stabilization of rubber. Since then, various systems of vulcanization have been developed to provide vulcanizates with improved thermal stability. The effect of vulcanization systems on the thermal stability of general purpose rubbers has been reviewed by Lewis (46) Though NR possesses a unique combination of many of the desirable physico-mechanical properties, one of its serious limitations is its lack of high temperature stability. The degradation of NR was found to commence between 250 and 320°C as determined by dynamic thermogravimetric analysis(47) Further, the additives such as plasticizers, fillers, curatives and flame retardants used for compounding the rubbers may affect the thermal and thermo-oxidative stability of the base polymer - a good information about which may be obtained from thermal analysis methods such as TGA, DSC and DTA

In the previous chapter, we have seen that the resistance to thermo-oxidative decomposition of PCNSL modified NR vulcanizates improves under the conditions of accelerated aging (48). The role of PCNSL in the crosslinking reactions during the vulcanization of NR has also been reported recently(49). Thus, it is evident that the phosphate group and the crosslinkable side chain component of PCNSL (after crosslinking) contribute to the enhanced thermal stability of PCNSL modified NR vulcanizates. Hence, the thermal stability and decomposition characteristics of PCNSL modified gum NR vulcanizates need to be studied in detail (in comparison with unmodified samples) using different thermal analytical tools such as TGA, DSC and DTA. The results of this study are described in the following section. The formulations of the mixes are given in Table VI.1. The physico-mechanical properties have been reported earlier in section 5.3 of chapter 5.

Table VI.1. Formulation of mixes-(Thermal stability of PCNSL modified NR)

Mix code	A	B
NR	100	100
ZnO	10	10
Stearic acid	2	2
Sulphur	2	2
MBT	1.5	1.5
TMTD	0.5	0.5
PCNSL	0	10

VI.2.Thermal decomposition and thermal stability of the vulcanizates.

The TG / DTG of the unmodified and PCNSL modified gum NR vulcanizates in air and nitrogen are given in Figures VI.1 and VI.2 respectively. The thermal decomposition characteristics of the vulcanizates such as IPDT and the decomposition temperatures at the various stages are given in Table VI.2.

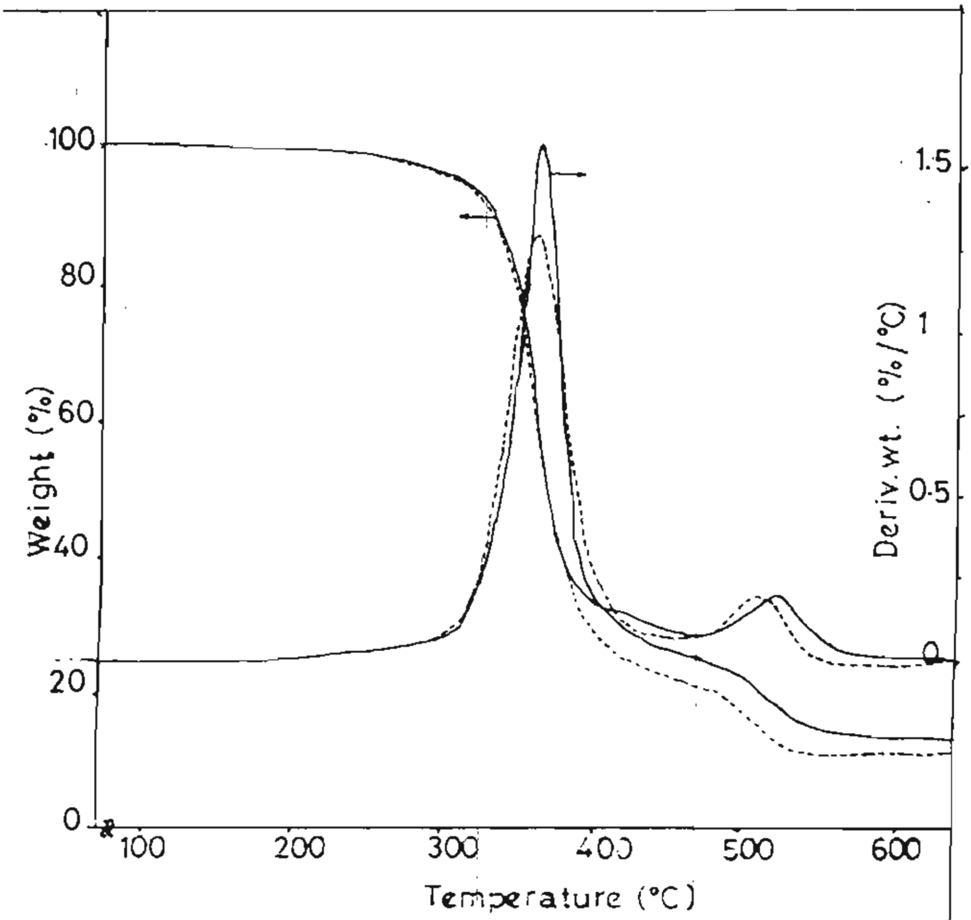

Fig.VI.J. TG/ DTG plots of un modified and PCNSL - modified NR vulcanizates in air

---- A . Un modified NR

—— B . PCNSL modified NR

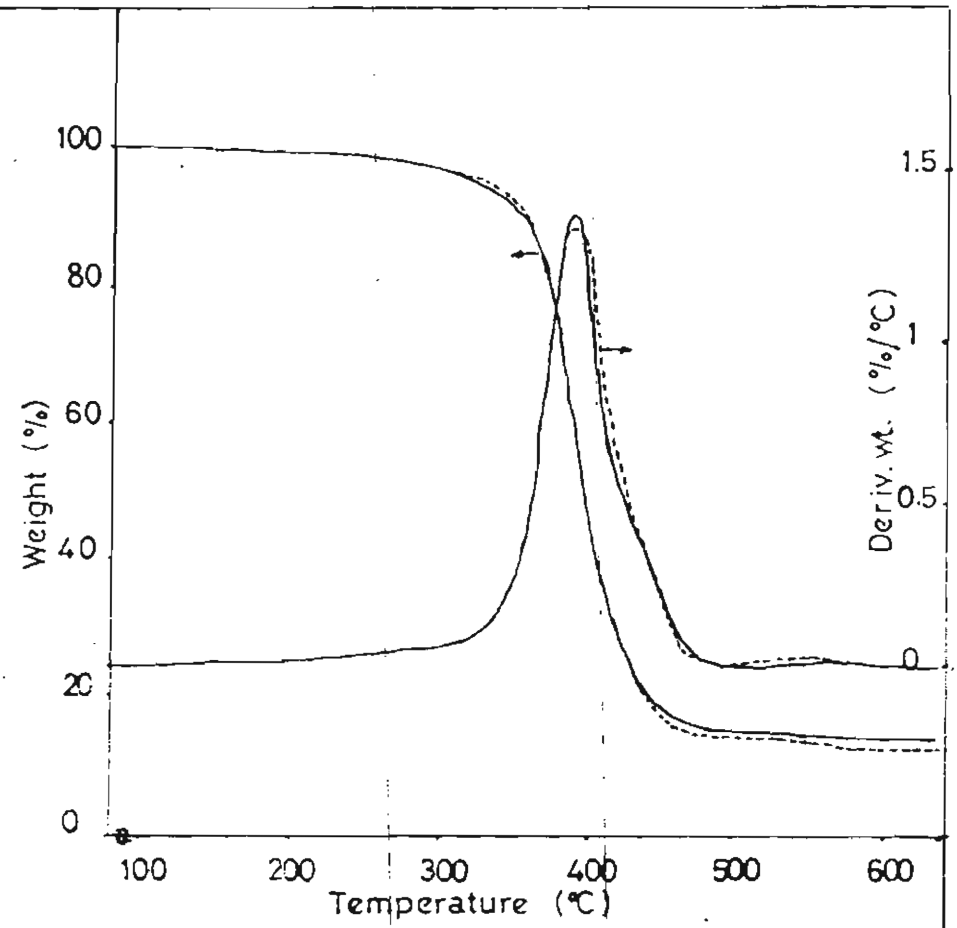

Fig. VI.2. TG / DTG plots of un modified and PCNSL - modified NR vulcanizates in nitrogen

----A. Un modified NR

——B. PCNSL modified NR

Table VI.2.Thermal decomposition characteristics of unmodified and PCNSL modified NR vulcanizates (TGA)

Medium	Air		Nitrogen	
Mix code	A	B	A	B
IPDT (°C)	347	366	373	373
Decompn. (%)	DT (°C)	DT (°C)	DT (°C)	DT (°C)
10	327	332	357	353
25	347	353	381	379
50	369	370	401	398
65	386	390	415	413
75	420	465	430	430

DT - Decomposition temperature

Table VI.2 shows that the IPDT of NR vulcanizate in air increases significantly by 19°C on modification with 10 phr of PCNSL. Also, the PCNSL modified NR vulcanizate shows comparatively higher decomposition temperature at the various stages during decomposition in air. The T_{50} value for the PCNSL modified NR vulcanizate in air is higher than that of NR indicating improved thermal stability. This may possibly be due to the formation of 'intermediate thermally stable structures' as a result of thermo-oxidative reactions in presence of PCNSL (50). This is evident from Figure VI.1 where the thermograms show two-stage degradation with the second stage occuring at a higher temperature of around 510 - 525°C.

The weight-loss of the vulcanizates in the major decomposition regions during TGA, along with the corresponding peak-temperature (T_{max}), temperatures at the different stages of decomposition such as T_i, T_{50}, T_f and the char yield are given in Table VI.3

Table VI.3. Weight loss of the vulcanizates in major decomposition regions (TGA)

Medium	Mix code	Temp. range (°C)	Decrease in mass (%)	Peak temp in DTG T_{max} (°C)	T_i (°C)	T_{50} (°C)	T_f (°C)	Char yield (%)
Air	A	300 - 420 460 - 560	70 11	358 510	292	369	512	11
	B	300 - 420 460 - 560	65 11	364 518	308	370	524	14
Nitrogen	A	300 - 420 460 - 560	66 3	394 -	340	401	540	11
	B	300 - 420 460 - 560	66 2	392 -	340	398	572	12

However, the decomposition temperatures of the PCNSL modified NR vulcanizate in nitrogen atmosphere, are slightly lower than that of the unmodified sample as shown in Table VI.2, probably due to a different mechanism of decomposition

In TGA, both the unmodified and PCNSL modified NR vulcanizates showed a characteristic two-stage decomposition pattern in air, as against the single stage decomposition in nitrogen (fig VI.1 and VI.2). The DTG for the decomposition of the samples in air (Fig VI.1) shows two prominent peaks in the regions 300 - 420° C and 460 - 560° C. Table VI.3 shows that the major decomposition of the vulcanizates occurs in the temperature range from 300 °C to 420 °C. It is note-worthy that in presence of 10 phr of PCNSL, there is a reduction in the weight loss from 70% to 65% in this temperature range. Also, the temperature for the maximum rate of decomposition (T_{max}) shifts from 358 °C to 364 °C and the second decomposition region from 510 °C to 518 °C for the PCNSL modified NR vulcanizate, indicating an improvement in thermal stability. The occurrence of two peaks in the DTG curves for the decomposition of elastomers in air, often indicates the formation of 'thermally stable intermediate products' (18,51) decomposing subsequently at higher temperatures whereas in nitrogen atmosphere the residual weight and the T_{max} remain the same.

The thermograms shown in Figure VI.1 and the results given in Tables VI.2 and VI.3, show the improvement in thermal stability of the PCNSL modified NR vulcanizate in air, compared to the unmodified sample.

It has been reported earlier that PCNSL and its analogue PCP enhance the thermal stability of poly ethylene (52). PCP itself has been found to exhibit higher thermal stability and resistance to thermo-oxidative degradation than cardanol (53).

The higher resistance to thermo-oxidative decomposition of the PCNSL modified NR vulcanizate in air was further confirmed from the results of DTA. The DTA-thermograms of the vulcanizates in air showed a sharp endotherm peak for the unmodified NR vulcanizate and a shallow endotherm peak for the PCNSL modified sample, corresponding to the major decomposition around 375 °C (Fig.VI.3). In nitrogen, the endotherms are shallow for both the vulcanizates.

The TGA of the raw polymer (ISNR-5) and PCNSL are given in Figure VI.4. It shows that the decomposition of NR occurs in the temperature range 375 to 450 °C as reported earlier (54). But the PCNSL commences degradation at a much lower temperature of 200 °C. However, it exhibits a two stage degradation and the final degradation occurs in the temperature range from 400 to 550°C. Thus, the PCNSL modified NR vulcanizates exhibit higher stability than the NR vulcanizate itself, may be due to obscuration of oxidative sites of NR by PCNSL.

The key role of sulphur in the oxidative degradation of polyisoprene networks has been highlighted by Bevilacqua (55). Vulcanizates with sulphur crosslinks are reported to oxidise more rapidly than the raw rubber. A recent study by Slusarski and Janowska (56) on the mechanistic aspects of thermo-oxidative decomposition of cis 1,4 -polyisoprene vulcanizates emphasizes the crucial role of polysulphidic crosslinks in the decomposition pattern of the rubber. They proposed that transformation of some of the polysulphidic crosslinks at elevated temperatures to sulphenic or thio-sulphoxylic acid groups prevented the autocatalytic thermo-oxidative decomposition of poly isoprene. There is a high probability for such a mechanism to operate in the PCNSL modified NR vulcanizate, since it has got a comparatively higher proportion of polysulphidic crosslinks in the vulcanizate(49). The possibility of formation of stable cyclized structures and secondary crosslinks during the initial decomposition stage of cis 1,4 - polyisoprene vulcanizates are known, as reported by Janowska and Slusarski (57). They have suggested that the degradation of vulcanizates having low energy di- and polysulphidic crosslinks proceeds primarily by S-S bond cleavage, giving rise to macro radicals terminated by S which are subsequently stabilized either by cyclization or secondary crosslink formation. This type of transformations are also possible in the PCNSL modified NR vulcanizate during the thermo-oxidative decomposition stage, because of its higher proportion of di- and polysulphidic crosslinks. Sircar (8) has also observed earlier that in NR and IR vulcanizates the DSC exotherms at 350°C correspond to the simultaneous formation of cyclized structures and the volatilization of chain fragments.

The results in Table VI.3 show that during decomposition of the vulcanizates in nitrogen, the thermal stability of the PCNSL modified NR vulcanizate does not improve over that of the unmodified sample like that in air. Also, the absence of the second DTG peak in the temperature range from 460 to 560 °C in nitrogen (Figure VI 2) shows a 'single stage decomposition' without the formation of any intermediate products

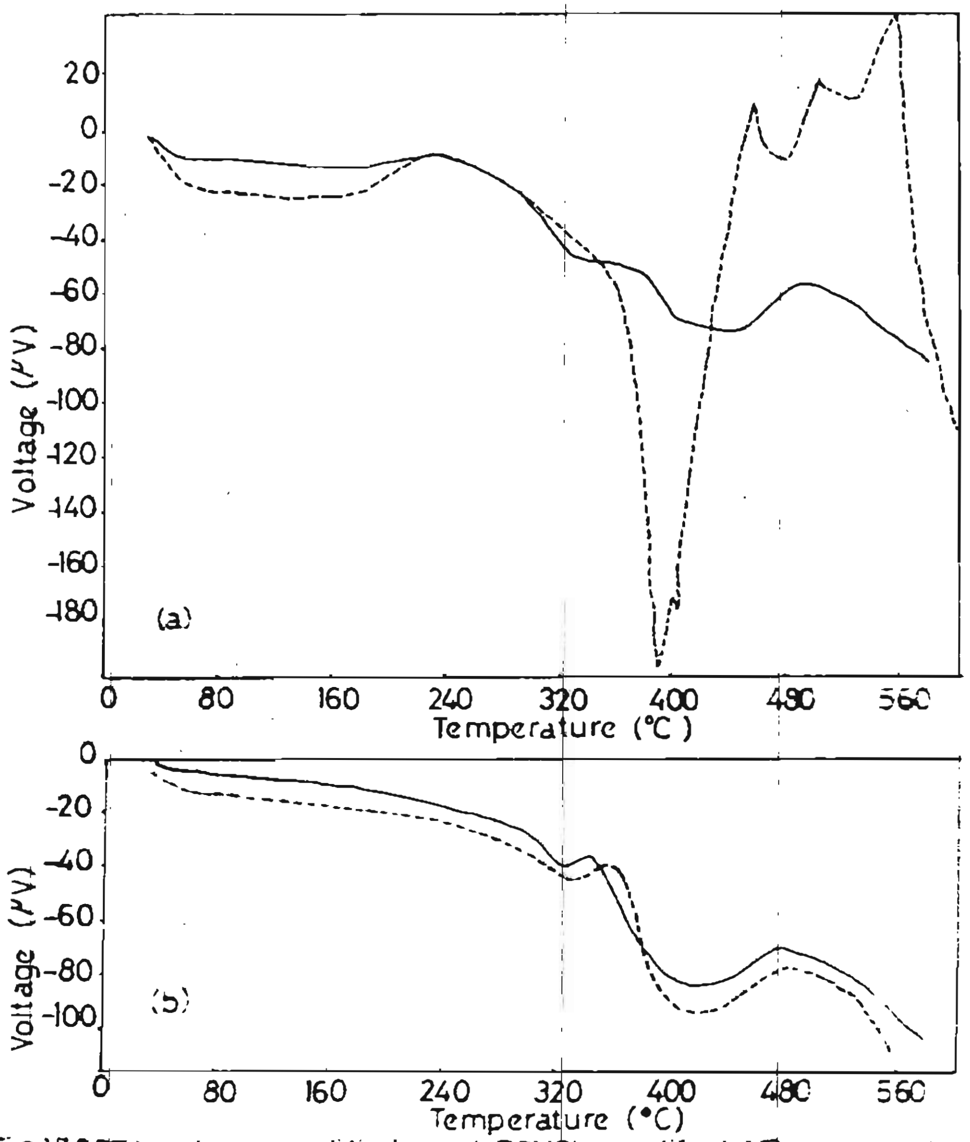

Fig.VI.3 DTA of un modified and PCNSL modified NR vulcanizates in (a) air and (b) nitrogen

----Un modified NR ——PCNSL (10 phr) modified NR

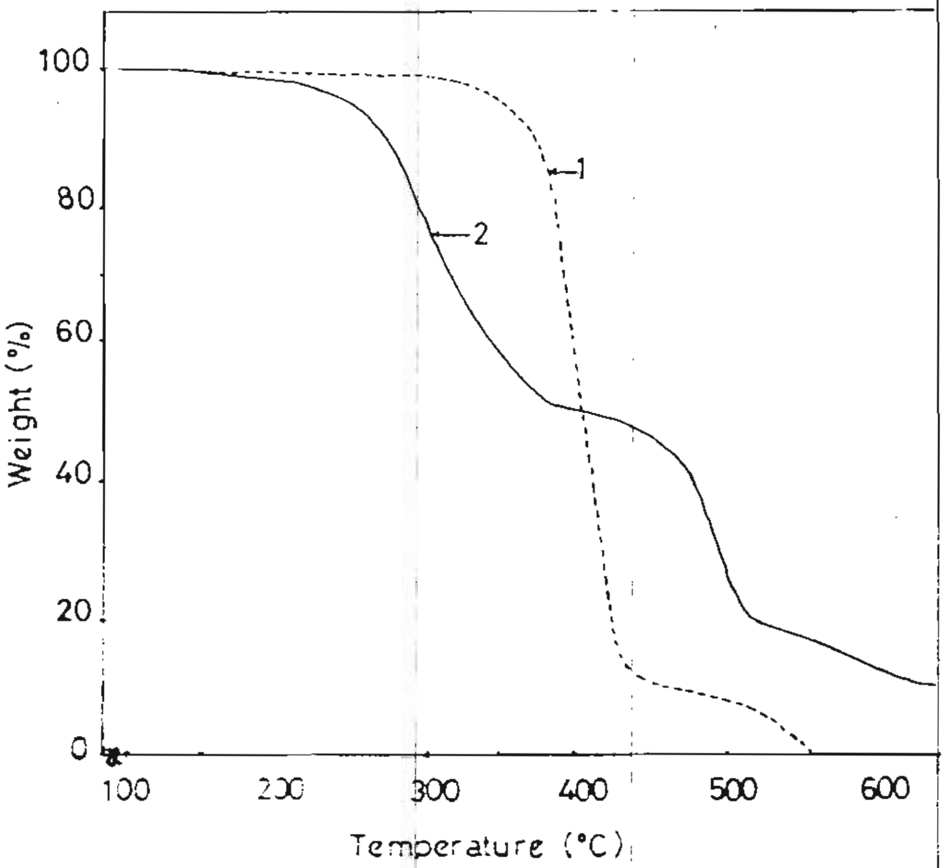

Fig. VI.4. TGA of NR and PCNSL in air

-----1. NR (ISNR-5) ____2. PCNSL

VI.3. Decomposition residue(char yield)

The carbonaceous matter deposited on heating or burning a sample of organic matter is the char yield. This is significant in polymers and polymer composites. The TGA studies of NR and PCNSL modified NR shows the char yield as per Table VI.3. It shows that there is an increase in the decomposition residue of PCNSL modified NR on heating upto 600 °C in air as well as in nitrogen atmosphere as compared to the unmodified NR vulcanizate itself. This increase is found to be 11 to 14% in air and from 11 to 12% in nitrogen atmosphere. It is believed that the char yield on pyrolysis depends on the type of mechanism occuring during the condensed phase reactions (58). As seen from Fig.VI.4 the PCNSL undergoes a two stage degradation on increasing the temperature. The first phase of degradation occurs at a temperature lower than 300 °C, but the second phase of degradation starts at a temperature much above 500 °C. The PCNSL containing NR has the advantage of PCNSL and does not yield to the low temperature degradation of PCNSL. Thus, the thermal stability of PCNSL modified NR increases as compared to that for NR itself. This high temperature stability of PCNSL modified NR may be considered to be due to the formation of nonvolatile complexes during combustion as observed for phosphorous containing compounds (59) and formation of a protective layer of carbonaceous char on the surface of the polymer as observed by Morchat and Hiltz (60) in the case of phenolic resins.

VI.4. Kinetics of thermal degradation of the vulcanizates.

The relevance of kinetic parameters of thermal decomposition such as activation energy (E_a) and specific rate constant (k) during the pyrolysis and combustion of polymers is well established. Higher value of the former generally indicates better thermal stability and a lower value of the latter represents a lower rate of combustion

It has been reported that above 300°C, NR volatilizes at a rapid rate and completes substantially at temperatures near 400 °C (61). In cis 1,4- polyisoprene vulcanizates, the transitions occuring above 300°C have been found to be of greater significance because of the strong correlation between the thermal properties and elastomer combustibility (62). Therefore the kinetic parameters have been evaluated only for the major decomposition observed between 300 and 400 °C. The results are given in Table VI.4.

Table VI.4.Kinetic parameters for the thermal decomposition of the vulcanizates - (TGA).

Medium	Mix code	Temp. range (°C)	Order n	Activation energy, E_a (kCal/mol)	Specific rate constant, k $(min)^{-1}$
Air	A	300 - 360	1.3	13.04	0.29
	B	300 - 360	1.4	15.10	0.28
Nitrogen	A	300 - 400	0.5	19.04	1.23
	B	300 - 400	1.4	15.79	0.30

The thermal decomposition reactions of the NR vulcanizate containing PCNSL in air and nitrogen have been found to follow near first order kinetics. The results in Table VI.4 show that the activation energy for decomposition of the unmodified NR vulcanizate increases from 13.04 kCal/mol to 15.10 kCal/mol and the specific rate constant decreases from 0.29 min^{-1} to 0.28 min^{-1} on modification with 10 phr of PCNSL. This again shows the improved resistance to thermo-oxidative decomposition of the PCNSL modified gum NR vulcanizate, which is expected to be due to the formation of thermally stable structures during the initial stages of the thermo-oxidative decomposition reactions. The results also show that in nitrogen atmosphere, the decomposition of the PCNSL modified NR proceeds at a slightly faster rate than that for NR presumably due to a change in the decomposition path-way.

VI.5. Resistance to thermo-oxidative decomposition (Antioxidant activity)

Low concentrations (from 2 to 4 phr) of PCNSL were found to impart better antioxidant property to gum NR compounds than those containing styrenated phenol (63). The PCNSL modified NR vulcanizates showed greater retention in physico-mechanical properties after aging in a hot air oven at 70 °C upto 7 days than unmodified NR vulcanizates. Also, superior retention in tensile properties of NR vulcanizates in accelerated aging tests have been reported at a higher concentration of PCNSL (48). The resistance to thermo-oxidative decomposition is indicated quite often by a reduction in the enthalpy of oxidation as obtained from DSC (9). The reduction in the enthalpy of oxidation (as shown by the reduction in the area of the exotherm peaks) has been reported as a measure of the 'antioxidant effectiveness' in BR and SBR (9,10). The DSC profiles for the decomposition of the unmodified and PCNSL modified NR vulcanizates in oxygen are shown in Figure VI.5. The enthalpy of oxidation of the vulcanizates in the temperature ranges from 300 °C to 420 °C and 420 °C to 500 °C are given in Table VI.5.

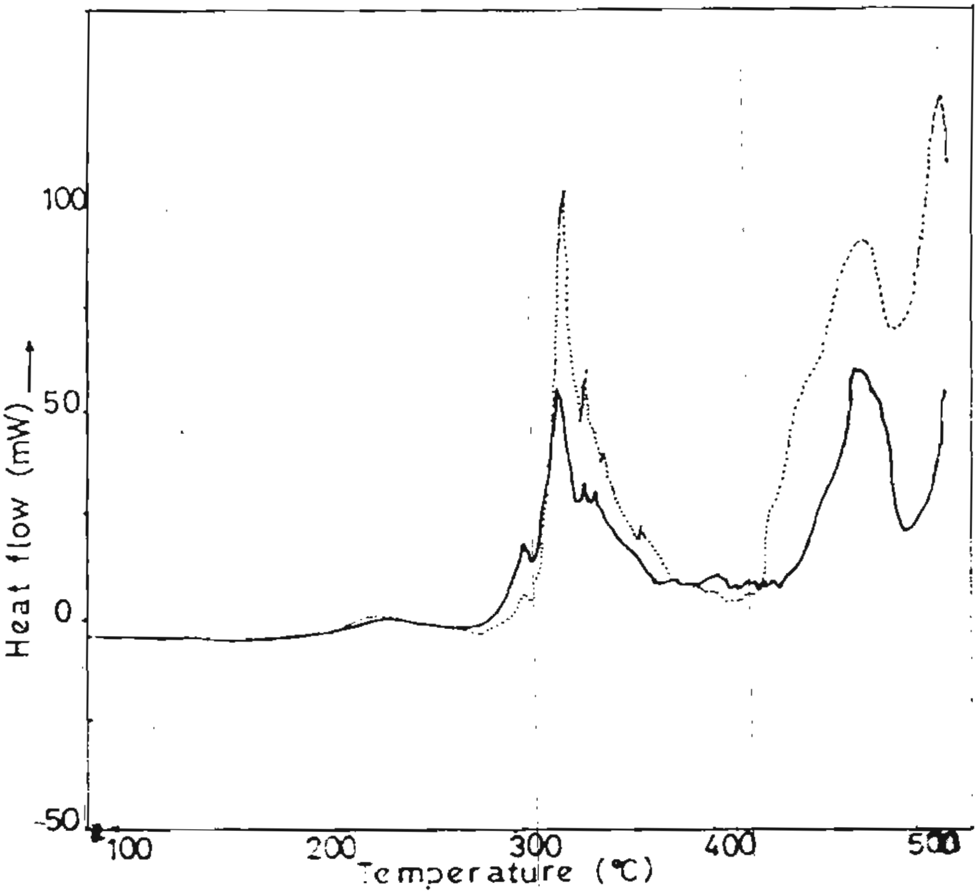

Fig. VII.5. DSC of unmodified & PCNSL modified NR vulcanizates in oxygen

..... Unmodified NR ___PCNSL modified NR

Table VI.5. Enthalpy of oxidation of unmodified and PCNSL modified NR vulcanizates from DSC (ΔH)

Temperature range (°C)	300 - 420	300 - 420	420 - 500	420 - 500
Mix code	S_0	S_{10}	S_0	S_{10}
Δ H (kCal/mol)	21.29	11.69	35.09	11.86

S_0 - Unmodified S_{10} - PCNSL (10 phr) modified

The substantially lower values of the enthalpy of oxidation for the PCNSL modified NR vulcanizate compared to that of the unmodified sample reflect the higher resistance to thermo-oxidative decomposition of the former.

Thus, the improved resistance to thermo-oxidative decomposition of the PCNSL modified NR vulcanizates at low and high temperatures as mentioned above, indicate the possible antioxidant action of PCNSL in NR vulcanizates. Yarmolenka and Novikava (64) studied the protective action of antioxidants of the phenolic type on the aging of NR. They suggested that these antioxidants either get oxidized themselves, act as retarders of oxidation or are adsorbed by rubber at double bonds, thus preventing atmospheric oxidation. The structural features of the molecule of PCNSL with secondary hydroxyl groups on the phosphate group that are oxidizable and unsaturation on the C_{15} side chain may perform similar functions and delay the process of oxidative degradation in diene rubbers as observed in case of phenolic antioxidants such as styrenated phenols (63).

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CHAPTER - VII

COMPARISON OF PCNSL WITH COMMERCIAL PLASTICIZERS IN NR

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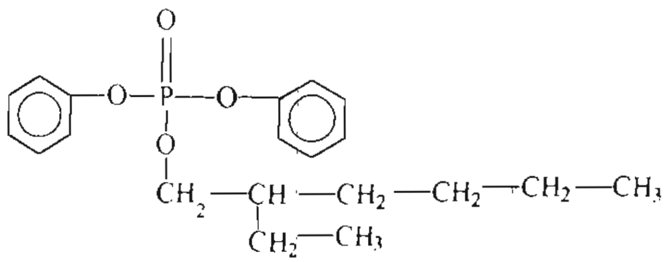
VII.1.Introduction

The role of PCNSL as a plasticizer in NR has been discussed in detail in chapter III. However, in any of the 'commercial formulations' designed for specific performance requirements, the cure characteristics of the mixes and physico-mechanical properties of their vulcanizates are factors of utmost importance. These are influenced to a very great extent by the type and dosage of the plasticizer used in the system. Since PCNSL is a phosphatic plasticizer and 2-ethyl hexyl diphenyl phosphate ('Santicizer 141') is a commercially available 'flame retardant plasticizer', a comparison between the two has been made particularly with respect to their cure characteristics and physico-mechanical properties. Also, comparison with a commercially available non-phosphatic plasticizer (Spindle oil) has been carried out to assess the differences in cure characteristics and physico-mechanical properties. The results of these studies are discussed in the following sections.

VII.2. Comparison of PCNSL with a phosphatic plasticizer (2-ethyl hexyl diphenyl phosphate) in NR.

Modification of polymers with plasticizers has long been practised as a means to improve the processability of compounds and the physico-mechanical properties of the final products. In many of the specialized applications where flame-retardancy of the products is an essential service requirement, it is imperative that the plasticizer used should be of the flame retardant type. In this respect, phosphatic plasticizers hold a place of great significance (1), which is evident from the amount and variety of such plasticizers being used in the modification of plastics and elastomers (2). However, while using such plasticizers, it should be ensured that the improvement in processability is not at the expense of the desired level of flame-retardancy and other physico-mechanical properties of the final product. Derouet(3) reported that an attempt to improve the flame retardancy of epoxidized liquid natural rubber by modification with di butyl phosphate resulted in a decrease in the rate of cure and mechanical properties. PCNSL is an 'oligomeric flame-retardant plasticizer' compatible with a variety of plastics and elastomers (4). The advantage of oligomeric flame-retardants over the low molecular weight counter-parts with respect to permanence / durability in service is well known (5). These have low volatility and combine more readily with the polymer base (6). The possibility for presence of highly toxic impurities in commercial grades of flame-retardant plasticizers such as tri cresyl phosphate (TCP) and tri xylyl phosphate (TXP) limits their wide-spread use in polymers (7). Other phosphatic plasticizers such as 2-ethyl hexyl diphenyl phosphate and iso-decyl diphenyl phosphate are reported to offer a compromise between flame-retardancy and low temperature properties in rubber products (8). 2-ethyl hexyl diphenyl phosphate ('Santicizer 141') (I) (9) has been shown to be an ideal non-toxic flame-retardant plasticizer for poly vinyl chloride (10) (PVC) and nitrile rubber (NBR) (11).



(I)

NR has been modified with 10 to 20 phr each of PCNSL and Santicizer 141in an SEV system. The formulations are given in Table V.13. (Ch.V, sec. V.3.vi.a.). The cure characteristics of the formulations and physico-mechanical properties of the vulcanizates such as tensile property, flame-retardancy and resistance to thermo-oxidative aging and decomposition have been studied ; the results of which are discussed below.

i. Cure characteristics

Figures VII.1 (a)&(b) give the rheographs of the formulations, obtained at 150°C using a Monsanto oscillating disk rheometer (Model R-100). The cure parameters such as scorch time, optimum cure time and cure rate of the mixes are given in Table VII.1.

Table VII.1. Comparison of PCNSL with Santicizer 141 - Cure characteristics.

Mix code	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
Scorch time at 150°C, t_{s2} (s)	109	101	146	131	109	120	124
Maximum cure, L_f (dNm)	53	40.5	26	15.3	50	47	44.8
Optimum cure time at 150°C, t_{90}, (s)	165	169	225	240	154	165	163
Cure rate , (s^{-1})	1.8	1.5	1.3	0.9	2.2	2.2	2.6

Table VII.1 shows that the scorch time for the mixes modified with 15 and 20 phr of PCNSL are higher than that without PCNSL and even higher than that containing the same dosage of Santicizer. The rate of cure of the PCNSL modified NR formulations are considerably lower than that of the unmodified sample and also that samples containing similar dosages of Santicizer. Also, an increase in concentration of PCNSL from 10 to 20 phr resulted in a steady decrease in the rate of cure from 1.5 s^{-1} to 0.9 s^{-1} and a drastic reduction in the maximum state of cure from 40.5 dNm to 15.3 dNm. The optimum cure time also increased with increase in dosage of PCNSL in NR. The reduction in the crosslinking efficiency in presence of higher dosages of PCNSL is expected to be due to

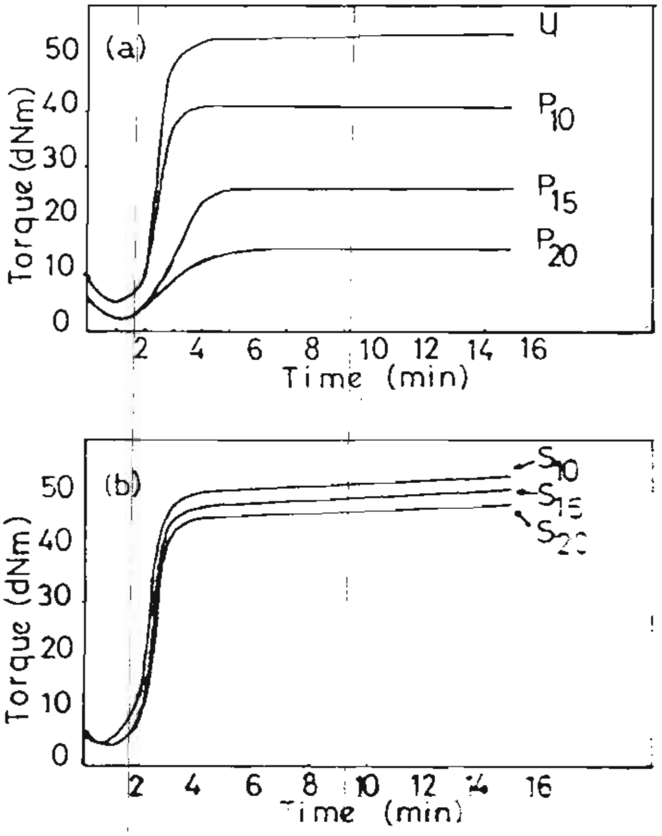


Fig.VII.1. Rheographs of NR formulations at 150°C

(a) Unmodified NR & PCNSL modified NR

(b) Santicizer modified NR

the blocking of the activation effect of ZnO at the normal dosage of 5 phr [12]. The reductions in chemical crosslink density at higher concentrations of PCNSL and at lower doses of ZnO are supposed to be due to a complex formation between the phosphate group of PCNSL and the ZnO leading subsequently to cure-retardation [13]. The relatively higher rate and state of cure of the Santicizer modified formulations (even at the higher concentrations of 15 and 20 phr) indicates higher degree of crosslinking , possibly due to the lack of interactions (eg:- H-bonding) between the phosphate group of Santicizer and ZnO, as mentioned above. This may be due to the presence of two bulky phenyl groups at the phosphate moiety, debarring the oxygen atoms to take part in H-bond formation.

ii. Compatibility of the plasticizer with rubber

The dispersion of PCNSL in the NR matrix is very good. There is no leaching of the PCNSL at all concentrations studied upto 20 phr. However, the Santicizer modified vulcanizates showed an undesirable 'surface-bloom' (especially at the higher concentrations of the plasticizer), possibly due to the poor compatibility with the NR matrix. From the above, it seems that PCNSL acts as a 'primary plasticizer' in NR and Santicizer as a 'secondary plasticizer' as per the grading based on the compatibility of a plasticizer with base polymer [11]. Primary plasticizers are highly compatible with a polymer and do not exude to form droplets or a liquid surface film or bloom as a crystalline surface crust, whereas secondary plasticizers exude or bloom on standing [11] .

iii. Physico mechanical properties of the vulcanizates

Table VII.2 shows the results on the tensile properties and flammability of the vulcanizates.

Table VII.2 Physico-mechanical properties of the NR vulcanizates containing PCNSL as well as Santicizer 141.

Mix code	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
Modulus - 100% (MPa)	0.87	0.52	0.42	0.23	0.70	0.63	0.60
Tensile strength (MPa)	2	17	16	7	2	2	12
Elongation at break (%)	240	1060	1170	1340	300	330	840
Limiting Oxygen Index (LOI)	17	17.5	18	18	17	17.5	17.5

Modification of NR with PCNSL resulted in comparatively 'softer' vulcanizates with lower 'stiffness' and greater flexibility. This is evident from the relatively higher reduction in tensile modulus from 0.52 MPa to 0.23 MPa for the PCNSL modified NR vulcanizates as compared to the reduction from 0.70 MPa to 0.60 MPa for the Santicizer modified NR vulcanizates, with the increase in dosage of plasticizer from 10 to 20 phr. The vulcanizate containing 10 phr of PCNSL in NR showed the highest tensile strength of 17 MPa as against 2 MPa for the sample containing the same dosage of Santicizer. The reduction in tensile strength of the PCNSL modified NR vulcanizates at higher concentrations of PCNSL may partly be due to the lower extent of cure of the vulcanizates. Though the elongation at break of all the vulcanizates increased with the increase in concentration of the plasticizer, the PCNSL modified NR vulcanizates showed comparatively higher elongations. The possiblity for higher degree of interactions of the unsaturated side chain of PCNSL with NR and the probable formation of 'entangled network structures' in the vulcanizates are held responsible for the higher tensile strength and elongation at break of the PCNSL modified NR vulcanizates (13). Since PCNSL as such on heating with sulphur at curing temperature of 150°C undergoes vulcanization through the side chain double bonds, as is evident from its resistance to swelling after treatment with sulphur, it is evident that PCNSL also undergoes intermolecular crosslink formation with unsaturation present in NR. This has been exemplified in chapter V, sec.V.4(ii).

iv. Flame retardancy

The results in Table VII.2 show that with the increase in dosage of PCNSL from 10 to 15 phr, there is a marginal improvement in the Limiting Oxygen Index (LOI) of the NR vulcanizate compared to that of the Santicizer modified sample. Generally, phosphatic flame retardants find their largest use in hetero-atom polymers, with the highest efficiency apparent in highly oxygenated polymers like cellulose (14). Considerable improvement in flame retardancy has been reported for cellulose modified with phosphatic flame-retardants, where the mechanism of flame retardance involves mainly the 'condensed phase reactions'(14). Also, reactive phosphatic flame retardants are used extensively in polyurethane foams by virtue of their effectiveness in reducing the flammability by char-forming through condensed phase mechanism (14). However, significant increase in LOI along with self extinguishing characteristics and very good tensile properties can be obtained for NR vulcanizates by modification with a bromo derivative of PCNSL (15,16). Further increase in LOI of NR vulcanizates to an extent of 42 has been obtained by the use of a 'synergistic' combination of brominated PCNSL and antimony trioxide(17).

v. Resistance to thermo-oxidative aging and decomposition

(a). Thermo-oxidative aging

The vulcanizates are aged in air oven at 70 °C for 12 hrs. Table VII.3(a) shows the results on the retention of tensile properties after aging.

Table VII.3.Resistance to thermo-oxidative aging of NR vulcanizates containing PCNSL and Santcizer

VII.3(a) Retention in tensile properties of the vulcanizates after aging at 70 C for 12 hrs.*

Mix code	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
Modulus - 100% (%)	101	103	103	110	99	101	106
Tensile strength (%)	96	76	93	118	71	78	17
Elongation at break (%)	95	90	96	99	73	79	33

* - % of original unaged value

The superior resistance to aging of the PCNSL modified NR vulcanizates over that of the Santicizer modified samples is evident from the higher retention in tensile properties of the former, at the various concentrations of the plasticizer. Thus, the increase in concentration of the plasticizer from 10 to 20 phr results in considerable increase in the retention of tensile modulus, tensile strength and elongation at break of the PCNSL modified NR vulcanizates as compared to that of Santicizer modified NR vulcanizates. The higher retention in tensile properties of the PCNSL modified NR vulcanizates was attributed mainly to the 'post-vulcanization reactions' leading to the formation of additional crosslinks (13). The absence of unsaturation in the alkyl groups of 2-ethyl hexyl di phenyl phosphate (Santicizer) rules out the possibility of any crosslink formation through sulphur with NR matrix during vulcanization with the result that no additional crosslinks are formed.

v (b). Thermo-oxidative decomposition

Since thermally induced polymer decomposition is the first step in the ignition process (18), a knowledge of the thermal and thermo-oxidative degradation of polymeric materials is essential in understanding the nature of decompositions occuring under pyrolytic conditions. Thus, results from a typical TGA curve give valuable informations on the thermal stability (19) in addition to the nature of decomposition and its kinetics (20). The temperature at which 50% of the weight of a given polymer is vaporized under standard pyrolytic conditions (T_{50}) has been considered to be a quantitative measure of thermal stability (21). The magnitude of the activation energy for decomposition may also be considered as a measure of thermal stability / resistance to thermo-oxidative decomposition. The average rate of decomposition during the major degradation step gives an indication of the extent of volatile / flammable hydrocarbons liberated during pyrolysis. The rate of energy input (which inturn determines the rate of thermal decomposition) is a critical factor for polymer ignition (18). Hence, the TGA of the NR vulcanizates was carried out at three different heating rates (10, 20 and 40°C/ min).

The results on the decomposition characteristics of the different vulcanizates are given in Table VII.3 (b) and the thermograms in Figures VII.2 & VII.3.

Table VII.3 (b) Thermal decomposition characteristics of PCNSL and Santicizer-141 modified NR vulcanizates

Heating rate (°C/min)	Parameter	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
10	$T_{50}^{\dagger}$ (°C)	374	365	359	369	362	344	361
	Activation energy, E_a (kCal/mol)	130.8	100.7	48.4	35	72.2	28.3	22.9
	Rate of decompn. (%/min)	6	6	6	5	5	5	5
	Residue at 600°C (%)	10	15	12	17	16	14	13
20	$T_{50}^{\dagger}$ (°C)	385	385	387	387	387	366	362
	Activation energy, E_a (kCal/mol)	124.6	75.4	38.6	26	31.3	21.1	19
	Rate of decompn. (%/min)	12	12	11	11	10	11	12
	Residue at 600°C (%)	9	11	13	11	11	10	12
40	$T_{50}^{\dagger}$ (°C)	378	377	384	381	381	380	372
	Activation energy, E_a kCal/mol)	51.2	62.5	53.8	28.2	34.4	32.3	11
	Rate of decompn. (%/min)	26	26	23	22	21	21	23
	Residue at 600°C (%)	11	18	21	21	21	14	14

†T_{50} - Temperature for 50% decomposition

The results given in Table VII.3(b) show clear changes in the decomposition pattern and the kinetic parameters of decomposition with the increase in concentration of the plasticizer from 10 to 20 phr and the increase in heating rate from 10 to 40 °C / min. It shows an increase in the thermal stability of the PCNSL modified NR vulcanizates which is particularly prominent at the higher heating rates of 20°C and 40°C. Thus, at the heating rate of 20°C/min an increase in dosage of PCNSL from 0 to 20 phr results in an increase in the thermal stability index (T_{50}) from 385°C to 387°C and a decrease in the rate of decomposition from 12%/min to 11%/min. Also, at the heating rate of 40°C/min the corresponding increase in T_{50} is from 378°C to 381°C and the decrease in rate of

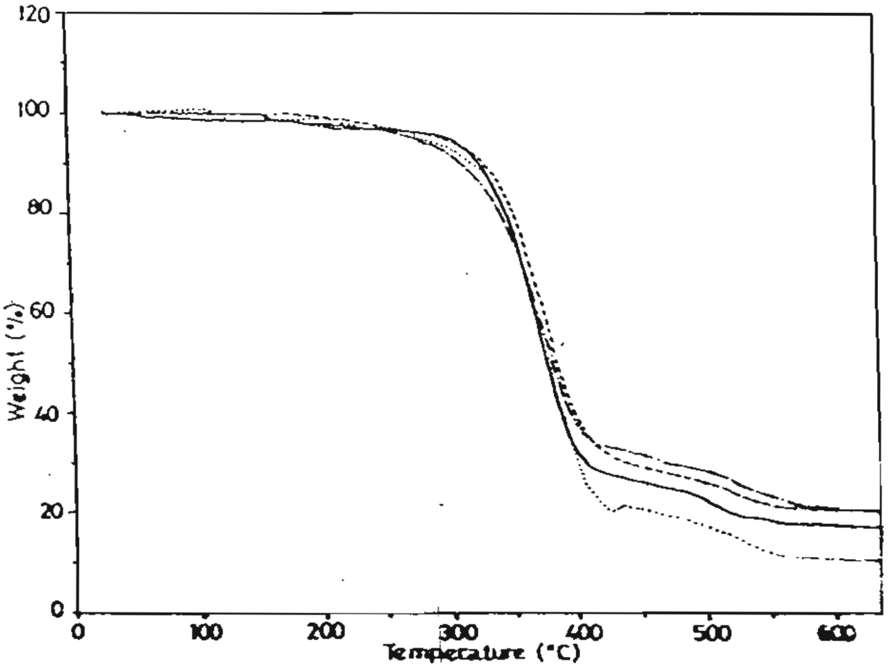


Fig.VII.2. Thermograams of unmodified & PCNSL modified NR vulcanizates

.... U ——P_{10} ----P_{15} —·—P_{20}

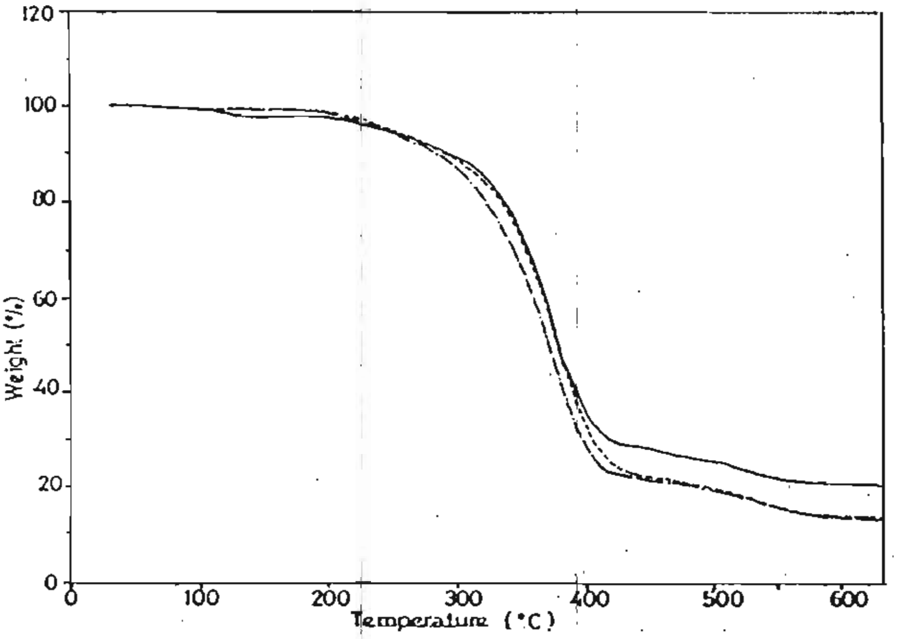


Fig.VII.3. Thermograms of Santicizer modified NR vulcanizates

——S_{10} ----S_{15} —·— S_{20}

decomposition is from 26%/min to 22%/min. However, the results show that an increase in dosage of Santicizer from 10 to 20 phr leads to a decrease in the thermal stability index (T_{50}) and an increase in the rate of decomposition at the different heating rates. Also, while the yield of pyrolysis residue at 600°C increases with the dosage of PCNSL at the different heating rates, a decrease in the yield is observed at the corresponding dosage of Santicizer which indicates the possibility of occurrence of a greater extent of condensed phase reactions during the thermal decomposition of PCNSL modified NR vulcanizates.

The thermograms of PCNSL modified NR vulcanizates and Santicizer modified NR vulcanizates at a heating rate of 20°C/min are given in Figures VII.2 and VII.3 respectively. The distinct change in the decomposition pattern of gum NR vulcanizates in presence of various dosages of PCNSL and Santicizer is evident from these figures. Thus, Figure VII.2 shows a progressive shift in the decomposition profile to the higher temperature and a decrease in its slope with the increase in concentration of PCNSL from 0 to 20 phr. Also, the yield of residue at 600°C increases with the increase in dosage of PCNSL. This type of decomposition behaviour and the increase in thermal stability may be due to the formation of thermally stable structures during the intermediate stage of decomposition, as explained in chapter VI (sec.VI.4) . The thermograms given in Figure VII.3 show the decrease in thermal stability of NR vulcanizates with an increase in the dosage of Santicizer from 10 to 20 phr. In presence of 15 and 20 phr of Santicizer in the NR vulcanizates, the decomposition commences at progressively lower temperatures. The major decomposition in the 300-400°C range also occurs at lower temperatures in presence of 15 and 20 phr of Santicizer

The decomposition pattern of NR vulcanizates containing PCNSL and Santicizer is found to be influenced considerably by the rate of heating. The activation energy for thermal decomposition of all the vulcanizates (in the temperature range from 310 to 360°C) decrease with the increase in heating rate. However, in all the cases, the values of the PCNSL modified NR vulcanizates are consistently higher than that of the Santicizer modified samples at similar dosages of the plasticizer. This again is an indication of the improved resistance to thermo-oxidative decomposition of the PCNSL modified NR vulcanizates compared to that containing Santicizer. The average rate of decomposition of the vulcanizates in the initial major decomposition region (from 310 °C to 380 °C) increases from 6 to 26% with the increase in heating rate from 10 to 40 °C/min. However, above the heating rate of 20°C/min, a change in the decomposition pattern is discernable between the vulcanizates containing PCNSL and Santicizer - the rate of decomposition of the former decreases with the increase in content of plasticizer as against an increase under the same conditions for the latter. Since, the pyrolytic decomposition products of NR at the initial stages (mostly of the flammable hydrocarbon type) contributes greatly to its flammability, the reduction in the rate of liberation of such products from the PCNSL modified NR vulcanizates is thought to be partly responsibile for their better flame retardancy compared to Santicizer modified NR vulcanizates. This is further supported by the higher values of LOI and higher yields of decomposition residue of the former as compared to the latter, given in Tables VII.2 and VII.3 (b) respectively. This is in agreement with the observation of Johnson that there exists a positive correlation between oxygen index and char-yield from pyrolytic data (22).

These results, particularly the reduction in rate of decomposition and increase in solid decomposition residue of NR vulcanizates containing higher concentrations of PCNSL, at higher heating rates indicate the probable contributions from condensed phase reactions typical of phosphatic flame retardants apart from the mechanism of decomposition of NR from a free radical type. This in turn may be responsibile for the observed improvement in their resistance to thermo-oxidative decomposition.

VII.3. Comparison of PCNSL with a conventional plasticizer (Spindle oil)

Aromatic, aliphatic and naphthenic oils which are non-phosphatic plasticizers are conventionally used in rubber compounding. These oils improve the processability of the rubber compounds and impart the desired physico-mechanical properties to the vulcanizates. Since PCNSL acts as a plasticizer and improver of physico-mechanical properties of the NR compounds it is essential that a comparative study be made between PCNSL and a commercially available plasticizer for rubber compounding with respect to the cure characteristics and physico-mechanical properties, inorder to assess their relative efficiency. The results of such a study carried out for NR gum compounds vulcanized by a semi-efficient vulcanization system in presence of 0 to 10 phr of the plasticizers are reported below.

i. Cure characteristics

The formulations as given in Table VII.4 were mixed on the roll mill as per the same standard procedure (ASTM D-3182-74). The lower value of Mooney viscosity of the Spindle oil modified mix as against that of the mix containing the same dosage of PCNSL indicates a higher degree of plasticization for the former.

Table VII.4 Composition of the NR mixes containing PCNSL and Spindle oil.

Mix code*	SN_0	SN_{10}	SNO_{10}
NR	100	100	100
ZnO	10	10	10
Stearic acid	2	2	2
Sulphur	1.6	1.6	1.6
MBT	1.5	1.5	1.5
TMT	0.3	0.3	0.3
PCNSL	-	10	-
Spindle oil	-	-	10
Mooney viscosity ML(1+4)100°C	35.5	23.25	14.5

* Subscript indicates the proportion of the plasticizer

The cure characteristics of the mixes obtained using an oscillating disk rheometer at 150°C and 180°C are given in Table VII.5 and the corresponding rheographs in Figure VII.4(a&b)

Table VII.5.Cure characteristics at 150°C of the NR mixes containing PCNSL and Spindle oil

Temp. (°C)	Mix code*	SN_0	SN_{10}	SNO_{10}
150	Scorch time, t_2 (s)	100	120	135
	Optimum cure time, t_{90} (s)	165	203	195
	Maximum cure, L_f (dNm)	51	38.25	41
	Cure rate, (s^{-1})	1.54	1.20	1.67
180	Scorch time, t_2 (s)	68	68	64
	Optimum cure time, t_{90} (s)	90	120	89
	Maximum cure, L_f (dNm)	27.5	23.3	22
	Cure rate, (s^{-1})	4.55	1.92	4
	Reversion time, (s)	210	338	143

* Subscript indicates the proportion of the plasticizer

The results given in Table VII.5 and Figure VII.4 show lower rate of cure and final state of cure for the PCNSL modified mix as compared to the oil modified mix and the unmodified mix. The lower state of cure of the PCNSL modified NR vulcanizate is further evidenced by the comparatively lower value of tensile modulus at 300% extension and chemical crosslink density of the vulcanizate as shown in Table VII.6. This may be due to the steric hindrance caused by the phosphate group and aliphatic side chain segment of PCNSL which prevents the attainment of a higher degree of crosslinking.

The rheographs given in Figure VII.4(b) and the results given in Table VII.5 show a distinct improvement in the reversion resistance during curing at high temperature of the PCNSL modified NR mix as compared to that of the unmodified and oil modified mix. The improved reversion resistance of the PCNSL modified mix may be due to the formation of crosslinks between the unsaturation sites in the aliphatic side chain segment of PCNSL and that of NR in addition to the rubber-rubber crosslinks.

ii. Physico-mechanical properties of vulcanizates

The physico-mechanical properties of the NR vulcanizates containing PCNSL and spindle oil are given in Table VII.6. It shows an improvement in the tensile properties and resistance to fatigue failure of the PCNSL modified NR vulcanizate (despite the lower chemical crosslink density) as compared to that containing the same dosage of spindle oil. The lower tensile modulus and hardness of the PCNSL modified NR vulcanizate as against that of the oil modified NR vulcanizate indicates a higher degree of softening effect of the PCNSL. Probably the higher flexibility of the NR matrix in presence of PCNSL helps in

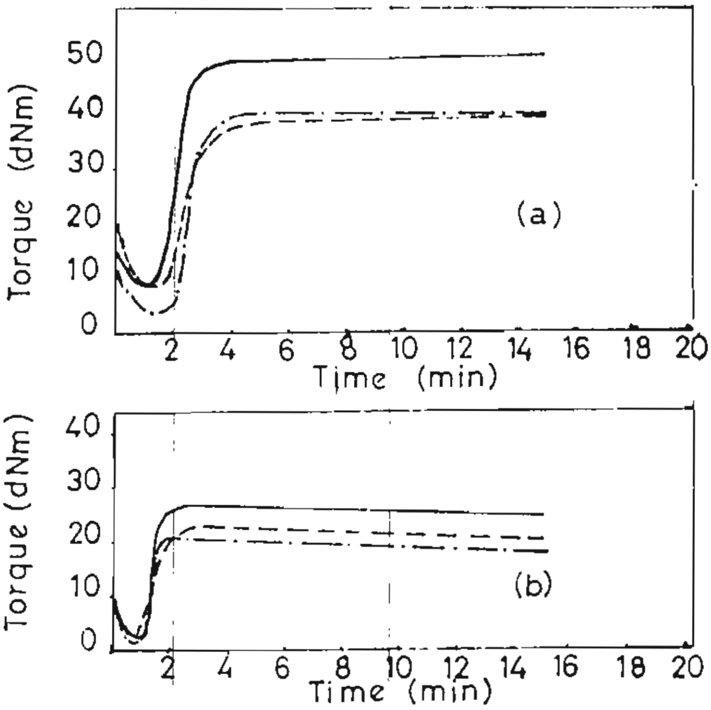


Fig.VII.4. Rheographs of unmodified NR, PCNSL-modified NR and oil modified NR

(a) 150 °C (b) 180 °C

____Unmodified NR ___PCNSL modified NR

_._Oil modified NR

faster dissipation of stress, thus hindering the easier propagation of cracks in the tensile and fatigue failure tests to a greater extent than that of the vulcanizate containing spindle oil resulting in the observed improvements in tensile strength and resistance to fatigue failure This has been further evidenced from the improved resistance to fatigue failure of the PCNSL modified NR vulcanizates during the De Mattia fatigue to failure test. It may be explained as due to the lower CLD and the resultant higher flexibility of the PCNSL modified NR vulcanizate which exhibits greater flex crack resistance property.

Table VII.6. Physico-mechanical properties of the NR vulcanizates containing PCNSL and Spindle oil.

Mix code*	SN_0	SN_{10}	SNO_{10}
Tensile strength (MPa)	18	17	16
Elongation at break (%)	1060	1120	1080
Modulus - 100% (MPa)	0.56	0.44	0.54
Modulus - 200% (MPa)	1.17	0.86	0.97
Modulus - 300% (MPa)	1.83	1.37	1.49
Hardness (ShoreA)	36.5	26	31
Tear strength (kN/m)	30.6	23.9	23.9
Monsanto fatigue to failure freq (kC)	42	>72.7	>50.3
De Mattia fatigue to failure			
Length of crack (mm/ 30kC)	23.5	9.5	25
CLD $X10^4$ (mol/g RH)	0.74	0.54	0.69

* Subscript indicates the dosage of the plasticizer

iii. Retention of mechanical properties after aging

The results given in Tables VII.7 show the retention of tensile properties of the NR vulcanizates containing PCNSL and spindle oil after accelerated aging in a hot air oven at 70°C for 24 and 48 hours.

Table VII.7. Retention of tensile properties after air aging at 70°C (%)

Period of aging (hrs.)	Mix code*	SN_0	SN_{10}	SNO_{10}
24	Tensile strength Elongation at break Modulus-100%	105 89 114	113 95 125	109 94 109
48	Tensile strength Elongation at break Modulus-100%	108 84 129	110 91 125	124 92 109

* Subscript indicates the proportion of the plasticizer

The results in TableVII.7 show improved retention in tensile strength, elongation at break and tensile modulus of the PCNSL modified NR vulcanizate after aging at 70°C for 24 and 48 hours as compared to that of the unmodified and oil modified NR vulcanizates. This may be due to the post-curing reactions taking place in the PCNSL modified NR vulcanizate during the aging period leading to formation of additional cross links and an increase in crosslink density as reported earlier (12,13). This may also be supported by the antioxidant activity of the PCNSL in NR

iv. Resistance to thermo-oxidative decomposition

The decomposition characteristics of the vulcanizates obtained from dynamic thermo-gravimetric analysis of the vulcanizates in air are given in Table VII.8. The thermograms are given in Figure VII.5 which shows a shift in the decomposition profile towards higher temperatures in presence of PCNSL as compared to that containing the same dosage of oil. The results in Table VII.8 show increases in the thermal stability index T_{50} and activation energy for thermal decomposition in the 300 - 360°C range for the PCNSL modified NR vulcanizate as compared to that of the unmodified and oil modified NR vulcanizates. Thus, the increase in T_{50} (4°C) and the activation energy of decomposition (36.4kCal/mol) of the PCNSL modified NR vulcanizate over that of the oil modified NR vulcanizate clearly indicates and improved resistance to thermo-oxidative decomposition of the PCNSL modified NR vulcanizate.

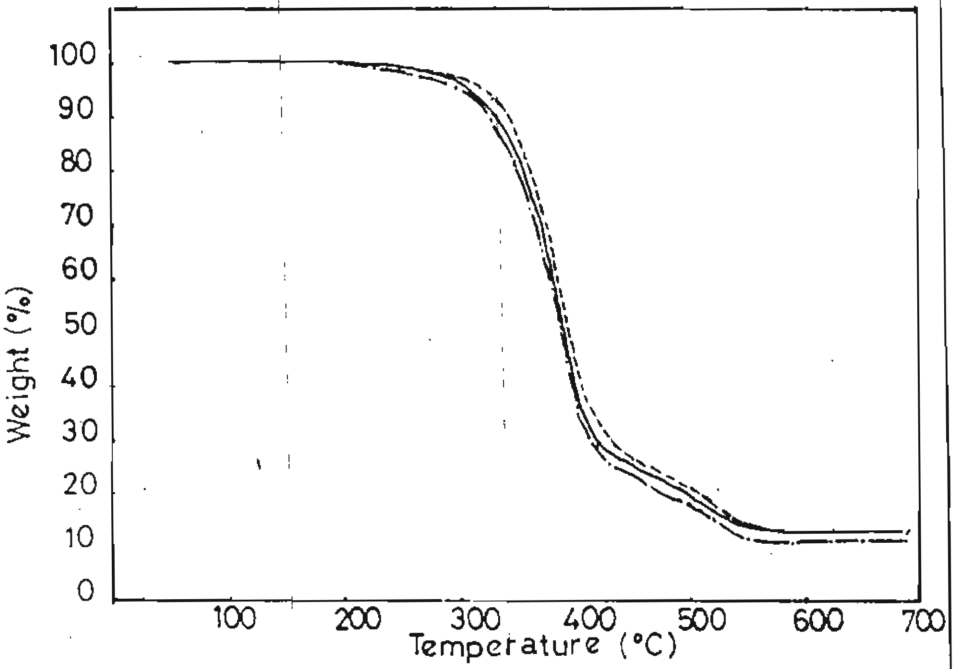


Fig.VII.5. Thermograms of unmodified NR vulcanizate, PCNSL modified NR vulcanizate and oil modified NR vulcanizate

____ Unmodified NR

----PCNSL modified NR

_._Oil modified NR

Table VII 8 Thermo-oxidative decomposition characteristics - (Dynamic thermogravimetry*)

Mix code	SN_0	SN_{10}	SNO_{10}
Thermal stability index, T_{50} (°C)	392	396	392
Activation energy, E_a (kCal/mol)	5 7	75.5	39.1
Residue at 600°C (%)	13	13	11

* Medium -air, Heating rate = 20°C/min

Also, the results from TGA shows an increase in the residue obtained at 600°C for the PCNSL modified NR vulcanizate (13%) in comparison with that of the oil modified NR vulcanizate (11%) This indicates a probable change in the decomposition path-way from a free radical type for the oil modified NR vulcanizate to one involving more of condensed phase reactions in the PCNSL modified NR vulcanizate leading to intermediate thermally stable structures, higher char yield and consequently, improved thermal stability and resistance to thermo-oxidative decomposition.

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CHAPTER VIII

EFFECT OF FILLERS ON PHYSICO-MECHANICAL PROPERTIES OF PCNSL MODIFIED NR

A part of this chapter has been accepted for publication in J. Appl. Polym. Sci., (in press) (1998).

VIII.1. Introduction

Often fillers, both reinforcing and non-reinforcing types play a significant role in elastomer compounding and in imparting the desirable processable characteristics as well as vulcanizate properties to the final product. Generally, fillers help in improving the processability of rubber compounds by reducing the 'nerve' during mixing, in imparting the necessary physico-mechanical properties to the vulcanizates and in reducing the cost of the compound especially when these are used at higher loadings. Since the fillers are often used at higher proportions, it is essential to know whether the desirable effect of the additives such as plasticizer or modifying resin is reflected in the filled compounds. The results reported in the previous chapters have shown that PCNSL improves the processability of gum NR compounds and imparts very good physico-mechanical properties to the vulcanizates in the concentration range of 0 to 20 phr. At the same time the loading of fillers such as carbon black, silica and china clay in NR compounds may be facilitated by the presence of PCNSL. Therefore, in this chapter the concentration of PCNSL was varied from 0 to 20 phr in a typical semi efficient vulcanization system of NR containing the same dosage of these fillers. The cure characteristics and physico-mechanical properties of these systems have been studied, results of which are presented in the following section.

VIII.2. Cure characteristics

Elastomer formulations are seldom used without incorporating a filler for most of their applications. Quite often, they contain a variety of fillers of the reinforcing or non-reinforcing type simultaneously at dosages ranging from low to high, depending on the specific end use properties. In such cases, it is absolutely essential to see that the plasticizer used does not affect the cure characteristics of the final formulation adversely.

The effect of increase in the dosage of PCNSL from 0 to 20 phr on the cure characteristics and physico-mechanical properties of NR compounds containing 40 phr each of the fillers such as HAF (N-330), silica (HiSil) and china clay (soft) has been studied. The composition of mixes are given in Table VIII.1 and the cure characteristics in Table VIII.2. The rheographs obtained from the ODR at 150 °C are given in Figure VIII.1.

TableVIII.1.Composition of PCNSL modified NR mixes containing different fillers

Mix code	H_0	H_5	H_{10}	H_{20}	Si_0	Si_5	Si_{10}	Si_{20}	CC_0	CC_5	CC_{10}	CC_{20}
Compn												
HAF black	40	40	40	40	-	-	-	-	-	-	-	-
Silica	-	-	-	-	40	40	40	40	-	-	-	-
EG*	-	-	-	-	4	4	4	4	-	-	-	-
CC*	-	-	-	-	-	-	-	-	40	40	40	40
PCNSL	0	5	10	20	0	5	10	20	0	5	10	20

*EG - Ethylene glycol, CC- China clay

Base mix (phr) - NR-100, ZnO-10, Stearic acid-2, Sulphur-2, MBT- 1.5, TMT-0.5

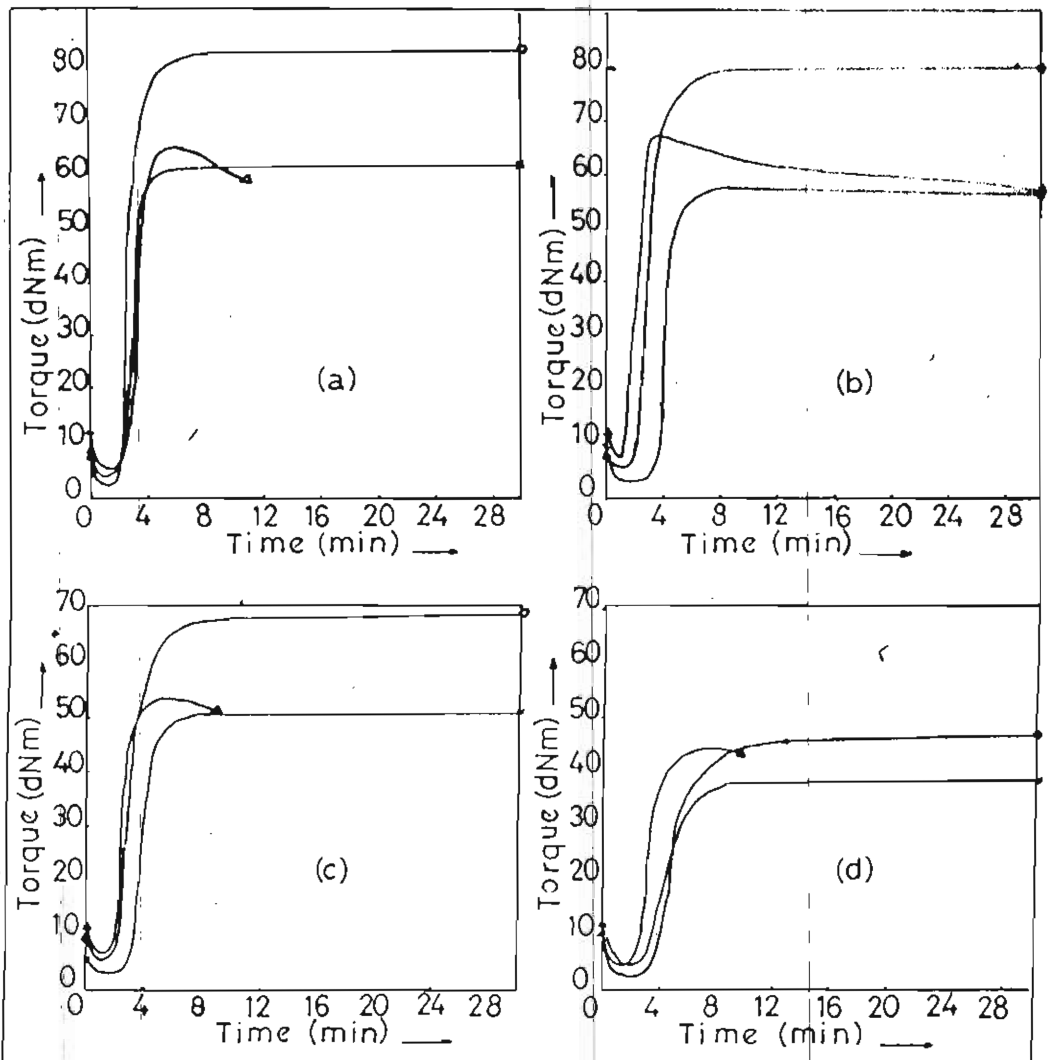

Fig. VIII.1. Rheographs of filled NR formulations

Fillers ○—○ HAF black ▲—▲ Silica •—• China clay

PCNSL (phr) – (a) 0 (b) 5 (c) 10 (d) 20

Table VIII.2 Effect of dosage of PCNSL on the cure - characteristics at 150°C of filled NR compounds

Mix code*	H_0	H_5	H_{10}	H_{20}	Si_0	Si_5	Si_{10}	Si_{20}	CC_0	CC_5	CC_{10}	CC_{20}
Parameter												
Scorch time, t_2 (s)	124	120	120	175	154	98	120	150	150	210	180	203
Optimum cure time, t_{90} (s)	236	255	285	510	250	143	195	263	229	300	285	375
Cure rate, (s^{-1})	0.9	0.7	0.6	0.3	1	2.2	1.3	0.9	1.3	1.1	1.0	0.6
Maximum cure, L_f (dNm)	82	80	69	47	64	67	54	44	61	57	51	38

* Subscript indicates the amount of PCNSL in the mix

The results in Table VIII.2 show that with the increase in dosage of PCNSL, a distinct improvement in the 'scorch safety' is obtained for the black and clay filled NR compounds at higher concentration of PCNSL viz., 20 phr. Also, the cure rate and maximum state of cure of the compounds decrease progressively with an increase in concentration of PCNSL. However, at a concentration of 10 phr of PCNSL all the compounds give an optimal combination of high cure rate, state of cure and scorch time whereas for the silica filled compounds the changes are marginal.

VIII.3. Physico-mechanical properties

The versatility of NR as a 'commodity polymer' and as an 'engineering elastomer' for wide-range of applications is mainly due to its unique combination of physico-mechanical properties. Two of the most important properties to be considered for any engineering application are its mechanical strength and aging behaviour (1). Among the compounding ingredients used to modify elastomers, fillers and plasticizers constitute two of the key elements affecting the strength properties of the vulcanizates. A variety of black and non-black fillers of the 'reinforcing', 'semi-reinforcing' and 'non-reinforcing' types and plasticizers of the 'reactive' and 'non-reactive' types often cater to this need (2).

The effect of increase in dosage of PCNSL from 0 to 20 phr on the cure characteristics of NR compounds containing 40 phr each of carbon black (HAF N330) black, silica (HiSil) and china clay (soft) has been discussed in the previous section. The physico-mechanical properties of these vulcanizates such as hardness, tensile properties, tear strength and resistance to thermo-oxidative degradation have also been measured ; the results of which are given in Table: VIII.3

Table VIII.3. Physico-mechanical properties of the vulcanizates

Mix code*	H_0	H_5	H_{10}	H_{20}	Si_0	Si_5	Si_{10}	Si_{20}	CC_0	CC_5	CC_{10}	CC_{20}
Parameter												
Reinforcement index, RI	0.47	0.74	0.68	0.21	0.1	0.26	0.31	0.16	0.07	0.26	0.30	0.04
Hardness (Shore A)	65	63	59	52	58	57	55	43	47	43	37	35
+T_{50} (°C)	404	405	402	445	399	399	401	444	451	424	418	405
IPDT(°C)	420	404	401	426	384	383	382	413	429	400	393	392
E_a kCal/mol	2.0	1.8	0.6	12.9	2.1	3.7	14.3	13.4	3.9	7.3	4.3	1.9
Modulus-300% (MPa)	12.1	9.0	6.4	3.2	4.3	3.9	3.3	2.3	3.3	2.9	2.4	1.8
TS (MPa)												
EB (%)	20	24	24	16	23	22	21	19	17	20	17	12
Tear	500	630	700	830	890	910	930	1000	790	930	960	1020
strength (kN/m)												
	57	63	106	86	69	74	76	80	30	30	30	26

* Subscript indicates the amount of PCNSL in the mix

\+ T_{50} - Thermal stability index, IPDT - Integral Procedural Decomposition Temperature, E_a - Activation energy for decomposition, TS- Tensile strength, EB - Elongation at break,

i. Reinforcement index

The rheographs of the mixes (given in Fig. VIII.1) show progressive decrease in the cure-plateau with the increase in concentration of PCNSL from 0 to 20 phr in the compounds containing different types of fillers. The 'filler reinforcement index' (α) was calculated from the maximum rheometric torques using the following relation as reported by Boonstra [3] viz.,

$\alpha = (\Delta L_{max(X)} - \Delta L_{max(gum)}) / \Delta L_{max(gum)}$ where $\Delta L_{max(X)}$ is the maximum change in torque during vulcanization due to the addition of X phr of the filler and $\Delta L_{max(gum)}$ is the maximum change in torque during the vulcanization of the gum compound. The results are given in Table VIII.3 which show that the reinforcement index reaches a maximum in all the compounds at concentrations of PCNSL ranging from 5 to 10 phr. This may be due to the better dispersion of the filler in the NR matrix in presence of 5 to 10 phr of PCNSL which helps in wetting the filler and lowering the interfacial energy between the filler and the rubber matrix

The interaction of particulate fillers with an elastomer is known to be dependent on various factors such as (i) the surface area of the filler, (ii) specific activity of the filler surface determined by its physical and chemical nature and (iii) the 'structure' and 'porosity' of the filler [1] A variety of chemical groups such as phenolic, ketonic and carboxylic acids are known to be present on the surface of carbon blacks [2]. Hence, it is presumed that there may be interactions between the carboxyl groups on the surface of the carbon black and the phenolic hydroxyl groups of PCNSL, leading to an increase in the reinforcement index The lower value of reinforcement index at higher dosage of PCNSL (20 phr) may be due to the plasticizing effect

ii. Dispersion of filler in PCNSL modified NR

The dispersion of PCNSL (10 phr) in the NR matrix is found to be very good as evidenced by the polaroid optical microscope. The photomicrographs (Fig.VIII.2) show a dispersion rating of "9" for the PCNSL modified NR gum vulcanizate which compares well with the unmodified NR vulcanizate indicating better dispersion of PCNSL in NR. The dispersion of carbon black (HAF N330) in the NR matrix in presence of 0 to 20 phr of PCNSL has also been studied; the results of which are discussed in the following section.

While studying the processing characteristics in an internal mixer, Palmgren[4] has identified five distinct stages in the mixing of a filler with rubber . They are :- (i) sub-division of the filler to smaller sizes, (ii) incorporation of the filler in the polymer matrix, (iii) dispersion of the filler, (iv)simple mixing of the filler in the polymer or distribution of the filler uniformly throughout the matrix and (v) viscosity reduction of the mix. Though each of the different steps mentioned above has its own importance in the whole mixing procedures, the role of dispersion of the filler in the polymer matrix is critical with respect to adequate processability of the mix and physico-mechanical properties of the cured product. Thus, the post-extrusion swelling of black filled mixes is found to be dependent on the degree of dispersion of the filler [5]. The dispersion of carbon black in NR has been studied extensively by Coran [6]. Coran and Donnet [7] have proposed a rapid method for assessing the quality of dispersion of carbon black in rubber They have also studied the kinetics of dispersion of carbon black in NR [8] and the effect of quality of dispersion of the black on the dynamic mechanical properties of filled NR [9] .

A variety of methods have been reported in the literature for the analysis of the dispersion of carbon black in polymers A quantitative method for carbon black dispersion analysis has been suggested by Hess et al. [10] . Some of the indirect methods of measuring the dispersion of carbon black in rubber compounds have been described by Guerbe and Freakley[11] These include measurements of (i) a.c. electrical conductivity (ii) micro wave -energy absorption and (iii) cut - surface light scattering ('Dark Field Cut Surface method' based on reflected light microscopy). Among the different methods, the microscopic - technique has gained wide acceptance for the rapid estimation of dispersion of carbon black in polymers. Some of its variations include (i) split-field microscopy [12,13], (ii) dark field reflected light microscopy [14,15] and (iii) transmitted light microscopy [16] Stumpe and Railsback [17] used a conventional microscope in combination with a standard Polaroid Land camera (with effective magnification 30X) for measuring carbon black dispersion. They

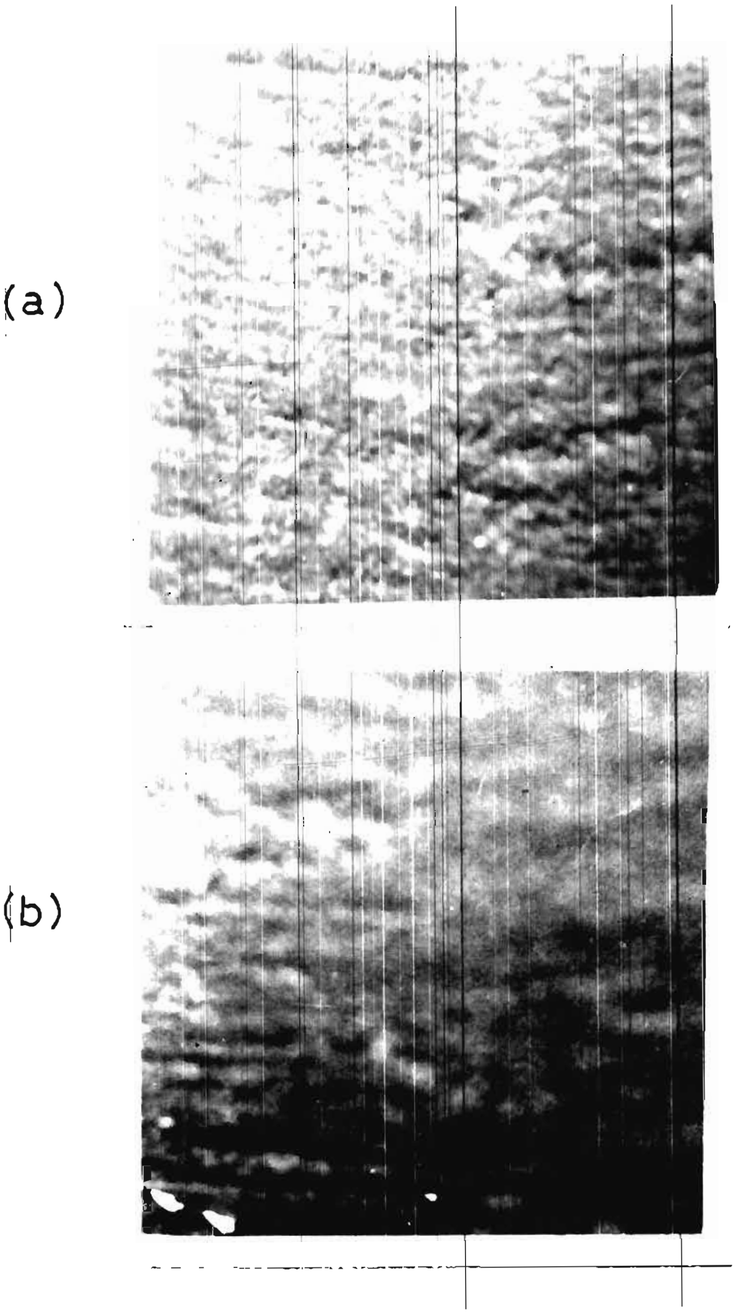

Fig. VIII.2. Polaroid photomicrographs of NR vulcanizates, (a) Unmodified NR (b) PCNSL (10 phr) modified NR (X 30) proposed a numerical rating (for assessing the quality of dispersion) from 1 to 10 ranging from "Very Poor" to "Excellent".

The dispersion of carbon black in the NR formulations containing 0 to 20 phr of PCNSL was measured using the polaroid photographic technique mentioned above. The composition of the mixes are given in Table VIII.1

The polaroid optical photomicrographs of the vulcanizates containing 0 to 20 phr of PCNSL are given in Figure VIII.3 (a-d). A numerical dispersion rating of "7" was assigned to the vulcanizates containing 5 and 10 phr of PCNSL, thereby showing a "good" degree of dispersion of the black in the NR matrix. The dispersion rating of the unmodified NR vulcanizate and that containing 20 phr of PCNSL were only "6" indicating a "fair" degree of dispersion of the black. The dispersion ratings of vulcanizates containing 5 and 10 phr of spindle oil in the same base formulation (Table VIII.1) were "6" and "5" corresponding to a rating of "fair" and "poor to fair" respectively.

The rate of dispersion of carbon black in rubber is found to be dependent on the 'mixing torque' developed in the processing equipment (18). A better dispersion of carbon black in NR in presence of 5 to 10 phr of PCNSL is expected to be due to an 'optimal reduction' in the viscosity of NR by virtue of the softening effect of PCNSL on it. Bolen et al.(19) have pointed out the requirement of a minimum shear- stress in a polymer matrix for optimum dispersion of the additives. Boonstra (20) has reported the probability for poor dispersion of fillers in low viscosity rubbers. The higher degree of softening action of PCNSL on NR at the higher concentration of 20 phr lowers the viscosity of the NR matrix considerably leading subsequently to a lowering of the shear- induced dispersion of the filler, resulting in a lower dispersion rating

iii. Mechanical properties of the vulcanizates

(a). Hardness

The results given in Table VIII.3 show that irrespective of the type of filler, the hardness of the vulcanizates decreases steadily with an increase in dosage of PCNSL from 0 to 20 phr. A similar softening effect due to plasticization has been reported in PCNSL modified gum NR vulcanizates also (21)

(b). Tensile properties

Boonstra (3) has given the definition of a 'reinforcing filler' as one that improves the modulus and 'failure-properties' such as tensile strength and tear strength of the final vulcanizate. In order to determine the extent of reinforcement of the different fillers in PCNSL modified NR vulcanizates, the variations in these properties with respect to the dosage of PCNSL were measured ; the results of which are shown in Figure VIII.4.

Generally, the most prominent physical effect of a filler in polymers is that of 'stiffening' or an increase in modulus (22). Figure VIII.4 shows that the tensile modulus at

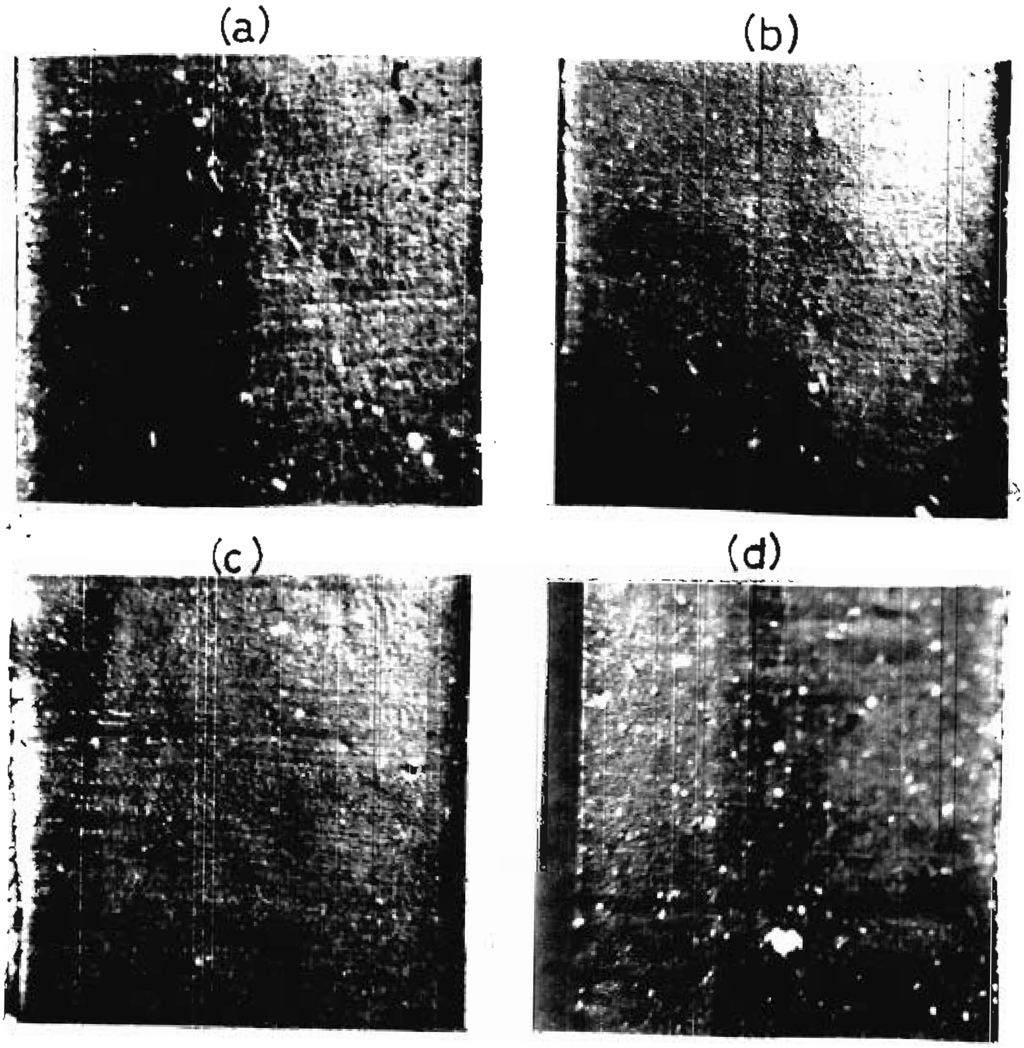

Fig. VIII.3. Polaroid photomicrographs of dispersion of carbon black in NR matrix in presence of PCNSL, (a) 0 phr, (b) 5 phr, (c) 10 phr & (d) 20 phr (X 30)

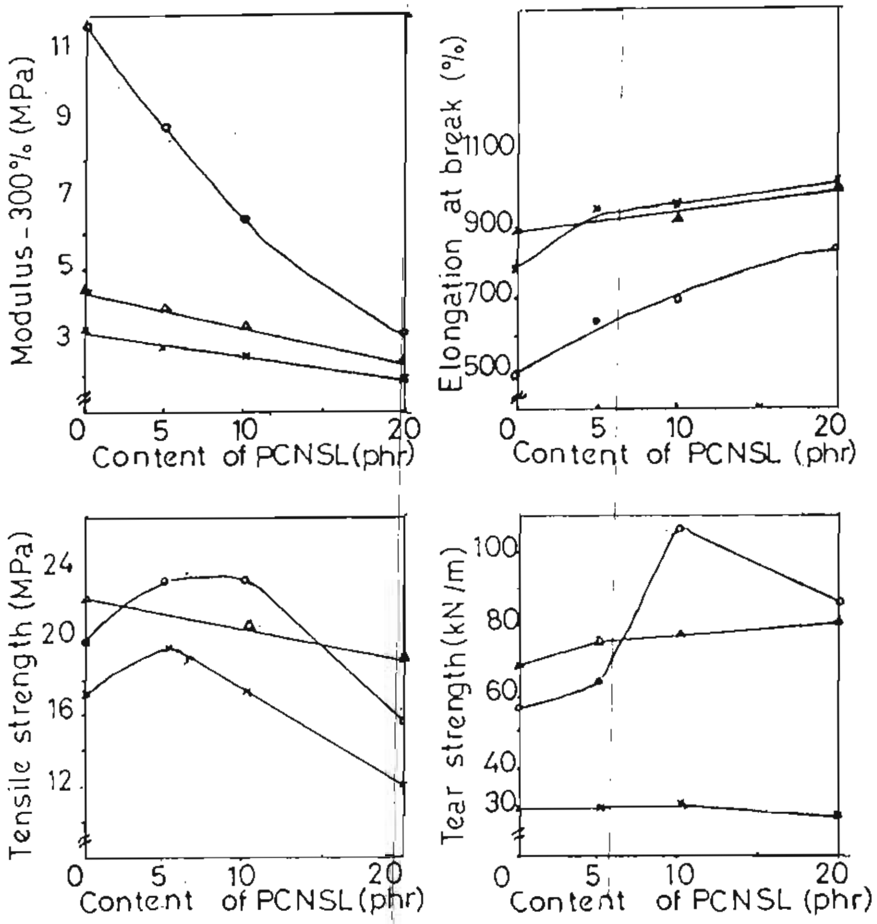

Fig. VIII.4. **Mechanical properties of filled NR vulcanizates with variation in the dosage of PCNSL**

o——o HAF △——△ Silica ×——× Clay

300% elongation of the HAF black filled NR vulcanizate decreases at a higher rate compared to that containing silica and china clay, with the increase in concentration of PCNSL. This shows the efficiency of PCNSL in reducing the stiffness of NR vulcanizates to a higher degree when HAF black is used as the reinforcing filler.

The softening effect of PCNSL on NR in the filled vulcanizates as indicated by the reduction in hardness and tensile modulus, is reflected in the elongation at break also. Figure VIII.4 shows that the elongation at break of the vulcanizates increases steadily with the increase in content of PCNSL - the rate of increase being higher for the black filled vulcanizates compared to that of others.

With the increase in dosage of PCNSL, the tensile strength of the black filled vulcanizate reaches a maximum (24 MPa) in presence of 5 to 10 phr of PCNSL. Also, the maximum tensile strength for the china clay filled NR vulcanizate (20 MPa) is obtained in presence of 5 phr of PCNSL. The silica filled NR vulcanizate do not show any improvement in tensile strength on modification with PCNSL. A simultaneous increase in tensile strength and elongation break of the black and clay filled NR vulcanizates upto the PCNSL dosage of 5 to 10 phr is analogous to the results reported earlier for PCNSL modified gum NR vulcanizates (21). The presence of a higher proportion of polysulphidic linkages in the PCNSL modified gum NR vulcanizates and the probable formation of an entangled network structure between PCNSL and the isoprene chains of NR are considered to be responsible for such a behaviour (23). It is possible that these mechanisms may operate in the filled vulcanizates. Besides, the plasticizing effect of PCNSL may facilitate better dispersion of these fillers in NR which is reflected in the improvements in tensile properties. Thus, the carbon black filled NR vulcanizates containing 5 to 10 phr of PCNSL have superior tensile properties and exhibit higher dispersion ratings as is evident from the polaroid optical photomicrographs (Fig.VIII.3).

Scanning Electron Microscopy (SEM) has been used as an efficient tool to study the fracture behaviour of filled rubber vulcanizates and to assess the extent of interactions between the elastomer matrix and the filler particles (27,28). The SEM photomicrographs obtained from such studies often helps in distinguishing fillers of the 'reinforcing' and 'non-reinforcing' types and in correlating the observed mechanical properties with failure-patterns.

The scanning electron microphotographs of the fracture surfaces of specimens obtained from tensile failure of black filled NR vulcanizate containing 10 phr of PCNSL are given in Figure VIII.5 (a-c). Figure VIII.5(a) shows the initiation of failure at an edge and the propagation of crack along a major crack-path. Figure VIII.5(b) shows the location of crack under a higher magnification with flow-lines spreading from locus towards periphery. Figure VIII.5(c) clearly shows the deviation in the propagation of a major crack-path. In general, the fracture surfaces are rough with considerable deviations in flow lines and crack-path and a higher degree of homogenity in the distribution of the filler. This in turn leads to higher strength properties as given in Table VIII.3. Very good interaction between filler particles and elastomer leading to adherence is known to be a basic requirement for

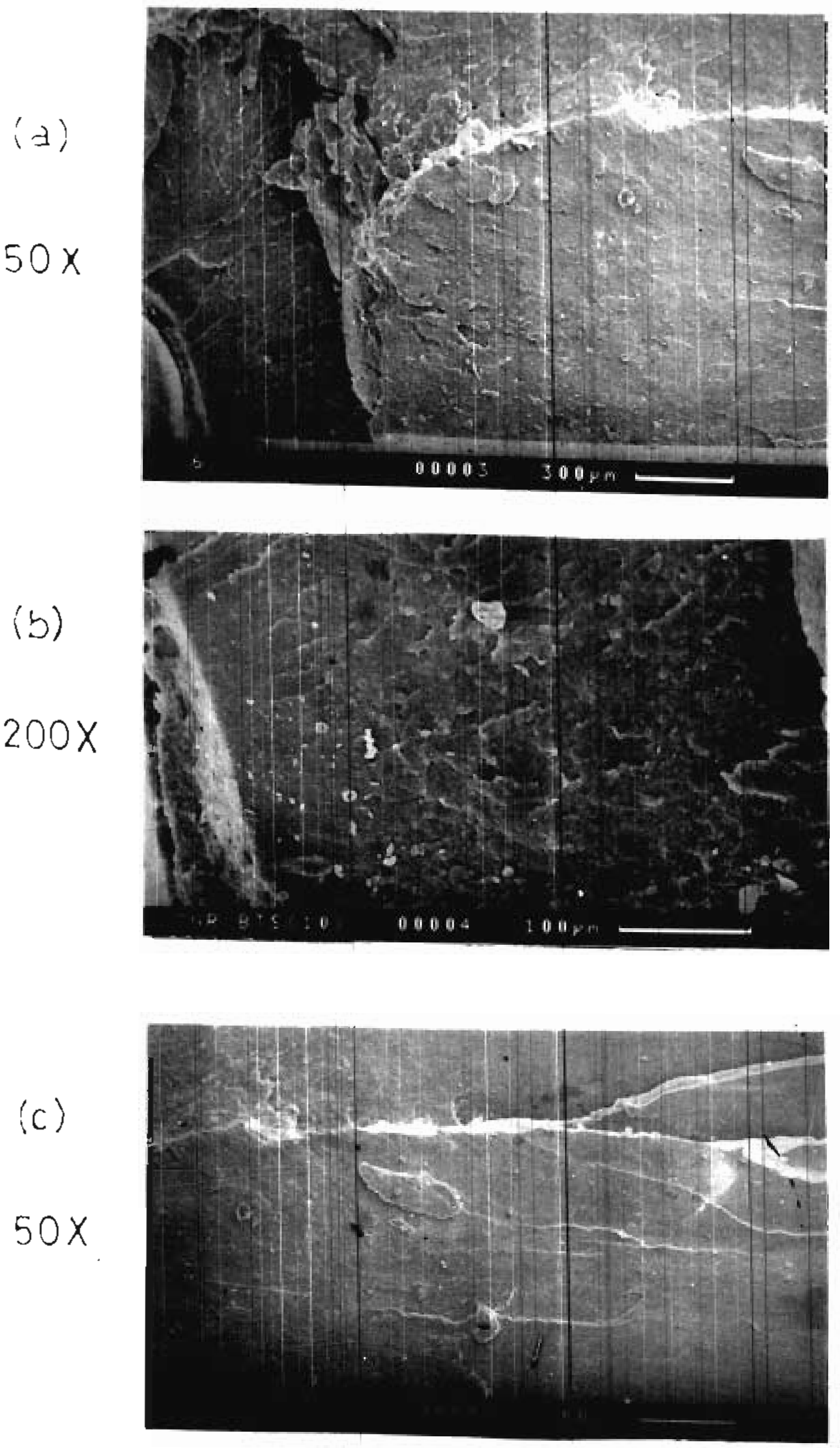

Fig. VIII.5. SEM photomicrographs of tensile fracture surfaces of PCNSL modified NR vulcanizate containing HAF black reinforcement (22) In such cases, the particles can delay or side-track crack formation and blunt or slow down the developing cracks

(c). Tear strength

The variations in the tear strength of the vulcanizates with an increase in the dosage of PCNSL are also shown in Figure VIII.4.

The increase in tear strength of the vulcanizates with an increase in concentration of PCNSL is much more prominent for the black filled vulcanizate with a higher value (106 kN/m) in presence of 10 phr of PCNSL, as against 57 kN/m for the control. The higher tear strength for the PCNSL modified vulcanizates may be due to the lateral deviations in the major 'tear-path' of these vulcanizates as a result of enhanced flexibility of NR matrix in presence of PCNSL.

iv. Resistance to aging

The retention of mechanical properties of the NR vulcanizates after aging in a hot air oven at 70°C for 48 hrs is plotted against the proportion of PCNSL and is shown in Figure VIII.6.

Retention of the properties after aging is found to be higher indicating good resistance to thermo-oxidative degradation of the filled vulcanizates modified with 5 to 20 phr of PCNSL. The retention in tensile strength and elongation at break of the vulcanizates containing HAF black and china clay increased with the increase in content of PCNSL from 5 to 20 phr. A significantly high retention, especially at 20 phr of PCNSL may be due to the post-curing reactions during the aging period. Unfilled NR vulcanizates modified with PCNSL also showed similar high retention in tensile properties after ageing (21) along-with an increase in crosslink density (23).

v. Thermal stability and thermo-oxidative decomposition characteristics

The thermal degradation characteristics of the filled NR vulcanizates containing PCNSL were determined by thermogravimetric analysis over the temperature range from 25 to 700 °C at a heating rate of 20 °C/min in air. The results are given in Table VIII.3 and Figures VIII.(7-9). Integral Procedural Decomposition Temperature (IPDT) of the vulcanizates were calculated from the area under the thermograms as per the method reported by Reich and Levi (24). Activation energy of decomposition (E_a) of the vulcanizates was calculated by the Freeman - Carroll method(25).

Table VIII.3 shows a significant increase in the thermal stability indices such as T_{50} and IPDT of the black and silica filled NR vulcanizates with an increase in the dosage of PCNSL from 0 to 20 phr. This result also shows a decrease in the thermal stability of china clay filled NR vulcanizates on increasing the concentration of PCNSL from 0 to 20 phr. Earlier thermogravimetric studies of unfilled NR vulcanizates containing 10 phr of PCNSL

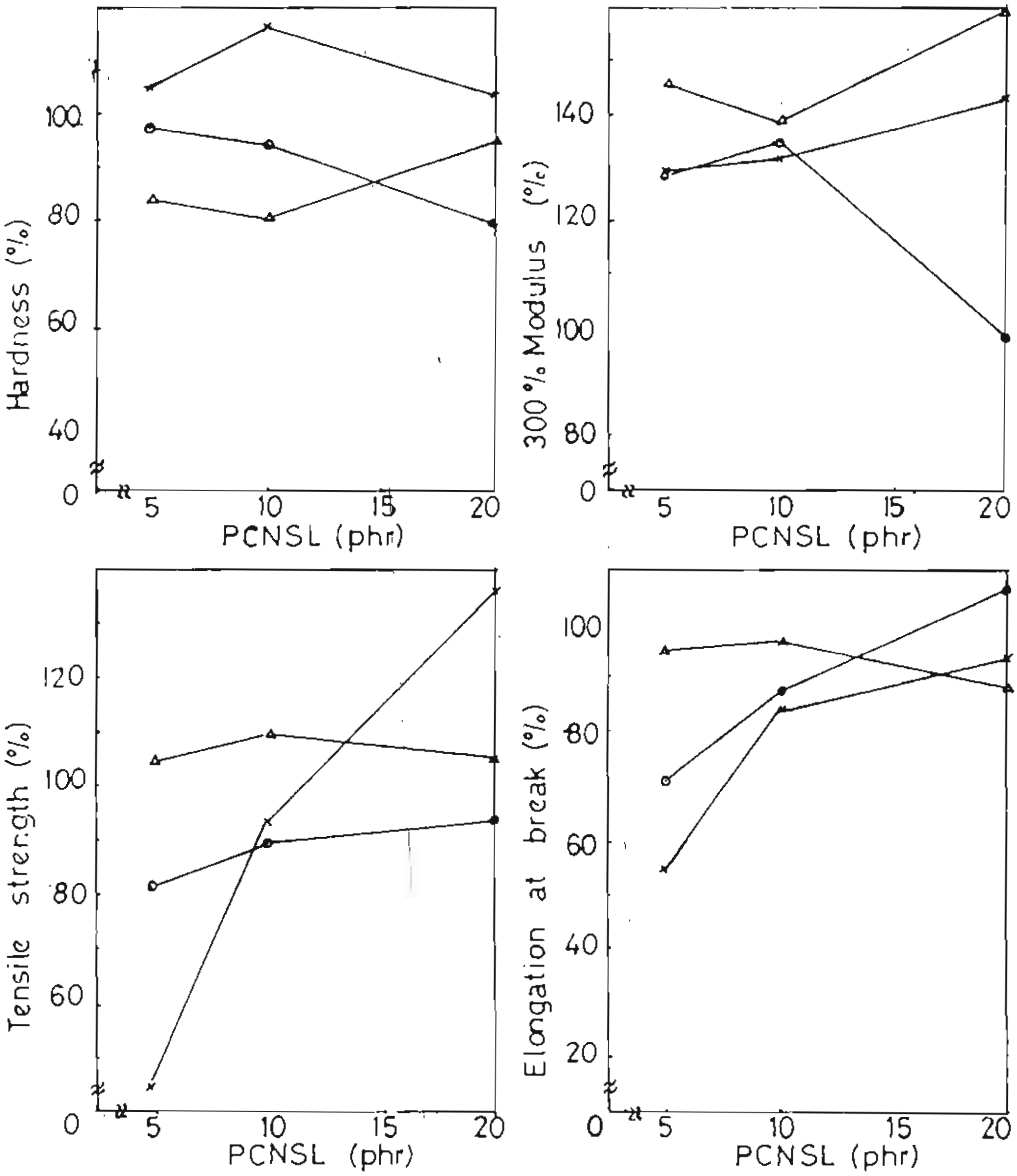

Fig. VIII.6. **Retention in mechanical properties of the vulcanizates after air aging at 70°C/48 hrs**

o——o HAF △——△ Silica ×——× Clay

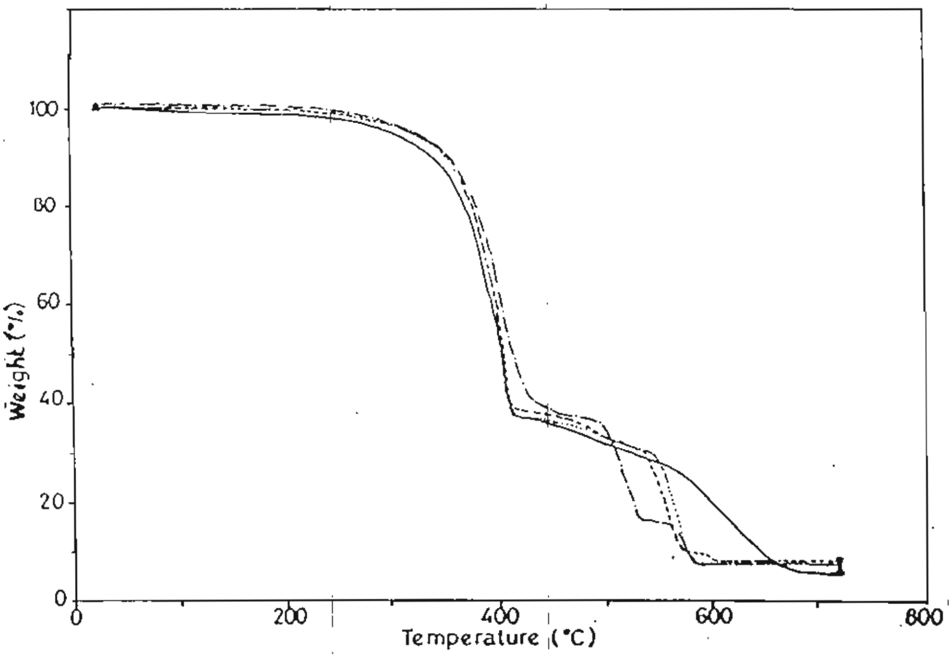

Fig. VIII.7. **Thermogravitograms of HAF black filled NR vulcanizates containing PCNSL.**

·········· 0phr   - - - - - 5 phr   ——— 10phr   —·— 20 phr

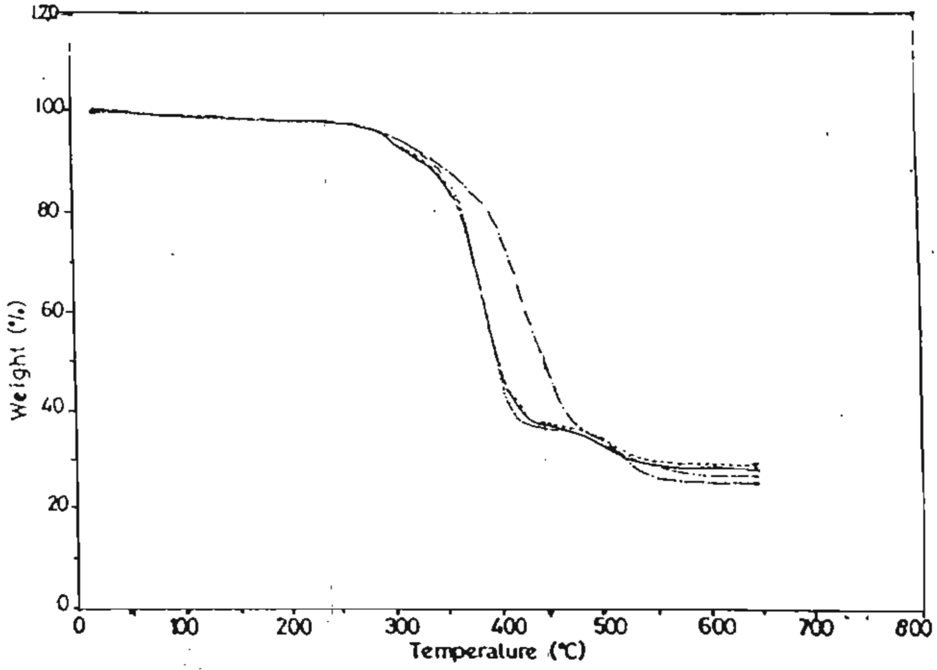

Fig. VIII.8. Thermogravitograms of silica filled NR vulcanizates containing PCNSL.

0phr 5 phr 10phr 20 phr

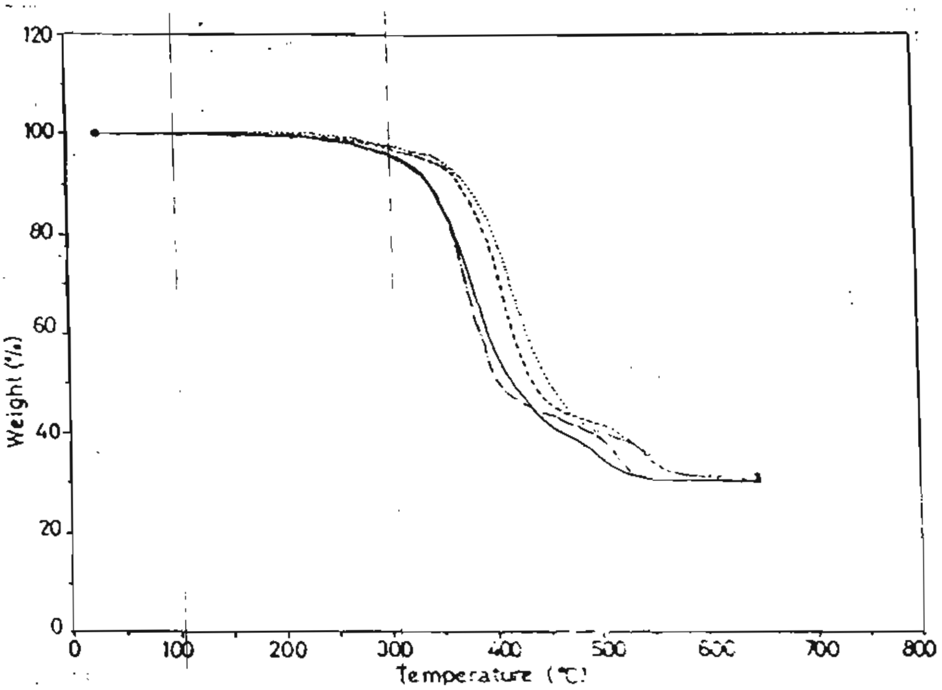

Fig. VIII.9. **Thermogravitograms of china clay filled NR vulcanizates containing PCNSL.**

0phr 5 phr 10phr 20 phr

in air and nitrogen showed a marginal improvement in thermal stability of the PCNSL modified vulcanizate in air as compared to that of the unmodified sample (26). Also, modification with 20 phr of PCNSL resulted in further improvement in thermal stability of the gum NR vulcanizates.

The results in Table VIII.3 also show that the activation energy (E_a) of thermal decomposition for the black filled vulcanizate reaches a maximum (12.9 kCal/mol) in presence of 20 phr of PCNSL. The maximum value of activation energy (14.3 kCal/mol) was obtained for the silica filled sample with 10 phr of PCNSL. The china clay filled NR vulcanizate containing 5 phr of PCNSL decomposed with a maximum activation energy of 7.3 kCal/mol. The considerably higher values of T_{50} , IPDT and activation energy for decomposition of the black and silica filled NR vulcanizates containing 20 phr of PCNSL, indicate their improved resistance to thermo-oxidative decomposition over that of the samples not containing PCNSL. The thermogravitograms of the NR vulcanizates (Figures VIII(7-9)) show that there is a considerable increase in the thermal stability of the carbon black and silica filled NR vulcanizates in presence of 20 phr of PCNSL in contrast to a decrease for the china clay filled NR vulcanizate. This is evident from the shift in the decomposition profile of the vulcanizate (in the 300-400°C range) towards higher temperatures with the increase in concentration of PCNSL from 0 to 20 phr.

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CHAPTER- IX

SUMMARY AND CONCLUSION

Chapter I gives an introduction to the role of additives in compounding of rubbers with special reference to 'multifunctional additives' (MFA) and their significance The various points discussed are examples of multifunctional additives reported for the compounding of elastomers, structural and other reqiurements of molecules for the synthesis of MFAs, suitability of derivatives of Cashew Nut Shell Liquid (CNSL) for the same, the various applications of derivatives of CNSL particularly for the modification of elastomers and preliminary results on the multifunctional role of Phosphorylated Cashew Nut Shell Liquid (PCNSL) and bromo derivative of PCNSL (BrPCNSL) in NR. The scope and objectives of the present work viz. to study the processability characteristics and vulcanizate properties of NR modified with PCNSL bringing out its multifunctional role is also presented towards the end of this chapter.

In chapter II, the characteristics and specifications of the materials used in the present study and the different experimental techniques and test methods followed for the evaluation of the 'processability characteristics' of the formulations and the physico-mechanical properties, chemical structure and thermal decomposition characteristics of their vulcanizates are described.

Chapter III gives a detailed account of the processability characteristics of NR modified with various doses of PCNSL(from 0 to 20 phr), under the conditions of mixing and extrusion along with relevant studies on their melt-rheology parameters. Also, a comparative study has been carried out using NR modified with the same dosages of an aromatic process oil (*Spindle oil*). The plasticizing action of PCNSL in NR was confirmed by the results obtained from a Monsanto Processability Tester (MPT) as evidenced by the higher 'pseudoplasticity index', lower 'consistency index' and melt-viscosity and lower activation energy of melt-flow of the PCNSL modified NR. The lower die-swell ratio of the PCNSL modified NR showed the reduction in 'melt-elasticity' of NR in presence of PCNSL. The decrease in principal normal stress difference of NR in presence of PCNSL indicated good 'compatibility' between NR and PCNSL. The results from MPT showed the improved extrusion characteristics of NR in presence of 10 phr of PCNSL. The DSC thermograms of the PCNSL modified gum NR vulcanizates at low temperatures (upto -100°C) showed a clear and progressive shift in the glass-transition temperature of NR to lower values, with the increase in concentration of PCNSL from 0 to 20 phr, thereby showing its effectiveness as a plasticizer at low temperatures. Studies on a Brabender Plasticorder at different rotor speeds and temperatures, showed improved mixing characteristics for PCNSL modified NR mixes as compared to unmodified samples. The lower values of melt viscosity, melt elasticity and energy requirement for mixing of the PCNSL modified NR mixes, as against that of the unmodified sample indicated the improvement in the processability of NR in presence of PCNSL.

Chapter IV describes the self adhesion characteristics of NR modified with various dosages of PCNSL under various conditions of sample preparation and testing. Modification of NR with upto 10 phr of PCNSL resulted in an improvement in the self adhesion strength ('tack strength') of unfilled NR compounds. In the standard 180° peel test, while the unmodified NR compound showed a maximum self adhesion strength of 2.01 kN/m at a contact time of 60 seconds, the samples containing 5 and 10 phr of PCNSL showed maximum values of 2.26 kN/m and 2.33 kN/m respectively. Also, the self adhesion strength of NR compounds containing 5 to 15 phr of PCNSL increased significantly with the increase in storage time prior to testing indicating a higher degree of 'time-dependent interfacial diffusion' of the macromolecules of NR in presence of PCNSL

Thus, the results in chapters III and IV show the multifunctional role of PCNSL in NR compounds as a plasticizer and as a tackifier.

Chapter V deals with the cure characteristics of PCNSL modified NR, various physico-mechanical properties of its vulcanizates and chemical analysis of PCNSL modified NR vulcanizates including the determination of crosslink density. PCNSL modified NR formulations with the semi-efficient vulcanization (SEV) system showed higher cure rate and maximum state of cure compared to the conventional vulcanization (CV) and efficient vulcanization (EV) systems along-with very good resistance to cure reversion The increase in dosage of PCNSL from 0 to 20 phr resulted in progressive reduction in the maximum state of cure in all the systems. The cure retardation effect of PCNSL observed at the higher concentration (20 phr) was eliminated by an increase in the ZnO/PCNSL ratio to 1:1. The lower value of activation energy for crosslinking of the PCNSL modified NR compound, as against that of the unmodified sample indicated the ease of crosslinking of NR in presence of 10 phr of PCNSL.

In the SEV system of NR, the tensile and tear strength of the vulcanizate increased significantly with an increase in concentration of PCNSL from 0 to 20 phr, reaching a maximum at 10 phr, as against the decrease for the CV and EV systems. In the SEV system, the elongation at break of the vulcanizate increased progressively with the increase in concentration of PCNSL from 0 to 20 phr. The tensile modulus and hardness decreased with the increase in dosage of PCNSL in all the systems. This shows the 'softening effect' of PCNSL in NR vulcanizates The mechanical properties of the vulcanizate containing 20 phr of PCNSL were improved by an increase in the concentration of ZnO from 10 to 20 phr, which was later found to be due to an increase in the crosslink density of the vulcanizate. Modification of NR with PCNSL resulted in an enhancement of the 'toughness' of the vulcanizate as shown by the increase in area under the stress-strain plot. The NR vulcanizates containing 10 and 20 phr of PCNSL showed higher heat-buildup under tensile and compressive deformation cycles along with lower rebound resilience, higher compression set, lower abrasion resistance and lower surface and volume resistivities as compared to the corresponding unmodified gum NR vulcanizate. However, modification of NR with 10 and 20 phr of PCNSL resulted in significant improvements in the resistance to tensile fatigue-failure. Scanning electron microscopy (SEM) of the fracture surfaces of PCNSL modified gum NR vulcanizates showed considerable deviations in the tear lines and crack-paths, partly accounting for the observed improvements in tensile and tear strengths and resistance to fatigue failure. The dynamic mechanical properties of unmodified and PCNSL modified NR vulcanizates measured over the temperature range from -100 °C to 50 °C at the frequencies of 3, 10 and 30 Hz showed a progressive widening of the 'tan δ' plot for the PCNSL modified sample, with the increase in temperature and frequency, showing increasing energy dissipation via. hysteresis at and above room temperature. This is considered to be responsible for delaying the rate of propagation of crack-growth and consequently the improvement in fatigue resistance.

The results on the chemical analysis of PCNSL modified gum NR vulcanizates, particularly those related to the elucidation of the network structure of the vulcanizate such as the chemical crosslink density, the proportion of different types of sulphidic linkages and the 'sulphur inefficiency parameter' in vulcanizates of the conventional, semi-efficient and efficient vulcanization systems are also presented in chapter V. The chemical crosslink density (CLD) and network structure of gum NR vulcanizates containing PCNSL were studied by equilibrium swelling in solvent and other physico-chemical methods. The PCNSL modified NR vulcanizates showed lower CLD than the unmodified NR samples, the decrease being lesser for the SEV system as compared to the CV and EV systems. The superior tensile characteristics of the PCNSL modified NR vulcanizates of the SEV system was presumed to be partly due to the presence of an 'entangled network structure' between the aliphatic segment of PCNSL and the isoprene chains as evident from the X-ray diffraction studies. The decrease in the solubility of PCNSL heated with various proportions of sulphur at 150°C indicated the 'crosslinkable' nature of PCNSL and the probable involvement of the unsaturated aliphatic segment of PCNSL in the vulcanization reaction with NR. The critical role of Zn^{++} ions in the crosslinking reactions, especially at higher concentrations of PCNSL was evident from the increase in CLD at higher concentrations of ZnO. The reduction in the IR absorption intensity in presence of ZnO indicated the probable complex formation of Zn^{++} ions with the phosphate group of PCNSL. These results show the role of PCNSL as a 'crosslinkable plasticizer' in NR

The above results show the role of PCNSL in NR vulcanizates as an improver of physico-mechanical properties such as tensile properties, toughness, tear strength, resistances to tensile fatigue failure and thermo-oxidative decomposition and as a softening agent.

Chapter VI describes the studies on the thermal analysis of PCNSL modified gum NR vulcanizates. The thermal and thermo-oxidative decomposition characteristics of NR vulcanizates modified with PCNSL were studied by thermo-gravimetric analysis, differential scanning calorimetry and differential thermal analysis. The PCNSL modified NR vulcanizate showed improved thermal stability in air, unlike that in nitrogen, which is presumed to be due to the formation of thermally stable structures during the intermediate stage of degradation. The kinetic parameters for the initial stage of degradation in air and nitrogen were evaluated by the Freeman - Carroll method. The higher value of activation energy for thermo-oxidative degradation of PCNSL modified NR (15.10 kCal/mol) and the Integral Procedural Decomposition Temperature (IPDT) (366°C) as against that for unmodified NR (13.04 kCal/mol and 347 °C respectively) indicate the improved thermal stability of the former. The higher resistance to thermo-oxidative decomposition of the PCNSL modified NR vulcanizate was shown by the lower values of enthalpy of oxidation as obtained from DSC and higher retention in tensile properties after accelerated heat aging.

Chapter VII deals with a comparative study of PCNSL modified NR and NR modified with two other commercially available plasticizers viz., 2-ethyl hexyl diphenyl phosphate (*Santicizer -141*) and an aromatic process oil (*Spindle oil*). The PCNSL modified NR vulcanizates showed higher tensile properties and resistances to thermo-oxidative decomposition and flame, compared to that containing the same dosage of Santicizer Also, the NR vulcanizate with the SEV system containing 10 phr of PCNSL showed higher tensile strength and resistance to fatigue failure and thermo-oxidative decomposition compared to that unmodified NR vulcanizate and that containing the same dosage of spindle oil.

Chapter VIII deals with the effect of different fillers such as carbon black, silica and china clay on the cure characteristics and physico-mechanical properties of PCNSL modified NR A distinct improvement in scorch safety was observed in carbon black and china clay filled NR compounds with an increase in dosage of PCNSL from 0 to 20 phr The reinforcing effect of black and non black fillers were found to be maximum at concentrations of PCNSL ranging from 5 to 10 phr as indicated by the increase in tensile and tear strengths. Polaroid micro-photography of the carbon black filled NR vulcanizate containing 5 and 10 phr of PCNSL showed improved dispersion of the black particles in the NR matrix in presence of PCNSL. Also, the SEM photomicrograph of the fracture surfaces of the specimens obtained from tensile failure of the carbon black filled NR vulcanizate containing 10 phr of PCNSL showed considerable deviations in the crack-path accounting for its higher tensile strength. The filled vulcanizates also showed improved resistance to thermo-oxidative aging and decomposition, especially at higher concentration of PCNSL viz., 20 phr

Chapter IX gives an over all summary and conclusions of the present work The results so far discussed establish that PCNSL acts as a 'multifunctional additive' in the compounding of NR as (i) a plasticizer, (ii) a co-agent for curing with improved resistance to cure reversion, (iii) an aid for filler dispersion, (iv) a tackifier , (v) a softening agent and (vi) an improver of physico-mechanical properties of the vulcanizates such as tensile strength, tear strength, elongation at break, thermal stability, and resistances to tensile and flex -fatigue failure and thermo-oxidative decomposition.

In addition to the multifunctional nature, the low cost, easy availability, abundancy and renewability of CNSL - a byproduct of the cashew industry, it serves as a precursor for the synthesis of PCNSL, thus widening the scope for using PCNSL for a variety of applications in NR. Thus PCNSL may be used as a good plasticizer / process aid , softening agent and improver of scorch safety in the compounding of re-tread rubber formulations for tires. The improved filler dispersion characteristics and self adhesion strength of PCNSL modified NR can be used advantageously in this application. The low rate of stress relaxation of NR formulations containing lower dosages of PCNSL (10 to 15 phr) can be made use of in applications such as gaskets or seals which reqiure dimensional stability under prolonged service conditions. On the other hand, the higher rate of stress relaxation of the NR formulation containing a higher concentration (20 phr) of PCNSL may be of use in formulating adhesives for stress-free joints. The improved fatigue resistance, toughness, higher energy dissipation characteristics and resistance to thermo-oxidative decomposition of the PCNSL modified NR indicate its potential application in vibration damping, shoe upper, etc. The improvement in the resistances to fatigue failure and thermo-oxidative decomposition of the PCNSL modified NR along with the antioxidant property of PCNSL in NR may extend its range of application in the manufacture of side wall of tires. There is a lot of scope for use of this material in synthetic rubbers too.

LIST OF PUBLICATIONS

The following papers based on this thesis have been published :-

1. *"Effect of phosphorylated cashew nut shell liquid on the physico-mechanical properties of natural rubber vulcanizates"*
   A.R.R.Menon, C.K.S.Pillai and G.B.Nando, *Kauts. Gummi Kunsts.*, 45(9), 708 (1992).

2. *"Chemical crosslink density and network structure of natural rubber vulcanizates modified with Phosphorylated Cardanol Pre-polymers"*
   A.R.R.Menon, C.K.S.Pillai and G.B.Nando, *J.Appl.Polym.Sci.*, 51(13), 2157 (1994).

3. *"Self-adhesion of natural rubber modified with phosphorylated cashew nut shell liquid"*
   A.R.R.Menon, C.K.S.Pillai and G.B.Nando, *J.Adhesion Sci. Technol.*, 9(4), 433 (1995).

4. *"Thermal degradation characteristics of natural rubber vulcanizates modified with phosphorylated cashew nut shell liquid"*
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5. *"Stress relaxation characteristics of natural rubber modified with phosphorylated cashew nut shell liquid pre-polymer"*
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