STUDIES ON DICHLOROCARBENE MODIFICATION AND BLENDING OF NATURAL RUBBER WITH HYDROGENATED NITRILE RUBBER TO IMPROVE THE AGING CHARACTERISTICS WITH RESPECT TO OIL, OZONE AND HEAT

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Certificate

This is to certify that the thesis entitled "***Studies on Dichlorocarbene Modification and Blending of Natural rubber with Hydrogenated Nitrile rubber to improve the aging characteristics with respect to Oil, Ozone and Heat***" is an authentic record of research work carried out by Mrs.K.I.Elizabeth under our joint supervision and guidance in partial fulfillment of the requirements for the award of the degree of ***Doctor of Philosophy*** in Polymer Chemistry under the faculty of Science of Mahatma Gandhi University, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma earlier. It is also certified that Mrs. K.I.Elizabeth has fulfilled the course requirements and exempted from the qualifying examination for the Ph.D. degree of Mahatma Gandhi University.

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Declaration

I hereby declare that the thesis entitled "***Studies on Dichlorocarbene Modification and Blending of Natural rubber with Hydrogenated Nitrile rubber to improve the aging characteristics with respect to Oil, Ozone and Heat***" is an authentic record of research work carried out by me under the joint supervision of Dr. N.R.Peethambaran, Deputy Director (Trg) and Dr. Rosamma Alex, Rubber Technologist, Rubber Research Institute of India, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma earlier.

Elizabeth

Kottayam
October 2005

Elizabeth K.I.

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Elizabeth K.I.

List of Notations and Abbreviations

ABS	- poly(acrylonitrile-co-butadiene-co-styrene)
BIIR	- bromobutyl rubber
BR	- butadiene rubber
CBS	- N- cyclohexyl benzothiazole- 2 sulphenamide
CIIR	- chlorobutyl rubber
CNR	- chlorinated natural rubber
CR	- chloroprene rubber
CSM	- chlorosulphonated rubber
CTNR	- caboxy terminated liquid natural rubber
CV	- constant viscosity
DCNR	- dichlorocarbene modified natural rubber
DPNR	- deproteinised natural rubber
DMA	- dynamic mechanical analysis
DSC	- differential scanning calorimeter
DTG	- differential thermo gravimetry
ECO	- epichlorohydrin
ENR	- epoxidized natural rubber
ENPCAF	- ethyl-N-phenylcarbamoylazoformate
EPDM	- ethylene propylene diene rubber
EV	- effective vulcanization system
FEF	- fast extrusion furnace black
FFKM	- perflourocarbon rubber
FPM	- fluorocarbon rubber
FTIR	- fourier transform infrared spectroscopy
G	- elastic modulus

ΔGm - free energy of mixing
HAF - high abrasion furnace black
HNBR - hydrogenated nitrile rubber
ΔH - enthalpy change
ΔHm - enthalpy change of mixing
IIR - butyl rubber
ISNR-5 - Indian Standard Natural Rubber –5 grade
LNR - liquid natural rubber
MBT - mercaptobenzothiazole
MEK - methyl ethyl ketone
NA-22 - ethylene thiourea
NaOH - sodium hydroxide
NBR - acrylonitrile butadiene rubber
NDB - negatively deviating blend
NMR - nuclear magnetic resonance
NR - natural rubber
n' - flow behavior index
OENR - oil extended natural rubber
phr - parts per hundred parts of rubber
PMMA - polymethyl methacrylate
PU - polyurethane
PVC - poly vinyl chloride
PVNRL - prevulcanized natural rubber latex
SBR - styrene butadiene rubber
SEM - scanning electron microscopy
SPNR - superior processing natural rubber

S_R - recoverable shear strain

ΔS - entropy

ΔSm - entropy of mixing

TEM - transmission electron microscopy

TGA - thermo gravimetric analysis

Tg - glass transition temperature

TMTD - tetramethylthiuram disulphide

TPNR - thermoplastic natural rubber

δ - solubility parameter

UTM - universal testing machine

Vr - cross link density

$\Phi 1$ - volume fraction

$\psi 1(\gamma)$ - viscosity coefficient

$(\tau_{11}-\tau_{22})$ - principal normal stress difference

Γ_w . apparent shear stress

η - shear viscosity

γ_w . shear rate at wall

γ_{wa} - apparent wall shear rate

Preface

This work was aimed to improve the performance of natural rubber towards degradation by heat, ozone and oil. Even though NR finds extensive application in many engineering and other fields, its poor performance towards degradation by oxygen, ozone, fuels and oils restricts its use for products, which has to be come in contact with oils, atmospheric exposure for longer time and for high temperature applications. Chemical modification and blending with synthetic polymers are the methods adopted to improve the aging behavior of NR. In this work dichlorocarbene modification of NR and blending of NR with hydrogenated nitrile rubber are carried out to improve the aging characteristics of NR. Dichlorocarbene modified NR is polar in nature and shows better solvent /oil and flame resistance. Blends of NR/HNBR exhibit very good degradation behavior. The use of DCNR as a modifier in this blend further improves the properties. This widens the use of NR in products for medium oil resistant, weather resistant and higher temperature applications.

This thesis is presented in eight chapters. The first chapter consists of a brief review of the earlier works in modified forms of NR, elastomer blends and scope of the present work. The second chapter deals with the materials used and experimental procedures adopted in this investigation. Chapter three describes the dichlorocarbene modification of NR, its characterization, properties and application in blends with hydrogenated nitrile rubber. In chapter four, blending of NR with HNBR, its preparation, characterization and mechanical properties are described. Chapter five deals with the aging characteristics of NR / HNBR blends. Chemical changes taking place during aging in NR / HNBR blends are discussed in chapter six. Chapter seven contains mechanical properties and aging behavior of blends of NR with speciality rubbers. Rheological behavior of NR/HNBR blends is described in chapter eight. The summary of the work done and conclusions of the study are given separately towards the end of the thesis.

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Chapter 3. DICHLOROCARBENE MODIFICATION OF NATURAL RUBBER

Chapter 8- RHEOLOGICAL BEHAVIOR OF BLENDS OF NR AND HNBR

CHAPTER 1

INTRODUCTION

Polymer modification and blending of elastomers have attained a prominent place in the field of polymer technology, as it is realized that synthesis of new elastomers are not always necessary for applications requiring specific properties. It can be met by modification of existing polymers or by blending suitable elastomers. So chemical modification and polymer blending have become a growing stimulation for research in the field of rubber chemistry and technology since the last few decades. Modification is attained by the incorporation of reactive functional groups on to the polymer chains. Functionalization of polymers results in new materials with wide spectrum of properties not available in parent polymer. Chemical modification of polymer backbone, grafting on to polymer chains, inter chain reactions and the formation of interpenetrating networks are the subject of many reviews.[1-3] Modification carried out on synthetic elastomers often result in enhanced properties as compared to original elastomers, where as chemical modification on naturally occurring polymers are generally accompanied by a loss in their basic characteristics. The first commercial carboxylated elastomer butadiene-styrene- acrylic acid terpolymer latex was introduced in 1949 by Goodrich under the trade name HYCAR 1571. Carboxylated nitrile rubber lattices find extensive use in leather-based products, oil resistant seals, gaskets, paper coatings and textile applications. The good abrasion resistance of carboxylated styrene butadiene rubber (SBR) enables it to find application in tyre tread compounds. Bromobutyl rubber, a modified form of butyl rubber (IIR) was first introduced commercially by BF Goodrich in 1955. The combination of low air permeability, good aging properties and better compatibility with natural rubber (NR) makes bromobutyl rubber an ideal choice for tyre industry. Successful materials prepared by modification of natural rubber that have got a lot of commercial applications include cyclised rubber, chlorinated rubber, hydrochlorinated rubber, epoxidized and grafted natural rubber. In these products the degree of modification is extensive and the products no longer possess the high elasticity of the raw material.

Polymer blending is another important route for developing polymer materials with tailor made physical properties.[4-7] Blending of thermoplastics is of recent origin, where as elastomer blends have been used in rubber industry since long time especially in tyre and mechanical goods. Blends of nitrile rubber (NBR) and poly vinyl chloride (PVC) have became commercially significant for use in hose, wire and cable industry.[8] Thermoplastic NR prepared by blending NR with plastics like, polyethylene and polypropylene and blends of NR with ethylene propylene rubber (EPDM) are materials that have been widely used in cable insulators, auto bumpers, hoses and gaskets.[9,10]

1.1.ELASTOMERS

Elastomers form a special class of polymeric materials characterized by a unique combination of useful properties such as elasticity, flexibility, toughness and impermeability. They are macromolecular substances capable of passing, under the effect of vulcanization from a predominantly plastic state to a predominantly elastic state.[11-13]

Generally elastomers are classified as commodity or general purpose elastomers [such as NR, styrene butadiene rubber (SBR), isoprene rubber (IR) etc.], high volume speciality elastomers [such as ethylene propylene rubber (EPM, EPDM), Chloroprene rubber (CR), acrylonitrile butadiene rubber (NBR)] and low volume speciality elastomers [such as polyurethane (PU, AU, EU), silicone (VMQ, FMQ), fluorocarbon (FKM, FPM, FFKM), polyacrylate (ACM,AEM), epichlorohydrin (ECO), chlorosulphonated elastomer (CSM)etc].

Elastomers may also be classified in groups, according to different aspects including chemical saturation of the polymer chain, oil resistance, flame resistance and service performance.[14] According to the chemical saturation of polymer chain of the basic rubber, classification is as in Table.1.1

Table 1.1

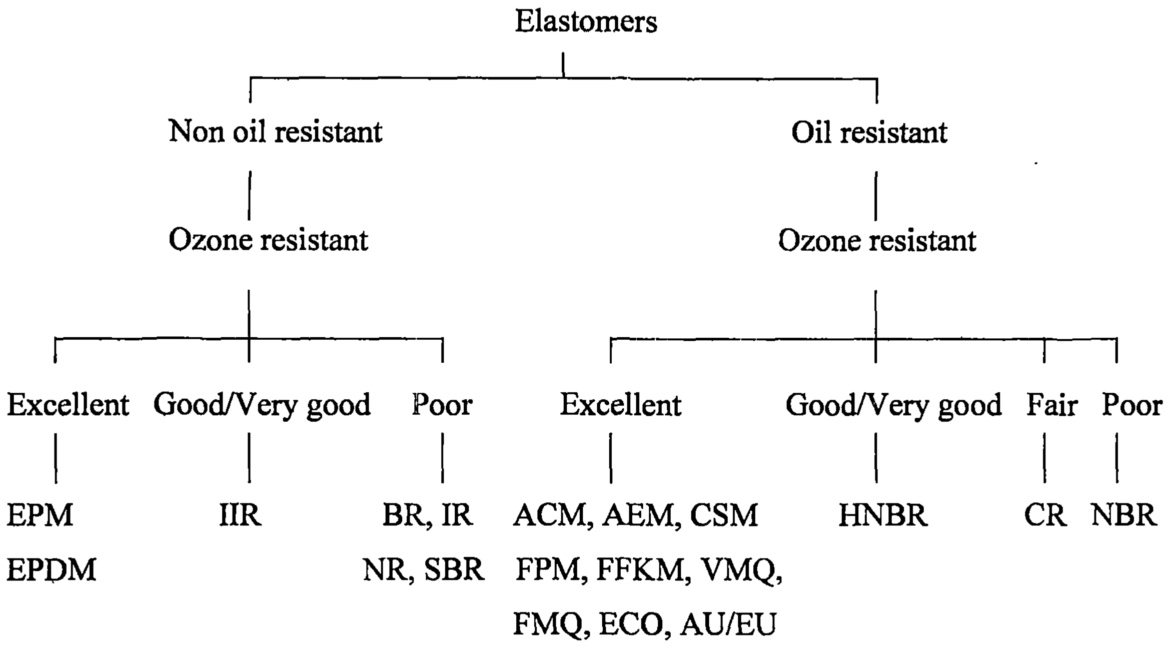
Elastomer

With saturated back bone	With slightly unsaturated back bone	With highly unsaturated back bone	
Ozone resistance Excellent	Ozone resistance Good/ Very good	Ozone resistance Fair	Poor
ACM, AEM, CSM, EPDM, EPM FPM, FFKM. VMQ, FMQ, ECO, AU, EU	IIR, HNBR	CR	BR, IR, NBR, NR, SBR

Elastomers that exhibit high resistance to ozone and weather are characterized by a saturated backbone. Elastomers with highly unsaturated backbone like NR and polybutadiene (BR) are not inherently ozone resistant. Therefore antiozonents and protective waxes are added during compounding to improve the ozone resistance.CR though highly unsaturated, like NR show fair ozone resistance due to the presence of chlorine atom which reduces the reactivity of double bonds to oxidizing agents including oxygen and ozone.

Elastomers having polar groups in the polymer chain show resistance to mineral oils. Table 1.2 shows grouping of most common elastomers based on their oil and ozone resistance.

Table 1.2



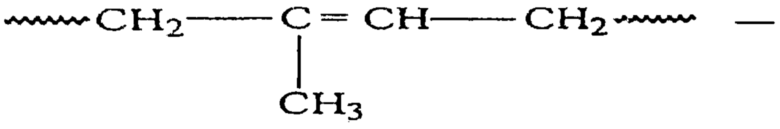
Halogen containing polymers like perflourocarbon rubbers (FFKM), fluorocarbon rubbers (FPM), chloroprene rubber (CR), chlorosulphonated rubber (CSM), and epichlorohydrin rubbers (CO, ECO) are inherently flame resistant and flame resistance improves as the polymer halogen content increases. Halogen free elastomers are not flame resistant unless they contain a high concentration of flame-retardants.

1.1.A.Natural Rubber

NR remains the best choice of elastomer for many applications that require low heat build up such as,in large tyres, carcasses of passenger car tyres, vibration dampers, springs, engine mountings and bearings. Other products like, hoses, conveyor belts, gaskets, seals, rollers, rubberized fabrics, elastic bands, latex foams, adhesives, pharmaceutical and medical products also consume a major part of NR.

It is the most widely used naturally occurring elastomer which is a homopolymer of isoprene having a cis 1,4 configuration as in Figure 1.1 and available in a variety of types and grades including latex, technically specified grades, sheets, crepes,etc.[15]

NR vulcanizates have high tensile strength over a wide hardness range due to its "strain induced crystallization".[16] It has the highest resilience (except BR) which is responsible for its very low heat build up. It shows very low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue.



$$\sim\sim \mathrm{CH_2} - \underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}} = \mathrm{CH} - \mathrm{CH_2} \sim\sim \quad -$$

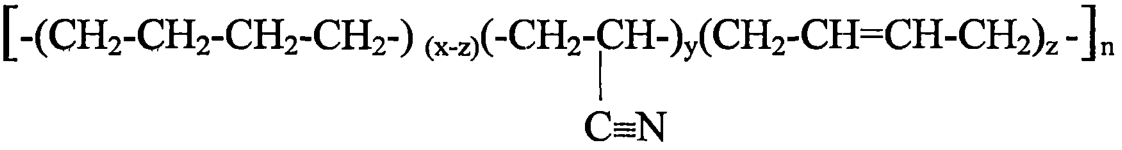
Figure 1. 1.

As an unsaturated elastomer, NR vulcanizates are susceptible to attack by atmospheric oxygen and ozone and hence it has poor heat and weather resistance. It is not resistant to petroleum-based oils and fuels, as it contains no polar groups, but can be used with a wide range of organic and inorganic chemicals such as non-petroleum based automotive break fluids, silicone oils and greases, glycols, alcohols, water and non-oxidizing aqueous solutions of acids, alkalies and salts.

The properties of NR can be improved either by chemically modifying or blending with speciality elastomers.

1.1.B.Hydrogenated nitrile rubber (HNBR)

HNBR as designated by ASTM D1418 was first commercialized in 1984 by Zeon Corporation (Nippon Zeon Co. Ltd., Japan) under the trade name Zetpol. Later, in the same year Bayer also announced the commercialization of their new HNBR under the trade name Therban. Tornac is another commercial grade by Polysar International S.A, Switzerland. This family of elastomer is manufactured by the hydrogenation of diene containing polymers, by a well-known and established reaction process, which starts with an emulsion polymerized acrylonitrile butadiene copolymer (NBR). The NBR base polymer is dissolved in a suitable solvent. Then through the addition of a particular catalyst in combination with a pre determined pressure and temperature, it undergoes a selective hydrogenation process producing a highly saturated nitrile elastomer.[17,18] Recently a bimetallic complex catalyst for hydrogenation of nitrile rubber is reported by D.M Yue and co_workers.[19] A new commercial grade trade named as Thortan is reported by DSM Nv, a Dutch Co. , based on a new technology which reduces the production cost of HNBR.[20] Hydrogenation of NBR latex is also reported.[21]The structure of HNBR is as shown in figure 1.2. The subscript (x-z) after the initial ethylene unit shows the variation in the ethylene unit concentration as a function of degree of hydrogenation of the butadiene units.



$$\left[-(CH_2-CH_2-CH_2-CH_2-)_{(x-z)}(-CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}-)_y(CH_2-CH=CH-CH_2)_z-\right]_n$$

Figure I.2

Through control of this reaction many different grades of HNBR are currently produced. The available grades vary in hydrogenation level, acrylonitrile content, and Mooney viscosity and are given Table 1.3(a).

Table 1. 3(a)

% Hydrogenation	**% ACN content**	**Mooney Viscosity, ML(1+4)100 °C**
85-99+	17-50	50-150

The grade names of commercialized HNBR, trade named as Zetpol by Nippon Zeon Co.Ltd. are shown in Table 1.3(b)

Table 1. 3(b) Commercial grades of Zetpol

Grade	Bound ACN, %	Iodine value, g/100g	Mooney Viscosity, ML(1+4)100°C
Zetpol 1010	44 ± 2	10	85
Zetpol 1020	44 ± 2	24 ± 4	78
Zetpol 2000	36 ± 2	7 max.	85
Zetpol 2000 L	36 ± 2	7 max.	65
Zetpol 2010	36 ± 2	11	85
Zetpol 2010 L	36 ± 2	11	57 ± 5
Zetpol 2020	36 ± 2	28	78
Zetpol 2020L	36 ± 2	28	57 ± 5
Zetpol 2030 L	36 ± 2	56 ± 5	57 ± 5
Zetpol PBZ 123	28 ± 9	24 ± 4	48
Zetpol PBZ 521	40 ± 2	27	49

HNBR is very tough, and provides outstanding stress-strain characteristics and abrasion resistance along with an excellent balance of low temperature and fluid resistance properties.[22-24] As the acrylonitrile content increases, oil and fuel resistance improves. As the acrylonitrile content decreases, low temperature properties improve. The static heat resistance of HNBR elastomers depends on the level of saturation within the elastomer. However, as the saturation level decreases, the dynamic heat generated as a result of flexing, decreases. So one has to determine the most appropriate saturation level depending on the desired end use in question. There is a convenient wide grouping of Mooney viscosity available which enables a manufacturer to produce products from HNBR.

Compounding is similar to NBR with some notable exceptions.[25] Peroxide cure is preferred for fully saturated grades. Both sulphur and peroxide cure are applicable for slightly unsaturated grades. One can use a wide range of carbon blacks, white fillers, anti oxidants and processing aids. Most commonly used plasticizer is triisooctyl trimellitate (TOTM), which provides the best balance of high and low temperature performances. Although HNBR elastomer is sulphur curable, most are peroxide cured, because of the enhanced heat and ozone resistance obtained via this cure chemistry.[25-28] The most common peroxides used are 1,4 bis(t-butylperoxy) di isopropyl-benzene, dicumylperoxide and 2,5,dimethyl-2,5-di-(t-butyl peroxy)hexane. HNBR uses a significantly higher quantity of peroxide and commonly use 6-12 phr. Although not used in all cases coagent may play a key role in both the cure chemistry and processability of HNBR compounds. Electron beam irradiation is also used for vulcanization of HNBR compounds.[29] Both fully and partly hydrogenated grades are reported to be suitable for radiation induced cross linking.[30]

Largest single use of HNBR is in synchronous timing belts for automotive industry.[31,32] Other uses[33] are in power steering, air conditioning, fuel systems and as O-rings, packings, gaskets, oil seals, hoses, drilling pipe protector, fuel hoses, diaphragms in tank insulator, etc. It is also used in cable jacketing and in many different industrial, aerospace, oil fields and food contact applications. Very recently, a multifunctional elastomeric coating based on HNBR for use on rubber compounds is reported to form tough, high strength coating with good ozone and weather resistance coupled with excellent oil and fuel resistance.[34] Blends of HNBR with Nylon[35] and other elastomers such as,CR and NBR are also reported.[36]

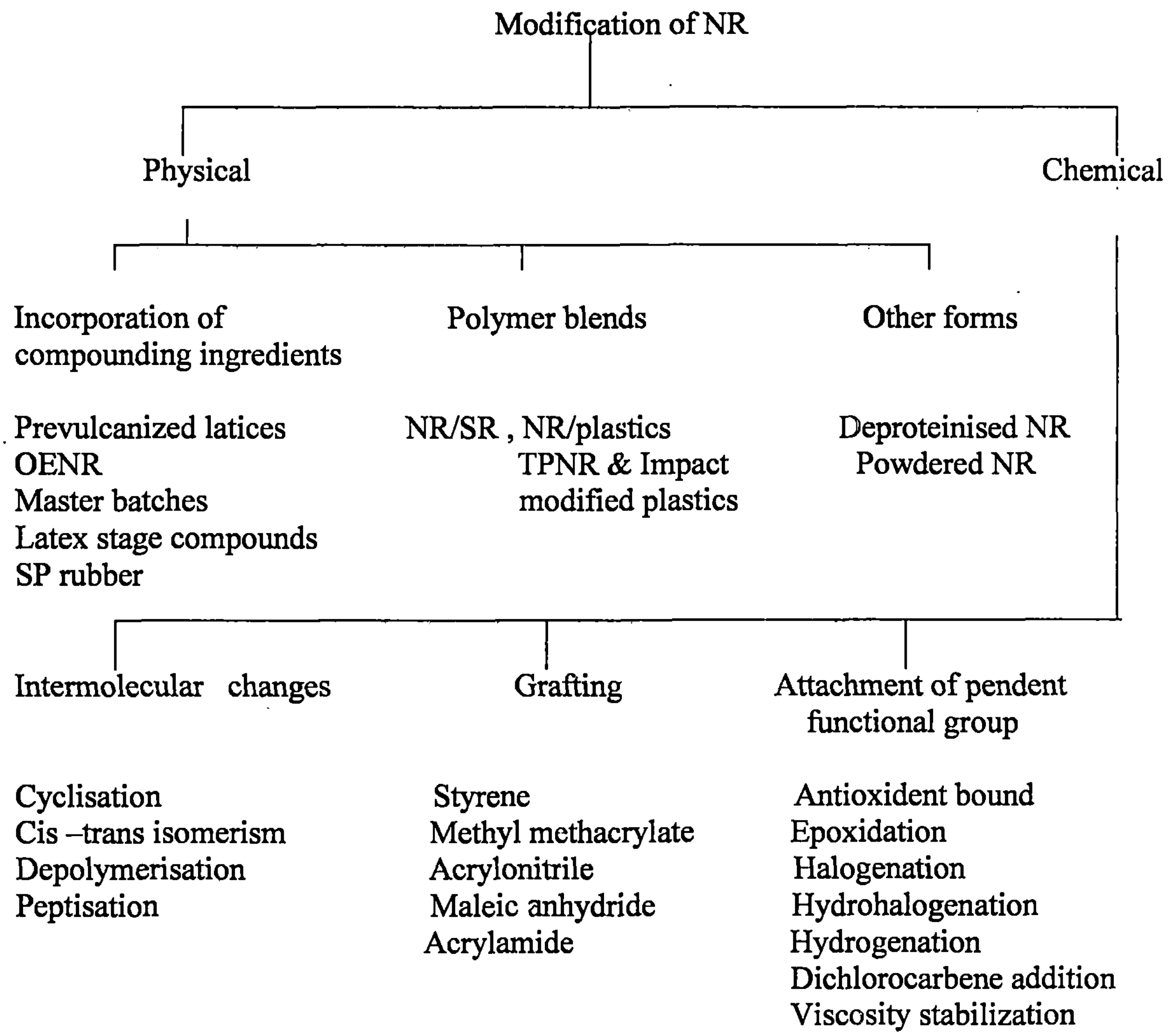
1.2.MODIFIED FORMS OF NR

NR can be modified by physical or chemical means and in some cases by a combination of the two.[37] Table1.4 gives most of the different types of modifications in NR.[38,39] Physical methods involves incorporation of additives that do not chemically react with rubber. Examples are oil extension, blending with other polymers, masterbatching, deproteinisation, prevulcanization, etc. NR is deproteinised to reduce water absorption and protein allergy which is effected by either enzymatic hydrolysis[40] /radiation process[41] or by multiple centrifugation. Deproteinised rubber (DPNR) is used in electrical and medical applications. Prevulcanization is usually done on latex stage.[42] Prevulcanized latex (PVNRL) is used for the production of casted or dipped articles. Superior processing natural rubber (SPNR) is prepared by blending ordinary and vulcanized lattices in 80:20 ratio before coagulation.[43] Unfilled and lightly filled compounds made with SPNR give smoother and less swollen extrudates compared to those prepared from regular NR.

1.2.1.Chemical modification of NR

A chemical modification depends on the chemical reactivity of the NR molecule. Being unsaturated, NR is highly reactive and several chemical reactions could be carried out resulting in materials having entirely different properties. Depending on the extent of modification, four classes of products are identified[37] as in Table 1.5. Low levels of modification have the object of retaining high elasticity while providing the means for

Table 1. 4. Modification of NR



altering specific properties to make the rubber suitable for particular application or conditions of use. For example, reactive site might be provided for new type of cross-linking for binding antioxidants or other materials or substrates. At moderate degree of modification, physical properties are altered due to the change in glass transition temperature (Tg) and a rubber with new properties is obtained. More drastic modifications leads to non-rubbery resinous or plastic materials. Finally modification only on the surface may be useful for increasing adhesion to other surfaces or protection against hostile environments.

Table 1.5. Classification of modified forms of NR

Degree / type of modification	**Approximate extent of modification (mole%)**	**Effect on elastic properties**
Slight	< 5	Essentially unchanged
Intermediate	5 - 25	Modified
Extensive	> 25	Lost
Surface	< 1	Bulk unchanged

Chemical modifications can be broadly grouped into

1) Attachment of a pendant functional group
2) Grafting of a different polymer at one or more points along the NR molecule
3) Inter molecular changes without the introduction of a new chemical group

1.2.1.A. Attachment of pendant functional group

1.2.1.A. i. *Chlorinated rubber*

Chlorinated natural rubber (CNR) is one of the first forms of chemically modified NR which find use in many commercial applications.[44] Chlorination is carried out either in solution or latex[45] stage and the reaction involves substitution and cyclisation along with addition of chlorine.[46] For the industrial preparation, batch and continuous process are now available and in all cases carbon tetra chloride is used as solvent for NR to perform the chlorination.[47] Recently liquid chlorine is reported to be used instead of carbon tetra chloride.[48] Use of depolymerised NR as starting material is reported to give higher yield of product.[49] Chlorinated rubber of 65% chlorine content is a pale , cream colored thermoplastic powder which is non inflammable and highly resistant to ozone, weather and chemicals up to 100 °C. CNR prepared from latex (CNRL)is characterized by IR, TGA and DTA investigations and is reported to exhibit poorer thermal and thermo oxidative stabilities than CNR prepared from solution (CNRS).[50] The effect of copper oxide on thermal stability of CNRL is studied by Yu,et.al.[51] The thermal degradation of CNRL in nitrogen atmosphere is a one step dehydrochlorination reaction. In air it degraded with two distinct steps of weight loss. In the first step, the hydrogen chloride is eliminated along with the release of a little amount of carbon dioxide. In the second step, the backbone of CNR is oxidized into carbon dioxide. The presence of copper oxide is shown to reduce the thermal stability by accelerating the dehydrochlorination reaction.

CNR is used in anticorrosive and heat resistant paints and coatings, adhesives, printing inks, paper coatings and textile finishes by mixing with an oppertune solvent. The composition contains at least 10% of chlorinated rubber with plasticizers and pigments. It is also used to protect wood, steel, cement, etc. from the environmental attacks and has been recommended as traffic paints on roads. Commercial grades are available under several trade names like,Pergut, Alloprene etc.

1.2.1.A. ii. *Epoxidised NR*

Latex stage epoxidation of NR under controlled conditions gives epoxidised NR (ENR) with improved resistance to hydrocarbons and oils, low air permeability, increased damping and good bonding properties while retaining the high strength properties of NR.[52-56] Improvement of these properties depends on the degree of epoxidation. Two grades of epoxidised NR, ENR 25 and ENR 50 with 25 and 50 mole percent of epoxidation respectively have attained commercial importance. It is reported that the volume swelling value of ENR 50 in ASTM oils approaches that of medium acrylonitrile NBR and is superior to that of polychloroprene rubber. Another distinctive feature of ENR is the high degree of reinforcement achieved with silica fillers without the addition of silane coupling agent.[57] ENR can be used as cover compound for PVC core conveyor belts. The processing characteristics and physico chemical properties of thioglycolic acid modified low molecular weight ENR (ELMWNR-TGA) and its blend with NR is reported recently.[58] It is shown that ELMWNR-TGA exhibits lower tensile strength, higher elongation at break but better resistance to solvents and mineral oils.

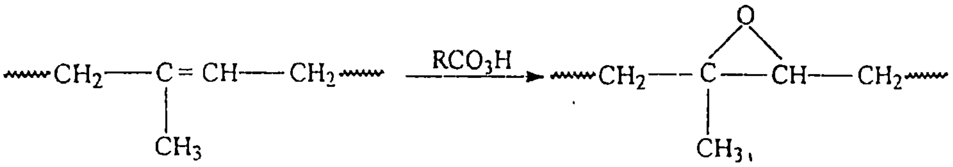


Figure 1.3.

1.2.1.A. iii. *Constant viscosity and low viscosity NR*

Increase in viscosity of NR during storage under ambient conditions known as storage hardening is caused by the cross linking reaction involving the randomly distributed carbonyl groups present on the main rubber chain and the amino acids present among the non-rubber constituents.[59] This can be inhibited by the addition of small amount of hydroxyl amine hydrochloride or hydroxyl amine neutral sulphate to the latex before coagulation. These chemicals effectively block the carbonyl groups and preserve the Mooney viscosity of the rubber. Viscosity stabilized rubber is technically specified and is available in two forms. Indian Standards Natural Rubber, ISNR 5CV and ISNR 5LV as per Indian standards with Mooney viscosity range of 60-65 for CV and 50 ± 5 for LV.

1.2.1.A. iv. *Carbene addition*

Carbenes (>C:) react readily with NR and is facilitated by the use of quaternary ammonium salts as phase transfer catalyst. The latter compounds bring the aqueous reagents into contact with the organic phase containing the polymer.[60,61] Treatment of cis poly isoprene in dilute aromatic solvent with dichlorocarbene prepared insitu from ethyltrichloro acetate with sodium methylate gives a white powder. The double bonds are converted into gem dichlorocyclopropane rings.[62] Similarly reaction of polyisoprene with dibromocarbene formed insitu from bromoform gives 70-75 % saturation of polymer double bonds. Carbene derived from the photolytic or thermal decomposition of 3,5 di-tert butyl benzene-1,4 diazoxide was used to introduce a polymer bound hindered phenol antioxidant on to NR[63]

1.2.1.A. v. *ENPCAF modification*

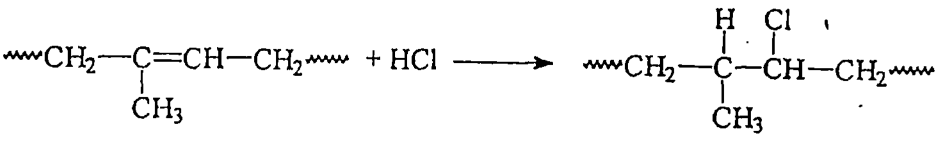
Ethyl-N-phenylcarbamoylazoformate (ENPCAF) modified NR shows the influence of bulky polar pendant groups on the physical properties of NR.[64,65] This modification can be carried out in an intermix or mixing mill at 110 °C on dry rubber. The reaction can also be carried out in latex stage at 30°C using deammoniated latex. The chemical modification results in the formation of hydroester pendant groups and is accompanied by an increase in Tg of the polymer along with high damping properties, improved gas impermeability and solvent resistance. The highly polar group introduced has a dramatic effect on the physical properties as shown by changes in stress relaxation and recovery of peroxide cured NR modified by ENPCAF. [66]

1.2.1.A. vi.*Hydrogenation*

Hydrogenation of NR was first reported by Berthalot [67] and there had been a steady stream of research publications on this subject.[68-70] Reaction of hydrogen at 30-35 atmosphere with a 2% solution of pale crepe rubber in cyclohexane over Nickel-Kiesleguhr catalyst in an autoclave at 200°C -220 °C for 12 hours leads to the formation of fully hydrogenated NR. More recently, homogeneous two component system based on a variety of Nickel and Cobalt compounds in combination with tri isobutylaluminium is reported to give complete hydrogenation in solution after 1 hour at 28°C.[71] Hydrogenation of diene elastomers, their properties and applications are discussed by Singha,et al.[72] in a recent review. Hydrogenated rubber is colorless and transparent. It is a plastic, elastic waxy solid with the peculiar characteristic of forming threads when stretched. Potential area of application is in cable industry, which would utilize its insulation properties.

1.2.1.A. vii. *Hydrohalogenation*

NR can be modified with hydrogen fluoride, hydrogen chloride, hydrogen bromide or hydrogen iodide to get the respective rubber hydrohalides.[73-79] The aim of this modification is same as that of halogenation, i.e. to reduce chemical reactivity of NR to oxygen and ozone by addition to the double bond. Bunn and Garner[77] reported that addition of HCl to polyisoprene obey Markownikov's rule. (Figure1.4) The rubber hydrochloride is a highly crystalline material. It is unaffected by dilute acids and bases at room temperature. NMR studies by Golub and Heller[73] have established that cyclization reaction also occours during hydrohalogenation.



$$\sim CH_2-\underset{CH_3}{C}=CH-CH_2\sim \; + HCl \longrightarrow \; \sim CH_2-\overset{H}{\underset{CH_3}{C}}-\overset{Cl}{CH}-CH_2\sim$$

Figure 1.4

1.2.1.B. Grafting

NR can be modified to graft copolymers by polymerizing vinyl monomers either in latex or solution. Methylmethacrylate (MMA),[80] styrene[81] and acrylonitrile [82] are the prominent monomers used for grafting on to NR. Among these polymethylmethacrylate grafted NR (PMMA-g-NR) is the most popular and has been commercialized since mid 1950's in Malaysia under the trade name Heveaplus MG. Generally grafting can be achieved by two methods viz.,by use of chemicals or by irradiation with γ rays.[83,84] The developments on this topic during the period of 1950-1990 had been recently reviewed by Blackly.[85] In later years, considerable efforts had been made to achieve thermoplastic elastomer characteristics to these graft polymers by controlling the polymerization conditions.[86,87] Recently Schneider, et al. reported that styrene and methylmethacrylate can be graft polymerized on NR latex in two step emulsion polymerization and can be used as toughening agent for SAN and polystyrene.[88,89] Lehrle, et. al.[90] reported the effect of using small quantity of vinyl aceatate on the efficiency of grafting methylmethacrylate in NR latex using AIBN as initiator. Fukushima, et. al[91] compared the grafting efficiency of styrene on to NR prepared from highly deproteinised latex and high ammonia concentrated latex using t-butyl hydroperoxide / TEPA redox system. The results are favorable towards high ammonia concentrated latex.

Polymethylmethacrylate is a hard plastic and when grafted on to NR, it increases the modulus of rubber depending on the percentage of methylmethacrylate grafted to it. Major use of Heveaplus MG is in adhesives.[92] In automotive industry for applications such as light shield, soft fronts, rear ends, rubbing strips and bumpers, blends of Heveaplus MG49 with NR can be used. It can also function as a compatibilizer in rubber/ plastic blends.[93] Styrene grafted NR (SG 50) can find application in micro cellular soleings in place of high styrene resin grade SBR[94].

Attempts to modify NR latex particle to produce NR interpenetrating networks was made by Hoursten, et al.[95,96] Recently Subramanian, et. al.[97] reported NR latex seeded emulsion polymerization of a highly hydrophobic monomer, vinyl neo-deaconates, under carefully controlled conditions. The DSC studies of the particles so formed shows a 5° C rise in Tg of the NR indicating the formation of a relatively homogeneous semi interpenetrating network or graft microphase.

1.2.1.C. Intramolecular changes

1.2.1.C.i. *Liquid NR (LNR)*

Liquid NR is prepared either by thermal or by chemical depolymerization of NR. In thermal depolymerization, rubber with 0.2 to 0.6 phr peptizer is first masticated to a Mooney viscosity of 25-30 and depolymerized by heating to 220°C -240 °C under stirring for 3-7 h. LNR with viscosity average molecular weight (Mv) in the range of 5000 – 20000 is reported to be produced by this method.[98] Chemical depolymerization is carried out in the latex stage by a redox reaction involving phenylhydrazine and air.[99] The mechanism of depolymerization involves the oxidation of phenyl hydrazine by air to give phenyl radical which through addition or transfer reaction initiates the formation of hydroperoxides. These peroxides lead by chain breakage to liquid NR with molecular weight range 6,000 –20,000 depending on the quantity of reagent used. The low molecular weight NR has been found to have similar properties with NR, for example affinity for ingredients during compounding, chemical behavior and service life performance.[100]

Liquid NR is used in elastic moulds, printing industry, as binder in grinding wheels, as reactive plasticizer[101]and as bulk viscosity modifier [102]in rubber compounds. Carboxy terminated liquid NR (CTNR) is reported as an adhesive in bonding rubber to rigid and non-rigid substrates.[103]

1.2.1.C.ii. *Cyclised NR*

Cyclised NR is a resinous material, obtained by treating NR with acidic reagents like, sulphuric acid, p-toluene sulphonic acid and by Lewis acids like, $SnCl_4$, $TiCl_4$, BF_3, and $FeCl_3$. Cyclisation could be done in solid, solution or latex stage.[104] Cyclised NR is found to have increased softening point, density and refractive index than NR. The preparation of cyclised NR latex on commercial scale was well established as early as 1947.[105] It is used in soling compounds as on heating it changes to a hard thermoplastic material.

1.3. POLYMER BLENDS

Developments of polymeric materials have been driven by the desire to make better products at minimum cost. Polymer blending technique is quite attractive based on the fact that, already existing polymers can be used and the costly development of new polymers via co-polymerization or by polymerization of new monomers can be avoided to achieve the requirement more rapidly and economically. As there is no generally accepted definition for polymer blends, they are generally considered as physical mixtures of two or more polymers. Normal methods of obtaining polymer blends are dry blending, solution blending, latex blending ,etc. In these cases, no chemical bonds exist between the component polymers forming the blend.

1.3. 1. Reasons for blending

The flexibility associated with blending of elastomers is such that it can be carried out to suit the requirements of both producer and user. The user related advantages are as follows. Developing materials with a full set of desired properties, improving a specific property like, high temperature, oil, ozone resistance etc. and adjusting the requirements at lower cost.

The producer related advantages are as follows. Better processability and less scrap rejects, product tailorability to specific customer needs, better customer satisfaction, plant flexibility, high productivity and increased economy.

1.3. 2. Preparation of elastomer blends.

Corish[106] has reviewed the general techniques for preparing elastomer blends namely, latex, solution and dry blending. A brief description of blending technology is given below.

1.3. 2. i) Latex blending.

Angrove[107] has reviewed latex blending, giving particular attention to processing, properties and economics. This technique has the potential for fine dispersion of the components, as the particles in the latex are very fine and well dispersed. Blends of NR/BR have been investigated by Blackly.[108] Blends of BR/SBR and BR/NR prepared by latex blending are reported to give a homogeneous dispersion of carbon black.[109]However, latex blending does not provide any cost advantage, since coagulation, removal of water and drying are cost intensive process.

1.3. 2. ii) Solution blending

This technique gives coarser particles because the low solution viscosity promotes rapid coalescence. Walters and Keyte[110] indicate greater heterogeneity (for NR/SBR blend) in solution mixed blends as did Livingstone Rongone.[111] Shunda,et al.[112] prepared a satisfactory blend of NR/BR by this technique. However, the drying process needs adequate amount of energy that makes it costly.

Combination of solution and latex blending is also used for master batching.[108] In the Columbian hydro dispersion process, the elastomer blend is kept in solution and the black is dispersed in solution, which transfers into the solution quite rapidly and produces a master batch. In the reverse process, the black dispersed in a solvent is blended with latex so as to provide a good dispersion.

1.3. 2. iii) Dry blending

This technique is applied for the preparation of most of the elastomer blends by using a mill, Banbury or extruder. This is because the process is economical and facilitates the incorporation of compounding ingredients in one operation. Again, blending is facilitated by mastication, which not only reduces viscosity but also under proper conditions provides opportunity for reaction (block or graft polymerization) and covulcanization. While Evans and Patridge[113] suggest that incorporation of all the ingredients in single step is desirable, Shunda [112]suggests that mill mixing provides better dispersion. Avgeropolos,et.al.carried out extensive mixing studies on EPDM/BR blends.[114]

These methods may be further divided into two general categories as pre blending[115] and phase mixing[116,117]. In the first case, the compounding ingredients are generally added to the premixed elastomers. In the phase mix, an attempt is made to control the specific location of filler and curing agents. This is generally accomplished by the preparation of separate master batches which are then blended mechanically[118,119].

In addition to these a number of special mixing techniques have been developed to control more precisely the different aspects of the overall homogeneity, phase morphology, filler distribution and interfacial interaction of the different components of elastomer blends. Hindemarch and Gale[120] developed a Cavity Transfer Mixer (CTM), designed to improve blending efficiency through better flow patterns which enhances distributive mixing in blends like NR/EPDM and SBR/BR. Coran and coworkers[121-122] have applied dynamic vulcanization technique to enhance properties of EPDM/NR and ACR/NBR blends.

1.3. 3. Factors affecting properties of elastomer blends

For the last few years, a large quantum of research and development has been occurred in the area of polymer blends. The importance of elastomeric blends has lead to extensive literature on this subject including several reviews [106,123-125] and many patents[126-128]. Fairly recent reviews by Roland [129] and Dhuryodhan Mankaraj[130] summarize the different aspects of elastomer blends. Antony et al. have reviewed blends of self cross-linking elastomers [131]. These studies revealed that the properties of polymer blends depend on many factors like,

- Blend ratio [132-137]
- Properties of component polymers[138-139]
- Viscosity of component polymers[140-142]
- Morphology[145-148]
- Compatibility or miscibility between polymers[149-150] and
- Interaction between the components during blending.[151-152]

Unlike plastics, elastomers contain a large number of compounding ingredients and the problems related to these materials also have to be taken care of. Based on this, factors affecting properties of elastomeric blends are :

- Interfacial adhesion / cross linking[153-156]
- Distribution of filler between elastomers[157-163]
- Distribution of cross links between elastomers [164]and
- Distribution of other non-reactive ingredients between elastomers.[165-170]

While true miscibility may not be required for good rubber properties, adhesion between the polymer phases is necessary and the respective interfacial energies are important. Shershnev[154] has summarized the importance and requirement of *covulcanization of the component elastomeric blends. Covulcanization was defined in* terms of a single network structure including cross-linked macromolecules of both polymers. They should be vulcanized to similar level with cross-linking across the micro domain interfaces.

The distribution of filler particles between the separate phases of an elastomeric blend is affected by a number of factors like,unsaturation, viscosity, polarity, etc. Carbon black has the tendency to migrate to the more unsaturated polymer. Butadiene has the highest affinity for carbon black and the affinity of carbon black follows the order BR > SBR > CR > NBR > NR > EPDM > CIIR > IIR. These findings are in agreement with that of Sircar and Lamend[156]. Cotton and Murphy[158,159] have applied GC technique to quantify carbon black phase distribution in blends of SBR with NR and NBR . In all instances there is a preferential location of carbon black in the SBR phase, which also supports the above study.

Ashida[160] found that when HAF black is added to a pre blend of BR/IR, the black concentration is initially greater in the IR phase, but with the time of mixing, it gradually decreases to a level lower than that in BR. The effect of carbon black loading in 50/50 blend of NR/SBR was studied by Laminday[168] and found that the anomaly of modulus observed is due to the early crystallization of NR inside the matrix. Manna, Tripady and De[161] have carried out in depth study on carbon black – rubber interactions, particularly using polar rubbers such as, ENR and oxidized carbon black. They suggest that both primary covalent bond and secondary bonds (H-bonding, dipole-dipole interaction, and dispersion type Vander Wall bonds) exist between carbon black and rubber that break down under dynamic stress. Klupel, Schuster and Schafer[162] have analyzed carbon black distribution in elastomer blends by measuring increase in loss modulus maxima in the glass transition region. They found that in EPDM/BR/N550 compound, carbon black is preferentially located in BR phase and in NR/SBR/N530 blend, black concentration is higher in SBR phase

The factors affecting the migration of crosslinking ingredients are the difference in cure rate, solubility and diffusion of these ingredients by the components of the blend. Differential distribution of vulcanizing agents such as, sulphur, accelerator and ultra accelerator in sulphur cure system and peroxide as well as coagents in peroxide cure systems happens in elastomer blends, particularly when the two elastomers differ in the concentration of reaction sites such as, degree of unsaturation and polarity.[171] This is because sulphur and most of the accelerators are polar in nature and are likely to partition preferably into polar phase. Common accelerators and sulphur are more soluble in highly unsaturated elastomers as compared to lightly unsaturated elastomers. Hence, curatives migrate from the low unsaturated elastomer to highly unsaturated ones. This type of migration is accelerated by higher curative reaction rates in higher diene elastomers. In blends of NR and NBR, [170] polar accelerators like, TMTD preferably migrate to NBR phase. The practical consequence of this problem is that the blend components will be either uncured or overcured. This problem can be solved by selecting a proper mixing schedule, masterbatching, or by using curatives that have almost the same rate of diffusion and cross linking independent of rubber polarity.[172,173]

The possibility of uneven distribution of cross links between the phases of a vulcanized blend has long been seen as a potential cause for poor physical properties within the blends of highly unsaturated elastomers such as NR with elastomers containing only low level unsaturation like, EPDM.[174]Recently 'reactive mixing' method[176] is applied to improve the properties of NR/EPDM blends which is similar in nature to that described by Hopper[175] in which a functionality –(alkylphenol monosulphide, caprolactum or morpholino)- derived from the sulphur donor is bound to EPDM via a sulphur linkage.

Covulcanization at the interphase of a rubber blend is important to provide mechanical compatibility and improved performance. This is best achieved if the cure rates are similar in both phases. Covulcanization is difficult in blends of saturated elastomer like, EPDM with high diene elastomers. It is better achieved by using fast accelerators such as, thiuram di and tetra sulphides. The interfacial bonds are largely monosulphidic at the initial stage, maturing to polysulphidic as the vulcanization progresses. Yoshimura and Fujimoto[176] showed that separate dynamic mechanical peak observed at initial stage, merged on continued vulcanization to give a single peak characteristic of compatible blend. Numerous efforts have been made to improve the cross link density of EPDM phase in elastomer blends.[177] Use of modified forms of EPDM when blended with NR is shown to give better modulus and tensile strength than unmodified EPDM/NR blends.[178,179]

In normal rubber vulcanizates, the concentration of the plasticizer is not very high and does not much affect the properties of the blends. However, when substantial quantities of plasticizer are used, the distribution of this ingredient can affect the properties of the rubber blends.[166,169] The relative solubility and diffusivity can be estimated using the empirical model given by Mangaraj , Pfau and Luttinger.[165] Goonetilleke and Billingham[166] have measured solubility and diffusivity of a series of phenolic antioxidants in NR and polyethylene. They found that where as solubility depended largely on the additive size, polymer- antioxidant interaction and melting point of the antioxidant, diffusivity depended largely on the size of the additive molecule and its polarity. Greater polarity and smaller size gave higher diffusivity.

1.3. 4. Thermodynamic criteria of miscibility

The term miscibility can be explained in terms of thermodynamics. The thermodynamic relation connecting the free energy, enthalpy and entropy is

$$\Delta G\ \text{mix} = \Delta H\ \text{mix} - T\ \Delta S\ \text{mix} \qquad \text{......................} (1)$$

Where ΔH mix, the change in enthalpy, ΔS mix, the change in entropy and T, the absolute temperature. For miscibility ΔG mix must be negative and satisfy the additional requirement

$$\frac{\delta^2 (\Delta G\ \text{mix})}{\delta (\Phi_1)^2} > 0 \qquad \text{....................................} \quad (2)$$

which ensures stability against phase segregation. The volume fraction Φ1 of component is employed here, but any other measure of mixture concentration could be used. The thermodynamic treatment of the phase behavior of mixtures became more useful when specific models for the enthalpic and entropic terms are used. The simplest model, which introduces most important elements needed for polymer blends, is that developed by Flory Huggins originally for the treatment of polymer solutions.[180,181] It assumes that the only contribution to the entropy of mixing is combinatorial in origin and is approximately given by the relation:

$$\Delta S\ \text{mix} = -R\,(V_A + V_B)\,[(\Phi_A / V_A) \ln \Phi_A + (\Phi_B\ / V_B) \ln \Phi_B\,] \qquad \text{.........}(3)$$

For mixing a volume V_A with volume V_B of polymer blend. Here Φ refers to the volume fraction of i in the mixture and Vi is the molar volume of i which is simply related to molecular weight and density by Mi / ρi. For simplicity, each component is assumed to be monodisperse, as more complex expressions result when polydispersity is considered.[182]

The Florry-Huggins treatment assumes the heat of mixing follows a Van Laar type relation.

$$\Delta H\ \mathrm{mix} = (V_A + V_B)\ B\ \Phi_A\ \Phi_B \qquad \ldots\ldots\ldots\ldots(4)$$

where B is an interaction energy for mixing segments of the two components and can be alternatively expressed as a χ parameter. ΔH mix does not depend on polymer molecular weight, where ΔSmix does. Thus for a fixed mass or volume of a blend, the combinatorial entropy of mixing becomes progressively smaller as the molecular weights of the components increase, and becomes zero as they approach infinity. Endothermic mixing, the case when $B > 0$, does not favor miscibility. Thus for mixing, the favorable entropic contribution must be large enough to yield a negative free energy of mixing, but as molecular weights are increased, a point is reached where this fundamental requirement can no longer be satisfied and phase separation occurs. On the other hand, for the exothermic mixing, $B < 0$, the Florry-Huggins theory predicts that all the conditions for miscibility are satisfied no matter how large are the molecular weights. Thus as the most simple rule, miscibility of high molecular weight polymers is only assured when mixing is exothermic.

1.3. 5. Compatibilization

There are several hundreds of report about polymer – polymer miscibility which emphasize that miscibility is limited to a specific set of conditions, while immiscibility dominates.[183] Only a very few polymers form truly miscible blends.[184-185] Examples are poly (phenylene oxide)/polystyrene (PPO/PS), poly vinyl chloride (PVC)/polymeric plasticizer, etc. Besides these, there are a few polymer blends, which are found to be compatible in solution. These include cellulose nitrate/ poly(vinylacetate), cellulose nitrate/poly(methylmethacrylate) and cellulose benzoate/polystyrene blends. The rest of the blends, which are either partially miscible or immiscible, may undergo micro or macrophase separation leading to heterophase polymer blends.

So far only few elastomer blends are reported to be truly miscible.[186-188] In elastomer blends, immiscibility is the general observation and miscibility is only an exception. The properties of miscible blends are an additive average of the properties of components, while those of immiscible polymers, a combination of the properties of the components is observed. Most of the high molecular weight polymer blends are immiscible. Generally, immiscible blends are preferred to miscible blends as it is possible to tailor the properties of component polymers, when they are not miscible. The immiscible blends often exhibit high interfacial tension, which leads to poor degree of dispersion of the phases and lack of phase stability, that is phase coarsening or stratification.

Figure 1.5(a) shows the narrow interface between two immiscible homopolymers of infinite molecular weight.[189] The interfacial density profiles of the two homopolymers through the interface region is shown in Figure 1.5(b). The number of contact points between two different polymers is less in the case of sharp profile and hence the enthalpic or interaction energy contribution to the total free energy is minimized.

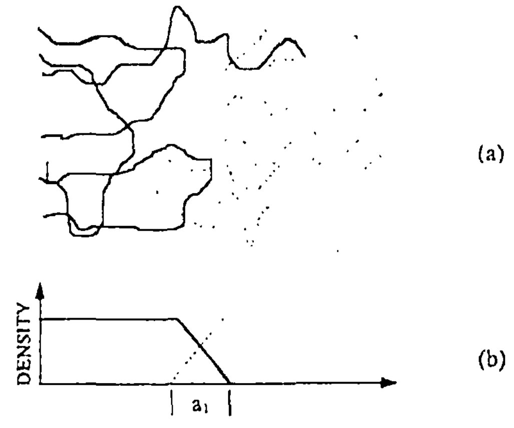


Figure.1. 5 .a) Interface between immiscible polymers and **b)** interfacial density profile between immiscible polymers.

However, the entropic contribution on the free energy arising from the turning – back entropy of the polymer chain is also smallest for narrow interface, leading to an increase in the total free energy. The interfacial adhesion between the phases is also low and hence immiscible blends usually give poor mechanical properties. The incompatibility or immiscibility between the polymers lead to complex rheological behavior and anisotropy in strength of fabricated articles. The problems associated with the immiscible blends can be alleviated by compatibilizing the blend, either by adding a third component called compatibilizer or by enhancing the interaction of the two component polymers, chemically or mechanically[190].

1.3.5. A. Methods of compatibilization

Compatibilization is carried out in non-reactive and reactive mode. In non-reactive mode, an external polymeric material is added where as in reactive mode, block and graft polymers are formed insitu during mixing of the two components. The essential function of compatibilization is to wet the interface between the two phases. The role of a compatibilizer is to

- Reduce interfacial energy and improve adhesion between phases
- Achieve finer dispersion during mixing and
- Stabilize the fine dispersion against agglomeration during processing and through out the service life.

1.3.5. A .i) Non- reactive compatibilization

Here an external polymeric material, preferably a block copolymer is used.[191-192] Diblock copolymers are favoured, although in many instances tri-block copolymers, random and graft copolymers have also been used. It wets the interface between the two phases which is achieved by spreading at the interphase and mixing with both phases through their component parts which are similar to the phase or the other (Figure 1.6)

Ashaletha and Thomas[193] have made an in depth study of compatibilization of NR and polystyrene (PS) blends using a graft copolymer of styrene and NR. Reiss and co workers[194] had shown that for polyisoprene polystyrene blend, block copolymers provide better compatibilization than graft copolymers and solubilization of compatibilizer by blend components take place when the molecular weight of them are comparable or smaller than the molecular weight of the corresponding block in the compatibilizer. Teysie and co-workers[195] have examined the compatibilizing action of many copolymers and concluded that the structure and molecular weight of the copolymer control the efficiency of compatibilization and tapered block copolymers are more effective as compatibilizer than linear block copolymer. Gailand and co-workers[196] have found that addition of styrene butadiene block copolymers reduce the interfacial tension in PS/BR blends. Coran and Patel[197] on blending polypropylene with several elastomers found that parameters such as critical surface tension for wetting the interface, critical entanglement spacing, crystallinity and tensile strength of the hard phase determines the mechanical properties of the blend. Leibler, Noolandi and Herg have developed thermodynamic basis[198] for copolymer compatibilization.

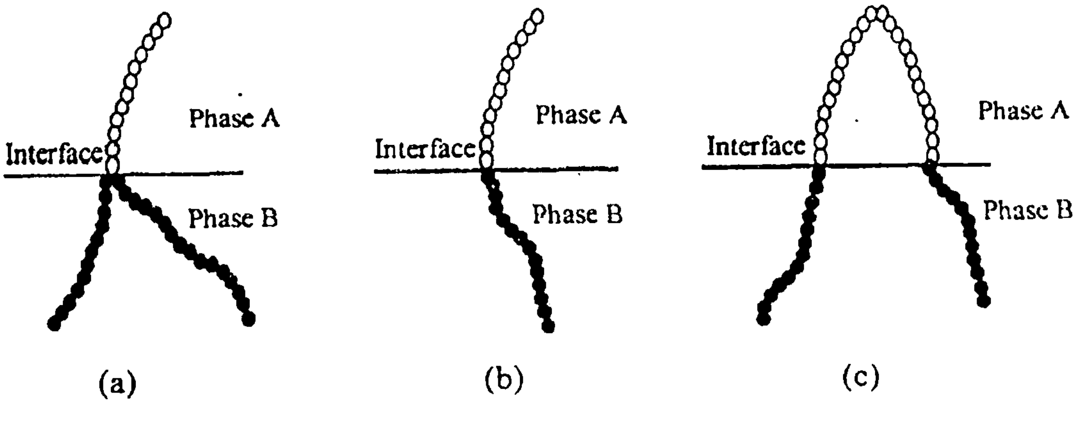


Figure. 1.6. Conformation of the copolymer at the blend interface: a) graft, b) di block and c) tri block copolymers extending into the homopolymers

1.3.5. A.ii) ***Reactive compatibilization***

This type of compatibilization is carried out during the blending process by adding a reactive material, either as a blend component or a reactive third component.[199-204] The classical example is Du Pont's production of super tough nylon by blending with maleic anhydride grafted EPDM. Blending nylon with functionalized elastomers have been carried out by several authors and recently by Scott and Macosko.[205] Coran and Patel studied the effect of polyolefins modified by phenolic, triethylenetetramine and chlorine as reactive compatibilizer in polyolefin-nitrile rubber blend[206] and found that the polyolefin-rubber block co-polymer, formed insitu acted as a compatibilizer for this immiscible rubber blend.

1.3. 5.A.iii) ***Compatibilization by surface activation***

Chemical modification of particle surface aids compatibilization by inducing chemical and physical interaction between the two phases[207,208]. Mangaraj has reviewed the use of surface activation in scrap tyre recycling.[209]

1.3. 5. A.iv) ***Compatibilization by cross linking***

Even though most elastomer blends exhibit phase separation, depending on their polarity, there is evidence that co curing may lead to destruction of phase boundary[210-215]. Contrary to expectations, many elastomer blends, particularly immiscible before vulcanization, develop mechanical homogeneity after vulcanization possibly due to the formation of a block copolymer insitu. Woods and Mass[216]have discussed the occurrence of covulcanization at phase interface of rubber blends and its beneficial effects in blends.

1.3.6. Characterization of elastomer blends

A variety of methods including solubility, spectroscopy, microscopy, thermo analytical techniques and dynamic mechanical and electrical measurements have been used to characterize elastomer blends. Hess, Herd and Vergi[125] have made an excellent review on this topic.

1.3.6. i) Microscopy

Phase contrast optical microscopy can be used to differentiate components in gum and lightly colored blends. However, most of elastomer blends contain large volume of fillers and hence, they are mostly characterized by electron microscopy. Different methods like swelling[217], staining[218], etching[219] and freezing[220]are used to improve contrast between the phases. Scanning electron microscopy (SEM) is used to characterize surfaces and transmission electron microscopy (TEM) is used to examine morphological features in bulk.

1.3.6. ii) Solution behavior

Solubility of polymers are limited to solvents which have interaction parameter χ less than 0.4 and two polymers are not miscible unless the difference in their interaction parameter in the same solvent is less than 0.05. Hence, if two polymers are not soluble in a common solvent, they are immiscible. This technique is used for testing miscibility of polymers[221,222].

I.3.6. iii) Thermal techniques

Thermo analytical techniques such as, differential scanning calorimetry (DSC), differential thermo gravimetry (DTG) have been used for analysis of polymers. DSC measures changes in specific heat of systems as a function of temperature[223]. TGA measures weight loss at different temperature[224]. In the case of miscible blends, there will be a single Tg or Tm whereas for immiscible blends, there will be two Tgs, which may be same or slightly different from Tg of individual components. Compatible blends may have a broad Tg indicating some interaction between the polymers. Sircar and Galaska et al.[225] recently reviewed the application of thermal analysis techniques such as DSC, TGA, thermo mechanical analysis (TMA) and thermal simulated current (TSC) for determining Tg of elastomers in their blends.

Dynamic mechanical analysis (DMA) provides information on change in internal damping as well as Tg of polymeric materials and their blends. Mazich and Samus et al.[226] have used DMA analysis to study blends of NR with IIR and BIIR.

1.3. 7. Processing techniques of elastomers and their blends

By processing we denote the operations that come between the initial mastication of elastomer and the vulcanization of the finished article. The techniques involved are mixing, calendaring, frictioning, extrusion, molding and combing with textiles or chords. Mixing mill and internal mixers are commonly employed for the preparation of rubber compounds. The shaping operations involve molding, calendaring and extrusion. Basis of all these process is the flow or viscous deformation of elastomers. The rate of shear occurring in these operations range from 10^1 s^{-1} to 10^4 s^{-1}.[227] Knowledge of viscosity of compounds over a wide range of shear rate is essential to standardize the conditions for each of these process.

Elastomers are strongly non-Newtonian, that is the rate of shear deformation is not proportional to shear stress except at very low stresses. At any given stress, the shear rate increases with temperature by a factor of roughly 1.3 per °C.[228] The rate of flow under a fixed stress is time dependent, that is rubber shows thixotropy and this is very marked in mixes containing reinforcing fillers like carbon black. All rubbers and mixes show more or less elastic recovery when deforming force is removed.

In mixing a filler with rubber, the surface of every particle should be thoroughly surrounded and wetted by the rubber.[229] The ability of the rubber to flow is important as the surface area involved is enormous and hence low viscosity would be desirable. On the other hand, filler agglomerates have to be broken down, which is favored by a high viscosity and higher stresses are needed to produce broken chain molecules necessary for filler reinforcement. Hence for practical application a right compromise is to be chosen.

Similarly extrusion, calendaring and frictioning involve vigorous working and hence considerable heat generation. The stiffer the mix, greater the heat and hence higher the risk of scorching. So a soft mix is desirable. In calendaring, a soft mix reduces the degree of bending of the bowls and hence adjustments needed to get a uniform gauge. In frictioning, soft mix penetrates more easily to the interstices of the fabric, whereas high viscosity is desirable when calendared sheet is to be wrapped on a fabric liner. Such apparently conflicting requirements may be reconcilable. It is quite possible to have a rubber with low effective viscosity at higher stress and high viscosity at low stresses. A rubber can have an effective viscosity of 2×10^4 poises at a shear stress of 2×10^6 dynes /cm^2 rising to 10^8 poise when the shear stress falls to 2×10^4 dynes /cm^2.

Mooney Viscometer and Wallace plastimeter are commonly used to measure flow properties. But they are operating at a particular temperature and shear rate, which is far less than those typical of modern processing equipments. Studies on viscosity of elastomers, and their compounds as a function of shear rate or shear stress and temperature is of much importance due to its direct dependence on processing methods followed in the rubber industry. These types of measurements are possible with capillary type viscometers.

1.3.8. Processability and rheology of elastomer blends

Miscible blends constitute one phase and are processed like a homopolymer or random copolymer, however, two phase blends have unique processing characteristics.[230] Multiphase blends can exhibit phase segregation and orientation under high shear processing conditions. The degree of orientation depends on many factors including relative viscosities to separate phases, the degree of shear and degree of which dispersed phase is cross linked.

Rheological properties are generally studied from measurement of their viscometric flow behavior. The rheological parameters influencing the processability are viscosity and elasticity as determined by die swell ratio, principal normal stress difference, recoverable shear strain, shear modulus and extrudate characteristics.

The major aspect of the processing step is the flow behavior of elastomers. The influence of fillers and blending of rubbers on flow properties of elastomers has great industrial importance as elastomers are seldom used without fillers and in most cases a blend of elastomers are preferred to achieve a particular end use. Einhorn and Turetzky showed the use of capillary rheometry to characterize elastomeric flow.[231]A number of researchers have investigated the rheology of polymer blends.[232-237] A comprehensive review on dependence of rheological properties on blend composition has been given by Plochoki.[238-239] Generally viscosities of blends vary monotonically with blend composition. Several workers have reported the rheological behavior of NR with plastics[240-243], ENR with PVC[244] , blends of ethylene propylene diene rubber (EPDM) and bromobutyl rubber (BIIR)[245] and butyl rubber (IIR)[246]as well as many other elastomers[247-249] thermoplastic elastomers,[250-254] composites [256-257] and elastomer blends[258].

Several models for viscosity of blends have been applied to polymer blends, from knowledge of their composition[259-261]. The different blend additivity rules, logarithamic rule, Hashin's upper control rule, Heitmillers inverse additivity rule and sheath-core rule have been used for polymer melts. Agreement between additivity rules and experimental results varies with blends.[262]

Elasticity of polymer melts respond differently to changes in extrusion conditions like increasing the residence time in the capillary and increasing temperature.[263] The behavior of elastomers is concerned with three functions- the viscosity coefficient $\eta(\gamma)$, principal normal stress coefficient $\psi_1(\gamma)$ and secondary stress coefficient $\psi_2(\gamma)$. [264-265] The behavior of an elastomer blend is determined not only by dependence of shear stress or shear rate, but also of normal stress on shear stress or shear rate. The die swell of extrudate depends on fundamental properties of the polymers such as molecular weight and its distribution as well as on flow conditions such as temperature, shear rate, shear stress and L/D ratio of the capillary. Fillers depending on their concentration and type generally reduce die swell in elastomers.

1.3. 9.Commercially successful elastomeric blends

Elastomeric products can be generally divided into two categories, tyre and non-tyre products. Non- tyre products include a variety of extruded, calendared and molded products like, automotive hoses, belts, foot wear, seals, O-rings, roofing materials and numerous other products. Elastomeric blends are being widely used in many products for a long time. Recently, Roger and Waddel have reviewed the past work on the use of blends of butyl (IIR), chlorobutyl (CIIR), bromobutyl (BIIR) and brominated methyl styrene- isobutylene co-polymer (BIMS) with NR and SBR in many tyre and non - tyre applications[266].

A large number of rubber blends have been patented for tyre application. The earlier patents have been discussed by Baranwal, Mc Donnel and Andries,[267] Walsh and Higgins[268] as well as by Hess and Vequari et al[269]. Pneumatic tyre is a highly engineered product made of several components including chafer, apex, black side wall, white side wall, belts, radial ply, bead and liner. Elastomeric blends used for making them[270] are given in Table 1.5.

Blends of NR or SBR with polybutadiene rubber (BR) are used in tread compounds to achieve better abrasion resistance and wet skid resistance.[271-74]Levitin and coworkers showed that 50/50 blends of cis polyisoprene rubber with methyl styrene butadiene copolymers provide optimum processing and physical properties required for tyre carcass.[275] A ternary blend of IR/NR/BR provide good physical properties for giant tyre treads used for truck and agricultural equipments.[276] Kim and Hammed showed that passenger tyre side wall based on blends of NR and cis-polybutadiene give good resistance to fracture over a wide range of conditions covering rapid as well as slow crack growth, retention ability for longitudinal crack branching, catastrophic rupture resistance and good resistance to slow fatigue crack growth.[277] For black side walls, blending of halobutyl rubbers and EPDM with NR/BR compound increases both dynamic and static ozone resistance as well as resistance to flex strain.[278] Addition of butyl and halo-butyl rubber to tyre tread compounds based on NR/SBR or NR/BR blends can lower resilience and improve skid resistance.[266] Addition of bromobutyl rubber to oil extended SBR/ carbon black compounds improves tread traction but decreases tread wear in tyre tests.[279-281] Both rolling resistance and wet grip properties are reported to be improved by partially replacing NR by NBR in NR/BR tyre tread compound.[282]

Table 1.5. Rubber blends used in typical tyre component formulations

Component	Rubber blends	Ratio
Passenger tyre tread		
Side wall, black	SBR/NR	50/50
Side wall, white	NR/CIIR/IR	25/55/20
Body ply (carcass)	NR/BR	70/30
Inner liner	BIIR/NR	70/30
Truck tyre		
Tread	BR/SBR	50/50
Carcass	NR/BR	80/20

Blends of NR and SBR are commonly used for foot wear applications.[270,284,285] (Table 1.6) It consists of a sole cemented to an upper part having the configuration of the foot. They are either injection moulded or calendared, followed by cutting in size and bonding.

Table 1.6. Rubber blends used for foot wear application.

Component	**Rubber blend**	**Ratio**
Out sole (Injection moulded)	NR/SBR	50/50
Boot upper (Injection moulded)	NR/SBR	80/20
Out sole / Foxing (Calendared)	NR/SBR	80/20
Out sole (Compression moulded)	NR/SBR	70/30
Boot lining Gum	NR/SBR/IR	40/20/40
Heel (High quality)	SBR/BR/IR	30/60/10
Heel (Standard quality)	SBR/BR/NBR	70/20/10

SBR, NR or IR blends with BR provides bulk of the rubber compounds used in belt applications that is largely used to transport heavy tonnage over long distance. It usually consists of a load bearing component carcass and a protective component called cover. The carcass consists of layers of fabric reinforcement impregnated with rubber. Table 1.7 shows the elastomers used in belt compounds.[270] NBR and CR are blended to the base rubber to resist oil present in grain or treated coal transport. EPM and chlorosulphonated polyethylene (CSM) rubbers are used for high temperature power transmission belts.[283]

Table 1.7. Rubber blends used in belt compounds

Component	Rubber blend	Ratio
Friction and skim coat		
First grade	SBR/NR	80/20
Heat resistant	SBR/NR	90/10
Belt cover		
First grade	NR/BR	80/20
Second grade	NR/BR/SBR	60/20/20
High temperature	EPDM/CSM	80/20

Nitrile / PVC blends with different flame retardants are used in applications such as, fire hose roll cover, electrical cover, plugs, etc. For covers of rubber hoses, whose main function is to protect carcass from deterioration by environmental conditions, the compounds used are blends of nitrile rubber with PVC or hypalon with polybutadiene rubber. Adhesion of elastomers to wire components in wire reinforced rubber articles such as, steel belted radial tyres, hoses and belting is very important as failure at rubber to wire can cause catastrophic consequences. Croft has studied the use of elastomer blends in wire reinforced hoses to improve rubber to wire adhesion.[286] In cables, blends of EPDM and EVA offer good electrical properties combined with weathering and aging characteristics. Blends of EPDM and NR [287]or blends of nitrile rubber and PVC are used for better ozone resistance. NR or EPDM is blended with PP or HDPE and have been commercialized the production of thermoplastic elastomers.[288]

The effect of high curing temperature on physical properties of blends of BR with NR is discussed by Glanvelle.[289] The heat stability imparted by cis- BR when blended with NR or SBR is confirmed by Svetlik.[290]Similar improvements in thermal properties are claimed for blends of emulsion BR with NR by Mc Call.[291] Addition of cis-BR is reported[292] to decrease the tensile strength and modulus of NR vulcanizates and increase the elasticity and abrasion resistance. Flannigan,[293] commenting on the future consumption of SBR reports that blends with highly saturated EPDM could lead to new applications. The tread wear and wet skid resistance of SBR 1500 series and their blends are dealt with by Kienle.[294] The hard rubber poly blends of SBR and butyl rubber vulcanized with sulphur have been studied in detail by Meltzer.[295-296] According to his report, Tg was found to increase with degree of vulcanization and dual or stepwise transition from glassy to rubbery characteristics of polyblends was found in all mixes. Reversion occurred on over cure and the temperature coefficient of vulcanization of SBR/butyl blends was also calculated. Sulton[297] reported that blends of EPDM with NR, SBR, NBR or CR gave compounds having good ozone aging and compression set characteristics. Stake[298] compared laboratory studies of the tyre tread compounds based on SBR/EPDM and SBR/BR/EPDM blends with field performance. Results of the tests of heat aging, groove cracking and abrasion resistance compared with those of SBR and SRR/BR controls indicated that the EPDM blends could be used in treads without antioxidants.

In blends of NR for inner liners of tubeless tyre, two characteristics of butyl rubber, which are particularly advantageous, are its damping properties and impermeability. Blends of chlorobutyl with nitrile rubber are studied in an attempt to develop vulcanizates having the desirable properties of the components at lower cost.[298,300] EPDM/NBR blends have also been considered for obtaining moderate resistance to oils and ozone combined with an acceptable level of general mechanical properties.[301] Takenaka reported a blend of fluorosilicone and silicone can be easily bonded using fluorosilicone adhesive , has better processing and technological properties and is cheaper than fluorosilicone itself.[302] By blending BR with ENR, improvement in wear resistance is reported.[303-305] Various blends of NBR with PVC and EPDM has been reported to improve ozone resistance.[306-310] Nagoda and Roland[311] noted that CR and ENR blends are miscible in all ratios when prepared by solvent casting from carbon tetra chloride. Self vulcanizing blends of CR and ENR are studied by Alex and coworkers.[312]Superior processing NR when blended with EPDM shows improvement in properties.[313] Covulcanized HNBR/EPDM is reported to exhibit superior thermal and oxidative aging properties.[314] Blends of silicone rubber with other elastomers enhanced bio compatibility. Medical research Associates Co. has taken several patents[315] on SEBS block copolymers with silicone for various medical applications. Improved medical grade adhesive has been reported[316] for the blend of poly isobutylene, IIR and radial styrene block copolymer.

I.4. SCOPE OF THE WORK

NR is the only naturally occurring elastomer, which finds extensive application in many engineering and other fields. Major part of it (nearly 70%) is consumed in the tyre industry. Mechanical goods like, hoses, conveyor belts, rubber lining, gaskets, seals, rubber rollers, rubberized fabrics, etc. and latex products like dipped goods, foam, carpet backing, elastic threads, adhesives, medical goods etc. also consume a significant amount of NR. Other uses include footwear, solution adhesives and many engineering products used in dynamic applications such as springs, anti vibration mountings, bushes, etc. The combination of high tensile strength with a high rebound elasticity, very good low temperature flexibility, excellent dynamic properties and very low heat build up make NR indispensable in several applications despite the availability of a great number of synthetic elastomers. Due to the strain crystallization of NR, which also occurs in vulcanizates, it has a high tensile strength and tear strength in gum vulcanizates, contrary to most type of synthetic elastomers.

However, due to the presence of unsaturation on the backbone of NR, it is highly susceptible to attack by atmospheric ozone and resistance to degradation by heat and oxygen is very poor like all unsaturated elastomers. Also due to the absence of polar groups on the NR, its vulcanizates swell extremely in petroleum fuels. These restrict the application of NR for such products, which has to be come in contact with oils and atmospheric exposure for longer time and for high temperature applications.

Many attempts have been made to improve these properties by chemical modification and by blending with speciality elastomers as discussed earlier. Resistance to thermo oxidative degradation is an important criterion to be satisfied for rubber products used in outdoor application. It is well known that degradation of rubber is due to its reaction with molecular oxygen. This reaction can be suppressed by reducing the double bonds, or by the introduction of groups that can deactivate the double bonds. The introduction of polar group can bring about the enhancement in resistance to polar solvents and petroleum oils and fuels.

Dichlorocarbene addition to double bond is an attempt to modify elastomers, which attracted much attention earlier. Dichlorocarbene modification has been reported for diene rubbers.[317-318] However, the products of dichlorocarbene modification have not so far found any good commercial application. Recent studies on dichlorocarbene modification of SBR reported improvement in gum strength, oil resistance and flame resistance.[319]

By dichlorocarbene modification, it is possible to have a reduction in double bonds in the main chain. Introduction of polar functional groups can deactivate the double bonds and also bring about polarity in the molecule as a whole resulting in increased resistance to fuels and oils. As the introducing group contains chlorine atoms, flame retardency can also be expected for the dichlorocarbene modified NR (DCNR). Thus for DCNR with its unique combination of properties, could find application either alone or in blends with other rubbers or as compatibilizer in blends of NR with polar rubbers. Hence, dichlorocarbene modification is carried out in NR so as to improve the fuel, oil, thermal and flame resistance.

HNBR is the hydrogenated form of nitrile rubber with excellent oil, ozone and thermal aging resistance due to its saturated backbone and the presence of polar acrylonitrile group. Blending of NR with HNBR is expected to improve the properties of NR with respect to oil, ozone and high temperature resistance. However, on thermodynamic conditions these two rubbers are immiscible due to the high difference in their solubility parameter and saturation level. So compatibilization of this blend is essential to alleviate the problems due to immiscibility. The blend can possibly be made miscible by using DCNR as an interface modifier. Due to the presence of chlorine within the repeat unit of DCNR, there is a possibility of dipolar interaction with the polar units of HNBR. The properties of the blend can also be improved by proper selection of cure system. Mixed cure system and incorporation of fillers may result in blends having good mechanical properties and good aging resistance.

Blends of NR and HNBR would be suitable for applications requiring a combination of good resistance to attack by ozone, better resistance to swelling by oils and fuels and resistance to high temperature, along with good mechanical properties at lower cost.

In this thesis, a detailed work on chemical modification and blending is presented with the following specific objectives:

1. Preparation, characterization and evaluation of dichlorocarbene modified natural rubber.
2. Improvement in resistance to aging of natural rubber by heat, oxygen, ozone, oils, fuel and radiation by blending with hydrogenated nitrile rubber.
3. Evaluation of the role of dichlorocarbene modified natural rubber as an interface modifier in blends of natural rubber and hydrogenated nitrile rubber with reference to the variation in curatives and filler.
4. Characterization of the flow behavior of the natural rubber / hydrogenated nitrile rubber blends.

Thesis is divided into 8 chapters. The first chapter is introduction, which includes literature survey on elastomers, chemical modification of NR and elastomer blends. The second chapter deals with the materials used and the experimental techniques followed throughout the course of the study. Third chapter contains the results of the preparation, characterization and properties of DCNR and its miscibility with a polar rubber like, HNBR. The fourth chapter discusses the different aspects of blending of NR with HNBR with reference to blend ratio, role of DCNR as an interface modifier, blending methods, type of cure system, fillers, etc., characterization techniques and mechanical properties. The fifth chapter deals with the aging behavior of vulcanizates of NR/HNBR blends under different conditions such as high temperature, immersion under oils and fuels and exposure to ozone and γ radiation. The sixth chapter focuses on the chemical changes taking place during aging of the blends of NR/HNBR by stress relaxation and solvent swelling methods. The seventh chapter is a comparative study of aging behavior of blends of NR with four speciality elastomers. The eighth chapter discusses the rheological behavior of the blends of NR/HNBR. The summary and conclusion based on the present work is given towards the end of the thesis.

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CHAPTER 2

MATERIALS
AND
EXPERIMENTAL TECHNIQUES

2.1 Materials

2.1.1 Natural rubber (NR)

Natural rubber used was ISNR 5 (Indian Standard Natural Rubber, 5 grade), obtained from M/s Pilot Crumb Rubber Factory, Kottayam, Kerala, India. The specification parameters for ISNR 5 grade as per IS 4588:1988 [1] and the values obtained are given in Table 2.1.

Table 2.1 Properties of NR (ISNR 5 grade)

Properties	Requirements as per IS:4588:1986	Values obtained
Dirt, % by mass, max.	0.05	0.006
Volatile matter, % by mass, max.	0.80	0.14
Ash, %by mass, max.	0.50	0.15
Nitrigen, % by mass, max.	0.60	0.38
Initial plasticity, Po, min.	30	50
Plasticity retention index, PRI, min.	60	84

2.1.2 Hydrogenated nitrile rubber (HNBR)

Hydrogenated nitrile rubber, Zetpol 2010 grade was obtained from Nippon Zeon Company, Japan. The detailed specification of this rubber is given in Table 2.2.

Table 2.2 Specific characteristics of Zetpol 2010

Bound acrylonitrile content, %	36
Iodine value, g/100g	11
Mooney viscosity, ML (1+4), 100 °C	85
Density, g/cm^3	0.97

2.1.3 Nitrile Rubber (NBR)

Acrylonitrile butadiene copolymer of medium acrylonitrile content, Chemaprene N3309 supplied by Synthetics and chemicals Ltd., Bareilly, U.P., India. The detailed specifications of the rubber are given in Table 2.3.

Table 2.3 Specific characteristics of Nitrile rubber

Volatile matter (%, max)	0.75
Ash (%, max)	1.0
Antioxidants (%)	1.0
Bound acrylonitrile content (%)	31-35
Mooney viscosity, ML (1+4) 100 °C	40-60
Soap (%)	0.05

2.1.4 Ethylene propylene rubber (EPDM)

EPDM, Royalene 521, manufactured by Uniroyal Chemical Co., U.S.A was used. The detailed specifications of the rubber are given in Table 2.4.

Table 2.4 Specific characteristics of EPDM

Mooney viscosity, ML (1+4), 100 °C	50
E/P Ratio	52/48
ENB (%)	5
Volatile matter (%)	1.0
Ash (%, max)	0.15
Stabilizer type	Non- staining
Molecular weight distribution	Medium
Specific gravity	0.86

2.1.5 Polychloroprene rubber (CR)

Neoprene (W type) was obtained from DuPont de Nemours Co., Germany. It consists of chloro 2 butylene in trans 1,4 addition (85%), cis 1,4 addition (10%), 1,2 addition (1.5%) and 3,4 addition (1%).

2.1.6 Solvents

Toluene, chloroform, isopropyl alcohol, methylethyl ketone, iso octane, etc. were of reagent grade and supplied by Merk India Ltd., Mumbai, India.

2.1.7 Chemicals and fillers.

N-Cetyl-N,N,N-trimethyl ammonium bromide(CTAB) was obtained from E Merk India Ltd., Mumbai. Sodium hydroxide and other chemicals like, silver nitrate, magnesium carbonate, sodium carbonate, ammonium thiocyanate, ferric alum indicator, etc. used for the estimation of chlorine content of the modified NR were guaranteed reagents obtained from Merchem, Kochi. All the rubber chemicals used for the preparation of rubber compounds were of industrial purity. The curatives zinc oxide (Sp. gravity 5.5), stearic acid (Sp. gravity0.92) , sulphur (Sp. gravity 1.9) were of commercial grade obtained from Bayer India Ltd., Mumbai. Dicumylperoxide (DCP) of 40% activity

(Sp.gravity 1.55) was obtained from M/s Peroxide India Ltd. Accelerators such as, tetramethylthiuram disulphide (TMTD), N-cyclohexyl-2-benzothyazyl sulphenamide (CBS) and mercaptobenzothiazole (MBT) were obtained from Merchem, Kochi, India. Antioxidants, HS (polymerized 2,2,4 trimethyl 1,2 dihydroquinoline - Sp. gravity 1.08 and melting point 75-90 °C) and 4010 NA (N-isopropyl N^1 phenyl p-phenylene diamine- (Sp. gravity 1.10 and melting point 73°C) were obtained from Bayer India Ltd., Mumbai.

Carbon blacks used were high abrasion furnace black (N330), fast extrusion furnace black (N550) and general purpose black (N660) supplied by Philips carbon India Ltd., Durgapur. Silica used was Ultrasil VN3 grade (Sp. gravity 2.0, particle size 40-60, pH 6.7) of Degussa, Germany.

The processing oils- Naphthenic oil (sp. gravity at 25°C- 0.9, aniline point 77.8°C, flash point 180°C and pour point 6°C) was obtained from Bharath Petroleum, India, and Dioctylphthalate (refractive index 1.484, Sp. gravity at 23°C- 0.986, viscosity at 30°C –60 cps, pour point 46°C, flash point 218°C) was obtained from Ceyenar Chemicals, Kottayam.

2.1.8 ASTM Oils

ASTM oil Nos.1, 2 & 3 were manufactured by R.E Carroll, Inc., New Jersey, Akron, Ohio and supplied by Apar Ltd., special refinery division, Mumbai, India.

2.2. Preparation of dichlorocarbene modified natural rubber (DCNR)

Addition of dichlorocarbene to natural rubber was carried out by the alkaline hydrolysis of chloroform using a phase transfer catalyst, according to the method suggested by Makosza [2]and later modified by Joshi, et al.[3] NR was dissolved in toluene and the phase transfer catalyst, cetyltrimethyl ammonium bromide was added to this and the mixture was stirred well. To this chloroform was added dropwise under constant stirring, followed by a 50% solution of sodium hydroxide, in a water bath at constant temperature. The reaction product was separated from solution and washed with hot and cold water until free of chlorine. The product was coagulated with isopropyl alcohol and reprecipitated from toluene solution. The modification was monitored at different intervals by measurement of chlorine content by chemical analysis.

2.3 Estimation of chlorine content of the modified NR

The percentage chlorine content of the modified NR was estimated using Volhard titration method[4]. About 0.2 grams of the modified rubber was weighed accurately into a platinum crucible and covered it with about 2grams of fusion mixture. The fusion mixture was prepared by thoroughly mixing equal proportions of sodium carbonate and potassium carbonate. The contents of the crucible were fused at 900 °C in a muffle furnace. The fused material was extracted in about 100 ml of distilled water, acidified with concentrated nitric acid and the solution was heated on a water bath for one hour. 40 ml of standard silver nitrate solution was added to the hot solution. After precipitation of the chloride, the solution was filtered and washed down with distilled water. The filtrate was titrated against standard ammonium thiocyanate using ferric alum as indicator to estimate the unreacted silver nitrate. The end point was the formation of a faint red colour. A blank determination was also carried out simultaneously.

$$\% \text{ of chlorine} = \frac{(B-V) \times N \times 35.5}{W} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots \qquad (1)$$

Where B - the volume of ammonium thiocyanate used for the blank

V - the volume of ammonium thiocyanate used for the sample

W- the weight of the sample

N- Normality of ammonium thiocyanate.

Rate constant (k) of the reaction at different temperatures was calculated by plotting $\log(C_{\propto} - C_t)$ versus time, where $C_{\propto}$ is the maximum chlorine percentage obtained at a particular temperature and Ct is the chlorine percentage at a particular time t. The activation energy of reaction was calculated from linear plots of log k versus 1/T where T is the temperature in Kelvin.

2.4 Test for Flammability

Flame resistance of vulcanizates of DCNR of varying chlorine content was evaluated as per UL 94 Overview- Test for flammability[5] of plastic materials for parts in devices and appliances. Method 94V, used for vertical burn test was applied. The test specimens were (strips of 12mm x 100mm and thickness 2.0 mm cut from molded vulcanizates) held at one end in the vertical position. A burner flame was applied to the free end of the specimen for two-ten seconds intervals, separated by the time it took for flaming combustion to cease after the first application. Two sets of three specimens were tested. The following were noted for each specimen.

Duration of flaming combustion after the first burner flame application.
Duration of flaming combustion after the second burner flame application.
Duration of glowing combustion after the second burner flame application.
Whether or not flaming drips ignite cotton placed below specimen.
Whether or not specimen burns up to holding clamp.

2.5 Preparation of mixes of elastomers and elastomeric blends

The mixes were prepared on a laboratory size two roll mixing mill (325 x 150 mm) at a friction ratio of 1:1.5 according to ASTM D3182-89 by careful control of temperature, nip gap, time of mixing and by uniform cutting operation. The compounding ingredients were added in the following order after mastication of rubber, zinc oxide, stearic acid, antioxidant, filler, plasticizer and finally curatives.

2.5.1 NR/HNBR blends

NR/HNBR blends were prepared by two different methods, method A and method B. In method A, both NR and HNBR were vulcanized by same cure system - NR and HNBR were first masticated separately to get comparable viscosity, cross blended and the accelerators and curatives were added. In method B, different cure systems were added to each phase. Here separate master batches of NR and HNBR were prepared and then cross-blended to get 25/75, 50/50 and 75/25 compositions. For the preparation of the modified blends, the required quantity of DCNR was first masticated and then blended with HNBR prior to the addition of curatives.

2.5.2 HNBR/DCNR blends

Both HNBR and DCNR were first masticated and then blended together, again masticated to get a uniform mix and then the curative, peroxide was added. For the filled blend, compounding ingredients, filler, plasticizer and anti oxidants were added prior to the addition of curatives.

2.5.3 Blends of NR with NBR/CR/EPDM

Separate master batches of NR, EPDM, CR and NBR were prepared and then cross-blended to get 50/50 compositions.

2.6 Processing characteristics.

2.6.1 Scott Mooney Viscometer

Scorch time is the induction period before the development of a noticeable modulus in the rubber compound. An appreciable level of scorch time ensures processing safety of the compound. The instrument (SMV-202) consists of a motor driven rotating disk within a cylindrical cavity formed by two dies maintained at special conditions of temperature and die closure force. Mooney viscometer measures the effect of temperature and time on the viscosity of rubber compound. Scorch time was determined at 120°C. The time required to get a rise in torque by 5 Mooney viscosity units from the minimum value was taken as scorch time.

2.6.2 Monsanto rheometer

The cure characteristics were determined using a Monsanto rheometer model R-100 and MDR 2000 at 150/160°C according to ASTM D 2084-93 test method.

2.6.2.1 Measurement procedure

The test specimen of vulcanizable rubber compound was inserted into the cure meter test cavity and after a closure action was contained in a sealed cavity under positive pressure. The cavity was maintained at elevated temperature. The rubber totally surrounded a biconical disk after the dies were closed. The disk was oscillated at 100 cycles per minute through rotational amplitude of 0.5° and this action exerted a shear strain on the test specimen. The force required to oscillate the disc to the set amplitude was continuously recorded as a function of time with the force being proportional to the shear modulus of the test specimen at the test temperature. This stiffness first decreased as it warmed up, then it increased due to vulcanization. The test was completed when the recorded torque rose to a maximum value. The time required to obtain a definite level of cure is a function of the characteristics of the rubber compound and the test temperature.

Optimum cure time (t90) is the time required for the development of 90% of maximum rheometric torque. It is calculated using the equation,

$$t90 = 0.9(Mh-Mn) + Mn \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Where Mh and Mn are maximum and minimum torque respectively.

Rheometric scorch time is the time required for the torque value to increase by two units above the minimum torque at the temperature denoted by ts2.

2.7 Kinetics of vulcanization

Kinetics of vulcanization of the different cure systems for 50/50 blends was studied by measuring the torque developed during the course of vulcanization[6] by using a rheo TECH MD+ moving die rheometer of oscillating speed 1.67 Hz and arc of ± 0.5^0 according to ASTM D 6204. The temperatures selected were 150°C, 160°C and 170°C.

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

$$(\ln a-x) = -kt + \ln a \quad \ldots\ldots\ldots(3)$$

where a = initial reaction concentration

x = reacted quantity at time 't', and

k = first order reaction rate constant

The rate of cross link formation is usually monitored by measuring the torque developed during the course of vulcanization by using a curometer and the torque values thus obtained are proportional to the modulus of the rubber. Hence,if a physical property such as modulus is being measured rather than the change in reactant concentration, then the following substitution can be made

$$(a - x) = (M_\alpha - M) \qquad \text{.........} \quad (4)$$

$$a = (M_\alpha - M_L) \qquad \text{............}(5)$$

where M_α = maximum modulus

M_L = minimum modulus, and

M = modulus at time 't'

Substituting torque values for modulus, we get,

$$(a - x) = (M_H - M_t) \qquad \text{............}(6)$$

where M_H = the maximum torque developed, and

M_t = the torque at time 't'.

If the reaction is of first order, a plot of ln $(M_H - M_t)$ against 't' should give a straight line whose slope will be the specific reaction rate constant 'k'. A guideline to calculate 'k' value is shown in Figure 2.1.

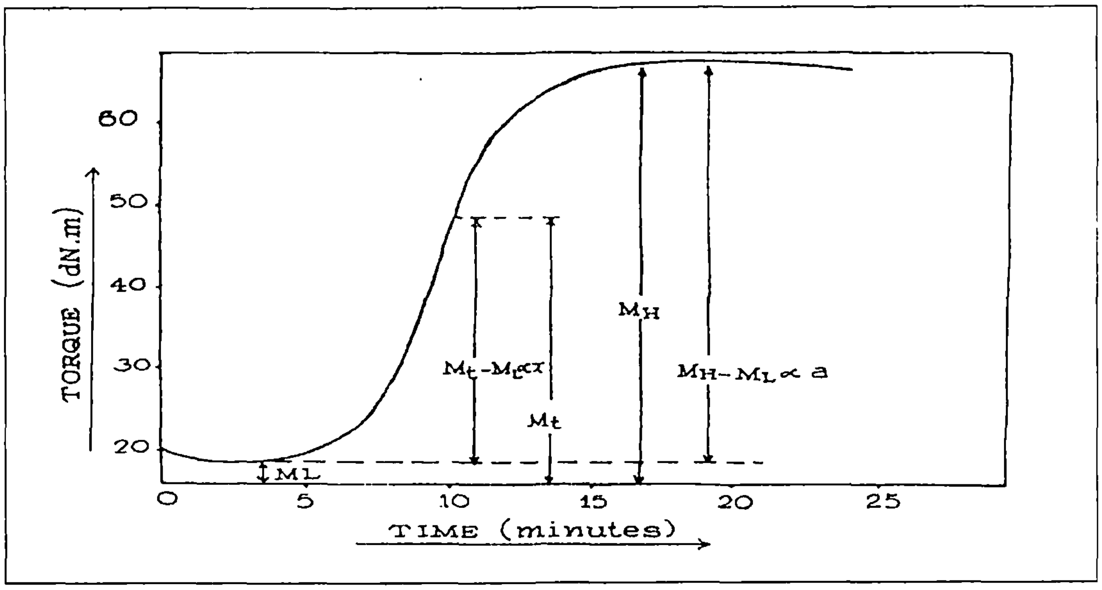

Figure 2. 1 . Guideline to find 'k' value.

To find out the activation energy of the vulcanization reaction, the modified Arrhenius equation was used.

$$t_{90} = A\, e^{E/RT} \qquad \text{.......................(7)}$$

$$\log t_{90} = \log A + \frac{E}{2.303\, RT} \qquad \text{..........................(8)}$$

where E - activation energy

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

T - absolute temperature, °K , and

R - universal gas constant.

A plot of log t_{90} vs 1/T gave a straight line, from the slope of which E was calculated.

2.8 Preparation of vulcanized samples

The test samples were compression molded at 150/160 ^{0} C at a pressure of 45 kg /cm^2 by placing 5% excess of the uncured mixes in the cavity of the required mould and vulcanized to their respective optimum cure time in an electrically heated hydraulic press. The samples were immediately cooled after removal from the mould.

2.9 Technological Properties

2.9.1 Modulus, tensile strength and elongation at break

Modulus, tensile strength and elongation at break were determined according to ASTM D 412-99A, using dumb bell specimens. The test specimens were punched out from molded sheets of thickness (2 ± 0.2) mm using the C – type die, along the mill grain direction. The thickness of the specimen within the gauge length was measured using a dial gauge of accuracy 0.001 mm. Five test pieces per sample were used for this test. The specimens were tested on a Zwick Universal Testing Machine (UTM) model 1474 at ambient temperature and at cross head speed of 500 mm per minute. The machine used was having a sensitivity of 0.5% of the full load scale. Modulus, tensile strength and the elongation at break, were obtained as a printout and reported as MPa and % respectively.

2.9.2 Tear resistance

Tear resistance of the samples was tested as per ASTM D 624-2000 using un nicked 90° angle test specimens that were punched out from molded sheets of thickness (2 ± 0.2) mm, along the mill grain direction. Five test pieces per sample were used for this test. This test was also carried out on a Zwick Universal Testing Machine (UTM) model 1474 at ambient temperature and at crosshead speed of 500 mm per minute and reported in kN/m.

2.9.3 Hardness

Hardness of samples was measured according to ASTM D 2240-2000 using a Shore A type durometer, which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indentor and the sample, the recordings immediately after establishment of firm contact were taken.

2.9.4 Compression set

The compression set was measured as per ASTM D 395 –2002 (Method B) Test samples (circular shape of 29mm diameter and 12.5 mm thickness) in duplicate, compressed to give 25 % deflection, were kept in an air oven at 70 / 125 /150 °C for 22 hours. After the heating period, the compression was released, the samples were kept at room temperature for half an hour and final thickness was measured. Compression set was calculated using the equation,

$$\text{Compression set} = \frac{t_o - t_f}{t_o - t_s} \times 100 \qquad \text{................(9)}$$

where t_o and t_f are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used.

2.9.5 Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader according to DIN No: 53516-1977 test method.[7] It consists of a drum on_to which a standard abrasive cloth was fixed. The drum rotated at a speed of 40 ± 1 rpm and the total abrasion length was 42 meters. The test specimen, cylindrical in shape with a diameter of 16 ± 0.2 mm and thickness 6-10 mm were molded out and kept on the rotating sample holder and 10N load was applied. Three test pieces per sample were used for this test. Initially pre run was given for the sample and its weight was taken. The weight after the final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test specimen getting abraded away by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows

$$V = \Delta m / \rho \qquad \text{...(10)}$$

Where Δ m - mass loss

ρ - density

V - abrasion loss in mm^3

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

2.9.6 Heat build up

Heat build up of the samples was measured as per ASTM D 623 –1999 test method. The test specimen was cylindrical in shape with diameter of 17.8 ± 0.1mm and a height of 25 ± 0.15mm. It was subjected to rapidly oscillating compressive stresses in

Goodrich Flexometer at 1800 cycles per minute. Test was conducted at 50°C. A constant initial compressive load was applied to the specimen through a lever having high inertia and imposing on the specimen an additional high frequency cyclic compression of definite amplitude. The stroke given was 4.45 mm. The increase in temperature at the base of the test specimen was measured with a thermocouple, which provided indication of the heat generated in flexing the specimen.

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

2.9.7 Rebound resilience

The rebound resilience of the vulcanizates was measured using Dunlop Tripsometer as per BS 903, part22, 1950 [8]. The test specimens used were of circular disc shape with a diameter 44 ± 0.5mm and a height of 4 ± 0.5mm. The specimens were held in position by applying vacuum. It was conditioned by striking it with the indenter six times. A freely falling hammer was dropped from a given height against the specimen at a known angle. The pendulum rebounded and the rebound angle was noted. The temperature of the specimen holder and sample was kept constant at 30 °C. Rebound resilience was calculated as

$$\text{Rebound resilience } \% = \frac{1 - \cos\theta_2}{1 - \cos\theta_1} \times 100 \qquad \text{......................(11)}$$

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

2.9.8 Flexing resistance

Test for dynamic fatigue was conducted as per ASTM D 430 –95, by method B. This method was designated to simulate the continually repeated distortions received in service by many rubber articles such as tires, belts, hoses, foot wear etc. and many molded goods. The distortions may be produced by extension, compressive and bending forces or a combination of these, the effect of which is to weaken the product until surface cracking or actual rupture occur. The test specimens of thickness 6.35mm, length

150 mm and breadth 25mm with a groove of 2.35 ± 0.03 rad at middle perpendicular to the length were molded out, conditioned for 42 hours and repeatedly flexed on a Demattia flexing machine with a frequency of 300 cycles run per minute at 25°C. The essential features of the apparatus were as follows. It has an adjustable stationary head or member provided with suitable grips for holding one end of each of the test specimens in a fixed position and a similar reciprocating member for holding the other end of specimen. The reciprocating member was so mounted that its motion was straight in the direction of and in the same plane as the central line between the grips. The travel of the moving members shall be adjustable and shall be obtained by means of a connecting rod and eccentric having a minimum length ratio of 10 to 1.The eccentric shall be driven by a motor operating at a constant speed under load and giving 300 ± 10 cycles per minute. The capacity of the machine was such that at least 12 specimens can be tested at the same time. The grips should hold the specimen firmly throughout the test and those on the reciprocating member clamp each specimen individually to facilitate proper adjustment of specimen. Samples were observed at regular intervals to check crack initiation. Number of cycles for crack initiation and failure of the sample were noted. Three specimens per sample were tested and the results averaged.

2.10 Selective solvent swelling

Interfacial adhesion in vulcanizates of polymer blends was investigated by selective or differential solvent swelling method.[9] The solvents used were methyl ethyl ketone and n-heptane. The scission and cross linking reactions occurring during vulcanization and aging for the individual matrices were studied by selective solvent swelling of the unaged and aged samples. The vulcanizates of blends were subjected to aging at 70^{0}C for 5 days, 120^{0}C for 5 days and 150^{0}C for one day. Test pieces of 20 mm diameter were cut from the aged and unaged samples, weighed and subjected to selective swelling of the individual matrices by immersion in the solvents to equilibrium swelling time which was taken as 48 hours at room temperature. After the swelling, samples were taken out, blotted with filter paper and weighed quickly in a stoppered weighing bottle. The weight of solvent absorbed per gram of the sample was calculated from measurement of swollen weight.

2.11 Calculation of volume fraction of rubber

The volume fraction of rubber in the swollen sample was calculated by the method reported by Ellis and Welding[10], which take into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0\rho_s^{-1}} \qquad \ldots\ldots\ldots\ldots(12)$$

where, D - deswollen weight of the test sample ,

F - the weight fraction of the insoluble component,

T - initial weight of the test sample,

A_0 - weight of solvent absorbed, corrected for swelling increment

ρ_r - density of rubber, and

ρ_s - density of solvent.

Samples of approximately 20 mm diameter and of thickness (2 ± 0.2) mm, weighing about 0.3 g were punched from the central portion of the vulcanized sheets and allowed to swell in the solvent at 25^0C . The swollen samples were taken after the equilibrium period, blotted with filter paper and weighed quickly in a stoppered weighing bottle. Samples were dried in an air oven for 24 hours at 70^0C and in vacuum and finally weighed after allowing them to cool in a dessicator. Duplicate readings were taken for each sample.

2.12 Characterization studies.

2.12.1 FTIR

The IR spectra of samples were recorded with a Shimadzu-8101 M Fourier transform infrared spectrophotometer, using thin film or pyrolysate of the samples. The thin film was prepared by dissolving the polymer in chloroform and then the concentrated solution (5%) was directly cast on a leveled glass plate to form a thin film. For the preparation of pyrolysate, samples were heated in a fusion tube and the condensed vapors were collected on the surface of sodium chloride cell to form a uniform film and this film was used to record the IR spectra. The light source (an electrically heated solid, eg.a nichrome wire) produces a beam of infrared radiation, which is divided (by a system of mirrors) into two parallel beams of equal intensity radiation. The sample is in the path of one beam a and the other may be used as a reference beam when a solution is to be analyzed. A slowly rotating diffraction grating or prism varies the wavelength of radiation reaching the sample and the detector. The detector records the difference in intensity between the two beams on a recorder chart as percentage transmittance. Maximum transmittance is at the top of the vertical scale, so absorbance is observed as a minimum on the chart even though it is called a peak.

2.12.2 Thermal analysis

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

2.12.2.A Differential scanning calorimeter

Direct calorimetric measurements, characterization and analysis of thermal properties of the samples were made using Toledostar S W 7 model, supplied by Mettler Co., Germany at a heating rate of 20 °C. Sub ambient operation was carried out by cooling the specimen and the specimen holder with liquid nitrogen. Exactly weighed (about 5mg) of samples was used for the studies. Samples were encapsulated in standard aluminium pans and covers were sealed by crimping. For purging the sample holders, pure nitrogen gas (99.99%) was used. The inlet gas pressure was adjusted at 2 kg/cm^2 to attain a flow rate of about 25 ml/min. Scanning rate was 20 °C/min.

2.12.2.B Thermogravimetry

A Perkin Elmer model thermogravimetric analyzer was used for the studies. It is a computer-controlled instrument, which permits the measurement of weight change in the sample as a function of temperature or time. It is programmed in the required temperature range to measure the weight change resulting from chemical reaction, decomposition, solvent and water evolution, curie point transitions and oxidation of the sample materials. The temperature is scanned at a linear rate. The Perkin Elmer model had two components, an ultra sensitive micro balance and a furnace element. The balance is sensitive to 0.1 micrograms and the furnace could be heated from ambient to 1000°C at rates of 0.1 to 200 °C per minute. For purging tile sample holder, gases commonly used are oxygen, air (a mixture of 80% nitrogen and 20% oxygen) or nitrogen so as to study the oxidation, burning and thermal stability of the materials. The purge gas flows directly over the sample. The recommended flow rate of the sample purge was kept less than the flow rate of the balance purge at all times.

2.12.3 Scanning electron microscopy studies

The scanning electron microscopy (SEM) photographs given in this work were taken using SEM model H600 with H 6010 a scanning electron image accessory supplied by Hitachi Ltd., Japan at 500 magnifications. The SEM utilizes a focused beam of high-energy electrons that systematically scans across the surface of the specimen.[11] The interaction of the beam with the specimen produces a large number of signals at or near the specimen surface. These interactions include lower energy electrons termed secondary electrons, which makes them a conveniently collected signal for scanning

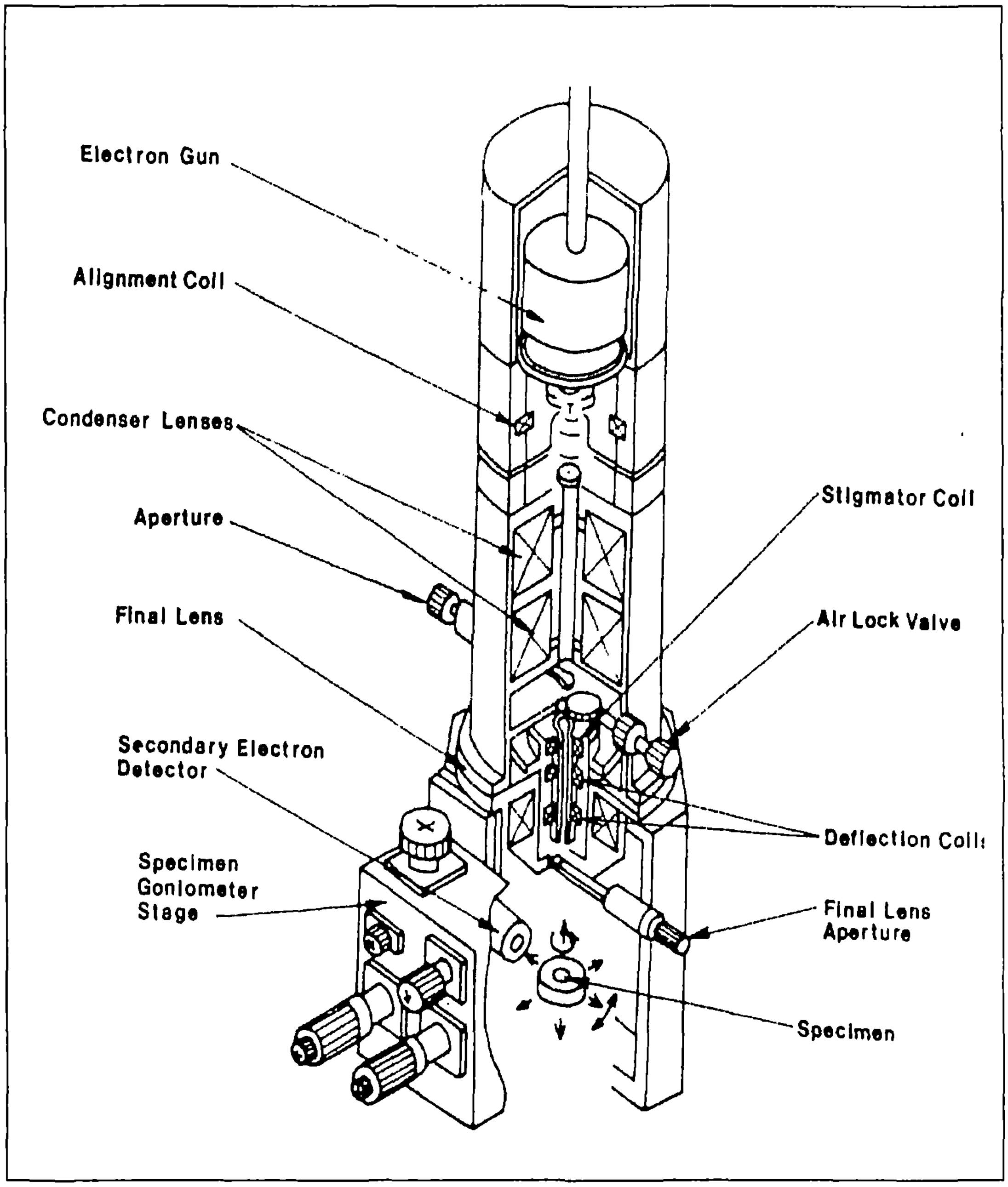

Figure 2 .2. Schematic representation of a scanning electron microscope column. (Courtesy of Hitachi, Ltd.)

electron microscopy. The electron signal is eventually converted to an electronic signal which is portrayed on a cathode ray tube .The scanning of the beam is synchronized with the scanning of the cathode ray tube, thus producing a one- to – one relation between the points on the specimen and points on the CRT. Electrons emitted from a surface, which faces away from the detector are partially blocked by the specimen and the image of such a surface is darker than that of a surface, which faces towards the detector.

The component parts of a typical scanning electron microscope includes the gun assembly which produces a primary electron beam, the electromagnetic lenses and apertures which focus the electron beam on the specimen, the vacuum system which allows the passage of the electron beam through the column without interference of air molecule, the specimen stage and the signal detection and display components which permits the observation and photographing of an enlarged image of the specimen. (Figure 2.2.) The samples were freeze fractured by immersing in liquid nitrogen and the fracture surfaces were carefully cut without touching the surfaces and were sputter- coated with gold within 24 hours of testing.[12] The fractured test specimens and gold coated samples were stored in a desiccators and the SEM observations were made within 24 hours of gold coating. There should not be any change in the fracture pattern when the SEM observations were made one month after gold coating.[13]

2.13 Degradation studies

2.13.1 Thermal aging

Dumb bell shaped tensile test samples of 2 ± 0.2 mm thickness were aged at 100°C, 120 °C and 150°C for 5 days and 24 hours respectively in an air circulated aging oven. The tensile strength and elongation at break were measured before and after aging. The percentage retention of properties after aging was calculated.

2.13.1.A. Stress relaxation studies

Stress relaxation is the stress decay with time under constant strain. The stress relaxation of the blends was studied using Zwick Universal testing machine (Model 1474) at 100^0C, 130^0C and 150^0C. Dumb bell specimens (as per ASTM D 412, die C) were used. The samples were pulled to the desired elongation at a strain rate of $0.03s^{-1}$. The decay of the stress as function of time was recorded. The slope and intercept of the stress relaxation plots [obtained from plots of (σ/σ_o) vs log time, where σo is the initial stress and σ is the stress at time t] were obtained by the method reported by Scanlan and Kackenzie[14]. The calculation of permanent set during stress relaxation was from the scission and cross linking reactions that take place during intermittent and continuous stress relaxation as reported by Andrews et al.[15]

2.13.2 Exposure to Ozonized Air

The ozone test chamber manufactured by MAST Development Company, USA was used to study ozone cracking. (Figure 2.3.) The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration selected was 50 $\overset{b}{pp}$m, which is generated by an UV quartz lamp.

The test was carried out as per ASTM D 1149 –99 specifications at 38.5°C. B type specimens were tested in duplicate and in the form of a bent loops. Rectangular strip of length 95mm, breadth 25mm and thickness 2 ± 0.2 mm cut with the grain in the length direction from tensile sheets were folded and tied at 25mm length from the edges to get the required strain (>20%). These were then conditioned for 24 hours. The conditioned samples were exposed to the ozonized air in the chamber. Periodic observations of the surface of the samples were made for crack initiation. Samples were exposed for longer time. Surfaces of the irradiated samples were scanned on a macro viewer of LEICA Q 500 IW image analyzer, images were acquired and the photo prints were taken.

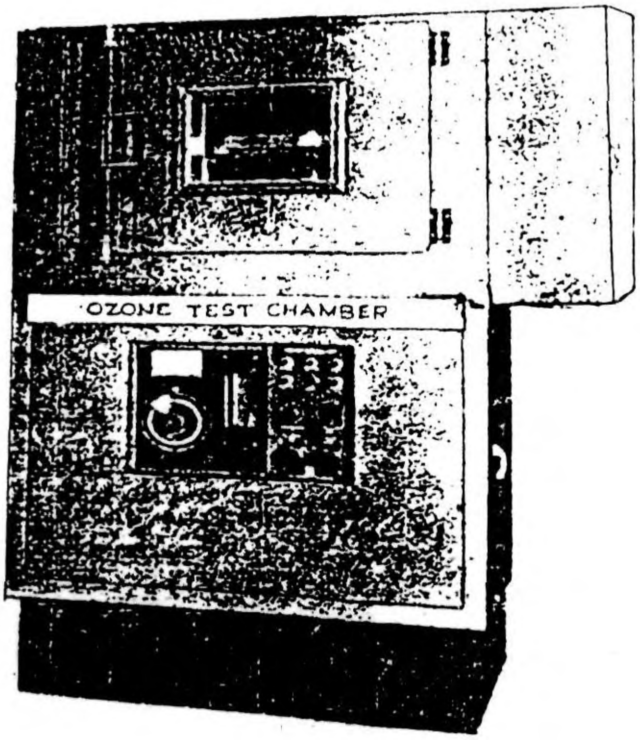

Figure 2. 3. Ozone chamber

2.13.3 Oil aging

2.13.3.A Change in mass

Oil aging was carried out as per ASTM D 471 –98. Test samples of circular shape (diameter 20mm and thickness 2 ± 0.2 mm) were punched out using a die from tensile sheets and initial weight in air were taken to the nearest 1 mg accurately. The test specimens were immersed in ASTM oil No. 1, 2 and 3 in a squat dish without touching the sides of the vessel for 5 days at three different temperatures- room temperature, 70°C and 100°C. After the immersion time, the test specimens were taken out, cooled to room temperature by transferring them to a cool clean portion of the test liquid for 30 minutes.

Then the specimens were quickly dipped in acetone at room temperature, blotted lightly with a filter paper free of lint and foreign material and final weight of the specimen was determined to the nearest 1 mg by placing in a tared, stoppered weighing bottle. The percentage change in mass was calculated as follows:

$$\Delta M, \% = \frac{(M2 - M1)}{M1} \times 100 \qquad \text{.........................(13)}$$

Where :

ΔM - change in mass, %,

M1 - initial mass of specimen in air, and

M2 - mass of specimen in air after immersion,

Test results were calculated for three test specimens of the same sample and the average value was taken.

2.13.3.B Change in tensile strength, elongation at break and tear strength

Test specimens were cut from vulcanized sheets of thickness 2 ± 0.2 mm according to ASTM test methods D412, Die C and D624. Three test specimens per sample were taken and the thickness was measured. The specimens were immersed in ASTM No.2 oil as described in 8.1, of ASTM D 471 test method for 5 days at room temperature. At the end of the immersion period, the specimens were taken out, quickly dipped in acetone and blotted lightly with a filter paper. Tensile strength, elongation at break and tear strength were measured as per the ASTM test methods using the immersed and original samples. The change in properties are expressed as a percentage change from the original values using the formula,

$$\Delta P, \% = \frac{(Po - Pi)}{Pi} \times 100 \qquad \text{...................(14)}$$

Where:

Po – original property before immersion,

Pi - property after immersion and

ΔP – change in property after immersion, %.

2.13.4 Fuel aging

ASTM reference fuel C prepared by mixing iso octane and toluene (Motor Fuels, Section 1, Test Method D 2699) in 50:50 volume % compositions was used for this study as per ASTM D 471 –98. Test specimens (in triplicate) were cut from vulcanized sheets of thickness 2 ± 0.2 mm and immersed in the fuel for 5 days at room temperature. The measurements were done as in the case of oil aging and the % change in properties were calculated.

2.13.5 Exposure to gamma radiation

Dumb bell shaped tensile test samples of 2 ± 0.2 mm thickness were irradiated with gamma (γ) rays in a Gamma Chamber 5000. (Figure 2.4). It is a compact self-shielded cobalt-60 gamma irradiator providing an irradiation volume of approximately 5000cc. The material for irradiation is placed in an irradiation chamber located in the vertical drawer inside the lead flask. This drawer can be moved up and down with the help of a system of motorized drive, which enables precise positioning of the irradiation chamber at the center of the radiation field. Radiation field is provided by a set of stationary cobalt-60 sources placed in a cylindrical cage. The sources are doubly encapsulated in corrosion resistant stainless steel pencils and are tested in accordance with international standards. The samples were irradiated for different radiation doses at a dose rate of 0.3 mega rad per hour in air at room temperature. The tensile strength was measured before and after irradiation and the percentage retention was calculated

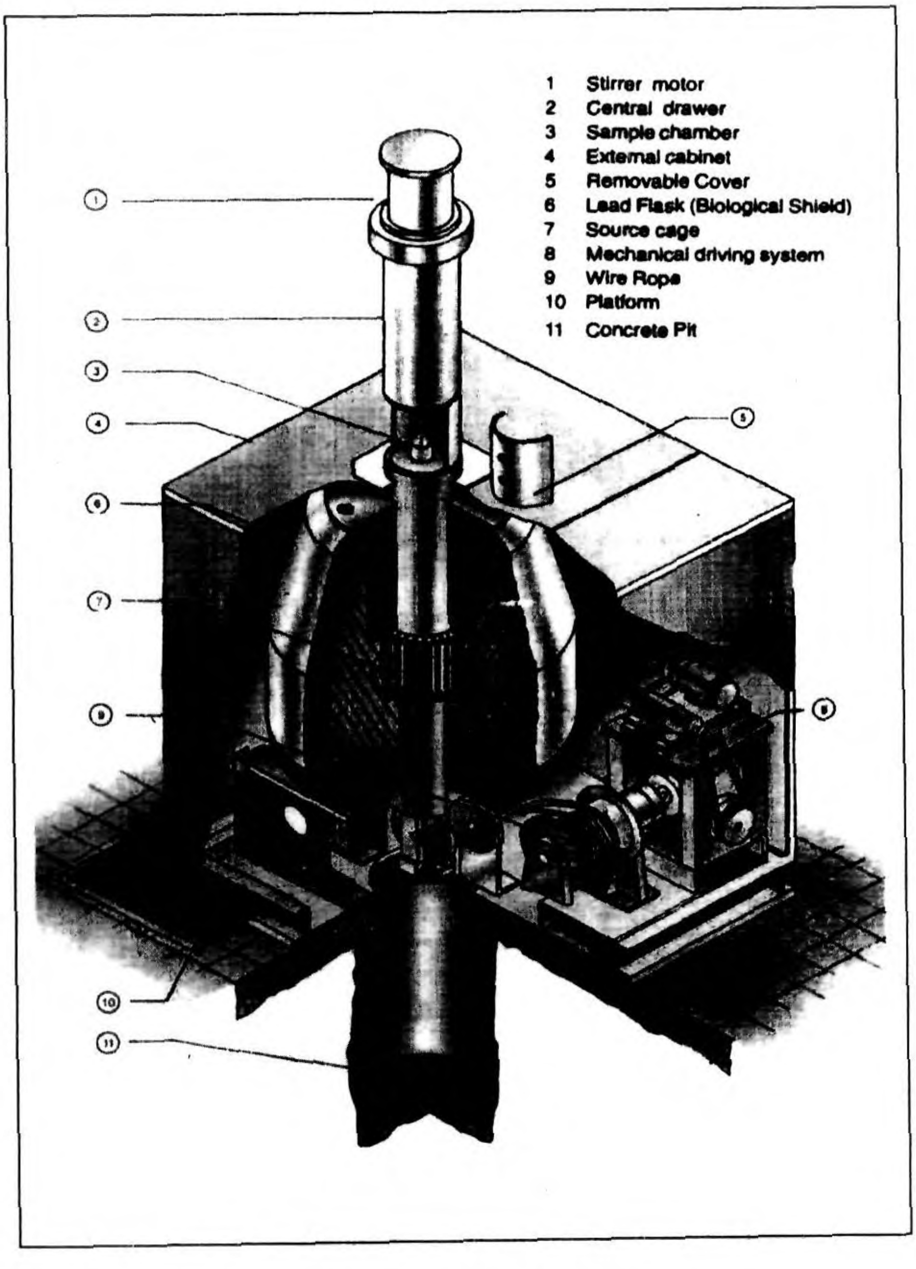

Figure 2.4. Gamma Chamber 5000

2.14 Measurement of Rheological Properties

2.14.1 Equipment details.

A capillary rheometer attached to Zwick UTM model 1474 was used to carry out the melt flow studies as per ASTM D 5099-1993. The extrusion assembly consisted of a barrel made of hardened steel, mounted on a special support, underneath the moving cross head of the Zwick UTM. A hardened steel plunger, which is accurately ground to fit inside the barrel is held to the load cell extrusion. An insulating ring thermally isolates the barrel from the rest of the machine and prevents heat losses due to conduction. The capillary is inserted at the bottom of the barrel and is locked using a clamping device. The capillary is made of tungsten carbide. The barrel was heated using a three-zone temperature control system. The difference between the successive temperature zones in the barrel was kept at 5 °C and the temperature of the lower zone, where the capillary is located, was taken as the test temperature.

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

2.14.2 Test procedure

Ten grams of the samples to be tested were placed inside the barrel, which was maintained at the test temperature. The sample was forced down to the capillary using the plunger attached to the crosshead. After a warming up period of three minutes, the melt was extruded through the capillary at pre-selected speeds of the crosshead. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give 8 different plunger speeds. Each plunger speed was continued until the recorded force was stabilized before changing the next speed. Forces corresponding to specific plunger speeds were recorded. The forces and cross head speed were converted into apparent shear stress (Γ_w) and shear rate (γ_w) at the wall by using the following equation:

$$\Gamma_w = \frac{F}{4Ap\,(lc/dc)} \qquad \text{.....................(15)}$$

$$\gamma_w = \frac{(3n' + 1)}{4n'} \times \frac{32\,Q}{\Pi dc^3} \qquad \text{...................(16)}$$

where:

F – force applied at a particular shear rate,

Ap - cross sectional area of the plunger,

lc - length of the capillary,

dc - diameter of the capillary,

Q - volume flow rate,

n' - flow behavior index defined by $d\,(\log \Gamma_w) / d\,(\log \gamma_{wa})$

γ_{wa} – apparent wall shear rate and

γ_w - actual shear rate at wall.

n' is determined by regression analysis of the values of Γ_w and γ_{wa} obtained from the experimental data. The shear viscosity was calculated as $\eta = \Gamma_w / \gamma_w$.

The shear stress at the wall requires corrections as suggested by Bagley.[16] But it was assumed that the correction factor is negligible at length to diameter ratio, 40. For the analysis of the data, the following assumptions were also made.

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

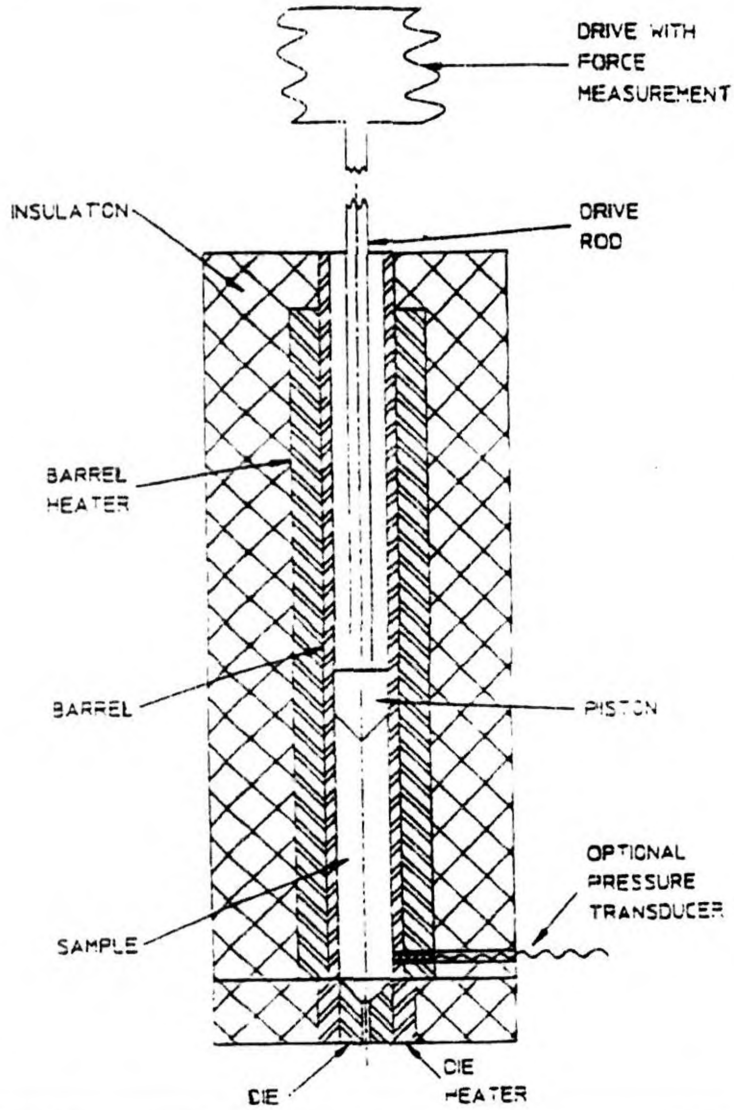

Figure 2.5. Schematic diagram of a Capillary rheometer

2.14.3 *Extrusion swell*

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

$$\text{Die swell} = \frac{de}{dc} \times 100 \qquad \text{......................(17)}$$

where dc is the diameter of the capillary.

2.14.4 *Elastic parameters*

The principal normal stress difference (Γ_{11} - Γ_{22}) was calculated from the die swell and shear stress according to Tanner's equation.[17]

$$(\Gamma_{11} - \Gamma_{22}) = 2\,\Gamma_w\,[2(de / dc)^6 - 2]^{1/2} \qquad \text{.......... (18)}$$

Recoverable shear strain S_R and elastic shear modulus G were calculated [18] from the equation:

$$S_R = (\Gamma_{11} - \Gamma_{22}) / 2\,\Gamma_w \qquad \text{....................(19)}$$

$$G = \Gamma_w / S_R \qquad \text{......................(20)}$$

where Γ_w is the wall shear stress.

2.14.5 *Extrudate deformation; Optical photography*

Extrudates were collected carefully with minimum possible deformation and allowed to relax for 24 hours. Representative samples at two different shear rates were cut from the extrudates and were scanned on a macro viewer of LEICA Q 500 IW image analyzer, images were acquired and the photo prints were taken.

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CHAPTER 3

DICHLOROCARBENE MODIFICATION OF NATURAL RUBBER

3.1.Introduction

For imparting special properties, general purpose rubbers can be chemically modified by reaction involving their double bonds.[1-7] It was found that the reaction of double bonds with various reagents resulted in improvement of flame retardency, oil resistance, air permeability and other properties.[8-10] The reaction of carbenes with olefins to form a cyclopropyl derivative had attracted much attention during the past years. Pinazzi and Levesque found that carbene addition had a significant influence on the properties of polydienes.[11] Dichlorocarbene modification on styrene butadiene rubber (SBR) was reported to increase the solvent resistance and flame resistance.[12] Cis -1,4 polyisoprene, natural rubber (NR) is a versatile elastomer which finds application in various products. However, it has very poor heat, flame and solvent resistance. A number of attempts have been made to improve the aging characteristics of NR. In most cases extensive modification reduced the elasticity of NR.

This chapter describes an attempt to improve the aging properties of NR by dichlorocarbene modification through the alkaline hydrolysis of chloroform using cetyl trimethyl ammonium bromide (CTAB) as a phase transfer agent. The modification was studied by chemically measuring the chlorine content of the modified sample, which was also characterized by FTIR, DSC and chemical analysis. The thermal stability of modified product was evaluated by thermogravimetry (TGA). The technological and oil/solvent swelling nature were also studied.

Modification is expected to improve the polar nature of NR and hence blends of modified NR with a polar rubber, hydrogenated nitrile rubber (HNBR) were prepared using peroxide vulcanization and evaluated for mechanical properties and aging resistance towards heat, oil and ozone.

3.2 Preparation of dichlorocarbene modified natural rubber (DCNR)

The concentration of the reagents, temperature and time of reaction are as given in Table 3.1. The experimental details are given in chapter 2.2.

Table 3.1. Formulation for the preparation of dichlorocarbene modified NR

ISNR 5	10 g
Toluene	300 ml
Chloroform	30 ml
50% NaOH	35 ml
CTAB[1]	0. 85 g
Time	0 - 25 hours
Temperature	40, 50 and 60 ^{0}C

1-Cetyltrimethyl ammonium bromide

3.3. Effect of time and temperature on chlorination

The extent of reaction based on chlorine content at three different temperatures 40^0 C, 50^0 C and 60 ^{0} C are shown in Figure 3.1. The dichlorocarbene addition was fast in

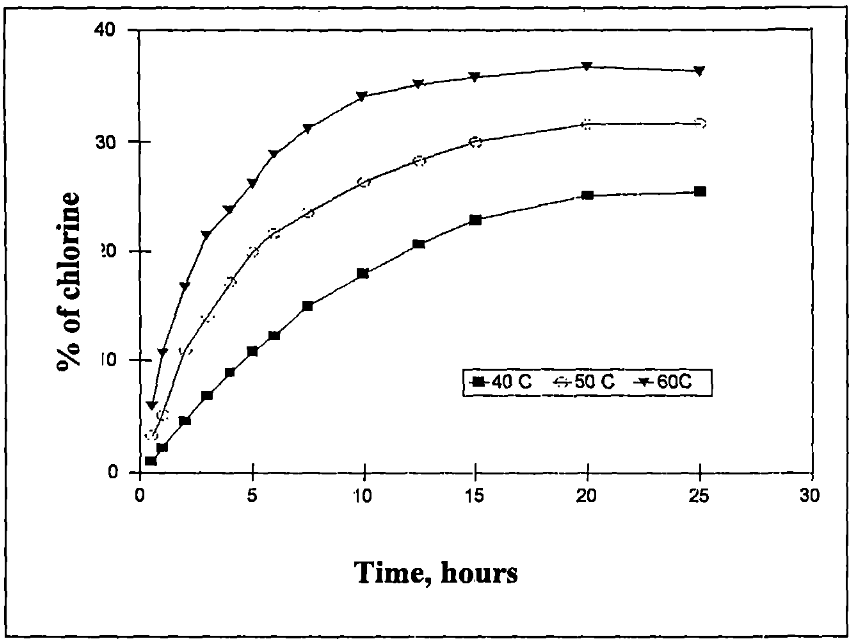


Figure 3. 1. Plots of percentage of chlorine versus time, at temperatures of 40^0 C, 50^0 C and 60 ^{0} C

the initial stages but decreased at later stages of reaction. The rate of reaction almost leveled off after about 17 h. As temperature of reaction increased the rate of reaction as measured by chlorine content also increased.

Figure 3. 2 shows change in chlorine content expressed as log(C_∞ –C_t) versus time, where C_∞ is the maximum chlorine percentage obtained at a particular temperature and C_t is the chlorine percentage at a particular time t. Linearity of the plots showed that

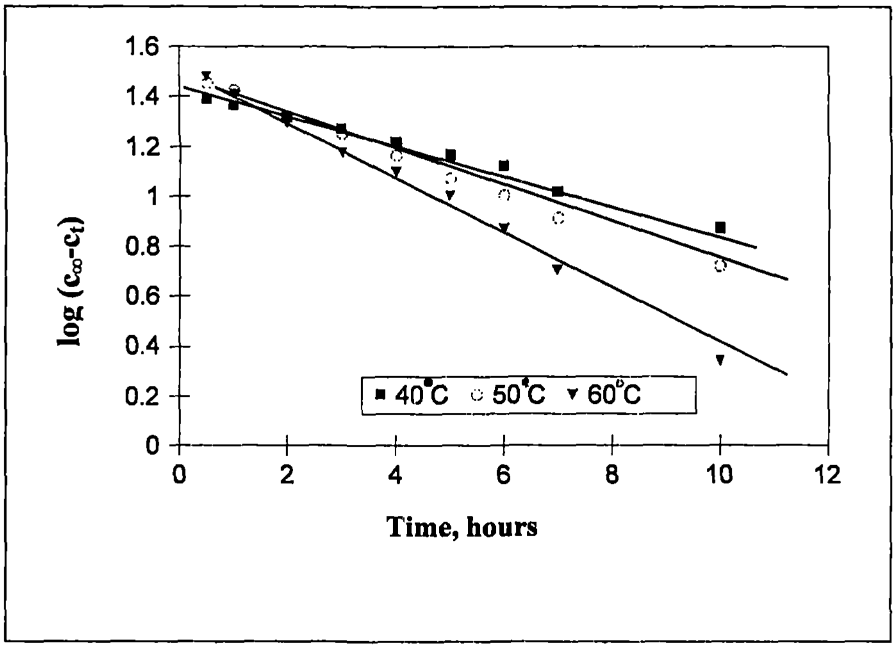


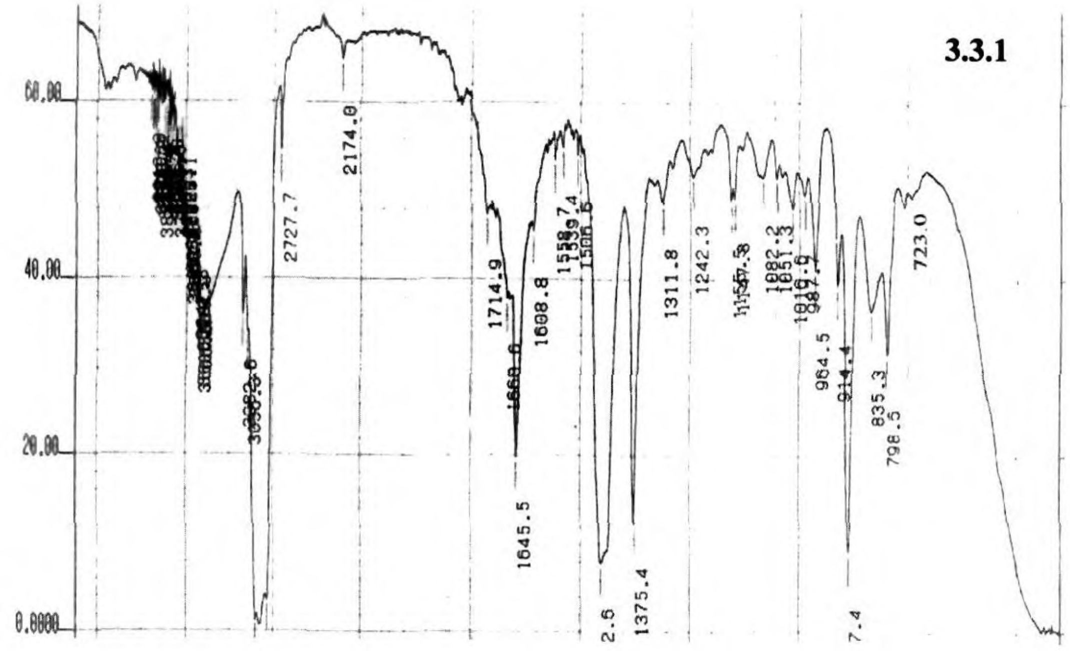
Figure 3.2. Rate of dichlorocarbene modification based on plots of log (C_∞ -C_t) versus time

modification reaction proceeded according to first order kinetics. Rate constant (k) of the reactions calculated were $1.33 \times 10^{-5}\ s^{-1}$, $2.48 \times 10^{-5}\ s^{-1}$ and $3.33 \times 10^{-5}\ s^{-1}$ at 40^0 C, 50^0 C and 60^0 C respectively. The activation energy of reaction calculated from linear plots of log k versus 1/T (where k is the rate constant and T is the temperature in Kelvin) was found to be 39.7 kJ/mole.

3.4.Characterization of dichlorocarbene modified natural rubber

3.4(a) FTIR characterization

The FTIR spectra of NR and modified NR of varying chlorine content are as in Figure 3.3. The band of interest is in the region 1050 cm $^{-1}$ to 740 cm $^{-1}$ and are given in Tables 3.2 and 3.3 As modification proceeded there was change in absorption due to cis double bond (-CH= CH-) and vinyl group (-CH=CH2-) while absorption due to trans double bond remained unchanged. Two new peaks appeared in the modified rubber, one at 780 cm $^{-1}$ due to incorporation of chlorine (-C-Cl) and the other at 1020 cm^{-1} due to presence of cyclopropyl ring. [16,17] The cis double bonds were readily attacked by dichlorocarbene and even at low levels of modification, the intensity due to double bonds was greatly reduced. The IR absorption characteristics are consistent with formation of cyclopropyl rings and loss of unsaturation of natural rubber and the modification is given in scheme 3.1.


60.00
40.00
20.00
0.0000
3030.3
2727.7
2174.0
1714.9
1645.5
1608.8
1375.4
1311.8
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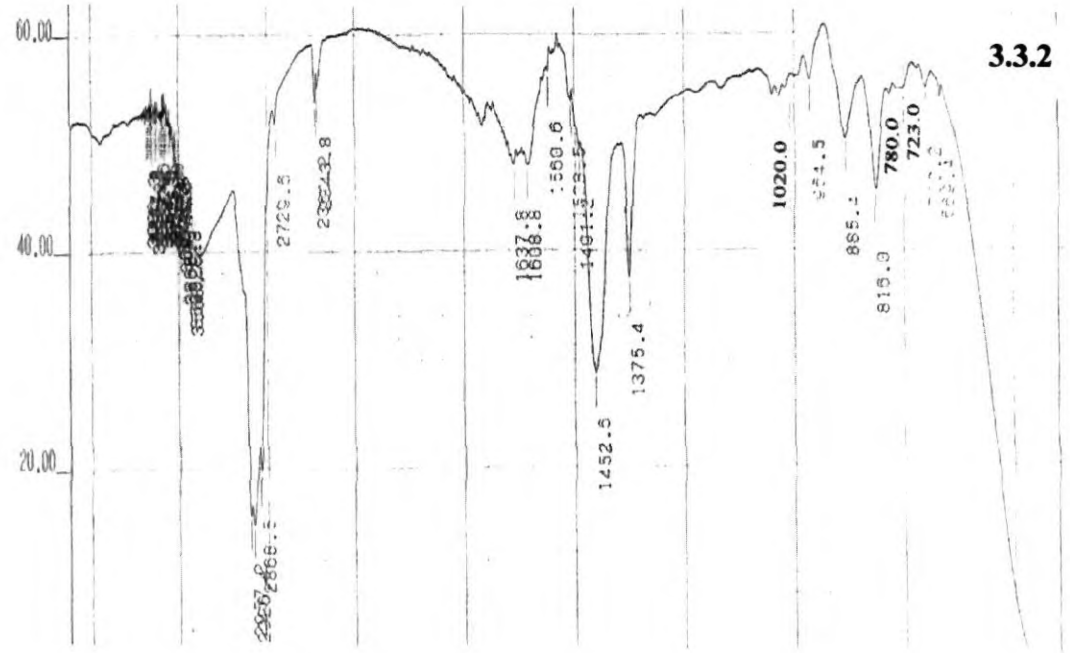
1082.2
1051.3
964.5
914.4
835.3
798.5
723.0

3.3.1


60.00
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3.3.2

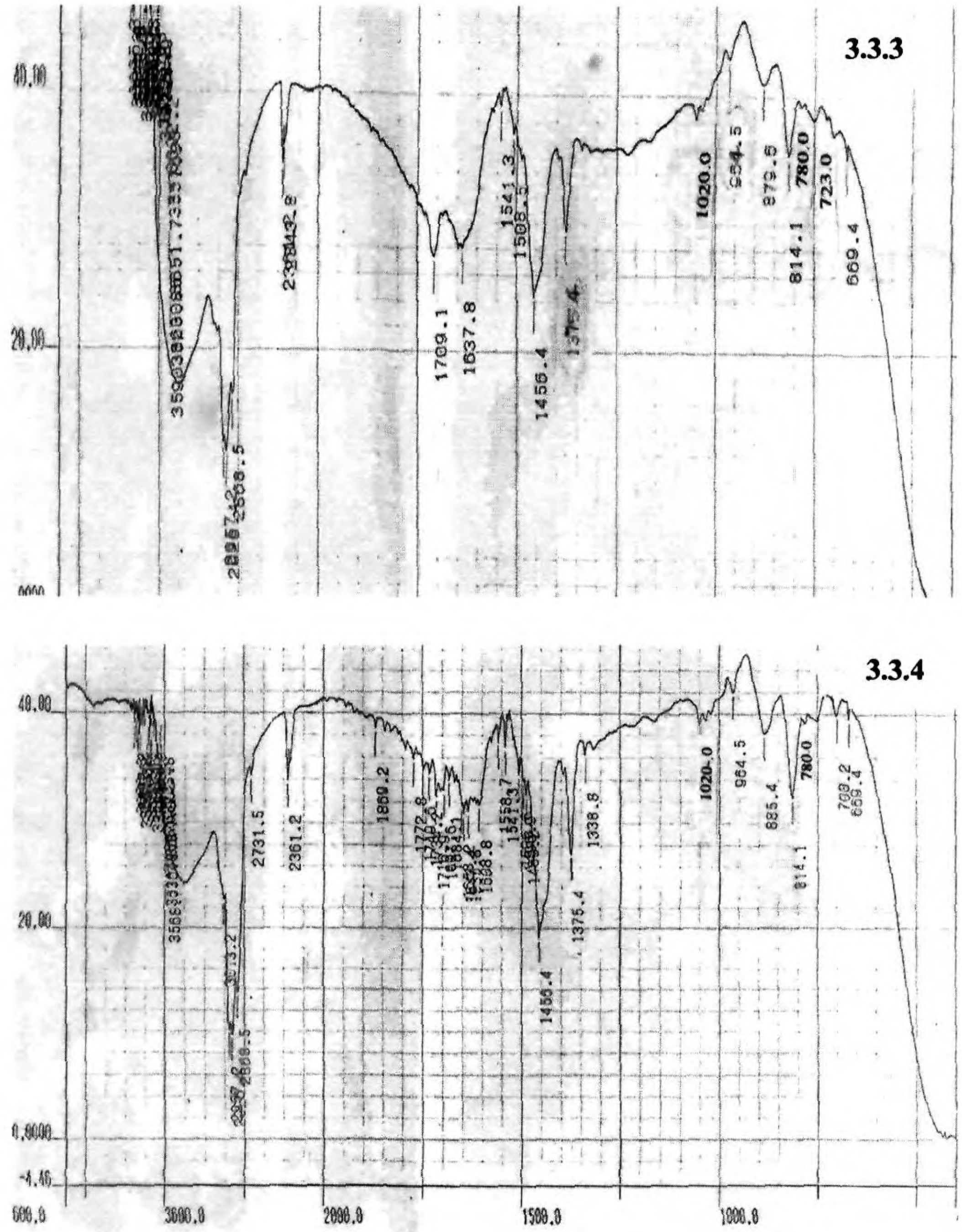


Figure 3.3. FTIR spectrographs of 1-NR and modified NR. of 2 -10%, 3 - 15% and 4 -30% Chlorine content.

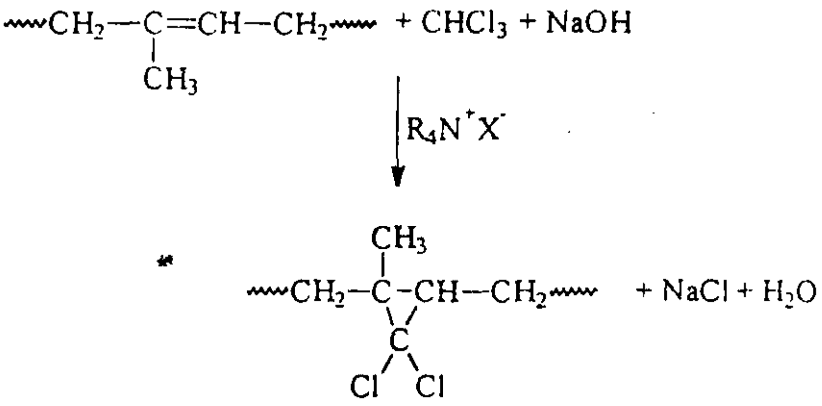
Table 3.2 IR absorption data for dichlorocarbene modified NR

IR absorption wave length,cm-1	NR	DCNR	IR spectral assignment
723	Present	Low intensity	Cis –CH=CH-
914	Present	Absent	$-CH=CH_2$
964	Present	Present	trans–CH=CH-
780	Absent	Present	-C-Cl
1020	Absent	Present	Cyclopropyl ring
1375	Present	Present	$-CH_3$

Table 3.3 IR absorption peak ratios for dichlorocarbene modified NR

Chlorine %	Cis –CH=CH-/ $-CH_3$ 723/1375	C-Cl /$-CH_3$ 780/1375	trans–CH=CH-/ $-CH_3$ 964/1375	Cyclopropyl/- CH_3 1020/1375
15	0.0416	0.0416	0.2183	0.0410
20	0.0196	0.0590	0.2176	0.049
30	723 absent	0.0937	0.2180	0.0968

Scheme 3.1. Chemical change taking place during dichlorocarbene modification



3.4(b) DSC analysis

The thermograms obtained from differential scanning calorimeter are as shown in Figure 3.4. The Tg of unmodified NR is at –63 °C, while that of modified NR of 15%, 25% and 35% of chlorine content are at -5 °C, 19 °C and above 40 °C respectively. This clearly showed the change of NR from rubbery to plastic nature. Increase in Tg considerably increased the stiffness of the polymer. NR changed from a flexible, tacky, elastic material to a hard, non-tacky and very stiff material as modification proceeded. Modified NR of 35% chlorine content was of powdery nature. Processability of NR decreased as the extent of modification increased.

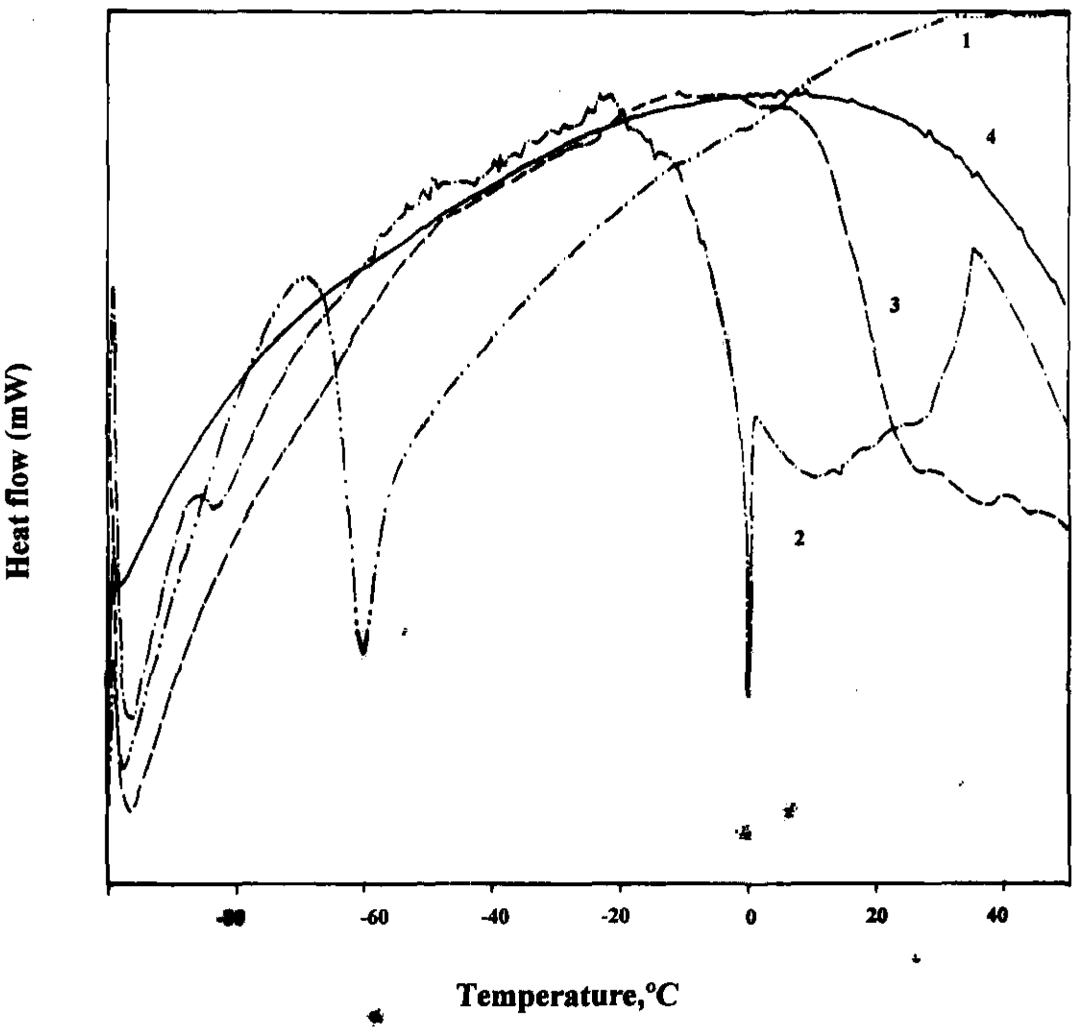


Figure. 3.4 DSC thermograms of 1- NR and DCNR of 2-15%, 3-20 % and 4- 35% chlorine content

3.4(c) Thermogravimetric Analysis

The thermograms of NR, modified NR and Chloroprene rubber (for comparison) are given in Figure 3.5. The decomposition pattern of dichlorocarbene modified NR was comparable with commercial chloroprene rubber. Pure NR (curve 1) showed single stage decomposition with initiation at 395°C. Dichlorocarbene modified NR showed considerable change in decomposition pattern (curve 2, 3 & 4). The decomposition of modified NR took place in two steps. The first degradation temperature appeared around 235 °C while the second degradation temperature appeared around 455 °C for DCNR of 15% chlorine content. The first degradation temperature as well as the second degradation temperature shifted towards the higher temperature side with increased level of chlorination. In fact lower amount of sample was degraded around 395 °C, as chlorination proceeded, compared to pure NR. This was also revealed from time taken for 50% weight drop presented in Table 3.4

Table 3.4. Time taken for 50% weight drop for NR and modified NR of varying chlorine content

Material	Curve	Time for50% weight drop (minutes)
NR	1	37.0
Modified NR (15% Cl)	2	40.1
Modified NR (20% Cl)	3	42.3
Modified NR (35% Cl)	4	43.7
Chloroprene	5	43.7

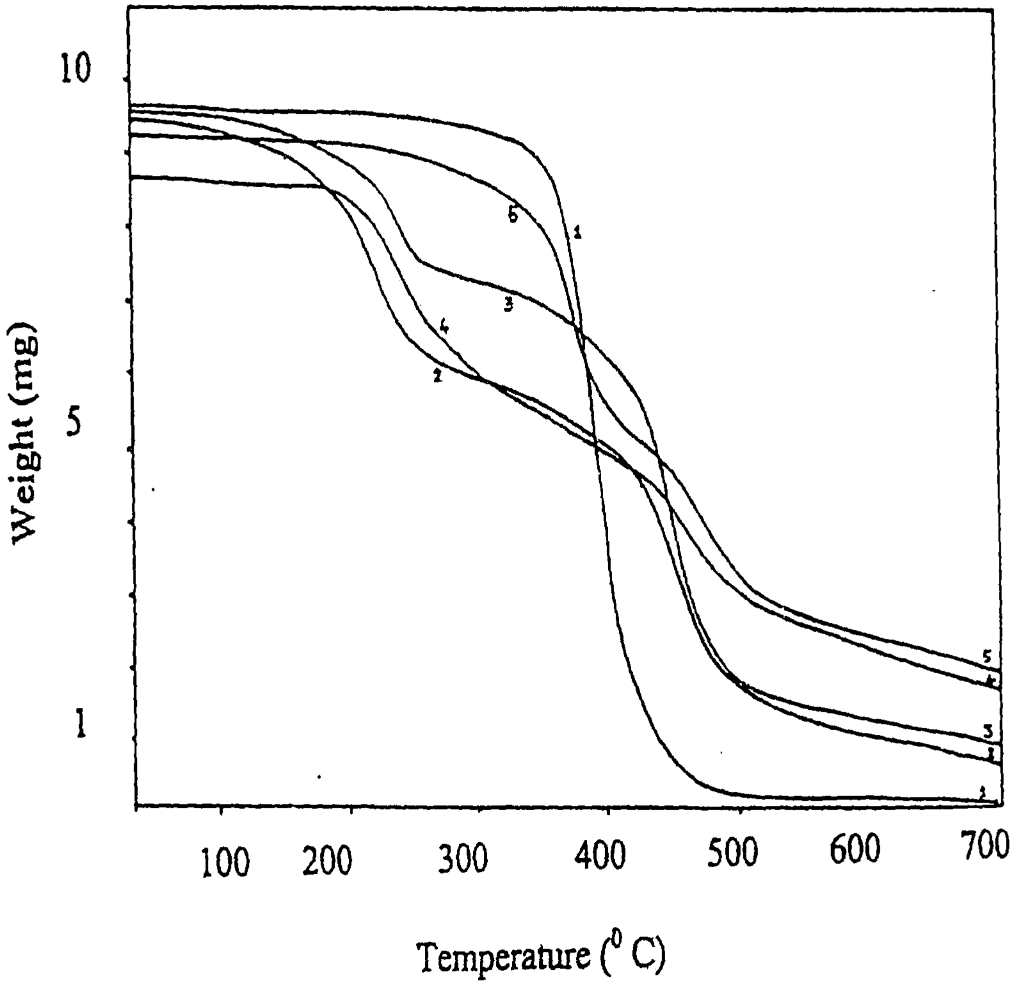


Figure 3.5. Thermograms of 1-NR, DCNR of chlorine content 2-15%, 3-20% , 4-30% and 5- chloroprene.

3.5. Cure characteristics and technological properties

Figure 3.6 shows the cure charts of NR and modified NR compounds containing two phr of dicumyl peroxide (DCP). Unmodified NR showed very little torque rise, while modified NR of 20% chlorine content showed higher torque rise. The stress-strain chart of molded pieces of NR and modified NR are given in Figure 3.7. It was seen that modified NR containing 20% chlorine showed brittle nature, which is in agreement with the physical appearance and the Tg values.

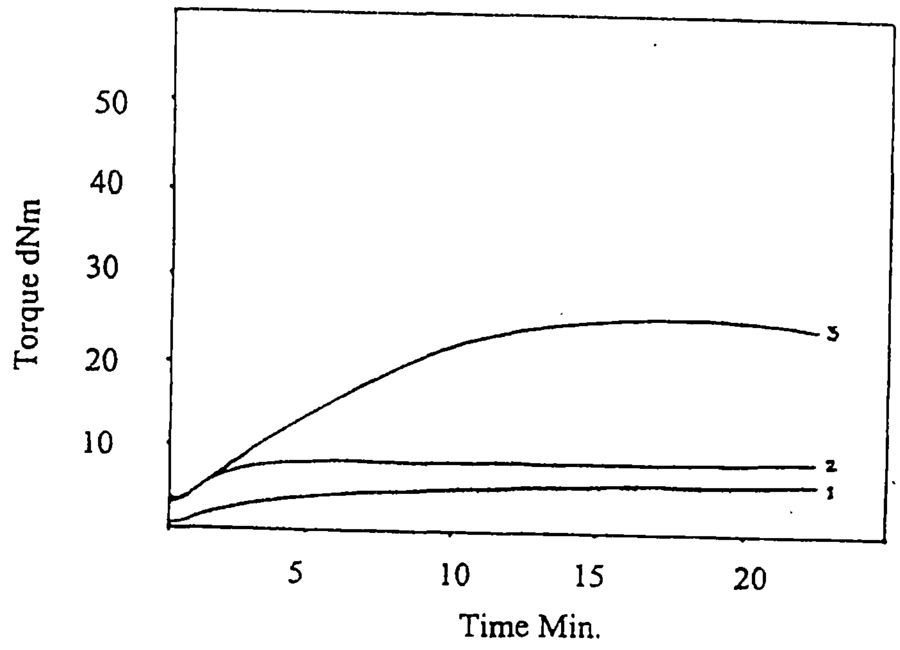


Figure 3.6. Rheographs of compounds (peroxide cure) of 1-NR, 2- DCNR (10% Cl) and 3- DCNR (20% Cl) at 160°C.

The physical properties of the peroxide vulcanized samples are as shown in Table 3.5. The peroxide vulcanized NR gave only very low tensile strength mainly due to the formation of C-C bond. Modified NR exhibited substantially better tensile strength and modulus than pure NR and increased as chlorine content increased. However, there was a progressive decrease in elongation at break, with increase in level of modification. Due to the introduction of polar groups and loss of flexibility at higher levels of chlorination, resilience showed a decrease as modification proceeded. Hardness considerably increased with the chlorine content.

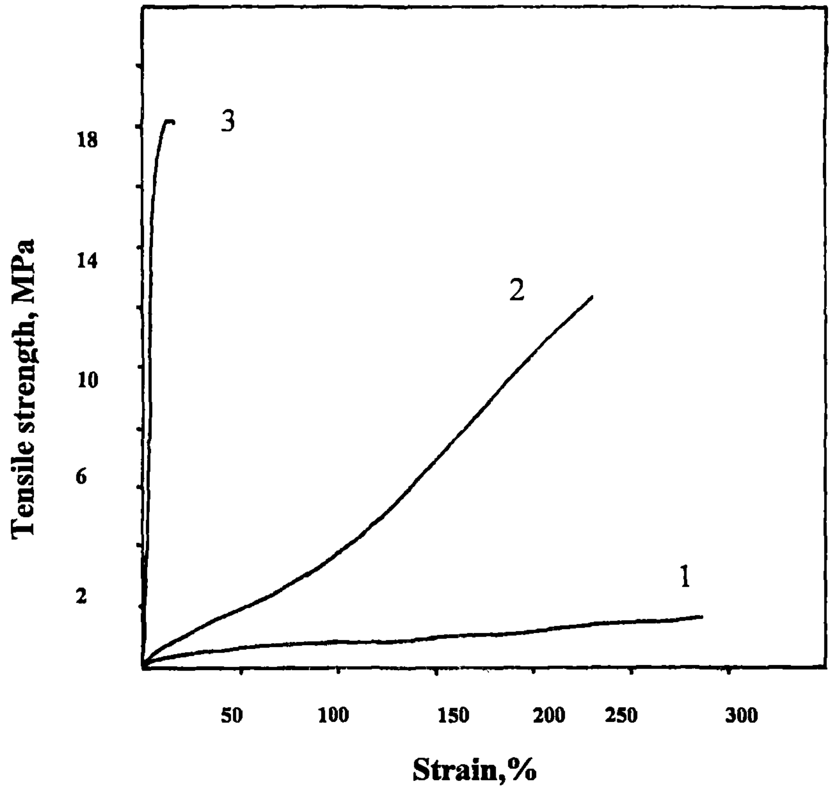


Figure 3.7. Stress- strain chart of peroxide vulcanisates of 1-NR, and DCNR of 2- 10% and 3- 20% Chlorine content.

Table 3.5. Physical properties of peroxide vulcanizates of NR and modified NR

Properties	NR	Modi.NR,10%Cl	Modi.NR,20%Cl
Tensile strength, MPa	1.6	12.2	18.1
Modulus, 100%, MPa	0.54	3.8	-
Modulus, 200%, MPa	1.40	10.3	-
Elongation at break, %	280	230	10
Hardness, Shore A	36	66	99
Resilience, %	63	45	40

3.6 Thermal aging characteristics

Tensile properties of the vulcanizates of NR and modified NR after aging in an air-circulating oven at 70°C for 5 days are as shown in Table 3.6. Tensile strength and elongation at break of the unmodified NR was improved due to the increased level of cross-linking possible at higher temperature in peroxide cure. Vulcanizates of modified NR showed degradation probably due to the liberation of HCl during aging.

Table 3.6 Physical properties of peroxide vulcanizates of NR and modified NR after aging

Properties	NR	Modified NR, 10% Cl	Modified NR, 20%Cl
Tensile strength, MPa	3.7	5.8	8.9
Elongation at break, %	370	110	2

3.7. Solvent swelling

Table 3.7 shows the swelling nature of modified NR in a non polar solvent, toluene and in a polar solvent, methyl ethyl ketone (MEK) at room temperature for 48 hours of immersion time. It was shown that weight of toluene absorbed per gram was highest for unmodified NR, and it reduced with increase in modification. This was due to the increased polar nature of the dichlorocarbene modified NR. This was again obvious from the swelling nature in MEK. Modified NR of higher chlorine content swelled more than unmodified NR, due to polarity introduced by chlorine.

Table 3.7. Weight of solvent absorbed per gram of peroxide vulcanizates of NR and modified NR

Solvent	NR	Modi.NR,10%Cl	Modi.NR,20%Cl
Toluene	3.15	1.42	0.69
MEK	0.42	0.52	0.69

3.8.Oil swelling

The percentage weight of oil absorbed per gram, by the peroxide vulcanized NR and modified NR, immersed in ASTM oil Nos. 1, 2 &3 for 5 days at room temperature, 70 °C and 100 °C are as given in Table 3.8. It was clear that dichlorocarbene modification considerably improved the oil resistance of NR. Modified NR of 20% chlorine content showed oil resistance comparable with that of HNBR of 36% ACN content at room temperature.

Table 3.8. Percentage weight of oil absorbed by peroxide cured NR, modified NR and HNBR vulcanizates

	Samples	ASTM No:		
		1	2	3
At room temperature (28°C)	NR	61.6	81.8	244.9
	DCNR(10%Cl)	1.6	4.2	10.7
	DCNR(20%Cl)	0.5	2.6	4.2
	HNBR	0.7	2.9	4.6
At 70 °C	NR	120.4	190.2	265.6
	DCNR (10%Cl)	4.5	17.7	83.5
	DCNR (20%Cl)	2.0	13.9	25.8
	HNBR	0.9	6.9	18.7
At 100 °C	NR	127.3	215.8	476.2
	DCNR (10%Cl)	5.9	59.0	96.7
	DCNR (20%Cl)	2.9	16.5	38.6
	HNBR	2.8	10.7	21.0

3.9.Flame resistance

Vulcanizates of DCNR of varying chlorine content were tested as per UL 94 by vertical burn test. DCNR of 35% chlorine content qualified UL94 V-0 (Best) Rating. That is burning stopped within 10 seconds after two applications of ten seconds each of a flame to the test bar and no flaming drips observed. DCNR of 25% chlorine content qualified UL94 V-1 (Good) Rating. That is burning stopped within 60 seconds after two applications of ten seconds each of a flame to the test bar and no flaming drips observed. As per the UL 94 flammability rating, these two belong to self-extinguishing grade. DCNR of 15% and lower chlorine content continued burning after the burner flame application and flaming drips ignited the cotton placed below the specimen, but took more time to complete burning than pure NR, indicating improvement in flame resistance. The improvement in flame resistance was due to the inclusion of chlorine into the NR molecule through the cyclopropyl group.

3.10 DCNR /HNBR blends

Blends of DCNR of 15% chlorine content and HNBR were prepared as per the formulations given in Table 3.9 and DCP cure was given. Addition of DCNR improved the flow characteristics of the compound. The cure properties of the mixes obtained from MDR cure meter at 160 °C is given in Table 3.10. It was seen that addition of DCNR reduced the torque minimum and torque maximum. Table 3.11 gives the technological properties of the mixes vulcanized at 160 °C by compression molding. It was seen that HNBR gave a lower tensile strength by peroxide vulcanization. Higher tensile strength for HNBR peroxide vulcanizates were reported in presence of co_agents or fillers.[18-19] Incorporation of DCNR into HNBR yielded better tensile strength.

Table 3.9. Formulations of HNBR/DCNR mixes

Ingredients	Parts per hundred HNBR rubber			
HNBR	100	100	100	100
DCNR	-	7	14	25
DCP	6	6	6	6

Table 3.10. Cure characteristics of peroxide vulcanizates of HNBR/DCNR blends at 160°C.

Properties	**Parts of DCNR**			
	0	**7**	**14**	**25**
Torque min., dNm	3.21	2.88	2.73	2.48
Torque max., dNm	26.00	23.59	22.57	21.50
OCT, 160°C, min.	13.21	10.28	10.58	10.57
tS_2, min.	0.90	0.94	0.97	0.92

Table 3.11. Physical properties of HNBR/DCNR vulcanizates

Property	**Parts of DCNR**			
	0	**7**	**14**	**25**
Tensile strength, MPa	1.4	4.3	4.5	8.3
Modulus, 100%, MPa	1.34	1.36	1.39	2.22
Modulus300%, MPa	-	3.48	3.80	6.90
Elongation at break, %	110	330	340	345
Tear strength, Kg/cm	9.2	14.6	14.8	22.3
Compression set, % (70° C/22h)	5.3	14.8	16.5	21.3
Heat buildup, ΔH, °C	13	17	23	29

Elongation at break and tear strength also improved considerably by the incorporation of DCNR. Hardness showed higher value at 25 parts loading of DCNR into HNBR mix. These observations indicated that there was some interaction between HNBR and DCNR, there_by acting as a coagent, that lead to a more uniform cross linking including interfacial cross linking which improved the physical properties.

3.10(a) Thermal aging

Table 3.12 shows the retention of tensile properties of the HNBR/DCNR vulcanizates after aging at 70°C for 5 days in an air oven. Tensile strength and elongation at break were improved after aging for all the vulcanizates. This indicated that the aging behavior of HNBR was not affected by the incorporation of DCNR.

Table 3.12. Physical properties of HNBR/DCNR vulcanizates after aging.

Properties	Parts of DCNR			
	0	**7**	**10**	**25**
Tensile strength, MPa	1.6	4.5	5.3	10.1
Elongation at break, %	115	340	365	380

3.10(b) Oil aging

By dichlorocarbene modification, NR improved its polar nature. Table 3.13 shows the percentage weight of oil absorbed per gram of the vulcanizates of HNBR/DCNR, immersed in ASTM oils at three different temperatures for 5 days. It was clear that the oil aging characteristics of HNBR was not adversely affected by the addition of DCNR even at higher temperature. This was due to the increased polarity of NR by the modification, which enabled better mixing of the two rubbers.

Table 3.13. Percentage weight of ASTM oils absorbed by HNBR/DCNR vulcanizates

Temperature	ASTM No:	**Parts of DCNR**			
		0	7	**14**	**25**
Room temperature (28°C)	1	0.7	0.6	0.4	0.3
	2	2.9	2.1	2.0	1.3
	3	4.6	4.3	4.1	3.9
70 °C	1	0.9	0.5	0.4	0.3
	2	6.9	4.3	3.6	3.0
	3	18.7	14.7	13.3	12.8
100 °C	1	2.1	1.9	1.4	1.3
	2	10.7	10.3	9.9	9.6
	3	21.0	20.6	20.4	20.0

3.10(c) Ozone aging

Photographs of ozone irradiated surfaces of HNBR and HNBR/DCNR blends for 50 hours in an ozone chamber are given in Figure 3.8. It was seen that ozone resistance of HNBR was unaffected by blending with DCNR up to 25 parts.

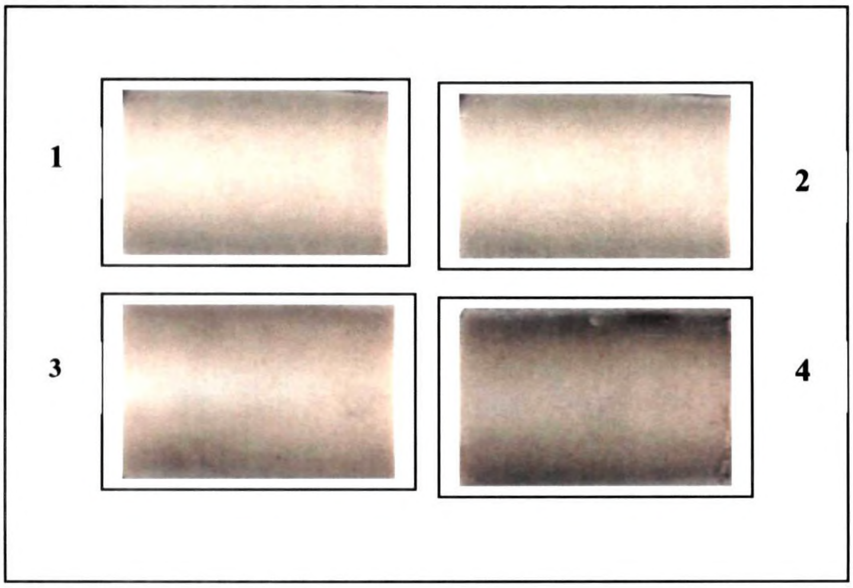


Figure 3.8. Ozone irradiated surfaces of 1. HNBR and HNBR/DCNR blends containing 2- 7 parts , 3-14 parts and 4- 25 parts of DCNR

3.10(d) Filled blends of HNBR/DCNR

HNBR and blends of HNBR/DCNR in 4:1 ratio filled with 30 parts of HAF black were prepared as per Table 3.14 and properties were evaluated. Cure characteristics are given in Table 3.15. It was observed that the torque maxima increased by the addition of DCNR. Torque minimum was also higher than pure HNBR, probably due to the hard nature of DCNR. Optimum cure time also showed higher value.

Table 3.14 Formulation of filled HNBR and HNBR/DCNR blends.

Ingredients	Mix	
	Hf	**HDf**
HNBR	100	100
DCNR	-	25
Dicumyl peroxide	6	6
Zinc oxide	5	5
Stearic acid	1	1
A/o 4010[1]	1	1
A/o HS[2]	1	1
HAF black	30	30
Dioctylphthalate	3	3

1-N phenyl N isopropyl paraphenylene diamine
2- Polymerised 1,2 dihydro 2,2,4 trimethyl quinoline

The physical properties of the black filled vulcanizates are as given in Table3.16. Carbon black filled HNBR showed better tensile properties and aging characteristics in comparison with DCNR mixed vulcanizate. (Table 3.17) The latter showed better tear strength, higher hardness and lower heat build up. It is interesting to observe that the percentage swell in fuel and oil was better for the blend probably due to the interactions possible between the two, which restricted the swelling. (Table 3.17)

Table 3.15 Cure characteristics of filled HNBR and HNBR/DCNR blend.

Mix.	CRI	MH, dNm	ML, dNm	t90, min.	ts2, min.
Hf	11.13	14.11	2.13	11.37	2.38
HDf	10.64	24.08	7.95	17.48	8.07

Table 3.16 Physical properties of filled HNBR and HNBR/DCNR blends.

Properties	**Hf**	**HDf**
Tensile strength, MPa	27.9	19.6
Elongation at break, %	370	90
Tear strength, Kg/cm	34.2	43.5
Resilience, %	55	48
Hardness, Shore A	60	78
Compression set, %, 150°C/22h	42.2	56.4
Compression set, %,125°C/22h	41.0	51.3
Heat build up, ΔH, °C	44	39
Dynamic set, %	1.99	1.45

Table 3.17 Aging properties of filled HNBR and HNBR/DCNR blends.

a) Air aging 150°C/24h

Properties	**Hf**	**HDf**
Tensile strength, MPa	27.7	17.0
Elongation at break, %	450	80
Tear strength, Kg/cm	45.9	31.1
Hardness, Shore A	64	84

b)Fuel aging. ASTM fuel C, at room temperature, 5 days

Properties	**Hf**	**HDf**
Fuel absorbed per gram	0.54	0.49
Tensile strength, MPa	26.0	16.7
Elongation at break, %	340	75

c) Oil aging, ASTM No;2 at room temperature, 5 days

Properties	**Hf**	**HDf**
Tensile strength, MPa	30.1	19.6
Elongation at break, %	480	110

d) Oil swelling, percentage of oil absorbed.

Temperature	**ASTM Oil No:**	**Hf**	**HDf**
At room temperature	1	-	-
	2	0.8	0.5
	3	5.4	4.5
At 70°C	1	-	-
	2	4.0	3.8
	3	9.4	8.3
At 100°C	1	-	-
	2	5.3	5.1
	3	11.2	11.0

3.11. Conclusion.

Polar nature can be imparted to NR by dichlorocarbene modification. Glass transition temperature of the polymer increased with the extent of modification. Modified NR showed different degradation pattern and took more time for 50% degradation than NR indicating better heat stability. DCNR of 10-20% chlorine content gave better physical properties with peroxide vulcanization than peroxide vulcanized NR. Vulcanizates of DCNR with 15% and above chlorine content exhibited oil aging properties comparable to that of HNBR of 36% ACN content at room temperature. DCNR containing 25% and above chlorine content showed flame retardant or self-extinguishing nature. Due to the better polar nature of DCNR, it could be blended with polar rubber like, HNBR without affecting its oil, ozone and heat aging characteristics and it acted as a coagent for peroxide vulcanization of gum HNBR.

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CHAPTER 4

BLENDS OF NR AND HNBR
PREPARATION, CHARACTERIZATION AND MECHANICAL PROPERTIES

4.1.Introduction

Elastomeric blends have been widely used in many commercial applications[1,2] particularly in automobile tires, vibration dampers, and products used in the oil field and weather resistant applications over the past few decades. By the process of blending, the characteristic properties of the polymers can be combined to get new materials with tailored properties more rapidly and economically.[3,4] For example, ethylene propylene based elastomers are usually blended with diene based elastomers to improve oxidation and ozone resistance while retaining cost and property advantages of the latter.[5,6] Similarly natural rubber is blended with acrylonitrile rubber for applications requiring resistance to swelling by oils, damping and good physical properties.[7]

Only very few polymers form truly miscible blends.[8-11] Most of the elastomers are incompatible with one another. Properties of polymer blends depend on many factors like blend ratio, component polymer properties, viscosity ratio, morphology, interaction between the components during mixing and miscibility of the polymers. In elastomeric blends, true miscibility may not be essential for getting good rubber properties.[12,15] The overall physico chemical properties of an immiscible blend are decided mainly by two factors.[16-17] One, a proper interfacial tension between the polymer phases which leads to a phase size small enough to allow the material to be considered as macroscopically homogeneous and two, an interfacial adhesion, strong enough to assimilate stress and strain without disruption of the established morphology.

Natural rubber (NR) is the only naturally occurring elastomer which find extensive application in variety of products.[18] The combination of properties like, high tensile strength with a high rebound resilience, very good low temperature flexibility, excellent dynamic properties, very low heat build up and low cost qualify, it as a good elastomer in many engineering and other applications, especially, for products which function in dynamic applications like, tires, vibration and suspension dampers, etc. However, NR vulcanizates have very poor resistance against oil, ozone and thermal oxidation. Hydrogenated nitrile rubber (HNBR) a versatile engineering elastomer is widely used in vibration dampers, timing belts, power transmission belts and bearings, because of its ideal balance of properties like, excellent heat and oil resistance coupled with good mechanical properties.[19-22] It combines the oil and fuel resistance of nitrile rubber (NBR) with heat and oxidation resistance of ethylene propylene diene rubber (EPDM). Blends of NR and HNBR would be ideal choice for application requiring good high temperature oil aging characteristics in dynamic conditions with low temperature flexibility like, seals, gaskets, etc and for products requiring good oil and ozone resistance at high temperature.

Blends of NR with polar/ saturated rubbers may result in materials with inferior physical properties due to the incompatibility arising from the difference in solubility parameter/cure rate.[23-29] These problems can be mitigated to an extent by the use of suitable modifiers that reduce the interfacial tension between the polymers, proper blending methods and by judicious choice of curatives. Arjunan and Kusznir[25] have shown that using a dual mode of compatibilizer, which, while having composition similar to one phase will interact or chemically react with the other phase, can compatibilize immiscible blends. Successfully compatibilized blends of chloroprene rubber (CR) and EPDM have been reported using ethylene maleic – anhydride- acrylic acid ter polymer and methyl methacrylate grafted EPDM.[24] Rankin[26] has shown that the difficulty in the covulcanization of blends of EPDM with NR and IR can be overcome by using chlorinated EPDM containing 1.5 to 2% chlorine in ethylene norborane. Compatibilization of blends of NBR and styrene butadiene rubber (SBR) using dichlorocarbene modified SBR has been reported recently.[27]

This chapter reports the results obtained from the preparation of blends of NR with HNBR. Different blend ratios, effect of vulcanization systems and fillers were studied. The effect of a chemically modified form of NR, dichlorocarbene modified NR (DCNR) was investigated in 50/50 blend to modify the blend properties.

4.2.Effect of blend ratio

Blends of NR/HNBR at different blend ratios were prepared as per the formulation given in Table 4.1. Table 4.2 shows the cure characteristics of the NR/HNBR blends at different ratios. Pure HNBR showed higher values of scorch time and torque at

120°C than NR. In the case of blends, values increased with the HNBR ratio. Optimum cure time at 150°C was also higher for HNBR. Blends showed higher OCT with increased HNBR content. Table 4.3 shows the technological properties of the blends. The tensile strength and modulus, 300% values of the blend were inferior to both NR and HNBR showing that blend was not miscible in any of these blend ratios as there was considerable difference in their solubility parameters and saturation level. The blends recorded higher values of tear strength and resilience in comparison with HNBR and higher hardness in comparison with NR. Higher values of compression set and heat build up indicated the immiscibility of the blend, which was expected. Among the blends, 50/50 blend maintain comparatively better mechanical properties and hence, this blend ratio was chosen for further study.

Table 4.1 Formulation of the mixes

Ingredients	**NR**	**75/25NH**	**50/50NH**	**25/75NH**	**HNBR**	**NHC**
NR	100	75	50	25	0	50
HNBR	0	25	50	75	100	50
DCNR	0	0	0	0	0	(3,7,10)
Zinc Oxide	5	5	5	5	5	5
Stearic Acid	1	1	1	1	1	1
TMTD	1.5	1.5	1.5	1.5	1.5	1.5
MBT	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5

Table 4.2 Blend ratio - Cure characteristics of the mixes

Properties	**NR**	**75/25NH**	**50/50NH**	**25/75NH**	**HNBR**
Scorch time, 120 °C, (min.)	16.8	12.3	11.9	16.1	47.9
Torque min., dNm	7.9	5.0	10.7	14.4	47.2
Torque max., dNm	16.9	13.7	30.6	64.5	112.0
OCT/150 °C, (min.)	5.5	5.8	6.0	10.5	21.7

Table 4.3. Blend ratio - Physical properties of NR, HNBR and blends of NR/HNBR

Properties	NR	75/25NH	50/50NH	25/75NH	HNBR
Tensile strength, MPa	18.0	10.7	10.6	14.2	21.1
Elongation at break, %	725	745	740	735	720
Modulus 100%, MPa	0.85	0.88	0.93	1.04	1.10
Modulus 300%, MPa	1.83	1.55	1.52	1.43	1.45
Tear strength, Kg/cm	20.8	20.6	20.5	19.1	16.9
Hardness, Shore A	37	40	44	45	49
Resilience, %	72	70	69	67	65
Compression set at 70 °C /22h, %	8.3	26.9	46.2	69.4	30.1
Heat build up, °C	6	16	56	57	25
Dynamic set, %	0.08	2.24	10.19	10.36	2.27

4.3.Effect of DCNR in 50/50 blends

4.3.a) Chlorine content of DCNR

DCNR of 5%, 15% and 25% Chlorine content were incorporated into 50/50 blends of NR/HNBR at 7 parts loading. DCNR of higher percentage of chlorine content were very difficult to incorporate due to its very hard and non-tacky nature. Table 4.4 gives the cure characteristics of the blends. Figure.4.1 is the Monsanto rheographs of the blends at 150 °C. Blend containing DCNR of 15% chlorine content exhibited higher torque maxima showing the possibility of higher cross linking. Scorch time at 120°C and cure time at 150°C were also higher for blend containing DCNR of 15% chlorine content.

Table 4.5 shows the physical properties of the blends. Better physical properties were obtained for blend containing DCNR of 15% chlorine content. Tensile strength and tear strength were higher for blend containing DCNR of 15% chlorine content. Modulus, showed only slight variation with the chlorine content of DCNR. The blend containing DCNR of 15% chlorine content gave a higher elongation, lower heat build up and lower compression set as compared to DCNR of higher and lower chlorine content. So it appears that in presence of DCNR of 15% chlorine content, there is the possibility of polar interactions that lead to the formation of higher cross-links in the blends. Chlorine content of 5% is probably not sufficient to have the required level of polar interactions. Similar effects were observed by dichlorocarbene modified styrene butadiene rubber (DCSBR) in SBR/ NBR blends.[28]

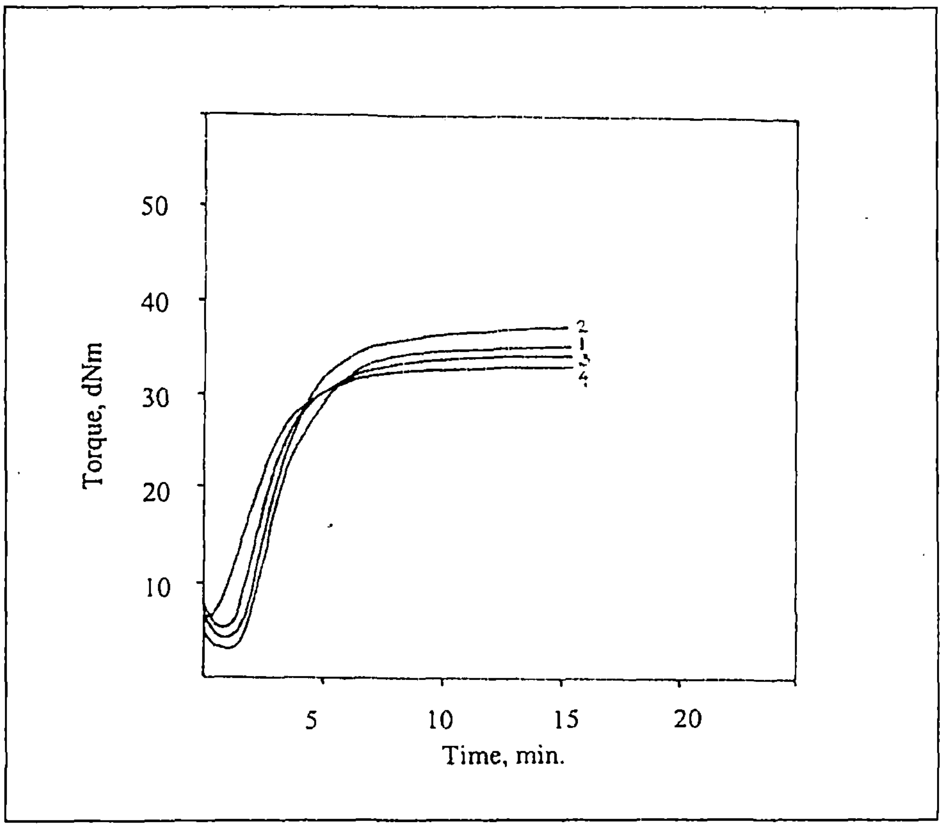

Figure 4.1 Monsanto Rheographs at 150°C of 1-50/50 blends of NR/HNBR and blends containing 7 parts of DCNR of 2-15%, 3-5% and 4-25% chlorine content.

Air aging properties were also better for blend containing DCNR of 15% chlorine content. (Table 4.6) This was probably due to the better interactions possible with the blend constituents. Hence,for further studies, DCNR containing 15 % chlorine only used.

4.3.b) Effect of DCNR loading

Figure 4.2 is the Monsanto rheographs of 50/50 blends of NR/HNBR containing DCNR of 15% of chlorine content at 3, 7 and 10 parts loading and cure characteristics are given in Table 4.4. The scorch time at 120°C was lower than pure blend and was increased with the loading of DCNR. OCT at 150°C was increased with DCNR loading. The torque maxima increased as loading of DCNR increased up to 7phr. With further increase in concentration of DCNR, the blend recorded a lower torque.

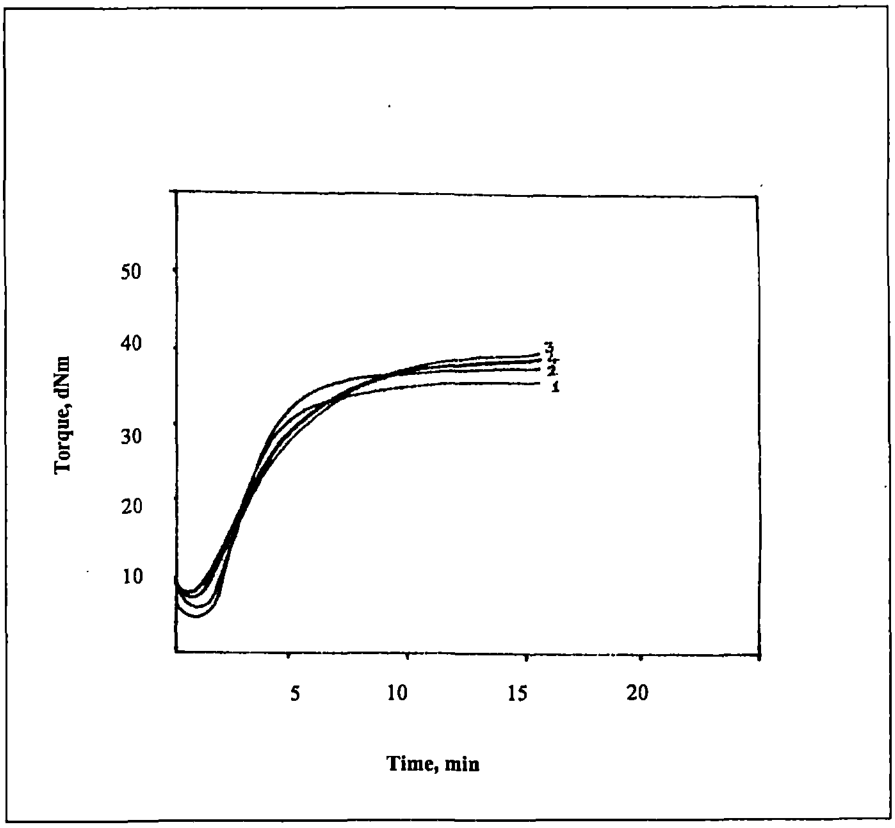

Figure 4.2. Monsanto rheographs at 150°C of 50/50 blends containing 1-0, 2-3, 3-7 and 4-10 parts of DCNR.

Table 4.4 Cure characteristics of 50/50 blend containing DCNR.

Properties	Parts of DCNR					
	0	7^a	7^b	3^c	7^c	10^c
Scorch time at 120°C, min.	11.9	8.9	6.6	8.8	9.8	9.8
Min.torque, dNm	10.7	16.2	28.6	18.8	16.9	16.8
Max.torque, dNm	30.6	29.4	113.0	37.6	39.8	38.1
OCT/150°C, min.	6.00	8.95	5.86	6.25	9.00	9.20

a – DCNR of 5% chlorine, b- DCNR of 25% chlorine, c- DCNR of 15% chlorine

Table 4.5 shows the technological properties of the blends. Tensile strength increased with increase in DCNR content and showed maximum value for 7 parts loading. EB values showed a slight reduction. Modulus increased with DCNR loading, indicating more cross linking in the presence of DCNR. Tear strength, hardness and resilience also showed improvement with the addition of DCNR. Considerable reduction in compression set and heat build up values indicated interaction in the presence of DCNR thereby imparting more cross linking and improving the properties. As TMTD accelerated sulphur vulcanization of NR was faster as compared to HNBR, there was chance for diffusion of sulphur and accelerator to NR phase, resulting in more cross links in one phase. Thus the rubber layer in the interface was not cross linked to the same level as the bulk. The phase structure stability of blends of thermodynamically incompatible polymers are reported to be increased by introducing block or graft copolymers comprising the fragments of macromolecule identical in structure with homopolymers being mixed.[28] As DCNR has the same backbone structure of NR, it retained in NR phase and its chlorine part interact with the acrylonitrile part of HNBR. So in presence of DCNR, as there was interaction with HNBR and NR, there was the possibility of covulcanization. This covulcanization could result in lower heat build up and compression set and higher tensile and tear properties. Incorporation of DCNR improved all the properties and showed highest increment with 7 parts DCNR, indicating most effective interaction at this loading.

Table 4.5 Mechanical properties of 50/50 blend containing DCNR.

Properties	Parts of DCNR					
	0	7[a]	7[b]	3[c]	7[c]	10[c]
Tensile strength, MPa	10.6	11.9	10.3	11.9	12.3	12.1
Modulus 100%, MPa	0.93	1.11	1.16	1.12	1.14	1.15
Modulus 300 %, MPa	1.52	1.56	1.69	1.56	1.58	1.59
Elongation at break, %	740	640	540	730	690	690
Tear strength, kN/m	20.5	20.9	20.6	21.8	23.9	22.9
Hardness, Shore A	44	44	47	45	45	46
Resilience, %	69	69	63	70	70	70
Compression set, %(22 h 70 °C)	46.2	42.6	44.8	40.9	39.0	39.8
Heat build up, ΔH, °C	56	65	71	48	47	48
Dynamic set, %	10.19	12.01	16.68	9.37	8.89	9.06

a – DCNR of 5% chlorine, b- DCNR of 25% chlorine, c- DCNR of 15% chlorine

Aging characteristics of the blends given in Table 4.6 also showed that better retention of properties were obtained at 7 parts loading. Hence for further studies, DCNR containing 15 % chlorine content at 7 parts loading only was used.

Table 4.6. Properties of 50/50 blend containing DCNR after aging at 120 °C, 5 days

Properties	Parts of DCNR					
	0	7[a]	7[b]	3[c]	7[c]	10[c]
Tensile strength, MPa	1.9	2.7	1.9	3.8	6.1	5.8
Modulus,100%, MPa	1.64	1.76	-	1.68	2.04	2.10
Modulus 300 %, MPa	1.88	-	-	2.04	3.96	3.90
Elongation at break, %	305	290	95	360	360	330

a – DCNR of 5% chlorine, b- DCNR of 25% chlorine, c- DCNR of 15% chlorine

4.4. Effect of method of blending

Variation in mixing technique can improve the properties of the blends. It was reported that the degree of cross linking of one of the elastomer can be considerably increased by introducing all the components of vulcanizing system into it and then mixing the master batch with the other elastomer.[30,31] Here for the preparation of 50/50 blends two methods were applied using the cure system given in Table 4.1. In method A, the rubbers were first blended together and then curatives were added. In method B,

Table 4.7. Effect of method of blending on mechanical properties of 50/50 blends.

Properties	**A**	**A** with 7parts DCNR	**B**	**B** with 7parts DCNR
Tensile strength, Mpa	10.6	12.3	10.9	12.4
Modulus, 100%, Mpa	0.93	1.14	0.96	1.20
Modulus, 300%, Mpa	1.52	1.58	1.54	1.59
Elongation at break, %	740	690	735	690
Tear strength, Kg/cm	20.5	23.9	21.0	24.3
Hardness, Shore A	44	45	45	46
Resilience, %	69	70	69	70
Compression set at 70 °C /22h, %	46.2	39.0	45.9	38.6
Heat build up	56	47	55	46
Dynamic set, %	10.19	8.89	10.01	8.69
After aging at 120 °C for 5 days				
Tensile strength, MPa	1.9	6.1	1.9	6.1
Modulus, 100%, MPa	1.6	2.0	1.6	2.1
Modulus, 300%, MPa	1.9	3.5	1.9	3.9
Elongation at break, %	305	350	310	360

master batches of the rubbers were prepared and then cross-blended. In both cases, for preparing the modified blend, DCNR was first blended with HNBR. The technological properties are given in Table 4.7. It was seen that even though both methods gave comparable properties, slight improvement was observed in method B probably due to the better miscibility of curatives in individual phases. Method B was used for further studies.

4.5. Effect of vulcanization system

The cure system plays an important role on the properties of the vulcanizates of elastomers and their blends.[32,33] For blends of elastomers differing in polarity, the deficiencies which arise from maldistribution of cross links can be alleviated by selection of appropriate cure system. [34-36] Provided a suitably higher level of cross-linking is achieved in both phases, it seems that there will also be adequate cross-linking between the elastomers. Hence,a judicious choice of curatives can bring about an even distribution of cross-links, which results in improved physical properties to the blend. Four cure systems applied for 50/50 blends were investigated in gum vulcanizates to establish an even distribution of cross-links in both phases of the blend. The cure systems used were (1) CBS/S· (2) TMTD/ MBT/S for NR and (3) DCP (4) TMTD/ MBT/S for HNBR. Master batches of NR and HNBR were prepared as per the formulation given in Table 4.8 and cross-blended to get 50/50 blends. Blends were identified as in Table 4.9.

The vulcanization systems selected for NR were an efficient vulcanization (EV) and a semi EV system. The accelerators investigated were the commonly used sulphenamides, CBS (N- cyclohexylbenzothiazole- 2 sulphenamide), TMTD (tetramethylthiuram disulphide) and MBT (mercaptobenzothiazole). Semi EV system selected was 1:1 sulphur : CBS system and EV system selected was TMTD/MBT with 0.3 parts of sulfur. For HNBR both peroxide and sulphur cure (TMTD/MBT/S) systems were tried.[37]

Table 4.8. Compound formulation.

Ingredients	NR		HNBR	
	1 CBS/S	2 TMTD/ MBT/S	3 Peroxide	4 TMTD/MBT/S
NR	100	100	-	-
HNBR	-	-	100	100
Zinc Oxide	5	5	-	5
Stearic acid	1	1	-	1
TMTD	-	3	-	1.5
MBT	-	0.5	-	0.5
CBS	1.5	-	-	-
Sulphur	1.5	0.3	-	0.5
DCP	-	-	6	-
DCNR	-	-	0, (14)	0, (14)

Table 4.9. Sample identification of 50/50 blends of NR/HNBR

Identified as	
5	CBS, sulphur cure for NR / Peroxide cure for HNBR
6	TMTD, MBT, sulphur cure for NR / Peroxide cure for HNBR
7	TMTD, MBT, sulphur cure system for both NR and HNBR
8	CBS, sulphur cure for NR / TMTD,MBT, sulphur cure for HNBR
5C	5 modified with 7 parts of DCNR
6C	6 modified with 7 parts of DCNR
7C	7 modified with 7 parts of DCNR

The cure characteristics of the mixes were studied using a rheo TECH MD+ moving die rheometer at an oscillating speed of 100 rpm and arc of ± 0.5 degree. The cure characteristics of NR (both semi EV and EV system) and HNBR (both

TMTD/MBT/S and peroxide) are as shown in Figure 4.3. Both NR and HNBR showed lower torque maxima and a slight reversion for TMTD/MBT/S system. CBS/ sulfur system for NR showed better scorch safety, whereas peroxide vulcanization of HNBR showed marching cure and higher torque.

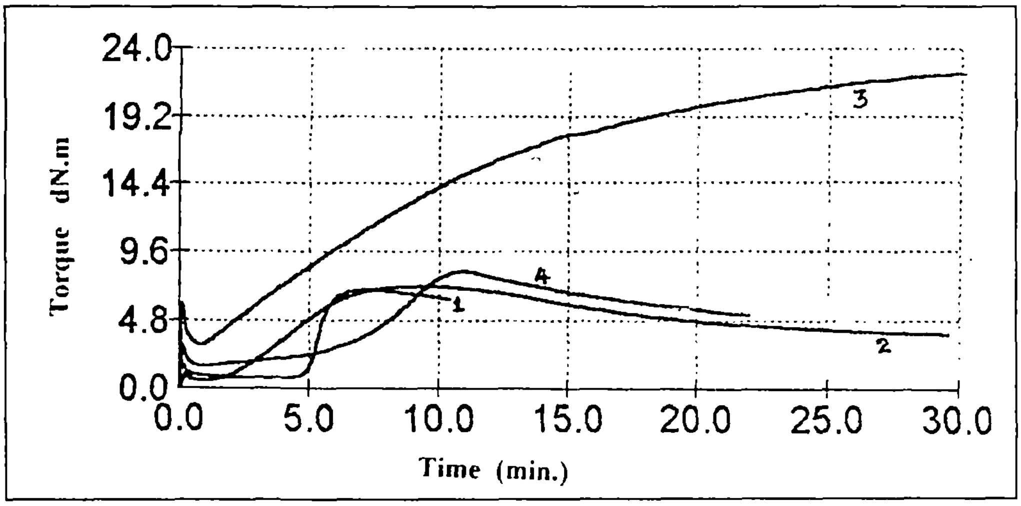

Figure 4.3. Rheographs at 160°C of 1. NR – CBS,S cure, 2. NR- TMTD,MBT,S cure, 3. HNBR- peroxide cure and 4.HNBR-TMTD,MBT,S cure

In respect of elastomer blends, the most essential cross linking characteristic is the ability of the two elastomers to covulcanize.[38] Covulcanization is a term which should be applied to the formation of a single network structure including cross linked macromolecules of the two elastomers. That is both elastomers became vulcanized to similar extents with cross-linking between the elastomers across micro domain interface. The nature and composition of vulcanization system considerably affects covulcanisation in elastomer blends. Different curatives depending on their polarity and reactivity affect the distribution differently. Uniform distribution of cross link density help to improve physical properties of blends.[35] The presence of an intermediate layer between rubber particles in a blend and its fixing during vulcanization process promotes covulcanisation of the mixture as a whole with similar solubilities of the vulcanizing agents in each elastomeric blend components.

Figure 4.4 shows the cure charts of 50/50 blend of NR/HNBR of different cure systems. It was seen that blends with mixed cure showed higher torque maximum. The maximum torque, which is a measure of the stiffness of the compound, could be roughly taken as a measure of cross-link density in the blend.[39] The highest torque was recorded for blends in which a mixed system of vulcanization, CBS/S and peroxide was used. Blends with TMTD/MBT/S system for NR and peroxide for HNBR showed next higher torque maxima. Blends with CBS/S for NR & TMTD/MBT/S system for HNBR and TMTD/MBT/S for both showed comparable torque maximum but lower than the other two. It was observed that sulphur vulcanization for both phases resulted in reversion, which was faster for blend with CBS/S system for NR & TMTD/MBT/S system for HNBR . This was probably due to the formation of more polysulphidic bonds, as the availability of sulphur was higher for the sulphur vulcanization for both phases. Hence, this system was not included for detailed study. However, reversion was absent for the blends where HNBR phase was vulcanized by peroxide.

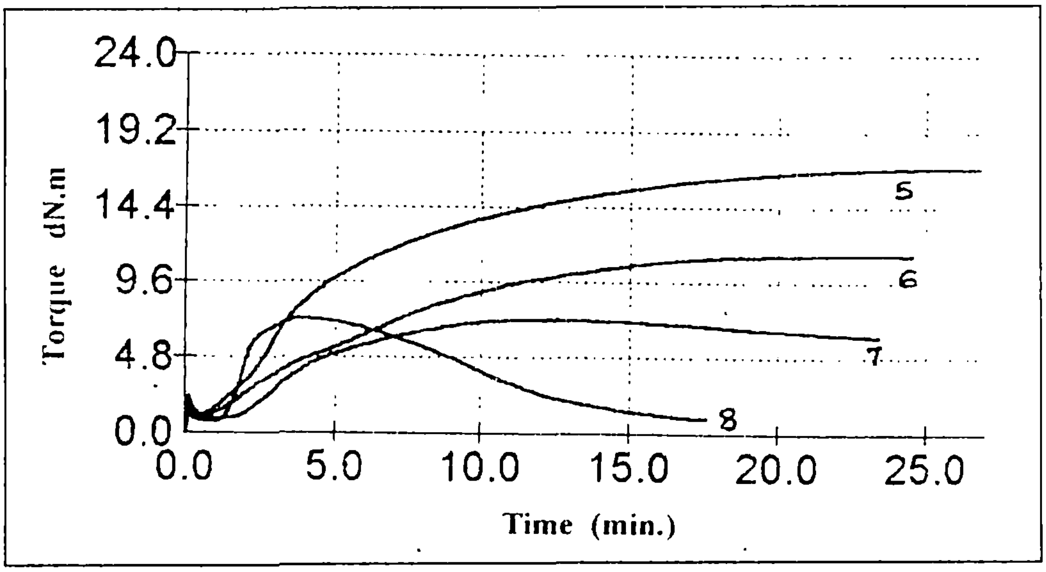

Figure 4.4 Rheographs at 160°C of 50/50 blends of NR/HNBR

In the first three vulcanization systems of binary blends, rheometric torque increased with the addition of 7 parts of DCNR. The cure charts of 50/50 pure blends and blends containing 7 parts of DCNR of 15% chlorine content, at three different temperatures are as shown in Figures 4.5, 4.6 and 4.7 respectively. The cure characteristics at 160°C are as given in Table 4.10. The cure time, torque minimum and torque maximum increased and scorch time decreased for all DCNR containing mixes. This was due to the interaction of DCNR with the blend constituents leading to higher cross-linking. The effect of DCNR in improving level of cross-linking was more pronounced in TMTD, MBT, S / peroxide cure system.

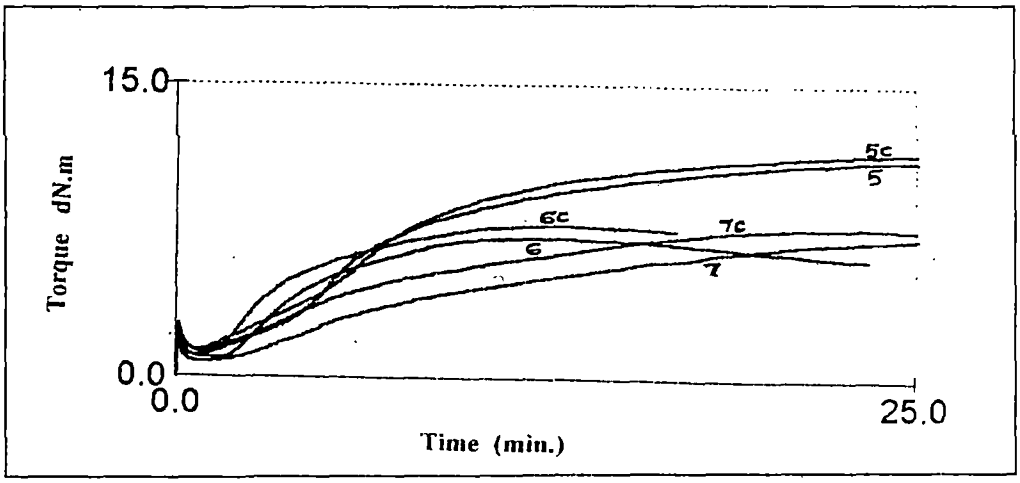

Figure 4.5. Rheographs of 50/50 blends of NR/HNBR and blend containing 7 parts of DCNR of different cure systems at 150° C

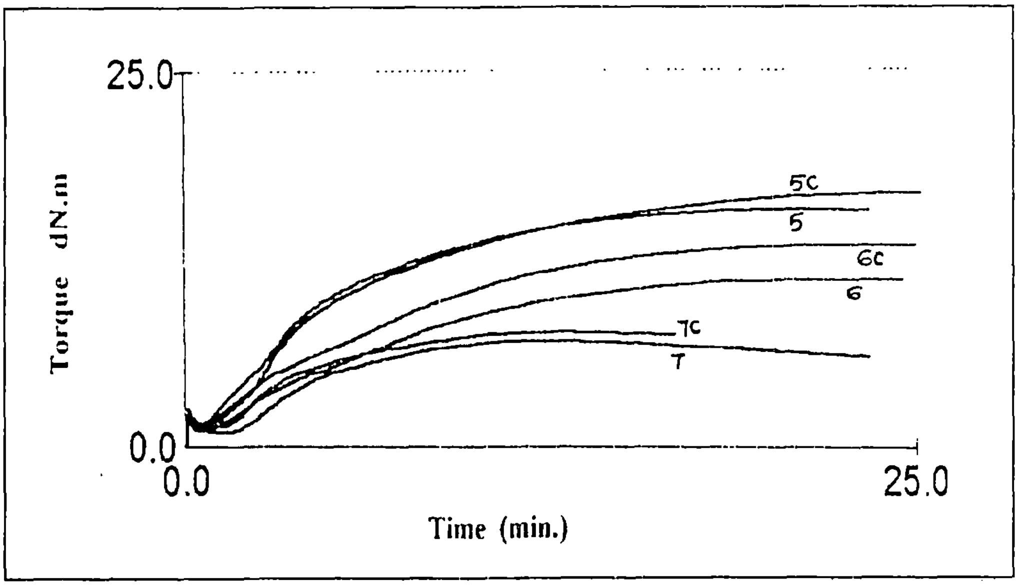

Figure 4.6. Rheographs of 50/50 blends of NR/HNBR and blend containing 7 parts of DCNR of different cure systems at 160° C

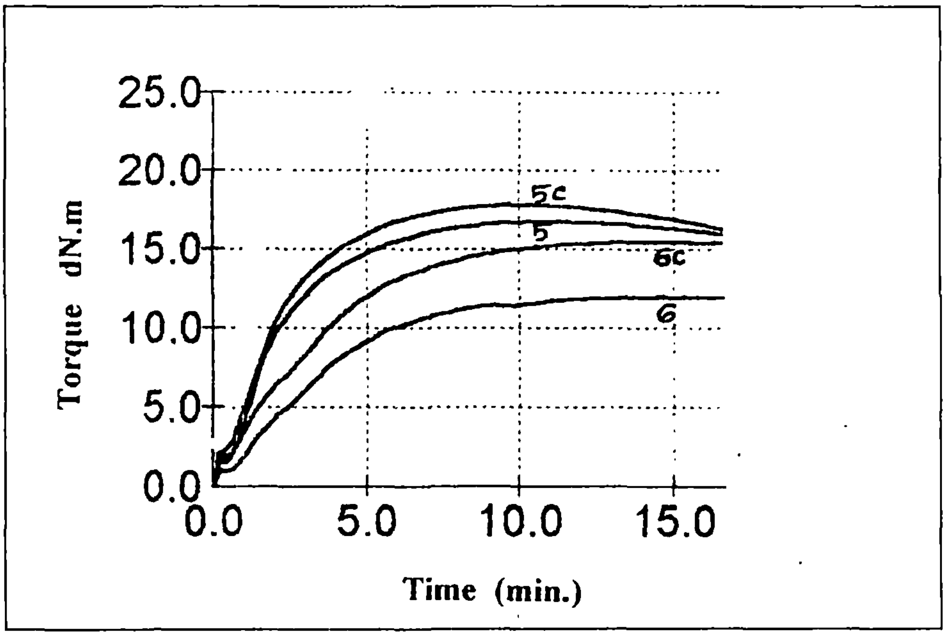

Figure 4.7. Rheographs of 50/50 blends of NR/HNBR and blend containing 7 parts of DCNR of different cure systems at 170° C

Table 4.10. Cure characteristics of the blends at 160 °C.

Properties	Mix No					
	5	5C	6	6C	7	7C
OCT/160°C, min	14.15	14.69	13.08	13.72	8.38	8.83
Torque,max, dNm	15.93	16.99	11.34	13.62	7.26	7.84
Torque,min, dNm	1.22	1.54	1.09	1.58	1.12	1.53
tS_2, min.	3.99	3.71	5.07	4.34	3.06	2.45

4.6. Vulcanization kinetics of the blends

The kinetics of vulcanization are determined based on rheometric torque, that depends on the migration of vulcanizing agents from one rubber to the other.[40-42] The nature of the polymers determine their reactivity with respect to cross linking agents. This naturally affects the ratio of vulcanization rates of the rubber in the blend. Vulcanizates of elastomeric blends, whose rates of reaction with a given vulcanizing agent are similar will have better properties than those with a noticeable difference in reaction rate.

Plots of $\ln(M_h - M_t)$ against time,'t' of blends for the four vulcanization systems at 160°C are as shown in Figure 4.8. A straight-line graph in each case indicated that reaction followed first order kinetics. The specific reaction rate constant 'k' for each system is given in Table 4.11. Even though the vulcanization rate was faster with the sulphur curing of both the matrices, a higher level of vulcanization was obtained when HNBR phase was vulcanized by peroxide.

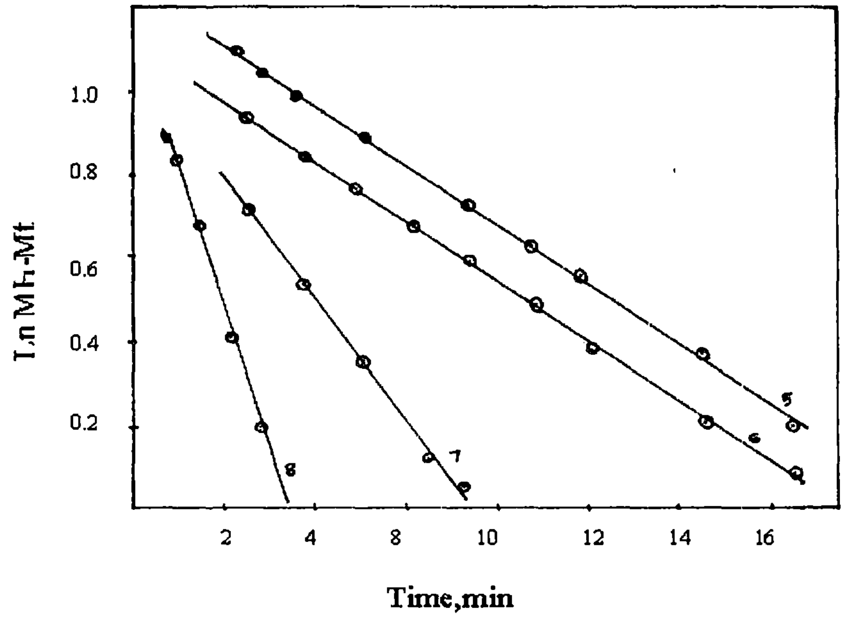

Figure 4.8. Plots of ln $(M_h - M_t)$ against 't' of different cure systems at 160°C.

Table 4.11. Specific reaction constants of vulcanization systems.

Mix No.	Specific reaction constant, k
5	0.7216
6	0.7241
7	1.476
8	3.333

Plots of log t_{90} vs 1/T for both pure and modified blends of CBS / peroxide and TMTD/ peroxide are as given in Figure 4.9. The slope of the line is an indication of the fastness of the cure reaction. The activation energy calculated is given in Table 4.12. DCNR containing blends gave higher activation energy. This showed that temperature sensitivity of vulcanization increased with the addition of DCNR.

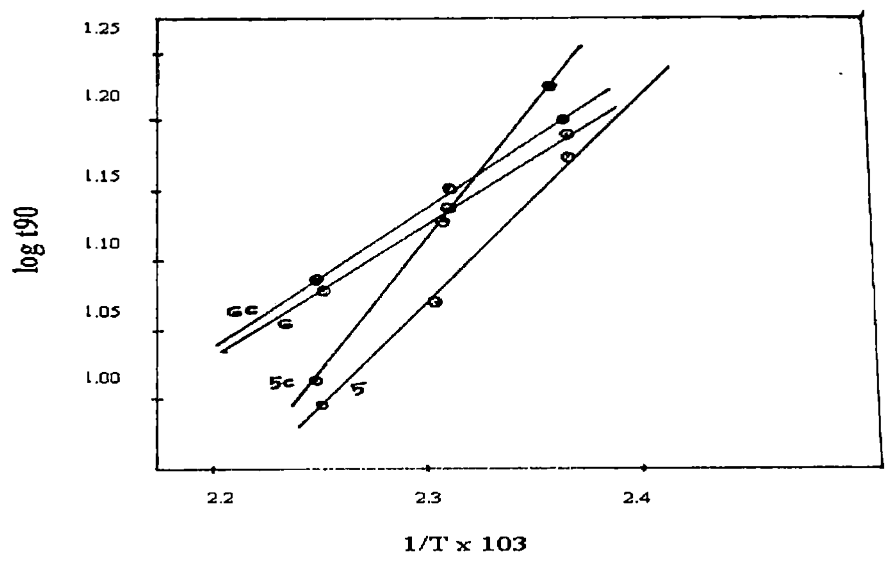

Figure 4.9. Plots of log t_{90} vs 1/T for both pure and modified blends of cure systems 5 & 6

Table 12. Activation energy of 50/50 blends of NR/HNBR

Mix No.	Activation energy, Cal/mol.
5	7.0165
5C	8.4739
6	4.1779
6C	5.1037

4.7.Blend characterization

4.7.i) *SEM characterization*

Figure 4.10 shows the scanning electron microscopic pictures of NR/HNBR blends at different blend ratios and 50/50 blend containing 7 parts of DCNR of 15 % chlorine content. It was clear that 75/25 and 25/75 blend ratios were immiscible due to clear phase separation.[43-45] Distinctive interfacial boundaries suggest very poor adhesion between the matrices.50/50 blend also showed immiscibility but to a lower extent as the phase separation was lower. By the incorporation of DCNR, the blend became more miscible as was seen from the SEM, the phase became more uniform and co_continuous. This better miscibility was due to the interaction of chlorine part of DCNR with the acrylonitrile part of HNBR simultaneously retaining with the NR part having the same backbone structure. This modified the interface between two phases and improved the morphology. This was evident from the improved mechanical properties of the modified blend.

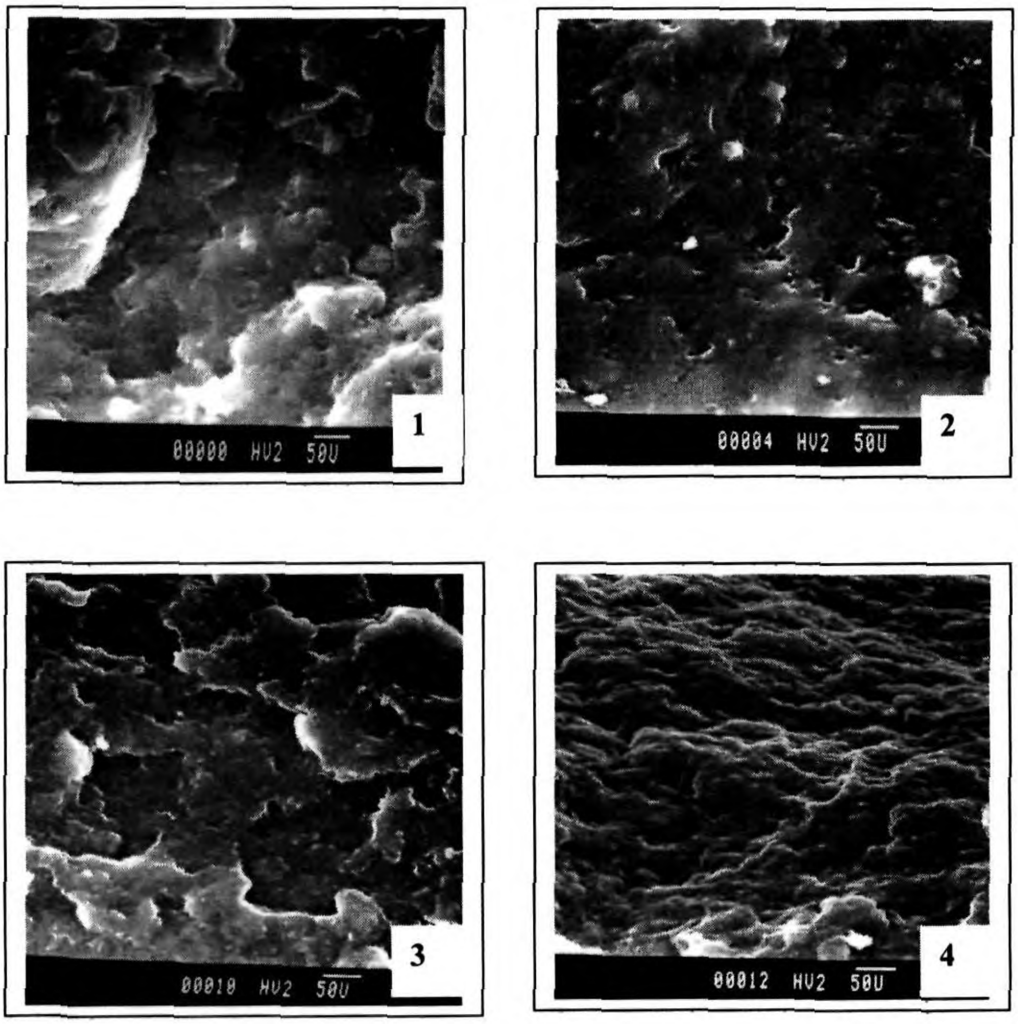

Figure.4.10. SEM pictures of blends of NR/HNBR of different blend ratio : 1-75/25, 2-50/50, 3- 25/75 and 4- 50/50 blend containing 7 parts of DCNR.

Figure 4.11 shows the scanning electron microscopic pictures of 50/50 NR/HNBR blends of different cure systems. It was seen that the mixed cure systems showed better co-continuity and hence miscibility of the phases. This shows the improved co vulcanization of the blend and explains the improved properties obtained for the mixed cure system.[46]

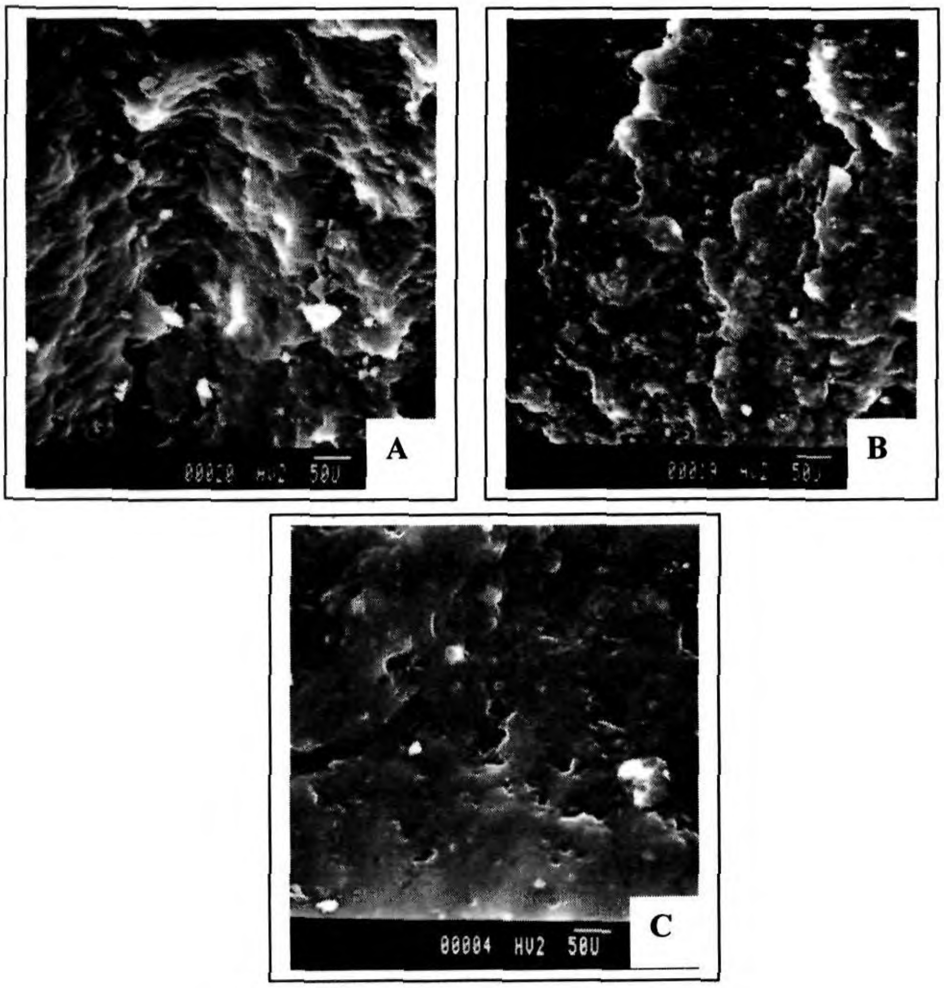

Figure 4.11 SEM pictures of 50/50 blends of NR/HNBR of different cure systems. A- CBS/S/Peroxide, B- TMTD/MBT/S/Peroxide and C-TMTD/MBT/S.

4.7.ii) *FTIR characterization*

Figure 4.12 shows the IR spectrographs of the pyrolysates of HNBR, 50/50 blends and that containing 7 parts of DCNR. The spectral data is given in Table 4.13. It is assumed that there would be polar-polar interactions between the –Cl group of DCNR and –CN group of acrylonitrile repeat unit present in HNBR. Similar interactions had been reported earlier for blends of SBR and NBR in presence of chlorine containing polymer.[27] Polar- polar interactions can affect the IR absorption peaks of concerned groups. Abdul Kader, et al.[47] reported a shift in carbonyl group in their studies of miscible blends of acrylate rubber and fluorocarbon rubber.

HNBR showed characteristic IR absorption at 2237.0 cm $^{-1}$ for –C≡N linkage and at 1641.6 cm $^{-1}$ for >C=O linkage. Formation of >C=O and –CHO groups in HNBR have been reported earlier due to oxidative degradation.[48] Examination of Figure 4.12 revealed two regions that show marked difference in their absorption for modified blend in comparison with pure blend: 2200 cm $^{-1}$ to 3000 cm $^{-1}$ and 1800 cm $^{-1}$ to 1500 cm $^{-1}$ regions which correspond to the absorption of –C≡N and >C=O respectively. Absorption due to –C≡N stretching at 2237.0 cm $^{-1}$ in pure NR/HNBR blend is shifted to 2239.6cm $^{-1}$ for the blend containing DCNR. Pure blend also showed absorption at 1641.6 cm $^{-1}$ due to -(C=O) stretching which is shifted to 1645.5 cm $^{-1}$ in modified blend. The absorption at 1016.6 cm $^{-1}$ due to –(C-O) stretching in pure blend shifted to 1018.5 cm $^{-1}$ in presence of DCNR. These observations indicated that there is interactions between the dichlorocarbene modified NR and HNBR.

Table4.13. Characteristic IR absorption for the blends of NR/HNBR

Mix	IR absorption, wave length, cm^{-1}	Peak assignment
HNBR	2237.0	-C≡N stretch
	1641.6	>C=O stretch
	1016.6	-C-O stretch
NH	2237.0	-C≡N stretch
	1641.6	>C=O stretch
	1016.6	-C-O stretch
NHC7	2239.6	-C≡N stretch
	1645.5	>C=O stretch
	1018.5	-C-O stretch

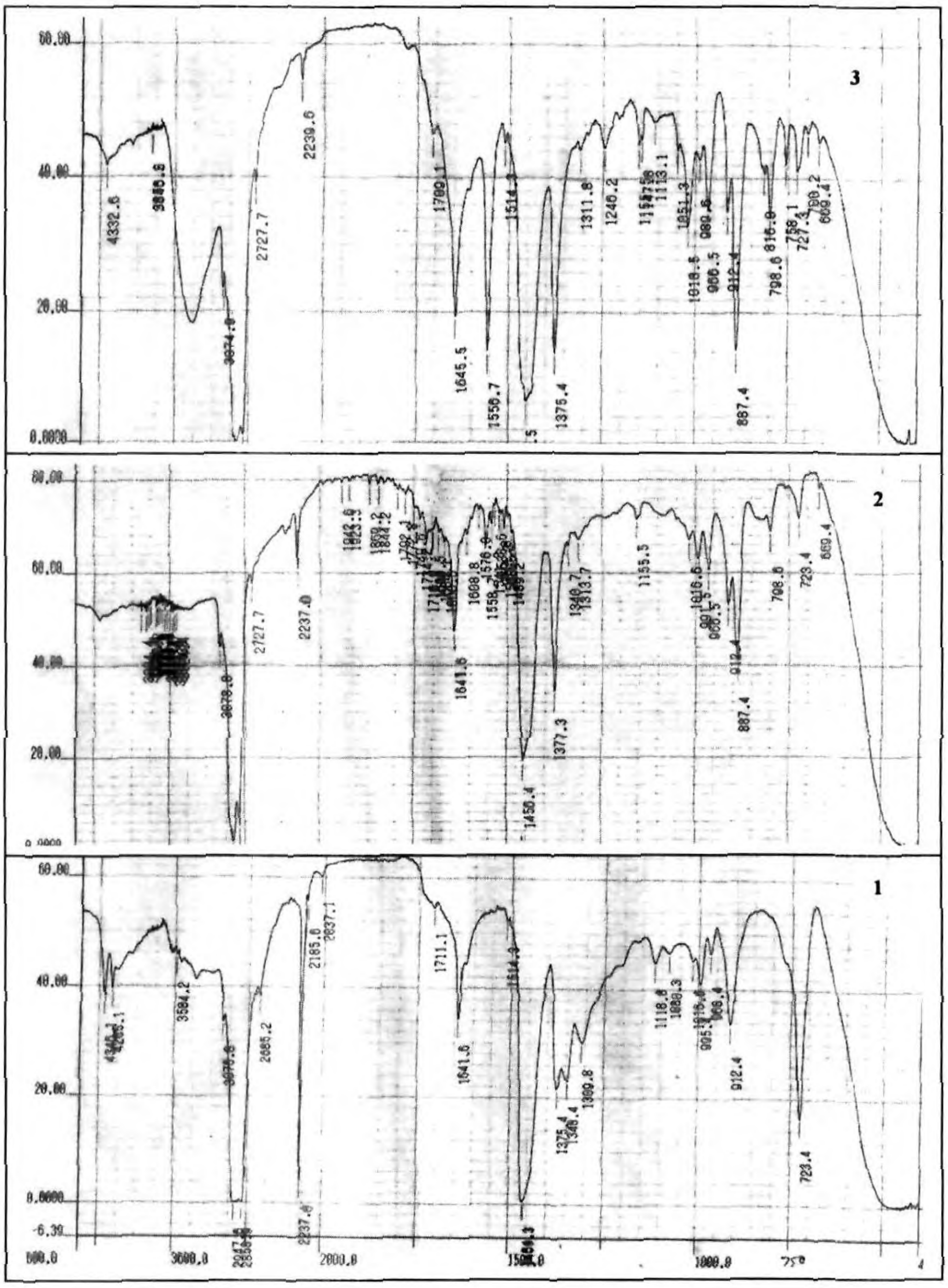

Figure 4.12. IR spectrographs of 1- HNBR, 2-50/50 blend of NR/HNBR and 3- blend containing 7 parts of DCNR

The addition of DCNR could promote dipole interaction in blends. Such interactions are known to affect the characteristic IR absorption peaks as reported earlier.[49-52] *Tabb and Koenig*[53] *described a shift in* –(C-O) *absorption frequencies* of dioctylphthalate (DOP) due to its interaction with polyvinylchloride. Coleman et.al.[54] have attributed a shift in –(C-O) absorption band of poly (methyl methacrylate) due to interactions involving carbonyl group in compatible blend of poly (vinylidene fluoride) and poly (methyl methacrylate) .

4.7.iii) *DSC characterization*

DSC traces of pure NR, HNBR, DCNR, 50/50 blend and blend containing two different levels of DCNR of 15% chlorine content are as shown in Figure 4.13 and results are summarized in Table 4.14. NR showed Tg at –63.7, HNBR at –24.4 and DCNR at –5 °C respectively. The blends exhibited two separate Tg's one at about -63^0 C and the other at about -25^0 C that correspond to the glass transition temperature of NR and HNBR respectively. The presence of two peaks for transitions of NR and HNBR in the binary blends revealed that blends of NR and HNBR are not compatible completely. There was only slight change in Tg of both NR and HNBR on addition of DCNR. This indicated that DCNR was not a very good compatibilizer. With the addition of DCNR to the blend, Tg of both NR and HNBR shifted to a slightly higher temperature. Shifting of Tg of a blend constituent to a higher temperature due to interaction with compatibilizer has been reported earlier.[55,56] This observation suggested the possibility of interactions between DCNR and the blend constituents and thus it acted as an interface modifier in blends of NR/HNBR.

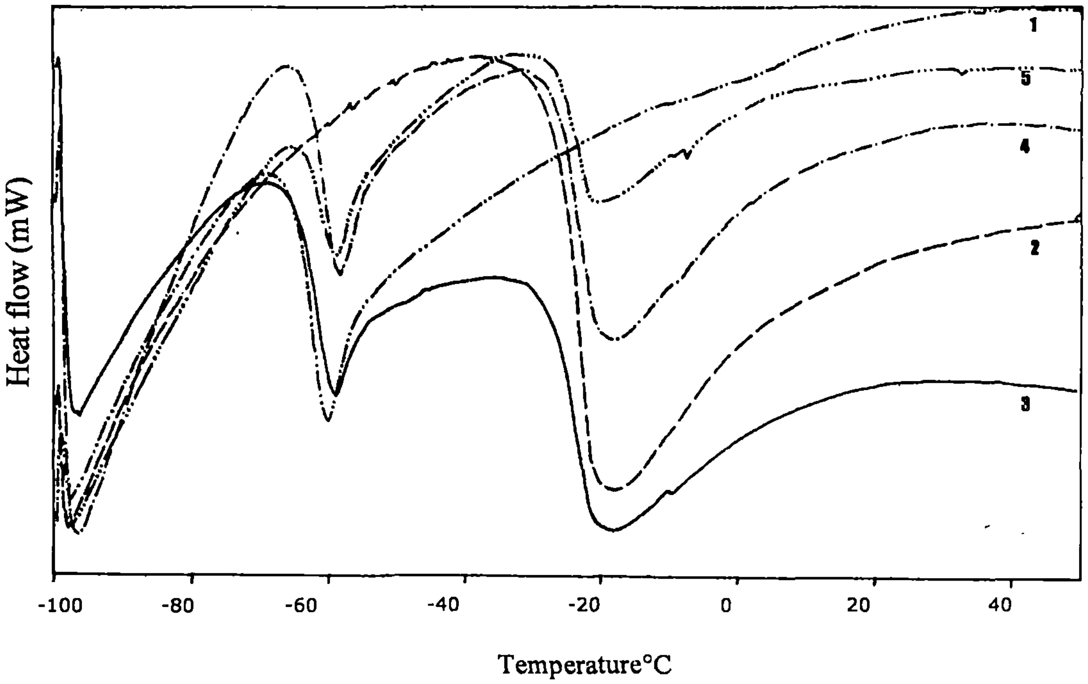

Figure 4.13 DSC thermograms of 1- NR, 2-HNBR, 3-NH, 4-NHC3 and 5-NHC7

Table 4.14 DSC peaks of NR, HNBR,DCNR (15% chlorine content) and blends (° C)

Sample	Tg1	Tg2
NR	-63.7	-
HNBR	-	- 24.4
DCNR	- 5.0	-
NH	- 63.6	- 25.8
NHC3	- 63.0	- 25.1
NHC7	-62.9	- 24.8

Figure 4.14 shows the DSC thermograms of the black filled 50/50 blend and that containing 7 parts of DCNR. Here also blends showed characteristic values at two transition temperatures indicating immiscibility. But in the case of DCNR containing blend, there was a shift in Tg. (Table 4.15) The transition region was more broadened and the transition temperature was slightly shifted to higher side showing that there is interaction of both NR and HNBR with DCNR. This interaction enhanced better miscibility, which was evidenced by SEM and other properties.

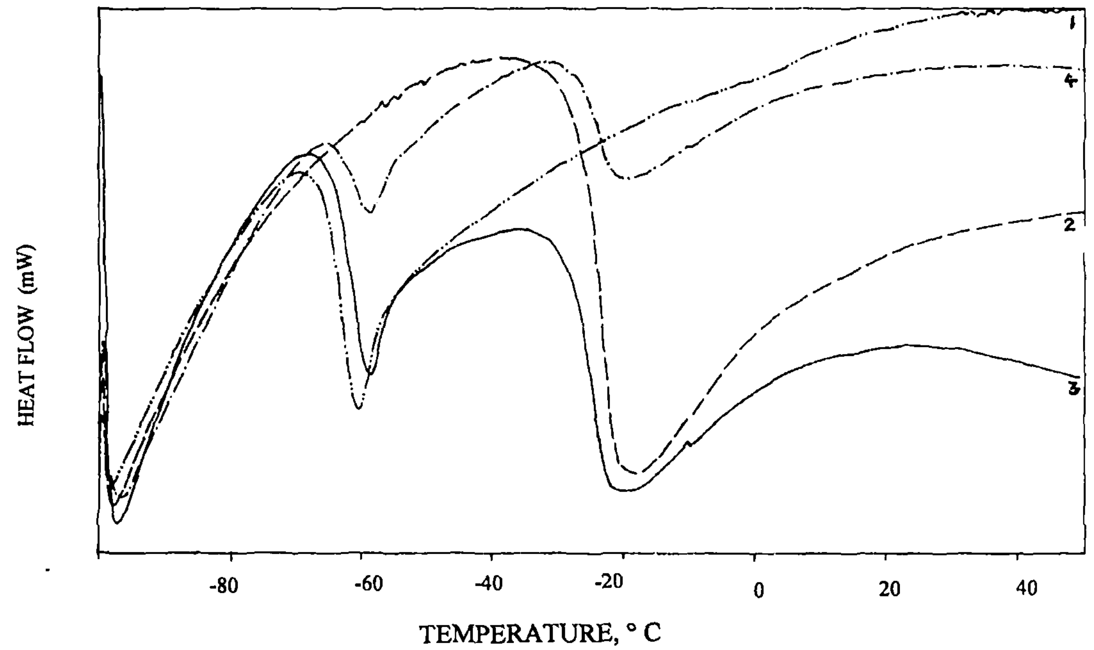

Figure.4.14 . DSC thermograms of black filled 1-NR, 2-HNBR, 3-NH and 4- NHC7

Table 4.15 Transition temperature and width of DSC peaks of black filled blends.

Property		NH	NHC7
Width of transition region	First	1.40	2.65
	Second	1.05	2.50
Transition temperature	First	-62.8	-61.6
	Second	-26.0	-24.6

4.8. Mechanical properties

The mechanical properties of the vulcanizates of NR (both semi EV and EV system) and HNBR (both TMTD/MBT/S and peroxide) and of the blends for the three vulcanization systems are as shown in Table 4.16. NR pure gum vulcanizates gave good mechanical properties, which were comparable for both systems, where as peroxide cure gave poor tensile properties for pure HNBR gum vulcanizates. HNBR vulcanizates are reported to show excellent mechanical properties in presence of suitable coagent or filler. [20,57,58]

Mechanical properties of blends can be affected considerably by the cure system.[59] In the case of blends, a mixed cure system consisting of CBS/S /peroxide gave best mechanical properties. TMTD/MBT/S/Peroxide cure system registered better properties than TMTD/MBT/S cure system. Higher tensile strength, modulus and lower elongation at break were observed for CBS/S/peroxide system showing higher levels of cross-linking. Comparatively a higher compression set and heat build up were observed for blends vulcanized by TMTD/MBT/S cure system indicating the possibility of lower cross link density. 50/50 blends containing 7 parts of DCNR registered higher tensile strength, modulus, elongation at break, tear strength and hardness along with lower heat build up and compression set as compared with pure blends in all the three vulcanization systems. This shows that DCNR has the ability to interact with the blend constituents, irrespective of the vulcanization system.

Table 4.16. Mechanical properties of NR, HNBR and the blends of different cure systems

	NR		HNBR		50/50 NR/HNBR					
Cure system → Mix No:	CBS/S	TMTD/MBT/S	Peroxide	TMTD/MBT/S	CBS/S/ Peroxide		TMTD/MBT/S /Peroxide		TMTD/MBT/S	
Properties ↓	**1**	**2**	**3**	**4**	**5**	**5C**	**6**	**6C**	**7**	**7C**
Tensile strength, Mpa	19.7	18.8	2.5	21.1	18.0	19.4	11.9	13.9	10.6	12.3
Modulus,100%,MPa	0.80	0.72	-	1.10	1.25	1.27	1.05	1.07	0.93	1.10
Modulus,300%,MPa	1.61	1.47	-	1.45	2.53	2.74	2.04	2.10	1.5	1.58
Elongation at break,%	750	735	100	720	320	330	325	350	740	690
Tear strength, Kg/cm	30.0	21.6	9.2	16.9	19.9	21.3	18.6	19.7	20.5	23.9
Resilience, %	76	74	69	65	64	63	63	64	69	70
Hardness, Shore A	42	42	57	49	46	48	44	46	44	45
Compression set, 70°C/22h,%	20.0	8.2	5.4	30.1	21.1	20.2	32.5	29.2	46.2	39.0
Heat build up, ΔH, ^{0} C	3	7	13	25	16	14	23	20	56	47
Dynamic set,%	0.40	0.88	0.48	2.27	2.47	1.96	4.46	2.64	10.27	8.89

4.9. Selective solvent swelling

. Interfacial adhesion in vulcanizates of polymer blends could be investigated by selective or differential solvent swelling.[60] Methyl ethyl ketone (MEK) and n-heptane were used as solvents at room temperature. During swelling by methyl ethyl ketone, the HNBR matrix of the blend swell highly while the NR phase swell lightly and the tendency was reversed during swelling by n-heptane. The percent volume of normal heptane and MEK absorbed by pure NR, HNBR and blend of the three cure systems are shown in Table 4.17 (a). The weight of normal heptane absorbed by NR matrix of the blend was lower than the additive average of the weight of solvent absorbed by NR and HNBR. Thus the level of cross-linking of the NR phase in the blend seems to be higher than that for the pure NR vulcanizate, which was highest for the blend having a mixed

Table 4.17 (a) Percentage weight of solvent absorbed during selective solvent swelling at room temperature for 48 h

Mix No	n-heptane	MEK
3 (HNBR, peroxide)	6.6	144.7
4 (HNBR, TMTD/MBT/S)	18.3	180.1
1 (NR, CBS/S)	150.6	43.9
2 (NR, TMTD/MBT/S)	170.4	42.8
5 (Blend)	52.3	131.9
5C (Blend)	51.1	120.5
6 (Blend)	63.9	202.3
6C (Blend)	57.9	160.8
7 (Blend)	84.5	220.3
7C (Blend)	80.1	203.9

cure system, CBS/S/ peroxide. The weight of solvent absorbed by the blend in the presence of DCNR was lower than the pure blend in all the three cure systems. It showed that there was restriction to swelling of NR phase by the lightly swollen HNBR phase and this indicated the formation of interfacial cross-links. The restriction to solvent swelling by formation of interfacial bonds had been reported earlier.[61] In the case of HNBR matrix of the blend the weight of MEK absorbed was higher than the additive average of weight of MEK absorbed by pure HNBR and NR. Thus the HNBR matrix in the blend was not vulcanized up to the same level as in pure HNBR. Here also the mixed cure system, CBS/S/ peroxide gave higher cross linking for HNBR phase and TMTD/MBT/S cure for both phases gave lowest. However, there were interfacial bonds formed, as there was restriction to penetration of HNBR phase by MEK in presence of DCNR. Thus it was due to the lower cross-linking of the HNBR phase that a lower rheometric torque is registered for these blends. The higher rheometric torque recorded for the modified blend should be due to the formation of interfacial bonds.

A measure of cross linking as obtained from Vr (volume fraction of rubber), given in Table 4.17(b), indicated a higher level of cross linking in blends in presence of DCNR.

Table 4.17 (b). V_r values of NR and HNBR phases of NR/HNBR blends

Mix No	V_r, NR phase	V_r, HNBR phase
5	0.379	0.164
5C	0.387	0.228
6	0.327	0.147
6C	0.355	0.177
7	0.106	0.108
7C	0.118	0.124

4.10. Effect of filler

Incorporation of fillers into elastomers and their blends lead to a wide range of interactions at the polymer filler interface, which considerably influence their properties. The major factors that control the properties are surface chemistry of the filler, nature, shape and size of particle, particle size distribution, specific surface area, etc.[62-65] The influence of fillers HAF, FEF and silica on properties of 50/50 blends was evaluated at 30 phr loading. Compounds of NR and HNBR were prepared as per formulation given in Table 4.18. Mixes of different blend ratios were prepared by cross blending NR (CBS/S cure) and HNBR (peroxide cure) filled with 30 parts of HAF at the required ratios. 50/50 blends were prepared with different cure systems and identified as given in Table 4.19.

Table 4.18 Compound formulations for filled NR and HNBR

Ingredients	NR CBS	NR TMTD	HNBR P	HNBR TMTD
NR	100	100		
HNBR	-	-	100	100
DCNR	-	-	0,(14)	0,(14)
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
A/o 4010 NA[1]	1	1	1	1
A/o HS[2]	1	1	1	1
Filler [a]	30	30	30	30
Aromatic oil	3	3	-	-
Dioctylphthalate	-	-	4	4
CBS[3]	1.5	-	-	-
Sulphur	1.5	0.3	-	0.5
TMTD[4]	-	3.0	-	1.5
Mercaptobenzothiazole	-	0.5	-	0.5
Dicumyl peroxide	-	-	6	-

a- HAF/FEF (30 and 60 phr) /Silica
1-N phenyl N isopropyl paraphenylene diamine
2- Polymerised 1,2 dihydro 2,2,4 trimethyl quinoline
3-1-N-Cyclohexyl benzothiazole-2 sulphenamide
4-Tetramethyl thiuram disulphide

Table 4.19. Identification of vulcanizates of NR, HNBR and blends.

N1h	NR- CBS/S cure, 30 phr HAF black	**N2f**	NR- TMTD/MBT/S cure, 30 phr FEF black
N1f	NR- CBS/S cure, 30 phr FEF black	**N2s**	NR- TMTD/MBT/S cure, 30 phr silica
N1s	NR- CBS/S cure, 30 phr silica	**Hp**	HNBR-Peroxide cure with 30 phr HAF black
N2h	NR- TMTD/MBT/S cure, 30 phr HAF black		

NHa	75 /25 NR / HNBR- CBS/S /Peroxide cure with 30 phr HAF black
NHb	25 /75 NR / HNBR- CBS/S /Peroxide cure with 30 phr HAF black
NH1h	50/50 NR / HNBR- CBS/S /Peroxide cure with 30 phr HAF black
NH1f	50/50 NR / HNBR- CBS/S /Peroxide cure with 30 phr FEF black
NH1s	50/50 NR / HNBR- CBS/S /Peroxide cure with 30 phr silica
NH2h	50/50 NR / HNBR- TMTD/MBT/S /Peroxide cure with 30phr HAF black
NH2f	50/50 NR/ HNBR- TMTD/MBT/S /Peroxide cure with 30 phr FEF black
NH2s	50/50 NR/ HNBR- TMTD/MBT/S /Peroxide cure with 30 phr silica
NH3f	50/50 NR / HNBR- TMTD/MBT/S cure with 30 phr FEF black
NH1Cf	NH1f containing 7 parts of DCNR
NH2Cf	NH2f containing 7 parts of DCNR
NH3Cf	NH3f containing 7 parts of DCNR

4.10.A Effect of different fillers on NR

The rheographs of NR vulcanized using CBS/S and TMTD/ MBT/S cure system with 30 phr of different fillers- HAF, FEF and silica- are as shown in Figure 4.15. Highest torque was obtained for silica filled one and lowest for FEF filled one. Both cure systems gave comparatively similar torque maximum.

Table 4.20 gives the mechanical properties of NR (both CBS/S and TMTD/MBT/S cure) with 30 phr each of the HAF, FEF and silica loading. It was seen that in filled systems, CBS/S cure gave better properties for NR than TMTD/MBT/S cure. HAF and FEF gave comparable values of tensile properties, hardness, tear strength,

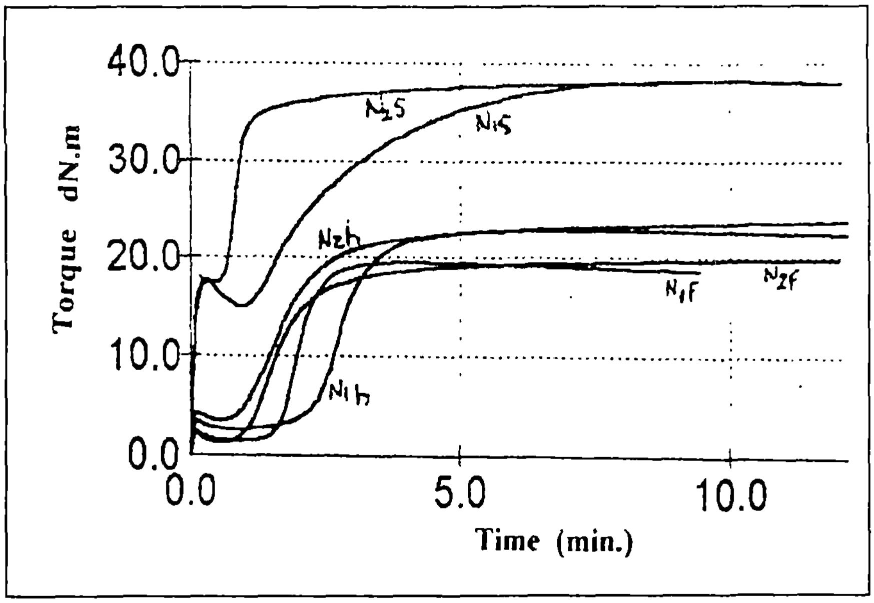

Figure 4. 15. Rheographs at 160° C of NR vulcanized by 1- semi EV and 2- EV cure with HAF, FEF and silica fillers.

resilience, abrasion resistance and flex resistance for the CBS/S cure. Better tensile properties, tear strength and hardness are obtained for HAF filled mixes in TMTD/MBT/S cure.[66,67] Heat build was comparable for both cure system.. TMTD/MBT/S cure showed better compression set values, which was due to the monosulphidic cross linking possible for this cure. Silica filled one gave inferior values except hardness and tear strength for both the cure systems. This was probably due to the absence of silane coupling agent in the cure system.

Table 4.20. Physical properties of filled NR vulcanizates

Properties	**N1h**	**N1f**	**N1s**	**N2h**	**N2f**	**N2s**
Tensile strength, MPa	31.3	31.5	18.9	29.3	25.3	19.5
Modulus 100%, MPa	2.8	2.8	2.7	2.8	2.9	2.8
Modulus 300 %, MPa	13.5	13.8	8.9	13.6	14.9	8.6
Elongation at break, %	470	470	415	440	390	470
Tear strength, k N/m	58.7	60.8	64.5	41.8	40.1	85.1
Hardness, Shore A	50	50	74	54	52	75
Resilience, %	68	66	52	69	68	55
Compression set, %(22 h 125 ^{0}C)	60.2	58.0	100.0	27.3	28.8	96.5
Heat build up, ^{0}C	17	15	45	16	16	48
Dynamic set, %	1.59	1.26	17.11	1.03	1.51	10.72
Din abrasion loss, /cm^3	125.4	126.0	259.6	119.8	139.7	205.4
Din Loss index	89.1	88.6	43.0	93.4	79.9	54.5
Demattia flexing, no.of cycles						
Crack initiation,	64,780	63,698	40,590	18,330	40,600	8,336
Failure	3,01,136	2,06,830	73,060	96,917	1,10,000	25,000

4.10.B.Effect of cure system on filled blends

4.10.B. 1. HAF black filled NR/HNBR blends cured by CBS/S /Peroxide system.

4.10.B.1.a) Blend ratio- Cure characteristics

The rheographs of NR (CBS/S cure), HNBR(peroxide cure) and NR/HNBR blends of 75/25, 50/50 and 25/75 ratios with a CBS/S/ peroxide cure containing 30 phr of HAF black are as shown in Figure 4.16. NR gave highest torque. 75/25 and 50/50 NR/HNBR blends showed torque maxima close to that of HNBR, where as 25/75 blend showed a lower torque than pure HNBR. The cure characteristics of the blends at 160 °C are given in Table 4.21(a). Optimum cure time of the blends increased as HNBR content in the blend increased. Scorch time also followed a similar trend for the blends.

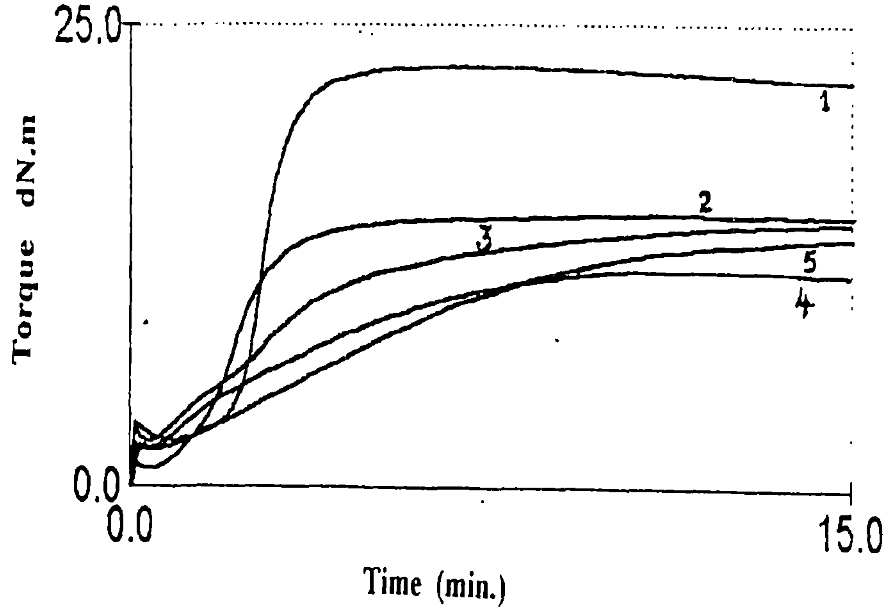

Figure 4.16. Rheographs of 30 parts HAF filled mixes at 160° C. 1-NR, 2-75/25, 3- 50/50, 4- 25/75 NR/HNBR blends and 5- HNBR.

Table 4.21(a). Cure characteristics of filled blends-effect of blend ratio

Mix ID →	NR	NH75/25	NH50/50	NH25/75	HNBR
Properties ↓	N1h	NHa	NH1h	NHb	Hp
OCT, 160°C, min	3.69	3.71	9.18	9.49	11.37
Min. torque, M_L, dNm	2.62	1.04	2.06	2.14	2.18
Max. torque, M_H, dNm	22.79	14.87	14.68	11.84	14.11
Scorch time, tS_2, min	2.20	1.35	1.38	1.46	2.38

4.10.B.1.b) Blend ratio- mechanical properties

The mechanical properties of blends are given in Table 4.21(b). It was seen that incorporation of black filler considerably improved the mechanical properties of the blends. In HAF filled system, all the blends showed better tear strength, resilience and heat build up than HNBR, better hardness and high temperature compression set than NR and better elongation at break than both the constituents. The flex resistance of blends containing 50 parts and above HNBR was superior to both NR and HNBR. However the tensile properties are inferior to both the components.

Table 4.21 (b) Blend ratio- Mechanical properties of the filled vulcanizates.

Mix ID. →	**NR**	**NH75/25**	**NH50/50**	**NH25/75**	**HNBR**
Properties ↓	N1h	NHa	NH1h	NHb	Hp
Tensile strength, MPa	31.3	21.9	21.8	25.6	27.9
Modulus, 100%, MPa	2.8	2.2	2.3	2.5	2.9
Modulus 300 %, MPa	13.5	6.8	7.4	9.6	20.9
Elongation at break, %	465	540	610	545	370
Tear strength, kN/m	58.7	42.7	42.3	40.3	34.2
Hardness, Shore A	50	54	58	60	60
Resilience , %	68	58	57	56	56
Compression set, %(22 h 125 ^{0}C)	67.2	66.6	60.6	60.0	41.0
Compression set, %(22 h 150 ^{0}C)	95.9	87.5	69.5	63.9	42.2
Heat build up, ΔH, ^{0}C	17	33	42	43	44
Dynamic set, %	1.59	3.19	3.39	2.23	1.99
Din abrasion loss,/cm^{3}	125.4	159.7	145.9	103.9	59.6
Din Loss index	89.07	69.93	76.53	107.54	187.48
Demattia flexing, no.of cycles					
Crack initiation,	64,780	18,766	2,49,859	2,81,080	1,59,650
Failure	3,01,136	91,646	4,60,600	5,12,980	4,07,425

4.10.B.1.c) Effect of type of filler on 50/50 blends of NR/HNBR cured by CBS/S/Peroxide system

Table 4.22(a) gives the cure characteristics of 50/50 blend of NR/HNBR cured by CBS/S/Peroxide system with 30 phr of HAF, FEF and silica. Silica filled mix recorded highest torque with least scorch time and FEF black filled mix recorded lowest torque maxima with a higher scorch time and highest optimum cure time.

Table 4.22(a). Cure characteristics of filled 50/50 NR/HNBR blend cured by CBS/S /Peroxide system .

Properties	NH1h	NH1f	NH1s
OCT, 160°C, min	9.18	11.10	9.05
Min. torque, M_L, dNm	2.06	2.33	7.90
Max. torque, M_H, dNm	14.68	13.95	25.81
Scorch time, tS_2, min	1.38	1.41	0.8

Mechanical properties of 50/50 blend of NR/HNBR cured by CBS/S/Peroxide system with 30 phr of HAF, FEF and silica are given in Table4.22 (b). Both HAF and FEF filled mixes exhibited comparable properties. Though higher torque was recorded for silica filled mixes, only inferior mechanical properties were obtained, except hardness and tear strength. This may be due to the lower cross-linking possible in NR phase as a result of the absence of silane coupling agent in NR mix.

Table 22(b). Mechanical properties of filled 50/50 blend of NR/HNBR cured by CBS/S/Peroxide system, effect of filler

Properties	**NH1h**	**NH1f**	**NH1s**
Tensile strength, MPa	21.8	22.1	19.2
Modulus, 100%, MPa	1.7	1.7	1.9
Modulus 300 %, MPa	5.4	5.7	4.3
Elongation at break, %	720	710	630
Tear strength, kN /m	42.3	42.3	57.8
Hardness, Shore A	58	58	68
Resilience, %	57	56	55
Compression set, %(22 h, 125 ^{0} C)	60.6	60.9	90.9
Heat build up, ΔH, ^{0} C	43	42	54
Dynamic set, %	3.39	3.9	13.9
Din abrasion loss,/cm^3	145.9	144.5	252.6
Din abrasion, loss index	76.5	77.3	44.2
Demattia flexing, no.of cycles			
Crack initiation,	2,49,859	1,76,917	76,910
Failure	4,60,600	3,26,000	3,24,370

4.10.B.1.d) Effect of filler loading in 50/50 blends of NR/HNBR cured by CBS/S/Peroxide system

The effect of FEF black loading on NR and 50/50 blend of NR/HNBR was evaluated, using CBS/S cure for NR and CBS/S/Peroxide cure for the blend. Table 4.23 shows the effect on mechanical properties of NR and the blends. It was seen that filler loading enhanced the mechanical properties of both NR and blend. Excessive loading slightly reduced the tensile strength of both NR and the blend. Reinforcement by filler loading was less effective in blends than in NR, which may be due to the immiscibility of the components. However, hardness, modulus and tear strength improved considerably with filler loading.

Table 4.23. Effect of FEF loading on NR and 50/50 NR/HNBR blend

Properties	NR, FEF loading, phr.			NH1, FEF loading, phr.		
	0	30	60	0	30	60
Tensile strength, MPa	17.6	31.5	27.7	17.9	22.1	19.3
Modulus 100%, MPa	0.8	2.8	3.2	1.3	1.7	3.1
Modulus 300 %, MPa	1.6	13.8	14.6	2.5	5.7	11.5
Elongation at break, %	750	470	440	320	710	590
Tear strength, kN/m	30.0	60.8	123.1	19.9	42.3	43.8
Hardness, Shore A	42	50	64	46	58	70
Resilience, %	76	66	51	67	56	47
Compression set, %(22 h 125 °C)	56.6	58.0	70.7	45.2	60.9	68.3
Heat build up, ΔH, °C	3	15	29	14	42	67
Dynamic set, %	0.4	1.26	1.50	0.96	3.90	8.61
Din abrasion loss,/cm^3	-	126.0	117.6	-	144.5	132.2
Loss index	-	88.6	94.9	-	77.3	84.5

4.10.B.2. Effect of different fillers on 50/50 blends cured by TMTD/MBT/S/Peroxide system

Table 4.24(a) gives the cure characteristics of 50/50 blend of NR/HNBR cured by TMTD/MBT/S/Peroxide system with 30 phr of HAF, FEF and silica. Here also silica filled mix recorded highest torque with least scorch time and FEF black filled mix recorded lowest torque maxima with a higher scorch time.

Table 4.24(a). Cure characteristics of filled 50/50 NR/HNBR blend cured by TMTD/MBT/S /Peroxide system.

Properties	NH2h	NH2f	NH2s
OCT, 160°C, min	12.31	11.22	15.98
Min. torque, M_L, dNm	2.63	2.02	8.10
Max. torque, M_H, dNm	12.18	11.16	24.43
Scorch time, tS_2, min	1.43	1.49	0.92

Mechanical properties of 50/50 blend of NR/HNBR cured by TMTD/MBT/S/Peroxide system with 30 phr of HAF, FEF and silica are given in Table 4.24(b). Here also properties were comparable for both the black filled mixes. However,

Table 4.24(b). Mechanical properties of 50/50 blend of NR/HNBR cured by TMTD/MBT/S/Peroxide system

Properties	NH2h	NH2f	NH2s
Tensile strength, MPa	16.0	17.7	14.4
Modulus 100%, MPa	1.7	1.8	2.1
Modulus 300 %, MPa	5.2	6.1	4.3
Elongation at break, %	600	590	595
Tear strength, kN/m	32.8	31.2	46.9
Hardness, Shore A	60	60	68
Resilience, %	59	59	56
Compression set, %(22 h 125 ^{0} C)	50.4	49.5	84.3
Heat build up, ΔH, ^{0} C	55	53	64
Dynamic set, %	5.3	4.9	16.9
Din abrasion loss,/cm^3	188.0	180.0	253.3
Din Loss index	59.4	62.1	44.1
Dematia flexing,no.of cycles			
Crack initiation,	85,440	49,00	18,330
Failure	4,55,750	1,59,650	76,917

FEF showed better tensile strength and modulus than HAF and the latter showed better flex resistance. Properties of silica filled mix were inferior except in hardness, tear strength and elongation at break.

The rheographs at 160^0 C of 50/50 blends of different cure systems and fillers are given in Figure 4.17. It showed the effect of fillers on the mixed cure systems 1 & 2. It was observed that system 1, ie. CBS/S/Peroxide cure recorded higher torque than TMTD/MBT/S/Peroxide cure with all the three fillers. Silica gave highest torque followed by HAF black and then FEF black.

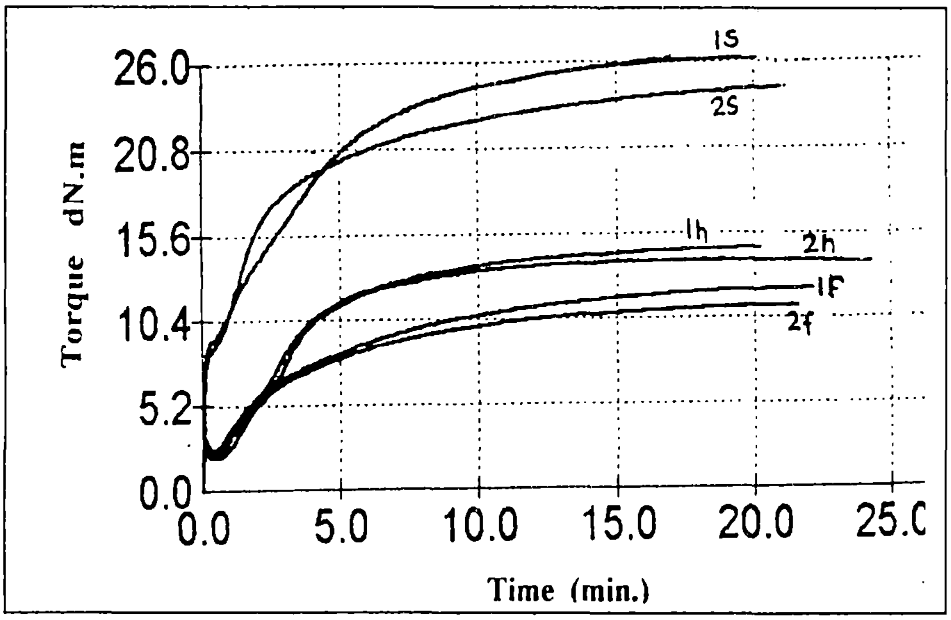

Figure 4.17. Rheographs at 160° C of 50/50 blends of NR/HNBR. Effect of different fillers on mixed cure systems, 1-CBS/S/Peroxide and 2-TMTD/MBT/S/Peroxode.

Figure 4.18 shows the rheographs at 160^0 C of NR (both EV and semi EV cure) and HNBR (peroxide cure) and the blends of three different cure systems, with 30 phr FEF loading. NR showed highest torque and was comparable for both cure systems. Blends with CBS / S/Peroxide cure (NH1) gave torque maxima close to that of HNBR, where as the other two -TMTD/MBT/S/Peroxide cure (NH2) and TMTD/MBT/S cure (NH3)- showed torque maxima close to each other, which was lower than that of both constituents.

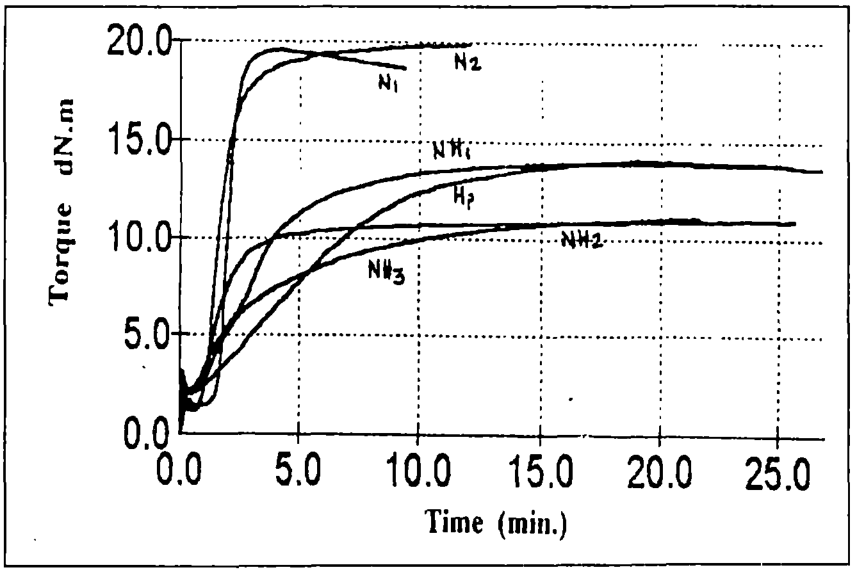

Figure 4.18 . Rheographs at 160° C of NR,HNBR and 50/50 blends containing 30 phr of FEF black of different cure systems.

4.10.C. Effect of DCNR in filled 50/50 blends of NR/HNBR

4.10.C.i) Cure characteristics

The effect of incorporation of 7 parts of DCNR in blends of NR/HNBR filled with 30 parts of FEF black of different cure systems on rheographs is given in Figure 4.19. It was seen that in all the three vulcanization systems, presence of DCNR improved the torque maxima. This showed that in filled systems also DCNR can interact with the constituents and can modify the interface.

The cure characteristics of the blends are given in Table 4.25(a). It was observed that optimum cure time was increased by the incorporation of 7 pars of DCNR to the mixes. Torque maxima was also increased along with decreased scorch time, irrespective of the cure system.

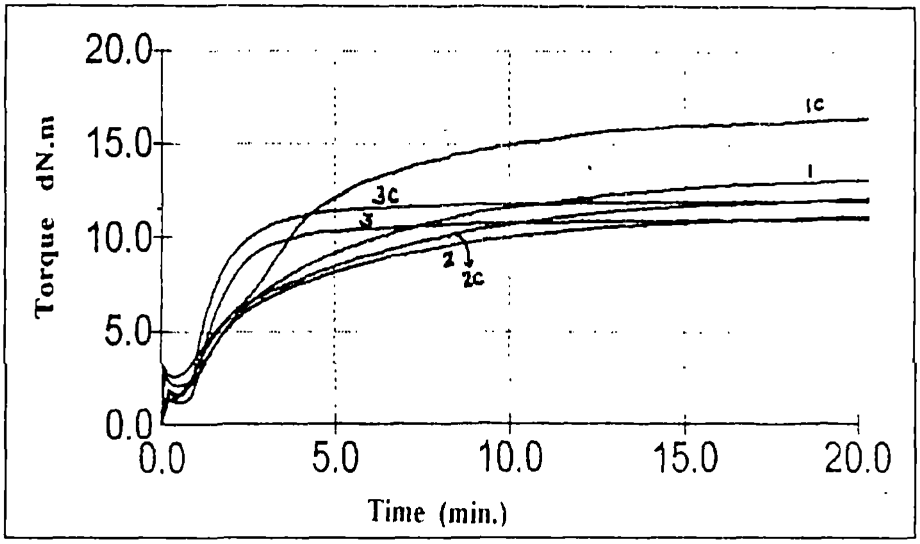

Figure 4.19. Rheographs at 160° C of FEF filled 50/50 blends of NR/HNBR and blends containing 7 parts of DCNR of different cure systems.

Table 4.25(a) Cure characteristics of filled 50/50 blends with different cure system – effect of DCNR

Properties	NH1f	NH1Cf	NH2f	NH2Cf	NH3f	NH3Cf
OCT, 160°C, min	11.10	13.21	11.22	12.98	6.03	6.63
Min. torque, M_L, dNm	2.33	2.68	2.02	2.12	1.98	2.01
Max. torque, M_H, dNm	13.95	16.60	11.16	13.511	11.42	12.01
Scorch time, tS_2, min.	2.41	2.36	2.49	2.41	1.52	1.48

4.10.C.ii) Mechanical properties

Table 4.25(b) gives the mechanical properties of filled blends of NR/HNBR and DCNR containing blends containing 30 phr FEF. Better properties were observed in the order- CBS/S/Peroxide > TMTD/MBT/S/Peroxide > TMTD/MBT/S cure. This was probably due to the more uniform cross linking possible in the mixed cure and possibility of curative migration in the third one (due to the large difference in the saturation level and polarity of the two elastomers) as same cure was used for both the phases.[68-70] However, better values were obtained for CBS/S/Peroxide cure with respect to tear strength, heat build up and flex resistance. For the modified blends containing 7 parts of DCNR, all the properties were improved, irrespective of the cure system, indicating the interfacial inter action resulting in more cross links. 50/50 blend of NR/HNBR modified with 7 parts of DCNR of 15% chlorine content with CBS/S/Peroxide cure containing 30 phr of EFF black recorded better properties like hardness, resilience, elongation at break, tear strength, heat build up and flex resistance than black filled HNBR, cured by peroxide. Tensile properties were comparable.

Table 4.24. Physical properties of the 50/50 blends of NR/HNBR- effect of DCNR.

Properties	**NH1f**	**NH1Cf**	**NH2f**	**NH2Cf**	**NH3f**	**NH3Cf**
Tensile strength, MPa	22.1	24.0	17.7	18.6	14.5	17.0
Modulus 100%, MPa	1.73	2.39	1.78	2.34	1.56	1.84
Modulus 300 %, MPa	5.71	8.81	6.10	8.64	2.77	3.77
Elongation at break, %	710	580	590	560	850	715
Tear strength, kN/m	42.5	50.5	31.2	37.5	28.3	37.8
Hardness, Shore A	58	64	60	64	58	60
Resilience, %	56	57	59	59	56	56
Compression set, %(22 h 125 °C)	60.9	55.6	49.5	47.1	67.8	64.1
Heat build up, ΔH, °C	42	40	53	51	63	60
Dynamic set, %	3.9	3.18	4.96	4.24	11.85	10.34
Din abrasion loss, /cm^3	144.5	126.4	180.0	130.6	161.7	156.8
Loss index	77.2	88.3	62.0	85.5	69.0	71.3
Demattia flexing, no. of cycles						
Crack initiation,	1,76,917	1,79,827	49,000	49,998	19,600	19,939
Failure	3,26,000	4,55,950	1,59,650	1,62,310	66,000	69,300

4.11.Conclusion

Blends of NR and HNBR were prepared by mill mixing without drastically affecting the mechanical properties. Immiscibility of the 50/50 blend of NR and HNBR was reduced considerably by the incorporation of 7 parts of dichlorocarbene modified NR of 15% chlorine content. The chlorine part of DCNR interacted with the acrylonitrile part of HNBR by polar- polar interaction and modified the interface. Consequently there was a higher level of cross-linking and enhancement in physical properties as compared with pure blend. This was revealed from differential solvent swelling studies, V_r values FTIR, SEM and DSC techniques. Properties of the blend were considerably improved by proper selection of cure system. A mixed cure system -CBS/S/Peroxide - yielded better properties to the blend. Incorporation of carbon black significantly improved the mechanical properties. In HAF filled system, all the blends showed better tear strength and heat build up than HNBR and better hardness and high temperature compression set than NR. The flex resistance of filled blends containing 50 parts and above HNBR was superior to both pure NR and HNBR vulcanizates. The tensile properties were slightly inferior to both the components. Properties of filled vulcanizates were further improved by the incorporation of DCNR Higher filler loading slightly reduced the mechanical properties.

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CHAPTER 5

BLENDS OF NR AND HNBR
AGING CHARACTERISTRICS

5.1.Introduction

Rubber products undergo aging during service, as they are exposed to different environmental conditions. These include higher temperature, weathering, contact with solvents and oils, exposure to ozonized air, radiation, light, etc. Rubber vulcanizates are degraded thermally, mechanically and chemically. The extent of these reactions depends on the type of polymer matrix and nature of cross-links employed. Aging behavior of vulcanizates of elastomers and blends have been extensively investigated.[1-6] Natural rubber being highly unsaturated, is easily subjected to the attack by oxygen, ozone and chemicals leading to degradation of polymer chains causing deterioration of properties.[7,8] Several methods have been reported to improve the aging characteristics of NR vulcanizates. Use of waxes[9], addition of anti oxiadants[10,11] and antiozonants[12], flexible coatings[13] and blending with less unsaturated rubbers[14-16] are some of the methods adopted to protect the polymer against such degradations. In order to assess the serviceability of products, it is essential that the aging characteristics of the vulcanizates are to be studied in detail,[17] since rubber is mostly exposed to atmospheric aging conditions. Now a days polymeric blends are used in many applications in nuclear field such as, packings, shock absorber, coatings, shields, constructional elements,[18,19] etc. Hence, this chapter discusses the effect of heat aging, immersion in ASTM oils and fuel, exposure to ozonized air and γ radiation on NR and NR/HNBR vulcanizates. Experimental details are given in chapter 2 and the physical properties of NR and NR/HNBR blends before aging are given in chapter 4.

5.2. Thermal aging

The effect of temperature on performance of polymers and the various degradation reactions including the mechanism were well discussed.[20,21] The air aging characteristics of vulcanizates of NR, HNBR and the blends vulcanized by TMTD/MBT/S (prepared as per Table4.1, method A) at three different temperatures (70^{0}C for 120h, 120^{0}C for 120h and 150^{0}C for 24h) are given in Table 5.1. As known already HNBR had excellent aging

Table 5.1. Physical properties after aging at 3 different temperatures

Properties	**NR**	**HNBR**	**NH**	**NHC7**
1. 70°C for 120 hours				
Tensile strength, Mpa	15.6	22.6	12.2	13.5
Modulus , 100%, MPa	1.1	1.3	1.1	1.5
Modulus , 300%, MPa	1.9	2.2	1.7	1.8
Elongation at break, %	680	720	680	650
2. 120°C for 120 hours				
Tensile strength, Mpa	0.9	18.0	1.9	6.1
Modulus , 100%, MPa	0.4	1.3	1.6	2.0
Modulus , 300%, MPa	-	1.5	1.9	3.5
Elongation at break,%	260	680	305	350
3. 150°C for 24 hours				
Tensile strength, Mpa	0.9	18.2	1.7	4.1
Modulus , 100%, MPa	-	1.1	1.3	2.9
Modulus , 300%, MPa	-	1.3	-	-
Elongation at break, %	50	680	250	275

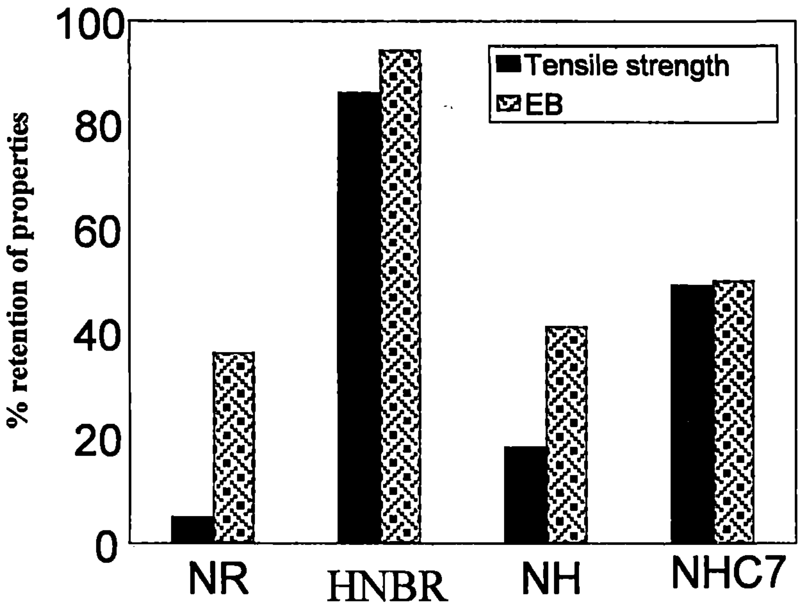

Figure 5.1. Percentage retention of tensile strength and elongation at break for samples aged at 120° C for five days.

characteristics [22,23]compared to NR. NR showed very poor aging behavior at all temperatures. It was clear from the table that at lower temperature, HNBR and the blends showed improvement in properties, probably due to the formation of more cross linking while NR showed degradation. At higher temperature, all compounds showed degradation. However, the blend containing 7 parts of DCNR showed a comparatively higher values for tensile strength and modulus than the pure blends after aging at all temperatures. The retention of the tensile properties at 120^0C is shown in Figure 5.1. The better aging properties of the modified blend may be due to the enhanced homogeneity during mixing and the formation of interfacial cross links that resulted in a lower level of scission reactions during aging.

5.2.i) Effect of cure system

During thermal aging, main chain scission, cross link formation and cross link breakage can take place. It is also possible that an existing cross link may break and a stable one be formed. Cure system can improve the degradation behavior of NR. [24-26] Table 5.2. gives the retention of properties of gum vulcanizates of NR, HNBR and blends of different cure systems (prepared as per Table 4.3, method B) after aging in an air oven at 120 °C for 120 h and 150 °C for 24 h. Here also NR gave very poor aging resistance for both CBS and TMTD cure systems where_as HNBR showed excellent aging resistance for both peroxide and sulfur vulcanization, as was expected. [27] By blending with HNBR, aging properties of NR was considerably improved for all the vulcanization systems. Even though the tensile strength was higher for blend having CBS/S /Peroxide cure, percentage retention of tensile properties after aging at 150°C was slightly higher for blend having TMTD/MBT/S/Peroxide cure. This was probably due to the type of cross-linking possible in the NR phase. Monosulphidic cross linking for the EV system favor the better retention of tensile properties.

By the incorporation of DCNR, aging properties of the blends were considerably improved for all the three cure systems indicating the effective interaction of DCNR, irrespective of the vulcanization system.

Table 5.2. Physical properties of gum vulcanizates after aging

Type of vulcanization →	NR CBS	NR TMTD	HNBR P	HNBR TMTD/ MBT/S	50/50 BLEND					
					CBS/S/PEROXIDE		TMTD/MBT/S / PEROXIDE		TMTD/MBT/S	
Properties ↓	1	2	3	4	5	5C	6	6C	7	7C
a) at 120 °C, 120h										
Tensile strength, Mpa	0.6	0.9	2.2	19.2	6.5	6.7	3.9	5.1	1.9	6.1
Modulus, 100%, MPa	0.4	0.3	1.7	1.3	2.3	2.5	1.9	2.0	1.6	2.0
Modulus, 300%, MPa	-	0.9	-	1.5	-	3.6	-	3.3	1.9	3.9
Elongation at break, %	170	310	105	680	280	320	225	300	310	360
b) at 150 °C, 24h										
Tensile strength, Mpa	1.1	1.1	2.3	19.1	4.9	5.4	3.8	4.9	1.7	4.1
Modulus, 100%, MPa	-	-	2.1	1.5	2.9	3.5	2.6	2.9	1.3	2.9
Modulus, 300%, MPa	-	-	-	1.43	-	-	-	-	1.9	3.1
Elongation at break, %	65	50	135	695	140	170	130	210	250	270

5.2.ii) Effect of filler

Introduction of fillers into polymers lead to a wide range of interactions arising at the polymer filler interphase.[28,29] These dispersed fillers considerably influence the properties of polymer blends including their degradation and stability.[30,31] Table 5.3 gives the retention of properties of NR vulcanizates filled with 30 parts of HAF black, FEF black and silica and HNBR vulcanizates filled with 30 parts of HAF black after aging at 150 °C for 24 hours. Filled HNBR vulcanizates showed excellent tensile strength after aging. Tear strength and hardness of filled HNBR were improved after aging, probably due to formation of more cross-linking. In filled systems also NR showed very poor aging resistance.[32] Tensile properties and tear strength were drastically reduced after aging. However, EV cure showed comparatively better retention of properties.

Table 5.3. Properties of filled NR and HNBR vulcanizates after air aging at 150 ^{0}C /24h

Cure system →	NR CBS/S/Peroxide			NR TMTD/MBT/S/Peroxide			HNBR Peroxide
Filler →	**HAF**	**FEF**	**Silica**	**HAF**	**FEF**	**Silica**	**HAF**
Properties ↓	N1h	N1f	N1s	N2h	N2f	N2s	Hp
Tensile strength, MPa	2.3	2.9	3.9	5.0	5.8	3.4	27.7
Modulus,100%, MPa	-	2.1	2.4	1.2	1.2	1.8	3.1
Modulus 300 %, MPa	-	-	-	-	-	3.0	17.3
Elongation at break, %	95	120	230	280	295	315	450
Tear strength, kN/m	9.1	9.9	19.3	21.8	18.6	18.3	45.9
Hardness, Shore A	48	46	70	44	46	62	64

5.2. ii.a) Effect of fillers on NR/HNBR blends cured by CBS/S/Peroxide system

5.2.ii.a)1. Blend ratio

Aging resistance of NR/HNBR blends of different ratios filled with 30 parts of HAF having CBS/S/Peroxide cure are as shown in Figure5.2. From the figure, it is clear that oxidative aging of NR improved considerably by the incorporation of HNBR. Blends containing 50 parts and above of HNBR exhibited very good resistance towards heat aging, with respect to tensile strength, elongation at break and tear strength.

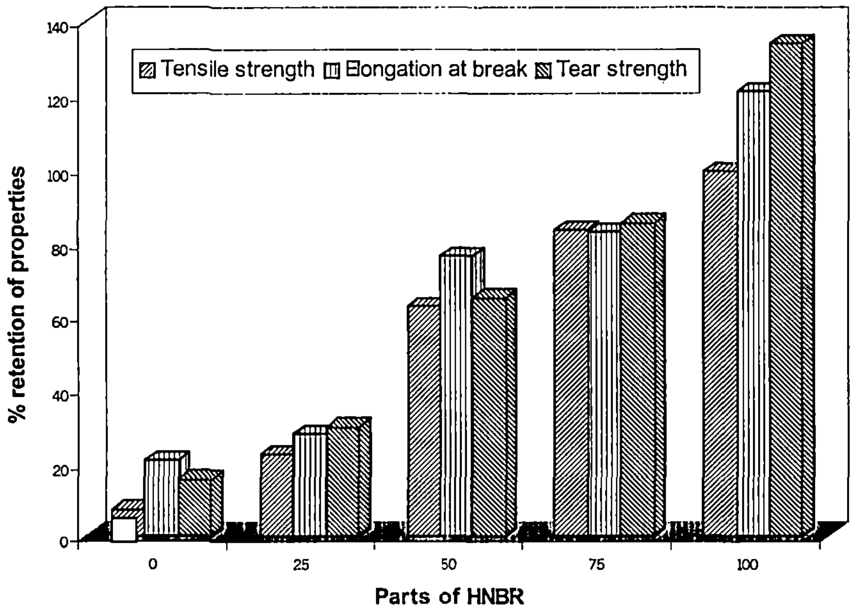

Figure 5.2. Physical properties after air aging at 150^0 C /24h- effect of blend ratio

5.2.ii.a)2. Effect of different fillers

Properties of 50/50 blends cured by CBS/S/Peroxide systems with different fillers after air aging at 150 ^{0} C /24h are given in Table 5.4(a). It was seen that in the case of 50/50 blends, retention of properties were very much improved by the incorporation of fillers. Among the blacks, retention of properties was better for HAF black. Silica filled systems also showed better aging resistance. In all cases, aging increased the modulus, decreased elongation at break and hardness, which is more prominent in the black filled mixes. Retention of tear strength was better in silica filled mix, which improved after aging.

Table 5.4(a). Properties after air aging at 150 ^{0} C /24h- Effect of different fillers on 50/50 blends cured by CBS/S/Peroxide system

Properties	**NH1h**	**NH1f**	**NH1s**
Tensile strength, MPa	13.6	12.2	13.9
Modulus 100%, MPa	2.3	2.3	2.7
Modulus 300 %, MPa	8.1	7.6	6.5
Elongation at break, %	465	465	570
Tear strength, kN/m	27.4	24.4	68.5
Hardness, Shore A	54	56	62

5.2.ii) b) Effect of fillers on NR/HNBR blends cured by TMTD/MBT/S/Peroxide system

Properties of 50/50 blends cured by TMTD/MBT/S/Peroxide systems with different fillers after air aging at 150 ^{0} C /24h are given in Table 5.4(b). In this case also incorporation of fillers considerably improved retention of properties. Both the black filled mixes exhibited comparatively better retention of properties. Silica filled systems also showed better aging resistance. In all cases, aging increased modulus, but to a lower extent than CBS/S/Peroxide system. Retention of hardness and tear strength were better in silica filled mixes.

Table 5.4(b). Properties after air aging at 150 ° C /24h: Effect of different fillers on 50/50 blends cured by TMTD/MBT/S/Peroxide system

Properties	**NH2h**	**NH2f**	**NH2s**
Tensile strength, MPa	13.9	12.3	14.2
Modulus 100%, MPa	1.7	1.8	2.3
Modulus 300 %, MPa	5.2	6.1	4.9
Elongation at break, %	600	590	595
Tear strength, kN/m	30.8	30.3	60.4
Hardness, Shore A	56	58	62

5.2.ii) c) Effect of DCNR on filled NR/HNBR blends of different cure system

Table 5.4(c) gives the properties of 50/50 blends and blends containing 7 parts of DCNR, cured by different vulcanization systems containing 30 phr of FEF black after air aging at 150 ° C /24h. It was observed that higher retention of properties was obtained for the modified blends than the corresponding pure blends. This may be due to the better interfacial interaction between the two phases which led to improved cross linking at the interphase. This resulted in better resistance to oxidative degradation of the filled blends in the presence of DCNR.

Among the different cure systems, TMTD/MBT/S and TMTD/MBT/S /Peroxide systems gave slightly better retention of properties, probably due to the formation of more monosulphidic cross-linking. Effect of DCNR was also more prominent in these cure systems than CBS/S/Peroxide cure.

Table 5.4(c). Properties of filled 50/50 blends of NR/HNBR and blends containing DCNR, of different cure systems after air aging, 150^0 C /24h

Cure system →	CBS/S/Peroxide		TMTD/MBT/S/Peroxide		TMTD/MBT/S	
Properties ↓	**NH1f**	**NH1Cf**	**NH2f**	**NH2Cf**	**NH3f**	**NH3Cf**
Tensile strength, MPa	12.2	13.7	12.3	14.9	12.3	14.6
Modulus 100%, MPa	2.3	2.9	1.7	3.3	1.9	3.1
Modulus 300 %, MPa	7.6	8.0	6.1	8.7	8.6	8.8
Elongation at break, %	465	400	590	515	555	545
Tear strength, kN/m	24.4	28.3	30.3	32.3	25.3	34.1
Hardness, Shore A	56	62	58	62	56	58

5.3. Oil aging

The usage of elastomeric components in the field of oil or gas production such as, hoses, sub sea flexible pipes and engineering applications such as, seals are increasing. Organic liquids tend to weaken elastomers by physico chemical means only causing swelling, where as corrosive liquids tend to attack chemically.[33-35]Different elastomers withstand such attack to different extends. A highly swollen elastomer is often too weak to be useful.

5.3. I) Effect of cure system

Table 5.5 gives the percentage swelling of gum vulcanizates of NR, HNBR and 50/50 blends of NR/HNBR of different cure systems in ASTM oils No.1, 2 and 3 at room temperature, 70°C and 100 °C for 5 days respectively. NR being a hydrocarbon elastomer, swelled highly. HNBR showed excellent resistance towards swelling due to the presence of polar acrylonitrile group. Blends showed swelling lower than the additive average of the components. Cure system affected the swelling slightly, TMTD/MBT/S cure for both phases swell more than the mixed cure, at higher temperature. This was probably due to the lower level of cross-linking of the NR phase and the interphase, which was discussed earlier. Among the 50/50 blends, the DCNR containing one showed better resistance, indicating that in presence of DCNR, blend became more miscible at the interphase. As a result of the interaction of polar chlorine atom present in the DCNR with the polar acrylonitrile group of HNBR, the interface became more continuous and the mix became more uniform. This restricted the swelling of NR phase and hence, the blend showed lower swelling.

Table 5.5. Percentage weight of oil absorbed by gum vulcanizates of NR, HNBR and 50/50 blends of different cure systems in ASTM oils for 5 days.

At room temperature	Cure system →	CBS	Peroxide	CBS/S/Peroxide		TMTD/MBT/S/Peroxide		TMTD/MBT/S	
	ASTM No;	NR	HNBR	5	5C	6	6C	7	7C
	1	47.5	0.8	17.6	13.2	12.5	11.9	13.8	12.9
	2	71.8	2.9	24.3	20.8	26.8	25.1	26.3	23.5
	3	180.7	4.7	54.3	53.7	58.7	54.3	77.6	68.6
At 70°C	1	126.9	0.9	33.7	32.6	34.9	33.5	47.4	42.5
	2	207.7	6.9	68.3	63.1	67.0	63.1	80.4	79.0
	3	285.9	18.7	101.9	99.9	100.3	98.8	155.5	145.3
At 100 °C	1	*	2.1	79.6	77.7	83.4	79.9	95.0	93.1
	2	*	10.7	99.8	96.6	99.8	97.8	143.1	138.9
	3	*	21.0	143.0	140.3	148.1	138.0	233.7	230.6

* Sample dissolved

5.3. ii) Effect of filler

Table 5.6 shows the retention of tensile properties of filled vulcanizates of NR (semi EV and EV cure with different fillers) and HNBR (peroxide cure with HAF black) after immersing in ASTM Oil No:2 at room temperature for 5 days. HNBR showed excellent retention of properties; tensile strength, modulus and elongation at break were slightly improved after aging. In the case of NR, silica filled vulcanizates showed better retention for both cure, probably due to the polar nature of silica. Effect of HAF and FEF black were comparable. CBS/S system showed better retention of properties, probably due to the higher level of cross-linking.

Table 5.6. Tensile properties of filled vulcanizates of NR and HNBR after oil aging Oil (ASTM No:2 at room temperature/5 days)

Cure system →	CBS/S			TMTD/MBT/S			Peroxide
Properties ↓	**N1h**	**N1f**	**N1s**	**N2h**	**N2f**	**N2s**	**Hp**
Tensile strength, MPa	9.7	9.4	16.9	7.2	5.9	13.5	30.1
Modulus, 100%, MPa	1.6	1.5	1.7	1.5	1.8	1.6	2.2
Modulus 300 %, MPa	7.7	7.2	3.0	-	-	2.6	13.8
Elongation at break, %	370	360	715	270	235	755	480

5.3.ii) a) Blend ratio

Table 5.7 gives the percentage swelling of filled blends of NR/HNBR cured by CBS/S/Peroxide filled with 30 parts of HAF in ASTM oils No.1, 2 and 3 at room temperature, 70°C and 100 °C for 5 days respectively. It was clear that oil resistance of NR was remarkably improved by blending with HNBR and oil swelling decreased with increased HNBR content. It was also observed that filled systems showed considerably lower swelling than gum mixes due to the lower polymer content of the filled blends.

Table 5.7. Percentage weight of oil absorbed by [illegible] filled blends of varying ratios after immersion in ASTM oils for 5 days.

	ASTM NO:	NR	NH75/25	NH50/50	NH25/75	HNBR
Room temperature	1	29.5	21.2	4.9	0.4	-
	2	46.1	34.1	9.1	3.0	0.8
	3	135.29	107.04	26.97	9.51	5.41
70 °C	1	67.52	52.1	17.1	1.4	-
	2	116.3	88.9	34.3	11.6	4.1
	3	161.1	148.3	69.5	27.8	9.4
100 °C	1	152.8	145.0	39.1	8.8	-
	2	280.1	251.8	86.4	38.3	5.4
	3	Dissolved	Swelled	133.7	53.5	11.3

Figure 5.3 is the photograph of oil-swelled samples NR/HNBR blends of different blend ratios vulcanized by CBS/S/Peroxide cure system containing 30 phr of HAF black in ASTM oil No:2 for 5 days at room temperature.

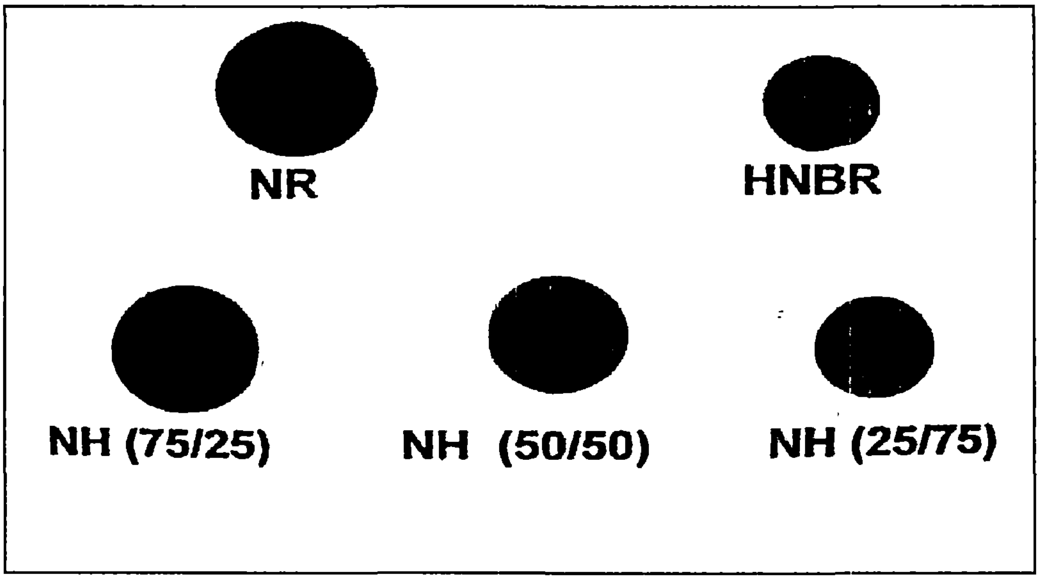

Figure 5.3. Oil swelled samples of NR/HNBR blends of different ratios in ASTM oil No:2 for 5 days at room temperature.

Figure 5.4 shows the percentage retention of physical properties of blends of different ratios after aging in ASTM No.2 oil at room temperature for 5 days. Retention of tensile properties after oil aging was remarkably improved with HNBR loading. The lower modulus value of HNBR after aging can be attributed to the increased elongation at break.

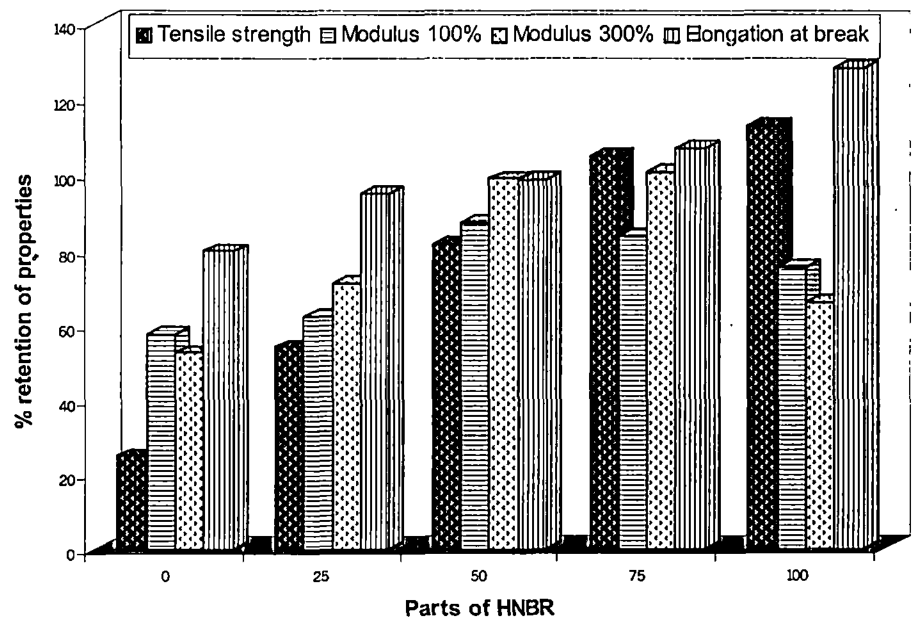

Figure 5.4. Retention of properties of filled blends of different ratios in ASTM oil No.2

5.3.ii) b) Effect of cure system, fillers and DCNR

Percentage weight of oil absorbed ~~per gram~~ by 50/50 blends having different cure systems, different fillers and blends containing 7 parts of DCNR, filled with 30 parts of FEF black in ASTM oils No.1, 2 and 3 at room temperature, 70°C and 100 °C for 5 days respectively are given in Table 5.8. Filled mixes showed strikingly lower swelling than the corresponding gum mixes. Cure system also showed the same trend as in gum mixes,

Table 5.8. Percentage weight of oil absorbed by 50/50 blends having different cure system and fillers after immersion in ASTM oils for 5 days.

	Cure system →	CBS/S/Peroxide				TMTD/MBT/S/Peroxide				TMTD/MBT/S	
	ASTM NO.	NH1h	NH1f	NH1Cf	NH1s	NH2h	NH2f	NH2Cf	NH2s	NH3f	NH3Cf
At room temperature	1	4.9	10.4	4.2	8.6	5.9	8.9	6.8	8.4	11.8	10.8
	2	9.1	16.5	9.8	15.6	12.0	14.3	10.9	14.7	19.9	16.9
	3	26.9	49.1	27.9	46.8	34.1	40.8	31.8	45.6	65.5	61.8
At 70°C	1	17.0	23.6	15.1	21.2	16.4	24.1	21.0	24.2	29.9	26.3
	2	34.3	47.8	31.0	48.3	30.4	47.7	38.9	47.5	55.1	52.0
	3	69.4	73.7	59.5	68.2	67.8	82.0	65.3	66.0	107.4	105.9
At 100°C	1	39.0	55.7	36.7	31.1	35.3	47.9	36.7	27.9	38.4	36.3
	2	86.4	108.2	76.4	71.4	65.3	98.1	77.1	60.2	91.5	83.8
	3	133.7	170.3	127.7	142.5	94.9	192.2	129.3	88.0	153.7	134.5

however, far better than gum mixes. In filled system also DCNR containing mixes exhibited enhanced resistance to oil swelling. Even at higher temperature blends showed remarkably better resistance than NR towards swelling by oils, especially in ASTM No.1 oil. Figure 5.5 is the photograph of oil-swelled samples of 50/50 blends of NR/HNBR cured by different vulcanization systems and blend containing 7 parts of DCNR in ASTM oil No:2 for 5 days at room temperature.

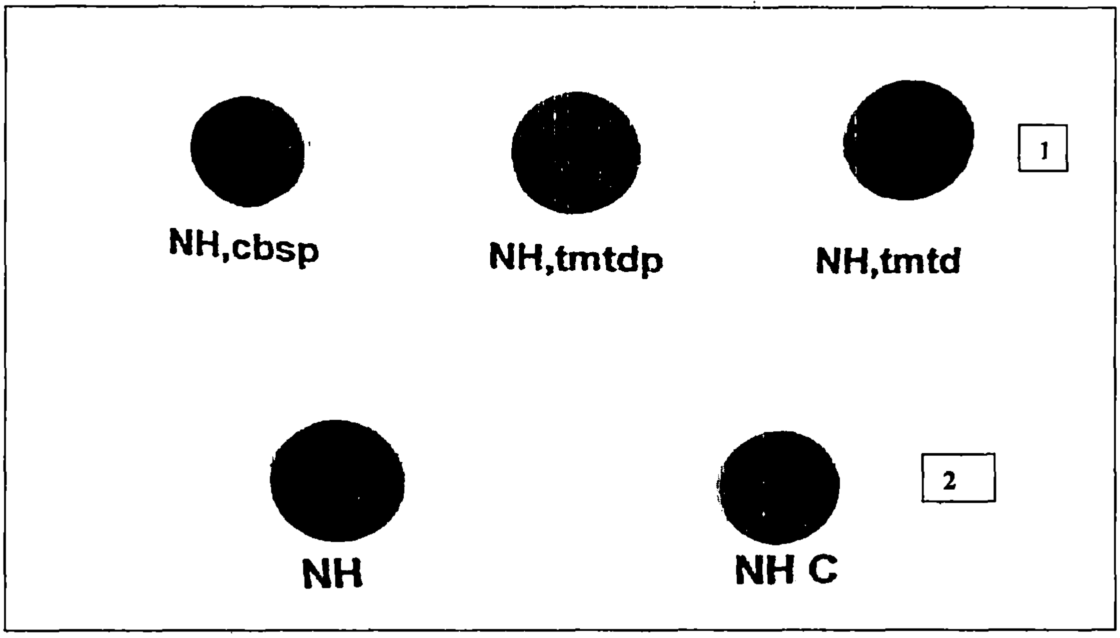

Figure5.5. Oil swelled samples of NR/HNBR blends in ASTM oil No:2 for 5 days at room temperature.1-vulcanization system and 2-effect of DCNR

. Table 5.9. shows the retention of tensile properties of 30 phr FEF filled vulcanizates of 50/50 blends after aging in ASTM No.2 oil at room temperature for 5 days. Here, the mixed cure systems exhibited better retention of properties than TMTD/MBT/S cure for both phases, due to the better interfacial mixing of the two rubbers and higher cross-linking possible. Modified blends exhibited considerably higher retention of properties than the corresponding pure blends in all the three cure systems.

Table 5.9. Tensile properties of filled 50/50 blends and modified blends of different cure systems after oil aging (ASTM No:2 oil at room temperature for 5 days)

Cure system →	CBS/S/Peroxide		TMTD/MBT/S/Peroxide		TMTD/MBT/S	
Properties ↓	**NH1f**	**NH1Cf**	**NH2f**	**NH2Cf**	**NH3f**	**NH3Cf**
Tensile strength, MPa	18.9	19.1	14.5	15.6	8.5	9.2
Modulus 100%, MPa	1.70	2.17	1.70	2.35	1.38	1.59
Modulus 300 %, MPa	6.46	7.78	5.90	7.42	2.57	3.51
Elongation at break, %	565	560	530	515	480	575

5.4. Fuel aging

Durability of elastomers in corrosive fluids has been studied earlier. [36-38]The effect of aging in ASTM fuel C on tensile properties of NR, HNBR and the blends of varying ratios at room temperature for 5 days are shown in Figure 5.6. NR swell highly and HNBR lightly in ASTM fuel C as shown in Figure 5.7. The volume swell of the blends in ASTM fuel C was reduced with the HNBR content. Retention of tensile strength of NR was slightly inferior to HNBR. Blends showed improved retention of properties.

Table 5.10 gives the effect of different fillers on retention of mechanical properties of NR vulcanizates in ASTM fuel C. Silica filled NR showed better retention than black. Volume swelling (expressed as weight of fuel absorbed /g) was also lower for silica filled vulcanizates. Table 5.11 shows the fuel aging of filled vulcanizates of 50/50 blends. Mixed cure system yielded better retention of properties for the blends than same cure for both phases. Retention of properties was further improved for the modified blends irrespective of the cure systems. In presence of DCNR, more interfacial bonds are formed which restricts the swelling by fuel and enhanced retention of properties.

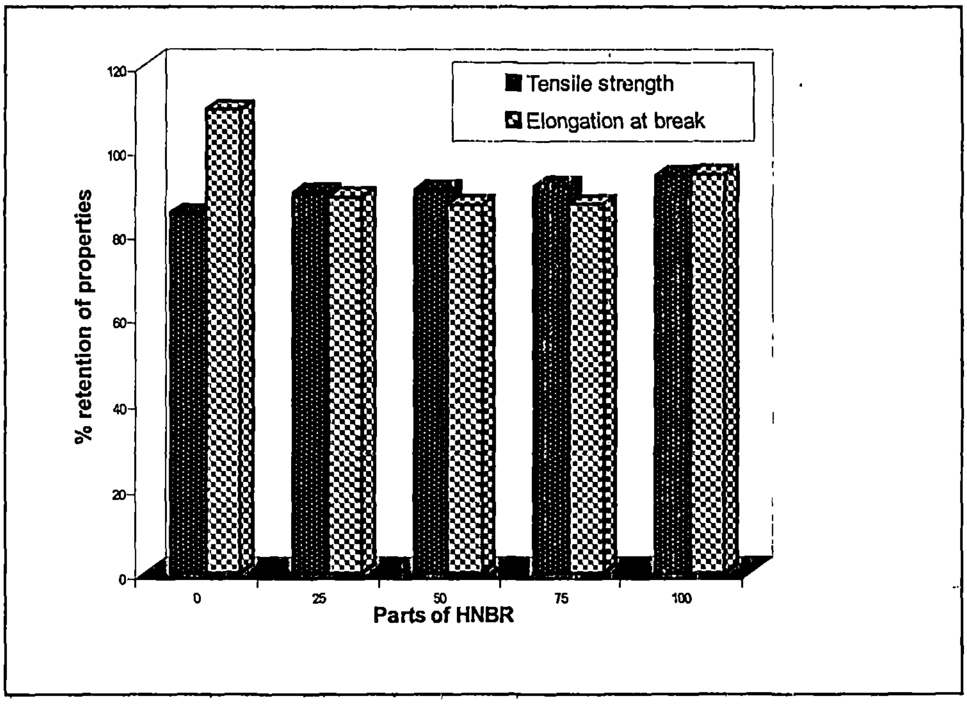

Figure 5.6. Effect of blend ratio on percentage retention of properties of filled NR/HNBR blends after fuel aging at room temperature.

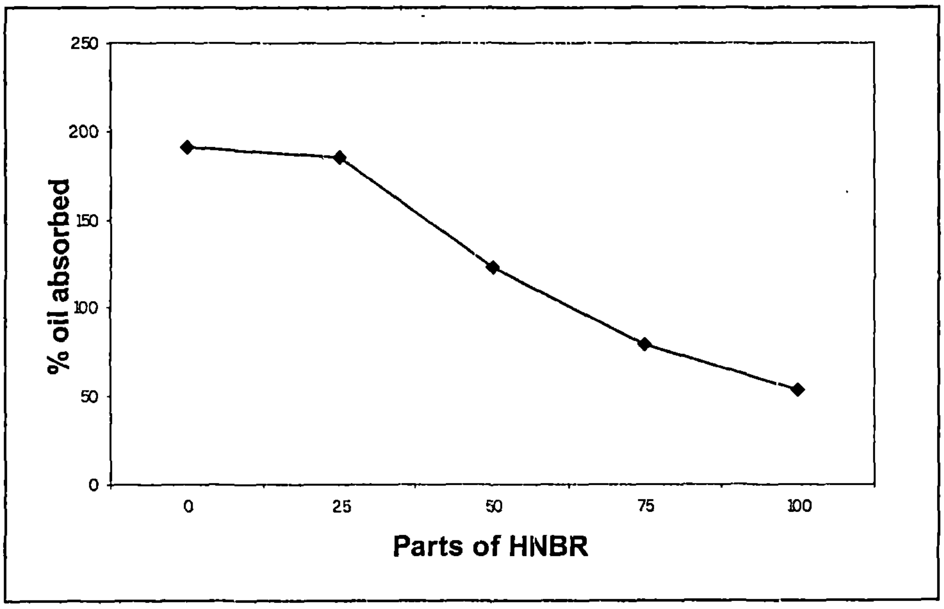

Figure 5.7. Effect of blend ratio on percentage of fuel absorbed by filled NR/HNBR blends

Table 5.10. Fuel aging of filled NR and HNBR vulcanizates in ASTM fuel C, at room temperature for 5 days.

Cure system →	CBS/S			TMTD/MBT/S			Peroxide
Properties ↓	**N1h**	**N1f**	**N1s**	**N2h**	**N2f**	**N2s**	**Hp**
Weight of fuel absorbed /g	1.9	1.9	1.3	1.9	1.9	1.4	0.5
Tensile strength, MPa	26.7	26.8	18.7	24.1	23.7	18.3	26.1
Modulus 100%, MPa	1.9	1.9	1.7	1.6	1.8	1.7	2.9
Modulus 300 %, MPa	8.0	8.0	4.6	4.4	7.9	4.4	21.2
Elongation at break, %	555	550	610	500	515	600	350
Hardness, Shore A	58	56	58	56	54	60	58

Table 5.11. Fuel aging of filled 50/50 blends (ASTM fuel C, at room temperature/5 days)

Cure system →	CBS/S/Peroxode				TMTD/MBT/S/Peroxide				TMTD/MBT/S	
Properties ↓	NH1h	NH1f	NH1Cf	NH1s	NH2h	NH2f	NH2Cf	NH2s	NH3f	NH3Cf
Weight of fuel absorbed /g	1.2	1.4	1.0	1.2	1.2	1.3	1.1	1.2	1.5	1.1
Tensile strength, MPa	18.6	19.3	22.9	17.6	14.1	16.7	17.1	15.1	14.7	15.7
Modulus 100%, MPa	2.9	2.5	3.6	2.3	2.5	2.3	3.6	2.3	2.0	2.2
Modulus 300 %, MPa	11.0	9.2	12.0	5.2	8.3	7.7	10.3	4.8	4.1	4.8
Elongation at break, %	420	480	440	550	405	470	475	550	500	480
Hardness, Shore A	60	60	64	64	58	58	64	64	58	60

5.5. Ozone aging

Ozone induced stress cracking is considered as a problem normally diminishing the appearance and serviceability of rubber products.[39,40] The cracking is the result of the rapid reaction of ozone with the olefinic double bonds to form an ozonide ring.[41] The scission of the ring produce surface cracks when the elastomer is stretched. The cracks formed on the surface perpendicular to the applied stress, is propagated catastrophically into the interior resulting in the failure of the product. Proper selection of cure system, incorporation of antiozonants and blending with saturated polymers are the methods adopted to reduce ozone attack.[42-44] Samples of NR, HNBR and the blends of different ratios, cure systems (both gum and filled) were exposed to ozone atmosphere of 50ppm ozone concentration, and the surfaces were observed for the development of cracks, periodically.

5.5. i) Effect of cure system

Figure 5.8 shows the photographs of ozone-irradiated surfaces of gum vulcanizates for 50 h. It was observed that, NR samples cracked within 2 hours of irradiation and the propagation was fast as NR contains active double bonds. HNBR samples being saturated remained unaffected. Blend having CBS/S/Peroxide cure showed cracks after 40 h of exposure. Other two systems showed no cracks up to 60 h. Blooming of the chemicals was also observed for TMTD/MBT/S cure for both phases. Modified blends showed better resistance due to the more homogeneous and higher level of cross-links in presence of DCNR.

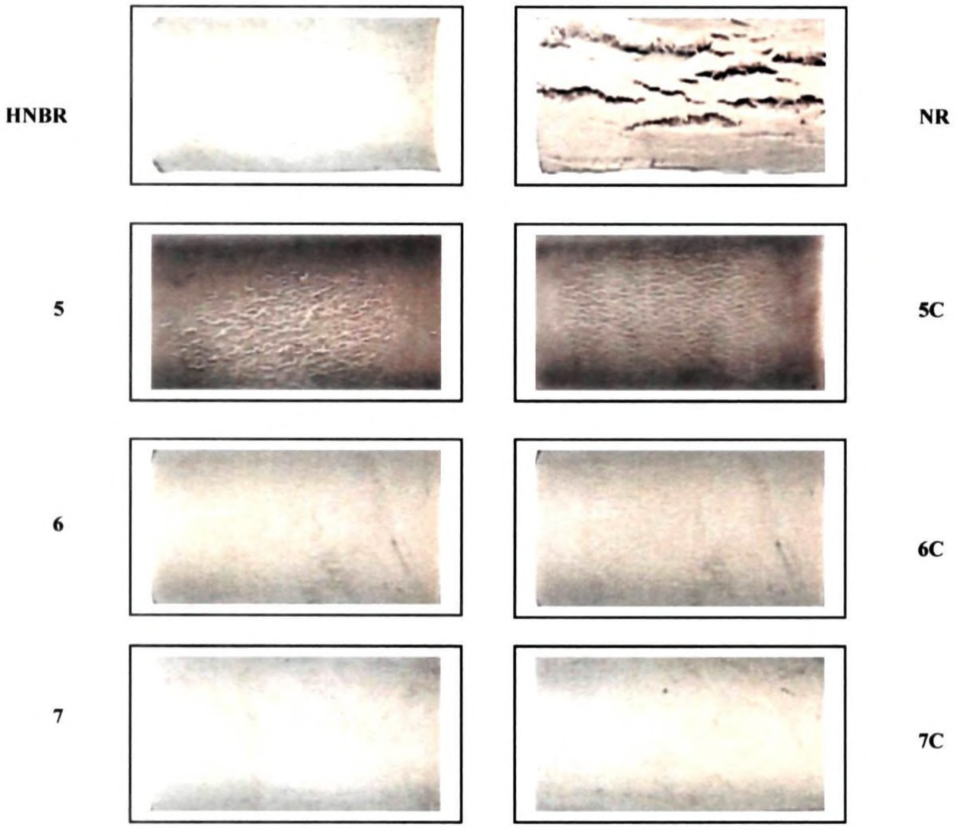

Figure 5.8. Ozone irradiated surfaces of gum vulcanizates of NR, HNBR and 50/50 blends, after 40 h of exposure.

5.5. ii) Effect of filler

Figure 5.9 shows the ozone irradiated surfaces of filled NR vulcanizates for 20 h. It was observed that filled NR also exhibited very poor resistance towards ozone degradation. The cracks formed within first two hours on all surfaces. In the case of black filled ones, cracks catastrophically propagated and fractured. Among the black filled vulcanizates, semi EV system showed faster development and propagation of cracks and ruptured within18 hours of irradiation. In the silica filled systems, crack propagation ie, widening and deepening of the crack was slower and did not break completely.

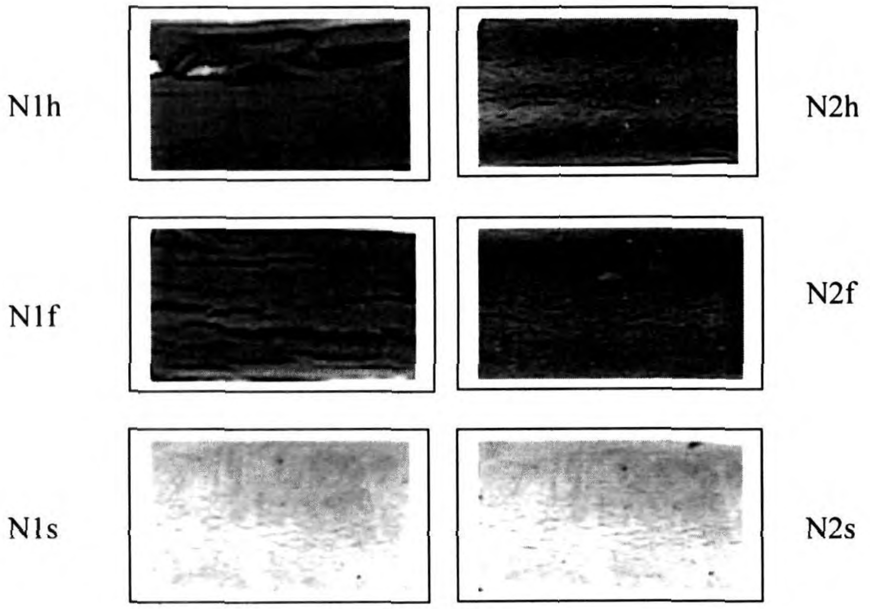

Figure 5.9. Ozone irradiated surfaces of filled NR vulcanizates of CBS/S and TMTD/MBT/S cure and different fillers after 20 h of exposure.

5.5. ii.a) Blend ratio

Figure 5.10 shows the ozone irradiated surfaces of vulcanizates of HAF filled NR /HNBR blends cured by CBS/S/Peroxide of different ratios. It was observed that in blends having higher percentage of NR, crack developed faster, where as blends having HNBR 50 parts and above remained unaffected even up to 150 h of irradiation. 75/25 NR/HNBR showed crack formation after 16 h of irradiation and the cracks developed from the sides of the sample. Widening and deepening of cracks was faster for both NR and 75/25 blends and broke under prolonged irradiation. 50/50, 25/75 blends did not show any cracks even up to 150 h of ozone irradiation

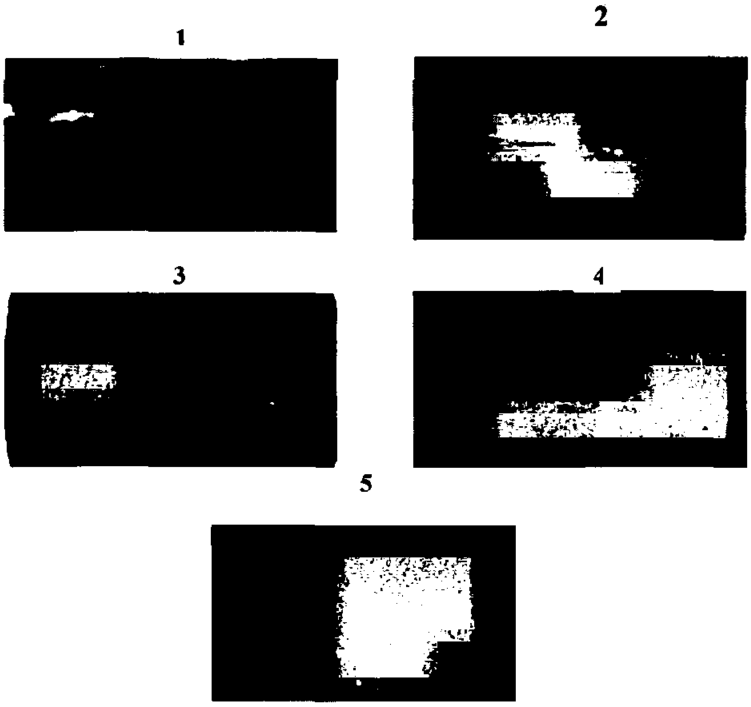

Figure 5.10. Ozone irradiated surfaces of 1- NR, 2- 75/25, 3-50/50, 4- 25/75 blends of NR/HNBR and 5. HNBR, after 20 h of exposure.

5.5.ii.b) Effect of DCNR

Figure 5.11 shows the ozone-irradiated surfaces of filled vulcanizates of 50/50 NR/HNBR blends and blends containing 7 parts of DCNR, after100 h of irradiation. It was observed that surfaces of all the filled 50/50 blends and modified blends were free of cracks, irrespective of cure system or filler. This was probably due to the reinforcing effect of the filler on the blend. [45,46] But in the case of TMTD/MBT/S cure for both phases, blooming was observed on the surfaces after exposure, which was obvious from the photographs. This may be due to the migration of the excess curatives present in the vulcanizates to the surface.[47] However,lower level of blooming observed for the modified blend, due to the higher consumption of curatives indicating higher level of cross linking

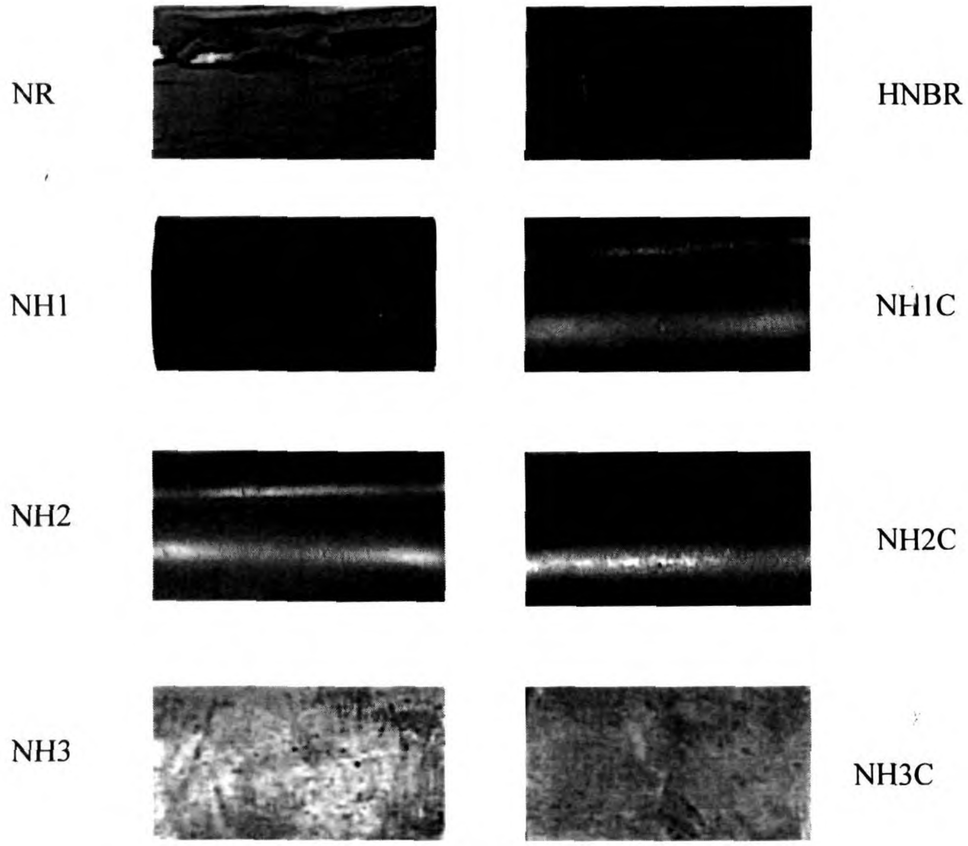

Figure 11. Ozone irradiated surfaces of NR, HNBR and 50/50 blends and modified blends of different cure systems after 100 h of exposure.

5.6. Exposure to γ radiation

Application of elastomer components in nuclear plants, radiation therapy medical equipments, etc. have been increasing. Much work has been done on the effect of radiation on elastomers[48,49] and blends.[50] Radiation is a powerful method for cross linking elastomers.[51,52] The extent of cross linking or degradation undergone by each polymer compounds depends on the nature of the polymer matrix, type of ingredients, presence of protective agents, etc. Table 5.12 and 5.13 show the retention of tensile properties of the filled vulcanizates of NR & HNBR and blends respectively after γ radiation for 25 and 35 M rad in a γ chamber. Reduction of tensile strength is a better measure of irradiation damage in rubber vulcanizates. Carbon black was found to protect rubber from degradation at lower levels of radiation.[53] It was observed that the NR vulcanizates gave lower tensile strength, modulus and higher elongation after irradiation. HNBR gave lower elongation, improved modulus and almost same tensile strength. Radiation has two major effects on mechanical properties. It can produce permanent cross-linking between carbon atoms and can reduce the crystallinity. These two effects operate in opposite directions; the former increases the stiffness while the latter reduces it. In the case of NR vulcanizates, degradation occurred which led to lower tensile properties where as in HNBR radiation increased cross linking[54] as was evidenced by the decreased elongation without affecting tensile strength and improved modulus at 25 M rad irradiation. However, on prolonged irradiation, both NR and HNBR vulcanizates undergone degradation as tensile strength was reduced after irradiation at 35 M rad.

In the case of blends, improved tensile strength, modulus and decreased elongation at break were observed which indicated that additional cross-linking was formed by radiation. This was more noticeable in the blends vulcanized by TMTD/MBT/ Sulfur /Peroxide cure. This was probably due to the excess peroxide present, which activates further cross-linking and or higher cross linking of HNBR phase. On further irradiation, tensile strength was slightly reduced showing the possibility of degradation. However the increased modulus indicated higher cross-linking with increased radiation. In all cases improved properties were obtained for modified blends.

Table 5.12. Tensile properties of filled NR and HNBR vulcanizates after γ irradiation.

Cure system →	CBS/S			TMTD/MBT/S			Peroxide
Properties ↓	N1h	N1f	N1s	N2h	N2f	N2s	Hp
25 M rad							
Tensile strength, Mpa	28.7	27.4	18.1	24.2	20.0	18.2	27.8
Elongation at break, %	615	590	630	570	485	685	270
Modulus 100%, Mpa	2.0	1.9	2.5	1.6	1.8	2.3	4.2
Modulus 300%, Mpa	8.3	8.4	6.5	6.9	7.9	6.6	-
35 M rad							
Tensile strength, Mpa	23.4	22.3	17.5	20.2	18.9	17.5	24.7
Elongation at break, %	495	495	525	470	460	525	210
Modulus 100%, Mpa	2.9	2.6	3.7	2.5	2.3	2.9	7.7
Modulus 300%, Mpa	10.5	10.6	8.0	8.8	8.7	7.8	-

Table 5.13. Tensile properties of filled NR/HNBR vulcanizates after γ irradiation.

Cure system →	CBS/S/Peroxide				TMTD/MBT/S/Peroxide				TMTD/MBT/S	
Properties ↓	NH1h	NH1f	NH1fC	NH1s	NH2h	NH2f	NH2fC	NH2s	NH3f	NH3fC
25 M rad										
Tensile strength, Mpa	24.8	23.8	24.6	20.2	24.8	25.3	25.9	20.9	22.0	22.9
Elongation at break, %	480	495	460	540	525	555	490	550	630	560
Modulus 100%, Mpa	2.4	2.0	3.4	2.6	2.0	2.3	4.6	2.7	1.9	2.6
Modulus 300% ,Mpa	11.0	7.8	14.4	5.9	8.6	9.2	17.7	6.0	5.3	7.7
35 M rad										
Tensile strength, Mpa	22.9	22.6	22.8	17.3	24.5	24.2	24.6	17.6	20.2	20.5
Elongation at break, %	420	425	400	405	410	425	390	415	450	425
Modulus 100%, Mpa	3.3	3.2	4.4	3.5	3.3	3.2	4.1	3.5	2.7	3.0
Modulus 300%, Mpa	13.9	13.4	17.1	8.4	14.9	13.8	15.5	8.4	8.3	9.9

5.7 .Conclusion

Aging characteristics of NR vulcanizates towards heat, oil, fuel, ozone and radiation can be remarkably improved by blending with HNBR. By proper selection of cure system and modification of the blend by incorporating 7 parts of dichlorocarbene modified NR of 15 % chlorine content, aging properties of blends of NR/HNBR can further be improved Incorporation of fillers like HAF, FEF or silica significantly enhanced the aging characteristics of the 50/50 blends. Among the different cure systems, TMTD/MBT/S and TMTD/MBT/S /Peroxide systems gave better retention of properties than CBS/S/Peroxide system. The thermal aging characteristics improved by the addition of filler in the order HAF ≥ silica > FEF. Very good aging resistance towards oils and fuels can be attained for NR/HNBR blend at higher loading of HNBR and filler. Excellent aging resistance towards ozone and γ radiation of the filled NR/HNBR blends were obtained at higher HNBR content.

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CHAPTER 6

BLENDS OF NR AND HNBR
CHEMICAL CHANGES TAKING PLACE DURING AGING

6.1.Introduction

Stress relaxation properties assume importance in static and dynamic application under stress. The stress under a constant deformation decays by an amount substantially proportional to the logarithm of the period of deformed state. The stress relaxation measurement is considered as a high speed method for predicting the long term behavior of rubber vulcanizates.[1-5] Stress relaxation of an elastomeric material is found to be depend on various factors such as,composition of the mix, nature and type of cross links, cross link density, hysterisis behavior of the compound, type of plasticizers and antioxidants used and testing conditions such as temperature, strain level and strain rate. Kalfayen, et.al[6] described stress relaxation as a tool to study aging characteristics since it gives an idea about the rate of network scission and formation during aging. Bhagvan,et.al[7] have been studied the stress relaxation behavior of jute fibre- nitrile rubber composites and reported a two stage relaxation pattern. Stress relaxation in rubber containing reinforcing fillers was reported by Cotton and Boonstra.[8]

In this chapter the stress relaxation behavior of NR and HNBR blends was studied at different temperatures and the effect of DCNR was evaluated. The scission and cross-linking reactions taking place during aging was studied by selective solvent swelling.

The stress relaxation of the blends was studied using Zwick Universal testing machine (Model 1474) at 100^{0}C, 130^{0}C and 150^{0}C. The calculation of permanent set during stress relaxation was from the scission and cross linking reactions that take place during intermittent and continuous stress relaxation as reported by Andrews, et al.[9]

For a homogeneous network in which all network chains are at equlibrium at length l, the equation relating stress and elongation to attain length lu in terms of concentration of network chains in rubber is given by

$f = skT\,[\,(l / lu)^2 - (l / lu)\,]$ ....(1)

Where f is the stress per unit cross sectional area, s is the number of network chains per unit volume of rubber, k is the Boltzmann's constant and T is the absolute temperature.

Thus at a fixed extension and constant temperature, the stress produced is entirely due to load sharing of rubber chains. Hence if network chains break, then the stress would decay. There for, at any time, t

$f(t) \alpha s(t)$

$f(t) / f(0) = s(t) / s(0)$ .... (2)

f(0) and s (0) denote the corresponding values at time = 0.

It is possible that if any new chains are produced, then some will bear load and some may not. Hence,in a rubber sample maintained at a fixed extension, there will be two types of network. One type of network is in equilibrium with the stretched condition. If the unstretched and stretched lengths are denoted by lu and lx respectively and the final length or set length by ls, then we may write for the two sets of network the following two equations.

$fu = s_u kT [(ls / lu)^2 - (lu / ls)]$ ....(3)

$fx = s_x kT [(lx / lu)^2 - (lx / ls)]$ ....(4)

where fu is the stress per unit attained cross sectional area which have their equilibrium at unstretched length and s_u the number of those chains. fx and s_x are the corresponding stress and number of chains which are in equilibrium at the extended length.

For equilibrium at permanent set, $fu = - fx$ ....(5)

Substituting (3) and (4) in (5) and on simplification we get

$s_u lx^2 / s_x lu^2 = lx^3 - ls^3 / lx^3 - lu^3$ ....(6)

% permanent set = $(ls - lu) / (lx - lu) \times 100$ ....(7)

$= (ls / lu - 1) / (lx / lu - 1) \times 100$ ....(8)

From simplification of equation (6) we get

$ls / lu = [\{ (lx / lu)^3 - 1 / (s_u / s_x)(lx / lu)^2 + 1 \} + 1]^{1/3}$ ....(9)

Substituting equation (9) in equation (8) we get

% permanent set $= [\{ C_1/(s_u / s_x) (C_2 + 1) + 1 \}^{1/3} - 1] C_3$ ....(10)

where C_1, C_2 and C_3 are constants.

The stress value given by continuous curve is proportional to s_u and that given by intermittent curve is proportional to $s_u + s_x$.

If f(t) / f(0) values given by continuous curve is designated as U and the difference in f(t) / f(0) values of the intermittent and continuous curves as X, then

$s_u / s_x = U/X$ ...... (11)

$\% \text{ Permanent set} = [\ \{\ C_1/(U/X)\ (C_2 + 1) + 1\ \}^{1/3} - 1]\ C_3$ ....(12)

$C_1 = (lx/lu)^3 - 1$

$C_2 = (lx / lu)2$

$C_3 = 100 / (lx / lu) - 1$

The test samples used were dumb bell pieces cut from tensile sheets vulcanized at 150^{0}C, from mixes of NR, HNBR, 50/50 blend of NR/HNBR and blend containing 7 parts of DCNR of 15% chlorine content prepared as per Table 4.1.

6.2. Stress relaxation characteristics

The net cross-linking and chain scission reactions occurring during aging was obtained from intermittent and continuous stress relaxation studies. The stress relaxation characteristics and permanent set obtained at temperature of 130^{0}C for 50/50 blend and blend containing DCNR are as shown in Figures 6.1 and 6.2. respectively. The experimental values of permanent set obtained for blends agreed with the calculated values and hence they obey the two-network theory of aging.[10,11] The continuous and intermittent stress relaxations of the blends at 100 ^{0}C and 130^{0}C are shown in Figure 6.3 and 6.4 respectively. The change in modulus for the intermittent stress relaxation was very less at 100 ^{0}C and 130 ^{0}C, due to the better aging characteristics of HNBR. It had been observed earlier that the relaxed modulus of HNBR was less sensitive to temperature changes and showed a slight increase at high temperature of 140^{0}C.[12] At both 100 ^{0}C and 130 ^{0}C, there were more scission reactions in the absence of DCNR as a higher stress relaxation was observed for both continuous and intermittent stress relaxation measurements. Probably interfacial bonds help in having a lower stress relaxation for the blend containing DCNR. The intermittent stress relaxation also showed a lower level of chain scission for the blend containing DCNR as compared to the pure blends during aging. However,at 150^{0}C, there was more cross-linking and more scission reactions for pure blend than DCNR containing blends as observed from Figure 6.5.

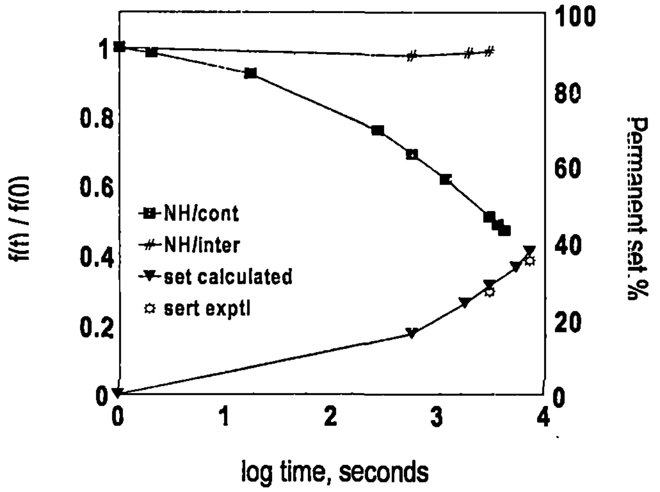

Figure 6.1. Intermittent and continuous stress relaxation along with calculated and experimental permanent set for 50/50 NR/HNBR blends at 130^0C

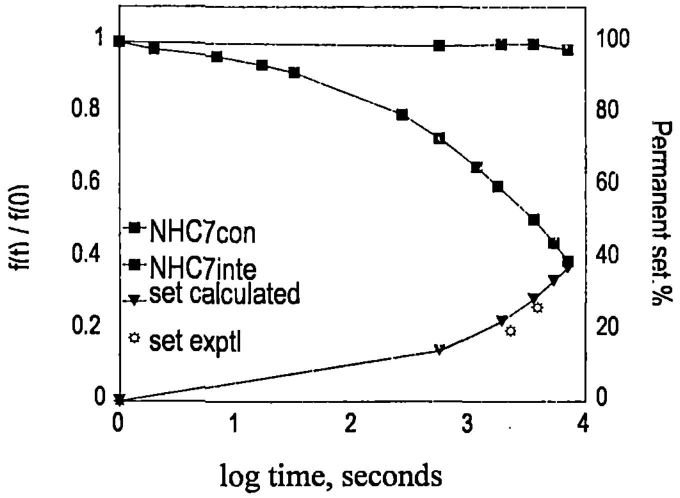

Figure 6.2. Intermittent and continuous stress relaxation along with calculated and experimental permanent set for the modified NR /HNBR blends at 130^0C

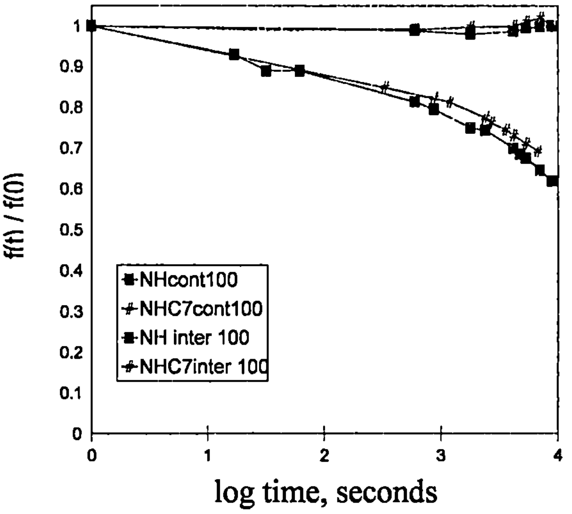

Figure 6.3 . Intermittent and continuous stress relaxation of pure and modified NR/HNBR blends at 100°C

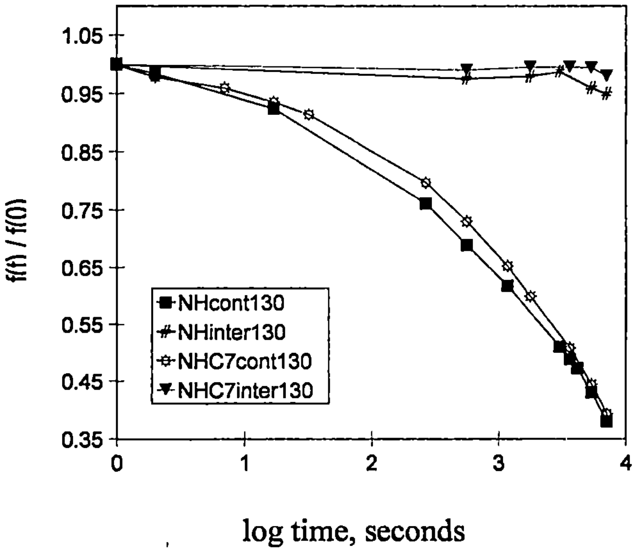

Figure 6.4. Intermittent and continuous stress relaxation of pure and modified NR/HNBR blends at 130°C

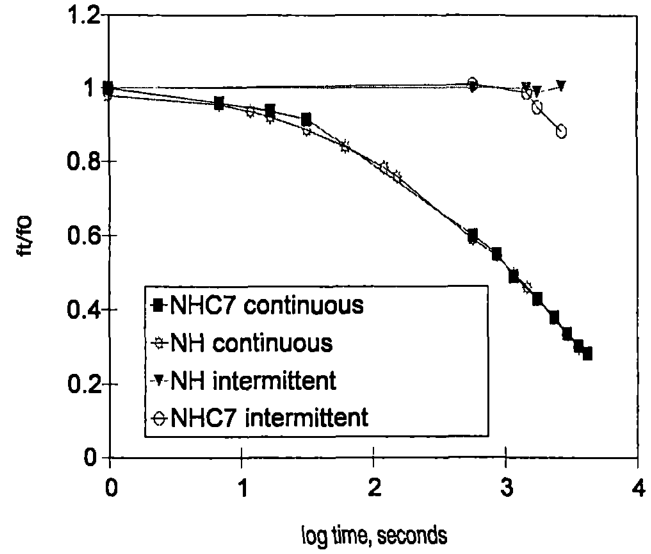

Figure 6.5. **Intermittent and continuous stress relaxation of pure and modified NR/HNBR blends at 150^{0}C**

6.3.Selective solvent swelling

The scission and cross linking reactions occurring during vulcanization and aging for the individual matrices were studied by selective solvent swelling of the unaged and aged samples. The samples were subjected to aging for 70^{0}C for 5 days, 120^{0}C for 5 days and 150^{0}C for one day. The aged and unaged samples were tested for selective swelling of the individual matrices by immersion in the solvents to equilibrium swelling time which was taken as 48 hours. The solvents used were methyl ethyl ketone and n-heptane. The weight of solvent absorbed per gram of the sample was calculated from measurement of swollen weight.

6.4.Network structure of blends by selective solvent swelling

During swelling by n-heptane the NR matrix of the blend swelled highly while the HNBR phase swelled lightly and the tendency was reversed during swelling by methyl ethyl ketone. The swelling characteristics of unaged and aged pure NR, HNBR, blend and modified blend in both MEK and n heptane are shown in Table 6.1. The per cent volume of n- heptane absorbed by pure NR, HNBR, blend and modified blend is shown in Figure 6.6.The weight of n- heptane absorbed by NR matrix of the unaged blend (shown as 30^0C in the figure) was the additive average of the weight of solvent absorbed by NR and HNBR. Thus the level of cross-linking of the NR phase in the blend was to the same level as observed for the pure NR vulcanizate. The weight of solvent absorbed by the blend in the presence of DCNR was less than the additive average (shown by dotted line in the figure). It was clear that there was restriction to swelling of NR phase by the lightly swollen HNBR phase and this showed the formation of interfacial cross-links. The restriction to solvent swelling by formation of interfacial bonds had been reported earlier.[13-14] This was also supported by the V_r values obtained from the selective solvent swelling of the blend using n- heptane and methyl ethyl ketone. (Table 6.2) DCNR added as an interface modifier in binary blends, was considered as filler during calculations of V_r. A higher V_r values in presence of DCNR as compared to pure blends show formation of interfacial bonds.

In the case of HNBR matrix of the blend, the weight of MEK absorbed was higher than the additive average of weight of MEK absorbed by pure HNBR and NR. Thus,the HNBR matrix in the blend was not vulcanized to the same level as pure HNBR. However,there were interfacial bonds formed, as there was restriction to penetration of HNBR phase by MEK in presence of DCNR. This was due to the lower cross linking of the HNBR phase that a lower rheometric torque was registered for the blends in comparison with either NR and HNBR. The higher rheometric torque recorded for the modified blend (Figure 4.2) should be due to the formation of these interfacial bonds. The better mechanical properties of the modified blend (Table 4.5) also attributed to this.

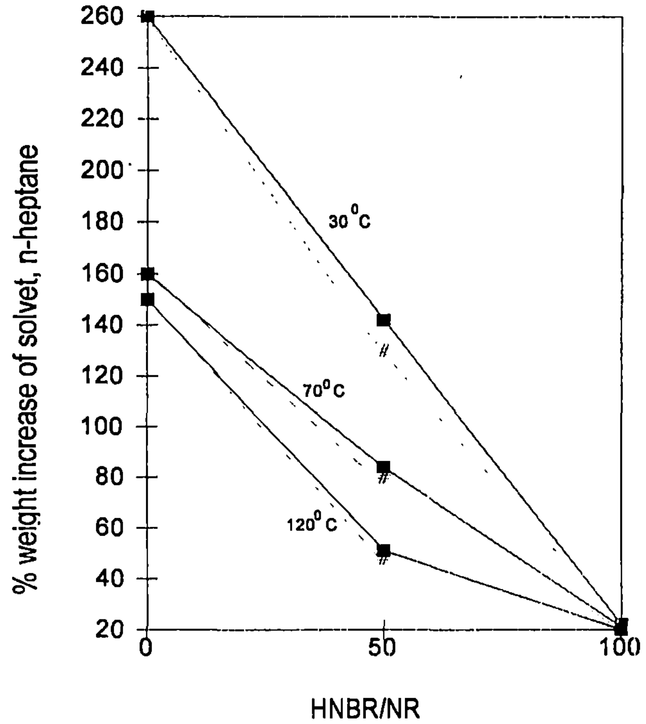

Figure 6.6. Solvent swelling of the unaged and aged NH (shown by solid line) and NHC7 (showed by dotted line) samples

6.5.Change in network structure during aging

NR matrix of the blend undergone cross linking reaction during aging at low temperatures and scission reactions during aging at high temperature as seen from a reduced swelling of the samples aged at 70°C for five days and 120°C for five days and a higher swelling of the samples aged at 150^{0}C for one day. HNBR phase was less sensitive to cross link formation during aging due to the observation that the weight of MEK absorbed by aged samples remained almost same. Weight of solvent absorbed by blend containing DCNR was lower for both the aged and unaged samples. This was in agreement with the physical properties obtained for the vulcanizates after aging (Table 5.1).

Table 6.1. Weight of solvent absorbed during selective solvent swelling by aged and unaged samples.

Solvent →	n-heptane (wt. of solvent absorbed/g of rubber)				MEK (wt. of solvent absorbed/g of rubber)			
Aging condition (^{0}C/days) →	150/1	120/5	70/5	unaged	150/1	120/5	70/5	unaged
NR	3.92	1.5	1.6	2.6	0.56	0.51	0.49	0.51
HNBR	0.23	0.20	0.21	0.22	2.40	2.20	2.22	2.81
NH	1.27	0.51	0.84	1.42	2.30	2.40	2.40	2.18
NHC7	1.05	0.48	0.80	1.30	2.13	2.30	2.32	2.17

Table 6.2. Vr of NR and HNBR matrices, in 50/50 binary blends, assuming DCNR as filler.

Vr	Parts of DCNR present	
	0	7
NR phase	0.102	0.108
HNBR phase	0.114	0.120

6.6. Conclusion

Stress relaxation studies showed that during aging, NR matrix undergone cross linking at lower temperature and scission at higher temperature, where as HNBR phase was less sensitive towards temperature up to 150°C. In the case of NR/HNBR blend, there were more scission reactions in the absence of DCNR. Solvent swelling studies also showed that, there was restriction to swelling of NR phase by the lightly swollen HNBR phase in the presence of DCNR indicating interfacial bonds which was further supported by Vr values.

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CHAPTER 7

BLENDS OF NR WITH SPECIALITY RUBBERS

MECHANICAL PROPERTIES AND AGING BEHAVIOR

7.1. Introduction

There is ever increasing technical interest in the use of dissimilar rubbers in order to improve specific vulcanizate properties. eg. Ozone resistance, oil resistance, etc. Unfortunately, this can often be at the expense of reduction in other properties like, modulus, tensile strength, etc. of the compound. In the case of blends of poly diene elastomers with elastomers having low olefinic content, the poor strength properties are thought to be a consequent of cure rate incompatibility between the polymers.[1] Blends of NR with speciality elastomers have been used in many commercial applications.[2-4] For getting better weather resistance NR/ EPDM blends[5-7] and for better oil/fuel resistance NR/NBR blends[8-10] have been used. Blending of butadiene rubber (BR) with NR[11,12] improved its processing characteristics and abrasion resistance.

In this chapter, 50/50 blends of NR with four speciality elastomers - HNBR, EPDM., CR and NBR -were prepared and the blends were evaluated for mechanical properties and aging resistance with respect to heat, oil, ozone and radiation. Mixes of NR, NBR, CR, EPDM and HNBR were prepared as per formulation given in Table 7.1. 50/50 blends of NR with NBR, CR, EPDM and HNBR were prepared by cross blending these mixes at the required ratio (method B) and compared the properties of the vulcanizates with that of NR.

Table 7.1. Compound formulation of mixes.

Ingredients	**NR**	**NBR**	**CR**	**EPDM**	**HNBR**
Elastomer	100	100	100	100	100
Zinc Oxide	5	5	5	-	-
Steric acid	1	2	-	-	-
Sulphur	1.5	1.3	-	-	-
CBS[a]	1.5	0.16	-	-	-
MBT[b]	-	0.16	-	-	-
Magnesium oxide	-	-	4	-	-
NA 22[c]	-	-	0.5	-	-
DCP[d]	-	-	-	6	6

a- N-cyclohexyl-2-benzothyazyl sulphenamide
b- Mercaptobenzothiazole
c- N-isopropyl N'phenyl p-phenylene diamine
d- Dicumylperoxide

7.2. Cure characteristics

Mixed cure systems were used for the blends. For EPDM and HNBR peroxide cure was selected, as these two were saturated elastomers. For CR metal oxide cure and for NR and NBR sulfur cure were used. Figure 7.1 shows the rheographs of NR and blends of NR with NBR, CR. EPDM and HNBR at 160 °C. It was seen that blend of NR with HNBR gave highest torque and that with CR showed lowest torque. Cure characteristics were as given in Table 7.2. Scorch time of the blends were shown to be lower than pure NR. Optimum cure time was higher for the blends of NR with EPDM and HNBR, probably due to the peroxide cure of the EPDM and HNBR.

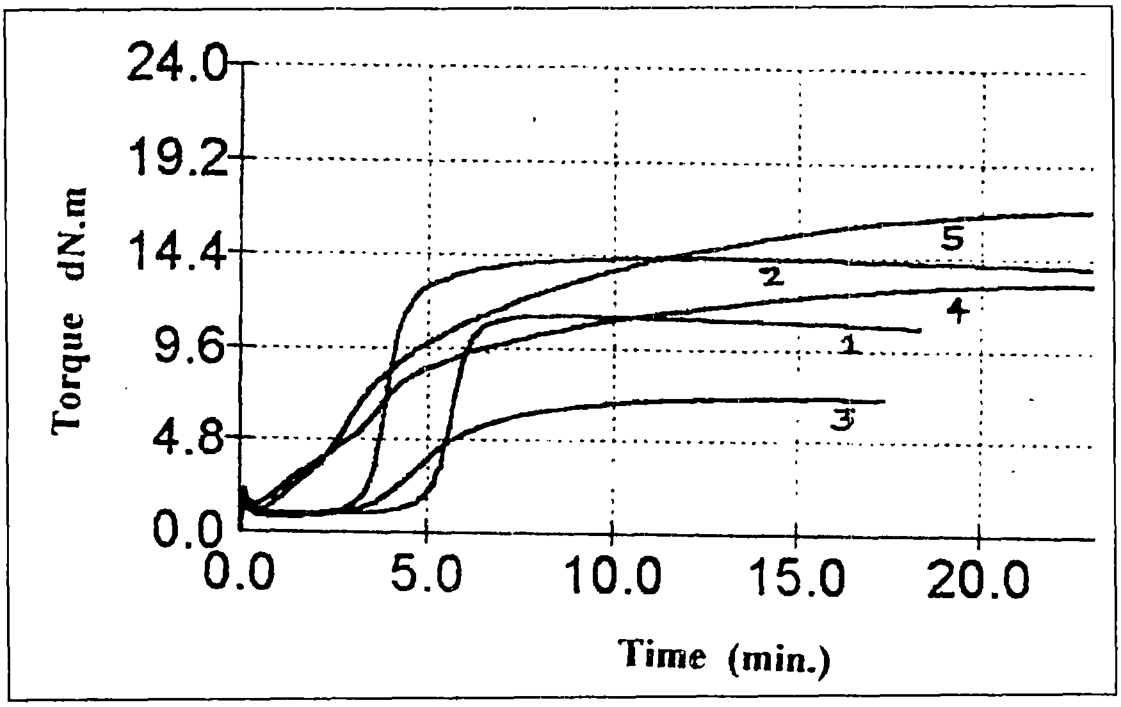

Figure 7.1. Rheographs of 1-NR and 50/50 blends of NR with 2-NBR, 3-CR, 4-EPDM and 5- HNBR.

Table 7.2. Cure characteristics of NR and the blends at 160 °C

Mix	CRI	M_H, dNm	M_L, dNm	t_{90}, min.	ts_2, min.
NR	99.92	11.34	0.96	6.24	5.24
NR/NBR	58.45	14.31	0.97	5.23	3.52
NR/CR	24.32	7.13	0.79	8.54	4.43
NR/EPDM	8.83	13.12	1.47	13.21	1.89
NR/HNBR	7.96	16.99	1.22	14.50	1.94

7. 3.Mechanical properties

Mechanical properties of NR and the blends are given in Table 7.3. All the blends exhibited lower tensile strength than NR indicating lower level of cross-linking due to the thermodynamic incompatibility of these elastomers with NR as a result of the difference in their solubility parameter/ saturation level. Blends of NR with NBR and HNBR gave comparably higher tensile strength than other two blends. NR/EPDM blend showed very low tensile properties, probably due to the incompatibility between these two as a result of the wide difference in their saturation level [13] and also due to the lower gum tensile strength of EPDM. Better values of hardness and compression set were shown by the blends with EPDM and HNBR. NR/EPDM blend showed very good high temperature compression set value while that of NR /CR was very poor. However, NR/NBR blend showed better high temperature compression set values than NR.

Table 7 .3. Mechanical properties of NR and the blends

Properties	**NR**	**NR/NBR**	**NR/CR**	**NR/EPDM**	**NR/HNBR**
Tensile strength, MPa	21.4	17.6	12.5	4.8	17.9
Elongation at break, %	620	870	895	330	320
Modulus 100%, MPa	1.44	0.95	0.91	1.58	1.25
Modulus 300%, MPa	3.24	1.75	1.52	3.85	2.53
Tear strength, Kg/cm	30.6	25.1	17.2	22.5	20.5
Resilience, %	76	58	49	58	62
Hardness, Shore A	42	42	36	46	44
Compression set, %					
At 125 °C/ 22 h	56.6	59.3	78.8	23.7	42.6
At 150 °C/ 22 h	87.4	68.14	96.5	32.8	56.1

7.4. Aging characteristics

7.4. A. Thermal aging

High performance and long-term heat and weather aging resistance are key requirements for many rubber applications. Figure 7.2 shows the retention of properties of NR and the blends after air aging at 150 C for 24 hours. NR and its blends with NBR[14] and CR[15] showed very poor thermal aging resistance as expected due to the unsaturation on their polymer backbone. Blends with HNBR showed better retention, where_as blends with EPDM exhibited very good resistance towards oxidation as a result of the stable saturated polymer back bone structure of these two elastomers.[16-19]

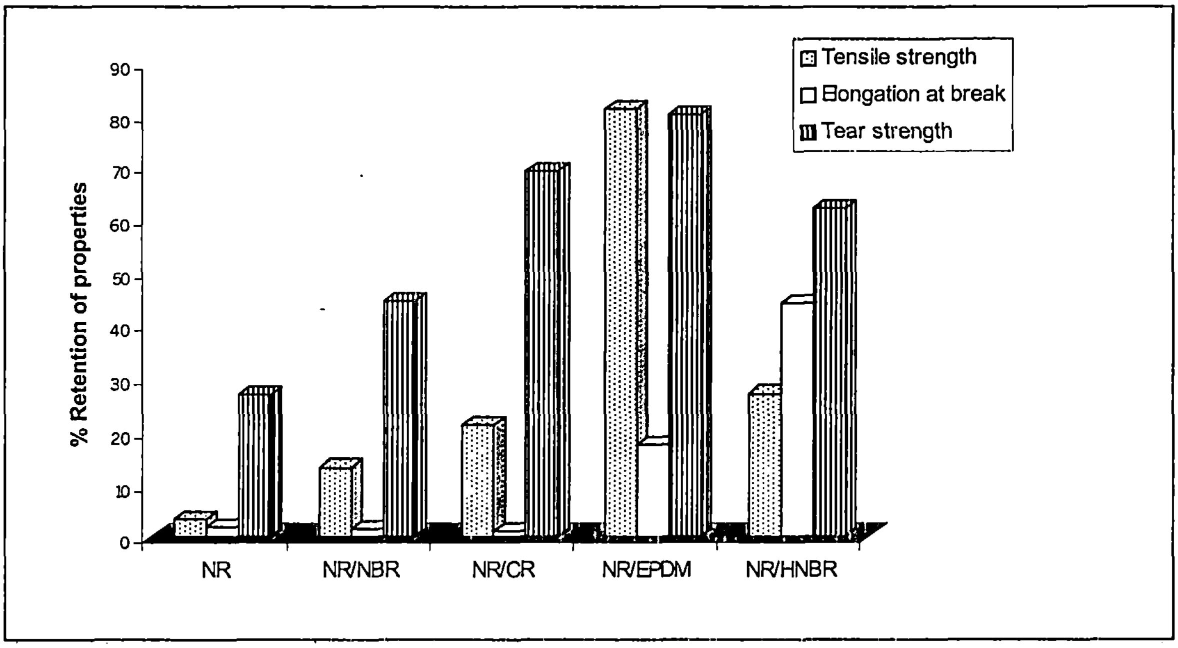

Figure.7.2 . Percentage retention of properties after aging at 150 C for 24 h.

7.4.B. Oil aging

Figure 7.3 shows the retention of properties of NR and its blends after immersion in ASTM No.2 oil at room temperature for 5 days. All the blends showed improved aging resistance than NR. As was expected, blends with NBR and HNBR exhibited good resistance, whereas blends with CR and EPDM showed comparatively poor resistance. Figure 7.4 shows the photographs of the swelled samples.

Table 7.4 gives the percentage swell of NR and the blends in ASTM oil Nos. 1, 2and 3 at three different temperatures- room temperature, 70°C and 100°C- for 5 days. NR exhibited least resistance and even dissolved in the oils at higher temperature. Blend of NR with EPDM showed least resistance among the blends, as EPDM contains no polar group and hence least resistant towards oils.[20] Blends with NBR and HNBR exhibited very good oil resistance. NR/HNBR blend gave better resistance at higher temperature than NR/NBR blend due to the excellent aging resistance of HNBR.[21] Selective hydrogenation of the C=C bonds, gave HNBR, excellent heat aging, while the nitrile group provided with very good oil/fuel resistance.[22] NR/CR exhibited better resistance than NR and NR/EPDM vulcanizates, as CR contains polar group.

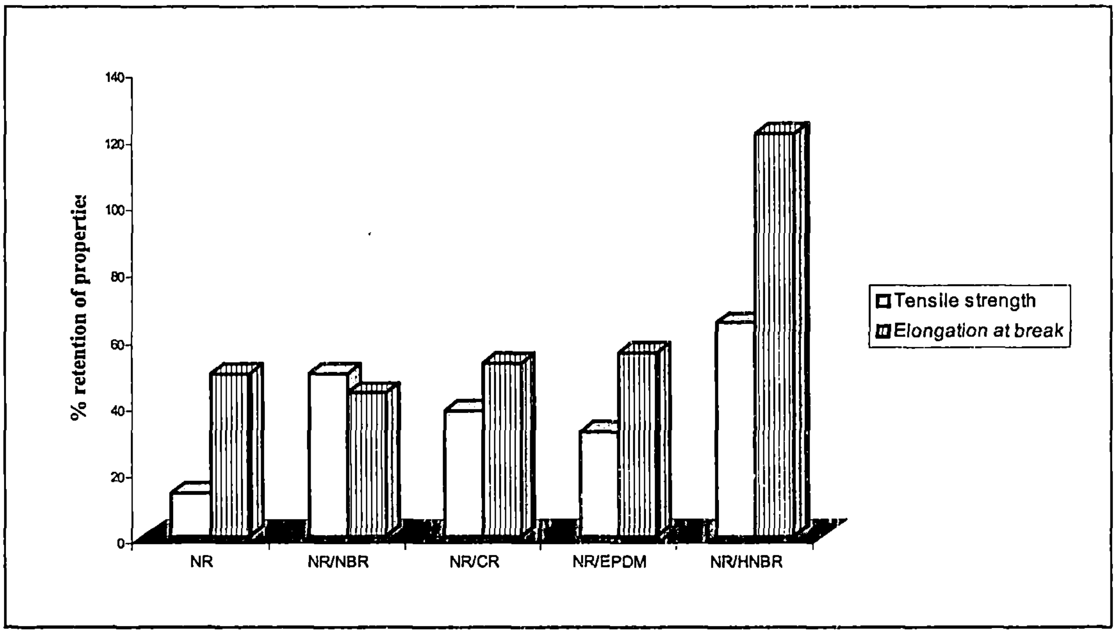

Figure.7.3. Percentage retention of properties after aging in ASTM oil No:2 for 5 days at room temperature.

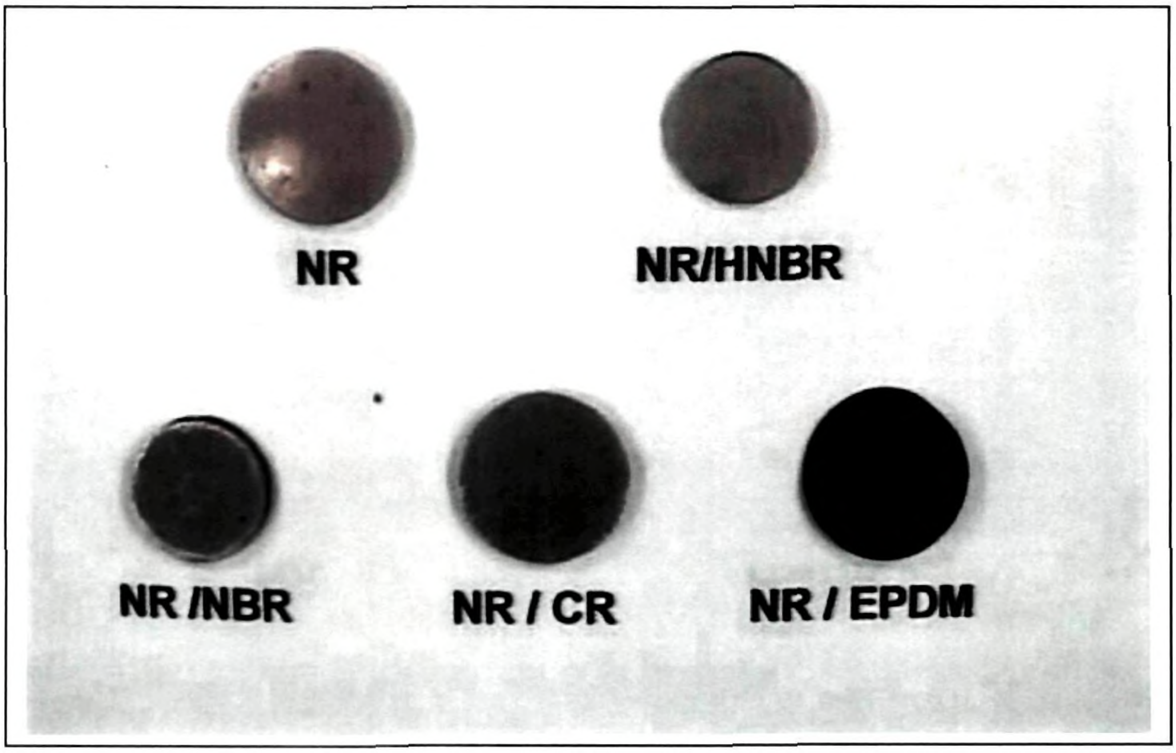

Figure.7. 4. Photographs of oil swelled samples of NR and its blends in ASTM No: 2 oil for 5 days at room temperature.

Table 7.4. Percentage swelling of NR and its blends in ASTM Oils (5 days at three different temperatures)

Temperature	ASTM NO.	NR	NR/NBR	NR/CR	NR/EPDM	NR/HNBR
At room temperature	1	47.5	16.1	24.9	30.5	15.6
	2	71.8	22.1	39.6	44.5	22.3
	3	180.7	63.9	147.4	151.9	54.7
At 70°C	1	126.9	42.8	95.5	124.0	33.6
	2	207.6	77.7	141.7	184.9	68.2
	3	285.8	115.2	272.2	283.2	101.9
At 100°C	1	Dissolved	83.4	94.0	182.9	79.5
	2	”	115.7	138.9	204.3	99.8
	3	”	198.0	279.0	409.0	143.0

7.4.C Ozone aging

One of the main types of degradation of elastomer products in service under natural conditions is caused by atmospheric ozone generated in nature by electrical discharge and also by solar radiation in the stratosphere.[23] Only a few pphm of ozone in air can cause cracking on surfaces which demolish the appearance and may destroy usefulness of the elastomer products. Ozonation and antioxidant efficiency of elastomers and blends had been extensively studied.[24-27] Figure 7.5 shows the optical photographs of the ozone irradiated surfaces of NR and its blends in an ozone chamber at 50 pphm ozone concentration at 38 °C. Within the first two hours itself cracks were formed on the surfaces of NR and NR/NBR blend and the deepening of the cracks was very fast. Cracks were developed only after 16 h on the NR/CR blend and propagated slowly, whereas blends of NR with EPDM and HNBR showed no cracks up to 50h of irradiation.

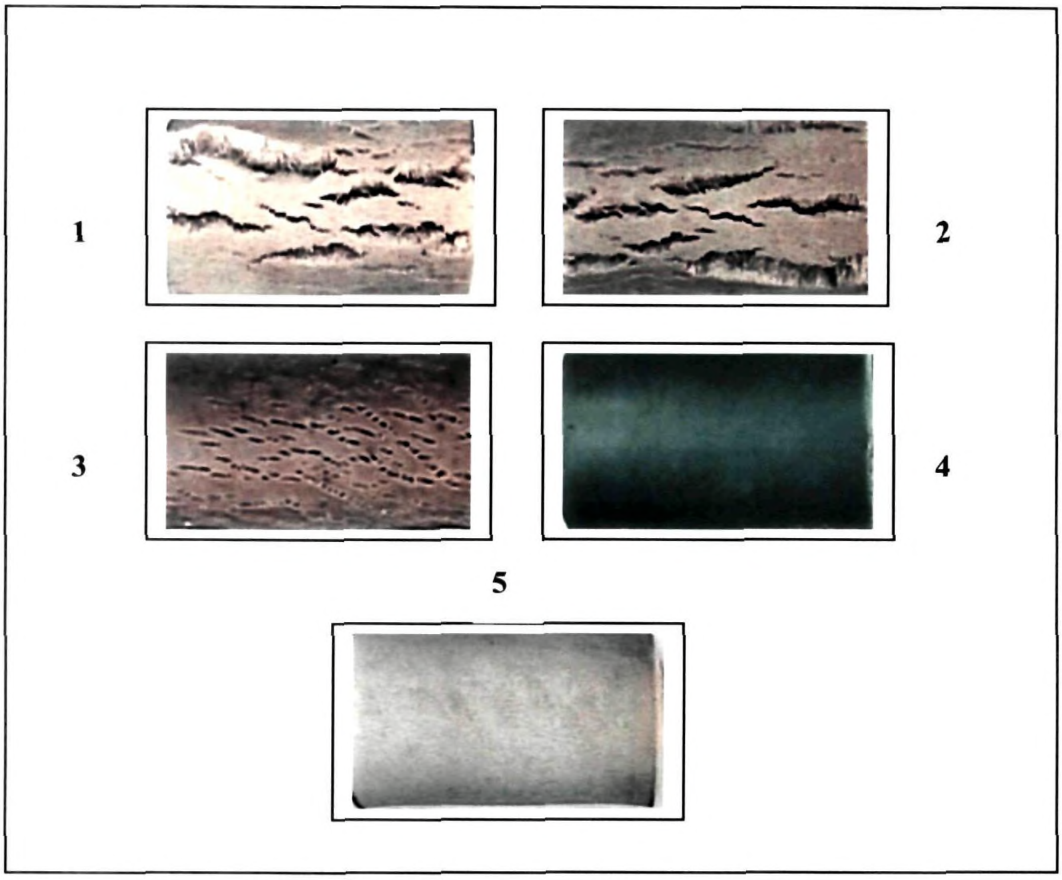

Figure.7.5 Photographs of ozone irradiated surfaces of 1. NR and its blends with 2. NBR, 3. CR, 4. EPDM, 5. HNBR for 40 h.

7.4.D. Exposure to γ radiation

Table 7.5 shows the retention of tensile properties of the blends after γ irradiation. All the vulcanizates showed decreased properties. It was seen that the properties were drastically reduced in NR and NR/CR blends. NR/EPDM exhibited higher retention of properties.[28] NR/NBR and NR/HNBR showed comparative retention of property. Higher degradation occurred on prolonged irradiation. However, NR/HNBR showed improved modulus and elongation, indicating additional cross-linking along with degradation.

Table 7.5. Tensile properties of vulcanizates of NR and blends after γ irradiation

Properties	**NR**	**NR/NBR**	**NR/CR**	**NR/EPDM**	**NR/HNBR**
15 M rad					
Tensile strength, MPa	7.6	12.7	6.7	4.0	12.5
Elongation at break, %	510	560	535	350	350
Modulus, 100%, MPa	1.07	1.64	0.97	1.37	1.53
Modulus, 300%, MPa	2.28	3.81	1.75	3.03	2.99
25 M rad					
Tensile strength, MPa	2.8	7.6	3.6	3.1	7.9
Elongation at break, %	415	500	390	385	410
Modulus, 100%, MPa	0.64	0.99	0.72	.917	1.31
Modulus, 300%, MPa	1.47	2.47	2.38	2.12	3.46

7.5. Conclusion

Aging characteristics of NR vulcanizates can be improved by blending with speciality elastomers like,CR, NBR, EPDM and HNBR. Among these NR/HNBR blend exhibited a combined effect of aging resistance towards heat, oil, ozone and radiation to a desirable level. NR/EPDM blend even though had good resistance towards ozone and heat aging, showed very poor resistance towards oil aging and had very low tensile properties. NR/NBR blend showed better oil and radiation resistance, but exhibited very poor resistance towards heat and ozone. Blend of NR/CR showed only slight improvement towards heat, oil and ozone.

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CHAPTER 8

RHEOLOGICAL BEHAVIOR OF BLENDS OF NR AND HNBR

8.1.Introduction

The processing behavior of elastomers which includes the behavior of materials during processing operations such as, mixing, shaping, molding, calendaring and extrusion is one of the major concerns of rubber industry. The flow behavior of elastomers is an important aspect in the processing step. [1-3] This is the reason why, the viscosity function of a polymer, that is the shear viscosity as a function of shear rate or shear stress and temperature becoming more important in trying to optimize the processing operations and in designing processing equipments such as extruders and dies required for various products.

The effect of blending of elastomers on flow properties is important as in many cases, blend of elastomers is preferred to achieve the required end use.[4-7] Most of the elastomeric blends are immiscible and hence suitable modifiers are used to improve the blend miscibility and the overall property.[8-10] Also elastomers are seldom used without fillers. Hence the influence of fillers and modifiers on the flow properties of elastomeric blends is very useful in designing rubber compounds.[11-12]

A number of rheological investigations have been reported on the behavior of NR compounds, [13-15] blends of NR with plastics, [16-17] cryoground compounds,[18] rubber reclaim[19]and other elastomer blends.[20-22]

Elasticity of a polymer melts responds differently to changes in extrusion conditions like, residence time in the capillary and temperature[23]. The behavior of an elastomer is controlled by the viscosity coefficient $\psi_1(\gamma)$ and secondary stress coefficient $\psi_2(\gamma)$. The behavior of an elastomer is determined by the dependence of shear stress on shear rate and by the dependence of normal stress on shear stress or shear rate[24].

We found that blending of NR with HNBR improved its aging properties to a great extent without much affecting the mechanical properties. Using 7parts of DCNR as a modifier in this blend further improved the properties. So this blend can be used in oil seals, hoses used in oil fields and other such applications requiring oil, weather and temperature resistance.

This chapter presents the results of rheological studies conducted for blends of NR and HNBR with respect to the effect of blend ratio, effect of DCNR dose, and effect of carbon black filler. The flow aspects considered are a) viscosity as a function of shear rate and b) elasticity as it appears in die swell and principal normal stress difference.

The mixes were prepared on a two roll mixing mill as per Table 8.1. NR and HNBR were individually masticated for about 1 min. and then blended together for a period of 4 minutes. For the preparation of the modified blends, DCNR was first masticated for 1 minute, incorporated with HNBR and then blended with NR. The filled mixes were prepared by adding carbon black FEF (N 550) after blending the rubbers. The total mixing time was 10 min. The temperature of the rolls was controlled by circulating cold water.

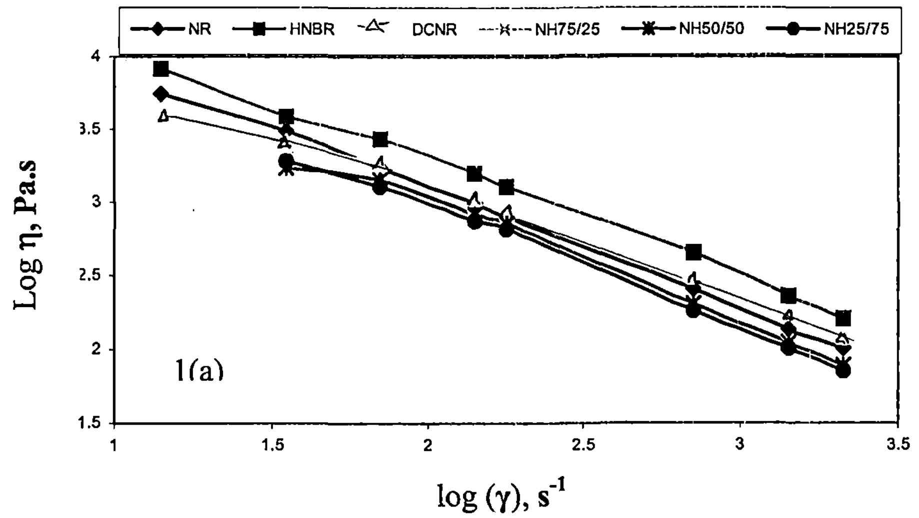
The rheological studies were carried out using a capillary rheometer, attached to a Zwick Universal Testing Machine, model 1474. Details are given in chapter 2.

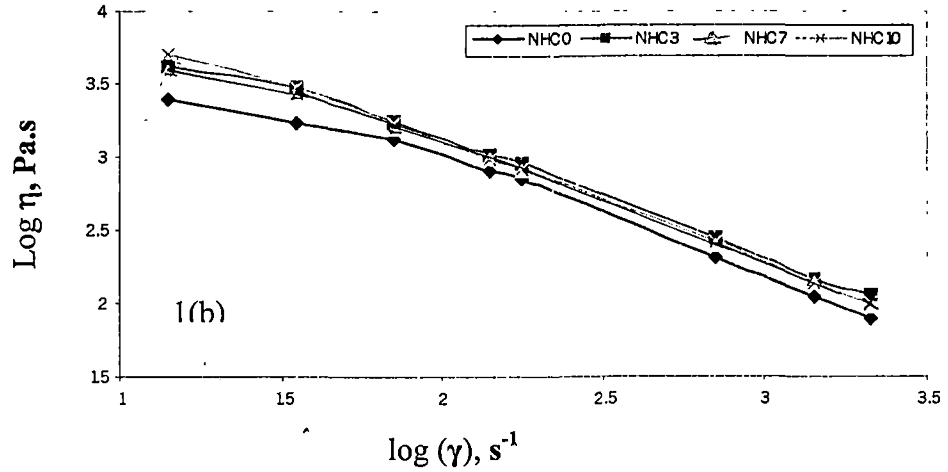
Table 8.1. Formulation of the mixes

	N	H	C	NHa	NH	NHb	NHC3	NHC7	NHC10	NHB	NHC7B
NR	100	-	-	75	50	25	50	50	50	50	50
HNBR	-	100	-	25	50	75	50	50	50	50	50
DCNR	-	-	100	-	-	-	3	7	10	-	7
FEF	-	-	-	-	-	-	-	-	-	30	30

8.2.Variation of viscosity with shear rate

Figure 8.1 shows the viscosity as a function of shear rate at 110°C for neat NR, HNBR, DCNR and different blends of NR/HNBR. Viscosity of all mixes decreased with increasing shear rate showing pseudoplastic flow behavior. The molecules, which are extensively entangled at normal conditions, became disentangled and oriented in the direction of flow under the application of shear. As NR has a very highly entangled matrix and as a result of this viscosity of NR reduced faster than HNBR. HNBR showed igher viscosity probably due to its polarity, as polarity results in association and hence n an increased apparent molecular weight[25]. Modified NR showed lower viscosity than





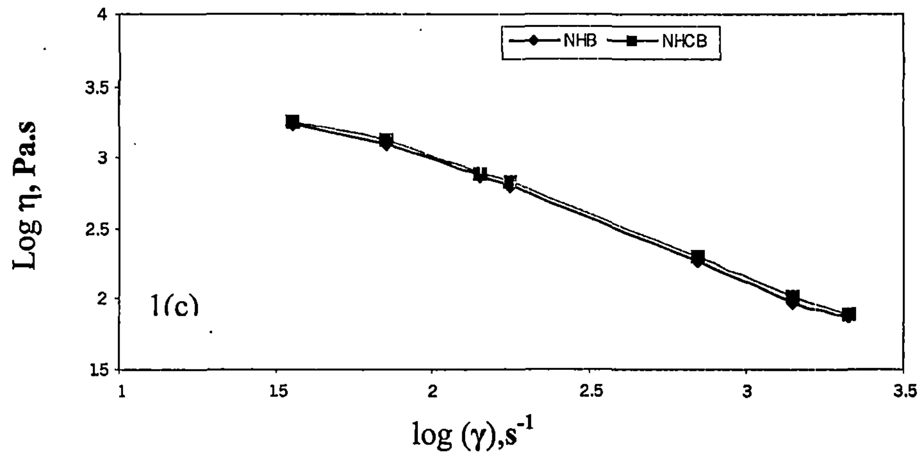


Figure 8.1. Variation of shear viscosity with shear rate. a) NR, HNBR, DCNR and the blends b) 50/50 blend containing different dosage of DCNR and c) filled blends with and without DCNR

HNBR at all shear rates. At shear rates less than 100 s^{-1} DCNR showed a lower viscosity than NR and at higher shear rates showed higher viscosity than NR, probably due to the presence of polar chlorine. This was also reflected in the flow behavior index given in Table 8.2. NR exhibited the highest pseudoplastic character among the different blend constituents.

8.2.i) Effect of blend ratio

The effect of blending of NR and HNBR on viscosity is shown in Figure 8.1(a). The blends showed a comparatively lower viscosity than NR, HNBR and DCNR. Viscosity of blends may be higher than the viscosity of pure components when there is interaction between blend components, or lower when there is the possibility of interlayer slip. At constant shear rate blend viscosity decreased as HNBR content of the blend increased. Blends showed lower viscosity than both the components at all ratios. This revealed the behavior of a negatively deviating blend (NDB), probably due to the interlayer slip possible in immiscible blends[26]. NR and HNBR are immiscible due to the large difference in their polarity and saturation level. In such immiscible blends, there is the possibility of interlayer slip. The lower viscosity recorded by the blends in comparison with the components may be attributed to this.

8.2.ii) Effect of DCNR

The effect of varying doses of DCNR on viscosity of 50/50 blend is shown in Figure 8.1(b). It was seen that incorporation of DCNR to the 50/50 blend increased its viscosity. In the case of filled blends also, the effect of DCNR was to increase the viscosity. (Figure 8.1 (c). This indicated that in the presence of DCNR there was some interfacial interaction occurring between the phases. These interactions reduced the possibility of interlayer slip and increased the formation of an associative network, resulting in a system with increased yield stress and a higher viscosity. However, contrary to the expectation, the black filled blends exhibited lower viscosity than gum mixes.

Table 8.2. Flow behavior of NR, HNBR, DCNR and the blends

Mix	Flow behavior index n’
N	0.1847
H	0.3831
C	0.2883
NH.	0.2004
NHa	0.1833
NHb	0.1760
NHC3	0.2407
NHC7	0.2276
NHC10	0.1969
NHB	0.1861
NHD7B	0.1886

8.3. Variation of viscosity with temperature

The temperature dependence of viscosity of both gum and filled 50/50 blends and blend containing 7 parts of DCNR at three different shear rates are given in Figure 8.2. It was seen that viscosity decreased with temperature at all shear rates and this effect was more pronounced above 100°C and at higher shear rates. Activation energy calculated for the gum and filled blends, based on the Arrhenius type equation, was given in Table 8.3.

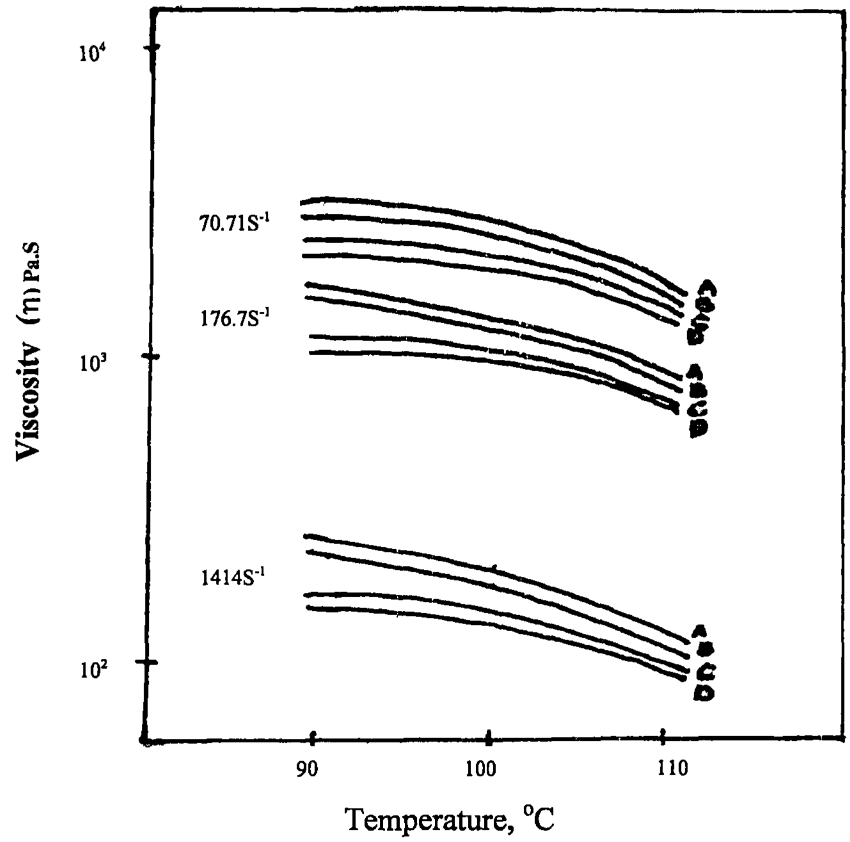


Figure 8.2. Variation of viscosity with temperature at three different shear rates. A- NHC7, B-NH, C- NHC7B and D- NHB

It was seen that activation energy was higher for the DCNR containing blend for both gum and filled blends. The polar interactions possible between DCNR and HNBR reduced disentanglement of molecules and hence higher amount of energy was needed for flow. Thus blends containing DCNR showed higher activation energy than the pure blend. The filled blend showed lower activation energy of flow as the temperature sensitivity reduced with filler loading.

Table 8.3. Activation Energy (K cal/mol) of the gum and filled blends at three shear rates.

Mix	Shear rate, s^{-1}		
	70.716	707.161	1414.4
NH	827	782	678
NHC7	848	794	691
NHB	684	628	564
NHC7B	734	696	586

8.4. Elasticity

The elastic parameters are important in the processing of polymers and can be characterized by principal normal stress difference (τ_{11}-τ_{22}), elastic modulus G, recoverable shear strain S_R and die swell ratio de/dc. Elastic parameters depend strongly on the extrusion history and are changed by filler incorporation.[27]

Values of (τ_{11}-τ_{22}), G and S_R at constant shear rate 1414 s^{-1} are given on Table 8.4. Higher values of (τ_{11}-τ_{22}) and S_R and lower values of G implied higher elasticity of the mixes. The data showed that higher elasticity of NR was considerably reduced by the addition of HNBR, a behavior seen similar to reduction in elasticity. Incorporation of 7 parts of DCNR to the blend exhibited only slight reduction in elasticity where as in corporation of filler reduced the elastic parameters to a considerable level. This was in accordance with observations from earlier works [12].

Table.8.4. The elastic parameters - principal normal stress difference $(\tau_{11}-\tau_{22})$, elastic modulus G, recoverable shear strain S_R of the blends

Mix	$(\tau_{11}-\tau_{22})$, N/m^2	G, N/m^2	S_R
N	1.53126x107	2.67x104	18.7013
H	4.7601x106	8.64x104	5.2470
C	8.4202x106	3.90x104	10.3774
NH	4.8045x106	4.10x104	7.6529
NHC7	4.3990x106	4.49x104	7.3802
NHB	9.097x105	1.893x105	1.6101
NHC7B	8.4119x105	2.245x105	1.3480

8.5. Die swell

Die swell is a relaxation phenomenon. When the molten polymer flows through the capillary, shearing tends to maintain the molecular orientation of polymer chains and when the melt emerges from the die, the molecules tend to recoil, leading to the phenomenon of die swell. The elastic recovery of the polymer chain is influenced by factors such as stress relaxation, cross-linking, presence of fillers etc.[28] In general die swell increase with increase in shear rate which is a common phenomena exhibited by almost all rubber compounds.[29] Figure 8.3 shows the die swell vs shear rate of NR, HNBR and 50/50 pure and DCNR containing blends and 50/50 blends containing 30 phr of FEF black. It was seen that NR showed highest die swell at all shear rates and increased greatly with increasing shear rate. HNBR showed a comparatively lower die swell with slight increase with shear rate. 50/50 blend showed a die swell intermediate

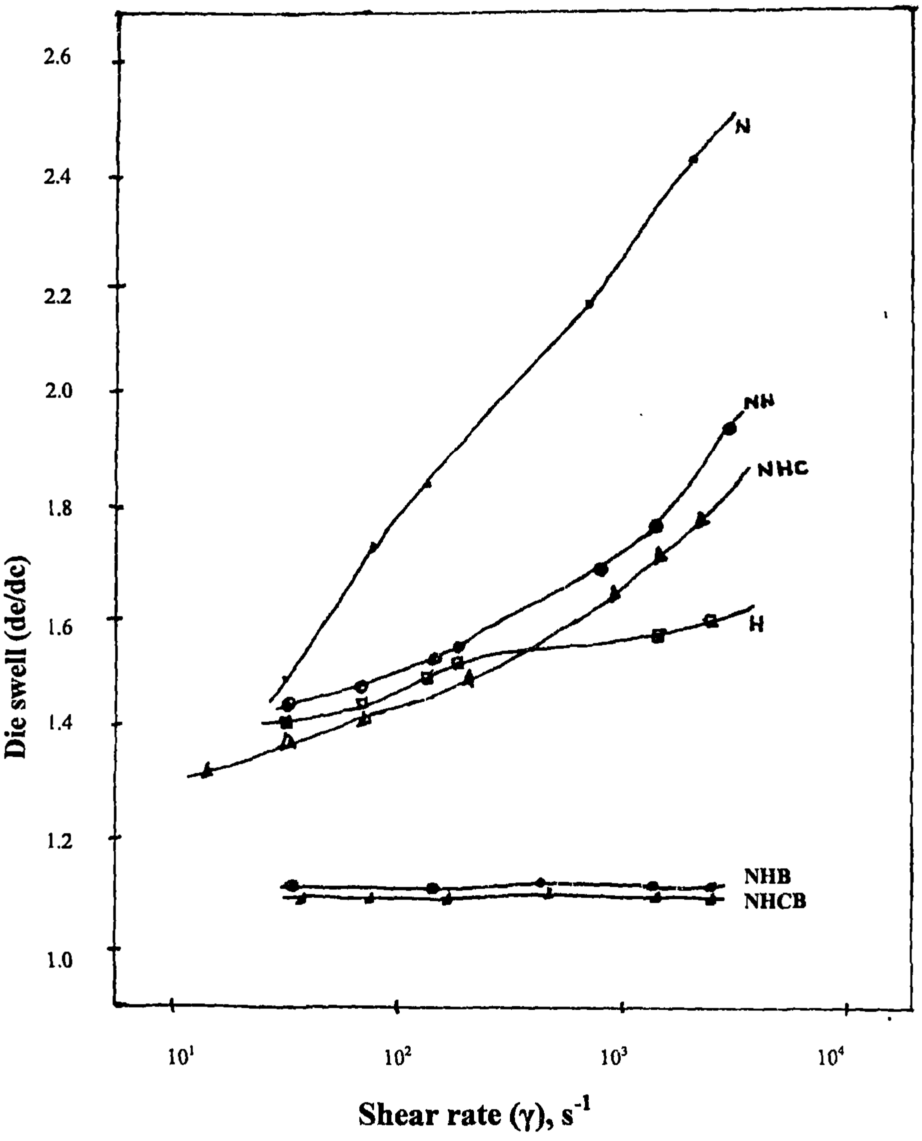


Figure 8.3. Variation of die swell with shear rate of NR, HNBR and blends

between NR and HNBR especially at higher shear rates. Die swell is generally related to shear stress and greater the shear strain that occurs in the capillary, less will be the die swell.[30]

Table 8.5 shows the die swell ratio of the elastomers and blends at two shear rates 70.716 s^{-1} and 707.16 s^{-1} at 110 °C. From the table it was clear that die swell of NR was reduced considerably by blending with HNBR. Similar effect was reported for blending NR with rubber reclaim[19]and with cryoground rubber compounds[18].

Table 8.5. Die swell ratio of gum and filled blends at two shear rates 70.716 s^{-1} and 707.16 s^{-1} at 110 °C .

Mix	Shear rate, s^{-1}	
	70.716	707.16
N	1.7400	2.1930
H	1.4629	1.6663
C	1.8099	1.9144
NHa	1.4967	1.8099
NH	1.4619	1.6707
NHb	1.3227	1.3922
NHC3	1.4614	1.775
NHC7	1.4270	1.6407
NHC10	1.5315	1.9144
NHB	1.1138	1.1486
NHC7B	1.0890	1.1138

8.5.i) Effect of blend ratio

Figure 8.4. shows the variation of die swell with blend ratio at three different shear rates at 110°C. It was clear that die swell of NR was reduced considerably with HNBR content. At lower shear rates, variation was less prominent. At all shear rates, 25/75 blend showed a die swell, which was less than both that of NR and HNBR.

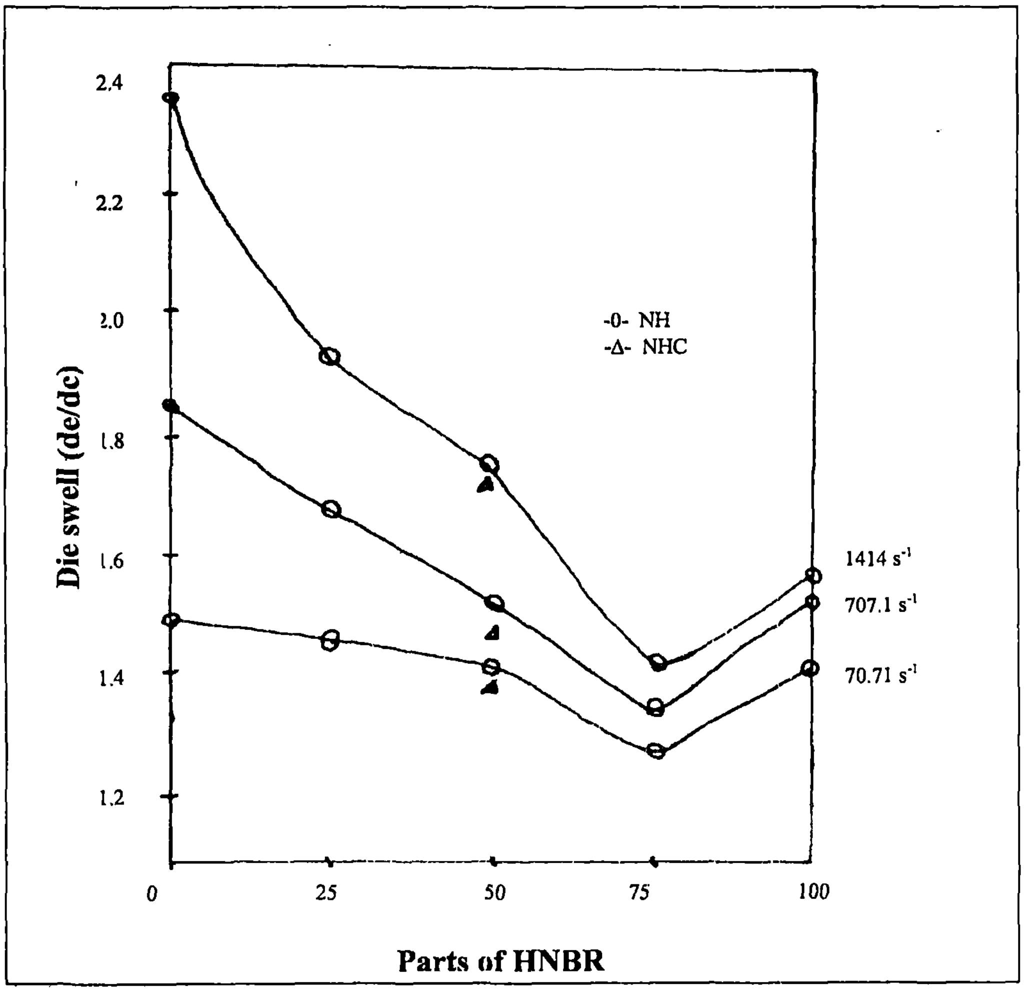


Figure 8.4. Variation of die swell with blend ratio at three different shear rates.

The occurrence of negative deviation in die swell may be explained in terms of morphology of the blends.[31,32] Both NR and HNBR are pseudoplastic and therefore they store part of the energy supplied to them as they enter the capillary. During flow the dispersed phase would dissipate less energy than the continuous phase which wets the passage wall. Therefore total recoverable energy in a two-phase system containing deformable particle would be greater than in a single-phase system or two phase system containing barely deformable particles.[29,34] In NR/HNBR blend, NR is more pseudoplastic than HNBR as evident from flow behavior index and die swell behavior of NR and HNBR. The volume fraction of highly deformable particle decreased with increase in HNBR content in the blend. Lower the volume fraction of the deformable particle, lower will be the energy stored during capillary flow. Therefore total recoverable energy in 25/75 blend will be lesser than other ratios. This may be the reason for the highest negative deviation in die swell exhibited by 25/75 NR/HNBR blend than other blend ratios.

8.5.ii) Effect of DCNR

From Figure 8.3 and Table 8.5 it was seen that incorporation of DCNR in 50/50 blend reduced the die swell due to the interactions between DCNR and HNBR. It was lowest at 7 parts loading indicating that effective interaction level was at this dose. At lower shear rates, modified blends showed even a lower die swell than HNBR. At higher shear rates it showed higher die swell than HNBR due to the increased elastic response of the blend. In filled blends also DCNR containing one exhibited extremely very low die swell and showed only slight variation with shear rate, due to the lower elastic response.

8.5.iii) Effect of filler

Filler addition drastically reduced the die swell in 50/50 blends as seen from Figure 8.3 and Table 8.5, which was in agreement with the previous reports.[12,32-34] A reinforcing filler like carbon black interact with rubber due to the presence of active chemical groups on the filler surface and form bound rubber, which increases the rigidity of polymers. The increase in rigidity implies less mobility and consequently reduced stretching of the macromolecular chains under the influence of applied shear stress. Hence elastic recovery and consequently the die swell of the filled mixes was less than that of unfilled mixes. It was also noted that for the filled blends, die swell variation with shear rate was very less.

8.6. Extrudate appearance

Figure 8.5 (a), (b)& (c) are the photographs of extrudates of NR, HNBR, DCNR , NR/HNBR blends and filled blends collected at 110°C. It was seen that neat NR and DCNR deformed to a great extent. This was due to the higher elastic recovery possible for them as a result of high molecular weight of the polymer. Neat HNBR extrudates showed lower distortion, probably due to its lower elastic response, as is evident from its flow behavior index.[17] It was seen that blending with HNBR, addition of filler and presence of DCNR improved the extrudate behavior of NR. Due to the polar interactions, DCNR acted as a modifier in blends of NR/HNBR to improve the flow behavior.

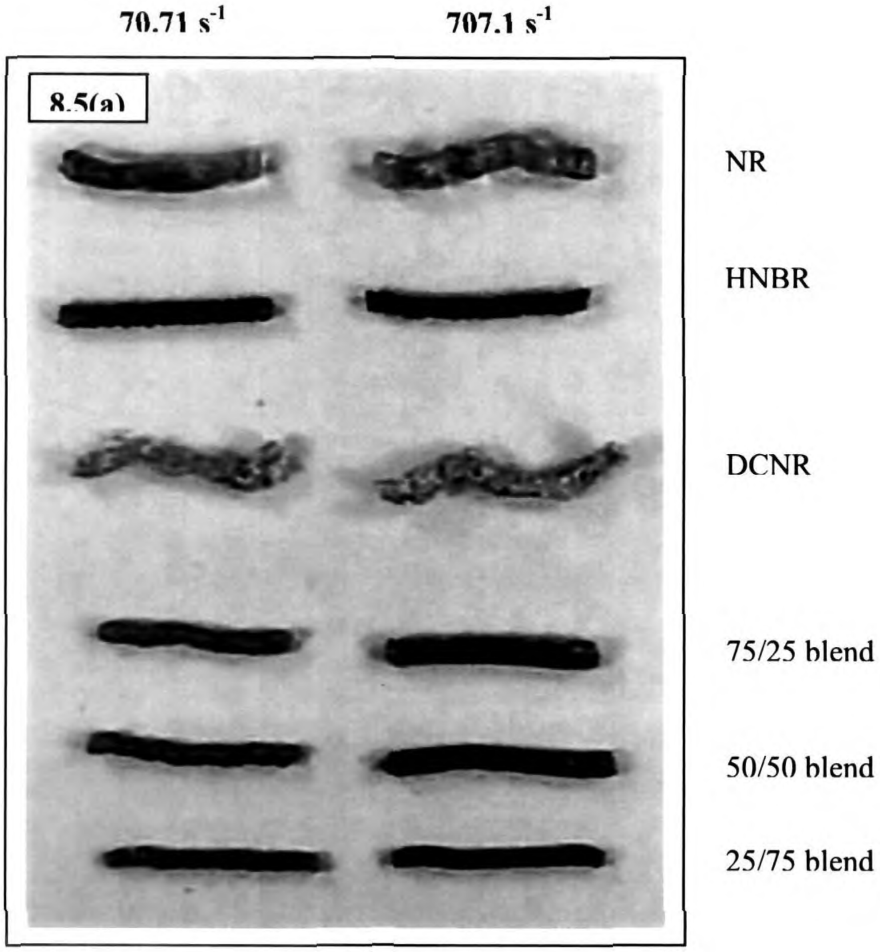
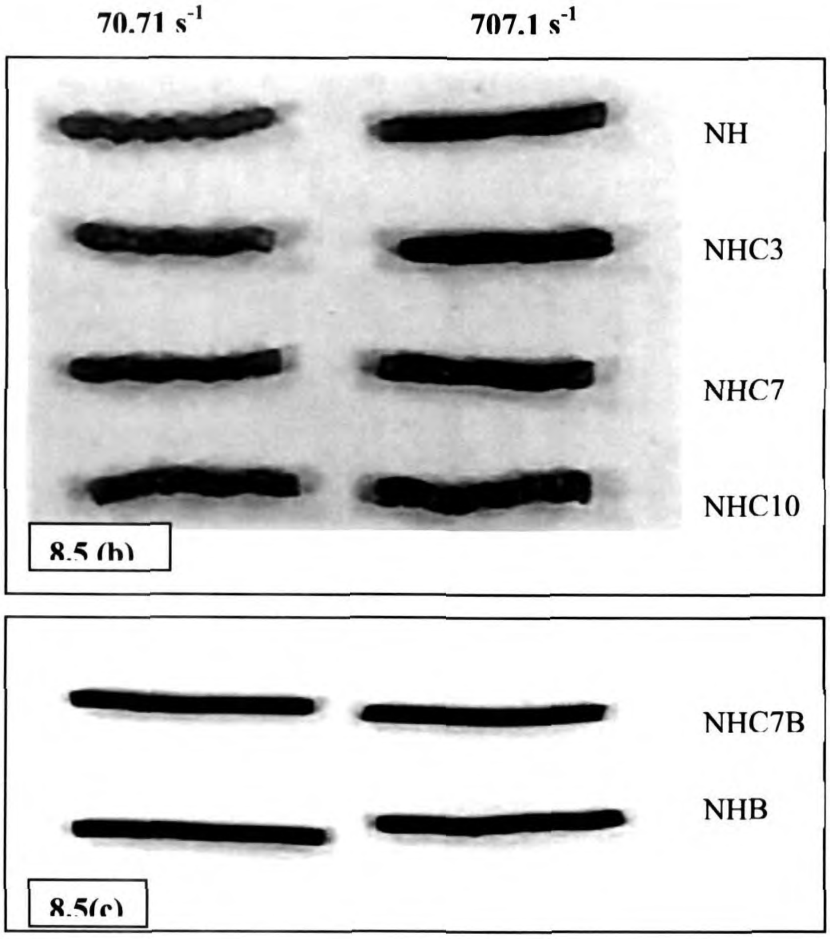


Figure 8.5(a). Photographs of the extrudates of NR, HNBR, DCNR and blends at two shear rates



Figures 8.5. Photographs of the extrudates - (b)-50/50 blend containing DCNR and (c)- filled blends with and without DCNR at two shear rates

8.7.Conclusion

The binary blends of NR and HNBR showed pseudoplastic behavior. These blends recorded a viscosity lower than both the constituents showing a behavior similar to a negatively deviating blend (NDB). Such immiscible blends exhibit lower viscosities than blend constituents due to slippage during flow. Addition of DCNR in NR/HNBR blend considerably improved their flow characteristics. DCNR containing blends showed a higher viscosity than pure blends due to the possibility of polar interactions among the blend constituents. They also exhibited higher activation energy of flow, which was considerably reduced by the addition of filler. Blends showed a lower elasticity than pure NR. Presence of 7 parts of DCNR further reduced the elasticity of the blend and resulted in extrudates with very low die swell, which was lower than both blend constituents at lower shear rates. The effect of filler in DCNR containing blend was to reduce die swell further with less sensitivity to variation with shear rate.

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SUMMARY AND CONCLUSION

The chemical modification of NR can be carried out through dichlorocarbene nodification by the alkaline hydrolysis of chloroform using a phase transfer catalyst, etyltrimethyl ammonium bromide (CTAB). The percentage chlorine content of the nodified NR as estimated by titration method showed that the chlorine content increased vith temperature of the reaction and the reaction followed first order kinetics. The lichlorocarbene addition was fast in the initial stages but decreased at later stages of eaction. The rate of reaction almost leveled off after about 17 h. As temperature of eaction increased, rate of reaction as measured by chlorine content increased. The FTIR tudies revealed the attachment of chlorine through cyclopropyl ring to the main chain of NR, during its dichlorocarbene modification. As modification proceeded, there was hange in absorption due to cis double bond (-CH= CH-) and vinyl group (-CH=CH2) vhile absorption due to trans double bond remained unaffected. Two new peaks appeared n the modified rubber, one at 780 cm $^{-1}$ due to incorporation of chlorine (-C-Cl)) nd the other at 1020 cm^{-1} due to presence of cyclopropyl ring. The cis double bonds vere readily attacked by dichlorocarbene and even at low levels of modification, the ntensity due to double bonds was greatly reduced. Hence the dichlorocarbene nodification occurs at the cis double bond of isoprene unit.

The thermograms obtained from differential scanning calorimeter showed that lass transition temperature (Tg) of the modified NR increased with the extent of nodification. The Tg of unmodified NR was at –63 °C, while that of modified NR of 15%, 25% and 35% of chlorine content were at –5 °C, 19 °C and above 40 °C espectively. This drastic change in Tg indicated the change of NR from rubbery to lastic nature. NR changed from a flexible, tacky, elastic material to a hard, non-tacky and very stiff material as modification proceeded. Modified NR of 35% chlorine content was very powdery. Processability of NR decreased as the extent of modification increased. TGA studies showed that the decomposition pattern of dichlorocarbene modified NR were comparable with commercial chloroprene rubber. Modified NR showed different degradation pattern and took more time for 50% degradation than NR indicating better heat stability. Polar nature was imparted to NR by dichlorocarbene modification as observed from solvent swelling studies. DCNR of 15% chlorine content gave better physical properties with peroxide vulcanization than unmodified NR. Vulcanizates of DCNR with 15% and above chlorine content exhibited oil aging properties comparable to that of HNBR of 36% ACN content, at room temperature. DCNR with a higher chlorine content (above 25%) showed flame retardant and self-extinguishing nature. The presence of chlorine in the samples enables them to be safely used as a flame resistant material for indoor applications. Due to the better polar nature of DCNR, it blended easily with polar rubber like,HNBR without affecting its oil and ozone aging characteristics and it acted as a coagent for peroxide vulcanization of gum HNBR.

Blends of NR and HNBR exhibited inferior technological properties at different blend ratios. The tensile strength and modulus of the blend were inferior to both NR and HNBR showing that blend was not miscible in any of these blend ratios as there was considerable difference in their solubility parameters and saturation level. DCNR of different chlorine content was incorporated to the 50/50 blend to alleviate this immiscibility. It was found that DCNR of 15% chlorine content at 7 parts loading considerably improved the technological and heat aging properties. Blending methods indicated that master batching and cross blending yielded better properties to the vulcanizates. Cure system also played an important role in improving the mechanical properties. Among the four types of cure system studied for the 50/50 blends, a mixed cure with an efficient vulcanization (EV) or a semi EV system for NR and peroxide cure for HNBR gave excellent dynamic mechanical properties. Vulcanization kinetics showed that even though the vulcanization rate was faster with the sulphur curing of both the matrices, a higher level of vulcanization was obtained when HNBR phase vulcanized by peroxide. DCNR containing blends gave higher activation energy. This showed that temperature sensitivity of vulcanization increased with the addition of DCNR. Interfacial adhesion in blend vulcanizates as investigated by selective or differential solvent swelling using methyl ethyl ketone (MEK) and n-heptane at room temperature and V_r values indicated that higher cross-linking was observed in the order CBS/S/Peroxide > TMTD/MBT/S/Peroxide > TMTD/MBT/S cure system. The weight of solvent absorbed by the blend in the presence of DCNR was lower than the pure blend in all the three cure systems, indicating the formation of interfacial cross-links. The influence of fillers HAF, FEF and silica on properties of blends were evaluated at 30 phr loading. In HAF filled system, all the blends showed better tear strength and heat build up than HNBR and better hardness and high temperature compression set than NR at all blend ratios. The flex resistance of blends containing 50 parts and above HNBR was superior to both the constituents. The tensile properties were inferior to both the components, which was further improved by the incorporation of DCNR. IR spectroscopic studies showed a shift in the characteristic peak of the acrylonitrile group of HNBR corresponds to 2237.0 cm^{-1} to 2239.6 cm^{-1} for the DCNR containing blend. This was possibly due to the polar – polar interaction occurring between the acrylonitrile part and the chlorine atom of DCNR. In DSC studies, the presence of two peaks for transitions of NR and HNBR in the binary blends revealed that blends of NR and HNBR were not miscible completely. However,on close observation it was seen that with addition of DCNR to the blend, Tg of both NR and HNBR shifted to a slightly higher temperature. SEM characterisation also showed that the blend became more miscible by the incorporation of DCNR.

The degradation behavior of the blends under different conditions of exposure such as thermal, oils, fuel, ozone and radiation was studied. The effect of blend ratio, cure systems and filler on aging was investigated. NR showed very poor thermal aging behavior at all temperatures due to its highly unsaturated structure. The blends showed improvement in properties and that containing 7 parts of DCNR showed a comparatively higher values for tensile strength and modulus than the pure blends after aging at temperatures from 70°C -150°C. Mixed cure system / incorporation of filler considerably enhanced the thermal aging resistance. Among the different cure systems, TMTD/MBT/S and TMTD/MBT/S /Peroxide systems gave slightly better retention of properties than CBS/S/Peroxide system. The thermal aging characteristics improved by the addition of filler in the order HAF ≥ silica > FEF. During solvent aging, NR being non-polar swell considerably in organic fluids and oils. The swelling nature of NR in ASTM oils and ASTM fuel C was remarkably reduced by blending with HNBR, which varied with the HNBR content. It was also observed that filled vulcanizates showed far lower swelling compared to gum vulcanizates at different temperatures. Retention of physical properties of vulcanizates after immersion in oils/ fuel was also far better for the blends than NR. During ozone aging, due to the double bonds present on the main chain, NR surfaces readily underwent ozone cracking on exposure to weathering conditions. Significant improvement in ozone resistance was observed for the blends, which was affected by cure system and blend ratio. Incorporation of DCNR and filler further improved the property. Blends having 50 parts and above HNBR with CBS/S/Peroxide cure system and 30 phr HAF loading showed excellent ozone resistance. During γ ray irradiation, among the filled vulcanizates, HNBR showed better retention of properties than NR. In the case of filled blends, improved tensile strength, modulus and decreased elongation at break were observed which indicated that additional cross-linking was formed by radiation. This was more obvious in the blend having TMTD/MBT/ S/Peroxide cure system.

The chemical changes taking place during aging studied by stress relaxation method showed that there were more scission reactions in NR/HNBR blend during aging in the absence of DCNR. Solvent swelling studies also revealed that there was restriction to swelling of NR phase by the lightly swollen HNBR phase in the presence of DCNR indicating interfacial bonds which was further supported by V_r values.

A comparative study of mechanical properties and aging behavior of NR and its blends with HNBR, CR, NBR and EPDM showed that aging characteristics of NR vulcanizates were improved by blending with speciality elastomers. Among these NR/HNBR blend gave a combined effect of aging resistance towards heat, oil, ozone and radiation to a desirable level. Even though NR/EPDM blend had good resistance towards ozone and heat aging, its oil aging and physical properties were very poor. NR/NBR blend showed better oil and radiation resistance, but was very poor towards heat and ozone resistance. Blend of NR/CR showed only little improvement towards heat, oil and ozone.

The rheological behavior of the blends showed that flow pattern of the blends was similar to NR. Viscosity of all mixes decreased with increasing shear rate showing pseudoplastic flow behavior. HNBR showed higher viscosity than NR. Blends showed lower viscosity than both the components, the behavior of a negatively deviating blend (NDB) which was due to the interlayer slip possible in immiscible blends In the case of both gum and filled blends, blend containing DCNR showed higher viscosity than pure blend. This indicated the possibility of interfacial interaction occurring between the two phases, which reduce the possibility of interlayer slip with the formation of an associative network, resulting in a system with increased yield stress and hence higher viscosity. Viscosity of the blends decreased with temperature at all shear rates and this effect was more prominent above 100°C and at higher shear rates. Higher values of $(\tau_{11}-\tau_{22})$ and S_R and lower values of G imply higher elasticity of the mixes. The high elasticity of NR was considerably reduced by the addition of HNBR to it. Incorporation of 7 parts of DCNR to the blend showed only slight reduction in elasticity where_as incorporation of filler reduced the elastic parameters to a considerable level. NR showed highest die swell at all shear rates and increased highly with increasing shear rate. HNBR showed a comparatively lower die swell with slight increase with shear rate. Blends showed a die swell intermediate between NR and HNBR especially at higher shear rates. DCNR containing blends showed lower die swell than pure blends at lower shear rates, which could also be due to the interactions between DCNR and HNBR. At higher shear rate it showed higher die swell than HNBR due to the increased elastic response of the blend. Filled blends exhibited extremely very low die swell and had only slight variation with shear rate, due to the lower elastic response. NR and DCNR showed highest distortion on the extrudates due to the higher elastic recovery possible for them as a result of high molecular weight of the polymer. HNBR extrudates showed lower distortion, as it is less viscoelastic than NR. It was seen that blending, addition of filler and presence of DCNR improved the extrudate behavior of NR.

The essence of the findings of the present investigation can be summarized and concluded as follows: Dichlorocarbene modification of natural rubber is an easy and useful technique to improve its resistance towards solvents along with flammability characteristics. Introduction of chlorine enhances the polarity of rubber and make it suitable for blending with hydrogenated nitrile rubber. Due to the polar interactions possible between chlorine of dichlorocarbene modified natural rubber and acrylonitrile of hydrogenated nitrile rubber, this acts as a phase modifier in NR/HNBR blends resulting in better processing behavior and vulcanizates with remarkably enhanced mechanical properties and aging characteristics with respect to heat, oil, fuel, ozone and radiation.

LIST OF PUBLICATIONS

1. Elizabeth K.I, R.Alex, B.Kuriakose, S. Varghese, N.R.Peethambaran, " Dichlorocarbene modification of Natural Rubber and its role as a modifier in Blends of Natural Rubber and Hydrogenated Nitrile Rubber". *Journal of Applied Polymer Science.* (In Press).

2. Elizabeth K.I, R.Alex, B.Kuriakose, N.R.Peethambaran, "Blends of Natural Rubber and Hydrogenated Nitrile Rubber containing Dichlorocarbene modified Natural Rubber, Part I- Aging behavior". *Progress in Rubber, Plastics and Recycling Technology.* (In Press).

3. Elizabeth K.I, R.Alex, B.Kuriakose, N.R.Peethambaran, "Dichlorocarbene modified Natural Rubber". *Natural RubberResearch.* (In Press)

4. Elizabeth K.I, R.Alex, B.Kuriakose, N.R.Peethambaran, "Evaluation of Blends of Natural Rubber and Hydrogenated Nitrile Rubber containing chemically modified Natural Rubber". *Journal of Rubber Plastics and Composites.* (Communicated)

5. Elizabeth K.I, R.Alex, "Rheological behavior of Blends of Natural Rubber and Hydrogenated Nitrile Rubber", *Kauchuk Gummi Kunststoffe, Nov.2005, 1.*

PRESENTED PAPERS

1. Elizabeth K.I, R.Alex, B.Kuriakose, N.R.Peethambaran, "Aging behavior of Natural Rubber and Hydrogenated Nitrile Rubber blend containing Dichlorocarbene modified Natural Rubber as compatibilizer". Presented in the International Rubber Conference, Rubb. Tech.EXPO, 2002, New Delhi: *Conf. Proce.* P-28-30.

2. Elizabeth K.I, R.Alex, B.Kuriakose, N.R.Peethambaran, "Dichlorocarbene modification of Natural Rubber and its role as a compatibilizer in Blends of Natural Rubber and Hydrogenated Nitrile Rubber". Presented in the International Rubber Conference, seminar APT 2002, Dec.12-14, Kochi: *Conf. Proce.* p-258-265.

3. Elizabeth K.I, R.Alex, " Rheological behavior of Blends of Natural Rubber and Hydrogenated Nitrile Rubber containing Dichlorocarbene modified Natural Rubber." Accepted for presentation in International Natural Rubber Conference, November 2005 at Kochi.

Rubber blends · Natural rubber · Dichlorocarbene modified natural rubber · Hydrogenated nitrile rubber · Flow properties

The influence of dichlorocarbene modified natural rubber (DCNR) as a modifying agent on the rheological behavior of blends based on natural rubber (NR) and hydrogenated nitrile rubber (HNBR) was investigated. The binary blends of NR and HNBR showed a pseudoplastic flow behavior. The blends recorded a viscosity lower than both the constituents showing a behavior, characteristic of immiscible blends. The addition of small quantities of DCNR to the 50/50 blend resulted in an increase in the viscosity due to the interactions with the blend constituents. The temperature sensitivity of the DCNR containing blend decreased with incorporation of filler. The higher elasticity of NR was indicated by higher values of principal normal stress difference ($\tau_{11} - \tau_{22}$), recoverable shear strain (S_R) and lower values of elastic modulus (G) in comparison with other mixes. ~~Blending of NR with HNBR considerably reduced the elasticity of the blend.. At lower shear rates, DCNR containing blends recorded a die swell lower than both the blend constituents. Filled blends exhibited very low die swell and showed slight variation with shear rate.~~

Rheologische Eigenschaften von verschnitten aus Naturkautschuk und hydriertem Nitrilkautschuk

Kautschukverschnitte · Naturkautschuk · Dichlorcarben · modifizierter Naturkautschuk · hydrierter Nitrilkautschuk · Fließeigenschaften

Der Einfluss von mit Dichlorcarben modifiziertem Naturkautschuk (DCNR) auf das rheologische Verhalten von NR und HNBR wurde untersucht. die binären Verschnitte aus NR und HNBR zeigten ein pseudoplatisches Fließverhalten, mit einer Viskosität die unterhalb der der jeweiligen Reinkomponenten liegt. Dieses für unverträgliche Verschnitte typische Verhalten wird durch die Zugabe geringer Mengen an DCNR und der damit eingebrachten Wechselwirkungen dahingehend verändert, dass die Viskosität sich erhöht. die Temperaturabhängigkeit der DCNR enthaltenden Verschnitte nimmt durch die Zugabe von Füllstoff ab.

Rheological Behavior of Blends of Natural Rubber and Hydrogenated Nitrile Rubber

The processing behavior of rubbers which includes the behavior of materials during processing operations such as mixing, shaping, molding, calendaring and extrusion is one of the major concerns of rubber industry. The flow behavior of elastomers is an important aspect in the processing step [1–3]. This is the reason why, the viscosity function of a polymer, is becoming more important in trying to optimize the processing operations and in designing processing equipments such as extruders and dies required for various products.

The effect of blending of rubbers on flow properties of elastomers is important as in many cases, blends are preferred to achieve the required end use [4–7]. Most of the rubber blends are immiscible and hence suitable modifiers are used to improve the blend compatibility and the overall properties [8–10]. Also rubbers are seldom used without fillers. Hence the influence of fillers and modifiers on the flow properties of rubber blends are very useful in designing rubber compounds [11–12].

A number of rheological investigations have been reported on the behavior of NR compounds [13–15], blends of NR with plastics [16–17], cryoground compounds [18], rubber reclaim [19] and other elastomers blends [20–22].

Elasticity of a polymer melt responds differently to changes in extrusion conditions like residence time in the die and temperature [23]. The behavior of a rubber mix is controlled by the viscosity coefficient $\psi 1(\gamma)$ and secondary stress coefficient $\psi 2(\gamma)$. The behavior is determined by the dependence of shear stress on shear rate and by the dependence of normal stress on shear stress or shear rate [24].

Natural rubber (NR) is a versatile material, that has found various engineering and other applications. Due to its high degree of unsaturation and non-polar nature it is highly prone to degradation by temperature, ozone and oils [25]. Hydrogenated nitrile rubber (HNBR) is a new class of elastomer, highly resistant to degradation under severe conditions of temperature, ozone and oils [26]. Dichlorocarbene modified natural rubber (DCNR) is a modified form of NR prepared by the alkaline hydrolysis of chloroform on NR [27]. We found that blending of NR with HNBR improves its aging properties to a great extend without much affecting mechanical properties [28]. The incorporation of 7 parts of DCNR as a modifier in this blend further improves the properties. Thus, this blend can be used in oil seals, hoses used in oil fields and other such applications requiring oil, weather and temperature resistance.

This paper presents the results of rheological studies conducted for blends of NR and HNBR with respect to the effect of blend ratio, of DCNR and of carbon black filler. The flow aspects considered are a) viscosity as a function of shear rate and b) elasticity as it appears in die swell and principal normal stress difference.

Experimental

Materials

The NR used in this study was ISNR 5 grade obtained from Pilot Crumb Rubber Factory, Rubber Board, Kottayam, India. The HNBR used was a Zetpol 2010 grade (Nippon Zeon, Japan) with 36 % bound ACN content, an iodine value-11 g/100 g and a Mooney viscosity ML(1 + 4)100°C – 85. The dichlorocarbene modified NR was prepared by alkaline hydrolysis of chloroform using cetyltrimethyl ammonium bromide as phase transfer catalyst according to the reference [29].

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Carbon black N 330 was supplied by Philips Carbon India Ltd.

1 Formulation of NR/HNBR blends

	N	H	C	NHa	NH	NHb	NHC3	NHC7	NHC10	NHB	NHC7B
NR	100			75	50	25	50	50	50	50	50
HNBR		100		25	50	75	50	50	50	50	50
DCNR			100				3	7	10		7
FEF										30	30

Preparation of the blends

The blends were prepared on a two roll mixing mill as per Table 1. NR and HNBR were individually masticated for about 1 min. and then blended together for a period of 4 min. For the preparation of the modified blend, DCNR was first masticated for 1 min. incorporated with HNBR and then blended with NR. The filled mixes were prepared by adding the filler after mixing the rubbers. The total mixing time was 10 min. The temperature of the rolls was controlled by circulating cold water.

Rheological studies

The rheological studies were carried out using a capillary rheometer, attached to a Zwick Universal Testing Machine, model 1474. The extrusion assembly consisted of a barrel made of hardened steel, mounted on a special support, underneath the moving cross head of the Zwick UTM. A hardened steel plunger, which was accurately ground to fit inside the barrel was held to the load cell extrusion. An insulating ring thermally isolated the barrel from the rest of the machine and prevented heat losses due to conduction. The capillary used was inserted at the bottom of the barrel and was locked using a clamping device. The capillary was made of tungsten carbide with a L/D ratio of 40 and an angle of entry of 180°. The temperature inside the barrel and capillary was varied between 90°C and 110°C with an accuracy of 1°C.

The moving cross head of the Zwick UTM runs the barrel at a constant speed, irrespective of the load on the melt, maintaining a constant volumetric flow rate through the capillary. The cross head speed could be varied from 0.5 to 500 mm/ min giving shear rates ranging from 3 to 3000 s-1. The forces corresponding to specific plunger speeds were recorded on a strip chart recorder. These values were converted to shear stress.

The test sample (10 g) was placed inside the barrel, which was maintained at the test temperature. The sample was forced down to the capillary using the plunger attached to the moving cross head. After a warming up period of three minutes, the melt was extruded through the capillary at pre-selected speeds of the crosshead. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give 8 different plunger speeds. Each plunger speed was continued until the recorded force was stabilized before changing to the next speed. Forces corresponding to specific plunger speeds were recorded. The forces and cross head speed were converted into apparent shear stress (Γ_w) and shear rate (γ_w) at the wall by using the following equation:

$$\Gamma_w = \frac{F}{4Ap\ (lc/dc)} \qquad (1)$$

$$\gamma_w = \frac{(3n'+1)}{4n'} \times \frac{32Q}{\Pi dc^3} \qquad (2)$$

where:

F – force applied at a particular shear rate, Ap – cross sectional area of the plunger, lc – length of the capillary, dc– diameter of the capillary, Q – volume flow rate, n' flow behavior index defined by d (log Γ_w)/d (log γ_{wa}), γ_{wa} – apparent wall shear rate and γ_w – actual shear rate at wall.

The value n' is determined by a regression analysis of the values of Γ_w and γ_{wa} obtained from the experimental data. The shear viscosity was calculated as $\eta = \Gamma_w/\gamma_w$.

The dependence of the melt viscosity on temperature was determined by the Arrhenius type equation:

$$\eta = A\ e^{E/RT} \qquad (3)$$

where A is a constant, E, the activation energy and R the universal gas constant.

Extrudate characteristics of the blends

The extrudate emerging from the capillary was collected with minimum possible deformation. The diameter of the extrudate was measured after 24 hours of rest period, using a WILD stereo microscope model M650 at several points on the extrudate. The average value of 10 readings was taken as diameter (de) of the extrudate and die swell was calculated as:

$$\text{Die swell} = \frac{de}{dc} \times 100 \qquad (4)$$

where dc is the diameter of the capillary. Representative samples were cut from the extrudates and photographs were taken.

Elastic parameters

The principal normal stress difference ($\Gamma_{11} - \Gamma_{22}$) was calculated from the die swell and shear stress according to Tanner's equation [30].

$$(\Gamma_{11} - \Gamma_{22}) = 2\Gamma_w[2(de/dc)^6 - 2]^{1/2} \qquad (5)$$

Recoverable shear strain S_R and elastic shear modulus G were calculated from the equation [31]:

$$S_R = (\Gamma_{11} - \Gamma_{22})/2\Gamma_w \qquad (6)$$

$$G = \Gamma_w/S_R \qquad (7)$$

where Γ_w is the wall shear stress.

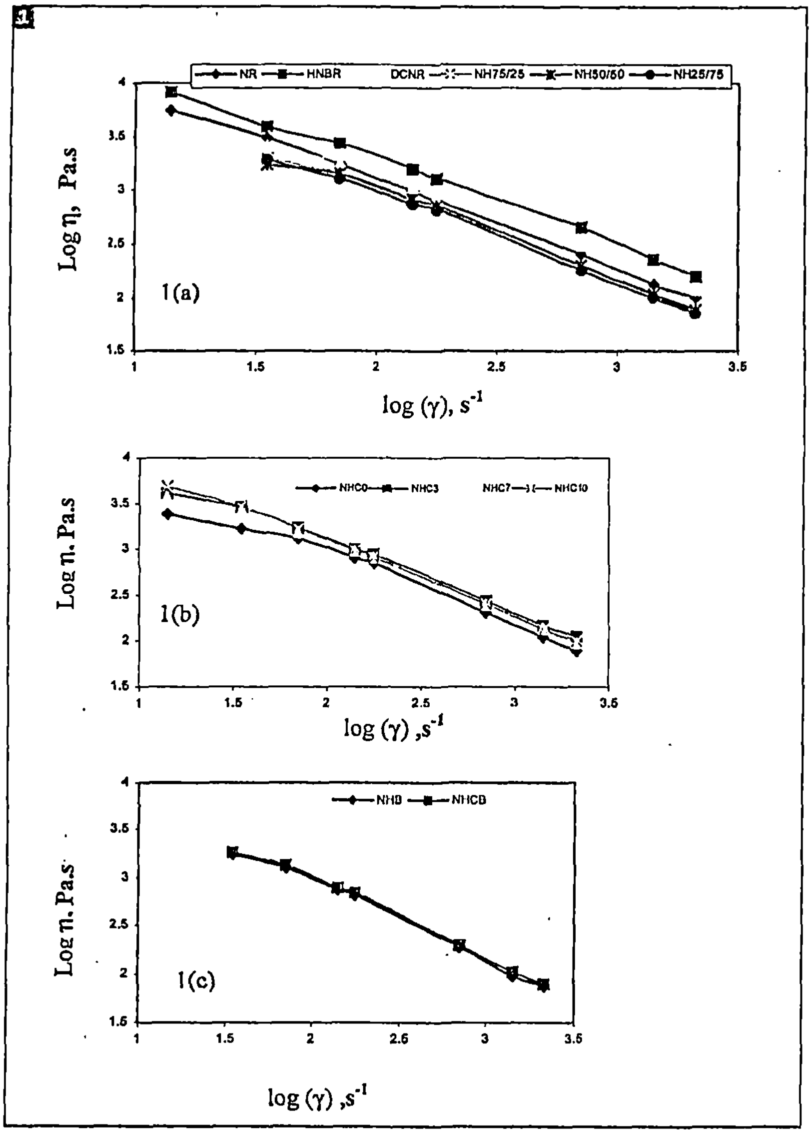
Results and discussion

Variation of viscosity with shear rate

Figure 1 shows the viscosity as a function of shear rate at 110°C for neat NR, HNBR, DCNR and different blends of NR/HNBR. The viscosity of all mixes decreases with increasing shear rate showing a pseudo-plastic flow behavior. The molecules which are extensively entangled at normal conditions become disentangled and oriented in the direction of flow under the application of shear. As NR has a very highly entangled matrix, during application of load, the viscosity of NR reduces faster than for HNBR. HNBR shows a higher viscosity probably due to its polarity which results from associative interactions [32]. Modified NR shows lower viscosity than HNBR at all shear rates. At shear rates less than 100 s^{-1} DCNR shows a lower viscosity than NR and at higher shear rates shows higher viscosity than NR. This is also reflected in the flow behavior index given in Table 2. NR shows the highest pseudoplastic character among the different blend constituents.

Effect of blend ratio

The effect of blending of NR and HNBR on viscosity is shown in Figure 1(a). The blends show a comparatively lower viscosity than NR, HNBR and DCNR. The viscosity of the blends may be higher than the viscosity of the pure components when there is interaction between blend components, or lower when there is the possibility of interlayer



1 Variation of shear viscosity with shear rate of a) NR, HNBR, DCNR and the blends b) 50/50 blend containing different dosage of DCNR and c) filled blends with and without DCNR

2 Flow behavior of NR, HNBR, DCNR and the blends

Blend	Flow behavior index n'
N	0.1847
H	0.3831
C	0.2883
NH	0.2004
NHa	0.1833
NHb	0.1760
NHC3	0.2407
NHC7	0.2276
NHC10	0.1969
NHB	0.1861
NHC7B	0.1886

slip. At constant shear rate the blend viscosity decreases as the HNBR content of the blend increases. The blends showed a lower viscosity than both the components at all ratios. This demonstrates showed the behavior of a negatively deviating blend (NDB), probably due to the interlayer slip possible in immiscible blends [33]. The lower viscosity recorded by the blends in comparison with the components may be attributed to this.

Effect of modifier

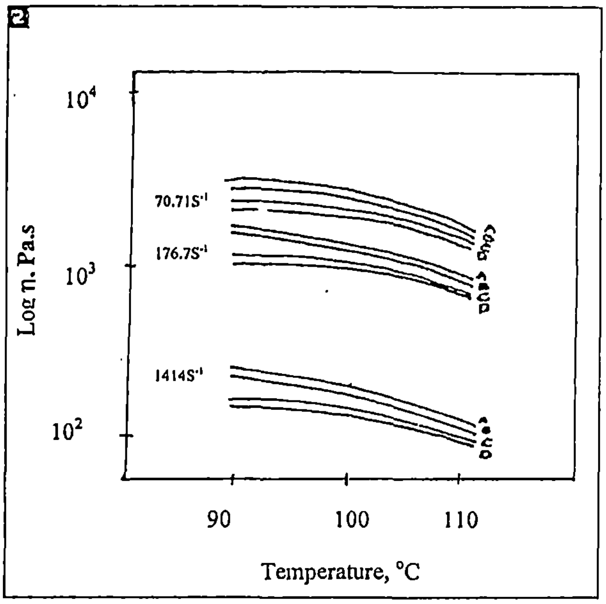
The effect of varying doses of DCNR on the viscosity of the 50/50 blend is shown in Figure 1(b). It is seen that incorporation of DCNR to the 50/50 blend increases its viscosity. In the case of filled blends also, the effect of DCNR is to increase the viscosity. (Figure 1(c). This indicates that in the presence of DCNR there is some interfacial interaction occurring between the phases. This interaction reduces the possibility of interlayer slip and increases the formation of an associative network, resulting in a system with increased yield stress and a higher viscosity. However contrary to the expectation, the black filled blends exhibits lower viscosity than gum mixes.

Variation of viscosity with temperature

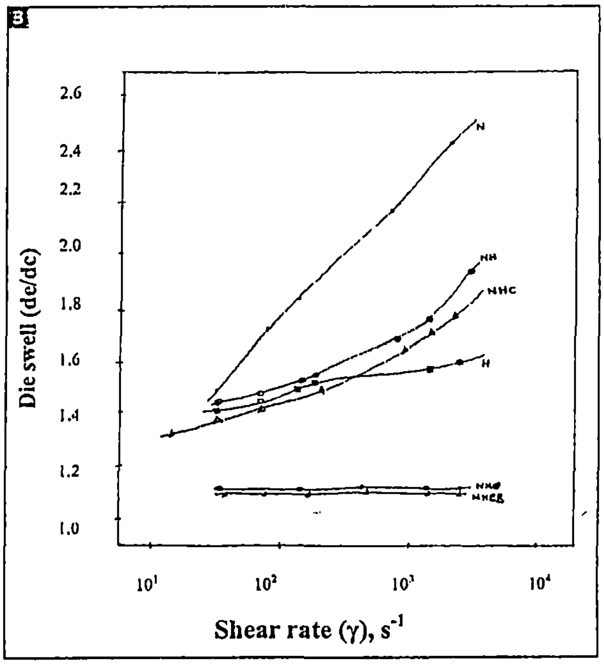
The temperature dependence of the viscosity of both the gum and the filled 50/50 blend and the blend containing 7 parts of DCNR at three different shear rates are given in Figure 2. It is seen that viscosity decreases with temperature at all shear rates and this effect was more pronounced above 100°C and at higher shear rates. The activation energy of flow calculated for the gum and filled blends is given in Table 3. It is seen that the activation energy is higher for the DCNR containing blend for both the gum and the filled blends. The polar interactions between DCNR and HNBR support the formation of entanglements of the chain molecules and hence a higher amount of energy is needed for the flow. Thus, blends containing DCNR show higher activation energy than the pure blend. The filled blend shows lower activation energy of flow as the temperature sensitivity reduces with filler loading.

3 Activation Energy (K cal/mol) of the gum and filled blends at three shear rates

	70.716	707.161	1414.4
NH	827	782.2	678.11
NHC7	848	794.4	691.6
NHB	684	628.54	564.5
NHC7B	734	696.6	586.67



2 Variation of viscosity with temperature. A – NHC, B -NH, C – NHCB and D – NHB



3 Variation of die swell with shear rate of NR. HNBR and blends

Elasticity

The elastic parameters are important in the processing of polymers and can be characterized by the normal stress difference ($\tau_{11} - \tau_{22}$), the elastic modulus G, the recoverable shear strain S_R and the die swell ratio de/dc. Elastic parameters depend strongly on the extrusion history and are changed by filler incorporation [34].

Values of ($\tau_{11} - \tau_{22}$), G and S_R at constant shear rate 1414 s^{-1} are given in Table 4. Higher values of ($\tau_{11} - \tau_{22}$) and S_R and lower values of G imply higher elasticity of the mixes. The data shows that high elasticity of NR is considerably reduced by the addition of HNBR, a behavior seen similar to reduction in elasticity. Incorporation of 7 parts of DCNR to the blend shows only slight reduction in elasticity where as in corporation of filler reduced the elastic parameters to a considerable level. This was in accordance with observations from earlier work [12].

Die swell

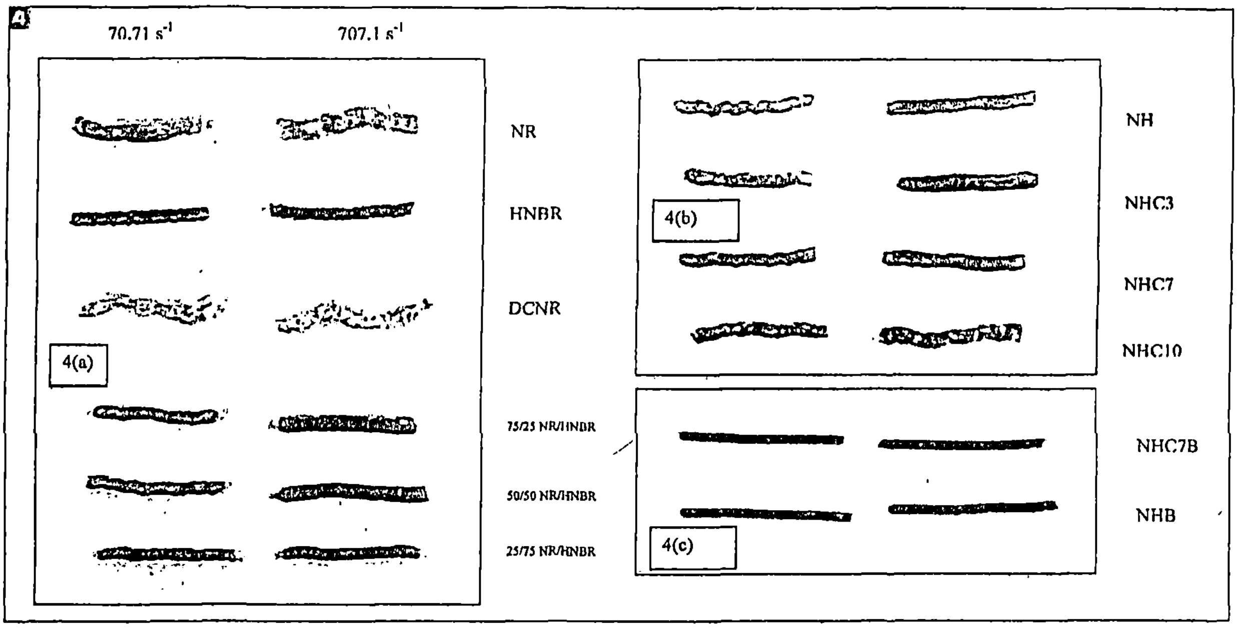
Die swell is a relaxation phenomenon. When the molten polymer flows through the capillary, shearing tends to maintain the molecular orientation of polymer chains and when the melt emerges from the die, the molecules tend to recoil, leading to the phenomenon of die swell. The elastic recovery of the polymer chains is influenced by factors such as stress relaxation, crosslinking, presence of fillers etc. [35]. In general die swell increase with the increase in shear rate [36]. Figure 3 shows the die swell vs shear rate of NR, HNBR and 50/50 pure and DCNR containing blends and 50/50 blends containing 30 phr of FEF black. It is seen that NR shows the highest die swell at all shear rates and increase highly with increasing shear rate. HNBR shows a comparatively lower die swell with a slight increase with shear rate. The blends show a die swell which is intermediate between NR and HNBR especially at higher shear rates (Table 5). Die swell is generally related to shear stress. The greater the shear strain that occurs in the capillary, the less will be die swell [37]. DCNR containing blends show lower die swell than pure blends at lower shear rates which could also be due to the interactions between DCNR and HNBR. At higher shear rate it shows higher die swell than HNBR due to the increased elastic response of the blend. Filled blends exhibit extremely very low die swell

4 The elastic parameters – principal normal stress dierence ($\tau_{11} - \tau_{22}$), elastic modulus G, recoverable shear strain S_R of the blends

	($\tau_{11} - \tau_{22}$), N/m²	G, N/m²	S_R
N	1.53126×10^7	2.67×10^4	18.7013
H	4.7601×10^6	8.64×10^4	5.2470
C	8.4202×10^6	3.90×10^4	10.3774
NH	4.8045×10^6	4.10×10^4	7.6529
NHC7	4.3990×10^6	4.49×10^4	7.3802
NHB	9.097×10^5	1.893×10^5	1.6101
NHC7B	8.4119×10^5	2.245×10^5	1.3480

5 Die swell ratio of gum and filled blends at two shear rates 70.716 s-1 and 707.16 s-1 at 110°C

	70.716	707.16
N	1.740	2.193
H	1.4969	1.5663
C	1.8099	1.9144
NH	1.4619	1.6707
NHC3	1.4614	1.775
NHC7	1.4270	1.6407
NHC10	1.5315	1.9144
NHB	1.1138	1.1486
NHC7B	1.089	1.1138



4 Photographs of the extudates. (a) – NR, HNBR, DCNR and blends (b) – 50/50 blend containing DCNR and (c) – filled blends with and without DCNR at two shear rates

and show only slight variation with shear rate, due to the lower elastic response. Table 5 shows the die swell ratio of the rubbers and the blends at two shear rates 70.716 s^{-1} and 707.16 s^{-1} at 110°C. It becomes clear that the die swell of NR is reduced considerably by blending with HNBR. A similar effect was reported for blending NR with rubber reclaim [19] and with cryoground rubber compounds [18]. Incorporation of DCNR in 50/50 blend further reduces the die swell. It is lowest at 7 parts loading indicating that effective interaction level is at this dose. Filler addition again reduces the die swell, which is in agreement with the previous reports. Reinforcing fillers result in low mobility of the polymer chains under the influence of applied shear stress. Hence the elastic recovery and subsequently the die swell decrease in filled blends. It is also noted that for the filled blends, die swell variation with shear rate is very low.

Figure 4 shows the photographs of extrudates of NR, HNBR, DCNR and NR/HNBR blends. It is seen that NR and DCNR shows highest distortion on the extrudates. This is due to the higher elastic recovery possible for them as a result of high molecular weight of the polymer. HNBR extrudates shows lower distortion, as it has a low molecular weight. It is seen that blending, addition of filler and of DCNR respectively improve the extrudate behavior of NR. Due to the polar interactions, DCNR is expected to act as a modifier in blends of NR/HNBR to improve the flow behavior.

Conclusion

The binary blends of NR and HNBR show a pseudo-plastic behavior. These blends exhibit lower viscosities than blend constituents due to slippage during flow. The addition of DCNR in NR/HNBR blend considerably improves their flow characteristics. DCNR containing blends show a higher viscosity than pure blends due to the contribution of polar interactions among blend constituents. They also exhibit higher activation energy of flow, which is considerably reduced by the addition of filler. The blends show a lower elasticity than pure NR. The presence of 7 parts of DCNR further reduce the elasticity of the blend and results in extrudates with very low die swell. The effect of filler in DCNR containing blend is to reduce die swell further with less sensitivity to variation with shear rate.

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Die höhere Elastizität des NR wird im Vergleich zu den Mischungen an der Normalspannungsdifferenz , dem Schubverformungsrest und dem elastischen Modul herausgestellt. ~~Durch Verschneiden von NR mit HNBR wurde die Elastizität herabgesetzt. Bei geringen Schergeschwindigkeiten zeigen die DCNR enthaltenden verschnitte eine geringe Spritzquellung als die jeweiligen Reinkomponenten. Gefüllte Verschnitte zeigen ebenfalls eine geringe Spritzquellung die zudem von der Spritzquellung nur geringfügig beeinflusst wird.~~