DICHLOROCARBENE MODIFIED STYRENE BUTADIENE RUBBER AND ITS APPLICATION IN RUBBER-RUBBER BLENDS

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BY

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Certificate

This is to certify that the thesis entitled ***Dichlorocarbene Modified Styrene Butadiene Rubber and its Application in Rubber-Rubber Blends*** *is an authentic record of the research work carried out by* ***Mr. M. T. Ramesan*** *under my supervision and guidance in partial fulfilment of the requirements for the award of the degree of* ***Doctor of Philosophy*** *in Polymer Chemistry under the Faculty of Science of Mahatma Gandhi University, Kottayam. The work presented in this thesis has not been submitted for any other degree or diploma earlier. It is also certified that Mr. M. T. Ramesan has fulfilled the course requirements and passed the qualifying examination for the Ph.D. degree of Mahatma Gandhi University.*

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Declaration

I hereby declare that the thesis entitled ***Dichlorocarbene Modified Styrene Butadiene Rubber and its Application in Rubber-Rubber Blends*** *is an authentic record of the research work carried out by me under the supervision of* ***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.*

M. T. Ramesan

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List of Notations and Abbreviations

ABS - poly(acrylonitrile-co-butadiene-co-styrene)
CBS - N-cyclohexyl-2-benzothiazyl sulphenamide
$CHCl_3$ - chloroform
CMC - critical micelle concentration
CPE - chlorinated polyethylene
CR - chloroprene rubber
CTAB - cetyl trimethyl ammonium bromide
CV - Conventional vulcanisation
DCP - dicumyl peroxide
DCSBR - dichloro carbene modified styrene butadiene rubber
DSC - differential scanning calorimetry
DTG - derivative thermogravimetry
E' - storage modulus
E'' - loss modulus
ENR - epoxidised natural rubber
EPDM - ethylene propylene diene terpolymer
EPM - ethylene propylene monomer
EPM-g-MA - maleic anhydride grafted EPM
EPR - ethylene propylene rubber
EVA - poly(ethylene-co-vinyl acetate)
HAF - high abrasion furnace black
HDPE - high density polyethylene
ISNR – 5 - Indian standard natural rubber – 5 grade
FTIR - fourier transform infrared spectroscopy
LDPE - low density polyethylene
LOI - limiting oxygen index
M - molecular weight of the polymer
M_c - molecular weight between crosslinks
MW - molecular weight
NA-22 - ethylene thiourea
NaOH - sodium hydroxide
NBR - acrylonitrile-co-butadiene rubber
NMR - nuclear magnetic resonance
NR - natural rubber
PE - polyethylene
PET - polyethylene terepthalate
PhPE - phenolic modified polyethylene
Phr - parts per hundred
PMMA - polymethyl methacrylate
PP - polypropylene
PVC - poly vinyl chloride
Q_t - mol% uptake
SAN - styrene-acrylonitrile copolymer
SBS - styrene butadiene styrene copolymer

SEM - scanning electron microscopy
SIS - styrene isoprene styrene copolymer
tan δ - dissipation factor
TDQ - 2, 2, 4 – trimethyl 1, 2 - dihydroquinoline
T_g - glass transition temperature
TGA - thermogravimetric analysis
TMTD - tetra methyl thiuram disulphide
vr - crosslink density
UTM - universal testing machine
X-NBR - carboxylated nitrile rubber
Z_c - degree of polymerisation of the copolymer
χ - Flory-Huggins interaction parameter
ν_{phys} - physical crosslinks
β - interaction parameter
γ - interfacial tension
ϕ_1 - volume fraction of component 1
ϕ_2 - volume fraction of component 2
ϕ_A - volume fraction of component A
ϕ_c - bulk copolymer volume fraction
Δd - particle size reduction
ΔG_m - free energy of mixing
ΔH - enthalpy
ΔH_m - enthalpy of mixing
λ - extension ratio
μm - micrometer
ρ_p - density of polymer
ρ_s - density of solvent
Δr - interaction tension reduction
ΔS - entropy
δ_s - solubility parameter of the solvent
ΔS_m - entropy of mixing

CHAPTER

1

INTRODUCTION

The emphasis on the synthesis of new polymers, to meet the requirement of a specific type, has begun to turn away, to polymer modification,since the last few decades. Chemical modification and blending of rubbers have become growing stimulation for research in the field of rubber chemistry, as it is realised that new elastomers are not always necessary for applications requiring specific properties because these can be met by modification of existing polymers or by blending of suitable rubbers. Chemical modifications on naturally occuring elastomers is generally accompanied by a loss of their basic characteristics. Modifications carried out on synthetic rubbers often results in enhanced properties as compared to original rubbers. New successful materials prepared by modification of natural rubber, that have a lot of commercial use include cyclised rubber, chlorinated rubber and hydrochlorinated rubber. In all these products the degree of modification is extensive and the products no longer possess the high elasticity of the raw material. Chlorinated rubber, one of the first modified forms of natural rubber has been used commercially in paints, adhesives, textile finishes, etc.[1,2] since a very long time. Modification of NR in the latex stage with hydrogen peroxide/formic acid to yield epoxide group, has been extensively studied.[3] The epoxidation process is unique as it improves the solvent and oil resistance of NR with preservation of the original gum strength. The first commercial carboxylated elastomer, butadiene-styrene-acrylic acid terpolymer latex was introduced by B. F. Goodrich in 1949 under the trade name HYCAR 1571.[4] Carboxylated nitrile rubber latices find extensive use in leather based product, oil-resistant seals, gaskets, paper coatings and textile applications. The good abrasion resistance of carboxylated SBR enables it to find application in tire tread compounds.[6] Bromobutyl rubber, a modified form of butyl rubber was first introduced commercially by B.F. Goodrich in 1955. The combination of low air permeability, good ageing properties, and better compatibility with NR makes bromobutyl rubber an ideal choice for the tire industry. Blends of NBR and PVC have become commercially significant for the use in hose, wire and cable industry.[7] Thermoplastic natural rubber made by blending natural rubber with plastics like polyethylene and polypropylene, and blends like NR/EPDM (ethylene propylene diene monomer) are materials that have wide acceptable as cable insulators, auto bumpers, hoses and gaskets.[8,9]

1.1 Chemical modification

The chemical modification on unsaturated elastomers is of particular interest because of the technological importance of parent materials and reactivity of the available double bonds.[10] Their high reactivity with a variety of chemical substances offer advantages for them to undergo extensive chemical modification. Chemical modifications carried out on rubber fall under four categories: (i) those resulting from attachment of a pendant group like epoxy, carbonyl etc. to the rubber molecule by addition or substitution reactions (ii) those obtained by grafting of a polymer at one or more points along the rubber molecule; (iii) those resulting from bond rearrangements without introduction of new chemical group like isomerised rubber; and (iv) those obtained by methods like depolymerisation.

1.1.1 Attachment of pendant groups

1.1.1.a Hydrogenation

Hydrogenation of synthetic rubbers is an excellent example of chemical modification, which imparts better physical properties to rubbers. Hydrogenated products are typically more stable than their unsaturated precursors.

The conversion of unsaturated polymers to saturated ones can be effected by both catalytic (homogeneous,[11] heterogeneous[12]) and non-catalytic (diimide,[13] hydrobortaion[14]) methods. Homogeneous, hydrogenation catalysts are usually of the co-ordination type organotransition metal such as cobalt or nickel in combination with triisobutyl aluminium. Heterogeneous hydrogenation catalysts are either of the low activity or high activity catalyst. Non-catalytic hydrogenation of olefinic polymers have been effected by hydroboration or diimide reduction. Degradation and cyclisation reaction generally accompany the hydrogenation process.[15]

Hydrogenation of cis-1,4-polyisoprene with triisobutylborane at high temperature and pressure yields a tough rubbery polymer which is a product similar to random copolymer of ethylene and propylene, prepared by Zeigler Nata catalyst. Hydrogenation of cis-1,4-polyisoprene with diimide generated in-situ from p-toluene sulphonyl hydrazide results in depolymerisation and cyclisation. Hydrogenation process generally require highly purified rubber in dilute solution, use of large amount of catalyst or use of high temperatures that cause degradation of rubber. Fully hydrogenated rubber is chemically inert and it is difficult to be vulcanised in conventional manner. Hydrogenated NR is transparent and colourless. It is a plastic, elastic waxy solid with the peculiar elastic characteristic of forming threads when stretched. Potential area of application is cable industry and automobile industry where its resistance to degradative agents like oxygen, ozone etc. is made use of. Partially hydrogenated material undergoes crosslinking by residual unsaturation and is of interest for a variety of application including adhesives and rubber-to-metal bonding. Hydrogenated polymers have also been used as model compounds[16] for the study of molecular theories and rheology.

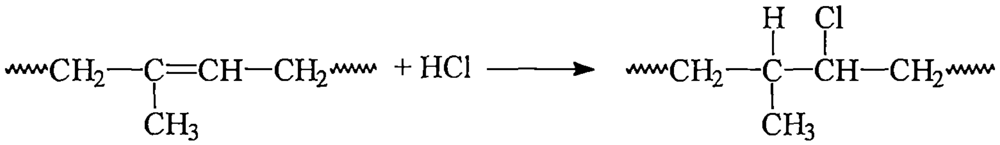
1.1.1.b Halogenation

The halogenation of unsaturated elastomers is of considerable interest in terms of its chemistry and applications of the resulting material. The extensive research on halogenation of small molecules served as a very important data base for the polymer reaction.[17] However, the reactions accompanying halogenation are complex and include addition, substitution, cyclisation, crosslinking and degradation. Rubber, in solid, solution and in latex forms reacts with gaseous chlorine. Graft copolymers of chlorinated SBR with isobutylene have been prepared by photochemical addition of tertiary butoxy chloride as the first step. Chlorination is carried out in EPDM rubber to improve adhesion and cure characteristics. 30% bromine emulsified in water has been used to brominate lattices of styrene-butadiene acrylic acid terpolymer. Brominated polymers are reported to have faster cure rates and better adhesive characteristics than those of chlorinated counter parts. Halogenated butyl rubber is used commercially with the advantages of retaining desirable features of regular butyl rubber and increased compatibility with unsaturated rubbers like NR, SBR and NBR.

Chlorinated natural rubber is a noninflammable thermoplastic powder which has high ozone, weather and chemical resistance. It is mainly used in chemical and heat resistant paints and coatings to combat corrosive environment. Chlorinated rubber is dispersed in a suitable solvent with appropriate plasticised pigments. Such paints contain 10-20% chlorinated rubber and can be applied by brush or spray. It is used to protect wood, steel, cement, etc. from the environmental attack and has been recommended as traffic paints on roads.

1.1.1.c Hydrohalogenation

Elastomers can be modified with chloride, bromide, iodide or fluoride to give rubber hydrochloride, hydrobromide, hydroiodide or hydrofluoride, respectively. HCl addition is the cheapest and most feasible. The aim of the modification is the same as that of halogenation; reduce chemical reactivity of elastomers to oxygen and ozone by addition to the double bonds.[18] The structure of rubber hydrochloride has been established by Bunn and Garner.[19] They reported that the addition of HCl to polyisoprene obey Markownikov's rule.



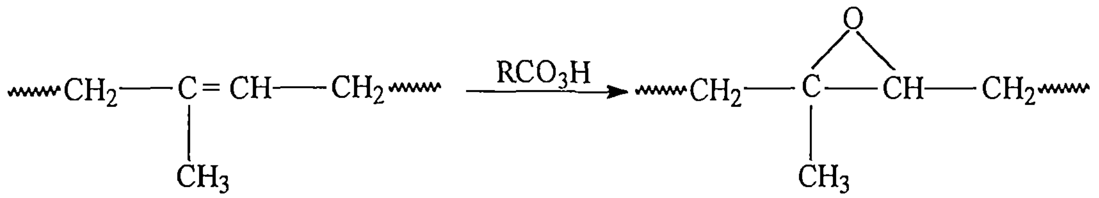
$$\sim CH_2-\underset{CH_3}{C}=CH-CH_2\sim + HCl \longrightarrow \sim CH_2-\underset{CH_3}{\overset{H}{C}}-\overset{Cl}{CH}-CH_2\sim$$

Hydrogen chloride adds readily to NR in the form of thin film solution or latex to give rubber hydrochlorides.[20] Polyisoprene with cis 1,4 and 3,4 structures reacts readily with HCl whereas 1,2 microstructure does not. Hydrochlorination of emulsion polyisoprene in benzene gives a product containing 14 -28% chlorine. The low chlorine content is possibly due to the segments with unreactive microstructure and a competing cyclisation reaction. For polyisoprene with micro structure of 79 % 3,4 polyisoprene, simultaneous hydrochlorination and cyclisation yield a product with a predominantly monocyclic structure. Cyclohydrochlorination proceeds through carbonium ion mechanism.

Hydrohalogenation of polybutadiene has been accomplished by phase transfer catalysis.[21] Hydrochlorination of 1,4-polyisoprene in chloroform yields soluble product that can be plasticised to give a tough flexible film useful in packaging.[22]

1.1.1.d Epoxidation

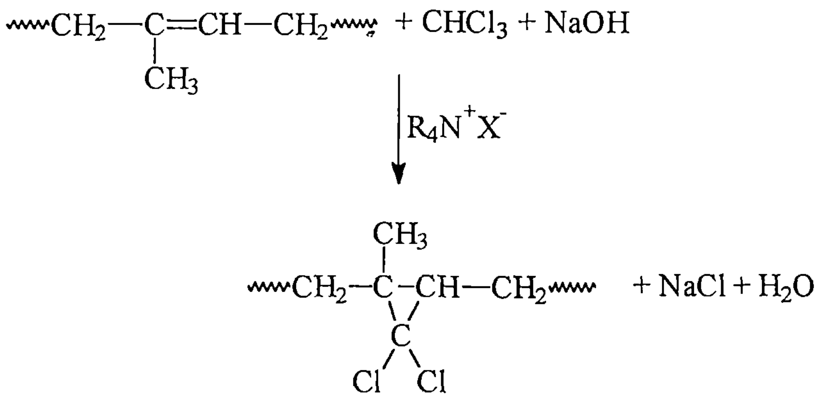
Epoxidation of NR and other unsaturated elastomers is of great interest and the reaction was first reported by Pumnerer and Burkard[23] and later developed by Rouse et al.[24] Epoxidation of polyisoprene gives structures containing oxirane rings. Organic acids, such as performic acid, perbenzoic acid, peracetic acid and monoperphthalic acid are used for epoxidation reaction.



Epoxidation of unsaturated elastomers bring about drastic changes in physical and mechanical properties.[25] Epoxidised NR is more damping and has improved solvent resistance, wet traction and gas retention as compared to NR in addition to excellent mechanical properties. It has oil resistance equivalent to that of nitrile rubber and low gas permeability near to that of butyl rubber. Epoxidation of 1,2-polybutadiene results in a material that has improved adhesive strength, heat stability and solvent resistance.[26] In turn, epoxidised EPDM has found use as a viscosity index improver in motor oils.[27]

1.1.1.e Carbene addition

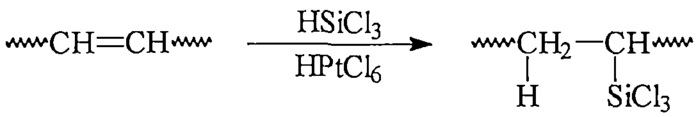
Carbenes (>C :) react readily with NR. Carbene addition is facilitated by the use of quaternary ammonium salts as phase-transfer catalysts. The latter compounds bring the aqueous reagents into contact with the organic phase containing polymer.[28,29] A dichlorocarbene derivative of natural rubber is prepared by use of phase transfer catalysts. The material with a chlorine content above 25% shows good flame retardent properties but poor thermal stability and processing behaviour. Treatment of cis polyisoprene in dilute aromatic solvent with dichlorocarbene (:CCl_2) prepared in-situ from ethyltrichloro acetate with sodium methylate, gives a white powder. The mechanism of the reaction is as shown below.



The double bonds are converted into gem- dichlorocyclopropane rings.[30] Similarly reaction of polyisoprene with dibromocarbene, formed in-situ from bromoform gives 70-75 % saturation of polymer double bonds. Carbene derived from the photolytic or thermal decompoisition of 3,5-di-ter-butylbenzene-1,4 diazooxide was used to introduce a polymer bound, hindered phenol antioxidant onto NR.[31]

1.1.1.f Hydrosilylation

Silyl groups have been introduced into unsaturated elastomers by (a) hydrosilylation (b) addition of vinyl silanes. Silane modified rubbers are of interest because such modified elastomers show improved adhesion to fillers[32] (metals, silicates, glass fibres) and better heat resistance[33] and serve as reactive substrates for grafting.[34]



$$\sim\sim\mathrm{CH{=}CH}\sim\sim \xrightarrow[\mathrm{HPtCl_6}]{\mathrm{HSiCl_3}} \sim\sim\underset{\mathrm{H}}{\mathrm{CH_2}}-\underset{\mathrm{SiCl_3}}{\mathrm{CH}}\sim\sim$$

1.1.1.g Sulphonation, carboxylation and phosphonylation

The introduction of ionic groups (e.g., COO^-, SO_3^-) in polymers results in enhanced physical and mechanical properties[35] and if the content of ionic group is high they become hydrophilic or water soluble. Sulfonation of block copolymers of styrene butadiene and styrene-isoprene are carried out with triethylphosphate-SO_3 and chlorosulphuric acid-diethyl ether.[36-38] $HSCH_2COOCH_3$ and $N_2CHCOOEt$ have been successfully used to attach carboxylate functionality onto the backbone of polypropylene. Polypentanamer has been phosphonylated by the free radical addition of dimethyl phosphite and their properties have been investigated.[39] Shazov et al.[40] reported the addition of PCl_3 to polybutadiene rubber through free radical mechanism.

1.1.1.h ENPCAF modification

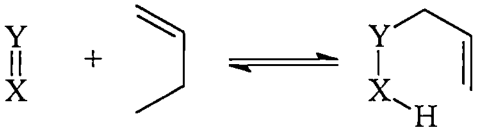
Ethyl N-phenylcarbamoylazoformate (ENPCAF) modified NR shows an indication of the influence of polar pendant groups on the physical properties of NR.[41,42] The ENPCAF modification can be carried out in an internal mixer or mixing mill at 110°C in dry rubber. This modification can also be carried out in latex stage. The modification reaction results in the formation of hydroester pendent groups. The modification reaction is accompanied by an increase in glass transition temperature (T_g) of the polymer, high damping properties and improved gas impermeability and solvent resistance.

1.1.1.i Maleic derivatives

Maleic anhydride has been found to be a useful compound for the modification of unsaturated polymers. Bacon and Farmer[43] showed that reaction between NR and maleic anhydride was accelerated by benzoyl peroxide. Infrared studies have indicated that on reaction of polyisoprene with maleic anhydride there is neither loss of any unsaturation nor any change in the cis trans ratio. It has been shown by Pinazzi et al.[44] that the reaction can be accelerated by a variety of catalysts such as azodiisobutyronitrile and chlorobromodimethyl-hydentoin as well as peroxides. The degree of addition (exprêssed as the number of maleic anhydride units added per 100 polyisoprene units) is usually less than 25. The tendency of the product to gel has been solved by the addition of amines like diethyl amine. Addition of maleic anhydride results in enhanced polarity for the unsaturated elastomers and the anhydride groups introduced can act as sites that can be converted into other functionalities. The reaction with maleic anhydride can be by a free radical or ene mechanism. In the presence of free radical initiators the reaction between NR and maleic anhydride occurs in solution at 70-80°C, to give succinic anhydride groups without the loss of unsaturation. At 200-250°C in absence of free radical, NR reacts with maleic anhydride to give a pendant maleic anhydride group in an ene reaction. Diels-Alder reaction of butyl rubber with maleic anhydride has also been described, which results in addition of 1-2 mol% succinic anhydride units.[45]

1.1.1.j Ene reaction

The ene reaction is a cycloaddition process involving a compound with a double bond (enophile) and olefine containing at least one allylic hydrogen (ene) as given below X and Y denote alkyl groups.



The mechanism of this reaction can be by free radical or concerted, depending on the presence and absence of free radical sources and also the reactivity of the reagents.

1.1.2 Grafting

1.1.2.a Grafting a polymer on the rubber molecule

Graft polymers are prepared by attaching one polymer as a branch to the chain of another polymer of different composition. This is usually accomplished by generating sites on the first polymer onto which monomer of the second polymer is grafted. The grafting may be carried out in bulk, solution or dispersion. Graft copolymers are prepared by polymerising monomers such as methyl methacrylate, styrene, acrylonitrile, maleic anhydride and acrylamide in presence of rubbers[46]. Grafting of different monomers impart improved properties to NR and the modified product is used in application such as substituent for high styrene resins in microcellular sheets for footwear etc.[47-49] Methyl methacrylate graft natural rubber is used as a stiffening agent and commercialised under to trade name Hevaplus MG. The most common commercial grafting reactions are of a thermoplastic polymer to produce impact-resistant thermoplastic of the ABS type. Methacrylate graft copolymers are commercially important. The graft copolymerisation of butadiene rubber with methyl methacrylate, acrylonitrile and styrene is carried out by dispersing polybutadiene rubber in a methyl methacrylate-acrylonitrile-styrene monomer mixture. These polymers are used in applications requiring a tough, transparent, highly impact resistant, thermally foamable material. Methyl methacrylate and styrene can be grafted to styrene butadiene rubber in an emulsion process which finds use as an impact modifier for rigid polyvinyl chloride.

1.1.3 Bond rearrangement reactions

1.1.3.a Cyclisation

Cyclisation, the first chemically modified derivative of NR, the oldest known modification of NR was reported by Bedford and Wilkinson.[50] Cyclisation results in the conversion of rubber to a hard resinous product. Cyclisation can be achieved by cationic, thermal, photolytic and radiation induced methods. NR or trans-1,4-polyisoprene undergoes cyclisation when treated at elevated temperatures with strong mineral acids (H_2SO_4), organic acids and their derivatives (p-toluenesulfonic acid and its chloride), Lewis acid ($SnCl_4$, $TiCl_4$, BF_3, $FeCl_3$) or other acidic catalyst. Cyclisation converts a long linear macro molecule into a much shorter polymer chain containing mono, di, tri,tetra and other polycyclic groups distributed randomly throughout the backbone and separated by unreacted isoprene units. Cyclised rubbers have been used in providing stiffness to diene rubber vulcanisates. It is a viable alternative for high styrene resins. A number of elastomers are blended with cyclised rubber for its use as stiffening agents in the absence of filler.

1.1.3.b Isomerisation

Cis-trans isomerisation of an unsaturated macromolecule was first achieved in 1957 when Goulb[51] reported that a high cis-1,4-polybutadiene was converted to a high trans-1,4-polybutadiene with a consequent increase in crystallinity. Isomerisation of NR takes place when thin films, sheets or crumbs are heated with SO_2 above 100°C. By isomerisation stereoregularity of NR is reduced, resulting in a reduced rate of low temperature crystallisation.[52] The tensile strength of NR decreases with progressive isomerisation. Isomerisation of elastomers can be achieved by thermal, photolytic, irradiative and catalytic methods.[53,54] Chemicals including selenium, NO_2, SO_2 and butadiene sulphone are effective isomerisation agents.

1.1.4 Other Modifications

1.1.4.a Depolymerisation

Synthetic rubbers have been offered in liquid or semiliquid form, liquid silicones and liquid butadiene rubbers have found wide acceptance amounting to 35,000 tonnes and 20,000 tonnes a year respectively in 1990. Synthetic rubber oligomers are readily prepared by controlling the degree of polymerisation during the production time (during polymerisation) from their respective monomer. NR is unique in its production from the plant as high molecular weight material and hence, depolymerisation techniques are adopted so as to convert it into the low molecular weight oligomers. However, the mechanical properties of liquid NR are inferior to those of its high molecular weight counterpart. Liquid or depolymerised natural rubber is prepared by the oxidative scission of natural rubber under controlled conditions. They find application as plasticisers, a binder in the manufacture of grinding wheels and bowling balls, a cement for brush bristles, in corrosion resistant paints, a sealant for pipe works and in the manufacture of printing rollers and battery boxes.[55,56]

1.2 Blending of elastomers

The progress in polymer blending is motivated by the realisation that new materials are not always required to meet specific requirements and that blending of two polymers can be carried out more rapidly and economically to achieve the requirement. Owing to the ease of preparation and achievement of easily controllable properties as per the need, the field of polymer blend has became very attractive. This method of simple mixing of selected polymers to achieve tailor made properties relieved the scientists from the costly development of new monomers and their polymerisation by various techniques. Normal methods for obtaining polymer blends are melt mixing, solution mixing, latex blending etc. In these cases, no chemical bonds exist between the component polymers forming the blend.

1.2.1 Reasons for blending

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

The producer related advantages are as follows.

- Better processability, more uniformity and less scrap rejection
- Better customer satisfaction
- Quick formulation changes, plant flexibility and high productivity
- Improved economy

1.2.2 Factors affecting properties of blend

A literature survey based on the past decade's research interests revealed that the properties of blends depend on so many factors such as

- Blend ratio[57-62]
- Properties of component polymers[63,64]
- Viscosity ratio of component polymers[65-67]
- Morphology[68-71]
- Compatibility or miscibility between polymers[72,73]
- Interaction between the components during melt blending

Unlike plastics since elastomers contain a large number of compounding ingredients the problems related to these materials have also to be taken care of. In particular factors affecting properties of elastomer blends are

- Interfacial adhesion/crosslinking
- Distribution of filler between elastomers
- Distribution of plasticiser between elastomers
- Distribution of crosslinks between elastomers

1.2.2.a Distribution of filler between elastomers

The distribution of filler particles between the separate phase of an elastomer blend is affected by a number of factors like unsaturation, viscosity, polariy, etc. Carbon black has a tendency to migrate to the more unsaturated polymers. Butadiene rubber has the greatest affinity for carbon black and the affinity of carbon black follows the order: BR > SBR > CR > NBR > NR > EPDM > IIR.[74]

1.2.2.b Distribution of plasticiser between elastomers

In the normal rubber vulcanisate the concentration of plasticizers is not very high and does not much affect the properties of blends. However, when substantial quantities of plasticizer must be used, the distribution of this ingredient can affect the properties of blends of rubbers.

1.2.2.c Distribution of soluble compounding ingredients

The factors affecting migration of compounding ingredients are, the differences in cure rate, solubility and diffusion for these ingredients by the components of the blend. Common accelerators and sulphur are more soluble in high unsaturated elastomers as compared to low unsaturated elastomers. Hence, the curatives migrate from the low unsaturated elastomer to the high unsaturated elastomer. This type of migration is accelerated by higher curative reaction rates in the higher diene elastomers. In blends of NR/NBR, polar accelerator like tetramethyl thiuram disulphide (TMTD) preferentially migrates to NBR phase. The practical consequence of the problem is that the blend components will either be uncured or overcured. This problem can be solved by selecting curatives that have almost the same rate of diffusion and crosslinking.

The possibility of uneven distribution of crosslink between the phases of a vulcanised 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 a low level of unsaturation, such as EPDM.

1.2.3 Thermodynamic criteria for miscibility

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

$$\Delta Gmix = \Delta H\ mix - T\ \Delta Smix \tag{1.1}$$

where ΔHmix, the change in enthalpy, ΔS mix, change in entropy and T, the absolute temperature. For miscibility ΔGmix must be negative and satisfy the additional requirement

$$\delta^2 (\Delta Gmix)/\delta(\phi_1)^2 > 0 \tag{1.2}$$

which ensures stability against phase segregation (P = pressure). The volume fraction ϕ_ι of component is employed here, but any other measure of mixture concentration could be used. The thermodynamic treatment of the phase behaviour, for mixtures becomes 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 and Huggins orginally for the treatment of polymer solutions.[75,76] It assumes that the only contribution to the entropy of mixing is combinatorial in origin and approximately by

$$\Delta S_{mix} = -R\ (V_A + VB)\ [\phi_A/V_A \ln \phi_A + \phi_B/V_B \ln \phi_B] \tag{1.3}$$

for mixing a volume V_A with volume V_B of polymer B. 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 M_i/ρ_i. For simplicity, each component is assumed to be monodisperse, as more complex expressions result when polydispersity is considered.[77] The Flory-Huggins treatment assumes the heat of mixing follows a van Laar-type relation.

$$\Delta H_{mix} = (V_A + V_B)\ B\ \phi_A\ \phi_B \tag{1.4}$$

where B is an interaction energy for mixing segmants of the two components and can be alternatively expressed as a χ parameter.[75] ΔH_{mix} does not depend on polymer molecular weight, whereas ΔS_{mix} 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 favour miscibility. Thus for mixing, the favourable 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 seperation occurs. On the other hand, for exothermic mixing, $B < 0$, the Flory-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.

1.2.4 Compatibilisation

Very few elastomer blends are so far reported to be truly miscible. In elastomer blends immscibility is the general observation and miscibility is only an exception. Compatibility of polymer blends is becoming a rapidly growing field since it provides a convenient procedure to change the mechanical, thermal or chemical properties of existing materials with out the expense of synthesis of new polymers. The dominance in the developments of compatibilised blends rather than synthesis of copolymers is an important development since it represents a conjunction of three favourable advantages of blends over new synthetic materials. These are: (i) Blends of materials at sufficiently small scale of dispersion have properties that are desirable but cannot be obtained otherwise. (ii) With the use of compatibilisers miscible blends of polymers can easily be prepared. (iii) Melt mixing has provided a reasonably economical path for the production of a wide variety of polymer blends.

The addition of an interfacial agent called compatibiliser[78] to immiscible blends is found to increase interfacial adhesion, provide stability of morphology against gross phase segregation and reduce the interfacial tension. Normally, block or graft polymers, functionalised polymers, and low molecular weight material are added as compatibilisers.[79] For these materials to function as compatibilisers, they must have segments identical to component polymers and must have specific interaction with them. Blends of high vinyl BR with natural rubber or cis-polyisoprene or SBR are some elastomer blends termed as homogeneous. The heterogeneity observed in elastomer blends is highly disadvantageous as it worsely affects the overall performance of resulting material.

1.2.4.a Techniques of compatibilisation

Several strategies of compatibilisation have been proposed: (1) addition of a small quantity of a third component that is miscible with both phases (cosolvent) or the addition of a third component which has an ability to interact with blend components, (block and graft copolymers and low molecular weight polymers) (2) reactive compatibilsation by compounding blends in presence of chemical reactants that leads to the modification of one of the components,resulting in the formation of an in-situ compatibiliser (3) mechanochemical blending that may lead chain break up and recombination, thus generation of copolymer.

1.2.4.b Use of block or graft copolymer

Block or graft copolymers which act as compatibilisers are of two types, reactive and nonreactive. In reactive copolymers, segments form strong covalent or ionic bonds with blend components. Non-reactive ones have segments capable of specific interaction with each of the blend components. Copolymers of both A-B type and A-C type can act as efficient compatibilisers in A/B system provided C is miscible with B. Tables 1.1 and 1.2 illustrate the polymer system that is compatibilised through reactive and non-reactive copolymers, respectively.

Table 1.1. Compatibility through reactive copolymers

Major Component	Minor Component	Compatibiliser
PP or PE	PET	PP-g-AA,
PE	PA-6 or PA-6,6	Ionomers, carboxyl functional PE's
PA-6	Acrylate rubber	EPM-g-MA
ABS	PA-6/PA-6,6 copolymer	SAN/MA copolymer
PP or PS-6	PA-6 or PP	EPM/MA copolymer

Table 1.2. Compatibility through nonreactive copolymers

Major Component	Minor Component	Compatibiliser
PS	PA-6 or EPDM	PS/PA-6 block copolymer or S-EB-S or PPE
PE or PP	PP or PE	EPM, EPDM
PP	PS or PMMA	S-EB-S
PF	PS/PMMA	PF-g-MMA or PF-g-S
PVC	PP or PE or PS	PCL/PS block copolymer or CFE
PVDF	PPE or PS	PS/PMMA block copolymer
EPDM	PMMA	EPDM-g-MMA
SAN	SBR	BR/PMMA block copolymer
PE or PS	PS or PE	S-B, S-EP,S-I-S,S-I-HDB, S-EB-S, , PS/PE graft copolymer
PEt	HDPE	S-EB-S

Certain low molecular weight materials can act as compatibilisers in many polymer blends as given in Table 1.3.

Table 1.3. Role of low molecular weight reactive compounds for compatibilisation

Major Component	Minor Component	Compatibiliser
NR	PA-6 or polyolefins	Peroxide and or polyfunctional monomers
PVC or PP	PP or PVC	Chlorinated paraffine
Fluoro rubber FPM	NBR or CHR	Triazine dithiol complex
PBT	EPDM-g-MA or MBS or NBR	Oligomers or epoxy silanes or polyfunctional epoxies.
PPE	PA-6,6	Aminosilane
PVC or LDPE	LDPE or PVC	Polyfunctional monomers plus peroxide
NBR	PP	NBR curative and interchain copolymer

1.2.4.c Compatibilisation by in-situ reaction

The compounding, mastication or polymerisation of one polymer in the presence of another leads to the formation of copolymers *in situ* that act as very good compatibilisers in many blends. The in-situ formation of compatibilisers employing functionalised polymers form the subject of several studies.[80] The functionalisation can be done in a compounding extruder which can bring about reactions such as halogenation, sulphonation, hydroperoxide formation and in-situ formation of block and graft polymers. Formation of maleic anhydride grafted PP in PP/PA-6 blend was reported by Ide and Hasegawa[81] Blending of polystyrene and polyethylene leads to the formation of styrene/ethylene graft copolymers.[82] Functionally active rubber on blending and vulcanisation from miscible blend, due to reduction with functional groups.[83]

1.2.4.d Compatibilisation by block and graft copolymers- basic features

The structure of the block or graft copolymer affects the compatibilisation efficiency. A diblock copolymer is much more effective than a triblock and among diblock systems itself, tapered diblock are more efficient[84] as they do not form domains of their own resulting in domains of segregated sequences. Therefore they will have a low viscosity and hence can be easily dispersed among the blend components. Block copolymers of equal segmental mass are more effective than those of unequal segmental mass. As far as graft copolymers are concerned, multiple branches should be avoided as they restrict penetration of backbone in to homopolymer phases.

Another factor is the chemical identity of the copolymer segment with the homopolymer phase. But even if there is no chemical identity, still the compatibilisation can be effective if the segments are miscible with homopolymer. Also the copolymer should have the property to disperse in the two phases and the copolymer should not be miscible as a whole in one of the homopolymer phases.

The amount of copolymer (m) to be added into a binary polymer blend depends on several factors and is given by[85]

$$m = 3\,\phi_A\, M/a\,RN \qquad (1.5)$$

where ϕ_A be the volume fraction of the polymer A, R is the radius of the dispersed particle A in a matrix B, N is the Avagadro's number, a is the area occupied by the copolymer and M is the molecular weight of the copolymer. For a copolymer to be effective, its molecular weight should be higher than the molecular weight of the homopolymers. The effect of molecular weight of the copolymer on the solubilisation was studied by Reiss and Jolivet.[86] When the homopolymer molecular weight is larger than that of the corresponding block segments, homopolymer form a separate phase and is not solubilised into the domains of block copolymer. In the case of high molecular weight copolymers, the long segments are able to anchor the immiscible phases firmly.

1.2.4.e Theories of compatibilisation

The actual function of a compatibiliser is to reduce the interfacial tension leading to a fine and uniform morphology of dispersed particles. The theory of Noolandi and Hong[87,88] is based on the reduction in interfacial tension in highly incompatible blends by the treatment of thermodynamic factors determining the state of block copolymers in the blend. According to the theory, the random distribution of copolymers is controlled by the entropy of mixing of the block copolymers with homopolymers. The preferential location of the block copolymers at the interface separates the homopolymers away from each other and this lowers the enthalpy of mixing of the homopolymer. Each block of the copolymer extends its chain to its compatibile homopolymer. This restriction of the blocks of the copolymer in the respective homopolymer and the preferential location of the copolymer at the interface increases the entropy.

Interfacial tension was found to be decreasing with increasing molecular weight since at highest molecular weight the interface is almost saturated with the homopolymer displaced away from the interface. The equation derived by Noolandi and Hong for the reduction in interfacial tension with increasing copolymer molecular weight and concentration, in the presence of a solvent is

$$\Delta\gamma = d\,\phi_c\,[(\tfrac{1}{2}\chi + 1/Z_c) - 1/Z_c \exp Z_c\chi/2] \qquad (1.6)$$

where d is the width at half height of the copolymer profile given by Kuhen statistical segment length, ϕ_c in the system is the bulk volume fraction of the polymer, χ is the Florry-Huggins interaction parameter between A and B segments of the copolymer and Zc is the degree of polymerisation of the copolymer. In the absence of a solvent the total polymer volume fraction ϕ_p goes to 1 and the equation for $\Delta\gamma$ reduces to

$$\Delta\gamma = \delta\phi_c \, ½\chi + 1/Z_c - 1/Z_c \exp(Z_c\chi/2) \qquad (1.7)$$

The above equation is not valid at copolymer concentrations higher than the critical micelle concentration (CMC) as at this concentration the copolymer forms miscelles in the bulk phase rather than locating at the interface as assumed by the theory. The testfication of the theory was done by Anastasiadis[89,90] by taking the PS/1,2-polybutadiene/poly(styrene-block-1,2-butadiene) system. The result showed a sharp decrease in interfacial tension with lower copolymer loadings with a levelling off at higher loadings resulting from interfacial saturation. On comparing the data with Noolandi's theory indicates that $\Delta\gamma$ varies linearly with copolymer concentration below CMC as predicted by Noolandi

The theory by Leibler[91,92] is a simple mean field formalisation for the interfacial properties of nearly compatible blend A/B compatibilised with A-B block copolymer. The addition of copolymers in nearly compatible blend first displaces the critical point of demixing and can some times convert a two phase system to a single phase system. The copolymer chains which are present in both phases favour a close mixing of the chemical species A and B. According to Leibler, for nearly compatible species, $[2 < \chi N < 4(2)^{1/2}]$, two mechanisms of interfacial activity of the copolymer chains are to be distinguished.

(1) The species A and B are closely mixed as copolymer chains are present in both the phases.

(2) Copolymers will have a certain tendency for interfacial location.

The interfacial tension γ can be expressed as

$$\gamma = \gamma_o - \gamma_I \tag{1.8}$$

Here γ_o represents the interfacial energy increase due to the first mechanism and γ_i the decrease in interfacial tension due to second mechanism.

With an interface with surface area (A), the interfacial thickness (D) and interfacial tension (γ_0 are given by

$$D = \frac{a}{\sqrt{6\chi}} \tag{1.9}$$

$$\gamma_0 = [KT/a^2] \sqrt{\chi/6} \tag{1.10}$$

where χ is the interaction parameter and a is the monomer length. Leibler discussed the formation of thermodynamically stable droplet phase in which one of the homopolymers is solubilised and potected by interfacial film. In order to get such a system, the copolymer should be symmetric and the condition for a symmetric copolymer is :

$$V^3{}_A/R_{GA}{}^2 = V^3{}_B / R_{GB}{}^2 \tag{1.11}$$

where V_A and V_B are the molar volumes, and R_{GA} and R_{GB} are the radius of gyration of A and B blocks, respectively.

1.2.5 Characterisation of the compatibilised blends

There are a large number of methods for studying the miscibility of polymer blends.[93-97] These include optical appearance, glass transition temperature, microscopy, small angle X- ray scattering, etc.

1.2.6 Compatibilisation studies on rubber-rubber blends

Blends of incompatible elastomers have been improved by the addition of small amounts of another elastomer. The presence of block or graft copolymers can also alleviate blending of incompatible elastomers, they can alter interfacial properties.[98] The block or graft component should contain a segment which is chemically identical to one of those in the respective phases, but the desired effect may still be achieved if one polymer of the graft is miscible with, or adhered to, one of the phases. The interfacial tension between the phases is lowered by this interfacial activity, and this plays an important role in blend morphology, reducing the phase sizes and also improving the physical properties and crosslink density distribution between the phases of the blend. Setua and White[99] used this techniques to increase the homogeneity of binary and ternary blends of CR, NBR and EPM. Chlorinated polyethylene acts as a compatibilising agent in NBR/EPM or CR/ EPDM blends.[100] Chloroprene rubber (CR) acts as a compatibiliser in NR/NBR blends.[101] CR has a solubility parameter intermediate between those of NR and NBR. Furthermore, the presence dipole within the repeat unit allows the possibility of dipolar interaction with the acrylonitrile repeat unit of NBR.

1.3 Scope of the present work

SBR finds extensive application in tyre treads, camelback, cycle tyres, roll covers, drive and conveyor belts, hoses, vibration mountings, shock absorbers, microcellular soles ebonite's, other hard rubber products, highly loaded goods and in production of any light coloured rubber product requiring stiffness or hardness combined with good physical properties. Compared to NR it has more resistance to heat and lower gas permeability. However, it has poor gum strength and poor resistance against thermooxidative degradation.

Many attempts have been carried out to increase the green strength of SBR by chemical modification. Green strength which is a cohesiveness in stretched uncured rubber compound is of great importance especially in the processing of tyres. For example, in the construction of radial tyres uncured stocks may be subjected to deformation of up to three times the original dimensions in the forming step. Carboxylation of emulsion SBR by copolymerisation with carboxylic acids (acrylic and methacrylic) results in products that have improved green strength. Carboxylated SBRs have better adhesion to fabrics and hence used in carpet backing application. Styrene-vinyl pyridine-butadiene terpolymer lattices have been developed principally for application as rubber-to-textile adhesives in particular as tyre cord adhesives. Copolymerisation of styrene and butadiene with tertiary amine containing monomers followed by reaction with dihalides to form a small number of labile (shear and temperature sensitive) crosslinks, also result in SBR with enhanced green strength.

Resistance to thermo-oxidative degradation is an important criteria to be satisfied for rubber products used in outdoor applications. It is well known that the degradation of rubber is due to its reaction with molecular oxygen. This reaction can be suppressed by reducing the double bonds, or by introduction of groups that can deactivate the double bonds. The introduction of polar groups also bring about enhancement in resistance to solvents.

Dichlorocarbene addition to double bond is an attempt to modify elastomers which attracted much attention earlier. Dichlorocarbene modification has been carried out on both NR and BR. However, the products of dichlorocarbene modification have not so far found any good commercial application.

By dichlorocarbene modification, it is possible to have reduction in double bonds in the main chain, introduce polar functional groups, which can deactivate the double bonds, and also bring about polarity in the molecule as a whole, resulting in increased resistance to fuels and oils and also flame retardency. Dichlorocarbene modified styrene butadiene rubber, with its unique combination of properties could find application either alone, or in blends with other rubbers like NR or as a compatibiliser in blends of SBR with other polar rubbers like NBR and CR in the production of useful rubber products.

Hence dichlorocarbene modification is carried out on SBR, so as to improve the ageing, fuel, oil and fire resistance while maintaining its comparatively good mechanical properties. The effect of various reinforcing fillers on the modified rubber to improve the mechanical properties.

Three types of blends are addressed here, each recognising the needs of particular types of application.

- Blend of NR and DCSBR intended to produce vulcanisates for applications requiring a combination of good resistance to attack by ozone, better resistance to swelling by oils, heat resistance and good strength properties.

- Blends of SBR and NBR used for applications requiring a measure of resistance to swelling by oils or damping with good physical properties.
- Blends of SBR and CR used for application requiring moderate resistance to ozone, oxygen or high temperature combined with good physical properties.

However, the blends of SBR/NBR, SBR/CR are immiscible. Detailed investigations have revealed that compatibilisation of these blends are essential to alleviate the problems due to immiscibility. These blends can possibly be made miscible by using DCSBR as compatibiliser, due to the presence of chlorine within the repeat unit of DCSBR, there is a possibility of dipolar interaction with dipole units of NBR and CR. In this thesis, a detailed work has been carried out to study the preparation characterisation and evaluation of properties of dichlorocarbene modified styrene butadiene rubber and also to analyse the influence of the modified polymer (DCSBR) on the compatibilisation of SBR/NBR and SBR/CR blends. Role of SBR as a compatibiliser in novel blends of NR and DCSBR has been also investigated.

The thesis divided into nine chapters. The first chapter is introduction and the second chapter deals with the materials used and the experimental techniques followed throughout the course of the study. The third chapter contains the results of preparation and characterisation of dichlorocarbene modified styrene-butadiene rubber. The fourth chapter discusses the vulcanisation behaviour, technological properties and effect of different fillers on dichlorocarbene modified SBR. The fifth chapter focuses on the blends of natural rubber and dichlorocarbene modified styrene butadiene rubber blends. The sixth chapter contains compatibilization of SBR/NBR blends with dichlorocarbene modified styrene butadiene rubber. The seventh chapter discusses the effect of different fillers on compatibilised and uncompatibilised

SBR/NBR blends. The eighth chapter deals with the effect of dichlorocarbene modified styrene butadiene rubber in compatibilisation of styrene butadiene rubber and chloroprene rubber blends. The ninth chapter presents the conclusion.

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CHAPTER

2

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials

2.1.1 Styrene butadiene rubber (SBR)

Styrene butadiene rubber (Synaprene 1502) was obtained from Synthetics and Chemicals Ltd., Bareilly, U. P., India. The basic characteristics of SBR are given in Table 2.1.

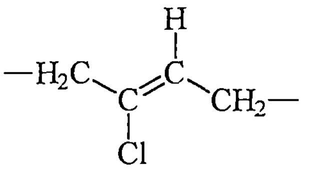
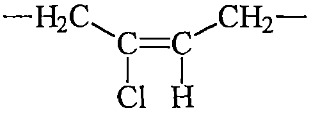
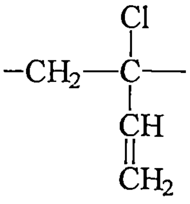
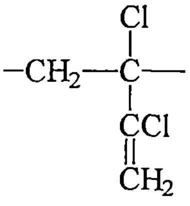
Table 2.1. Basic characteristics of SBR

	Percentage
Styrene	21.5-25.5
Volatile matter	0.75
Soap	0.70
Ash	0.5
Antioxidant	0.5-1.5
Cis-1,4	18
Trans-1,4	65
1,2(vinyl)	17

2.1.2 Polychloroprene rubber (CR)

Neoprene (**W** type) was obtained from DuPont de Nemours and Company. The structural units in the neoprene polymer chain are in Table 2.2.

Table 2.2. Structural changes in the neoprene polymer chain

Type of addition	Formula	Approximate per cent
Tran-1,4	 $-H_2C-C(Cl)=C(H)-CH_2-$	85
Cis-1,4	 $-H_2C-C(Cl)=C(H)-CH_2-$	10
1,2	 $-CH_2-C(Cl)(CH{=}CH_2)-$	1.5
3,4	 $-CH_2-C(Cl)(CCl{=}CH_2)-$	1.0

2.1.3 *Nitrile rubber (NBR)*

Butadiene acrylonitrile copolymer of medium acrylonitrile content, Chemaprene N-3309 supplied by Synthetics and Chemicals Ltd., Bareilly, U.P., India. The detailed specifications of this rubber are given in Table 2.3.

Table 2.3. Specification of nitrile rubber

Volatile matter (% max)	0.75
Ash (% max)	1.0
Antioxidants (%)	1.0
Bound acrylonitrile content (%)	31-35
Mooney viscosity $M_{L(1+4)}$ at 100°C	40-60
Soap (%)	0.05

2.1.4 Natural rubber (NR)

Natural rubber (ISNR 5, Indian Standard Natural Rubber-5) was obtained from Rubber Research Institute of India, Kottayam, Kerala, India. The specification parameters for ISNR-5 grade natural rubber is given in Table 2.4.

Table 2.4. Specification of ISNR-5 grade NR

Parameters	%/Mass
Dirt content	0.5
Volatile matter	0.5
Nitrogen	0.3
Ash	0.4
Initial Plasticity P_0	38
Plasticity Retention Index PRI	78

2.1.5 Solvents

Toluene, chloroform, isopropyl alcohol, n-heptane were of reagent grade and supplied by Merck India Ltd., Mumbai.

2.1.6 Chemicals and fillers

Cetyl trimethyl ammonium bromide was obtained from E-Merk India Ltd., Mumbai. All the chemicals used for the preparation of rubber compounds were of industrial purity, sodium hydroxide, dicumyl peroxide (40% active), zinc oxide, stearic acid, N-cyclohexyl-2-benzothiazyl sulphenamide, ethylene thiourea, tetramethyl thiuram disulphide, 2,2,4-trimethyl 1,2-dihydroquinoline and sulphur were supplied by Bayer (India) Ltd., Mumbai.

Fillers

HAF: High abrasion furnace black (N220) was obtained from Philips Carbon Black Ltd., Durgapur.

Silica: Precipitated silica was supplied by Bayer (India) Ltd., Mumbai.

2.2 Preparation of dichlorocarbene modified styrene butadiene rubber (DCSBR)

Addition of dichlorocarbene to SBR was carried out by the alkaline hydrolysis of $CHCl_3$ using phase transfer catalyst, according to the method by Makosza[1] and later developed by Joshi.[2] SBR was dissolved in toluene, the phase transfer catalyst was added to this and the mixture was stirred. To this, $CHCl_3$ was added drop wise followed by NaOH solution (50%). The reaction product was separated from the solution and washed with hot water and cold water, until free of chlorine. The product was coagulated with isopropyl alcohol and reprecipitated from toluene solution. The modification was monitored by the determination of chlorine percentage at different times using the method of chemical analysis.

2.3 Estimation of chlorine content of the polymer

About 2 g of rubber is accurately weighed and embedded in about 2 g of fusion mixture prepared by mixing equal proposition of sodium carbonate and potassium carbonate in a platinum crucible. The contents of the crucible are fused at 900°C in a muffle furnace. The fused material is extracted in about 100 ml of distilled water and acidified with concentrated HNO_3 till liberation of carbon dioxide stop and the solution is neutral. About 5 ml more of concentrated HNO_3 is added and the solution is boiled. 40 ml of standard silver nitrate is added to the hot solution. After precipitation of the chloride, the solution is filtered and washed down with distilled water. The filtered solution is titrated with standard ammonium thiocyanate using ferric alum as indicator, to estimate the unreacted silver nitrate. The end point is the formation of a faint red colour. A blank determination is also carried out simultaneously.

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

where B is the volume of NH_4CNS required for the blanks,

V is the volume of NH_4CNS required for the sample, and

W is the weight of sample.

2.4 Preparation of elastomers and elastomer 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 D3182-74 by careful control of temperature, nip gap, time of mixing and by uniform cutting operation.[3] The compounding ingredients were added in the following order after mastication of rubber, ZnO, stearic acid, antioxidant, filler, plasticiser and finally curatives.

2.4.a NR/DCSBR blends

Separate master batches of NR and DCSBR were prepared with all compounding ingredients without accelerator and sulphur. The master batches were blended at 70/30, 50/50 and 30/70 compositions and finalised with curatives on a two roll mixing mill. The compatibilised blends were prepared by adding the required concentration of compatibiliser to the blended master batches, before the addition of curatives.

DCSBR was vulcanised at 150°C in a hydraulic press by either sulphur vulcanisation system or peroxide vulcanising system.

2.4.b SBR/NBR blends

Master batches of SBR, NBR (without accelerator and sulphur) were prepared separately and then blended at different compositions of 70/30, 50/50 and 30/70. DCSBR, used as the compatibiliser with varying chlorine content from 15 to 35% was added to the preblended SBR/NBR blends at a constant dosage of 5 phr and compatibiliser having 25% chlorine content was added at various concentration of 1-10 phr. The required quantity of curatives were then added and mixed properly with the pre-blended mixes. The effect of loading of fillers such as carbon black and silica (10-40 phr) on 50/50 blend compatibilised by 5 phr DCSBR containing 25% chlorine are prepared. The effect of loading of carbon black and silica on SBR/NBR blend with different composition (70/30, 50/50, 30/70) in the presence (5 phr compatibiliser) and absence of DCSBR were carried out in a two roll mixing mill. In the case of filled mixes the fillers such as carbon black and silica were added after blending the rubbers. The curatives were added after addition of fillers.

2.4.c *SBR/CR blends*

Master batches of SBR and CR (without accelerator and sulphur) and were prepared separately and then blended at different compositions (70/30, 50/50 and 30/70). The compatibiliser (DCSBR) with varying chlorine content from 15 to 35% were added to the preblended SBR/CR at a constant dosage of 5 phr and DCSBR having 25% chlorine content was added at various dosage of 1-10 phr on 50/50 preblend compositions. The effect of loading of fillers such as carbon black and precipitated silica (10-40 phr) on 50/50 blend compatibilised by 5 phr DCSBR containing 25% chlorine. The effect of loading of carbon black and precipitated silica of 50/50 SBR/NBR blend in the presence (5 phr) and absence of DCSBR.

2.5 Processing characteristics

2.5.1 *Monsanto rheometer*

The cure characteristics were determined using a Monsanto rheometric model R-100. Optimum cure time (t_{90}) is the time for the development of 90% of maximum rheometric torque. It is calculated using the equation,

$$t_{90} = 90\,\frac{(\mathrm{Mh} - \mathrm{Mn})}{100} + \mathrm{Mn}$$

where Mh and Mn are the maximum and minimum rheometric torque respectively.

Rheometric scorch time is the time required for the torque value to increase by two units above the minimum torque at 150°C, denoted as t_2. Rheometric induction time (time required for the torque value to increase by one unit above the minimum torque at 150°C) denoted as t_1.

2.6 Preparation of vulcanised samples

Samples were cured to the optimum cure time in a hydraulic press using a pressure of 300 kg/cm^2. The samples were immediately cooled after removed from the mould.

2.7 Characterisation studies

2.7.1 ^{1}H FTNMR studies

SBR and modified SBR was dissolved in a proton-free solvent such as CCl_4 or $DCCl_3$ (Although deuterium is NMR active, it does not interfere because it does not absorb in the frequency range set in instrument for ^{1}H). If a more polar solvent is needed, dry $(CD_3)_2S{=}O$ (perdeuterodimethyl sulfoxide) issued. The solution is placed in a long thin glass tube which is spun in the magnetic field so that all the molecules are exposed to a uniform magnetic field. A small amount of a reference compound, tetramethyl silane $(CH_3)_2S_1$ is added to the sample. The spectrum is taken with a 90 MHz JEOL EX90 FTNMR and when the H_0 value is reached-enabling the proton to be in resonance at the resonance at the set frequency, a signal (peak) is traced on a calibrated chart paper that plots transmittance vs. H_0.

2.7.2 FTIR

IR spectra of samples were recorded with a Shimadzu-8101 M Fourier transform infrared spectrophotometer, using thin films and pyrolysate of polymer. The thin film was prepared by dissolving the polymer in chloroform and then the concentrated solution (5%) was directly caste on a levelled glass plate.[4] The light source (an electrically heated solid, e.g., 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 and the other may be used as a reference beam when a solution is to be analysed. A slowly rotating diffraction grating or prism varies the wavelength of radiation reaching the sample and then 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.

2.7.3 Gel permeation chromatography

Molecular weight determination was carried out by a Waters 510 gel permeation chromatography (GPC) instrument attached to a 410 diffraction refractometer. HPLC-grade toluene was used as a solvent with a flow rate set to 1 ml/min. The GPC columns were calibrated with polystyrene standards.

2.8 Thermal analysis

Thermal analysis was carried out using a differential scanning calorimeter (DSC) and a thermogravimetric analyser (TGA) and dynamic mechanical analysis (DMA).

2.8.1 Differential scanning calorimeter

Direct calorimetric measurements, characterisation and analysis of thermal properties of the sample were made using a Perkin Elmer 7 series differential scanning calorimeter. Sub-ambient operation was carried out by cooling the specimen and the specimen holder with liquid nitrogen. Exactly weighed (about 5 mg) of sample was used for the studies. Samples were encapsulated in standard aluminium pans and covers and sealed by crimping. For purging the sample holders pure dry 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 15°C/min.

2.8.2 Thermogravimetry

A Perkin Elmer make thermogravimetric analyser was used for the studies. It is a computer controlled instrument that permits the measurement of weight changes 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 instrument supplied by Perkin Elmer had two components, an ultrasensitive micro balance and a furnace element. The balance is sensitive to 0.1 microgram and the furnace could be heated from ambient to 1000°C at rates of 0.1 to 200°C per min. 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.

2.8.3 Dynamic mechanical thermal analysis

The dynamic mechanical properties of the blends were measured using a dynamic mechanical analyser (Polymer Laboratories DMTA MK-II), consist of a temperature programmer and a controller. It measures dynamic moduli (both storage and loss) and damping of the specimen under oscillatory load as a function of temperature. The experiment was conducted at a dynamic strain of 4% at a frequency of 0.1 Hz. Liquid nitrogen was used to achieve subambient temperature and a programmed heating rate of 1°C min^{-1} was used. Mechanical loss factor tan δ and the dynamic moduli (E′ and E″) were calculated with a microcomputer. Samples of dimension 70 × 10 × 2.5 mm were prepared for testing.

2.9 Flammability behaviour

2.9.1 Limiting oxygen index

The above test was carried out using a Limiting Oxygen Index (LOI) apparatus manufactured by Appireillage Industrial Scientific Company, France.[5] Both oxygen and nitrogen were connected to the equipment through pressure regulators (about 2 bars). The flow of gases was regulated at 17 litres per minute by adjusting the flow speed to 4 cm per minute on the glass tube.

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

A concentration of oxygen in the mixture was selected and the flow valves were adjusted so as to read the oxygen concentration. The test chamber was purged with the mixture for 30 seconds and the specimen was ignited with the ignition flame so that it was well lit and the entire top was burning. Subsequent trials were carried out with new specimens with varying concentration of oxygen. The level of oxygen flow was adjusted to the minimum at which the specimen burned for 3 minutes or more than 30 mm length, whichever is earlier. The test specimen was changed after each trial and the test continued until reaching the minimum oxygen concentration with a precision of at least 0.2%.

2.10 Scanning electron microscopy studies

The scanning electron microscopy (SEM) photomicrographs given in this work were obtained using JEOL 35C model scanning electron microscope. The fracture surfaces were carefully cut from the failed test specimens without touching the surface and were sputter-coated with gold within 24 h. of testing. The SEM observations were made within 24 h of gold coating. The fractured test specimens and the gold coated samples were stored in a desiccator till the SEM observations were made. There should not be any change in the fracture pattern when the SEM observations were made one month after gold coating.[6]

2.11 Crosslink density determination

2.11.a From mechanical measurements

The extent of physical crosslinks in an elastomer vulcanisate can be understood by the use of Mooney-Rivlin equation.[7]

$$F = 2A_0(\lambda-\lambda^{-1})\,(C_1 + \lambda^{-2}\,C_2) \qquad (2.1)$$

where F is the extension force required to stretch a piece of rubber vulcanisate of cross-section area A_0, to an extension ratio λ. A plot of $F/2A_0\,(\lambda-\lambda^{-1})$ Vs λ^{-1} gives a straight line whose λ intercept C, is directly related to the physically effective crosslink density (ν_{phys}) by the equation,

$$C_1 = \rho RT\,\nu_{phys} \qquad (2.2)$$

2.11.b From solvent swelling

The crosslink density of the samples was determined by the swelling method. The samples were allowed to swell in toluene and the equilibrium uptake is noted. The molecular weight between crosslinks M_c is calculated using Flory-Rehner equation.[8]

$$\frac{1}{2M_c} = \left[\frac{\rho_r V_s (V_r)^{1/3}}{\ln(1-V_r)+V_r+\chi^2 V_r^2}\right] \tag{2.3}$$

where M_c = molecular weight of polymer between two crosslinks

ρ_r = density of polymer

V_s = molar volume of solvent

V_r = volume fraction of polymer in swollen mass is calculated by the method of Ellis and Welding[9] is given by

$$V_r = \frac{(d-fw)\rho_r^{-1}}{(d-fw)\rho_r^{-1}+A_s\rho_s^{-1}} \tag{2.4}$$

where A_s = amount of solvent absorbed

ρ_r = density of rubber

ρ_s = density of solvent

d = deswollen weight of the sample

f_w = fraction of insoluble components

χ = interaction parameter which is given by Hildebrand[10] equation as

$$\chi = \beta + \frac{V_s}{RT}(\delta_s-\delta_p)^2 \tag{2.5}$$

where β = lattice constant; V_s = molar volume; R = universal gas constant; T = absolute temperature; δ_s = solubility parameter of solvent; δ_p = solubility parameter of polymer.

From molecular weight between crosslinks M_c, the crosslink density ν was calculated using the following equation.

$$\nu = 1/2M_c \tag{2.6}$$

2.12 Physical test methods

2.12.1 Modulus, tensile strength and elongation at break

These three parameters were determined according to ASTM D412-92,[11] using dumbbell specimens. The test specimens were punched out from moulded sheets using the C-type die, along the mill grain direction. The thickness of the specimen within the gauge length of the test specimen was measured using a dial gauge of accuracy 0.001 mm. The specimens were tested on a Zwick Universal Testing Machine (UTM) model 1474 at ambient temperature and at a crosshead speed of 500 mm per minute. The elongation at break, modulus and tensile strength were obtained as a print out.

2.12.2 Tear resistance

Tear resistance of the samples was tested as per ASTM-D-624-81,[12] using unnicked 90°C angle test specimens that were punched out from moulded sheets, along the mill grain direction. This test was also carried out on a Zwick UTM, at a crosshead speed of 500 mm per minute. The tear strength was reported in kN/m.

2.12.3 Hardness

Hardness of the samples was measured according to ASTM D-2240-81[13] 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.

2.12.4 Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader according to DIN No. 5351 test method. Circular sample having a diameter of 6 ± 0.2 mm and a thickness of 6-10 mm was kept on a rotating sample holder and 10 N load was applied. Initially a 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.

DIN abrasion loss of specimens in mm^3

$$= \text{DIN abrasion loss} \times \text{abrasion index of standard specimen} \quad (2.7)$$

where

Abrasion index of standard specimen

$$= \frac{200}{\text{Loss of weight in gm for the standard specimen} \times 1000} \quad (2.8)$$

$$\text{DIN abrasion loss} = \text{Loss of weight in gm of the rubber vulcanizate} \times 1000/\text{specific gravity of specimen} \quad (2.9)$$

2.12.5 Compression set

The compression set was measured according to ASTM D 395-71 (Method B). The samples (1.25 cm thickness and 2.8 cm diameter) in duplicate, compressed to give 25% deflection, were kept in an air oven at 70°C for 22 h. After the heating period, the compression was released, the samples were cooled to room temperature for half an hour and final thickness was measured. Compression set was calculated using the equation,

$$\text{Compression set } (\%) = \frac{t_0 - t_f}{t_0 - t_s} \times 100 \quad (2.10)$$

where t_0 and t_f are the initial and final thickness of the specimen, respectively and t_s, the thickness of the spacer bar used.

2.12.6 Rebound resilience

The rebound resilience of the composites was measured using Dunlop Tripsometer (BS 903, Part 22, 1950). The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as

$$\text{Rebound resilience (\%)} = \frac{1-\text{Cos}\theta_2}{1-\text{Cos}\theta_1} \text{ x } 100 \qquad (2.11)$$

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

2.13 Degradation studies

2.13.1 Ozone cracking

The ozone test chamber manufactured by MAST Development Company, USA, was used to study ozone cracking. The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration used as 50 ppm which is generated by a UV quartz lamp. The test was carried out as per ASTM D-1149-81 specification. The test was conducted at 38.5°C. Ozone determination was evaluated by determining to amount of cracks obtained in the specimen after exposure to ozone for a definite period.

2.13.2 Thermal ageing

Test samples (2 ± 0.2 mm thick) were aged at 70°C for 96 h in an ageing oven. The tensile strength, elongation at break were measured before and after ageing. The percentage retention of properties after ageing was calculated.

2.13.3 Oil ageing

Oil ageing was carried out by immersing the test specimen about 2 cm × 1 cm in ASTM oils 1, 2 and 3. The weight of oil uptake was evaluated by measuring the swollen weight of samples after a specific time. The swollen samples were immersed in acetone wiped with filter paper, and transferred to weighed bottle and the final weight of the sample were taken.

$$\text{Weight of oil absorbed} = \frac{M_2}{M_1} \times 100 \qquad (2.12)$$

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CHAPTER

3

PREPARATION AND CHARACTERISATION OF DICHLOROCARBENE MODIFIED STYRENE BUTADIENE RUBBER

Results of this chapter is published in *J. Appl. Polym. Sci.* 68, 153, 1998

3.1 Introduction

Chemical modification of general-purpose rubbers plays an important role in imparting special properties to them. The properties of unsaturated elastomers can be modified by reactions involving their double bonds.[1] It was found that the reaction of double bonds with various reagents could result in improvement of flame retardancy, oil resistance, and other properties.[2] The reaction of carbene with olefins to form a cyclopropane derivative had attracted much attention during the past years.[3-6] The addition of halocarbenes to cis-1,4-polyisoprene (NR)[7-10] and cis-1,4-polybutadiene was reported by Pinazzi and Levesque[11] and Barentsvich et al.[12] They found that carbene addition had a significant influence on the properties of polydienes. However, this material did not find any commercial application. A number of attempts have been made to increase the green strength of SBR and also to improve its oxidative and oil resistance. One attempt to increase the green strength was by introduction of carbonyl groups during the polymerisation. If 1,4-transbutadiene units are long enough in SBR, then it is shown to have low temperature crystallisation accompanied by good green strength.[13,14] In this chapter, an attempt is made to improve the resistance of SBR towards heat, flame, and solvents by dichlorocarbene modification without destroying the technological properties of SBR. The activation energy of the chemical reaction is calculated and the modification is characterized by proton NMR, FTIR, and chemical analysis. The thermal stability and flammability of modified products are evaluated by thermogravimetry (TG) and the limiting oxygen index (LOI), respectively. The melting and phase transition temperature is measured calorimetrically.

3.2 Effect of time and temperature on dichlorocarbene addition to SBR

The concentration of reagents, the temperature and the time of reactions are given in Table 3.1.

Table 3.1. Concentration of reagents for dichlorocarbene modification

SBR (g)	100
Toluene (ml)	2000
$CHCl_3$ (ml)	300
NaOH 50% (ml)	350
CTAB(g)	8.5
Time (h)	1-36
Temperature (°C)	28/40/60

Figure 3.1 shows the percentage of chlorine versus time at temperatures of 28, 40, and 60°C. The dichlorocarbene addition is fast in the initial stages but decreases at later stages of the reaction. The rate reaction almost levels off after 12 h of reaction. The rate of reaction and the chlorine content increases with the temperature of the reaction. As far as the first 15 min of the reaction are concerned, the reaction is extremely fast at 60°C.

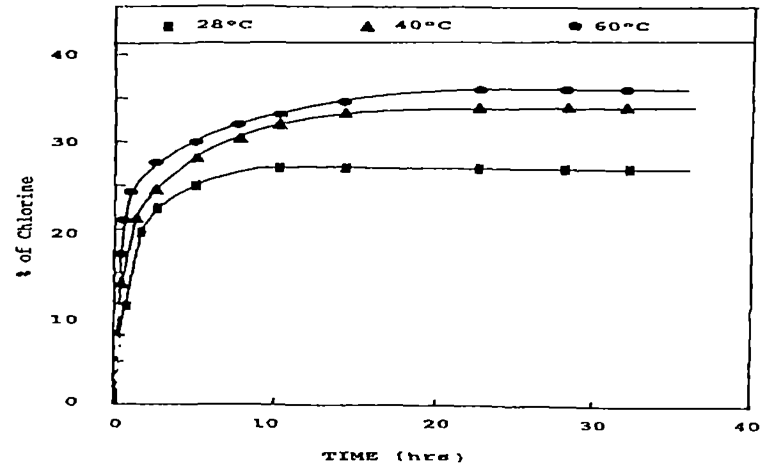


Figure 3.1. Plot of percentage of chlorine versus time, at temperature of 28, 40 and 60°C

Figure 3.2 shows the change in percentage of chlorine log(c_∞-c_t) versus time, where c_∞ is the maximum chlorine percentage obtained at a particular temperature and c_t is the percentage of chlorine at any time t. Linearity of the plots shows that the modification reaction proceeds according to first-order kinetics. Rate constants (k) of the reactions calculated are 3.24 x 10^{-5} s^{-1}, 2.05 x 10^{-5} s^{-1}, and 1.23 x 10^{-5} s^{-1} at 28, 40, and 60°C, respectively. The activation energy of the reaction calculated from the linear plot of log k versus 1/T (where *k is* the rate constant and *T is* the temperature in K) is found to be 35.89 kJ/mol.

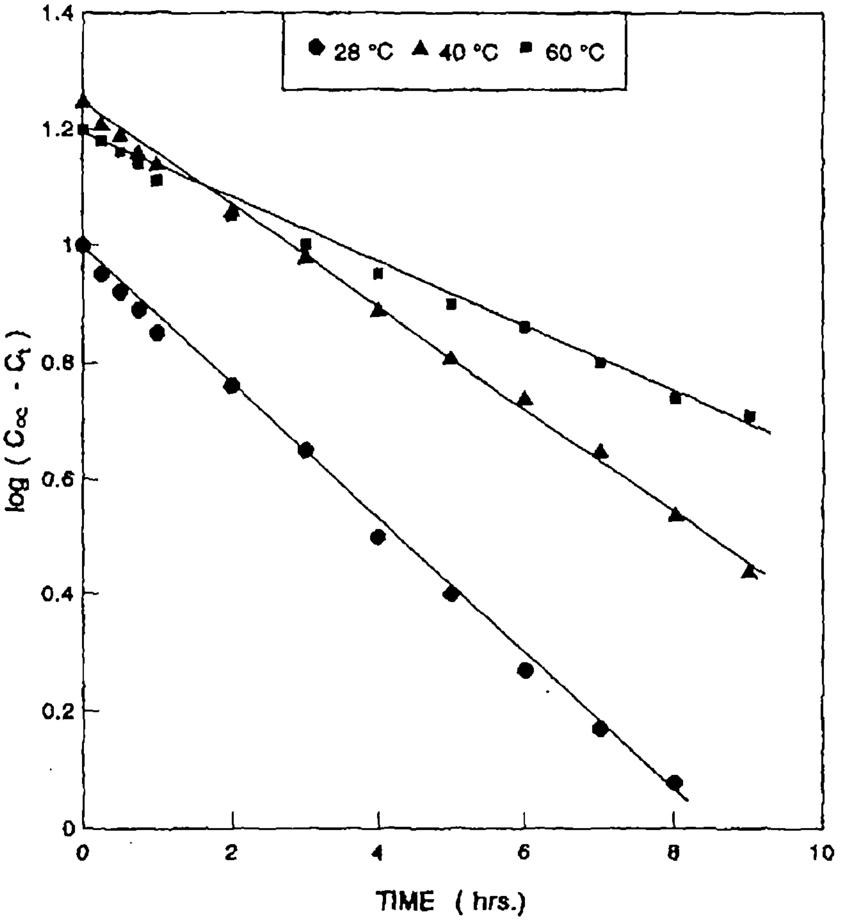


Figure 3.2. Plot of log (C_∞ - C_t) versus time for dichlorocarbene modified SBR

3.3 Characterisation of modified SBR

3.3.1 FT ^{1}H-NMR characterization

FT ^{1}H-NMR spectra recorded for SBR and dichlorocarbene-modified SBR are given in Figure 3.3. SBR and representative modified SBR exhibit signals for the hydrogen region of benzene at 7.3-7 ppm. Pure SBR displays signals at 2 and 1.4 ppm due to the methylene hydrogens ($-CH^2-$) and at 5.6 ppm (s) due to the unsaturated methine hydrogen (-CH=) of butadiene. Modified SBR displays a triplet for methylene hydrogens, in the region of 1.1-2 ppm. These additional signals can be attributed to the cyclopropyl ring. The doublet in the region 5.8 to 5.2 ppm shown by the modified SBR can be due to the hydrogen of the carbene bearing carbon and the hydrogen of the carbon attached to the benzene ring.

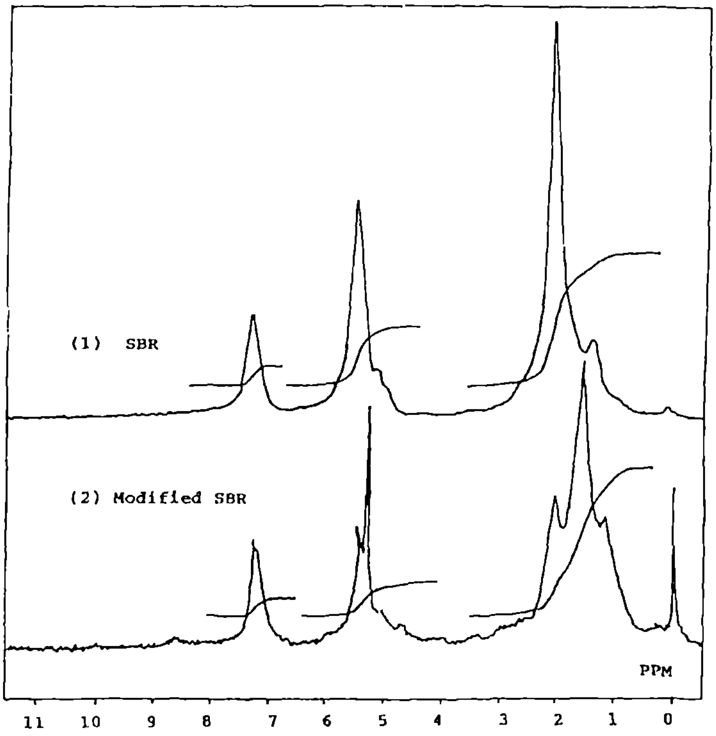


Figure 3.3. FT ^{1}H-NMR spectra of (1) pure SBR and (2) dichlorocarbene modified SBR (representative polymer) of 25% Cl

3.3.2 FTIR characterization

Figure 3.4 shows the IR spectra of the thin films (cast from $CHCl_3$) of SBR [Figure 3.4(1)] and modified SBR at I h [Figure 3.4(2)], 12 h [Figure 3.4(3)], and 24 h [Figure 3.4(4)].

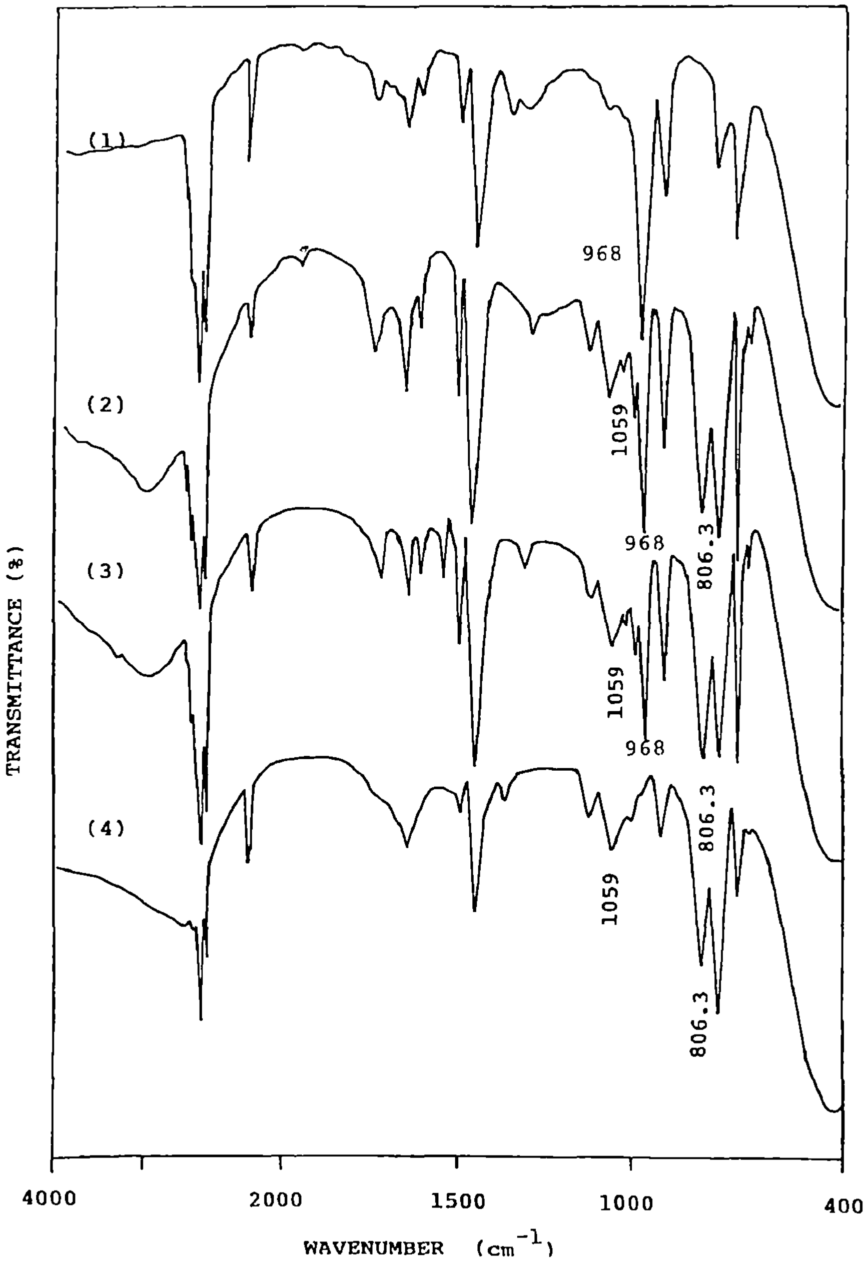


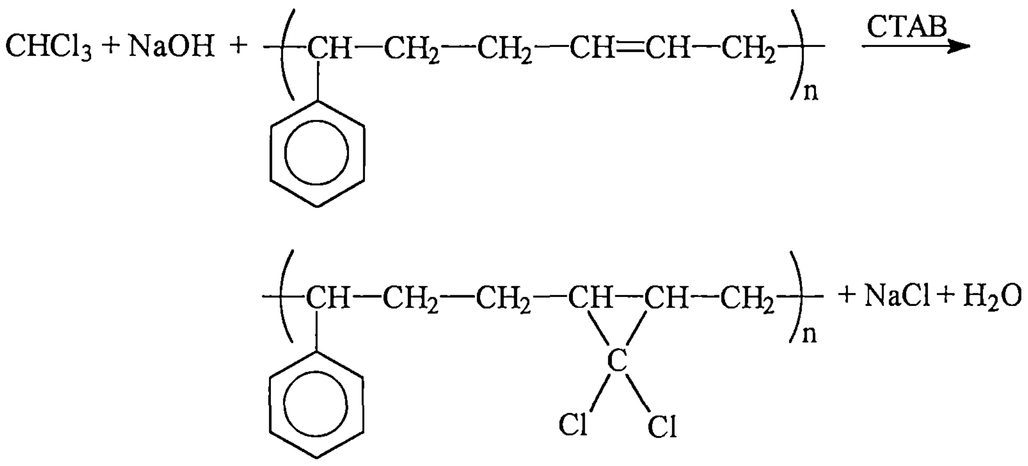
Figure 3.4. **FTIR spectra of thin films of (1) pure SBR, (2) dichlorocarbene modified SBR of 15%, (3) 25%, and (4) 35% chlorine**

The modified SBR shows characteristic C-Cl absorption peaks at 806 and 1059 cm^{-1} due to the cyclopropane ring.[15] It is likely that the cis-butadiene takes part in the reaction initially, as: CCl_2 more readily attacks the *cis* double bond. As the reaction time increases, there is a reduction in the intensity of the absorption at 968 cm^{-1} which is due to the *trans* -CH=CH and at 1653 cm^{-1} which is due to *cis* -CH=CH. The absorption at 698 cm^{-1} is due to the presence of an aromatic ring, whose concentration remains unaffected with modification. The absorption at 910 cm^{-1} (vinyl 1,2 content) remains almost unaffected after modification. There is a shift from 698 cm^{-1} absorption to 702 cm^{-1} due to the increase in chlorination; this may be attributed to steric hindrance of the cyclopropane ring. The peak ratio of absorption at 1653/806 cm^{-1}, 968/806 cm^{-1}, 910/806 cm^{-1} and 698/806 cm^{-1} is shown in Table 3.2.

Table 3.2. IR absorption peak height ratios

Time (h)	Chlorine (%)	1653/806 (cm^{-1})	968/806 (cm^{-1})	910/806 (cm^{-1})	698/806 (cm^{-1})
1	15	0.307	1.199	0.631	1.78
12	25	0.115	0.957	0.620	1.75
24	35	1653 absent	968 absent	0.619	1.71

With increase in the duration of the chemical reaction, there is a progressive reduction in the double-bond concentration and corresponding increase in the concentration of C-Cl bonds, whereas the styrene concentration remains almost unchanged. Hence, it can be inferred that it is the double bond[4,16,17] of butadiene that takes part in the chemical reaction. The proposed reaction is shown in Scheme 3.1.



Scheme 3.1. Proposed pattern of dichlorocarbene modification

3.3.3 Gel permeation chromatography

The molecular weight distribution curves of SBR and modified SBR (<20%) determined by GPC are given in Figure 3.5.

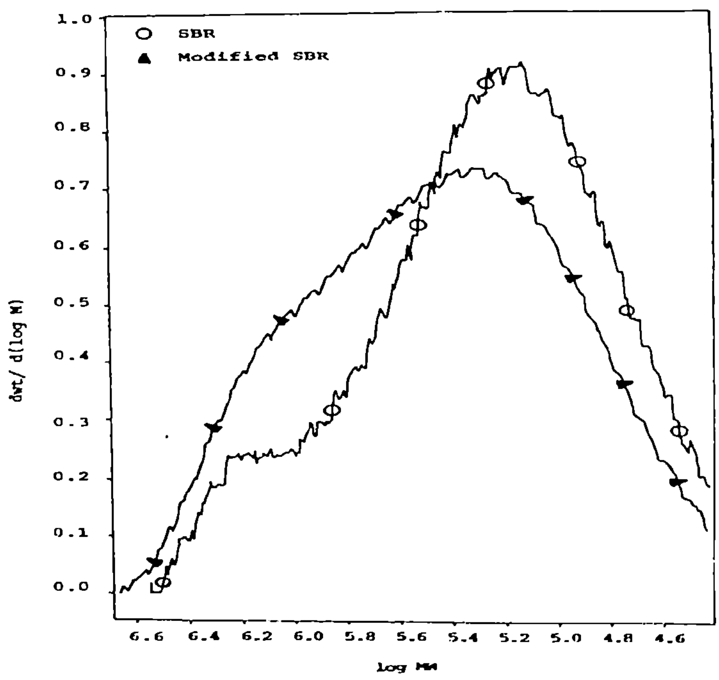


Figure 3.5. Molecular weight distribution curves of SBR and dichlorocarbene modified SBR (15% Cl)

From the figure, it is evident that high molecular weight fractions are formed in modified SBR as a result of the modification. The molecular weight ranges from 2.5 x 10^4 to 5.01 x 10^6 in both modified and pure SBR. The high molecular weight fraction above a molecular weight of 10^6 is higher for the modified samples (as seen from the area under the molecular weight distribution curve). The increase in $\bar{M}_n$, (number average molecular weight), $\bar{M}_w$ (weight-average molecular weight), and $\bar{M}_z$, (z-average or sedimentation-average molecular weight) with very little change in the polydispersity given in Table 3.3 shows that dichlorocarbene modification is accompanied by an increase in molecular weight due to the addition of chlorine through the cyclopropyl ring as a side chain.

Table 3.3. Molecular weights of dichlorocarbene modified SBR

Materials	$\bar{M}_n$ (Daltons)	$\bar{M}_w$ (Daltons)	$\bar{M}_z$ (Daltons)	Polydispersity
SBR	125550	359502	996026	2.8634
10% Cl	142260	421251	1225600	2.9611
15% Cl	164980	525782	1241151	3.1869

3.3.4 Differential scanning calorimetry

DSC thermograms of the modified rubber shown in Figure 3.6, readily demonstrate the presence of crystallinity with increasing chlorination. DCSBR containing 15% chlorine (Figure 3.6a) shows a clear thermal transition at -56°C corresponding to the T_g of SBR. Modified SBR containing 25% chlorine (Figure 3.6b) shows two thermal transitions at-56°C corresponding to the to T_g of SBR and at -36°C corresponding to T_g of chlorinated segments in addition to two melting endotherms at -22 and 20°C. As the level of modification increased to 30% (Figure 3.6c) the sample shows melting endotherms at -12 and 25°C in addition to thermal transitions due to the T_gs. This observation reveals that during dichlorocarbene modification there are structural changes, which can lead to crystallisations at low temperatures. The presence of specific groups which produce strong intermolecular bonds is one of the contributing factors for the development of crystallinity.[18] As modification proceed, greater amount of chlorine is incorporated into the butadiene units, leading to increased polar interactions.

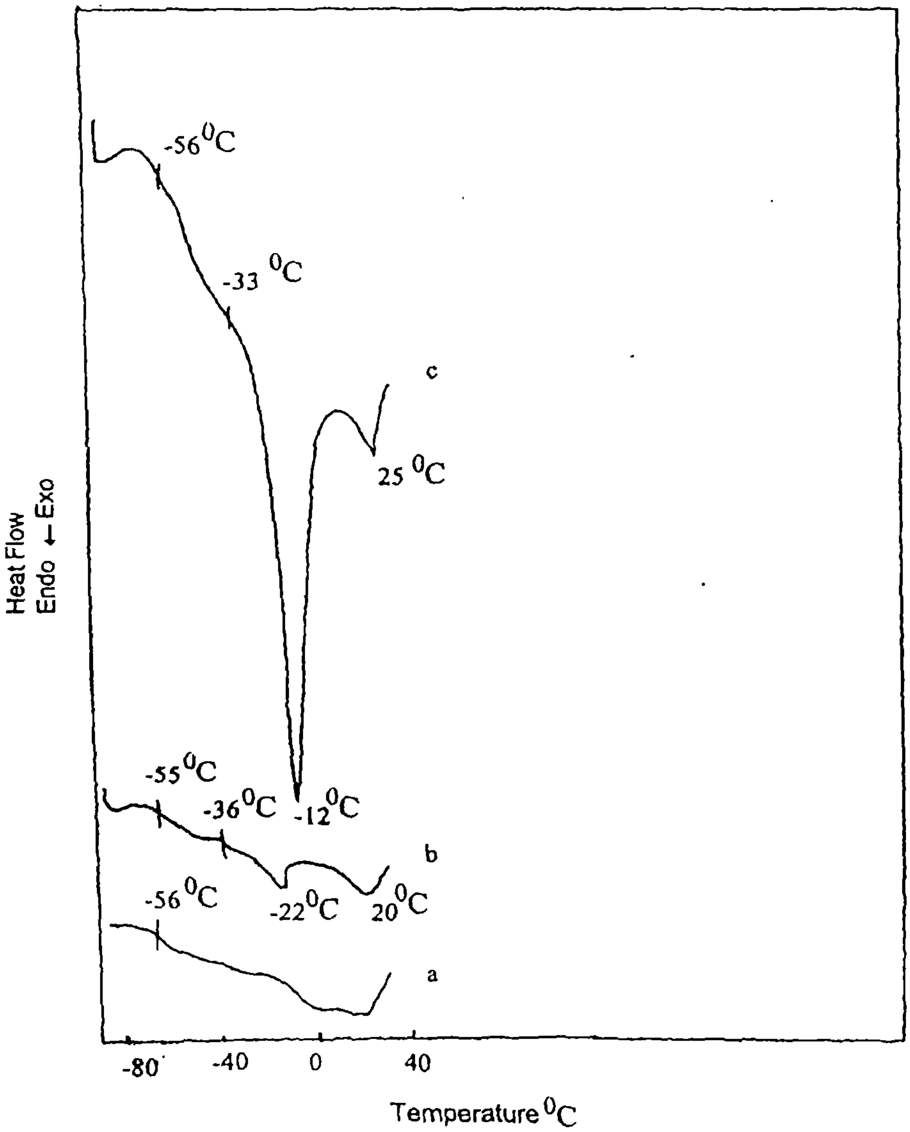


Figure 3.6. **DSC thermograms of dichlorocarbene modified SBR of varying chlorine contents: (a) 15%, (b) 25% and (c) 30%.**

3.3.5 Thermogravimetric analysis

The thermograms of SBR, modified SBR, and chloroprene rubber (Neoprene W) are given Figure 3.7. The decomposition pattern is compare with a commercial chloroprene rubber. Pure SBR (curve 1) shows a single-stage decomposition at a temperature of initiation of 454°C. As the chlorination increases, there is a considerable change in the decomposition pattern. The decomposition of chlorinated SBR (at a higher percentage of Cl) takes place in two steps (curves 2 and 3): The first decomposition begins at 286°C, and the second, at 454°C.

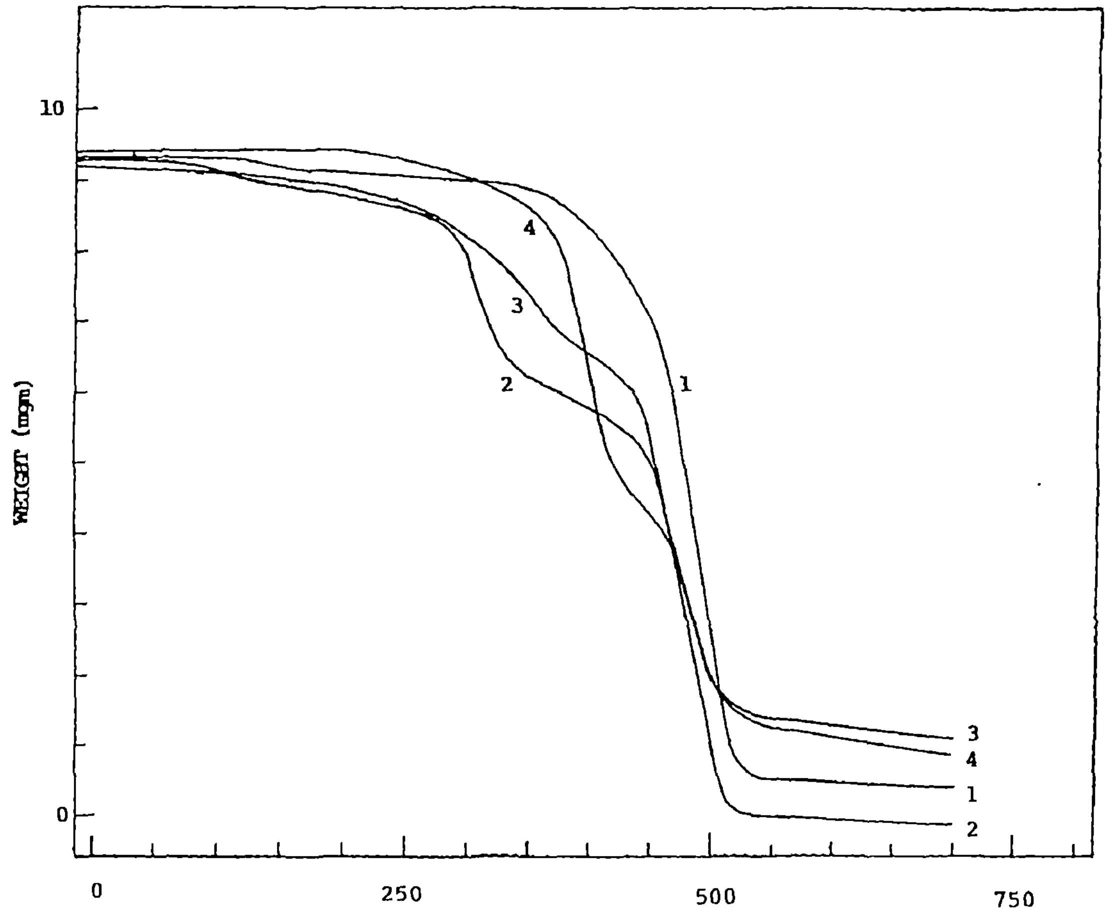


Figure 3.7. **Thermograms of (1) pure SBR, (2) dichlorocarbene modified SBR of 15% chlorine, (3) modified SBR of 35% chlorine and (4) commercial chloroprene rubber**

The time taken for a 50% weight drop for chloroprene rubber and chlorinated SBR are presented in Table 3.4. It is clear from the table that the time taken for a commercial chloroprene rubber for a 50% weight drop is lower than that of dichlorocarbene-modified SBR. This indicates that the chlorinated SBR has a superior thermal stability to that of commercial chloroprene rubber.

Table 3.4. Time for 50% weight drop

Material	Curve	Time for 50% weight drop (min)
SBR	1	44.8
Modified SBR (15% Cl)	2	43.3
Modified SBR (25% Cl)	3	43.5
Chloroprene	4	39.8

3.3.6 Flammability behavior

The limiting oxygen index (LOI) (which is a direct measure of the flame resistance of the materials) of pure SBR, modified SBR, and commercial chloroprene rubber are given in Table 3.5. When halogen-containing elastomers are ignited, they could exhibit an intumescence effect, due to which the char formed thermally insulates the polymer from the flame and thus inhibits combustion. From the table, it is clear that modified SBR shows better flame resistance than that of unmodified SBR. Moreover, the LOI value for SBR with a chlorine content of 25% is almost the same as that of commercial chloroprene rubber. Thus modified SBR can be recommended as a substitute for building materials, since materials with an LOI value[2] greater than 20.8 are considered to be safe for indoor applications, because these materials will be self-extinguishing even if ignited.

Table 3.5. **Limiting oxygen index (LOI) values**

Material	Chlorine (%)	LOI (%)
SBR	-	19
Modified SBR	15	24
Modified SBR	25	28
Chloroprene	40	28.4

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CHAPTER

4

VULCANISATION BEHAVIOUR, TECHNOLOGICAL PROPERTIES AND EFFECT OF DIFFERENT FILLERS ON DICHLOROCARBENE MODIFIED SBR

A part of this chapter is accepted for publication
in *Kautschuk Gummi Kunststoffe*

4.1 Introduction

Chemical modification carried out on SBR is mainly to improve its gum strength. One attempt to improve the green strength of SBR is improved by introduction of tertiary amine containing monomers during polymerisation, followed by reaction with dihalides to form a small number of labile crosslinks.[1,2] The technique of anionic polymerisation using modified alkyl lithium initiators has been used to prepare high vinyl SBR.[3,4] This material contain 90% diene as 1,2 vinyl units and exhibit high green strength. SBR has very poor resistance for attack by degradative agents like oxygen, ozone, oils and solvents. Dichlorocarbene addition to double bonds, an attempt to modify elastomers has been done earlier.[5] This chapter focuses on the vulcanisation characteristics and change in physical properties of the dichlorocarbene modified styrene butadiene rubber. The processing and technological properties of DCSBR (15% Cl) containing reinforcing fillers like carbon black and silica are also evaluated.

4.2 Vucanisation behaviour of dichlorocarbene modified SBR

(a) Sulphur vulcanisation

The formulation used in the study is given in Table 4.1.

Table 4.1. Formulation of mixes

Mix No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Styrene butadiene rubber	100	-	-	-	-	-	-	-		-	-	-	-
DCSBR containing 15% chlorine	-	100	-	-	-	-	-	-		100	-	-	-
DCSBR containing 20% chlorine	-	-	100	-	-	-	-	-		-	100	-	-
DCSBR containing 25% chlorine	-	-	-	100	100	100	100	-	-	-	-	100	-
DCSBR containing 30% chlorine	-	-	-	-	-	-	-	100	100	-	-	-	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.0	1.5	-	-	-	-	-
Zinc oxide	5	5	5	5	5	5	5	5	5	-	-	-	-
Magnesium oxide	-	-	-	-	-	-	4	-	4	-	-	-	-
CBS	1	1.5	1.5	1.5	1.0	1.5	-	1.5	-	-	-	-	-
TMTD	-	0.5	0.6	0.8	0.8	0.7	0.5	1	0.7	-	-	-	-
ETU (NA-22)	-	-	-	-	0.5	-	0.5	-	0.5	-	-	-	-
Sulphur	2.2	2.2	2.2	2.2	2.0	2.2	-	2.2	-	-	-	-	-
Dicumyl peroxide	-	-	-	-	-	-	-	-	-	4	4	4	4

1, 2, 3 and 4 denote DCSBR containing 15, 20, 25 and 30% chlorine content respectively.

A successful accelerated sulphur vulcanisation can be carried out on DCSBR when its chlorine content of DCSBR is either 25% or lower. The rheograph of conventional sulphur vulcanisation system on DCSBR is given in Figure 4.1. At lower level of modification, comparatively lower amount of accelerator can successfully bring about vulcanisation, but at a higher level of modification higher amount of accelerator is required. Since dichlorocarbene modification occurs at the double bond, reducing the active sites of vulcanisation, resulting in a requirement of higher dosage of accelerator to bring about satisfactory cure. This is clear from Figure 4.1 (Plots 4 and 6). A combination of accelerator CBS/TMTD/ ETU at a dosage 1/0.8/ 0.5 also brings appreciable state of cure (Figure 4.1) (Plot 5). However, comparatively poor scorch safety is exhibited by this combination. ETU is known to be scorchy in CR. When chlorine content increases up to 30%, there is no satisfactory level of cure, even by an accelerated sulphur vulcanisation (Figure 4.1) (Plot 8). At higher level of modification the negative inductive effect of chlorine (-I effect) is more pronounced and this leads to a deactivation of crosslinking sites.

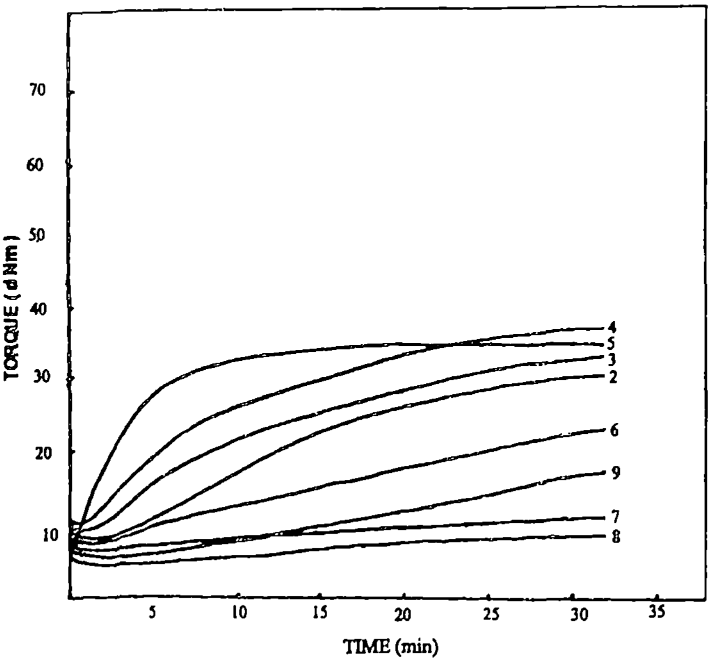


Figure 4.1 **Rheographs of DCSBR cured by conventional sulphur and metal oxide vulcanisation systems at 150°C**

(b) Metal oxide vulcanisation

DCSBR does not undergo any appreciable level of cure by metal oxides (Figure 4.1). A chlorine containing polymer like polychloroprene (CR) readily undergoes crosslinking by metal oxides.[6] For example, CR undergoes crosslinking in presence of metal oxide and ethylene thiourea [ETU] producing crosslinks that are monosulphidic in nature and it is already proved that these crosslinks occur due to the presence of labile chlorine.[7] In DCSBR reactive allylic or tertiary allylic chlorine which is responsible for crosslink formation by metal oxide[8] is absent. Therefore, in this case the above explained type of crosslink formation is prevented. This fact well explains the plots 7 and 9.

(c) Thermovulcanisation

CR is also known to undergo crosslinking by heat at 180°C without the use of any crosslinking agent (Thermovulcanisation).[9] However, DCSBR is found to be less susceptible to thermovulcanisation as evidenced from Figure 4.2. Thermovulcanisation of CR has been shown to be due to the liberation of chlorine from CR with the formation of HCl resulting in crosslinks. In the case of DCSBR the chlorine is attached to the main chain through a cyclopropyl ring.

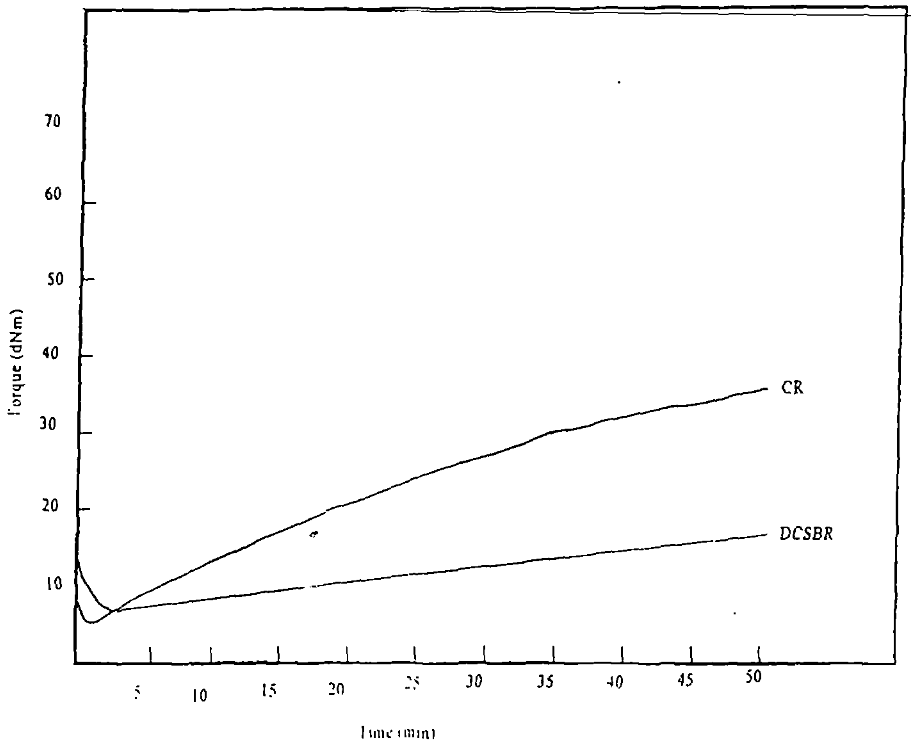


Figure 4.2. Thermovulcanisation of CR and DCSBR (containing 25% chlorine) at 180°C

(d) Dicumyl peroxide vulcanisation

A higher level of crosslinking is obtained with peroxide cure (Figure 4.3) (Plots 10-13). The state of cure attained for each modified compound is different and depends on the level of chlorination. The curing efficiency decreases as modification increases. The diene structure of a polymer, its type and amount is shown to influence the peroxide vulcanisation of an elastomer like EPDM.[10] The cure attained by peroxide vulcanisation can be increased by temperature as seen from rheographs of DCSBR containing 25% chlorine cured with 4 phr DCP (Figure 4.4). The level of crosslinking increases as dose of dicumyl peroxide (DCP) increases which is evidenced from the increase in torque (Figure 4.5).

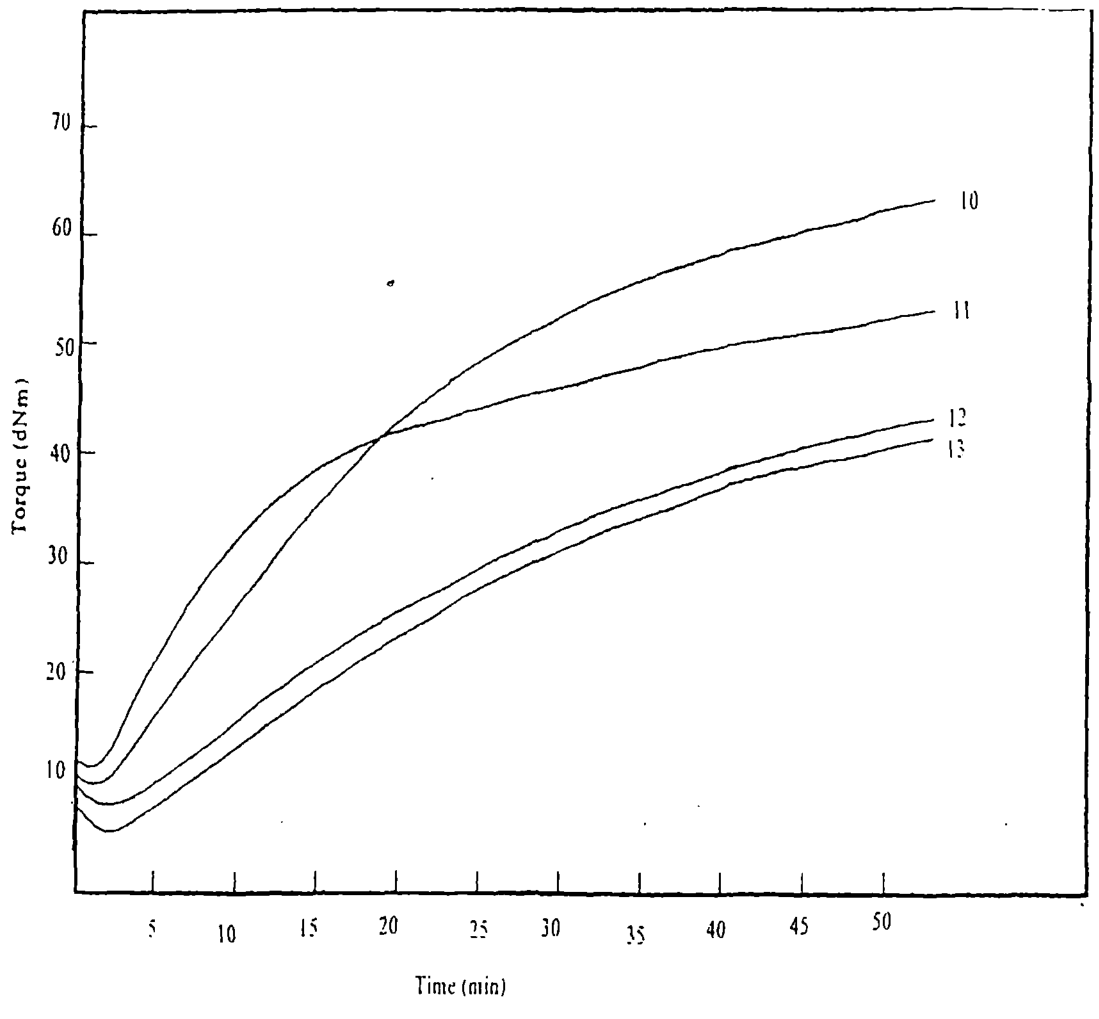


Figure 4.3. Rheographs of DCSBR containing varying percentage chlorine cured by DCP (4phr) at 150°C

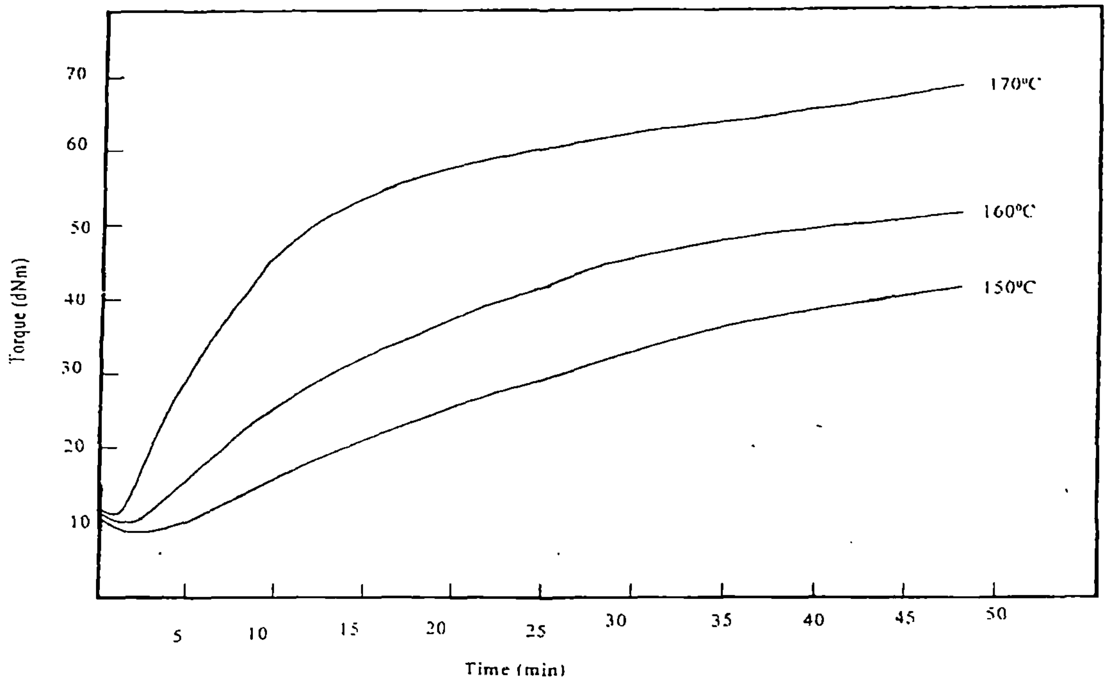


Figure 4.4. **Rheographs of 25% chlorine containing DCSBR cured by 4 phr DCP at 150, 160 and 170°C**

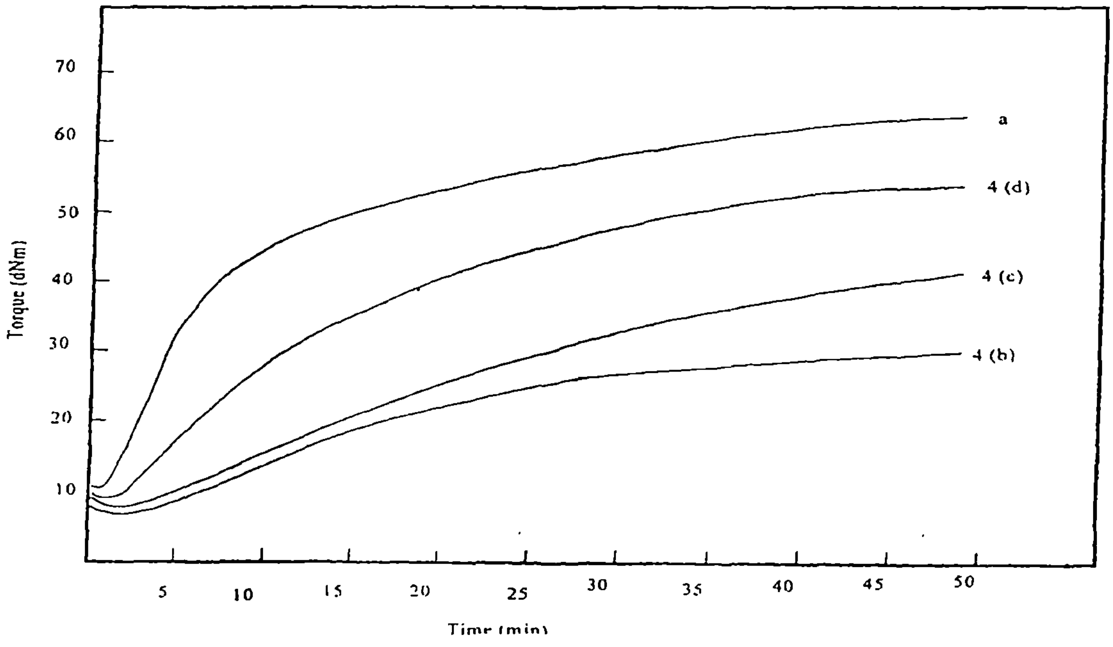


Figure 4.5. **Rheographs of (a)-CR cured by 4phr DCP, (b) -25% chlorine containing DCSBR cured by 2phr DCP, (c) -25% chlorine containing DCSBR cured by 4phr DCP, (d) -25% chlorine containing DCSBR cured by 6phr DCP**

It is known that in the case of peroxide vulcanisation, crosslinking is controlled by both temperature[11] of vulcanisation and concentration of peroxide. Even though the state of cure increases significantly, cure time does not change appreciably, with the concentration of DCP as indicated in Table 4.2.

Table 4.2. **Cure characteristics of DCSBR containing 25% chlorine cured by varying concentration of DCP**

Concentration of DCP (phr)	2	4	6
Difference in torque, Δ torque (dN-m)	23	32	44
Optimum cure time, t_{90} (min)	15	19	15

4.3 Physical properties

The physical properties of sulphur cured and dicumyl peroxide cured DCSBR are given in Tables 4.3 and 4.4, respectively. The tensile strength and modulus of the samples cured by an accelerated sulphur vulcanisation system increase progressively as the chlorine content increases. The tensile strength of DCSBR containing 25% chlorine is rather high (17 MPa, Table 4.3) with an EB of 520%, a behaviour similar to that of strain crystallising polymer. Resilience decreases with increasing level of chlorination whereas compression set, hardness and heat build-up increases. Tear strength increases with the chlorine content of modified samples. For DCP cured mixes the tensile strength and modulus increases progressively with chlorination as in the case of sulphur cured vulcanisates. For DCP cured mixes the EB increases with modification of SBR up to 25 % of chlorination and then decreases. Sample containing 30% chlorine becomes hard with low elongation at break as seen from Table 4.4. The physical properties of sulphur cured vulcanisates are superior to peroxide cured vulcanisates. It is well known that difference in technical properties is due to the type of bond formed during peroxide cure.

Table 4.3. Physical properties of accelerated S-cured DCSBR.

Mix No.	1	2	3	4
Tensile strength (MPa)	2.88	9.68	12.5	17.08
Modulus 300% (MPa)	1.86	2.51	3.0	3.9
Elongation at break (%)	340	410	480	520
Tear strength (kN/m)	24.4	37.8	43.7	58.1
Hardness (Shore A)	34	42	44	47
Resilience (%)	41	36	34	30
Heat build-up (°C)	12	15	17	20
Compression set (%)	11	13	14	16

Table 4.4. Physical properties of DCP cured DCSBR

Mix No.	10	11	12	13
Tensile strength (MPa)	6.6	8.1	14.0	20.0
Modulus 300% (MPa)	1.98	2.11	2.48	2.55
Elongation at break (%)	320	300	240	90.0
Tear strength (kN/m)	31	38	44	46
Resilience (%)	32	28	27	22
Heat build-up (°C)	12	16	18	20
Compression set (%)	12	13	15	17

4.3.1 Stress-strain behaviour

The stress strain curve for the samples shown in Figure 4.6 (1, 2 and 4). It reveals that up to chlorination of 25%, the modified samples are rubbery in nature and strain crystallising. The addition of halocarbenes to SBR is in a stereospecific manner. Chlorine containing polymers exhibit high polar interactions. As a consequence during stretching modified butadiene units can develop regular portions that can become incorporated in a crystalline lattice.[12]

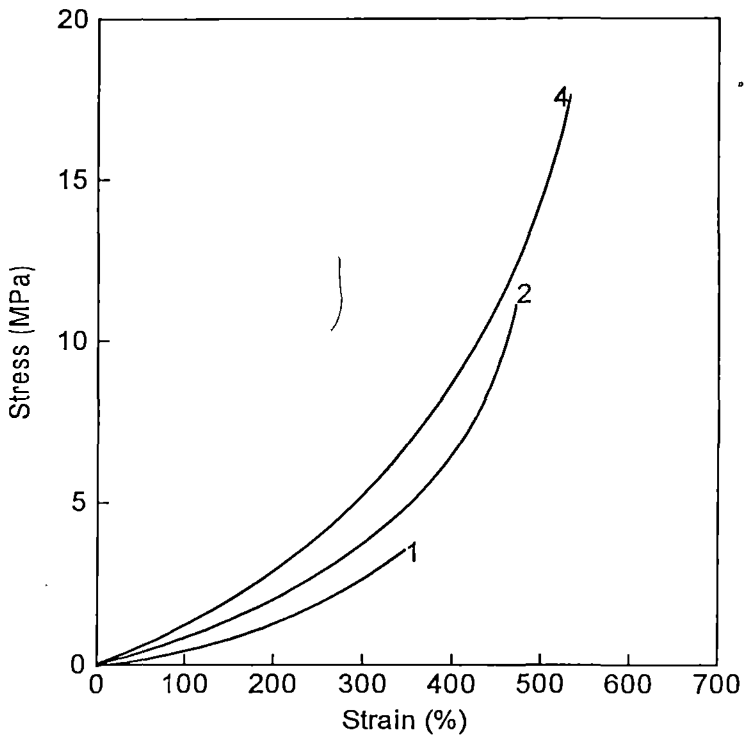


Figure 4.6. Stress-strain curves of SBR and DCSBR (1) SBR (2) DCSBR of 15 % Cl (4) DCSBR of 25% Cl

4.3.2 Air and oil ageing

Mechanical properties of samples aged in air at 70°C for 96 h is shown in Table 4.5. The materials show comparatively good mechanical properties and better resistance to oxidative degradation as seen from the change in percentage of tensile strength. This is attributed to the decrease in the concentration of double bonds obtained during chemical modification. Dichlorocarbene modification imparts excellent resistance to oil which is superior to CR and almost approaching that of NBR (medium AN content) as seen from Table 4.6. Oil resistance of DCSBR increase with increasing chlorine content of the samples. DCP cured DCSBR results in a product with much enhanced oil resistance, which is superior to conventionally cured NBR. As the level of modification increases, more and more polar groups are introduced which results in higher resistance to oil swell.[13]

Table 4.5. **Effect of air ageing on mechanical properties of modified SBR at 70°C for 96 h.**

Mix No.	Decrease in tensile strength (%)	Decrease in elongation at break (%)
1	32	19.8
2	26	17
3	22.6	21
4	17.3	14.4
10	21.7	17.1
11	15.4	13.2
12	12	9.4
13	9.8	9.0

Table 4.6. **Swelling behaviour of DCSBR, SBR, CR and NBR**

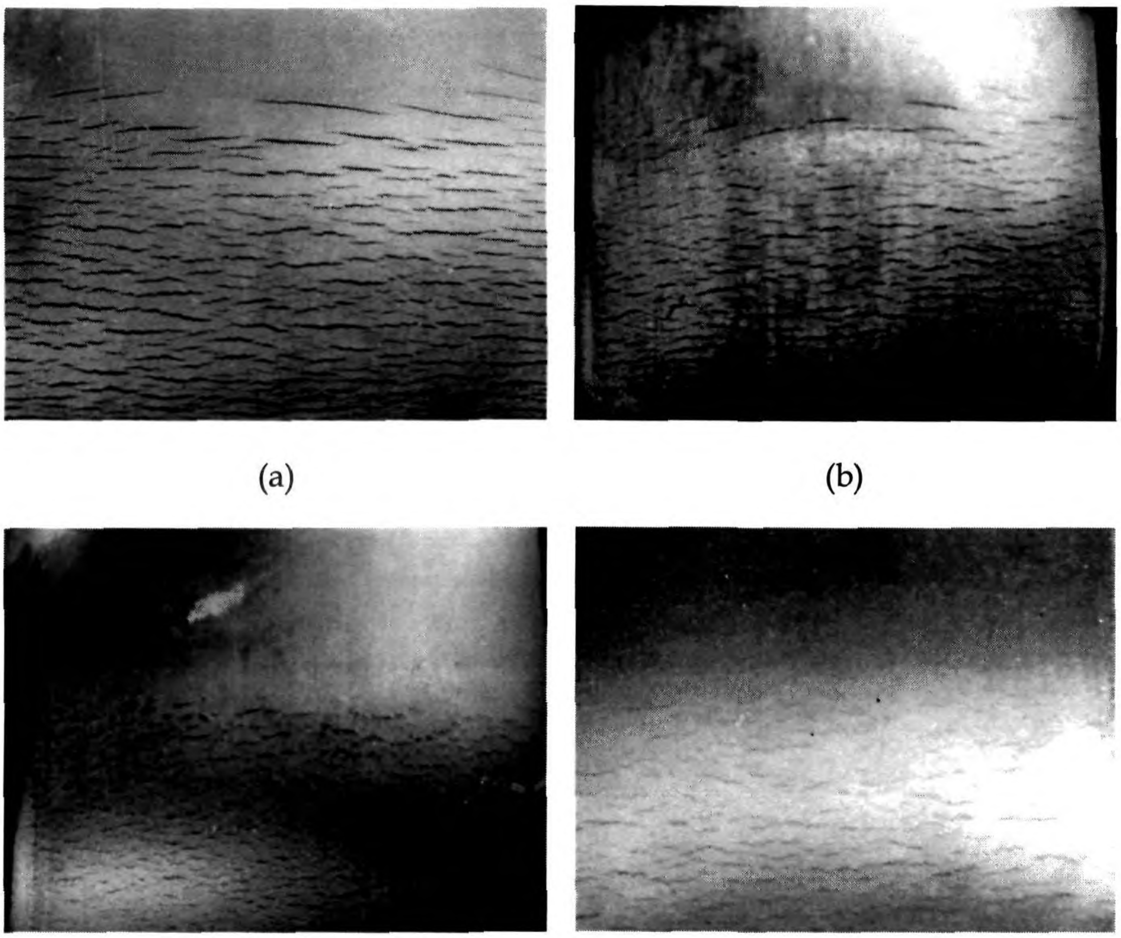
Mix No.	ASTM oil No. 1 (%)	ASTM oil No. 2 (%)	ASTM oil No. 3 (%)
CR[a]	2.12	4.37	16.21
NBR[b]	0.34	0.51	0.68
1	9.28	15.94	52.78
2	1.22	4.2	15.5
3	1.09	2.23	8.97
4	0.9	1.6	4.95
10	0.51	0.63	2.1
11	0.26	0.32	2.5
12	0.04	0.07	0.9
13	0.02	0.03	0.5

[a] CR – 100, stearic acid - 0.5, TMTD - 0.5, ETU - 0.5, MgO - 4, ZnO - 5.

[b] NBR - 100, stearic acid - 1, ZnO - 5, CBS - 1.5, TMTD - 1, Sulphur - 0.5

4.3.3 Ozone resistance

The optical photographs of 20 h of ozone exposed SBR and modified SBR are shown in Figure 4.7. Cracks were developed on the surface of SBR even after 2 h of exposure to ozone attack. However, the nature and level of crack developed due to ozone attack are different for different chlorine containing DCSBR. In the case of 15% chlorine containing DCSBR the cracks are developed after 3 h, 20% chlorinated samples take 4.5 h whereas 25% Cl containing DCSBR cracks developed only after 6 h. This is because as the level of modification increases more and more chlorine groups attached to the main chain. This is effectively prevents the generation and propagation of crack on the surface of DCSBR vulcanisate.



(a) (b)

(c) (d)

Figure 4.7. Optical photographs of 10 h of ozone exposed (a) SBR, (b) modified SBR with 15%, (c) 20% and (d) 25% chlorine content.

4.4 Effect of different fillers on sulphur cured 15% chlorine containing DCSBR

4.4.a Processing characteristics

The basic formulation used for the fillers in DCSBR are given in Table 4.7.

Table 4.7. Formulation of filler filled DCSBR

Chemicals	Mix No.								
	1	2	3	4	5	6	7	8	9
DCSBR (15% Cl)	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5	5	5
CBS	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
TMTD	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TDQ	1	1	1	1	1	1	1	1	1
Aromatic oil	-	0.7	1.4	2.1	2.8	0.7	1.4	2.1	2.8
HAF C-black	-	10.	20	30	40	-	-	-	-
Precipitated silica	-	-	-	-	-	10	20	30	40
Diethylene glycol	-	-	-	-	-	0.5	0.8	1.0	1.5
Sulphur	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2

The cure characteristics of different fillers on DCSBR containing 15% chlorine are shown in Table 4.8 and the rheographs of silica and carbon black filled samples are given in Figures 4.8 and 4.9. The optimum cure time is higher for silica filled compounds than carbon black filled compounds. This can be attributed to the dipole-dipole interaction between chlorine part of DCSBR and silanol group of silica. As the loading of fillers increases the optimum cure time decreases.

Table 4.8. Cure characteristics of different fillers on DCSBR (15% chlorine content)

Properties	Silica (phr)				Carbon black (phr)			
	10	20	30	40	10	20	30	40
Cure time (min)	24	23	21.5	20.5	19.5	18.5	18	17
Scorch time (min)	3	2.75	2.5	2.25	2.5	2.25	2	1.75
Max. torque (dNm)	37	39.5	43.5	49.5	43	46	49	55

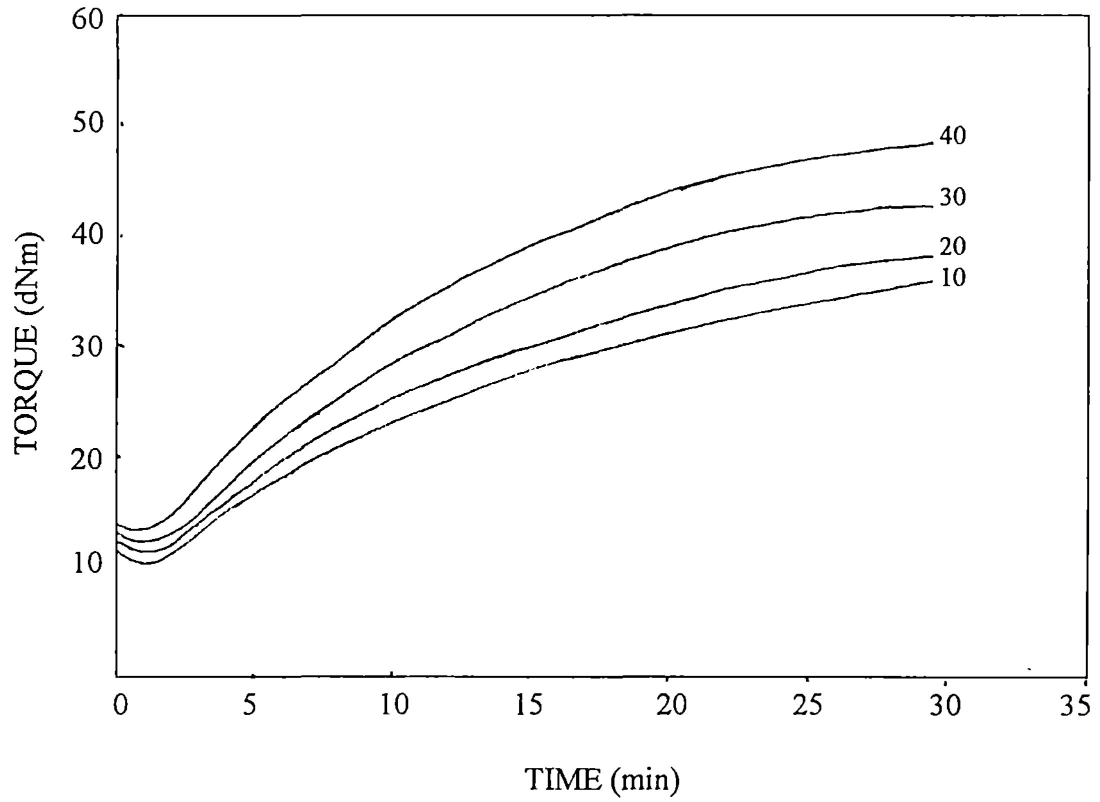


Figure 4.8. Rheographs of silica filled DCSBR (15% chlorine content) at 150°C

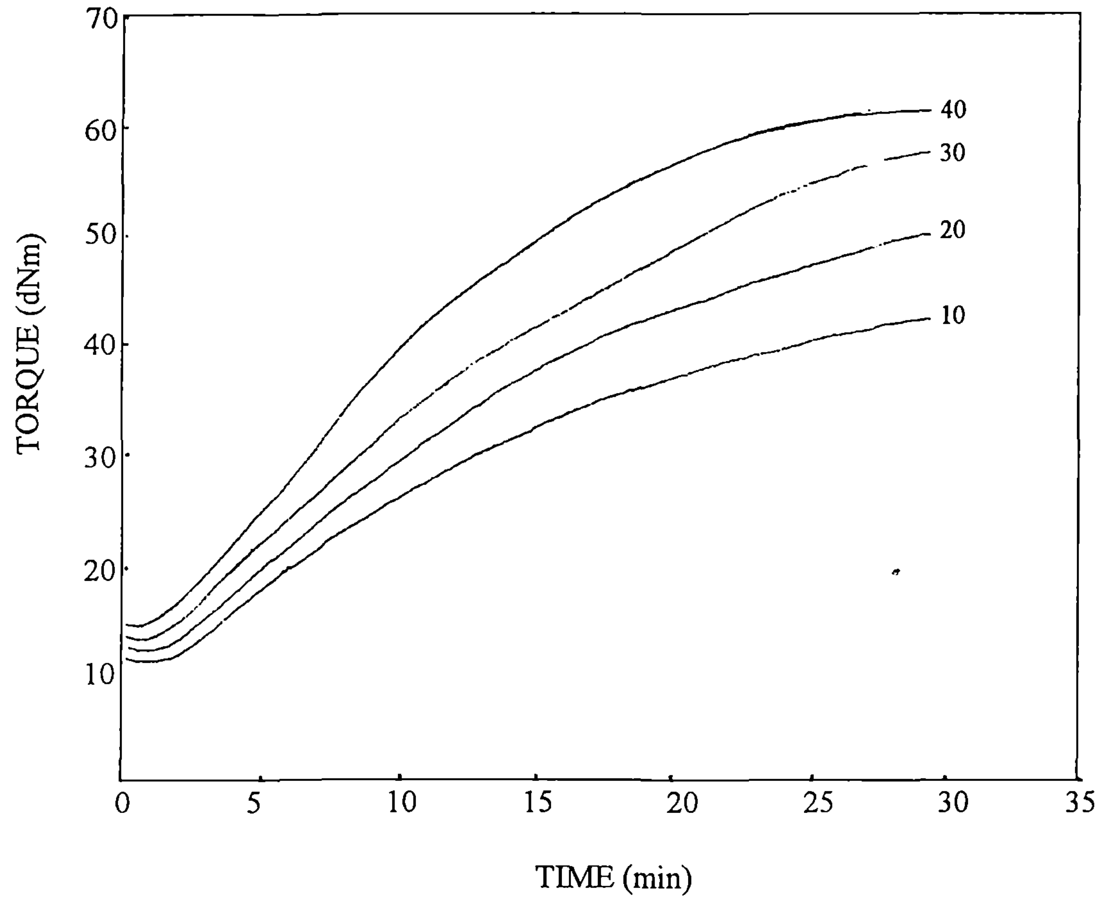


Figure 4.9. Rheographs of carbon black filled DCSBR (15% chlorine content) at 150°C

Rheometric scorch time of various fillers on DCSBR (Table 4.8) reveals that silica filled samples show good scorch time. As the loading of fillers increases the magnitude of scorch time decreases. A higher rheometric torque is obtained for carbon black filled mixes as compared to silica filled mixes.

4.4.b Effect of fillers on technological properties

Mechanical properties of different fillers on DCSBR vulcanisate is presented in Table 4.9. As the loading of fillers increases the tensile strength increases, among the fillers used carbon black exhibit better tensile strength.

This is due to the minimum particle size of black which provides a large interfacial area of contact, resulting in a better interfacial adhesion.

Table 4.9. Mechanical properties of carbon black and silica filled DCSBR

Properties	Silica (phr)				Carbon black (phr)			
	10	20	30	40	10	20	30	40
Tensile strength (MPa)	15.9	20.1	22.9	24.0	16.5	22.9	26.5	29.4
Modulus, 300% (MPa)	4.5	5.9	8.1	10.3	5.9	9.1	12.5	16.8
Elongation at break (%)	459	430	400	365	440	400	378	350
Tear strength (kN/m)	47.8	52.3	56.3	59	49.5	53	59	63
Hardness (Shore A)	46	49	52	57	49	53	58	64
Resilience (%)	32	30	27	24	30	27	29	35
Heat build-up (°C)	19	22	25	27	21	25	29	35
Compression set (%)	17	19	24	26	15	17	19	22

Tear strength is an important property which contributes towards resistance to crack growth. As filler loading increases beyond a certain limit, the vulcanisate tends to tear during production as well as in service. It can be seen from the table that tear strength is maximum for carbon black filled system, due to the reinforcing nature and the effective utilisation of the surface by polymer. The tear strength increases with increase in loading of filler, a number of filler particles will be present at the crack propagation tip to arrest the propagating cracks.

Rebound resilience of different fillers on DCSBR shows that as the filler content increases, resilience decreases. This is due to two reasons, one is the higher crosslink density of the vulcanisate resulting from filler matrix adhesion and the second is the reduction in the amount of the polymer in the system. Silica filled vulcanisate shows higher resilience than carbon black filled samples.

The compression set value of silica filled DCSBR vulcanisate are higher than the carbon black filled mixes. As the filler content increases set value increases.

Hardness of a material is a complex property which indirectly depends on concentration of filler and mechanical properties such as modulus, strength, etc. Hardness and modulus of vulcanisate are usually expected to increase by the use of fillers. Carbon black filled samples show higher hardness than silica filled ones. Hardness also increases with increase in loading of fillers.

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CHAPTER

5

BLENDS OF NATURAL RUBBER AND DICHLOROCARBENE MODIFIED STYRENE BUTADIENE RUBBER

Results of this chapter have been communicated
to *Plastics, Rubber and Composite*

5.1 Introduction

Blending of polymers for property improvement and economic advantage has gained considerable importance. Large number of polymer blends has been proposed for commercial purpose,[1] all of them do not have the required mechanical properties mainly due to their incompatibility. This arises because of the absence of specific interaction between the phases in such blends which can be significantly improved by adding suitable compatibilisers during processing.[2-9] The segments of these compatibilisers can be chemically identical with the respective phases[10-13] or miscible with or adhered to one of the phases.[14-16] According to Paul[17] this type of surface activity should reduce interfacial energy between the phases, permit a finer dispersion during mixing, provide a measure of stability against gross segregation[18] and result in improved interfacial adhesion.[19] A compatibilised blend hence gives a more homogeneous crosslink density during vulcanisation which results in enhanced technological properties. Blending of NR and DCSBR, can result in materials that have a combination of good resistance to attack by ozone, better resistance to oil swelling heat resistance and good strength properties. This chapter discusses the processing and the mechanical properties of NR/DCSBR blends containing SBR as compatibiliser and analyses the effect of loading of the compatibiliser on 70/30, 50/50 and 30/70 composition of NR/DCSBR blends.

5.2 Cure characteristics of NR/DCSBR blends

The basic formulation used in the study is given in Table 5.1.

Table 5.1. Formulation of NR/DCSBR blends

Ingredients	Mix No.				
	1	2	3	4	5
Natural rubber	100	70	50	30	-
DCSBR (25% Cl content)	-	30	50	70	100
Stearic acid	2.0	1.85	1.75	1.65	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0
Antioxidant TDQ	1.0	1.0	1.0	1.0	1.0
CBS	0.8	0.92	1.0	1.08	1.2
TMTD	-	0.24	0.4	0.56	0.8
Sulphur	2.5	2.41	2.35	2.29	2.2

The rheographs of NR/DCSBR blends and the blend containing SBR as a compatibiliser on different blend composition (70/30, 50/50, 30/70) are given in Figures 5.1-5.4. The data presented in Table 5.2 represent the detailed cure characteristics of the single and blended rubber mixes. In presence of SBR as a compatibiliser the optimum cure time, scroch time and induction time become higher for NR/DCSBR 70/30 and 50/50 blends as compared to uncompatibilised blends. In 30/70 NR/DCSBR blend a reverse behaviour is observed in the case of optimum cure time. The 70/30 blend show an increase in rheometric torque as concentration of SBR increases from 5-10 phr. Compatibilised 1:1 blend containing 5 phr SBR gives a higher torque than NR and the maximum torque decreases at higher loading of compatibiliser. As concentration of DCSBR in the blend increases further, the presence of SBR does not cause an increase in the rheometric torque. This observation reveals the variation in phase discontinuity of the blends with the compatibiliser. According to our investigation, the maximum compatibilisation in 70/30 NR/DCSBR composition is noted with a compatibiliser concentration of

10 phr (parts per hundred rubber) loading and in 50/50 NR/DCSBR composition with 5 phr loading of the compatibiliser and no effective compatibilisation in the concentration range of 5-10 phr of SBR in 30/70 NR/DCSBR blend (as evidenced from mechanical properties). Uniform distribution of microdomains increases the interfacial area. Since more time is needed for the formation of greater number of interfacial crosslinks, the optimum cure time found to be higher in compatibilised blends as compared to uncompatibilised slends. As the loading of compatibiliser increases, the compatibilisation effect decreases which ultimately ends due to coalescence of dispersed domains. This reduces the interfacial area and thereby causing a decrease in optimum cure in 50/50 blend.

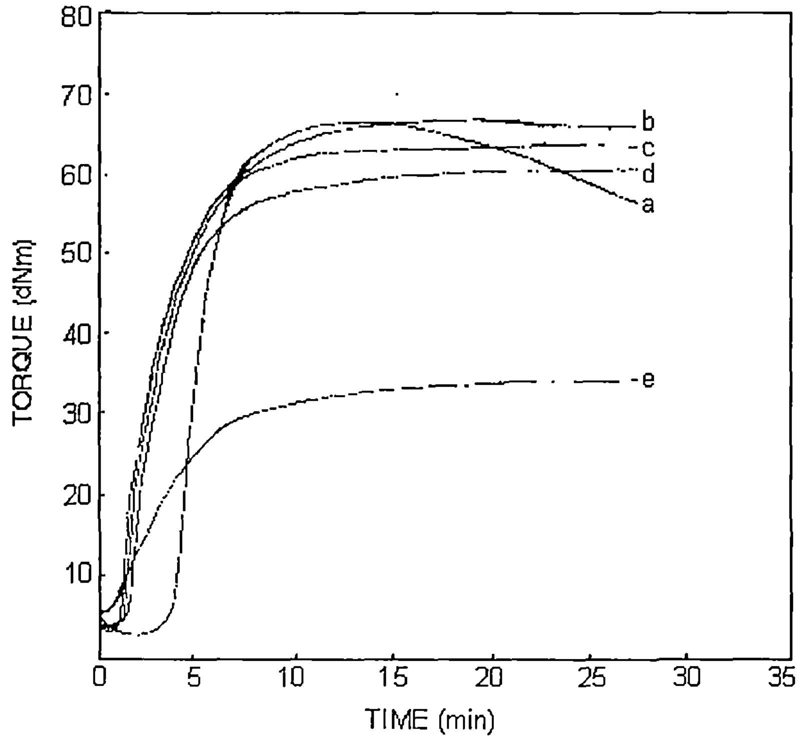


Figure 5.1. Rheographs of NR/DCSBR blend with different composition: (a) NR, (b) 70/30 NR/DCSBR, (c) 50/50 NR/DCSBR, (d) 30/70 NR/DCSBR and (e) DCSBR.

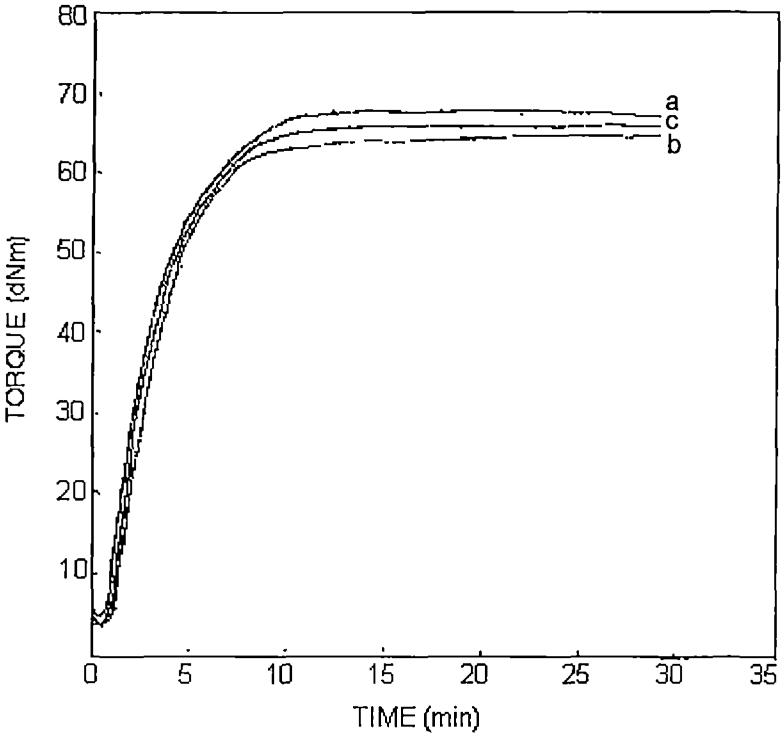


Figure 5.2. Rheographs of 70/30 NR/DCSBR blend containing (a) 0, (b) 5 and (c) 10 phr SBR as compatibiliser.

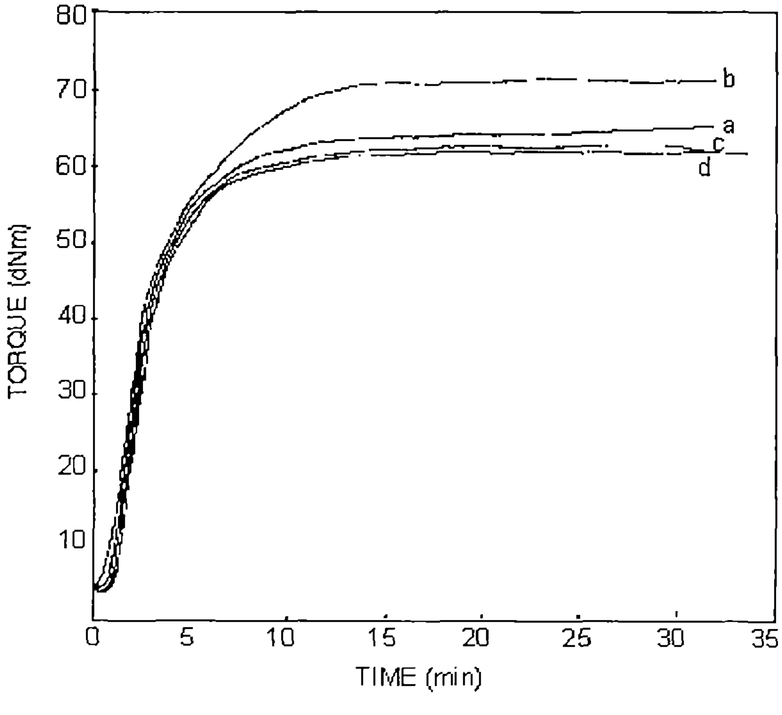


Figure 5.3. Rheographs of 50/50 NR/DCSBR blend containing (a) 0, (b) 5, (c) 10 and (d) 15 phr SBR as compatibiliser.

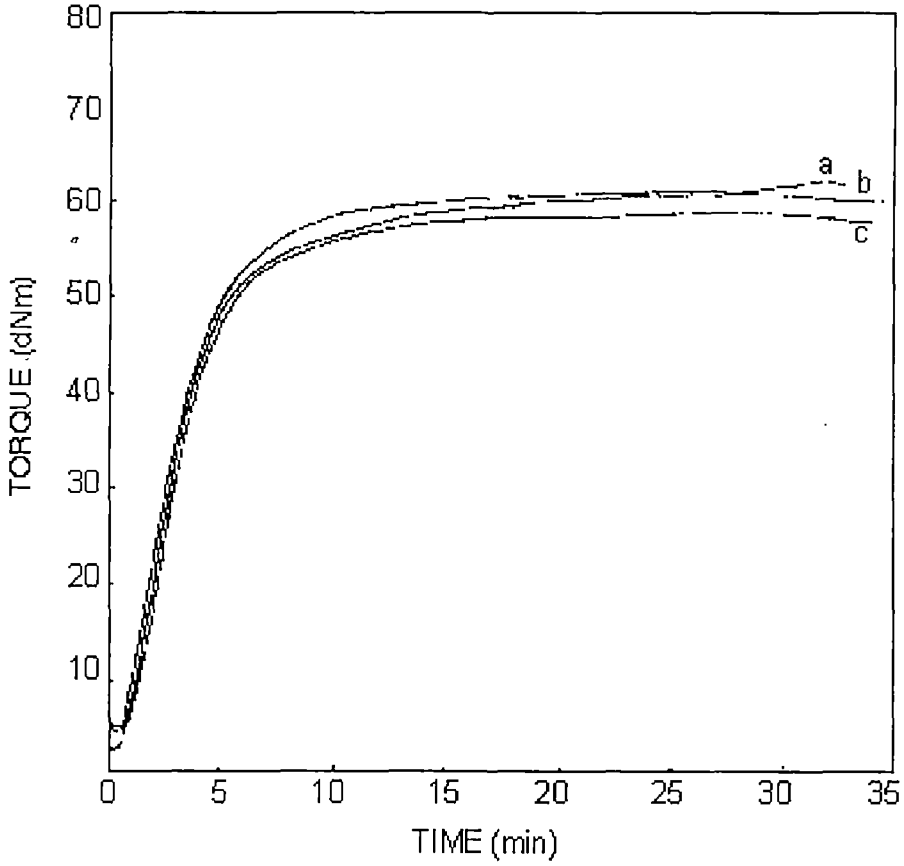


Figure 5.4. **Rheographs of 30/70 NR/DCSBR blend containing (a) 0, (b) 5 and (c) 10 phr SBR as compatibiliser**

Table 5.2. Cure characteristics at 150°C of NR/DCSBR blends compatibilised by SBR

Blend composition	T_{max} (dNm)	Optimum cure time (t_{90}) at 150°C	Scorch time (t_2) at 150°C	Induction time (t_1) at 150°C
NR	69	7.5	3.8	3.5
DCSBR	33	13.5	1.3	1.0
NR/DCSBR 70/30	67	5.3	0.7	0.5
NR/DCSBR 70/30 + 5 phr SBR	63	6.2	0.8	0.6
NR/DCSBR 70/30 + 10 phr SBR	65	5.7	1.1	0.9
NR/DCSBR 50/50	64	6.0	0.7	0.5
NR/DCSBR 50/50 + 5 phr SBR	70	6.5	0.9	0.7
NR/DCSBR570/50 + 10 phr SBR	62	6.2	0.8	0.7
NR/DCSBR 50/50 + 15 phr SBR	61	6.0	0.95	0.75
NR/DCSBR 30/70	61	7.0	1.1	0.9
NR/DCSBR 30/70 + 5 phr SBR	60	7.5	1.0	0.8
NR/DCSBR 30/70 + 10 phr SBR	59	8.5	0.75	0.6

5.3 Characterisation of blends

5.3.1 DSC thermograms

The DSC traces of 50/50 NR/DCSBR blend and the blend containing varying concentration of SBR (5-15 phr) are presented in Figure 5.5. For 50/50 blends, there are two transition, one around -72°C which corresponds to the transition of NR and the other at -55°C that related to the transition of DCSBR. For 1:1 blend containing 5 phr SBR the two thermal transitions merged to a single transition around -60°C. This shows that 5 phr SBR acts as a compatibiliser in NR/DCSBR blends. As the amount of SBR in the blend increases to 10 phr the transition shift to -58°C but still a single transition is observed (Figure 5.1c). When the dosage of SBR become 15 phr again there are two thermal transitions, one at -62°C and other at -50°C. This indicates that at lower concentrations in the range of 5-10 phr SBR acts as a compatibiliser in binary blends of DCSBR and NR, whereas at higher concentration of SBR (15 phr), does not act as a compatibiliser. This is good agreement with the overall mechanical properties, which will be discussed later.

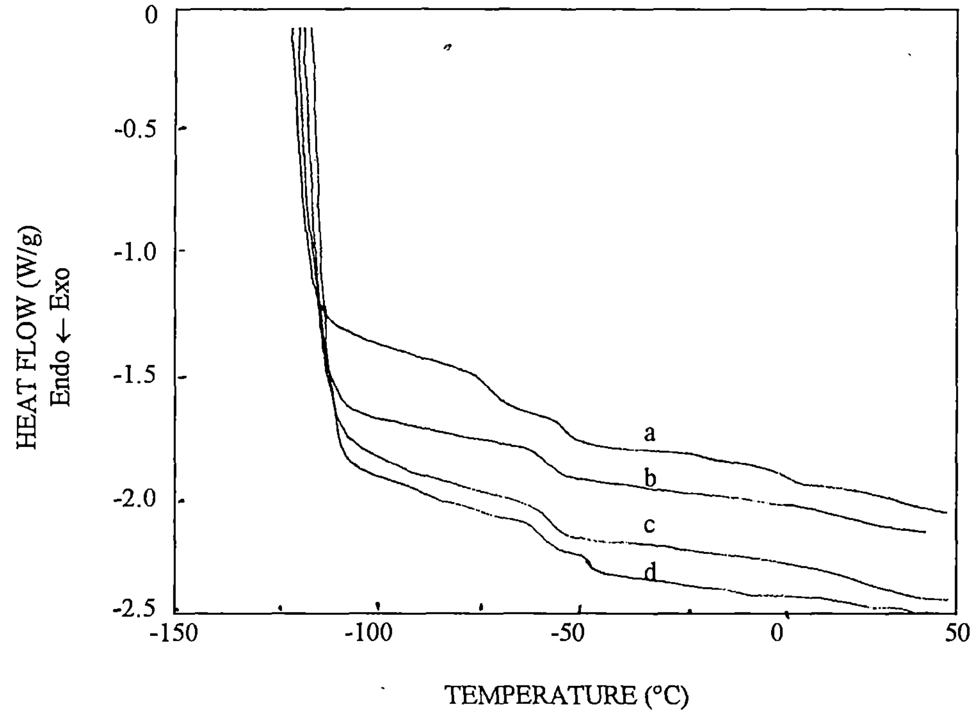
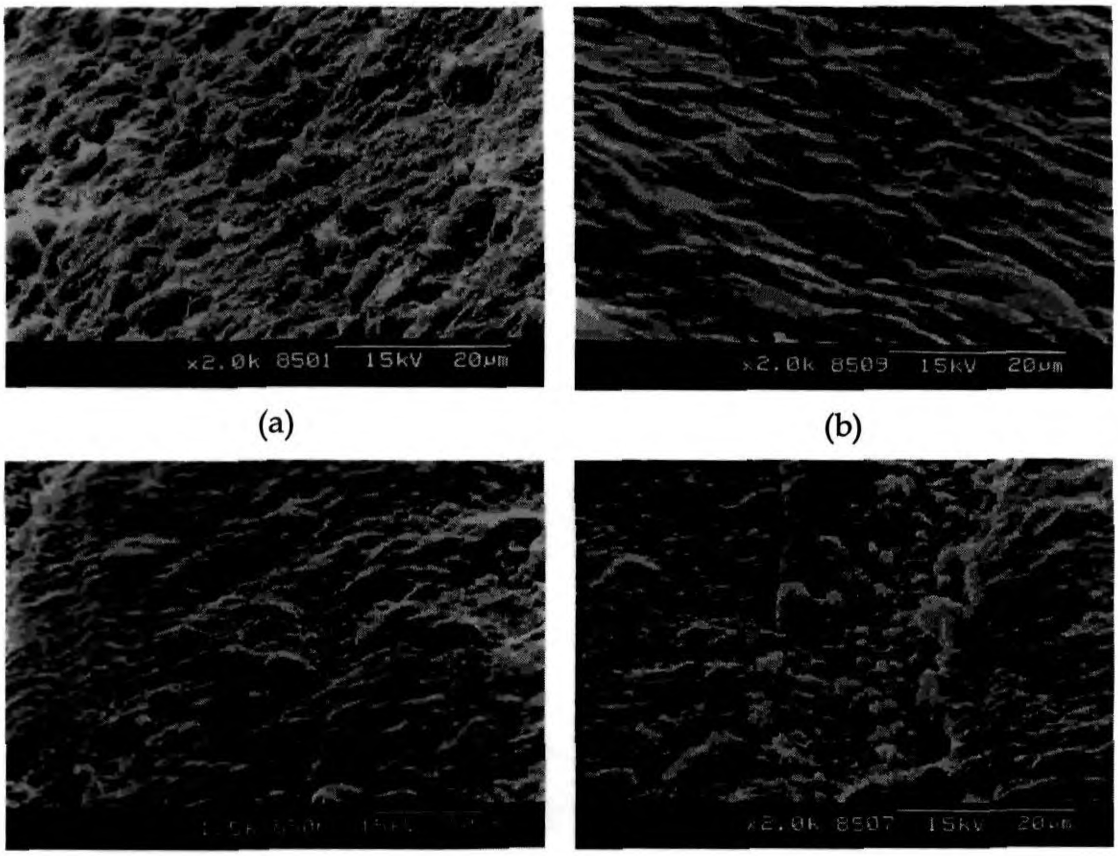


Figure 5.5. **DSC thermograms of 50/50 NR/DCSBR blend: (a) without compatibiliser, (b) compatibiliser with 5 phr, (c) 10 phr and (d) 15 phr**

5.3.2 Scanning Electron Microscopy

The SEM photograph of 1:1 NR/DCSBR blends having 5 to 15 phr loading of compatibiliser are presented in Figure 5.6. The presence of dewetted area indicate the low strength of the material (Figure 5.6a), the dispersed DCSBR phase is much polydispersed in size. But with the addition of 5 phr SBR (Figure 5.6b), the average size of the dispersed domains is much reduced, a fine morphology with uniform average dispersed domain size is observed. This is found to be the optimum compatibiliser loading. As the concentration of SBR increases further (Figure 5.6c), the average size of dispersed domains slightly increases and when the compatibiliser concentration becomes 15 phr (Figure 6d) the average size and polydispersity of the DCSBR phase again increases.



(a) (b)

(c) (d)

Figure 5.6. Scanning electron micrographs of 50/50 NR/DCSBR blends: (a) 0, (b) 5, (c) 10 and (d) 15 phr SBR as compatibiliser.

5.4 Effect of concentration of compatibilisers on technological properties of NR/DCSBR blends

5.4.a Mechanical properties

The mechanical properties of blends of NR/DCSBR are presented in Table 5.3. Compatibilisation with 5-10 parts of SBR greatly enhances the tensile properties of the blend when the concentration of DCSBR is lower or equal to NR. For 70/30 NR/DCSBR blend, higher values of tensile strength are obtained when concentration of SBR is 10 phr whereas in 1:1 composition, 5 phr loading of compatibiliser gives maximum tensile strength.

The improved tensile strength is due to the uniform distribution of the two rubber phases, the compatibiliser aids in the formation of strong interfacial crosslink which facilitate efficient stress transfer between the two phases. The excellent gum strength of the DCSBR compound and that of the compatibilised blend shows that DCSBR also undergoes strain induced crystallisation.[20] This is supported by the stress-strain data analysis using Martin, Roth and Stiechler equation.[21]

$$\ln \frac{\sigma\lambda^2}{\lambda^{-1}} = \ln E_0 + A(\lambda-\lambda^{-1}) \qquad (5.1)$$

where E_0 is Young's modulus at zero strain, λ is the extension ratio required to stretch a piece of rubber vulcanisate (dumbbell shape) and A is a constant at constant temperature. This equation provides a useful indication of the onset of strain-induced crystallisation.[31] A plot of $\ln \sigma\ \lambda^2/\lambda^{-1}$ vs. $\lambda-\lambda^{-1}$ undergoes an abrupt increase of slope (Figure 5.7). This clearly shows that the strain induced crystallisation operate in both NR and DCSBR and this phenomenon is rare in other rubber-rubber blends. Generally the strength of NR is drastically reduced when mixed with other rubbers. At higher dosage of SBR as compatibiliser, a decrease in tensile strength is obtained. This is due to the higher amount of amorphous and weak SBR.

Table 5.3. **Mechanical properties of NR/DCSBR blends**

Properties	NR	DCSBR	70/30 NR/DCSBR (phr)			50/50 NR/DCSBR (phr)				30/70 NR/DCSBR (phr)		
			0	5	10	0	5	10	15	0	5	10
Tensile strength (MPa)	22	17.05	22.48	25.5	33.1	20.2	31.7	25.4	22.1	16.0	16.5	15.4
Modulus 300% (MPa)	2.89	3.9	3.09	3.63	3.71	3.88	3.77	3.99	3.58	3.51	3.63	3.86
Elongation at break (%)	840	525	850	890	790	760	710	680	630	550	500	530
Tear strength (kNm^{-1})	30.4	58.4	43.71	59.09	61.1	36.45	47.97	46.5	39.6	40.4	42.4	43.5
Resilience (%)	77	30	50.8	52	53	36	35	35	36	32	30	30.7
Compression set (%) 22 h for 70°C	21.2	13.5	19.9	16.0	15.8	18	16.7	16.3	16.1	15.9	17.5	16.9
Heat build-up (°C)	10	11	12	12	11	13	14	13	13	15	18	14
DIN abrasion loss (mm^3)	140.3	69.8	118.5	97.3	86.8	107.1	76.2	79.6	71.4	85.7	78	71.4

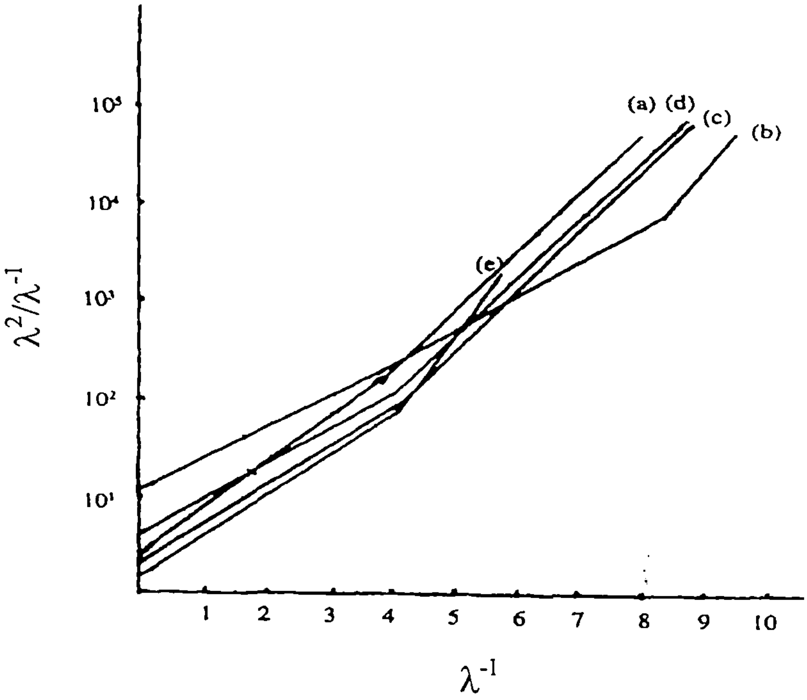


Figure 5.7. Stress-strain relationship in extension, plotted according to Martin, Roth and Stiehler equations of NR/DCSBR blend: (a) NR, (b) 70/30 NR/DCSBR, (c) 50/50 NR/DCSBR, (d) 30/70 NR/DCSBR and (e) DCSBR

Compatibilised blend shows a higher tear strength as compared to uncompatibilised blends (Table 5.3). The superior tear strength is observed for 70/30 NR/DCSBR blend, the compatibiliser creates efficient stress transfer leading to elongated DCSBR domains. The elongated DCSBR domains present in the tear path elongate to a higher strain and obstruct tear propagation. This increase the tear strength of 70/30 composition with 10 phr loading of compatibiliser while 5 phr loading is enough for 1:1 compositions.

Compression set value is strongly dependent on the elastic recovery of the sample. For compatibilised blends, the percentage of set is lower than that of uncompatibilised blends. As the loading of compatibiliser increases, the set decreases for 70/30 and 30/70 NR/DCSBR compositions. In 50/50 blends, a lower set is noted for 5 phr compatibiliser concentration. This is because the dispersed domains will respond differently in the stress-relaxation process (after compression period) and decreases the set values.

Table 5.3 reveals that the abrasion resistance of DCSBR is better than that of NR. Compared to uncompatibilised blends, compatibilised samples show a higher abrasion resistance. Similarly as the loading of compatibiliser increases the abrasion resistance also increases. This is due to the compatibilising action of SBR.

Heat build-up values of NR/DCSBR blends given in Table 5.3 indicate that all the three compatibilised blends presents the lower heat build-up values at 10 phr loading of SBR.

Resilience values of NR/DCSBR blends increase with increase in concentration of NR. Lower resilience is observed for compatibilised samples, but as the loading of compatibiliser increases up to 10 phr, resilience also increases (Table 5.3).

5.4.b Ageing resistance

The resistance of the rubber vulcanisates to thermal ageing is considered as an essential requirement for better service performance of products. The percentage of decreases in tensile strength as a result of ageing at 70°C for 96 h is presented in Table 5.4. The ageing resistance decreases with increase in NR content. Comparatively higher ageing resistance is obtained for compatibilised blend. As the concentration of compatibiliser increases above 5 phr in 50/50, a decrease of tensile strength is observed. This again confirms the compatibilisation efficiency of SBR in the blend.

Table 5.4. Effect of air ageing on mechanical properties of NR/DCSBR blend at 70°C 96 h.

Blend composition	Decrease in tensile strength (%)	Decrease in elongation at break (%)
NR	68.1	41.2
DCSBR	12.3	14.4
NR/DCSBR 70/30	59.9	39.5
NR/DCSBR 70/30 + 5 phr SBR	53.1	38.3
NR/DCSBR 70/30 + 10 phr SBR	51.3	36.0
NR/DCSBR 50/50	52.3	29.6
NR/DCSBR 50/50 + 5 phr SBR	52.0	17.6
NR/DCSBR 50/50 + 10 phr SBR	51.4	16.9
NR/DCSBR 50/50 + 15 phr SBR	51.0	20.3
NR/DCSBR 30/70	39.6	24.5
NR/DCSBR 30/70 + 5 phr SBR	40.3	14.9
NR/DCSBR 30/70 + 10 phr SBR	40.0	12.3

5.4.c Oil ageing

The ASTM oil swelling values of NR/DCSBR blends given in Table 5.5 indicates that dichlorocarbene modified SBR has a much higher oil resistance than NR. The oil resistance of DCSBR is comparable to that of NBR.[29] It is found that better oil resistance is obtained for the entire blend ratio, and the oil resistance is decreased with increase in concentration of NR. The combined effect of better oil resistance with a low compression set enables NR/DCSBR blend for oil seal application.

Table 5.5. Comparative evaluation of swelling behaviour of NR/DCSBR blend in ASTM oils for 5 days at room temperature.

Blend composition	ASTM oil (%)		
	No. 1	No. 2	No. 3
NBR*	0.34	0.51	0.68
NR	12.47	21.59	58.78
DCSBR	0.9	1.6	4.95
70/30 NR/DCSBR	9.62	15.85	52.91
50/50 NR/DCSBR	4.43	9.94	45.5
30/70 NR/DCSBR	2.59	5.25	29.3

*NBR - 100, stearic acid - 1, ZnO - 5, CBS - 1.5, TMTD - 1, Sulphur - 0.5

5.5 Crosslink density from swelling and stress-strain behaviour

The crosslink density values obtained from swelling data[22] for NR/DCSBR blends are given in Table 5.6. For uncompatibilised blends the crosslink density is decreases with increase in concentration of NR. Higher crosslink density is observed for compatibilised blends and as the dosage of compatibiliser increases the crosslink density also increases. This is because of the restriction of swelling which causes an increase in ϕ, which in turn increases the crosslink density. In a particular blend composition, crosslink density is higher for blends containing SBR (5-10 phr) as compared to blends without compatibiliser. As seen from the table the volume of solvent absorbed decreases as concentration of DCSBR in the blend increases, because DCSBR restricts swelling by hexane in the blends. Hence at higher concentration of DCSBR in blend a higher restriction to swelling is observed, even though there is a lower rheometric torque.

Table 5.6. Crosslink density values from swelling and stress-strain data

Blend composition	Swelling index (%)	Flory-Rehner equation	Mooney-Rivlin equation
NR	295	3.1×10^{-5}	3.04×10^{-3}
DCSBR	160	1.3×10^{-5}	1.06×10^{-3}
NR/DCSBR 70/30	279	2.5×10^{-5}	1.96×10^{-3}
NR/DCSBR 70/30 + 5 phr SBR	266	6.88×10^{-5}	2.04×10^{-3}
NR/DCSBR 70/30 + 10 phr SBR	250	1.24×10^{-4}	2.38×10^{-3}
NR/DCSBR 50/50	248	5.0×10^{-5}	1.75×10^{-3}
NR/DCSBR 50/50 + 5 phr SBR	240	9.81×10^{-5}	2.88×10^{-3}
NR/DCSBR 50/50 + 10 phr SBR	233	1.58×10^{-4}	2.27×10^{-3}
NR/DCSBR 50/50 + 15 phr SBR	230	2.36×10^{-4}	2.15×10^{-3}
NR/DCSBR 30/70	220	5.95×10^{-4}	1.02×10^{-3}
NR/DCSBR 30/70 + 5 phr SBR	216	6.03×10^{-4}	1.6×10^{-3}
NR/DCSBR 30/70 + 10 phr SBR	216	6.03×10^{-4}	1.8×10^{-3}

The crosslink density values (ν_{phys}) calculated using Mooney-Rivlin equation[23-25] is given in Table 5.6. It can be seen that ν_{phys} is following the same trend as given by swelling studies. The crosslink density increases in presence of SBR as a compatibiliser. Thus the observed tensile strength variation can be exactly correlated with the variation of ν_{phys} from Mooney-Rivlin equation and the crosslink density data from swelling studies. Moreover, the value of ν_{phys} is higher for compatibilised and uncompatibilised samples compared to that of crosslink density from swelling studies. In swelling studies of these samples, crosslinks are flexible to penetrants, but as the loading of compatibiliser increases, notable restriction of swelling is observed. The discrepancy between crosslink density determined by chemical analysis and by the application of stress-strain equation is partly due to the entanglements of interpenetrating network chains which behave as crosslinks and partly by the presence of elastically ineffective chain ends. This shows that there is sufficient molecular mixing of NR/DCSBR in presence of SBR.

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CHAPTER

6

COMPATIBILISATION OF SBR/NBR BLENDS WITH DICHLOROCARBENE MODIFIED STYRENE BUTADIENE RUBBER

Section 6.2 of this chapter has been communicated
to *J. Macromol. Sci. Pure Appl. Chem.*

Section 6.3 of this chapter has been communicated
to *J. Polym. Sci. Phys. Edn.*

6.1 Introduction

Polymer blends are considered as mixtures of macromolecular species. The necessary condition is that the amount of minor component must exceed at least five per cent by weight. Most of the polymer blends are found to be immiscible and incompatible. In the case of miscible blends, the overall physicomechanical properties depends on two structural parameters: (a) proper interfacial tension which leads to a phase size small enough to allow the material to be considered as macroscopically homogeneous, (b) an interphase adhesion strong enough to assimilate stresses and strains without disruption of the established morphology. This unfortunately is not the case for most polymer blends.[1-3]

Nitrile rubber is primarily noted for its oil and chemical resistance. Oil resistance specified for the rubber products vary to a considerable extent. It is possible to use a blend of high acrylonitrile NBR with styrene butadiene rubber to get a degree of oil resistance equal to that given by a low acrylonitrile NBR with an overall economy in cost. Products from high acrylonitrile NBR have a tendency to shrink in contact with hot lubricating oils and replacement of a part of it by SBR overcomes this defect. Along with oil resistance property, oil seals and gaskets sometimes require lower compression set resistance at higher temperatures. Compression set resistance can be improved by blending with SBR. SBR can also improve its processing properties. Blends of SBR and NBR are found to be immiscible[20] and they can possibly be made miscible by using compatibilisers that can have interactions with SBR and NBR. Some segments of the compatibilisers is chemically identical to SBR, and it is possible to have interaction with the chlorine of compatabilisers and acrylonitrile unit of NBR. This chapter discusses the effect of DCSBR with varying chlorine content and also the loading of DCSBR with 25% chlorine content as a compatibiliser in SBR/NBR blends with reference to their cure characteristics, mechanical properties, oil resistance and swelling behaviour.

6.2 Effect of chlorine content of dichlorocarbene modified styrene butadiene rubber on the miscibility and mechanical properties of SBR/NBR blends

6.2.1 Processing characteristics from rheometric data

The basic formulation using the study is given in Table 6.1. The commonly used sulphenamide (CBS) as primary accelerator and TMTD as secondary accelerator used in bends as they are known to produce satisfactory levels of cure in both SBR and NBR. An idea about the crosslinking within a phase and the crosslinking between the two phases can be obtained from the cure characteristics and mechanical properties of rubbers. There will be insufficient crosslinking between the phases if the two rubbers do not mix properly, which will be reflected in poor mechanical properties.

Table 6.1. Formulation of SBR/NBR blends

Ingredients	N_3	N_5	N_7	N_7*	N_5*	N_3*
SBR	70	50	30	70	50	30
NBR	30	50	70	30	50	70
DCSBR*	-	-	--	5	5	5
Stearic acid	1.2	1.0	0.8	1.2	1.0	0.8
Zinc oxide	5	5	5	5	5	5
Antioxidant TDQ	1.0	1.0	1.0	1.0	1.0	1.0
CBS	0.7	0.5	0.3	0.7	0.5	0.3
TMTD	0.3	1.0	0.7	0.3	1.0	0.7
Sulphur	1.69	1.35	1.01	1.69	1.35	1.01

*DCSBR containing (A) 15, (B) 20, (C) 25, (D) 30, (E) 35% chlorine content respectively.

The rheographs of the mixes are given in Figures 6.1-6.3. In all the blend composition there is a considerable enhancement in torque on addition of DCSBR of chlorine content varying from 15 to 35% at a concentration of 5 phr. The rheometric torque increases as the SBR content in the blend increases. TMTD has a tendency to migrate to the polar rubbers. As the content of SBR increases, there is lesser possibility for migration of accelerator, with the result in SBR/NBR there is a higher crosslinking. As NBR content increases it is probable that due to migration of TMTD, the overall crosslinking will be less. The torque increases progressively with the chlorine content of DCSBR, up to 25% and then decreases in all blend compositions. The presence of DCSBR enhances the effect of inter diffused chains leading to optimum vulcanisation.

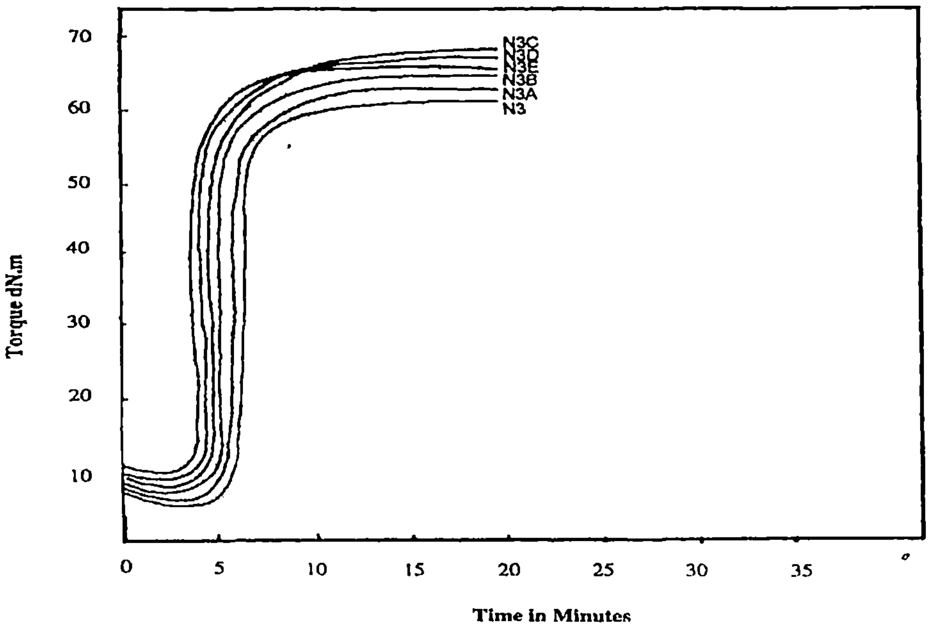


Figure 6.1. Rheographs of 70/30 SBR/NBR blend and compatibilised blend containing 5 phr DCSBR varying chlorine content: (A) 15, (B) 20, (C) 25, (D) 30 and (E) 35%.

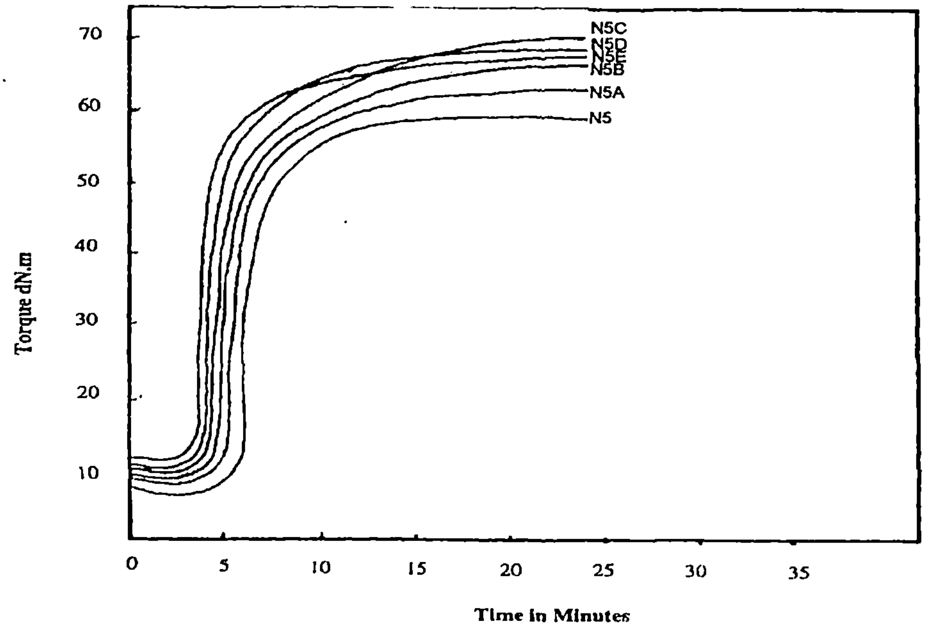


Figure 6.2. Rheographs of 50/50 SBR/NBR blend and compatibilised blend containing 5 phr DCSBR of varying chlorine content: (A) 15, (B) 20, (C) 25, (D) 30 and (E) 35%.

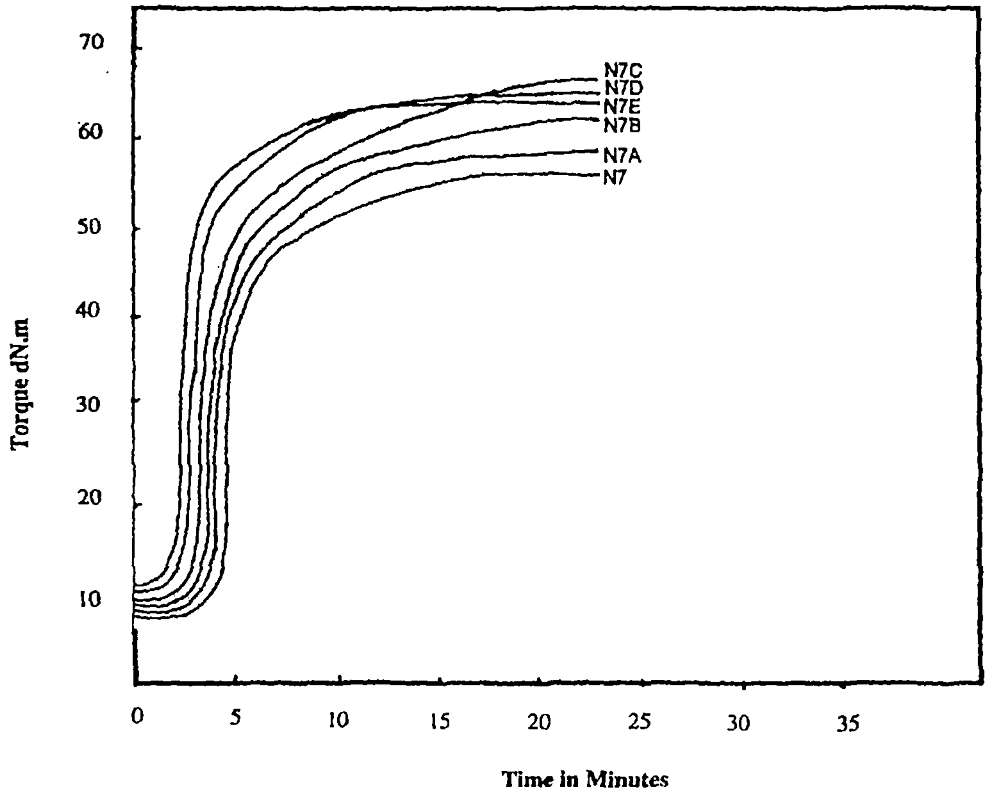


Figure 6.3. **Rheographs of 30/70 SBR/NBR blend and compatibilised blend containing 5 phr DCSBR of varying chlorine content: (A) 15, (B) 20, (C) 25, (D) 30 and (E) 35%.**

The cure characteristics of the blends are presented in Table 6.2. The optimum cure time of pure blends increases whereas scorch time and induction time decreases as the NBR content of the blend increases. The addition of DCSBR brings about a decrease in scorch time and induction time in all blends, showing effective crosslinking due to increased molecular level homogeneity. The optimum cure time of the blend increases as the chlorine content of DCSBR increases, up to 25% and then decreases in all the blend ratios. This is because of the large interfacial area formed by the uniformly distributed blend matrix. Since more time is needed for the formation of greater number of interface crosslinks, the optimum cure time is found to be maximum here. But as the chlorine content increases further the homogenising efficiency decreases which results in the coalescence of dispersed domains. This reduces the interfacial area and thereby causes a decrease in optimum cure time. This data predicts the behaviour of DCSBR as a compatibilised in SBR/NBR blend which is further confirmed by following techniques.

Table 6.2. Cure characteristics of SBR/NBR blends compatibilised by DCSBR

Blend composition	Chlorine content of DCSBR (%)	Optimum cure time at 150°C (t_{90}) (min)	Scorch time at 150°C (t_2) (min)	Induction time at 150°C (t_1) (min)
SBR/NBR 70/30	0	7.5	5.5	5
	15	7.5	5	4.5
	20	8.0	4.5	4
	25	8.5	4	3.5
	30	6.0	3.5	3
	35	5.0	3	2.5
SBR/NBR 50/50	0	9.0	4.5	4
	15	9.5	4	3.75
	20	10.5	3.75	3.25
	25	11.5	3.5	3
	30	9.0	3.25	2.75
	35	8.0	3	2.5
SBR/NBR 30/70	0	10.0	4.25	3.75
	15	10.5	3.75	3.25
	20	11.5	3.5	3
	25	13.5	3.25	2.75
	30	9.0	3	2.5
	35	7.0	2.75	2.25

6.2.2 Characterisation of blend

6.2.2.a *Thermal analysis*

The DSC traces of pure SBR, NBR and their blends (1:1 mix) in the presence and absence of compatibiliser are presented in Figure 6.4 and the thermal transition data are shown in Table 6.3. Pure SBR shows a T_g at -56°C[5] and pure NBR (containing 34% ACN) shows two transition[6] at -38°C and -28°C. For uncompatibilised 50/50 blend, there appears to be two transitions in the temperature range from -68 to -26°C which shows the presence of microlevel inhomogeneity. 50/50 blend with 5 phr DCSBR of 15% chlorine content shows some microlevel inhomogeneity with two transition at -58°C and -25°C revealing that DCSBR containing low level of chlorine content (up to 15%) is not very efficient as a compatibiliser in SBR/NBR blend. However 50/50 blend with 5phr (5 parts per100 parts rubber) of 25% chlorine containing DCSBR shows a single transition at -44°C in the temperature range of -68 to -29°C, showing that DCSBR acts as a compatibiliser in the blends of SBR/NBR. This is because, as chlorine content of DCSBR increase, there is enhanced interaction between chlorine of DCSBR with acrylonitrile unit of NBR, thus reducing interfacial tension. Many copolymers are known to reduce interfacial tension in blends of dissimilar polymers due to their interfacial activity.[7-14]

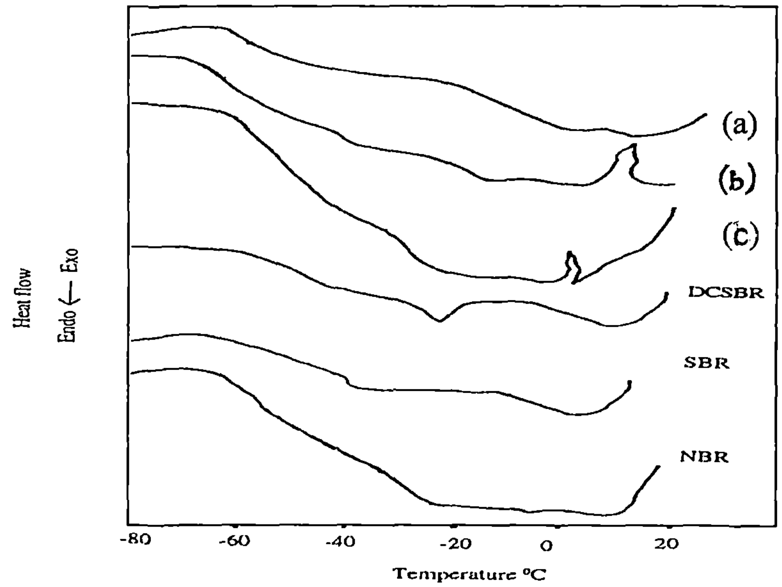


Figure 6.4. DSC thermograms of NBR, SBR, DCSBR, 50/50 SBR/NBR blend: (a) without compatibiliser, (b) compatibiliser with 15% and (c) with 25% chlorine content

Table 6.3. DSC thermal characteristics data of DCSBR, SBR, NBR and their blends

Samples	T_g, °C	Temperature range of transition, °C
DCSBR	-40	-58 to -20
SBR	- 56	-62 to -40
NBR	- 38, - 28	-65 to -35, -35 to -26
N5	- 56, - 28	-59 to -44, -33 to -18
N5A	- 56, - 28	-59 to -44, -33 to -18
N5 C	- 44	-59 to -28

6.2.2.b Dynamic mechanical analysis

Figures 6.5 represents the plot of storage modulus versus temperature for SBR and NBR. It is clear from the plot that there is a transition in storage modulus of SBR for a temperature range -35 to -14°C. In the case of NBR the transition in storage modulus occurs in the temperature range -49 to -32°C. There is also another weak transition in the temperature range -25 to -6°C. It can be seen that SBR shows slightly higher storage modulus than NBR.

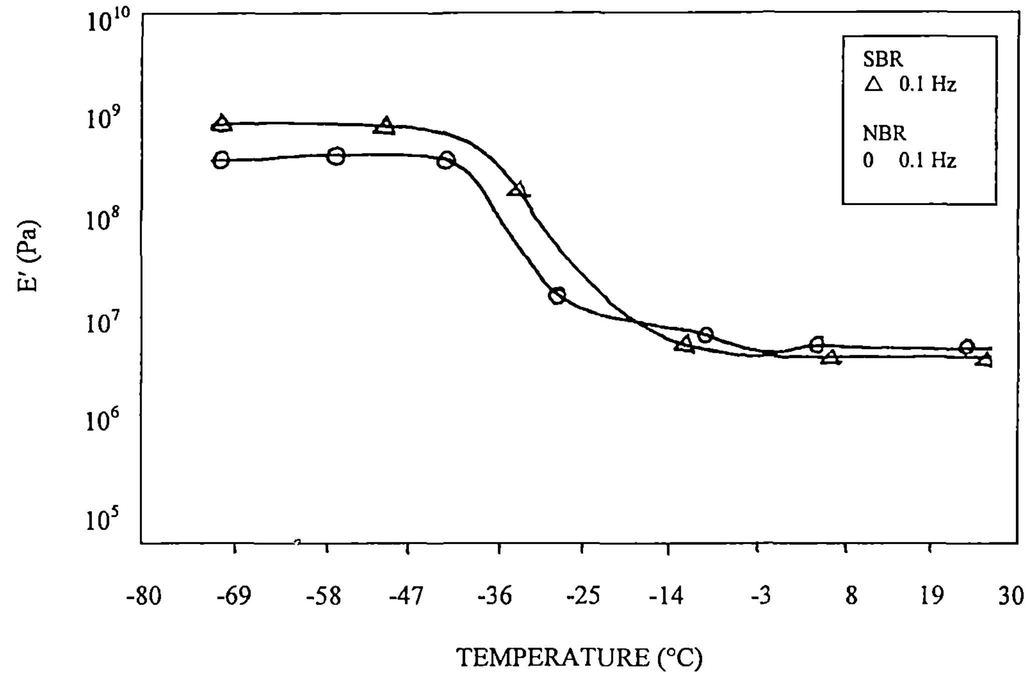


Figure 6.5. Variation of storage modulus E′ at different frequencies of SBR and NBR

The variation of storage modulus with temperature for the uncompatibilised and compatibilised 50/50 blend is presented in Figure 6.6. It is clear that uncompatbilised and compatibilised samples show higher storage modulus compared to individual components. The pure 50/50 blend shows two transition in storage modulus in the temperature -50 and -14°C. This reveals its incompatibility. After addition of 15% chlorine containing DCSBR (N5A) the drop in storage modulus is again in two step process. But when the chlorine content of DCSBR increases to 25% (N5C), there is only a single transition in storage modulus around -25°C, thus revealing that DCSBR acts as a compatibiliser in SBR/NBR blends.

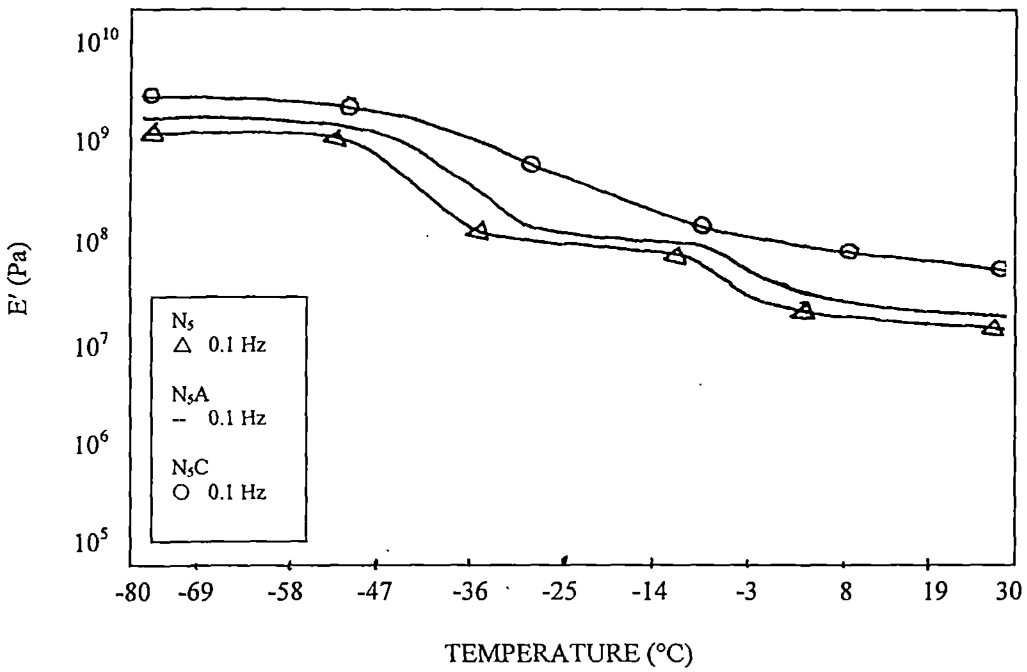


Figure 6.6. Variation of storage modulus E′ at different frequencies of 50/50 SBR/NBR blends (N_5), blend with 15% (N_5A) and 25% (N_5C) chlorine containing DCSBR, respectively

The above explained behaviour could be seen very clearly in the plots of loss modulus and tan delta. The loss modulus variation with respect to temperature is presented in Figure 6.7. The loss modulus reaches a peak value for SBR sample at -30°C while in the case of NBR, there are two maxima at -17 and -9°C. This presence of two T_g for NBR is already reported.[6]

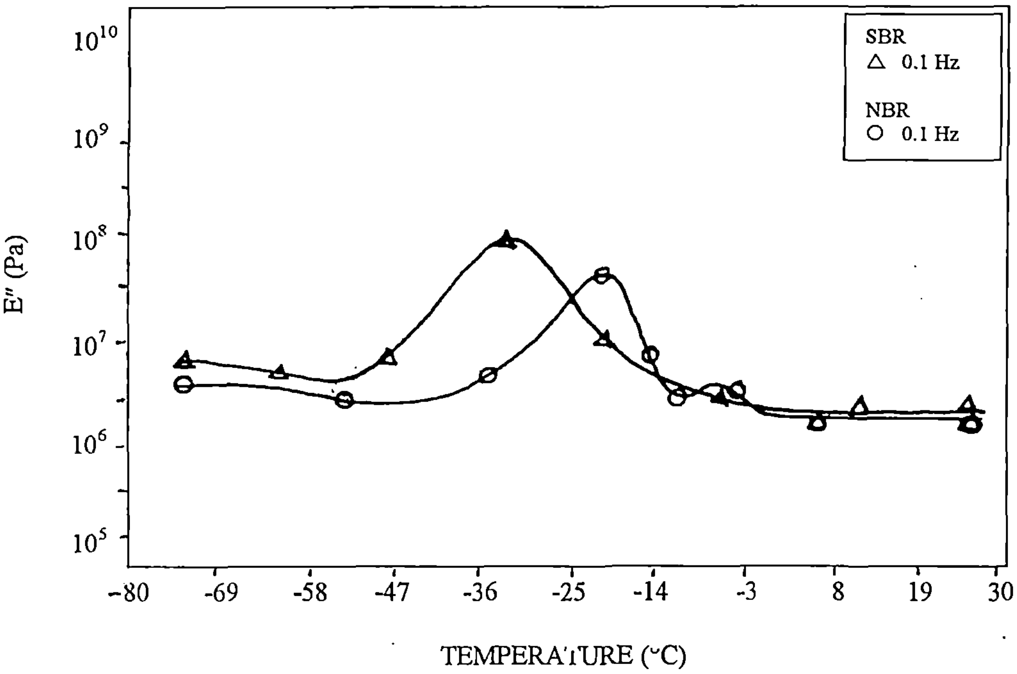


Figure 6.7. Variation of loss modulus E" at different frequencies of SBR and NBR

Blends record a lower value of loss modulus as compared to pure SBR and NBR (Figure 6.8). In the case of 50/50 blend there are two maxima in viscous modulus at -34.67°C and -12.7°C. However, with the addition of 5 phr of 25% chlorine containing DCSBR (N_5C), the presence of two peaks is no longer visible, instead a single peak at -25.8°C appears. When the chlorine content of DCSBR is 15%, (N_5A), then again two peaks with maxima at -32°C and -13°C. This shows that compatibiliser with a chlorine content of 15% is not sufficient to saturate the interface.

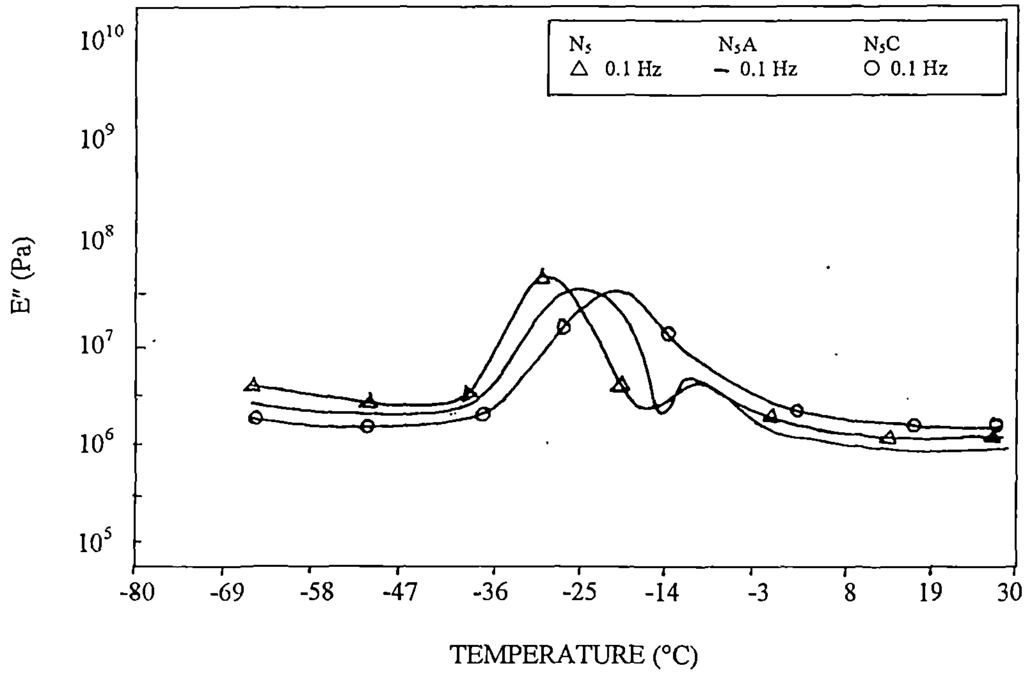


Figure 6.8. Variation of loss modulus E" at different frequencies of 50/50 SBR/NBR blends (N_5), blend with 15% (N_5A) and 25% (N_5C) chlorine containing DCSBR, respectively

The tan delta plots for the similar compositions are given in Figure 6.9 and 6.10. The T_g obtained from the temperature corresponding to a maximum in tan delta is shown in table 6.4. SBR presents a slightly higher tan delta value (damping) compared to NBR. SBR shows a T_g at -27.5°C while that of NBR shows two Tg's one at -22°C and another at -8°C. The blends have a lower values of damping as compared with the individual components. The 50/50 blend shows two T_g's at -36° and -18°C, due to the presence of two immiscible SBR and NBR phases. In the 50/50 blend containing 5phr 25% chlorine containing DCSBR (N5C), there is only one T_g at -25°C which proves the formation of a miscible SBR/NBR blend.

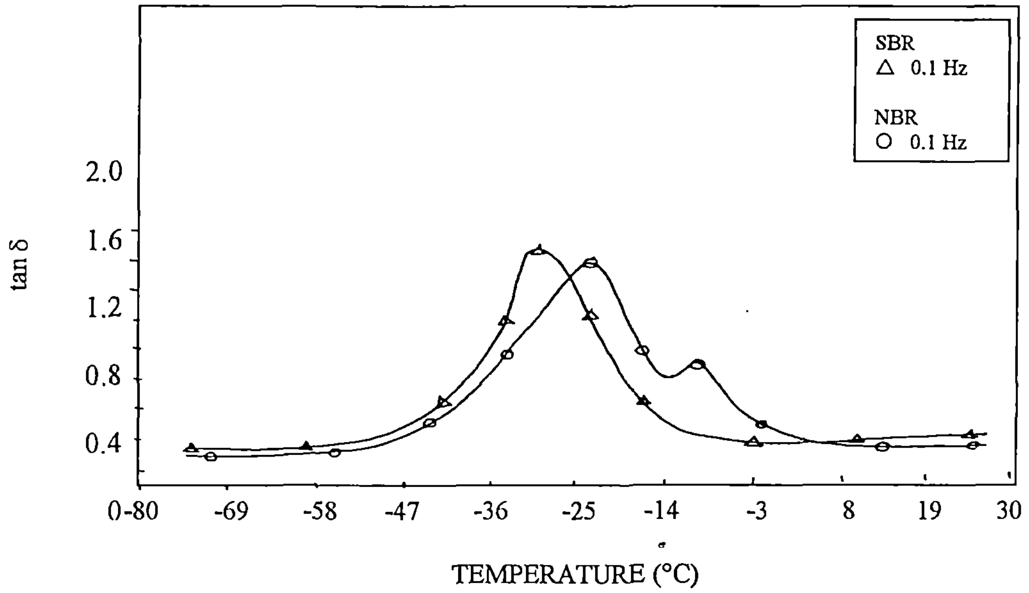


Figure 6.9. Variation of tan δ at different frequencies of SBR and NBR

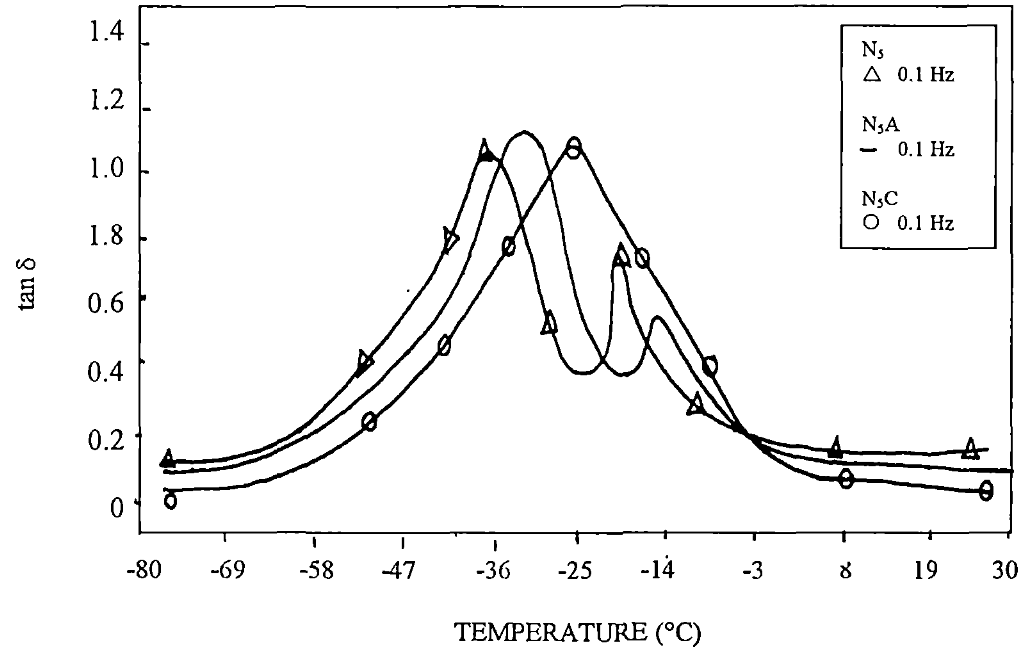


Figure 6.10. Variation of tan δ at different frequencies of 50/50 SBR/NBR blends (N_5), blend with 15% (N_5A) and 25% (N_5C) chlorine containing DCSBR, respectively

Table 6.4 **T_g determined from maxima in viscous modulus and damping at a frequency 0.1 Hz.**

Samples	Viscous modulus (°C)	Tan δ (°C)
SBR	- 29.5	
NBR	- 17, - 9	-22.5, -7
N5	- 34.67, - 12.7	-36, -18
N5A	- 32.4, - 12.1	-34, -14
N5 C	- 25.8	-26.5

6.2.3 Effect of compatibiliser on technological properties

The variation in mechanical properties with varying chlorine content of the compatibiliser on SBR/NBR blends is given in Tables 6.5a-c. Compared to uncompatibilised blends compatibilised sample show an increase in the over all tensile strength. A comparatively higher increase in tensile strength is observed for 30/70 and 50/50 SBR/NBR blends showing that compatibilising action is efficient in these compositions. The compatibilising action is due to the interaction of acrylonitrile of NBR and chlorine of DCSBR. Similar to compatibilising action of CR in NR/NBR blends.[15] There is structural similarity between some segments of compatibiliser and SBR. This also promotes compatabilising action of DCSBR in the blends. If the segments of the added copolymer are chemically identical,[12,16-19] with those of in the respective phases or adhered to one of the phases[20-22] then they acts as efficient compatibilisers. As the concentration of NBR in the blend decreases the probable interaction between the blend component and compatibiliser decrease. The tensile strength is not governed by overall crosslinking alone, it depends on crosslink distribution and phase size. There is higher homogeneity of mixing and more uniform mixing of the rubbers in presence of compatibilisers as the NBR content in the blend is higher or equal to that of SBR. In SBR/NBR blends, the tensile strength increases as the chlorine content of the compatibiliser increases, up to 25% and then decreases. Efficient compatibilisation by 25% chlorine containing compatibiliser creates strong interfacial crosslinks which facilitate efficient stress transfer to the well dispersed SBR/NBR domains. The tear strength increases with increase in NBR content and enhances considerably on addition of the compatibilising agent. DCSBR with 25% chlorine content brings about higher tear strength for all compatibilised blends.

It is obvious that the compression set decreases with increase in SBR content of the blend. Compatibilised blends show a lower compression set than that of the uncompatibilised blends. The decrease in drop is maximum for 25% chlorine containing compatibiliser for 30/70 and 50/50 SBR/NBR compositions. Similarly a higher resilience is observed for blends containing DCSBR. The resilience progressively decreases as SBR content in the blend decreases. Hardness increases as NBR content in the blend increases. The uncompatibilised blends exhibit lower hardness as compared to compatibilised blends. This is due to the higher crosslinking in presence of compatibiliser.

Table 6.5a. Physical properties of blends of 70/30 SBR/NBR compatibilised by DCSBR of chlorine content varying from 15-35%.

Properties	Percentage of chlorine containing DCSBR used at 5 phr concentration					
	0	15	20	25	30	35
Modulus, 300% (MPa)	2.8	2.24	2.76	3.47	2.36	1.91
Tensile strength (MPa)	2.9	3.1	4.7	5.2	5.1	4.4
Elongation at break (%	310	350	420	555	490	415
Tear strength (kN/m)	15.7	16.5	18.9	22.8	20.5	20
Hardness (Shore A)	40	40	42	44	46	48
Resilience (%) (Dunlop tripsometer)	68	68	70	71	70	69
Compression set (%) 22 h at 70°C	17.5	17.4	16	15.6	16.2	17

Table 6.5b. Physical properties of blends of 50/50 SBR/NBR compatibilised by DCSBR of chlorine content varying from 15-35%.

Properties	Percentage of chlorine containing DCSBR used at 5 phr concentration					
	0	15	20	25	30	35
Modulus, 300% (MPa)	2.51	2.73	2.81	3.18	3.01	2.62
Tensile strength (MPa)	3.5	4.0	4.6	6.2	5.5	5.1
Elongation at break (%	325	380	460	515	460	400
Tear strength (kN/m)	16.1	19.9	20.6	22.8	24.4	23.2
Hardness (Shore A)	41	41	42	44	46	48
Resilience (%) (Dunlop tripsometer)	62	63	65	67	63	67
Compression set (%) 22 h at 70°C	18	16.3	15.8	14.2	14.6	15.2

Table 6.5c. Physical properties of blends of 30/70 SBR/NBR compatibilised by DCSBR of chlorine content varying from 15-35%

Properties	Percentage of chlorine containing DCSBR used at 5 phr concentration					
	0	15	20	25	30	35
Modulus, 300% (MPa)	1.99	2.21	2.35	2.7	2.61	2.5
Tensile strength (MPa)	3. 0	4.1	4.7	6.8	4.6	4.2
Elongation at break (%	360	365	480	450	400	355
Tear strength (kN/m)	18.8	19.3	21.53	22.8	22.5	22
Hardness (Shore A)	42	42	44	46	47	48
Resilience (%) (Dunlop tripsometer)	58	59	60	62	64	66
Compression set (%) 22 h at 70°C	18.3	17.4	16.0	15.6	16.8	17.8

Oil resistance

The oil resistance of SBR/NBR blends in the presence and absence of compatibiliser are presented in Table 6.6. Blending SBR with NBR imparts considerable oil resistance to the blend which is improved by the addition of DCSBR. Compatibilised blend shows a higher oil resistance and lower compression set enabling it for use in oil seal application.

Ageing resistance

As seen from Table 6.6 ageing resistance of the blend improves with addition of compatibiliser and also with its chlorine content. This is attributed to the enhanced crosslink density obtained as revealed further from swelling studies.

Table 6.6. Air ageing (96 h at 70^0C) and oil resistance (5 days at 25^0C) of SBR/NBR blends

Blend composition	Chlorine content of DCSBR (%)	Swell in ASTM Decrease in % (w/w)			Change in tensile properties	
		ASTM oil No 1	ASTM oil No 2	ASTM oil No 3	Decrease in tensile strength (%)	Decrease in EB (%)
SBR	-	9.28	15.94	52.78	32	19.8
NBR	-	0.34	0.51	0.68	31	19.0
SBR/ NBR 70/30	0	6.68	11.31	37.15	39	20
	15	6.65	11.28	37	37	18
	20	6.61	11.25	36.5	36	17
	25	6.58	11.2	36.1	34	16
	30	6.55	11.18	35.6	35	15
	35	6.53	11.12	35.2	35	13
SBR/ NBR 50/50	0	4.81	8.32	26.73	42	24
	15	4.74	8.11	25.96	44	22
	20	4.69	7.97	25.51	46	21
	25	4.41	7.9	25.23	49	20
	30	4.56	7.81	25.03	48	19
	35	4.54	7.75	24.81	46	19
SBR/ NBR 30/70	0	3.02	5.14	16.31	45	26
	15	2.95	4.91	15.33	43	25
	20	2.88	4.69	14.73	41	22
	25	2.8	4.46	13.95	40	21
	30	2.74	4.23	13.16	38	20
	35	2.67	4.01	12.39	37	18

6.2.4 Effect of chlorine content of compatibiliser on swelling behavior

(a) Swelling parameters

The extent of swelling data of SBR/NBR blends after swelling in *n*-heptane at room temperature for 24 h is presented in Table 6.7. The swelling index and swelling coefficient (α)[23] values are calculated, using equations 6.1 and 6.2.

$$\text{Swelling index (\%)} = \frac{(W_2 - W_1)}{W_1} \times 100 \qquad (6.1)$$

W_1 = initial weigh of the sample
W_2 = final or swollen weight of the sample

$$\text{Swelling coefficient} = \frac{A_s}{m} \times \frac{1}{s} \qquad (6.2)$$

A_s = amount of solvent absorbed
m = initial weight of the sample
s = density of the solvent used

Higher these values higher will be the extent of swelling and less will be polymer-polymer interaction. It is clear from Table 6.7 that for any blend ratio, uncompatibilised blends, swelling is higher when compared to that of compatibilised blends and the value decreases progressively with increasing chlorine content of compatibiliser (up to 25%). For DCSBR containing a higher chlorine content (> 25%) the compatibilising action is less as seen from a higher swelling in n-heptane. This clearly indicates that the compatibilising efficiency is maximum for 25% chlorine containing compatibiliser. There is a decrease in swelling as concentration of NBR in the blend increases. This is due to the restriction of swelling caused by the polar NBR. As a consequence a higher crosslink density is observed as NBR content in the blend increases. In all the blend composition, the crosslinking increases with incorporation of compatibiliser which shows that there is formation of more crosslinks in presence of compatibilisers. The volume fraction of rubber in the solvent swollen sample is calculated by the method reported by Ellis and Welding,[24] and Figure 6.11 shows the change in V_r (apparent crosslink density) as function of compatibiliser concentration on different compositions of SBR/NBR blends. The maximum crosslink density is obtained, when chlorine content of DCSBR is 25%, in the range of chlorine content studied.

Table 6.7. Swelling parameters of SBR/NBR blends in the presence and absence of compatibiliser

	70/30						50/50						30/70					
	N3	N3A	N3B	N3C	N3D	N3E	N5	N5A	N5B	N5C	N5D	N5E	N7	N7A	N7B	N7C	N7D	N7E
Swelling index (%)	75.37	53.9	53.6	50.3	53.3	60.7	59.9	45.2	40.9	37.3	41.5	44.9	24.3	23.6	23.0	22.3	27.0	26.9
Swelling coefficient (α)	1.11	0.79	0.78	0.74	0.78	0.89	0.88	0.67	0.60	0.55	0.61	0.66	0.36	0.35	0.34	0.33	0.39	0.4
Crosslink density Flory Rehner $\times 10 \times 10^{-4}$ (gmmol/cc)	1.39	3.4	3.42	3.51	3.44	3.27	2.36	4.74	4.95	5.11	4.96	4.42	5.12	6.89	6.9	6.97	6.74	6.72
Crosslink density Mooney-Rivlin (10^{-3} gmmol/cc)	1.04	1.14	1.23	1.28	1.21	1.19	1.25	1.44	1.51	2.1	2.02	1.89	1.41	1.62	1.7	2.62	2.46	2.42

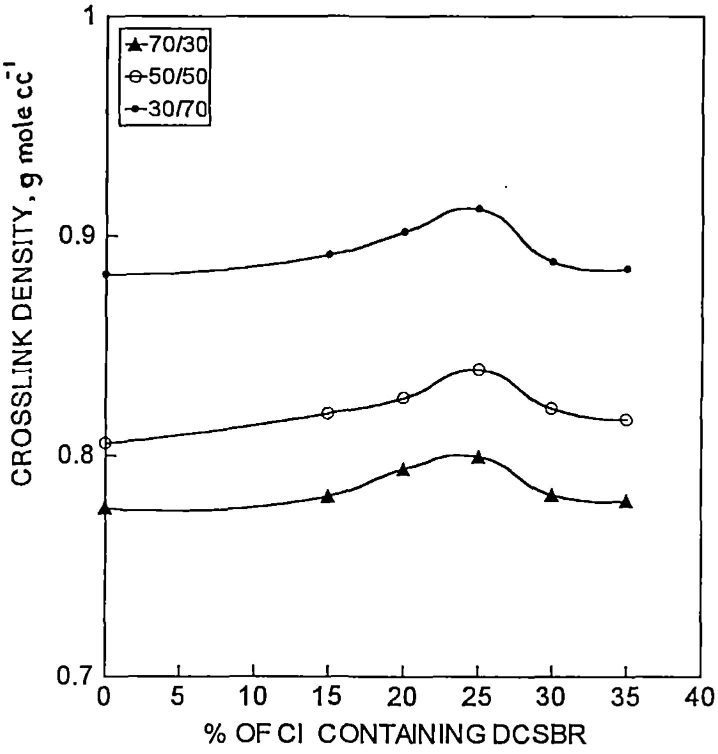


Figure 611. Change in crosslink density of SBR/NBR blends

6.2.5 Calculation of crosslink density

The crosslink densities were calculated from both the swelling data using Flory-Rehner[25] equation and stress-strain data using Mooney-Rivlin equation.[26]

(a) From swelling studies

The crosslink densities obtained from swelling data are given in Table 6.7. In agreement with the swelling data crosslink density of the compatibilised blend increases with increasing concentration of chlorine content of the compatibiliser up to 25% and then decreases. This is because of the restriction to swelling which causes an increase in V_r, which inturn increases the crosslink density, and the effect is maximum for 30/70 compositions and minimum for 70/30 SBR/NBR blends. Here the swelling contribution due to NBR is considered to be negligible and the swelling of only SBR is considered.

(b) From stress-strain data

The crosslink density is calculated using the equation[26]

$$C_1 = \rho RT\, \nu_{phys} \tag{6.3}$$

and the values are ν_{phys} in Table 6.7 reveals that the ν_{phys} has the same trend as given by the swelling studies. The ν_{phys} value increases with addition of compatibiliser and with its chlorine content up to 25% which indicates the presence of higher crosslinks in presence of compatibiliser. The values of ν_{phys} are found to be much higher than that from the swelling studies. For the uncompatibilised blends, due to weak polymer-polymer interactions there is greater penetration of the solvent. As the chlorine content of the compatibiliser increases (25% Cl content), they restrict swelling due to the greater amount of crosslinks produced. But in mechanical stretching of vulcanisate sample the physical entanglements of chain also get involved in the process. Therefore ν_{phys} values calculated from stress -strain data is higher than that obtained from swelling studies. This effect can be clearly understood from the increasing difference between crosslink density from swelling studies and mechanical data, with the addition of different chlorine content of compatibiliser. This difference is found to be reaching maximum at 25% chlorine containing compatibiliser and thereafter the values decrease. Thus as chlorine content of compatibiliser increases, the mixing between the two rubbers became more homogeneous and the blend behaves almost like a one component system.

6.3 Effect of concentration of DCSBR on the miscibility and mechanical properties of SBR/NBR blends

6.3.1 Effect of concentration o f DCSBR on processing characteristics

The basic formulation used in the study is given in Table 6.8. Figures 6.12-6.14 show the rheographs of SBR/NBR blends containing varying concentration of DCSBR with 25% chlorine content in different blend ratios. Table 6.9 represents the optimum cure time of SBR/NBR blends in the presence and absence of compatibiliser. Studies on the effect of loading of compatibiliser on the different blend composition makes it clear that the maximum cure time is reported at a concentration of 5 phr of DCSBR. When the compatibiliser concentration increases above 5 phr, the compatibiliser efficiency decreases, which result in the coalescence of, dispersed domains. This reduces the interfacial area and thereby causes a decrease in optimum cure time.

Table 6.8. Formulation of SBR/NBR blends of 25% chlorine containing DCSBR (1-10 phr)

Ingredients	N_3	N_5	N_7
SBR	70	50	30
NBR	30	50	70
DCSBR	0, 1, 3, 5, 10	0, 1, 3, 5, 10	0, 1, 3, 5, 10
Stearic acid	1.2	1.0	0.8
Zinc oxide	5	5	5
Antioxidant TDQ	1.0	1.0	1.0
CBS	0.7	0.5	0.3
TMTD	0.3	1.0	0.7
Sulphur	1.69	1.35	1.01

Table 6.9. **Cure characteristics of SBR/NBR blends compatibilised by DCSBR**

Blend composition	Dosage of DCSBR (phr)	Optimum cure time at 150°C (t_{90}) (min)	Scorch time at 150°C (t_2) (min)	Induction time at 150°C (t_i) (min)	Mh-Mn (dN.m)
SBR/NBR 70/30	0	7.5	5.5	5	56
	1	8	5	4.5	57
	3	8.5	4.5	4	58
	5	8.5	4	3.5	60
	10	8	3.5	3	57
SBR/NBR 50/50	0	9	4.5	4	53
	1	9.5	4	3.5	56
	3	10.5	3.75	3.25	59
	5	11.5	3.5	3	62
	10	10	2.5	2	59
SBR/NBR 30/70	0	10	4.25	3.75	54
	1	10.5	3.75	3.25	56
	3	11.5	3.5	3	58.5
	5	13.5	3.25	2.75	64
	10	11.5	2.75	2.25	61

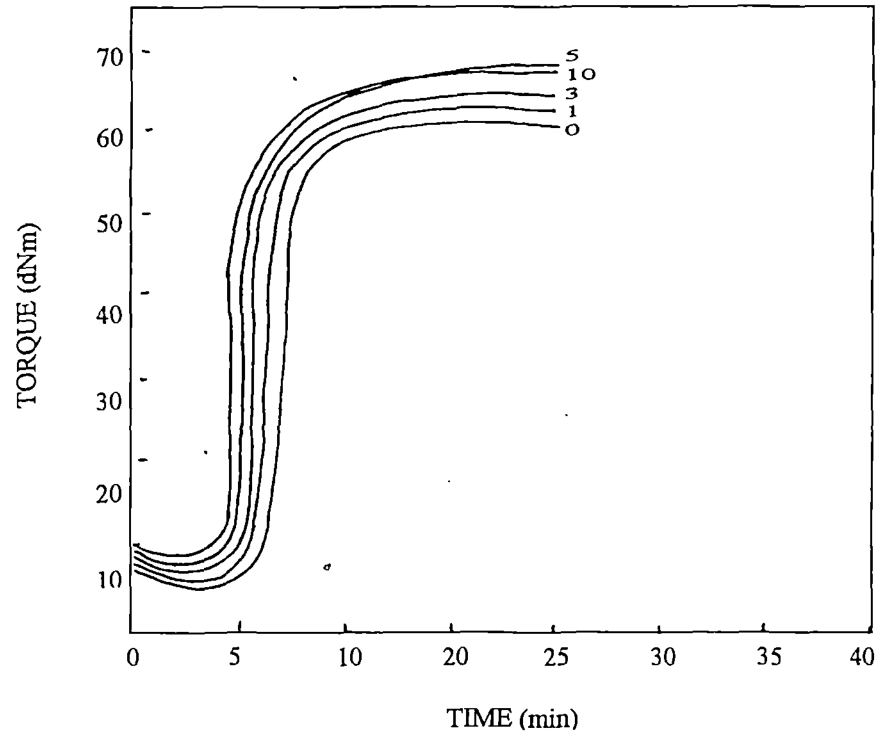


Figure 6.12. Rheographs of 70/30 SBR/NBR blends at 150°C with concentration of DCSBR varying from 0, 1, 3, 5 and 10 phr

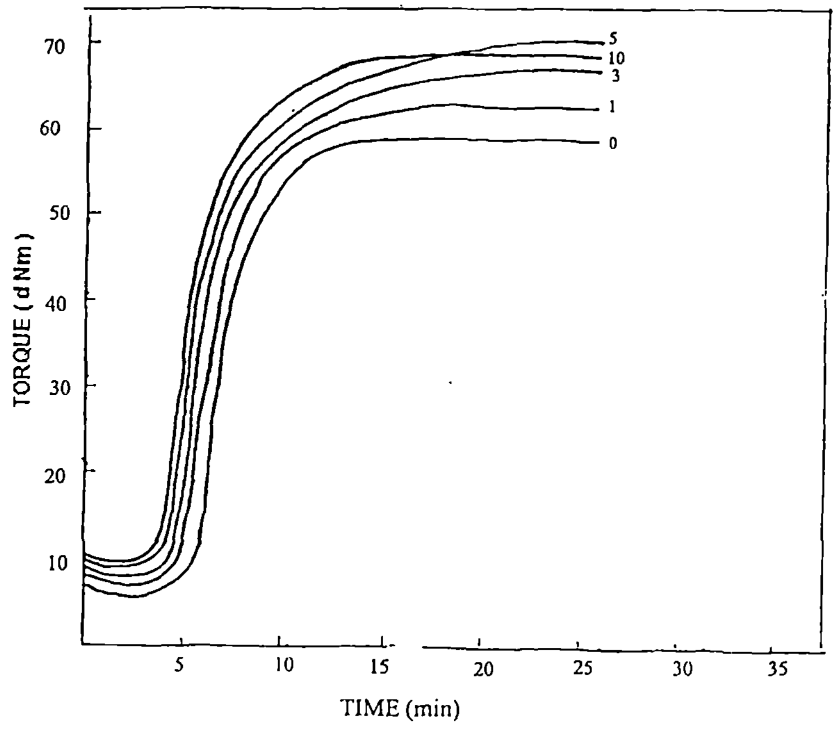


Figure 6.13. Rheographs of 50/50 SBR/NBR blends at 150°C with concentration of DCSBR varying from 0, 1, 3, 5 and 10 phr

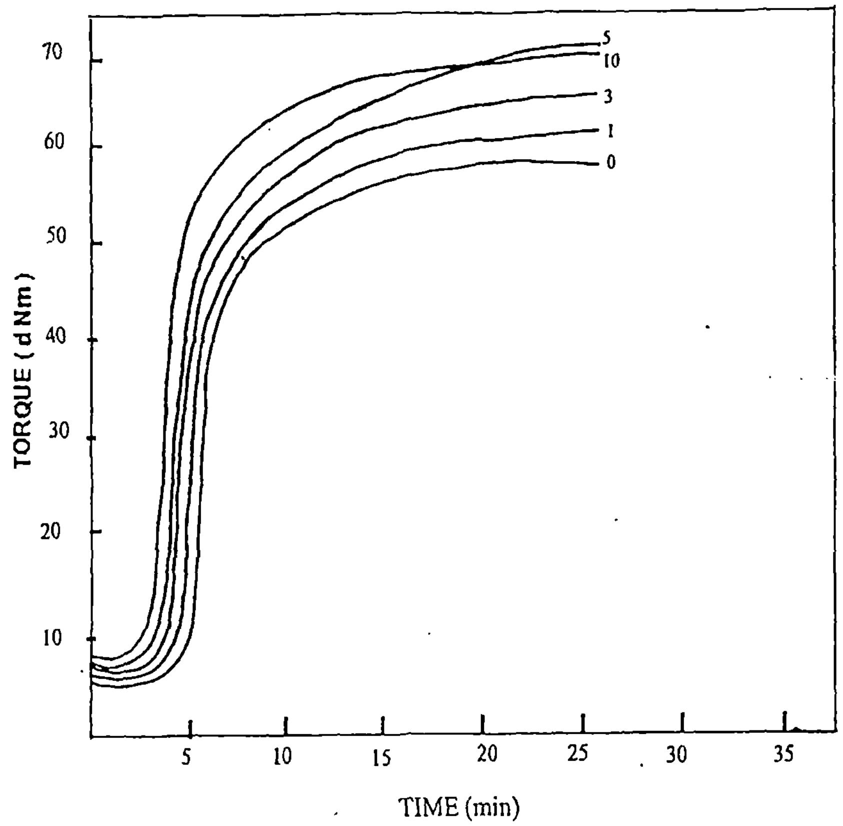


Figure 6.14. **Rheographs of 30/70 SBR/NBR blends at 150°C with concentration of DCSBR varying from 0, 1, 3, 5 and 10 phr**

The increase in torque due to the crosslinking process (Mh-Mn) of compatibilised and uncompatibilised SBR/NBR blends are shown in the Table 6.9. As the loading of compatibiliser increases the difference in torque value increases and then decreases in all blend compositions. At lower concentration of compatibiliser the torque variation with blend composition is negligible, but as the concentration of compatibiliser increases from 5 to 10 phr, the torque attained increases with concentration of NBR. In all the blend composition 5 phr DCSBR shows the maximum difference in torque. Hence at this concentration, the compatibiliser enhances the formation of inter diffused chains with higher crosslinking that leads to development of a higher torque.

6.3.2 Characterisation of blends

6.3.2.a Differential scanning calorimetry

The DSC traces of pure 50/50 SBR/NBR blend in the presence and absence of compatibiliser are presented in Figure 6.15. For uncompatibilised 50/50 blend, there appears to be two transitions in the temperature range from -68 to -28°C which shows the presence of microlevel inhomogeneity. The transition at -56 and -28°C for the blend corresponds to the transition of pure SBR and pure NBR respectively. 50/50 blend with 1 phr DCSBR (25% chlorine content) shows microlevel inhomogeneity with two transition at -50 and -38°C. As the concentration of DCSBR increases upto 5 phr the blend shows a single transition at -44°C in the temperature range of -68 to -29°C, showing that DCSBR acts a compatibiliser in the blends of SBR/NBR. When the concentration become 10 phr, the blend exhibit two transition at -55 and -35°C.

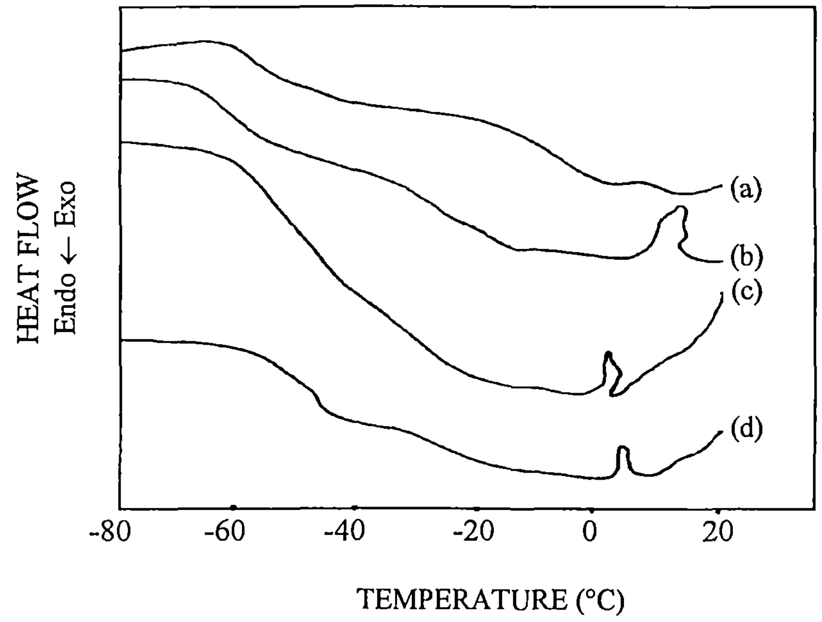


Figure 6.15. DSC themograms of SBR/NBR blends (a) 50/50 blend (b) blend containing 1phr, (c) 5 phr and (d) 10 phr DCSBR with 25% chlorine content.

6.3.2.b FTIR analysis

IR spectra of pyrolysate of SBR, NBR, DCSBR, 50/50 SBR/NBR and 50/50 blend containing 5 phr and 10 phr of 25% chlorine containing DCSBR are shown in Figure 6.16 and the corresponding IR absorption data in Table 6.10.

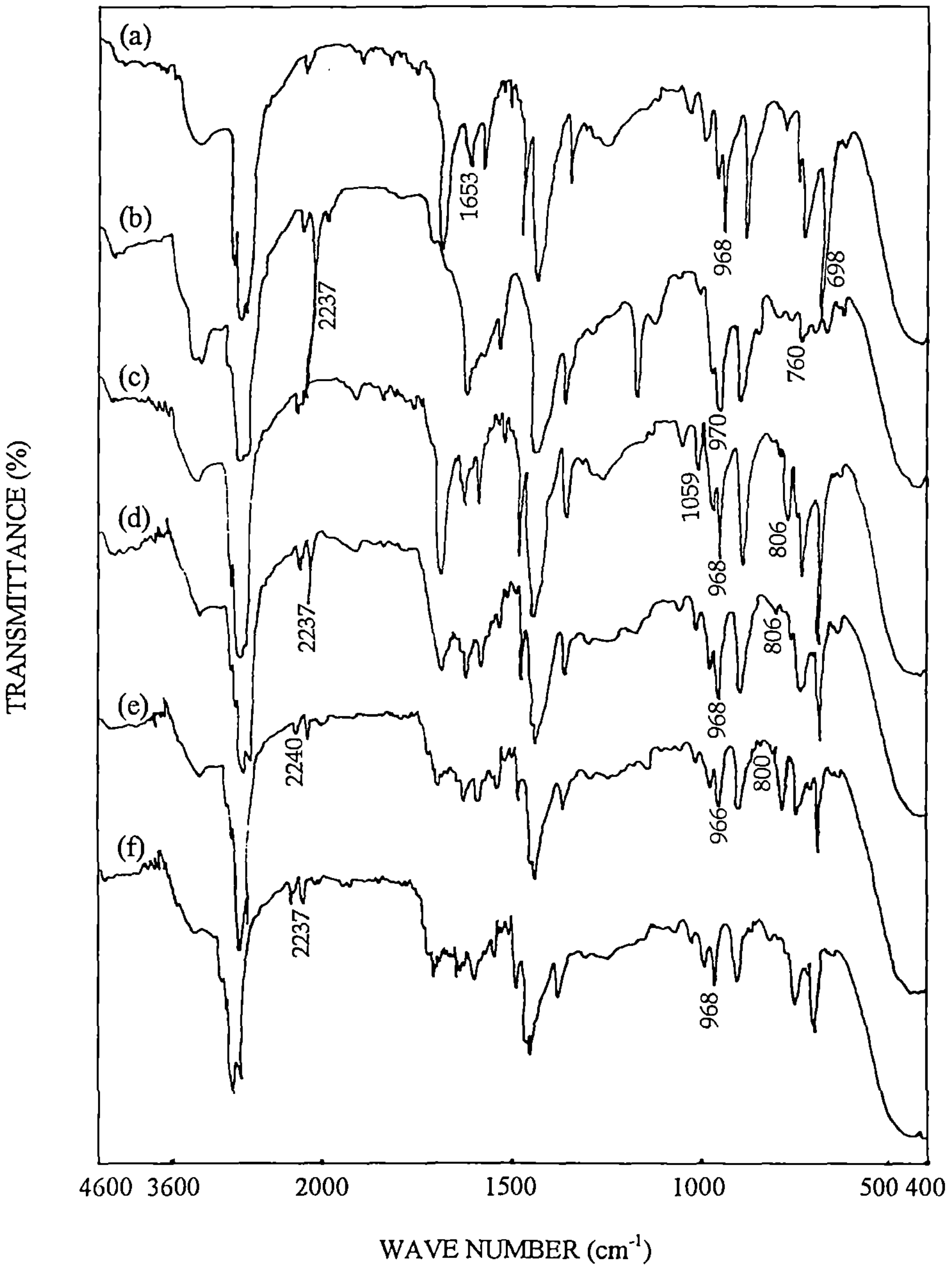


Figure 6.16. FTIR spectra of pyrolysate of (a) SBR, (b) NBR, (c) DCSBR, (d) 50/50 SBR/NBR, (e) 50/50 blend containing 5 phr DCSBR (25% Cl), and (f) 50/50 blend containing 10 phr DCSBR (25% Cl)

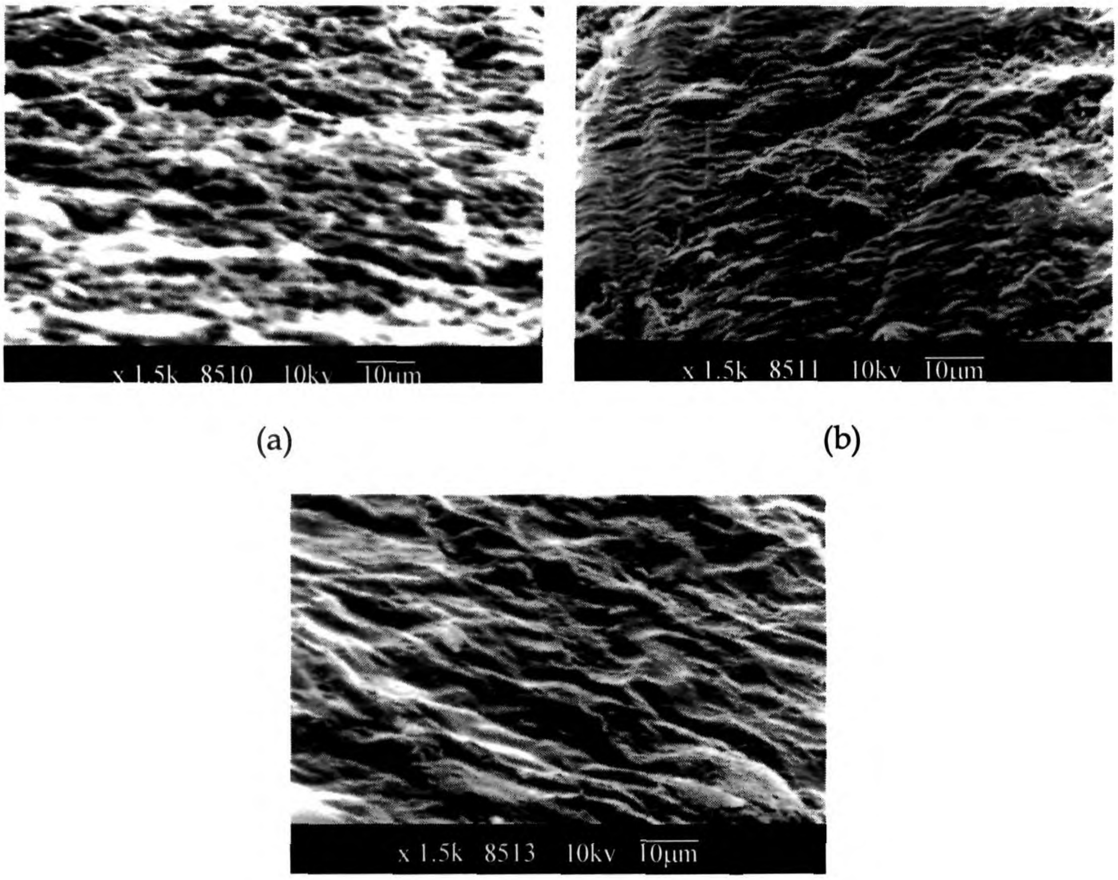
Table 6.10. IR absorption peak of (a) SBR, (b) NBR, (c) DCSBR, (d) 50/50 SBR/NBR, (e) 50/50 blend containing 5 phr DCSBR (25% Cl), and (f) 50/50 blend containing 10 phr DCSBR (25% Cl)

Materials	Wave number (cm^{-1})	Reputed assignment
(a)	968	Trans-CH=CH-
	698	Aromatic substitution
	1653	cis-CH=
(b)	2237	-C≡N
	970	Trans-CH=CH-
	760	Aromatic substitution
(c)	968	Trans-CH=CH-
	806	C-Cl
	1059	Cyclopropane
(d)	2237	-C≡N
	968	Trans-CH=CH-
	756	Aromatic substitution
(e)	2240	-C≡N
	800	C-Cl
	966	Trans-CH=CH-
	758	Aromatic substitution
(f)	2237	-C≡N
	968	Trans-CH=CH-
	806	C-Cl
	756	Aromatic substitution

It is assumed that there would be polar-polar interactions between the chlorine of DCSBR and cyanide group of acrylonitrile repeat units present in NBR which leads to miscibility in these blends. It has been shown earlier that methyl methacrylate grafted natural rubber and CR acts as compatibiliser in blends of NR/NBR due to the possible interaction between the compatibilised NBR. The polar-polar interaction affect IR absorption peaks of the concerned groups. As seen from the IR spectrograph and IR absorption data, in an optimum concentration of DCSBR there is sufficient polar interaction between DCSBR and NBR. Pure NBR and 50/50 blends of NBR and SBR, shows an IR absorption at 2337 cm^{-1} due to CN stretching. NBR/SBR blends containing 5 phr DCSBR shows a shift in absorption to 2339 cm^{-1}. There is no shift in the IR absorption due to CN stretch for NBR/SBR blends containing higher concentration of DCSBR. Hence in an optimum concentration, DCSBR acts as a compatibiliser in SBR/NBR blends.

6.3.2.c Morphological studies

The effect of concentration of DCSBR as a compatibiliser on the morphology of 50/50 SBR/NBR blend is shown by the scanning electron micrographs of Figure 6.17a-c. These micrographs show changes in phase morphology of blends containing 0, 5 and 10 phr compatibiliser, respectively. From scanning electron micrograph it is seen that the size of the dispersed NBR phase (as viscosity of SBR is lower than that of NBR) decreases with addition of modified SBR. This reduction in domain size with the addition of DCSBR is due to the reduction of interfacial tension between SBR and NBR phase.



(a) (b)

(c)

Figure 6.17. SEM micrographs of 50/50 SBR/NBR blend (a) without compatibiliser (b) with 5 phr DCSBR (c) with 10 phr DCSBR

The average domain size of the compatibilised blends analyzed as a function of compatibiliser concentration is presented in Figure 6.18. The average domain size of the uncompatibilised SBR/NBR blend is 4.1 μm. But with addition of compatibiliser up to 5 phr the domain size is reduced by 48% of domain size of the uncompatibilised 50/50 blend. Moreover, further addition of compatibiliser increases the domain size. The equilibrium concentration at which the dispersed NBR domain size levels off is called critical micelle concentration (CMC). The estimation of CMC from the plot of domain size vs. concentration is already reported in the literature.[27] The CMC corresponds to the critical amount of the compatibiliser to saturate the unit volume of the interface. When compatibiliser concentration exceeds CMC, micelle of the compatibiliser is formed in the continuous SBR phase. Several works are available from the literature, regarding the linear decrease of dispersed domain size with increasing compatibiliser concentration.[28-30] Therefore it can be confirmed that a concentration of 10 phr of compatibiliser is much above CMC and comparatively very good reduction of interfacial tension is achieved at a concentration of 5 phr. This is in good agreement with the overall mechanical properties obtained.

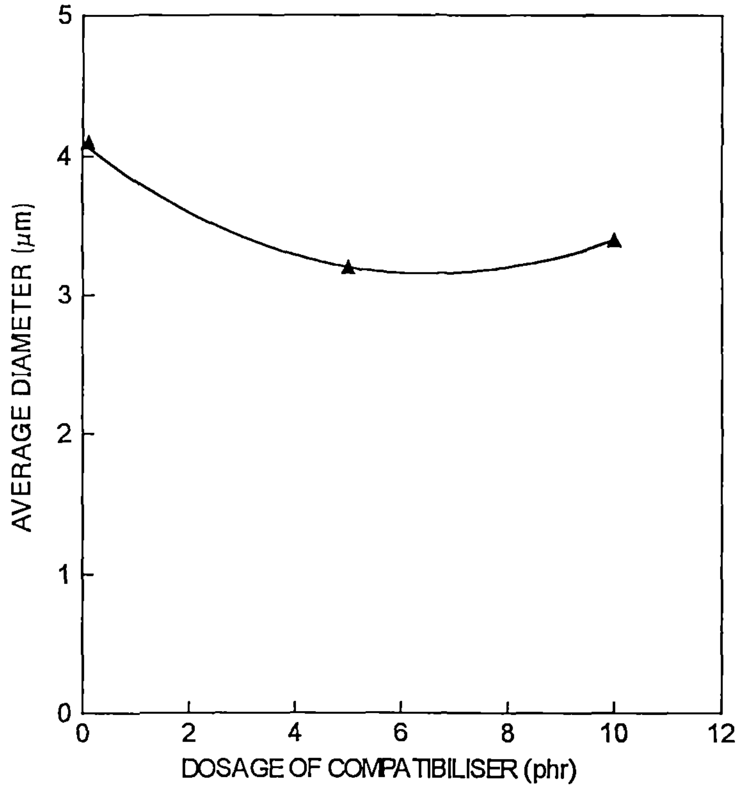


Figure 6.18. Effect of compatibiliser concentration on the domain size of 50/50 SBR/NBR blends.

The compatibilising effect of DCSBR is evident from the increased interfacial adhesion as revealed from processing characteristics and technological properties as detailed below.

6.3.3 Effect of concentration of compatibiliser on the swelling behavior

The swelling studies were carried out in n-heptane at room temperature.

According to Lorentz and Parks equation[31]

$$Q_c \big/ Q_u = ae^{-z} + b \qquad (6.4)$$

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

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight x } 100 \,/\, \text{Formula weight}} \qquad (6.5)$$

The subscripts c and u of the above equation refer to compatibilised and uncompatibilised vulcanisates, respectively. z is the ratio by weight of compatibiliser to rubber hydrocarbon in the vulcanisate, whereas a and b are constants. The higher the Q_c/Q_u values, lower will be the extent of interaction between the compatibiliser and rubber blends. Parks[32] also proved that the value of 1/Q can be used to study the effect of interaction between two polymers. Table 6.11 shows the Q_c/Q_u, 1/Q values for SBR/NBR blends as a function of concentration of compatibiliser after swelling in n-heptane. The lowest value of Q_u/Q_c is obtained for 5 phr loading of compatibiliser from all the blend ratios, which confirms that maximum interaction occurs between the polar segments of modified SBR with NBR and butadiene part with SBR phase, thereby reducing the interfacial tension. The result from 1/Q values also supports this observation. Plots of solvent uptake (n-heptane) versus blend composition are given in Figure 6.19. As seen from the figure the volume of solvent absorbed is below the additive average with increase in concentration of compatibiliser up to 5 phr. If interfacial bonds are formed during covulcanisation the lightly swollen phase will restrict swelling of the highly swollen phase below an additive average.[33] This confirm that interfacial bonds are formed in blends of SBR/NBR blends in presence of DCSBR.

Table 6.11. Swelling characteristics, crosslink density parameters C_1, C_2 and crosslink density values for SBR/NBR blends

Properties	Loading of compatibiliser (phr)														
	70/30					50/50					30/70				
	0	1	3	5	10	0	1	3	5	10	0	1	3	5	10
1/Q	1.3103	1.8132	1.8872	1.9272	1.5693	1.6286	2.4182	2.5437	2.5674	1.5697	3.8865	4.1179	4.1921	4.2019	2.9091
Q_c/Q_g	-	0.7289	0.7001	0.6799	0.6887	-	0.6734	0.6402	0.6269	1.0375	-	0.9559	0.9438	0.9249	1.3358
V_{r0}/V_{rc}	-	0.9381	0.9265	0.9115	0.9229	-	0.9045	0.8939	0.6269	1.0082	-	0.9926	0.9895	0.9881	1.0459
$2C_2$,N mm^{-2}	0.64	1,04	1.20	1.28	1.20	1.04	1.20	1.52	2.08	1.64	1.52	1.76	1.96	2.48	1.98
$2C_1$, N mm^{-2}	0.72	0.95	1.04	1.1	1.08	0.88	0.96	1.17	1.48	1.29	1.1	1.3	1.37	1.78	1.49
Crosslink density Mooney-Rivlin (10^{-3} gmmol/cc)	1.04	1.16	1.2	1.28	1.26	1.25	1.53	1.79	2.1	1.99	1.41	1.61	1.98	2.62	2.31

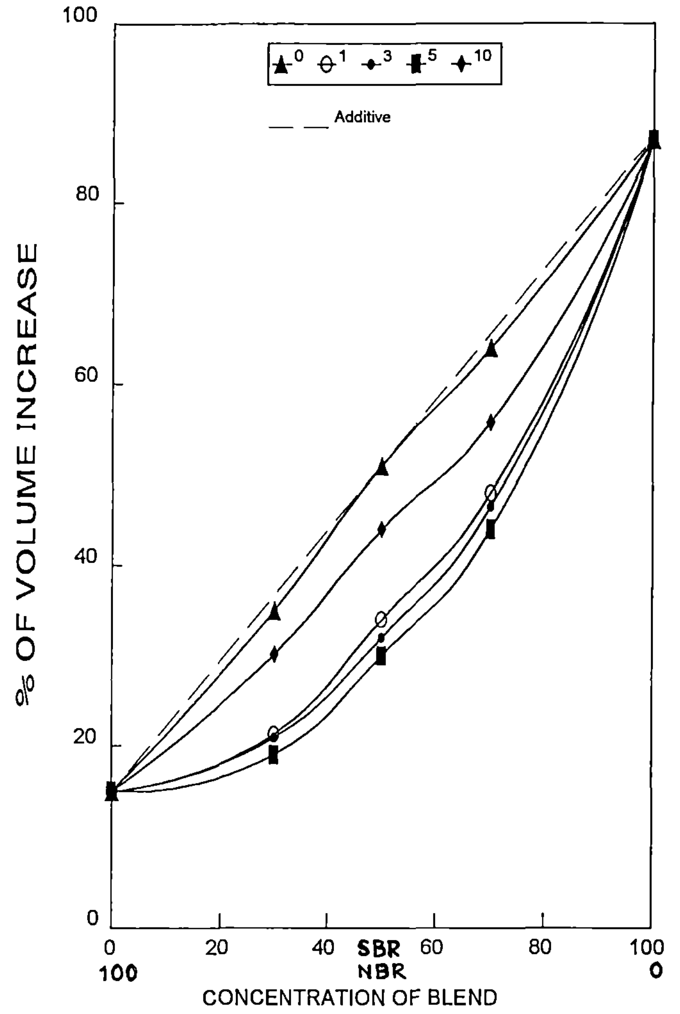


Figure 6.19. Interfacial bonding of SBR/NBR blends in presence of compatibiliser (DCSBR) at concentrations of 0, 1, 3, 5 and 10 phr

The volume fraction of rubber in the solvent swollen sample is calculated by the method reported by Ellis and Welding.[24] Kraus[34] theory can be applied to blends of SBR and NBR

$$Vr_0/Vr_c = 1\text{-}M\ (\phi/1\text{-}\phi) \qquad (6.6)$$

where Vr0 is the volume fraction of elastomer in the swollen gel when no dispersed phase is present Vr0 is the volume fraction of the continuous phase elastomer when a lightly swollen dispersed phase. Vrc is the volume fraction of dispersed phase in the unswollen covulcanisate, and M is a parameter depending on Vr0 and the extent of swelling restriction. A plot of Vr0/Vr as a function volume fraction of SBR in blends in the presence and absence of compatibiliser is given in Figure 6.20.

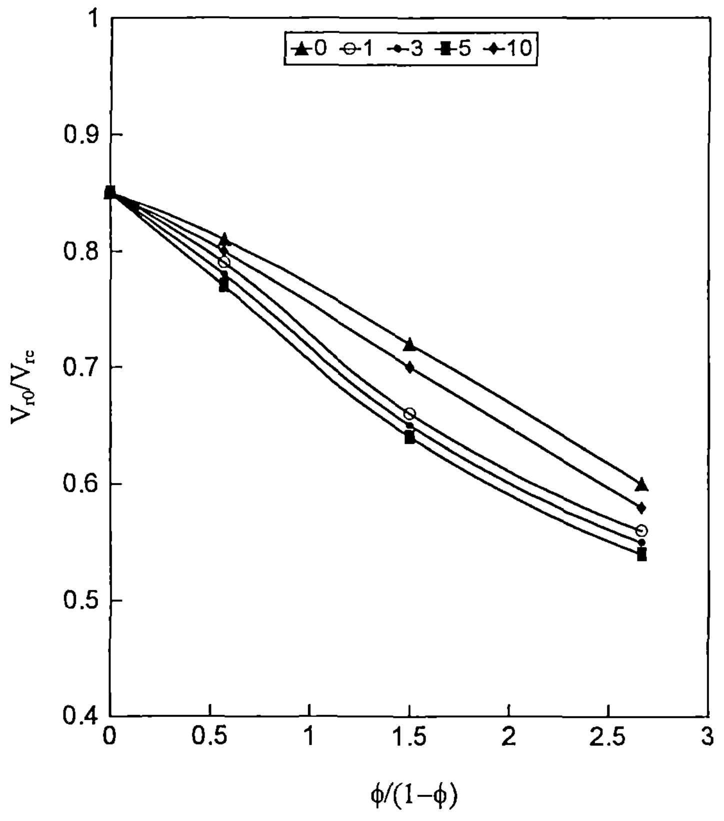


Figure 6.20. Kraus plot for SBR and blends of SBR with NBR in presence of compatibiliser (DCSBR) at concentrations of 0, 1, 3, 5 and 10 phr

Since Vr_0/Vr deviates from unity with addition of compatibiliser in all blend ratios there is formation of interfacial bonds.[35] But the interfacial bond formation increases only as the concentration of SBR in the blend increase from 0 to 50 phr, and at higher concentration the interfacial bond formation is not very effective since there is deviation from linearity for the Kraus plots. Thus the compatibilising action is higher when concentration of SBR in the blend is 50 phr or lower. This is clear from the mechanical properties discussed later.

6.3.4 Calculation of crosslink density from stress-strain data

The physical crosslinks in an elastomers can be understood by the Mooney-Rivlin equation (6.3).[26]

The plot obtained from stress-strain data for 70/30, 50/50 and 30/70 SBR/NBR blends are shown in Figures 6.21a-c and the values of crosslink density are presented in Table 6.11. It can be seen that the crosslink density increases as the concentration of DCSBR increases up to 5 phr and then decreases, which is in good agreement with rheometric torque. C_2 a term which serves as a measure of departure in the observed stress strain behavior from the form suggested by statistical theories[36] is given in Table 6.10. $2C_2$ value increases with the loading of DCSBR up to 5phr and then decreases. The higher C_2 values is noted for the 30/70 SBR/NBR blends shows the presence of higher chain entanglements.[36] Since the elastomeric matrix is composed of two components, a higher entanglements shows better molecular level mixing.

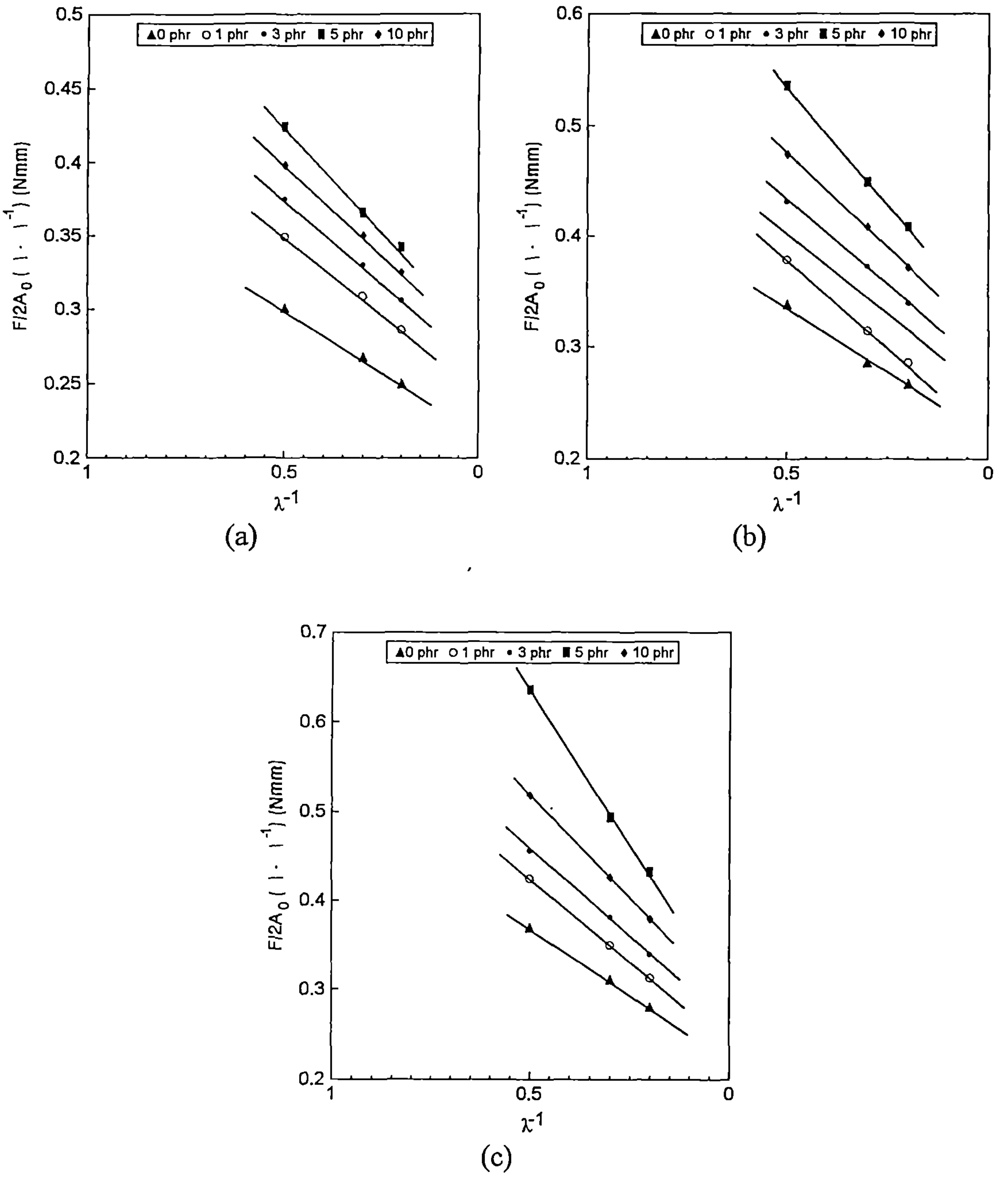


Figure 6.21. Plot of $F/2A_0(\lambda-\lambda^{-1})$ versus λ^{-1} of SBR/NBR blends (a) 70/30 SBR/NBR blends with concentration of DCSBR varying from 0, 1, 3, 5 and 10 phr (b) 50/50 SBR/NBR blends with concentration of DCSBR varying from 0, 1, 3, 5 and 10 phr (c) 30/70 SBR/NBR blends with concentration of DCSBR varying from 0, 1, 3, 5 and 10 phr.

6.3.5 Effect of concentration of compatibiliser on technological properties

The variation of mechanical properties with varying dosage of DCSBR on SBR/NBR blends are presented in Table 6.12. It reveals that the compatibilisation substantially increases the tensile strength. In compatibilised blends, tensile strength increases as concentration of NBR in the blend increases. The tensile strength value slowly increases with the compatibiliser concentration being at the peak at a concentration of 5 phr, and with further increase in the concentration of compatibiliser, the tensile strength drops. This may be due to the super saturation of the interface with the compatibiliser which increases interfacial tension. Moreover, with increased concentration the uniformly distributed domains may tend to agglomerates forming bigger aggregates.

As in the case of tensile strength, tear resistance improves on the addition of DCSBR. The value gets maximized at a concentration of 5 phr of the compatibiliser. Formation of uniformly distributed finer domains tend to elongate to higher strain and effectively prevents tear propagation. With increase in the concentration of compatibiliser above 5 phr, the tear strength decreases.

The compression set decreases and the resilience increases with increase in SBR content of the blend. Compatibilised blends show a lower compression set and a higher resilience than that of uncompatibilised blend. The compression set is minimum at a concentration of 5 phr of DCSBR in all blend ratios. The uncompatibilised blends show lower hardness as compared to compatibilised samples. Increased interfacial adhesion in compatibilised blend eliminates these air spaces and hence hardness increases.

Table 6.12. Physical properties of SBR/NBR blends containing DCSBR with dosage of 0-10 phr

Properties	70/30					50/50					30/70				
	0	1	3	5	10	0	1	3	5	10	0	1	3	5	10
Modulus, 300% (MPa)	1.98	2.46	2.82	3.47	3.01	2.51	2.73	2.91	3.18	3.01	1.99	2.11	2.49	2.7	2.64
Tensile strength (MPa)	2.9	3.4	4.7	5.2	5.0	3.5	4.1	5.3	6.2	6.0	3.0	4.0	5.6	6.8	6.0
Elongation at break (%)	310	350	440	555	510	325	390	470	515	495	360	300	425	450	430
Tear strength (kN/m)	15.7	16.9	19.0	22.8	21.6	16.1	18.9	22.8	24.2	24.0	18.8	20.9	23.7	26.4	25.8
Hardness (Shore A)	40	41	42	44	45	41	42	43	44	46	42	43	44	46	48
Resilience (%) Dunlop tripsometer)	68	68	69	71	69	62	63	65	67	64	58	59	60	62	63
Compression set (%) 22 h at 70°C	17.5	17.0	16.7	15.6	16.1	18.0	16.5	15.3	14.2	14.9	18.3	17.0	16.1	15.6	16.8

The oil aging in ASTM oils at room temperature and air aging at 70^{0}C for 96 h. of SBR/NBR blend in the presence and absence of compatibiliser are presented in Table 6.13. Blending of NBR with SBR imparts considerable oil resistance to SBR which is improved by the addition of compatibiliser and also with good ageing resistance. The change in tensile strength after ageing is lower when SBR concentration in the blend is high. In all blend composition, the change in tensile strength and elongation at break is minimum, when blends contain 5 phr of 25% chlorine containing DCSBR.

Table 6.13. Air aging (96 h at 70°C) and oil resistance (5 days at 25°C) of SBR/NBR blends

Blend composition	Dosage of DCSBR (phr)	Swell in ASTM Decrease in % (w/w)			Change in tensile properties after aging at 70 ^{0} C for 96 h	
		ASTM oil No 1	ASTM oil No 2	ASTM oil No 3	Decrease in tensile strength (%)	Decrease in EB (%)
SBR/ NBR 70/30	0	6.68	11.31	37.15	39	20
	1	6.63	11.28	37.3	36	18
	3	6.60	11.24	37	35	17
	5	6.58	11.2	36.1	34	16
	10	6.55	11.11	35.8	36	15
SBR/ NBR 50/50	0	4.81	8.32	26.73	42	24
	1	4.77	8.3	26.13	40	22
	3	4.69	8.11	25.92	36	20
	5	4.41	7.9	25.23	49	20
	10	4.56	7.3	24.81	34	19
SBR/ NBR 30/70	0	3.02	5.14	16.31	45	26
	1	2.98	5.02	15.8	43	25
	3	2.89	4.80	15	41	23
	5	2.8	4.46	13.95	40	21
	10	2.73	4.01	13.36	42	23

6.3.6 Different mechanical modeling for tensile strength variation of compatibilised blends

Mathematical equations can be used for the prediction of technological properties from experimental data. There are two common methods for obtaining an equation to fit the experimental data. The first method is the derivation of an equation from the experimental data and the second method is fitting an established equation with experimental data. The later approach is adopted in this chapter.

The following mathematical models, which are relevant to the broad field of this work.

(a) Einstein Equation

Einstein[37] has proposed for the tensile property of matrices with perfect interaction between the phases:

$$M_c = M_m (1 + 1.25 V_f) \tag{6.7}$$

where M_c is the tensile strength of the concerned matrix, Mm is the tensile strength inclusion of the second phase and V_f is the volume fraction of the inclusion.

Since these equations were found to be useful only at low concentration of compatibiliser, they were modified by Mooney.

(b) Mooney Equation

The equation by Mooney[38] considers the interaction of strain field around the two phases. Einstein equation is applicable at low volume fraction of the compatibiliser while Mooney equation is able to represent the data at higher volume fractions. It is given by the equation.

$$M_c = M_m \exp\left[\frac{2.5\ Vf}{1 - S\,Vf}\right] \tag{6.8}$$

where S′ is the crowding factor given by

$$S = \frac{\text{Volume occupied by the compatibilizer}}{\text{True volume of the compatibilizer}} \tag{6.9}$$

(c) Brodnyan Equation

Brodnyan[39] modified the Mooney equation by adding an aspect ratio by the equation

$$M_c = M_m \exp\left[\frac{2.5 V_f + 0.407(p-1)^{1.508} V_f}{1 - SV_f}\right] \tag{6.10}$$

where P is the aspect ratio $1 < p < 15$

(d) Guth Equation

Guth[40] modified Einstein equation for the perfect bonding between the phases as

$$M_c = M_m\,(1 + 2.5\,V_f + 14.1\,V_f^2) \tag{6.11}$$

(e) Kerner Equation

Kerner[41] equation is given as

$$M_c = M_m\left[1 + \frac{V_f\,15(1 - \nu_m)}{V_m(8 - 10\nu_m)}\right] \tag{6.12}$$

where V_m is the volume fraction of the matrix.

(f) Sato-Furukawa model

The weak adhesion between the matrix and the compatibiliser is better represented in literature by Sato-Furukawa model.[42]

The equation is

$$M_c = M_m\left[\left\{1+\frac{y^2}{2(1-y)}\right\}\left(1\frac{y^3T}{3}\left\{\frac{1+y-y^2}{1-y+y^2}\right\}\right)\right.$$

$$\left.-\left\{\frac{y^2T}{3(1-y)}\right\}\left\{\frac{1+y-y^2}{1-y+y^2}\right\}\right] \qquad (6.13)$$

where y is a concentration variable equal to $V_f^{1/3}$. If the adhesion is perfect T = 0 and if it is weak T = 1.

The experimentally observed variation in tensile strength of compatibilised and uncompatibilised SBR/NBR 50/50 blends with loading of compatibiliser is compared with several mechanical model predictions (Figure 6.22). All the models are in good agreement with experimental data and among the models, Kerner model is better to represent the experimental behaviour.

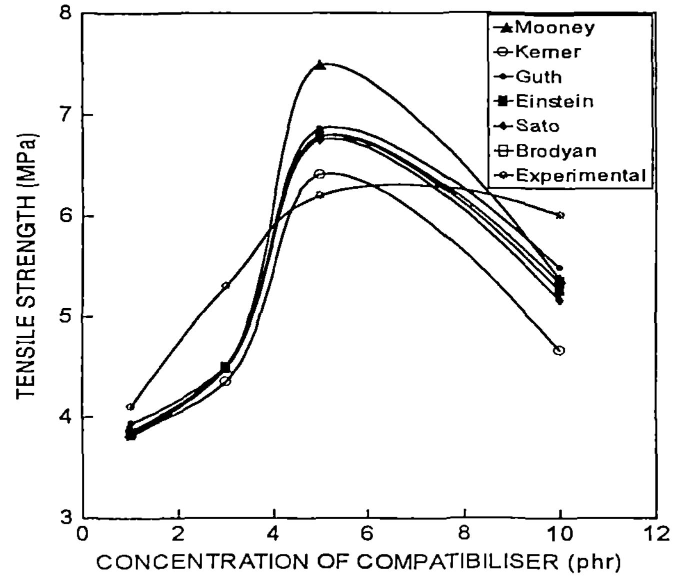


Figure 6.22. Mechanical modeling of tensile properties of SBR/NBR compatibilised blends

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CHAPTER

7

EFFECT OF DIFFERENT FILLERS ON COMPATIBILISED AND UNCOMPTIBILISED SBR/NBR BLENDS

Results of this chapter have been communicated
to *J. Elast. Plastics*

7.1 Introduction

Blending of polymers offers novel materials with tailored properties. Hence this technique has been extensively used in plastics, rubbers, composites, films, fibres, coating and adhesives.[1] The last few years have seen a remarkable increase in the production of new type of blends such as elastomer alloys[2-4] and interpenetrating networks.[5,6] The most important advantage of these systems is the ease of mixing procedure. Among the broad class of polymer blends, the field of rubber-rubber blends deserves a prominent place. The main factor which decides the ultimate properties of rubber-rubber blend is the diffusion of one rubber into the other. The factor in turn is depend on the interaction between the component rubbers. Expensive studies are available in literature on the inter diffusion of rubbers and its relation to ultimate properties. The main use of fillers in rubber-rubber blend is to improve the processability, mechanical properties and to reduce the overall cost. Fillers are considered to improve the phase morphology of the incompatible blends.[11] According to Lipatov et al.[12,13] the thermodynamic compatibility of many binary blends are further improved by many inorganic fillers. This ability of fillers comes from its tendency to reduce zone size of dispersed domains in polymer blends. Hence this chapter focuses on the effect of different fillers on SBR/NBR blends compatibilised by dichlorocarbene modified styrene butadiene rubber (DCSBR) with reference to cure characteristics, crosslinking and mechanical properties. SBR and NBR are both important commercial elastomers. Blending of these two polymers can result in materials that have excellent resistance to oils with good mechanical properties. Such a blend is suitable for a wide range of applications in automobile industry. However, this particular blend system has received limited attention in literature, owing to the immiscibility of these two elastomers.

7.2 Effect of different fillers on the processing characteristics

Formulation of silica and carbon black filled SBR/NBR blends are given in Table 7.1.

Table 7.1. Formulation of silica and carbon black filled SBR/NBR blends

Ingredients	S_7	S_5	S_3	S_{7C}	S_{5C}	S_{3C}
SBR	70	50	30	70	50	30
NBR	30	50	70	30	50	70
DCSBR(25% Cl content)	-	-	--	5	5	5
Stearic acid	1.2	1.0	0.8	1.2	1.0	0.8
Zinc oxide	5	5	5	5	5	5
Antioxidant TDQ	1.0	1.0	1.0	1.0	1.0	1.0
CBS	0.7	0.5	0.3	0.7	0.5	0.3
TMTD	0.3	1.0	0.7	0.3	1.0	0.7
Aromatic oil	0.7-2.8	0.7-2.8	0.7-2.8	0.7-2.8	0.7-2.8	0.7-2.8
HAF black (N330)	10-40	10-40	10-40	10-40	10-40	10-40
Precipitated silica	10-40	10-40	10-40	10-40	10-40	10-40
Diethylene glycol	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.69	1.35	1.01	1.69	1.35	1.01

The effect of addition of varying concentration of carbon black and precipitated silica on the cure characteristics of SBR/NBR blends at different compositions (70/30, 50/50 and 30/70), and corresponding blends containing 5 phr of 25% chlorine containing DCSBR are shown in Tables 7.2-7.4 and the rheographs of the mixes are given in Figures 7.1–7.6 (S_1, S_2, S_3 and S_4 represent the blend without DCSBR containing 10, 20, 30 and 40 phr fillers (70/30, 50/50 and 30/70); SC_1, SC_2, SC_3 and SC_4 with DCSBR containing 10, 20, 30 and 40 phr fillers (70/30, 50/50 and 30/70).

(a) Effect of blend composition

As seen from the rheographs the initial viscosity, induction time, scorch time and maximum torque increase with filler loading in all blend composition as it is well known that reinforcing fillers like silica and carbon black increase viscosity of rubber specifically non-crystallising rubbers depending on its concentration. Carbon black filled mixes record a higher rheometric torque than the corresponding silica filled mixes, as a general trend. The effect of fillers in small concentration (10 phr) in raising the rheometric torque increases as the concentration of SBR in the blend increases. The reinforcing effect of fillers attributed to better polymer filler interaction became more pronounced as concentration of SBR in the blend decreases.

As proportion of NBR in the blend increases it is probable that the polar accelerates like TMTD migrates more towards NBR phase resulting on a lower extent of crosslinking in SBR phase. As concentration of NBR in the blend decreases the extent of migration of polar accelerator is also reduced. Carbon black has a tendency to migrate to SBR phase compared to NBR phase.[14] As NBR content and concentration of filler increases, the extent of migration of carbon black to the SBR phase decreases. Hence the effect of filler in raising the rheometric torque increases as concentration of filler increases and when SBR content in the blend is 50% or lower. The optimum cure time and scorch time are higher for silica filled compounds than the carbon black filled compounds. This can be due to the accelerator adsorption by silanol groups present in silica.

(b) Effect of compatibiliser

With the addition of a small quantity of DCSBR, there is a rise in rheometric torque with the addition of filler as proportion of NBR in the blend is 50% or above. The increase in rheometric is due to an increaed level of crosslinking. It is already reported that maximum torque is dependent on the crosslink density and chain entanglement which result from higher interaction of SBR and NBR through DCSBR unit. As the loading of filler increases the difference in torque also increases and this is intense for carbon black filled samples. It is assumed that DCSBR reduces the interfacial tension giving increased interfacial crosslinking due to more homogeneous mixing of the two rubbers. The problem due to unequal distribution of curatives is minimised resulting enhanced crosslinking of the blend. Due to this there is a decrease scorch time and cure time blends containing DCSBR.

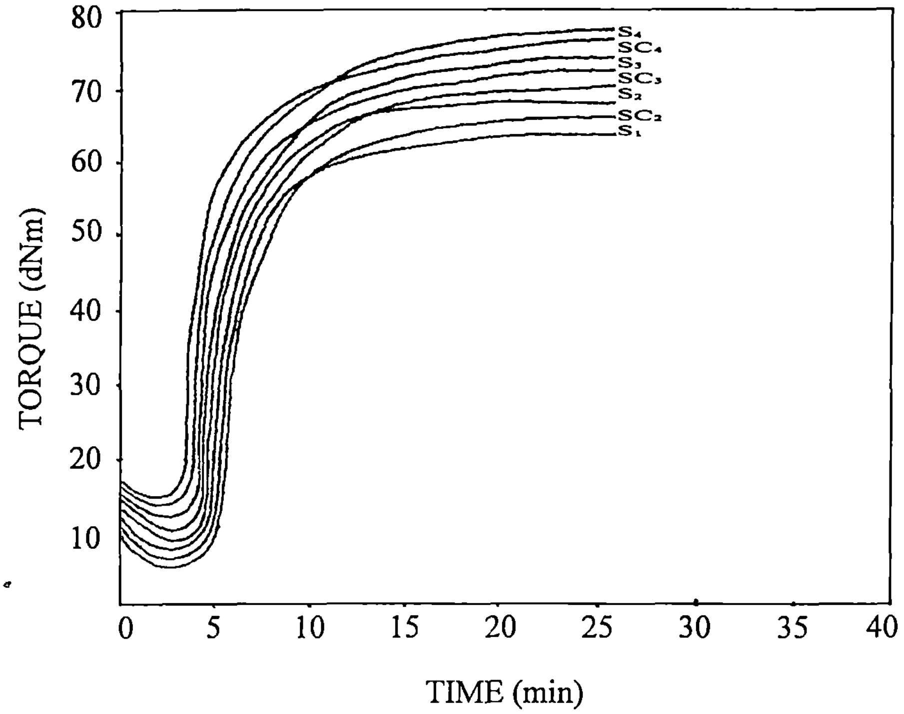


Figure 7.1. Rheographs at 150°C of silica filled 70/30 SBR/NBR blends

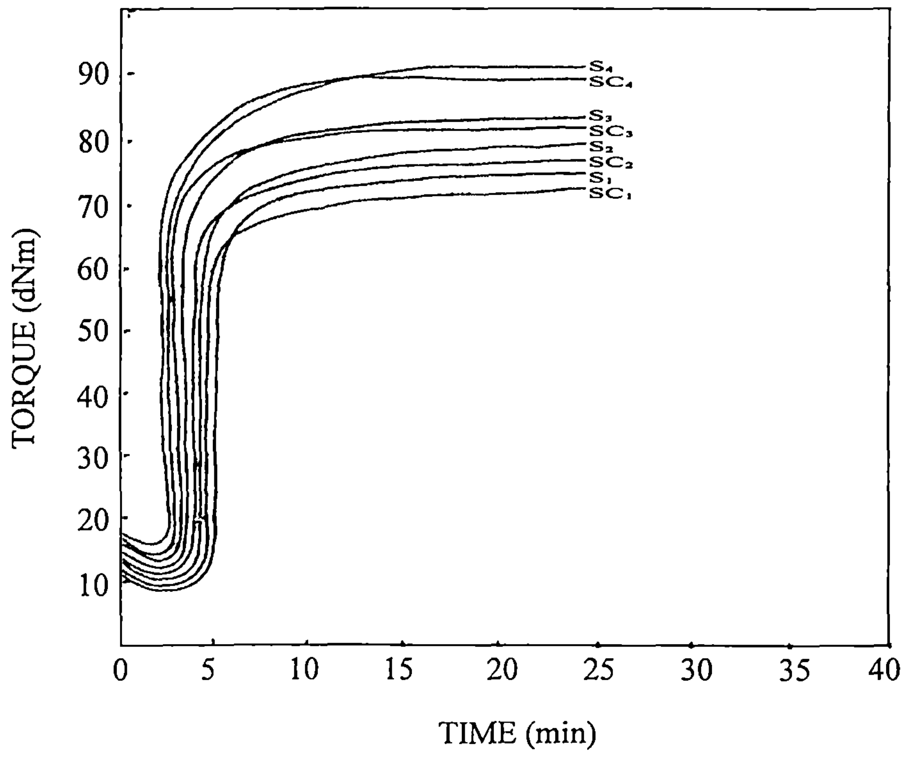


Figure 7.2. Rheographs at 150°C of carbon black filled 70/30 SBR/NBR blends

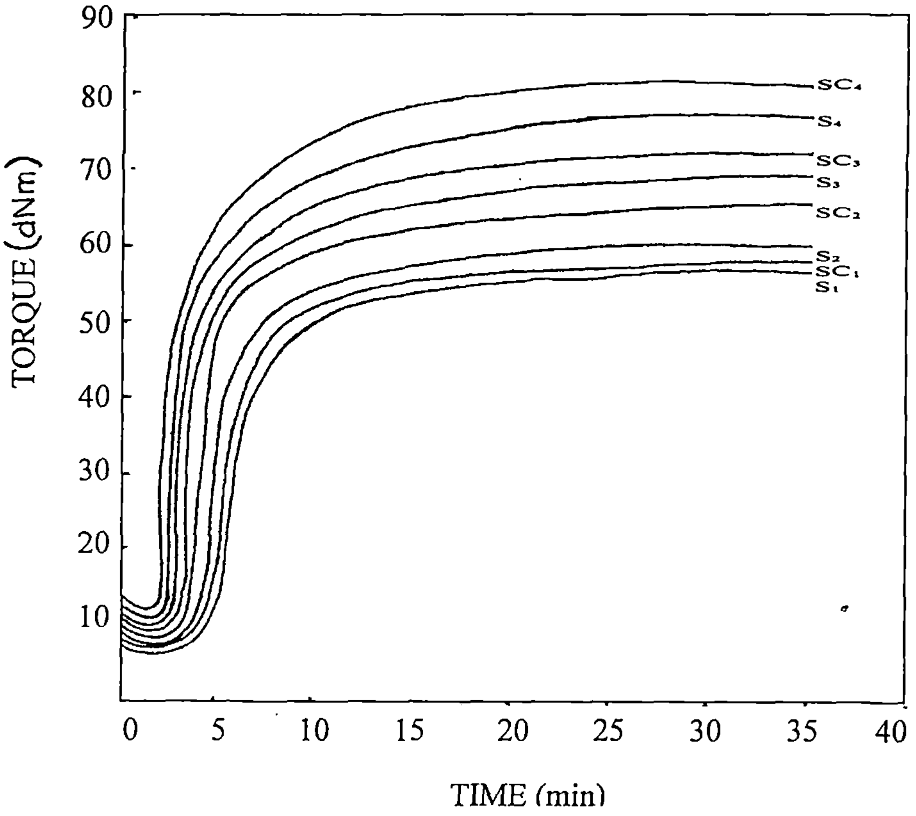


Figure 7.3. Rheographs at 150°C of silica filled 50/50 SBR/NBR blends

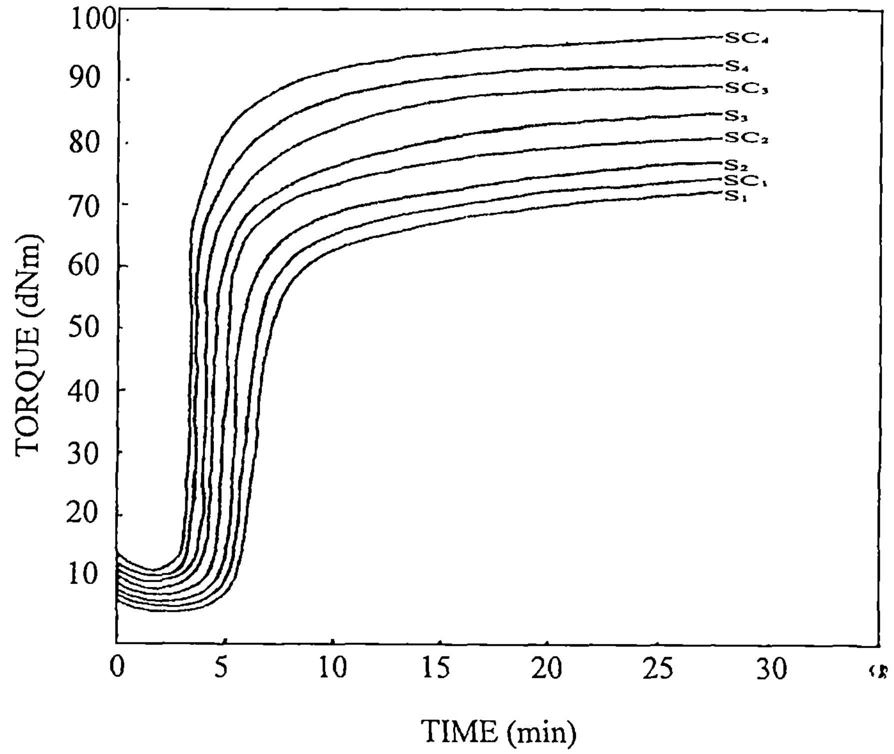


Figure 7.4. Rheographs at 150°C of carbon black filled 50/50 SBR/NBR blends

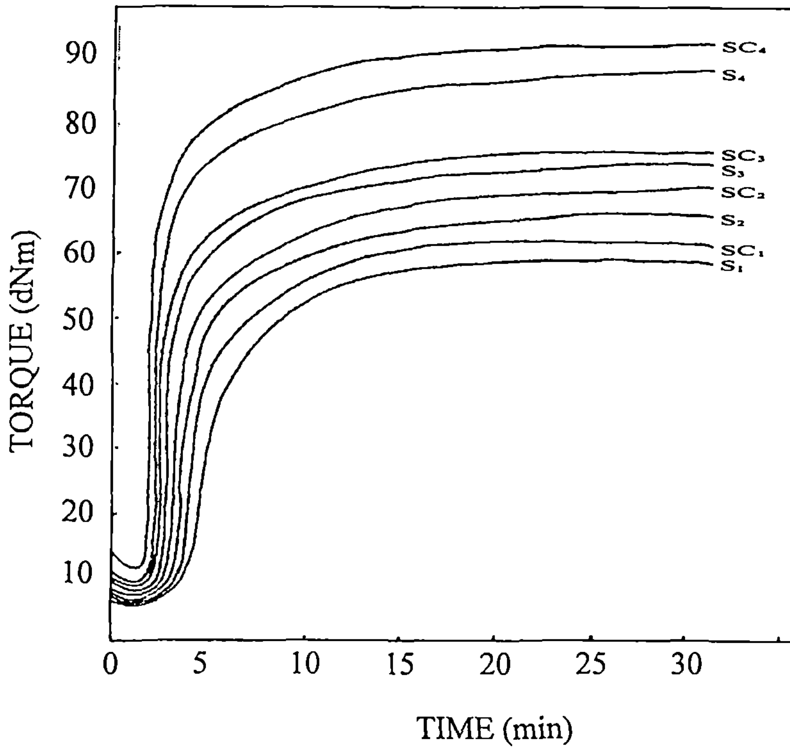


Figure 7.5. Rheographs at 150°C of silica filled 30/70 SBR/NBR blends

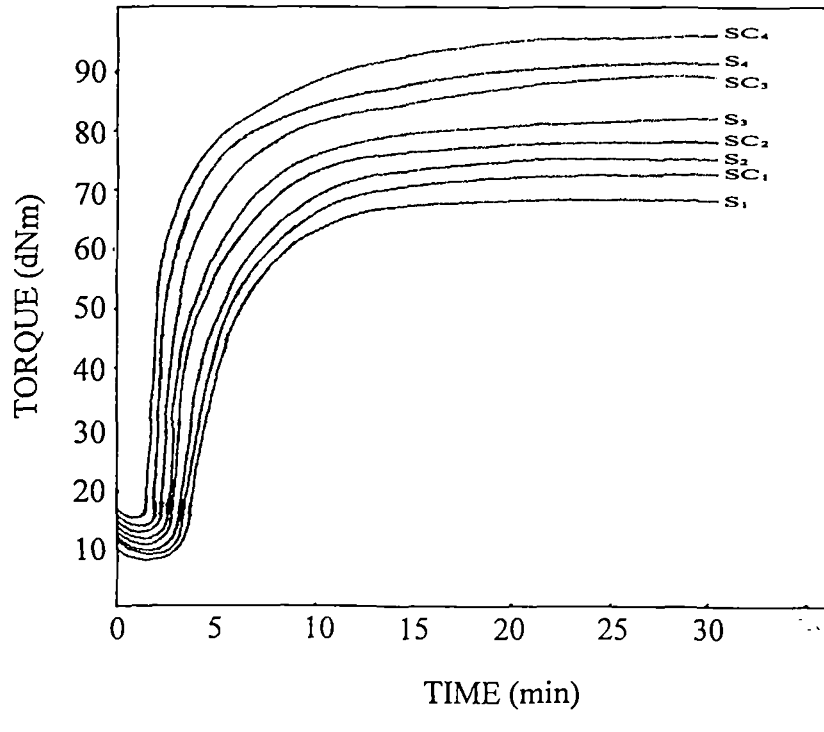


Figure 7.6. Rheographs at 150°C of carbon black filled 30/70 SBR/NBR blends

Table 7.2. Cure characteristics and swelling behaviour of carbon black and silica filled SBR/NBR (70/30) blends

Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
Optimum cure time (min)	11	10.5	10	10	10	9.5	9.5	9	6.5	6.5	5.5	5	6.5	6	5	4.75
Scorch time (min)	4.75	4.25	3.75	3.25	4.5	4	3.5	3	4.25	3.75	3.25	2.75	4	3.5	3	2.5
Mh-Mn (dN.m)	60.5	62.5	63	65	57	59.5	60	62	57	61	60.5	66	54	56	59	64
Swelling index (%)	255	236	215	196	234	202	191	192	190	180	174	160	173	169	162	149
Swelling coefficient	5.27	4.96	4.78	4.49	4.90	4.59	4.31	4.35	4.29	4.1	3.91	3.83	4.04	3.96	3.87	3.49
Volume fraction (V_r)	0.31	0.33	0.35	0.38	0.32	0.34	0.36	0.38	0.36	0.39	0.42	0.45	0.37	0.40	0.42	0.45
Crosslink density (Flory-Rehner) × 10^{-4}	4.3	5	5.8	6.5	4.4	5.2	6	6.7	6	7.1	8	8.9	6.1	7.3	8.2	8.97
Crosslink density (Mooney-Rivlin) × 10^{-3}	2.1	2.17	2.22	2.25	2.13	2.20	2.25	2.26	1.58	1.61	1.68	1.71	1.59	1.63	1.68	1.7

Table 7.3. Cure characteristics and swelling behaviour of carbon black and silica filled SBR/NBR (50/50) blends

Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
Optimum cure time (min)	12	11.5	11.5	10.5	11	11	11	10	13	11	10.5	9	12	10	9	8
Scorch time (min)	4	3.5	3	2.5	3.75	3.25	2.75	2.25	4.5	4	3.5	3	4.25	3.75	3.25	2.75
Mh-Mn (dN.m)	51	53.5	61	66	52	68	63	69	61	61	65	70	60	63	68	73
Swelling index (%)	240	222	200	185	210	101	169	142	187	174	156	135	171	149	140	122
Swelling coefficient	4.97	4.50	4.20	4.15	4.71	4.19	3.90	3.46	4.16	4.01	3.70	3.38	3.90	3.73	3.44	3.21
Volume fraction (V_r)	0.35	0.38	0.41	0.43	0.38	0.41	0.44	0.46	0.41	0.46	0.49	0.53	0.43	0.48	0.53	0.56
Crosslink density (Flory-Rehner) × 10^{-4}	3.63	4.15	5.3	6.1	4.01	4.7	6.1	6.9	5.3	6.8	7.7	8.8	5.9	7.5	8.6	9.1
Crosslink density (Mooney-Rivlin) × 10^{-3}	1.4	2.01	2.21	2.29	1.71	2.19	2.41	2.5	1.19	1.27	1.36	1.40	1.22	1.30	1.39	1.46

Table 7.4. Cure characteristics and swelling behaviour of carbon black and silica filled SBR/NBR (30/70) blends

Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
Optimum cure time (min)	11	10.5	9.5	8	9.5	10	8	7.5	10.5	9.5	9	8.5	10	9	8.5	8
Scorch time (min)	3.25	2.75	2.25	1.75	3	2.5	2	1.5	3.5	3	2.5	2	3.25	2.75	2.25	1.75
Mh-Mn (dN.m)	50	55	60.5	73	51.5	58	62	75	47.5	51	54.25	61	49.5	52	59.5	62.5
Swelling index (%)	220	206	190	181	232	202	192	179	184	176	172	158	169	141	126	115
Swelling coefficient	4.55	4.25	4.18	4.10	4.90	4.59	4.31	4.07	4.16	4.05	3.93	3.72	3.96	3.68	3.51	3.28
Volume fraction (V_r)	0.38	0.39	0.41	0.44	0.40	0.43	0.44	0.47	0.44	0.47	0.49	0.54	0.47	0.50	0.53	0.58
Crosslink density (Flory-Rehner) × 10^{-4}	3.16	3.9	5	5.7	3.56	4.5	5	6.4	4.81	6	7.3	8.2	5.7	6.9	8.3	9.1
Crosslink density (Mooney-Rivlin) × 10^{-3}	1.31	1.69	1.71	1.78	1.36	1.78	1.80	1.87	0.91	0.97	1.01	1.07	0.98	1.3	1.11	1.17

7.2.2 Effect of loading of fillers on technological properties

Effect of fillers on the mechanical properties of SBR/NBR blends in the presence and absence of compatibiliser are presented in Tables 7.5-7.7. The tensile strength values of compatibilised blends are higher than that of uncompatibilised blends as the NBR content increases there is more interaction between compatibiliser and blend constituents. Due to a reduction of interfacial tension on these blend compositions there is also an improved polymer filled interaction and more uniform distribution of filler in the two rubbers. Among the fillers [illegible] carbon black shows the maximum tensile strength in all blend compositions, owing to the higher reinforcing effect of rubbers.

Tear strength is an important property which contributes towards resistance to crack growth. Compatibilised blends exhibit higher tear strength than uncompatibilised samples. As filler loading increases the tear value also increases and the increase is maximum for carbon black filled vulcanisate due to its reinforcing nature, a number of filler particles will be present at the crack propagation tip to arrest the propagating cracks.

Resilience decrease as NBR content in the blend increases. Blends containing 5 phr DCSBR have higher resilience as compared to pure blends. Rebound resilience of different fillers on SBR/NBR blends with and without compatibiliser is presented in Tables 7.5-7.7. It reveals that resilence values are lower for compatabilised blend compared to uncompatabilised system in all the blend ratios. It is generally observed that as the filler content increases, resilience decreases.

Table 7.5. **Physical properties of carbon black and silica filled SBR/NBR (70/30) blends**

Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
Modulus, 300% (MPa)	3.2	4.16	5.38	6.48	3.25	4.3	5.5	6.8	4.17	6.2	8.1	9.9	4.1	6.5	8.1	9.8
Tensile strength (MPa)	5.0	6.3	8.16	9.33	5.1	6.4	8.4	9.5	6.09	9.8	12.98	16.0	6.11	9.89	13.4	16.3
Elongation at break (%)	290	270	245	220	300	275	250	225	300	280	255	230	310	290	265	235
Tear strength (kN/m)	18.7	21.6	26.8	31.9	19.2	22.1	28	32.4	31.2	35.6	41.3	47.9	31.6	37	42.6	49.4
Hardness (Shore A)	50	52	56	60	52	54	58	61	52	55	58	63	53	57	60	66
Resilience (%) Dunlop tripsometer)	56.8	51.3	49.4	46.2	56.0	50.9	48.0	44.6	53.4	49.7	46.3	43.9	53.0	48.8	45.0	42.2
Compression set (%) 22 h at 70°C	22.3	20.2	17.8	15.4	23.1	21.6	18.4	17.2	17.3	14.7	12.6	9.42	17.8	15.4	14	12.6
Heat build-up (°C)	20	22	28	34	22	25	32	39	20	21	26	31	21	23	29	35
Abrasion loss (mm^3)	128	139	155	169	127	140	160	174	59	69	77	84	59	71	81	86

Table 7.6. Physical properties of carbon black and silica filled SBR/NBR (50/50) blends

Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
Modulus, 300% (MPa)	2.98	4.1	7.4	9.2	3.16	4.8	9.1	10.2	5.1	7.8	9.2	10.8	5.3	8.6	10.2	11.1
Tensile strength (MPa)	4.78	6.66	104	11.8	7.06	8.08	11.28	13.0	8.22	12.1	15.8	18.1	9.36	13.8	16.98	20.01
Elongation at break (%)	300	280	256	243	350	335	310	280	330	312	293	270	370	350	328	300
Tear strength (kN/m)	15.9	20.2	26.4	30.1	20.1	24.8	30.6	34.1	32.8	37.0	39.4	42.9	34	38.6	42	46.4
Hardness (Shore A)	48	49	53	56	51	53	55	59	50	56	61	64	54	59	63	69
Resilience (%) Dunlop tripsometer)	57.94	55.21	53.76	49.6	58.88	56.3	55.0	50.2	52.95	49.4	44.71	40.13	53.42	50.8	45.96	41.81
Compression set (%) 22 h at 70°C	14.2	12.73	11.8	10.9	14.3	12.0	10.4	9.15	12.0	11.21	9.98	8.73	11.8	9.3	7.96	7.0
Heat build-up (°C)	23	26	29	35	20	22	24	30	22	26	33	39	19	23	30	34
Abrasion loss (mm^3)	135	168	179	204	130	160	170	192	71	78	89	92	66	71	80	88

Table 7.7. Physical properties of carbon black and silica filled SBR/NBR (30/70) blends

Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
Modulus, 300% (MPa)	3.1	4.3	6.9	8.2	3.3	5.02	7.4	9.1	4.18	6.3	9.8	12.4	4.5	7.18	11.4	13.1
Tensile strength (MPa)	5.8	7.1	9.8	11.7	6.2	8	11.1	13.2	7.3	12.7	15.4	17.8	8.1	13.9	16.7	18
Elongation at break (%)	340	325	305	280	380	362	340	315	365	345	320	295	345	320	295	270
Tear strength (kN/m)	16.09	19.73	21.9	23	18.9	24.8	29.3	33	28.7	34.75	39.6	44.8	30.1	36	42.9	52.1
Hardness (Shore A)	47	49	54	58	50	52	56	61	45	50	57	60	48	55	60	64
Resilience (%) Dunlop tripsometer)	58.7	55.4	50.1	47.2	59.9	56.5	51.4	48.0	54.08	50.6	44.7	41.8	55.81	51.8	45.1	42.3
Compression set (%) 22 h at 70°C	15.64	13.87	12.4	10.77	15.0	12.9	11.7	10.0	12.34	10.2	8.3	7.0	11.8	9.4	7.1	6.2
Heat build-up (°C)	26	29	37	45	20	26	28	36	25	30	36	42	19	22	28	36
Abrasion loss (mm³)	140	170	200	215	130	164	198	214	63	65	69	76	60	62	64	66

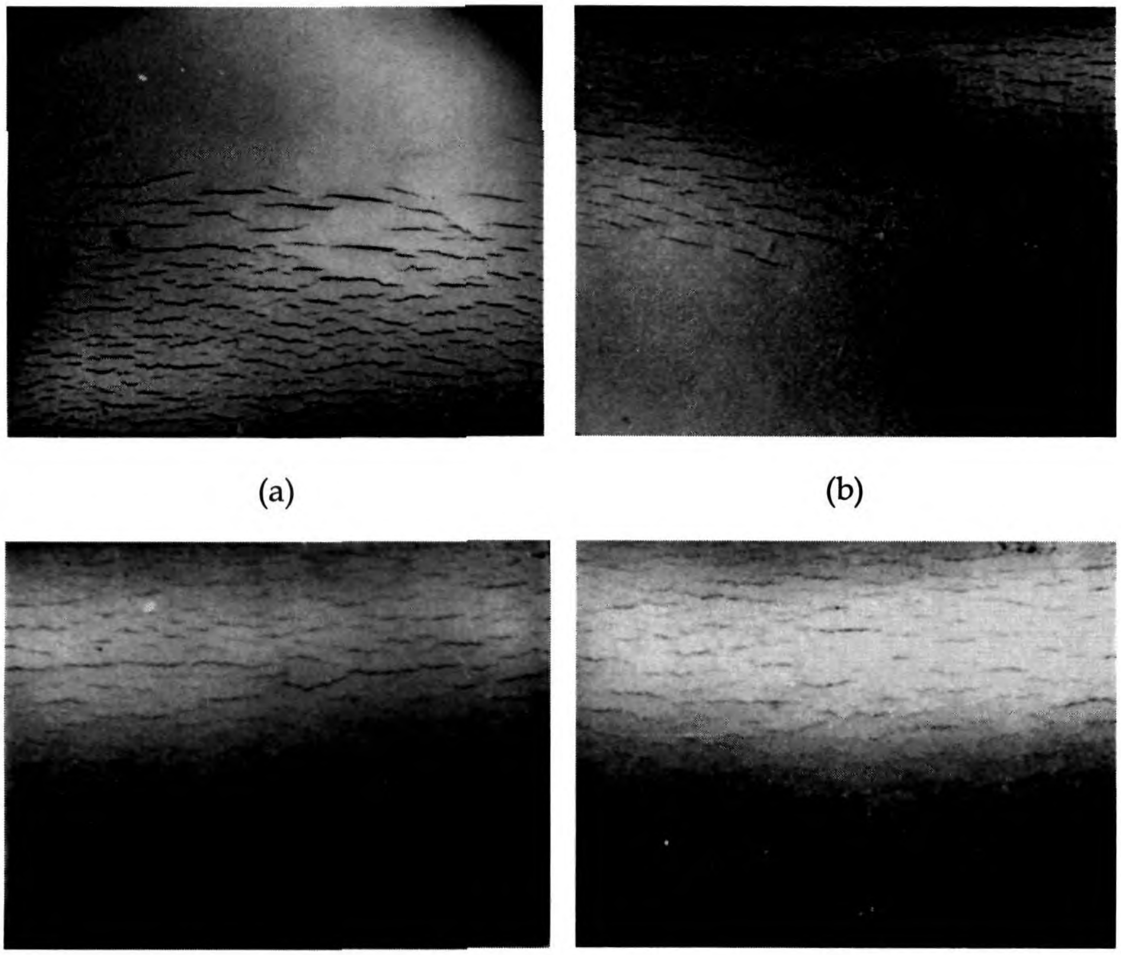
Heat build-up of an elastomer vulcanisate result from the internal friction in the sample. It can be seen from the table that compatibilised SBR/NBR blends exhibit lower heat build-up values. The presence of compatibiliser reduces heat build-up due to the formation of effective interface which avoids severe friction between the blend components and filler. Heat build-up registers an increase with increase in filler loading for all the fillers in both systems. Carbon black filled mixes have a lower resilience than the silica filled mixes.

Compression set of SBR/NBR blends with an without compatibiliser are shown in Tables 7.5-7.7. As the filler loading increases the set values are decreases in filled compatibilised blends compared to uncompatibilised system. The lower set values are noted for 30/70 filled composition and higher for 70/30 blends. It is found that the presence of black increases the set values due to a corresponding decrease in elastic recovery.

The carbon black filled mixes have a higher abrasion resistance as compared to silica filled mixtures. Compatibilised blends have a lower abrasion loss as compared to uncompatibilised blends.

Hardness of a material is usually expected to increase by the use of fillers. Carbon black filled compatibilised SBR/NBR blends exhibits higher hardness compared to that of the uncompatabilised one.

Rubber is prone to deterioration during processing and service. This is due to various chemicals such as oxygen, ozone solvents, etc. and physical agent such as heat and radiation. It also observed that addition of filler increases, ozone resistance of the compatibilised blends is shown in Figure 7.5 which shows the photographs of compatibilised SBR/NBR blends containing 10, 20, 30 and 40 phr carbon black, exposed to an ozone concentration of 50 pphm for 10 hours. From the photographs it is clear that as the loading of filler increases the ozone resistance also increases. The oil and air ageing behaviour of SBR/NBR blends with different fillers are given in Tables 7.8-7.10. The ageing experiments were conducted at a temperature of 70°C for 96 h. After ageing, the change in tensile strength of all the compatibilised samples is lower than the uncompatibilised blend. Thus ageing studies support the fact that there is a sufficient interaction of SBR and NBR through dichlorocarbene unit of SBR resulting in a higher crosslinking.



(a) (b)

(c) (d)

Figure 7.5. Optical photographs of 10 h of ozone exposed (a) 10, (b) 20, (c) 30, (d) 40 phr carbon black filled 50/50 compatibilised blend

Table 7.8. The oil resistance (5 days at 25°C) and air ageing (96 h at 70°C) of SBR/NBR 70/30 blends

Ageing Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
ASTM oil No. 1	6.63	6.57	6.51	6.45	6.53	6.48	6.42	6.34	6.60	6.53	6.45	6.37	6.59	6.42	6.35	6.26
ASTM oil No. 2	11.25	11.19	11.12	11.05	11.15	11.18	11.00	10.93	11.22	11.13	11.04	10.92	11.11	11.10	10.92	10.80
ASTM oil No. 3	36.4	35.65	34.89	34.12	35.5	34.74	33.96	33.16	36.35	35.5	34.64	33.79	35.42	34.56	33.68	32.82
Decrease in tensile strength (%)	40	42	45	48	39	41	44	48	38	40	43	45	36	38	40	44
Change in elongation at break (%)	30	35	40	50	28	33	38	49	28	34	38	48	26	30	35	46

Table 7.9. **The oil resistance (5 days at 25°C) and air ageing (96 h at 70°C) of SBR/NBR 50/50 blends**

Ageing Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
ASTM oil No. 1	4.56	4.42	4.27	4.11	4.21	4.08	3.91	3.74	4.53	4.36	4.19	4.0	4.19	4.0	3.82	3.63
ASTM oil No. 2	8.0	7.68	7.34	6.99	7.59	7.27	6.92	6.57	7.96	7.63	7.29	6.94	7.54	7.21	6.87	6.51
ASTM oil No. 3	25.62	24.60	23.57	22.51	24.23	23.18	22.14	21.06	25.59	24.55	23.50	22.44	24.18	23.12	22.06	20.98
Decrease in tensile strength (%)	42	45	48	49	37	40	42	43	41	43	46	48	36	39	41	44
Elongation at break (%)	35	42	48	57	30	35	40	50	33	39	46	55	30	35	42	50

Table 7.10. The oil resistance (5 days at 25°C) and air ageing (96 h at 70°C) of SBR/NBR 30/70 blends

Ageing Properties	Silica								Carbon black							
	Uncompatibilised				Compatibilised				Uncompatibilised				Compatibilised			
	10	20	30	40	10	20	30	40	10	20	30	40	10	20	30	40
ASTM oil No. 1	2.86	2.7	2.53	2.35	2.64	2.47	2.31	2.12	2.83	2.68	2.51	2.32	2.6	2.46	2.29	2.09
ASTM oil No. 2	4.69	4.23	3.77	3.33	4.05	3.58	3.12	2.67	4.62	4.17	3.71	3.25	3.97	3.51	3.06	2.59
ASTM oil No. 3	15.06	13.79	12.5	11.20	12.86	11.58	10.26	8.73	14.96	13.70	12.41	11.14	12.75	11.45	10.13	9.85
Decrease in tensile strength (%)	44	47	50	54	40	42	45	49	42	45	48	51	38	40	42	45
Elongation at break (%)	38	44	50	59	33	40	45	53	35	41	48	55	30	37	42	47

It can be seen from the Tables (7.8 - 7.10) that the oil and air ageing behaviour of compatibilised sample is better compared to that of uncompatibilised blends.

7.3 Effect of loading of carbon black and silica on swelling behaviour

7.3.1 Swelling parameters

The data obtained after swelling the blends in toluene at room temperature is given in Tables 7.2-7.4. It is clear from the table that the lower swelling is observed for compatibilised blends as compared with pure blends. Since NBR is more polar the SBR, there is restriction is swelling as NBR content increases, even if crosslink density is lower. As a consequence the solvent absorbed decreases as NBR content in the blend increases. Within a particular blend composition to restriction in swelling is due to the increased crosslinking.

The change in crosslink density (V_r) as a function of filler loading is presented in Tables 7.2-7.4. Compared to uncompatibilised samples compatibilised blend shows an increased in V_r with the addition of fillers due to the decrease in extent of swelling caused by higher polymer-filler interaction and a more crosslinking due to a homogeneous blend matrix. The carbon black filled blends have a higher volume fraction as compared to corresponding silica filled mixes showing that there is a higher polymer filler interaction or more crosslinking in its presence.

7.3.2 Calculation of crosslink density from swelling and stress-strain data

Knowing that diffusion is influenced by the polymer morphology, in addition to experimental variables, we have estimated the molar mass between crosslinks, M_c, from the sorption data.

The effect of fillers on the crosslink density values of SBR/NBR blend are presented in Tables 7.2-7.4. Higher crosslink density values are obtained for compatibilised samples and these increases with increase in filler loading. This shows that there is a greater crosslinking or polymer filler interaction in blends containing DCSBR.

7.3.3 *Stress-strain data*

The physical crosslinks in an elastomer vulcanisate can be understood by the use of Mooney-Rivlin equation.

$$C_1 = \rho RT\ \nu_{phys} \tag{7.1}$$

From Tables 7.2-7.4 it is obvious that ν_{phys} following the same trend as given by swelling data. Compared to swelling studies, the values of ν_{phys} are much higher. In swelling studies, the crosslinks are flexible to penetrants, but as the filler loading increases, they restrict swelling, which reduces the penetrant uptake which regularly increases the crosslink density. But in mechanical stretching of the samples, physical entanglements of chain also get involved in the process which result in higher ν_{phys} values.

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CHAPTER

8

EFFECT OF DICHLOROCARBENE MODIFIED STYRENE BUTADIENE RUBBER IN COMPATIBILISATION OF SBR/CR BLENDS

Results of this chapter have been communicated
to *Eur. Polym. J.*

8.1 Introduction

Blending of elastomers is being practised to achieve the best balance of physical properties, processability and cost. Elastomeric blends can either be miscible or immiscible depending on the free energy of mixing but the number of miscible elastomer blends has been very few.[1] Blending of two incompatible polymers yields a material with poor mechanical properties. However, different studies have demonstrated that the mechanical properties of such blends can be significantly improved by adding a suitable compatibiliser,[2-6] during processing. These materials decrease the macroscopic inhomogeneities and increase the stability of the morphology during processing by reducing the interfacial tension and subsequently reducing the dispersed phase size,[7-10] as expected from Taylor's theory.[11]

Specific interaction of polymer with functional group can increase the extent of thermodynamic compatibility. Compatibility of polymer blends can also be improved by use of copolymers containing segments chemically identical to the individual homopolymers.[12-15] If one of the polymers of a graft copolymer is miscible with one of the phases then also blend can be compatibilised.[16]

Blends of SBR and BR were found to be more compatible after vulcanisation by Livingston *et al.*[17] Blends based on functionally active rubbers are reported to be miscible due to crosslinking reaction by the functional groups.[18-25] Chlorinated polyethylene acts as a compatibiliser in chloroprene (CR)/ethylene propylene diene monomer rubber (EPDM) and acrylonitrile butadiene (NBR)/EPDM blends.[21] Polymethyl methacrylate

(PMMA) acts as a compatibiliser in blends of NR/NBR.[22] CR also is a compatibiliser in NR/NBR blends.[22]

Blending of SBR with CR has been done to have better crystallisation resistance, better compression set resistance, lower brittleness temperature and enhanced resistance to sunlight deterioration as compared with CR alone. Other important properties such as oil, heat, flame and ozone resistance decrease as the amount of SBR increases. There are miscible blends and they can be made miscible by use of certain interfacial agents that can have interactions with blend constituents. In this chapter, efficiency of dichlorocarbene modified SBR as a compatibiliser in SBR/CR blends is reported. Effect of level of modifications and the amount of modified SBR required for compaitbilisation are studied in detail.

8.2 Processing characteristics from rheometric data

The formulation of the mixes is given in Table 8.1. The rheographs of the mixes are shown in Figures 8.1-8.4 and cure characteristics are presented in Table 8.2. The maximum torque, optimum cure time, and scorch time change significantly with blend composition. In all blend compositions comparatively high optimum torque is obtained when concentration of either SBR or NBR in the blend is high. There is a progressive increase in scorch time as SBR concentration in the blend increase. Crosslinking of CR in presence of ZnO and accelerator like TMTD and ETU proceed very rapidly and ZnO or $ZnCl_2$ formed catalyses the reaction.[23] The mechanism of crosslinking by sulphenamide accelerator in SBR is accompanied by a great processing safety. With addition of 5 phr DCSBR of chlorine content varying from 15 to 35%, the maximum torque attained increases with a decrease in scorch time in all blend composition showing that there is a greater crosslinking. The presence of DCSBR brings about sufficient adhesion between the phases[24] due to the polar interaction among blend constituents. Thus there is a reduction of surface energy mismatch between polymers and there is sufficient interfacial crosslinks. This interfacial crosslink formation increases as concentration of chlorine in DCSBR increases.

Table 8.1. Formulation of SBR/CR blends in the presence and absence of DCSBR

Chemical	S7	S5	S3	S7*	S5*	S3*
SBR	70	50	30	70	50	30
CR	30	50	70	30	50	70
DCSBR*	-	-	-	5	5	5
Zinc oxide	5	5	5	5	5	5
Magnesium oxide	1.2	5	2.8	1.2	2	2.8
Stearic acid	1.15	1.0	0.8	1.15	1.0	0.8
CBS	0.7	0.5	0.3	0.7	0.5	0.3
TMTD	0.15	0.25	0.35	0.15	0.25	0.35
NA22	0.15	0.25	0.35	0.15	0.25	0.35
TDQ	0.7	0.5	0.3	0.7	0.5	0.3
Sulphur	1.54	1.1	0.66	1.54	1.1	0.66

*DCSBR containing (a) 15, (b) 20, (c) 25, (d) 30 and (e) 35% of chlorine content, respectively.
CBS - cyclohexyl benzathiazole; TMTD - tetramethyl thiuram disulphide; NA22 - ethylene thiourea; TDQ - 2,2,4-trimethyl 1,2-dihydroquinoline

Table 8.2. Cure characteristics of SBR/CR blends compatibilised by DCSBR

Blend composition	Chlorine content of DCSBR (%)	Optimum cure time at 150°C (t_{90}) (min)	Scorch time at 150°C (t_2) (min)	Mh-Mn (dN.m)
SBR/CR 70/30	0	26.5	5.5	30
	15	28	5	32
	20	29	4.75	33
	25	30	4.5	34
	30	26	4.25	34
	35	25	4	33
SBR/CR 50/50	0	22	4	28
	15	24	3.75	29
	20	25.5	3.5	30
	25	27	3.25	32
	30	25	3	31
	35	24	2.8	30
Dosage of compatibiliser (phr) having 25% chlorine content in 50/50 blend	1	23	3.75	29
	3	25	3.5	30
	5	27	3.25	32
	10	25	3	29
SBR/CR 30/70	0	16	3	31
	15	18.5	2.75	33
	20	20	2.5	34
	25	21	2	36
	30	18	1.75	35
	35	16	1.5	35

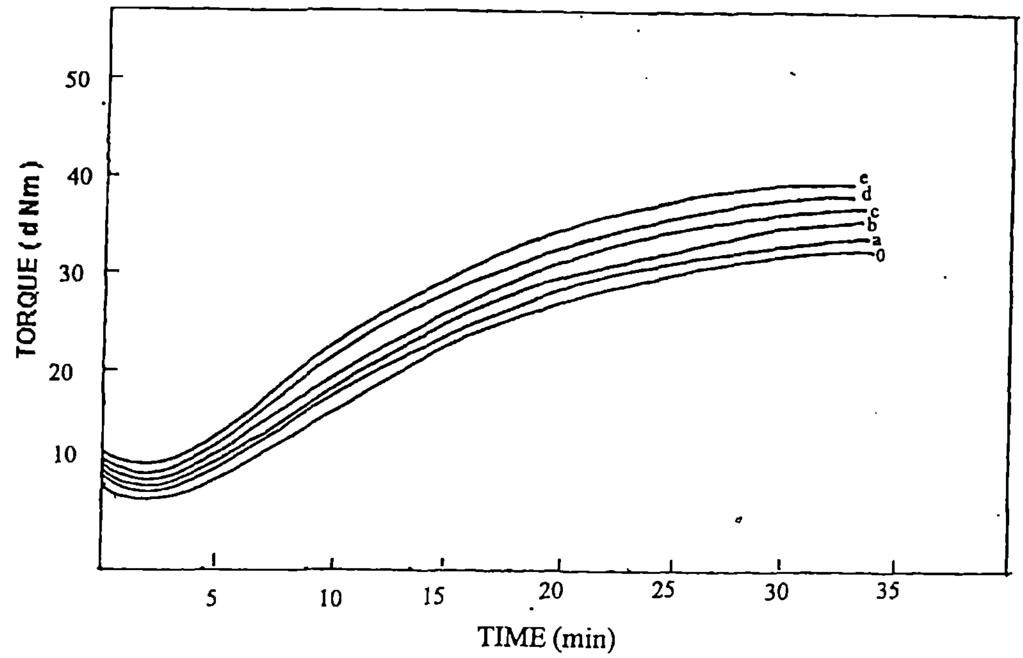

Figure 8.1. Rheographs of 70/30 SBR/CR blend and compatibilised blend containing 5 phr DCSBR of varying chlorine content at 150°C: (a) 15, (b) 20, (c) 25, (d) 30 and (e) 35%.

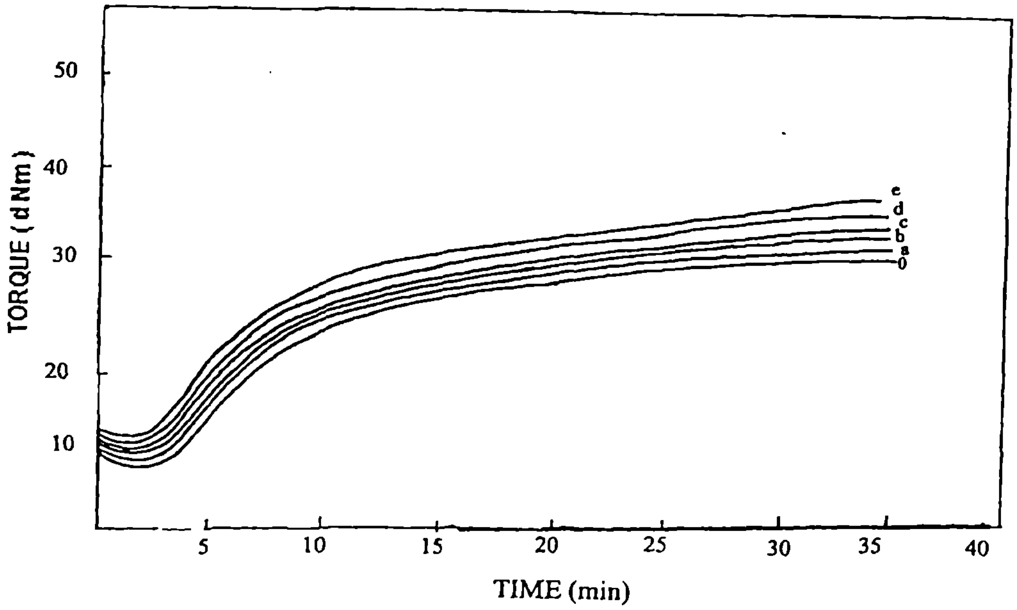

Figure 8.2. Rheographs of 50/50 SBR/CR blend and compatibilised blend containing 5 phr DCSBR of varying chlorine content at 150°C: (a) 15, (b) 20, (c) 25, (d) 30 and (e) 35%.

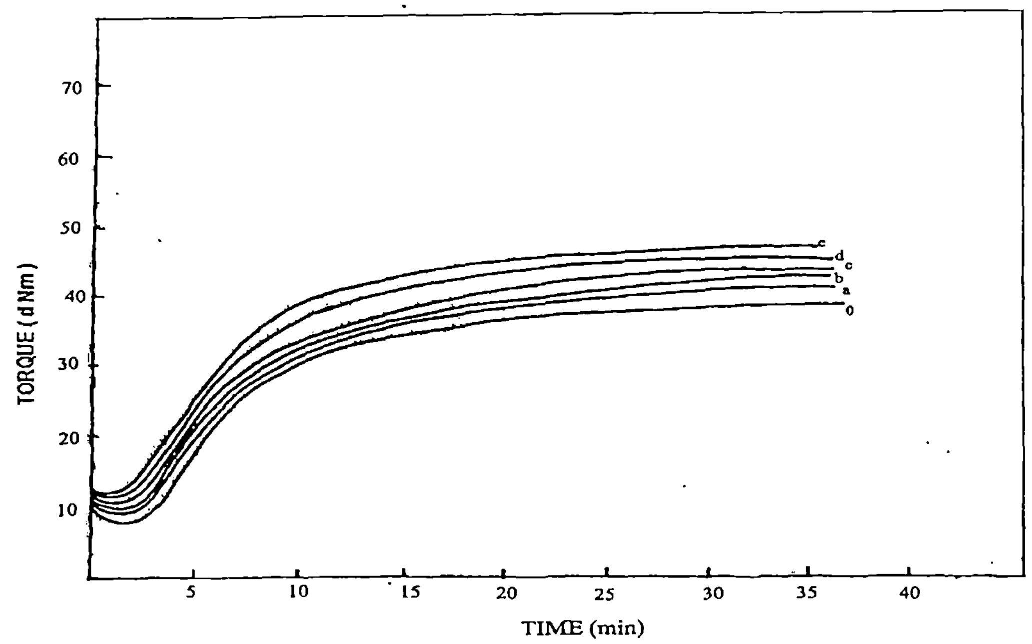

Figure 8.3. Rheographs of 30/70 SBR/CR blend and compatibilised blend containing 5 phr DCSBR of varying chlorine content at 150°C: (a) 15, (b) 20, (c) 25, (d) 30 and (e) 35%.

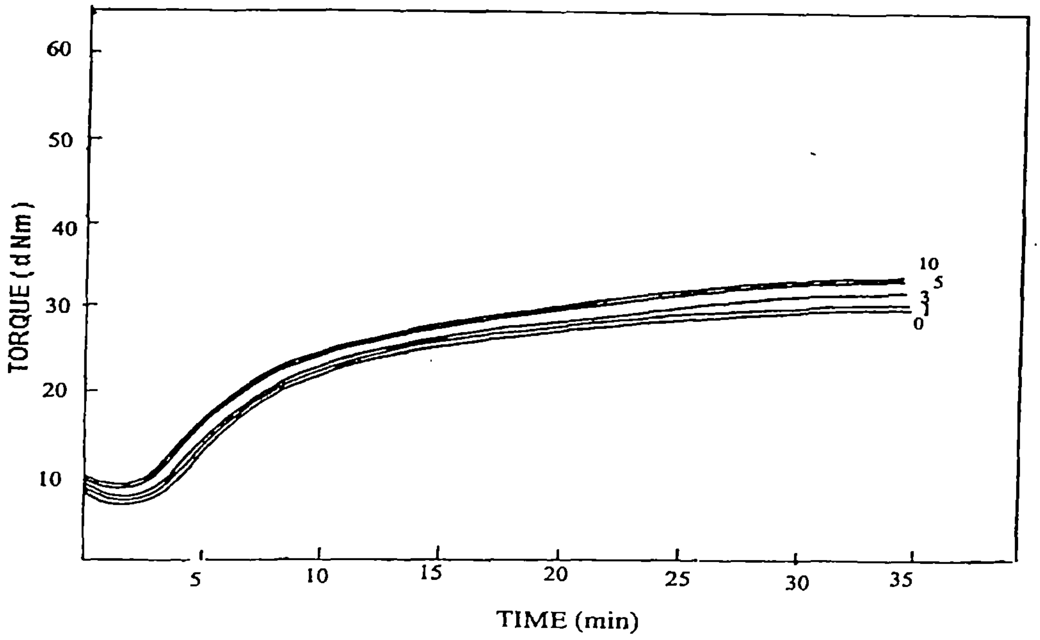

Figure 8.4. Rheographs of 50/50 SBR/CR blend and compatibilised blend containing different dosage of DCSBR (25%) at 150°C: (a) 0, (b) 1, (c) 3, (d) 5 and (e) 10 phr.

There is an increase in optimum cure time as chlorine content of DCSBR increase up to 25% beyond that level of chlorination the optimum cure time decreases. When the chlorine content is 25%, and the loading is 5 phr the compatibilising efficiency is maximum (as evidenced from tensile property). Since more reactants are needed for the formation of greater number of interface crosslinks, the optimum cure time is found to increase. But as the chlorine content increases further, the compatibiliser efficiency seems to decrease which ultimately ends or results in coalescence of dispersed domains. This reduces the interfacial area and thereby causing a decrease in optimum cure time. The effect of dosage of compatibiliser on rheometric torque is shown in Figure 8.2d. The maximum torque attained increases with the loading of compatibiliser. However at a dosage of 10 phr the maximum torque is only marginally higher than that obtained with 5 phr DCSBR. It is clear that as loading of the compatibiliser increases there is greater interaction among the constituents promoting interfacial crosslinks. The optimum cure time increases as the dosage of DCSBR increases up to 5 phr and beyond this dosage the value drops. Hence optimum vulcanisation characteristics are obtained with DCSBR of chlorine content 25% and at a dosage of 5 phr.

8.3 Characterisation of blends

8.3.1 Thermal analysis

The DSC traces of pure SBR and CR and their 50/50 blend in the presence and absence of compatibiliser are presented in Figure 8.5. Pure SBR shows a glass transition temperature (T_g) at -56°C and pure CR shows a T_g at -33°C. For uncompatibilised blend, there appears to be two transition in the temperature range from -60 to -35°C which indicates the presence of microlevel inhomogeneity. The transition at -56 and -33°C for the blends correspond to the transition of pure SBR and pure CR, respectively. However, the blend with 5 phr of 25% chlorine containing DCSBR shows a single transition in the temperature range -55 to -33°C with a mid point around -40°C, showed that DCSBR acts as a compatibiliser in blends of SBR/CR.

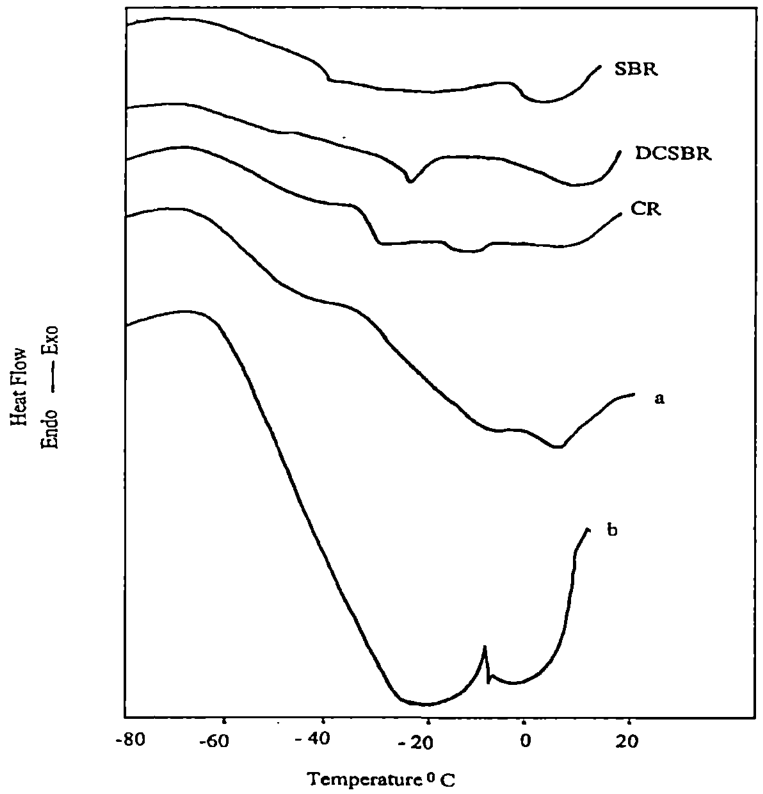

Figure 8.5. DSC thermograms of 50/50 SBR/CR blend: (a) without compatibiliser and (b) compatibiliser with 5 phr loading.

8.3.2 FTIR analysis

Figure 8.6 shows the IR spectra of pyrolysate of SBR, CR, SBR/CR 50/50 blend, 50/50 blend containing 5 and 10 phr DCSBR, and the IR absorption data are given in Table 8.3.

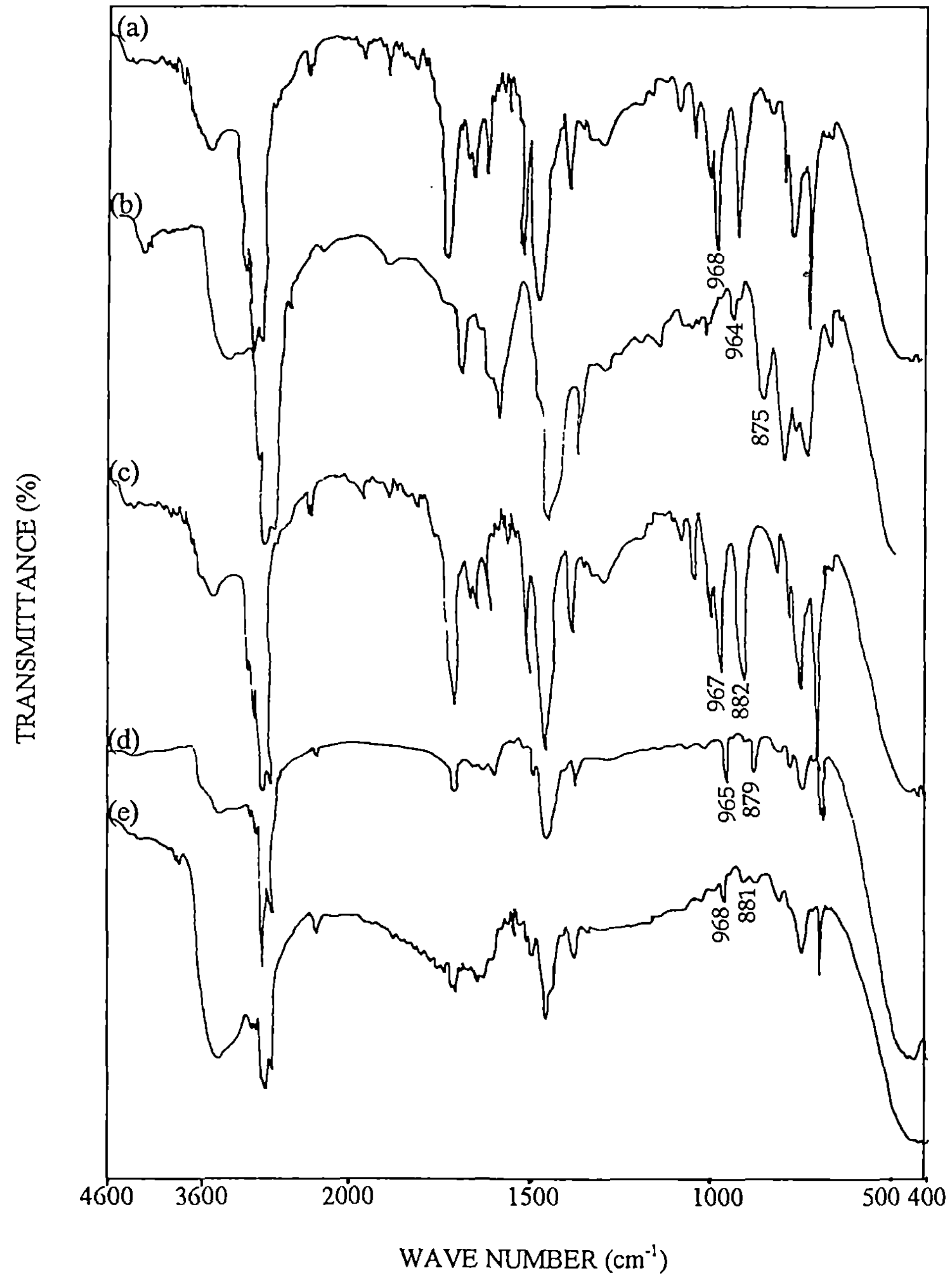

Figure 8.6. **FTIR spectra of pyrolysate of (a) SBR, (b) CR, (c) 50/50 SBR/CR blend (d) blend containing 5 phr and (e) blend containing 10 phr DCSBR**

Table 8.3. IR absorption peak of (a) SBR, (b) CR, (c) 50/50 SBR/CR blend (d) blend containing 5 phr and (e) blend containing 10 phr DCSBR

Materials	Wave number (cm^{-1})	Reputed assignment
(a)	968	Trans-CH=CH-
	698	Aromatic substitution
	1653	cis-CH=
(b)	964	-CH=CH_2
	876	C-Cl
	814	Aromatic substitution
(c)	967	-CH=CH-
	882	C-Cl
	814	Aromatic substitution
(d)	965	-CH=CH-
	879	C-Cl
	818	Aromatic substitution
(e)	966	CH=CH
	881	C-Cl
	814	Aromatic substitution

It is considered that there would be sufficient interaction between the polar segments of modified SBR with CR pahse and butadiene part with SBR phase, thereby reducing the interfacial tension. Pure CR shows an IR absorption at 875 cm^{-1}, due to the C-Cl stretching. In 50/50 blend the C-Cl absorption shift to 882 cm^{-1}. Blend with 5 phr DCSBR, the C-Cl stretching shift to 879 cm^{-1} and the corresponding trans-CH=CH shift to 965 cm^{-1}. There is no shift in the IR absorption for SBR/CR blend containing higher concentration of DCSBR. Hence at 5 phr DCSBR (optimum concentration), there is sufficient interaction between DCSBR and CR.

8.4 *Effect of compatibiliser on technological properties*

The physical properties of the blends are given in Tables 8.4-8.7. In pure blends tensile strength, elongation at break and modulus increases as CR concentration increases. The mechanical properties are not only governed by attainment of a higher rheometric torque, but also other factors like presence of crystallinity and uniform distribution of crosslinks in blend components. SBR has very poor gum strength while CR has comparatively very high gum strength. The resilience shows a decrease whereas compression set increases with the increase in CR concentration in the blends. Mechanical properties in all blend composition improve with addition of 5 phr DCSBR of chlorine content varying from 15-35%. The level of improvement depends on the chlorine content of DCSBR. Tensile strength and elongation at break, hardness and resilience increase while compression set decrease with increase in chlorine content of DCSBR up to 25% and then decreases. Efficient compatibilisation by 25% chlorine containing DCSBR creates strong interfacial crosslinks which results in an increase in tensile strength. The improvement in mechanical properties is more effective at 50/50 blend composition. A comparatively higher tensile strength, elongation at break and tear strength is obtained for the compatibilised 30/70 SBR/CR blend. The microscopic extension ratio of the dispersed CR domains is much higher than the macroscopic extension ratio during tensile test. Greater extension ratios causes strain induced crystallisation in CR which results better tensile properties in these cases. Owing to the absence of efficient interfacial crosslink the uncompatibilised blend show comparatively poor mechanical properties. The tensile strength values for compatibilised SBR/CR 70/30 are found to comparatively lower due to higher proportion of amorphous and weak SBR in this blend .

Table 8.4. Mechanical properties of blends of 70/30 SBR/CR compatibilised by DCSBR of chlorine content varying from 15-35%

Properties	Percentage of chlorine in DCSBR used at 5 phr loading					
	(1)	(2)[a]	(3)[b]	(4)[c]	(5)[d]	(6)[e]
Modulus, 300% (MPa)	1.7	1.8	1.82	1.67	1.83	1.85
Tensile strength (MPa)	3.2	3.3	3.4	3.8	3.5	3.19
Elongation at break (%)	430	370	380	500	420	390
Tear strength (kN/m)	19.4	16.6	18.8	19.1	19.8	19.4
Hardness (Shore A)	31	33	35	36	38	39
Resilience (%) (Dunlop tripsometer)	62	63	64	65	64	63
Compression set (%) 22 h at 70°C	18.6	17.5	16.6	15.4	15.8	16.9

a, b, c, d and e are the DCSBR containing 15, 20, 25, 30 and 35% of chlorine content, respectively.

Table 8.5. Mechanical properties of blends of 50/50 SBR/CR compatibilised by DCSBR of chlorine content varying from 15-35%

Properties	Percentage of chlorine in DCSBR used at 5 phr loading					
	(1)	(2)[a]	(3)[b]	(4)[c]	(5)[d]	(6)[e]
Modulus, 300% (MPa)	1.6	1.7	2.1	2.94	2.48	2.0
Tensile strength (MPa)	3.9	4.6	5.73	6.5	5.8	5.2
Elongation at break (%)	520	550	580	680	600	490
Tear strength (kN/m)	16.7	16.0	19.1	20.9	20.4	19.0
Hardness (Shore A)	33	33	36	39	41	43
Resilience (%) (Dunlop tripsometer)	60	61	63	64	62	61
Compression set (%) 22 h at 70°C	20.8	20.8	19.4	18.1	20.2	22.0

a, b, c, d and e are the DCSBR containing 15, 20, 25, 30 and 35% of chlorine content, respectively.

Table 8.6. **Mechanical properties of blends of 30/70 SBR/CR compatibilised by DCSBR of chlorine content varying from 15-35%**

Properties	Percentage of chlorine in DCSBR used at 5 phr loading					
	(1)	(2)[a]	(3)[b]	(4)[c]	(5)[d]	(6)[e]
Modulus, 300% (MPa)	2.39	1.71	1.31	1.80	1.28	1.65
Tensile strength (MPa)	8.10	6.9	7.0	8.4	6.4	6.6
Elongation at break (%)	690	650	750	800	750	700
Tear strength (kN/m)	25	20.5	21.6	25.8	21.7	18.9
Hardness (Shore A)	28	31	33	35	37	38
Resilience (%) (Dunlop tripsometer)	53	54	54	55	52	51
Compression set (%) 22 h at 70°C	32.5	31.6	28.8	25.8	27.8	28

a, b, c, d and e are the DCSBR containing 15, 20, 25, 30 and 35% of chlorine content, respectively.

Table 8.7. **Mechanical properties of blends of 50/50 SBR/CR compatibilised by DCSBR**

Properties	Loading of 25% chlorine containing DCSBR (phr)				
	0	1	3	5	10
Modulus, 300% (MPa)	1.66	1.98	2.35	2.94	2.8
Tensile strength (MPa)	3.9	4.6	5.73	6.5	5.8
Elongation at break (%)	520	400	440	680	570
Tear strength (kN/m)	16.7	17	18.4	20.9	21.3
Hardness (Shore A)	33	34	37	39	42
Resilience (%) Dunlop tripsometer)	60	62	63	64	61
Compression set (%) 22 h at 70°C	20.8	19.3	18.8	18.1	21.3

The tensile strength of 50/50 composition increases with loading of compatibiliser (Table 8.7) up to 5 phr and with further increase in the concentration of compatibiliser, tensile strength does not change much. This may be due to the super saturation of the interphase with the compatibiliser which increases interfacial tension.

8.5 Calculation of crosslink density

(a) Stress-strain isotherms

The extent of physical crosslinks in an elastomer vulcanisate can be assessed by using Mooney Rivlin equation.[25-27]

The plots obtained for stress-strain data are presented in Figure 8.7 and the values of crosslink density are shown in Table 8.8. It can be seen that the force and crosslink density increases as the concentration of DCSBR increases in 50/50 blend and is in agreement with the increase in rheometric torque. C_2 a term which serves as a measure of departure of observed stress-strain relationship from the form suggested by statistical theories[28] is given in Table 8.3. $2C_2$ value increase with the loading of compatibiliser up to 5 phr and then decreases. Observation of a higher $2C_2$ for the 50/50 blend containing 5 phr DCSBR shows the presence of higher chain entanglement.[28] Since the elastomer matrix is composed of two components a higher entanglement shows better molecular level mixing. At higher concentration of DCSBR there is probably less chain entanglement and hence molecular level mixing through there is a much enhanced polar interactions.

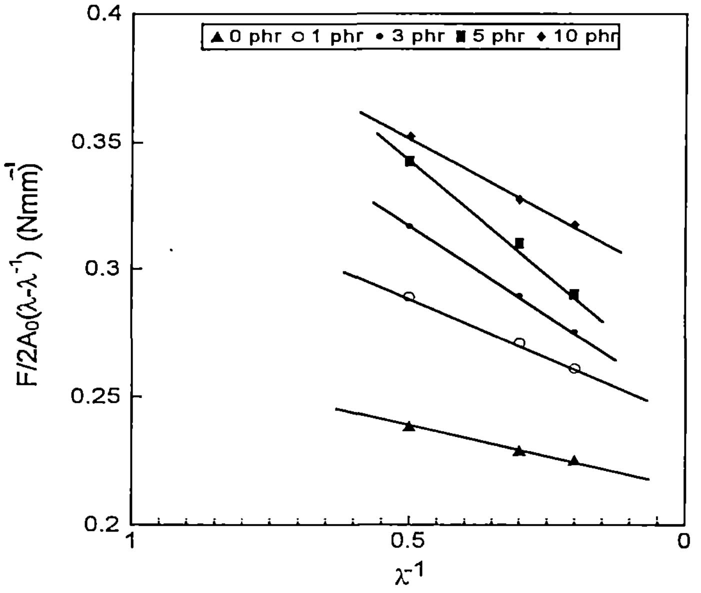

Figure 8.7. **Plots of $F/2A_0\ (\lambda - \lambda^{-1})$ vs. λ^{-1} of 50/50 SBR/CR blend with different dosage of compatibiliser.**

Table 8.8. **Crosslink density parameters C_1, C_2, ν_{phys}, V_r and difference in rheometric torque of 50/50 SBR/CR blend with varying concentration of compatibiliser**

Compatibiliser loading (phr)	$\nu_{phys} \times 10^{-3}$ (gmol/cc)	Mh-Mn (dN.m)	$2C_2$ (Nmm^{-2})	$2C_1$ (Nmm^{-2})	V_r (from swelling studies)
0	1.06	28	1.04	0.536	0.3364
1	1.22	29	2.32	0.686	0.3568
3	1.98	30	3.36	0.750	0.3685
5	2.75	32	4.0	0.890	0.3874
10	2.09	29	3.12	0.82	0.3766

(b) Swelling studies

Equilibrium swelling in toluene to assess the volume fraction (V_r) of the rubber network in the swollen gel was calculated. V_r increases with the addition of compatibiliser progressively up to 5 phr and at still higher concentration the value of Vr drops down. This is due to the decrease in extent of swelling caused by higher polymer-polymer interactions and increased interfacial crosslinks formed in presence of compatibiliser. This is in good agreement with the crosslink density obtained from stress-strain data.

8.6 Effect of different fillers on compatibilised SBR/CR (50/50) blends

The rheographs of carbon black and silica filled blends in the presence and absence of compatibiliser are presented in Figure 8.8 (CU^1, CU^2, CU^3 and CU^4 are the uncompatabilised blend containing 10, 20, 30 and 40 phr carbon black, CC^1, CC^2, CC^3 and CC^4 are the compatabilised blend containing 10, 20, 30 and 40 phr carbon black) and Figure 8.9 (SU^1, SU^2, SU^3 and SU^4 are the uncompatabilised blend containing 10, 20, 30 and 40 phr silica, SU^1, SU^2, SU^3 and SU^4 are the compatabilised blend containing 10, 20, 30 and 40 phr silica) and the formulation of the mixes are given in Tables 8.9 and 8.10. The rheometric torque increases with the addition of 5 phr of DSCBR. The optimum cure time increases whereas scorch time decreases with the addition of filler. The carbon black filled blends shows comparatively higher Mh-Mn value, higher optimum cure time and lower scorch time as compared to silica filled blends.

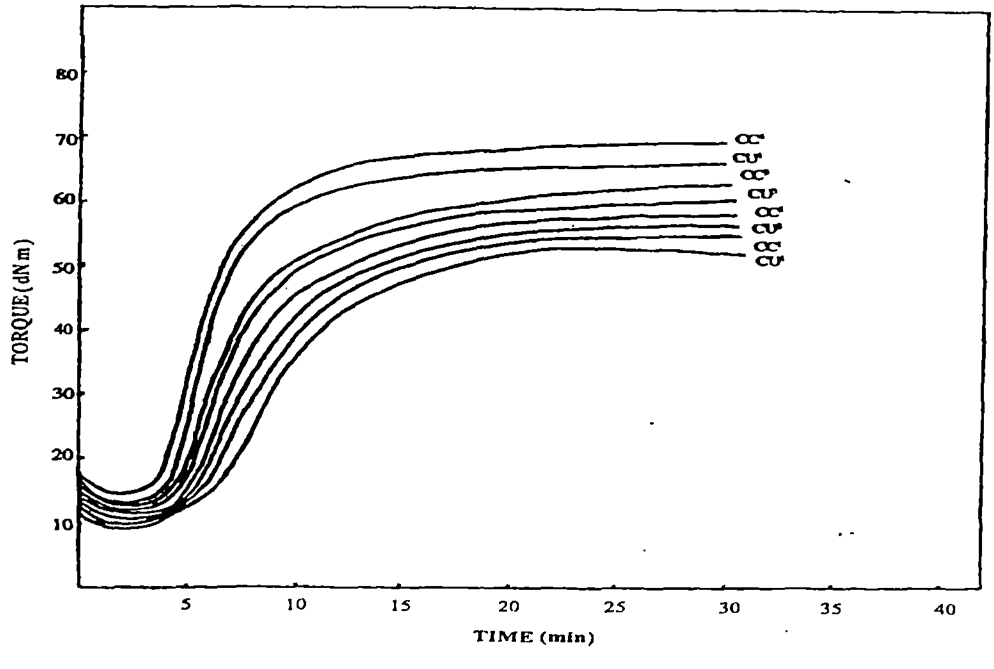

Figure 8.8. **Rheographs at 150°C of carbon black filled 50/50 SBR/CR blend and compatibilised blend.**

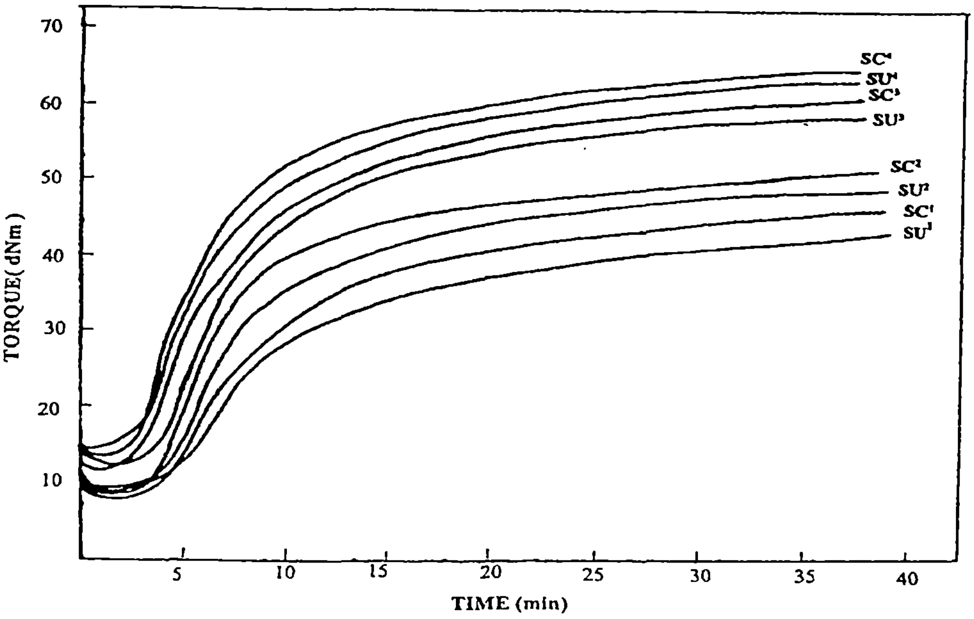

Figure 8.9. **Rheographs at 150°C of silica filled 50/50 SBR/CR blend and compatibilised blend**

Table 8.9. **Formulation of 50/50 SBR/CR carbon black filled blends in the presence and absence of DCSBR**

Chemical	CU^1	CC^1	CU^2	CC^2	CU^3	CC^3	CU^4	CC^4
SBR	50	50	50	50	50	50	50	50
CR	50	50	50	50	50	50	50	50
DCSBR*	-	5	-	5	-	5	-	5
Zinc oxide	5	5	5	5	5	5	5	5
Magnesium oxide	2	2	2	2	2	2	2	2
Stearic acid	1	1	1	1	1	1	1	1
CBS	5	5	5	5	5	5	5	5
TMTD	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
NA22	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Aromatic oil	0.7	0.7	1.4	1.4	2.1	2.1	2.8	2.8
HAF C-black	10	10	20	20	30	30	40	40
Sulphur	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1

*DCSBR containing 25% of chlorine content.

Table 8.10. Formulation of 50/50 SBR/CR precipitated silica filled blends in the presence and absence of DCSBR

Chemical	SU^1	SC^1	SU^2	SC^2	SU^3	SC^3	SU^4	SC^4
SBR	50	50	50	50	50	50	50	50
CR	50	50	50	50	50	50	50	50
DCSBR*	-	5	-	5	-	5	-	5
Zinc oxide	5	5	5	5	5	5	5	5
Magnesium oxide	2	2	2	2	2	2	2	2
Stearic acid	1	1	1	1	1	1	1	1
CBS	5	5	5	5	5	5	5	5
TMTD	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
NA22	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Aromatic oil	0.7	0.7	1.4	1.4	2.1	2.1	2.8	2.8
Ppt. silica	10	10	20	20	30	30	40	40
Diethylene glycol	0.5	0.5	0.5	0.5	1	1	1.5	1.5
Sulphur	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1

*DCSBR containing 25% of chlorine content.

There is enhancement in technical properties with the addition of filler as shown in Tables 8.7 and 8.8. The blend containing fillers of carbon black and silica show a higher tensile strength, tear strength and abrasion resistance as compared to uncompatibilised blends. This is due to the improvement in polymer filler interaction resulting from effective interfacial adhesion and the uniform distribution of the phases. In blends of SBR and CR, carbon black has a tendency to migrate to SBR phase. In blends containing DCSBR there is reduced interfacial tension, and filler distribution is more uniform resulting in better mechanical properties as compared to uncompatibilised blends.

Table 8.7. Mechanical properties of compatibilised 50/50 SBR/CR blend with different loading of carbon black filler

Properties	CU^1	CC^1	CU^2	CC^2	CU^3	CC^3	CU^4	CC^4
Modulus, 300% (MPa)	3.2	4.1	3.9	4.8	5.3	6.1	5.8	6.7
Tensile strength (MPa)	8.0	9.5	11.8	14.8	16.5	19.0	19.8	21.2
Elongation at break (%)	560	540	530	510	500	475	560	430
Tear strength (kN/m)	31.3	41.0	46.0	50.6	55.1	57.1	56.2	62.0
Din abrasion loss (mm^3)	196	162	129	105	111	93	96	70
Heat build-up (°C)	31	28	37	33	42	36	47	43
Compression set (%) 22 h at 70°C	16.8	15.2	15.4	13.0	13.4	11.2	12.4	10.9
Resilience (%) (Dunlop tripsometer)	60	60	52	58	49	55	41	50

Table 8.8. Mechanical properties of compatibilised 50/50 SBR/CR blend with different loading of silica filler

Properties	SU^1	SC^1	SU^2	SC^2	SU^3	SC^3	SU^4	SC^4
Modulus, 300% (MPa)	2.5	3.0	2.9	3.7	3.5	4.1	4.0	4.9
Tensile strength (MPa)	5.8	7.8	10.1	12.3	11.2	13.0	14.1	15.0
Elongation at break (%)	580	570	550	530	540	490	470	455
Tear strength (kN/m)	23.7	25.9	25.5	28.4	30.6	32.8	35.4	37.8
Din abrasion loss (mm^3)	254	216	181	150	132	119	114	109
Heat build-up (°C)	29	25	32	28	36	32	38	34
Compression set (%) 22 h at 70°C	24	21	21	19	20	18	18	16
Resilience (%) (Dunlop tripsometer)	64	65	62	64	57	62	52	60

The heat build up and compression set values decreases whereas resilience increase on compatibilisation. The compatibiliser present in the blend reduces the heat build-up due to the formation of effective interface which avoids severe friction between component and polymer filler friction. The heat build up increases with increase in filler loading and the effect is maximum for the carbon black filled samples.

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CHAPTER

9

SUMMARY AND CONCLUSION

The chemical modification of SBR can be carried out through dichlorocarbene modification by the alkaline hydrolysis of $CHCl_3$ using CTAB as a phase-transfer catalyst. The chlorine content increases with temperature of the reaction and the reaction follows first-order kinetics. The modification levels of after 12 h. At a temperature of 60^0C the rate of modification is very high in the first fifteen minutes. Dichlorocarbene addition of SBR occurs to levels of chlorine up to 35% in the modified sample. The molecular weight determination carried out by GPC reveals that chemical modification is accompanied by an increase in high molecular weight fraction. Proton NMR and FTIR studies reveals the attachment of chlorine through cyclopropyl ring to the main chain of SBR, during its dichlorocarbene modification. As reaction time increases, there is a reduction in the intensity of IR absorption at 968 cm^{-1} which is due to trans - CH=CH and at 1653cm^{-1} which is due to cis CH=CH. The IR absorption at 698 cm^{-1} which is due to the presence of an aromatic ring, remains unaffected during modification. The vinyl double bond (absorption at 910 cm^{-1}) also remains unaffected during modification. Hence the dichlorocarbene modification occurs at the cis and trans double bond of butadiene segment present in SBR, takes part in reaction. A satisfactory level of vulcanisation is achieved by either sulphur or peroxide when chlorine content of DCSBR is lower than 25% and by peroxide at a levels of 30% chlorine content. Vulcanisation with sulphur is not possible when chlorine content of modified sample is greater than 25%. This is due to the fact that as chlorine content of modified sample increases there is a reduction in reactive sites for vulcanisation along with electrophyllic effect of chlorine. DCSBR does not undergo crosslinking in presence of metal oxide alone, due to the absence of reactive allylic or tertiary allylic chlorine. Dichlorocarbene modification is accompanied by a reduction of double bonds and they can be vulcanised with an accelerated sulphur system that imparts excellent tensile strength and oxidative stability. Resilience decreases whereas compression set, hardness and heat build-up increases with increasing level of chlorination. Dichlorocarbene modification of SBR results in an improvement in mechanical properties, ageing and oil resistance depending on the chlorine content of modified SBR. The modification imparts excellent oil resistance superior to that of CR and approaching that of sulphur cured NBR. DCP cured DCSBR result in a much enhanced oil resistance superior to conventionally cured NBR. The structural change that takes place during modification brings about crystallisation of the material under low temperature transitions and this could be due to polar interactions. The basic decomposition pattern and thermal stability of the samples are superior to those of commercial chloroprene rubber. The presence of chlorine in the samples enables them to be safely used as a flame-resistant material for indoor applications. The modified SBR have excellent solvent resistance compared to other chlorine-containing elastomers like chloroprene, even at low levels of chlorination (16-20%), where they exhibit rubbery properties.

Blends of NR and DCSBR is accompanied by an excellent mechanical properties compared with other NR based rubber blends. Further improvement in mechanical properties is obtained by using 5-10 phr of SBR as a compatibiliser depending on blend composition. A higher rheometric torque obtained in 50/50 blend in presence of compatibiliser reveals the formation of higher crosslinks. In 1:1 blends the presence 5 phr of SBR (compatibiliser) imparts very good mechanical properties as compared to uncompatibilised blends. The presence of higher state of crosslinking in compatibilised blends is supported by the higher crosslink density obtained in these samples from swelling and stress-strain data. The observed improvement in mechanical properties of 50/50 blends with compatibiliser is supported by the differential scanning calorimetry and also by scanning electron micrographs, which confirms that SBR in small proportion of 5-10 phr acts as a compatibiliser in NR/DCSBR blends.

Blending of high acrylonitrile NBR with SBR can be carried to get a degree of oil resistance equal to that given by a low acrylonitrile NBR. Dichlorocarbene modified SBR acts as a compatibilizer in blends of SBR/NBR. The efficiency of compatibilization depends on the chlorine content of the compatibilizer, concentration of compatibilizer and the blend ratio of the components. The compatibilizing efficiency increases as the SBR content in the blend decreases and also when the chlorine content of DCSBR increases up to 25%. The addition of DCSBR is accompanied by an overall improvement in mechanical properties including air and oil resistance. The improvement in mechanical properties is due to the enhanced crosslinking obtained in presence of DCSBR The change in mechanical properties are in good agreement with change in crosslink density obtained from both swelling and stress-strain data.

The presence of dipole within the repeat unit of DCSBR allows the possibility of dipole interaction with the acrylonitrile repeat unit of NBR. Due to this specific interaction as revealed from IR absorption data DCSBR acts as a compatibilising agent for SBR/NBR blends by locating preferentially at the SBR/NBR interface. Addition of 25% chlorine containing DCSBR at a concentration of 5 phr to SBR/NBR blends, results in miscible blends. These blends show a single glass transition temperature as determined from DSC and DMA techniques. The SEM studies also reveals a more homogenous mixing of SBR/NBR blends in presence of 5 phr of 25% chlorine containing DCSBR. The addition of even 1 phr of DCSBR considerably enhances the interfacial adhesion in the blends. The compatibilizing action increases with concentration of compatibilizer up to 5 phr in all blend compositions. The effect of DCSBR as a compatibilizer increases with increase in NBR content in the blend. The addition of DCSBR enhances the overall mechanical properties including air and oil resistance. Mechanical modelling are good agreement with the observed experimental data.

The effect of carbon black and silica on compatibilised SBR/NBR blend with different blend composition shows an improvement in technological properties compared to that of uncompatibilised blends. The carbon black filled samples show an improvement in mechanical properties compared to that of silica filled samples.

Dichlorocarbene modified SBR acts as a compatibiliser in the otherwise incompatible blends of SBR/CR. The compatibilisation is accompanied by an improvement in mechanical properties and depends on chlorine content and concentration of DCSBR. The compatibilising action is more efficient in 50/50 blend and increases progressively with chlorine content of compatibiliser up to 25% and a dosage up to 5 phr, beyond which there is no further increment. The presence of chain entanglements as revealed from stress-strain isotherm, due to better molecular level mixing lead to enhanced physical properties. Incorporation of filler imparts enhanced the physical properties in compatibilised SBR/CR blends.

* * *

APPENDIX

List of Publications

1. Dichlorocarbene Modification of Styrene-Butadiene Rubber.
   M. T. Ramesan and R. Alex. *J. Appl. Polym. Sci.*, **68**, 153, 163 (1998).

2. Dichlorocarbene Modified SBR-Vulcanization Behaviour and Physical Properties.
   M. T. Ramesan and R. Alex. *Kautschuk Gummi Kunststoffe*, KGK5/2000.

3. Investigation on Compatibilisation of Natural Rubber and Dichlorocarbene Modified Styrene Butadiene Rubber Blends.
   M. T. Ramesan, B. Kuriakose and R. Alex (communicated to *Plastic, Rubber and Composite*).

4. Compatibilisation of SBR/NBR Blends Using Chemically Modified Styrene Butadiene Rubber, Part 1 - Effect of Chlorine Content of Compatibiliser.
   M. T. Ramesan, P. Pradeep and R. Alex (communicated to *J. Macromol. Sci. Pure and Appl. Chem.*).

5. Compatibilisation of SBR/NBR Blends Using Chemically Modified Styrene Butadiene Rubber, Part 2 - Effect of Loading of Compatibiliser.
   M. T. Ramesan, C. K. Premalatha, G. Mathew and R. Alex (communicated to *J. Polym. Sci. Polym. Phys. Edn.*).

6. Effect of Different Fillers on Compatibilised and Uncompatibilised SBR/NBR Blends.
   M. T. Ramesan, and R. Alex (communicated to *J. Elastomers and Plastics*).

7. Role of Dichlorocarbene Modified Styrene Butadiene Rubber in Compatibilisation of Styrene Butadiene Rubber and Chloroprene Rubber Blends.
   M. T. Ramesan, G. Mathew, B. Kuriakose and R. Alex (communicated to *Eur. Polym. J.*).

Dichlorocarbene Modification of Styrene–Butadiene Rubber

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ABSTRACT: Dichlorocarbene-modified styrene–butadiene rubber (SBR) prepared by the alkaline hydrolysis of chloroform using cetyltrimethylammonium bromide as a phase-transfer agent resulted in a product that showed good mechanical properties, excellent flame resistance, solvent resistance, and good thermal stability. The activation energy for this chemical reaction calculated from the time–temperature data on the chemical reaction by the measurement of the percentage of chlorine indicated that the reaction proceeded according to first-order kinetics. The molecular weight of the polymers, determined by gel permeation chromatography, showed that chemical modification was accompanied by an increase in molecular weight. The chemical modification was characterized by proton NMR, FTIR studies, thermogravimetric analysis, and flammability measurement. Proton NMR and FTIR studies revealed the attachment of chlorine through cyclopropyl rings to the double bond of butadiene. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 153–160, 1998

Key words: dichlorocarbene; modification; styrene–butadiene rubber; thermal; flammability

INTRODUCTION

Chemical modification of general-purpose rubbers plays an important role in imparting special properties to them. The properties of unsaturated elastomers can be modified by reactions involving their double bonds.[1] It was found that the reaction of double bonds with various reagents could result in improvement of flame retardancy, oil resistance, and other properties.[2] The reaction of carbene with olefins to form a cyclopropane derivative had attracted much attention during the past years.[3–6] The addition of halocarbenes to *cis*-1,4-polyisoprene (NR)[7–10] and *cis*-1,4-polybutadiene was reported by Pinazzi and Levesque[11] and Barentsvich et al.[12] They found that carbene addition had a significant influence on the properties of polydienes. Various other modifications of natural rubber and polybutadiene using *para*-toluene sulfenyl chloride have been carried out.[13–16] The studies revealed that a copolymer containing modified and unmodified blocks arranged in a sequential manner was formed as a result of the modification.

Styrene–butadiene rubber (SBR) is a versatile elastomer, which finds application in various products. However, it has poor heat, flame, and solvent resistance. In this article, an attempt was made to improve the resistance of SBR toward heat, flame, and solvents by dichlorocarbene modification through the alkaline hydrolysis of chloroform using cetyltrimethylammonium bromide (CTAB) as a phase-transfer agent without destroying the technical properties of SBR. The activation energy of the chemical reaction was calculated and the modification was characterized by proton NMR, FTIR, and chemical analysis. The thermal stability and flammability of modified products were evaluated by thermogravimetry (TGA) and the limiting oxygen index (LOI), respectively.

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Table I Composition of SBR-1500

Chemical Constituents (%)	Min	Max
Styrene	21.5	25.5
Volatile matter		0.75
Organic acid	4.75	7
Soap		0.5
Ash		1.5
Antioxidant	0.5	1.5
cis-1,4	—	18
trans-1,4	—	65
1,2 (vinyl)	—	17

EXPERIMENTAL

SBR (Synaprene 1500) was obtained from Synthetics and Chemicals Ltd., Bareilly, U.P., India, and its composition is given in Table I. All other chemicals were of analytical grade. The modification of SBR was done by the alkaline hydrolysis of $CHCl_3$ using a phase-transfer agent, according to the method first suggested by Makosza and Wawrzyniewicz[17] and later developed by Joshi et al.[18] SBR was dissolved in toluene, the phase-transfer catalyst was added to this, and the mixture was allowed stir. To this, $CHCl_3$ was added dropwise followed by an NaOH solution (50%). The reaction product was separated from the solution and washed with hot water and cold water, until free of chlorine. The product was coagulated with isopropyl alcohol and reprecipitated from the toluene solution. The concentration of reagents, the temperature, and the time of reaction are given in Table II. The modification was monitored by the determination of the chlorine percentage at different times using chemical analysis.

The ^{1}H-NMR spectrum of SBR and modified SBR in $CDCl_3$ (10% w/v solution) was recorded with a 90-MHz JEOL EX90 FT NMR spectrometer with tetramethylsilane as the internal reference. IR spectra of samples were recorded with a Shimadzu-8101 M Fourier transform infrared spectrophotometer, using thin films of polymer. The thin films were prepared by dissolving the polymer in chloroform and then the concentrated

Table II Concentration of Reagents for Dichlorocarbene Modification

SBR (g)	10
Toluene (mL)	200
$CHCl_3$ (mL)	30
NaOH 50% (mL)	35
CTAB	0.85
Time (h)	1–36
Temperature (°C)	28/40/60

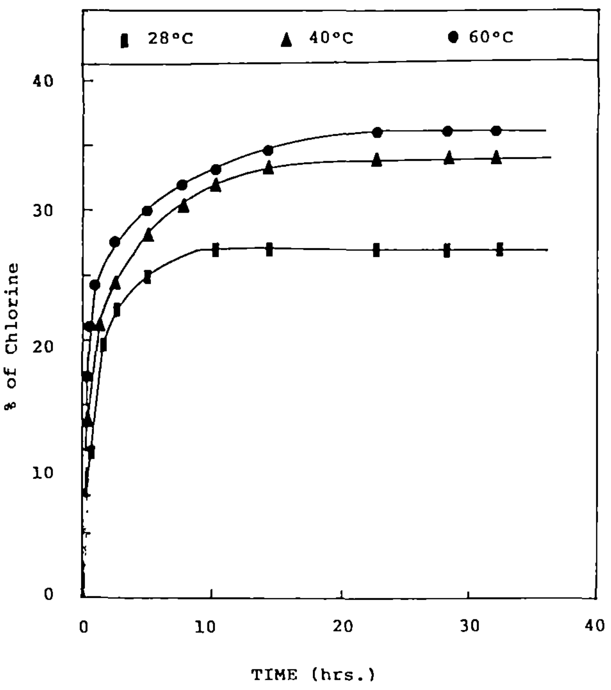


Figure 1 Plots of percentage of chlorine versus time, at temperatures of 28, 40, and 60°C.

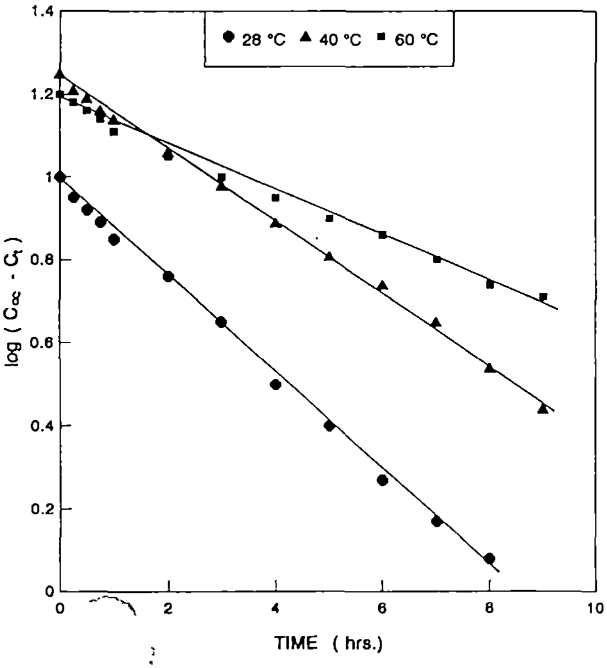


Figure 2 Plots of $\log(C_\infty - c_t)$ versus time for dichlorocarbene-modified SBR.

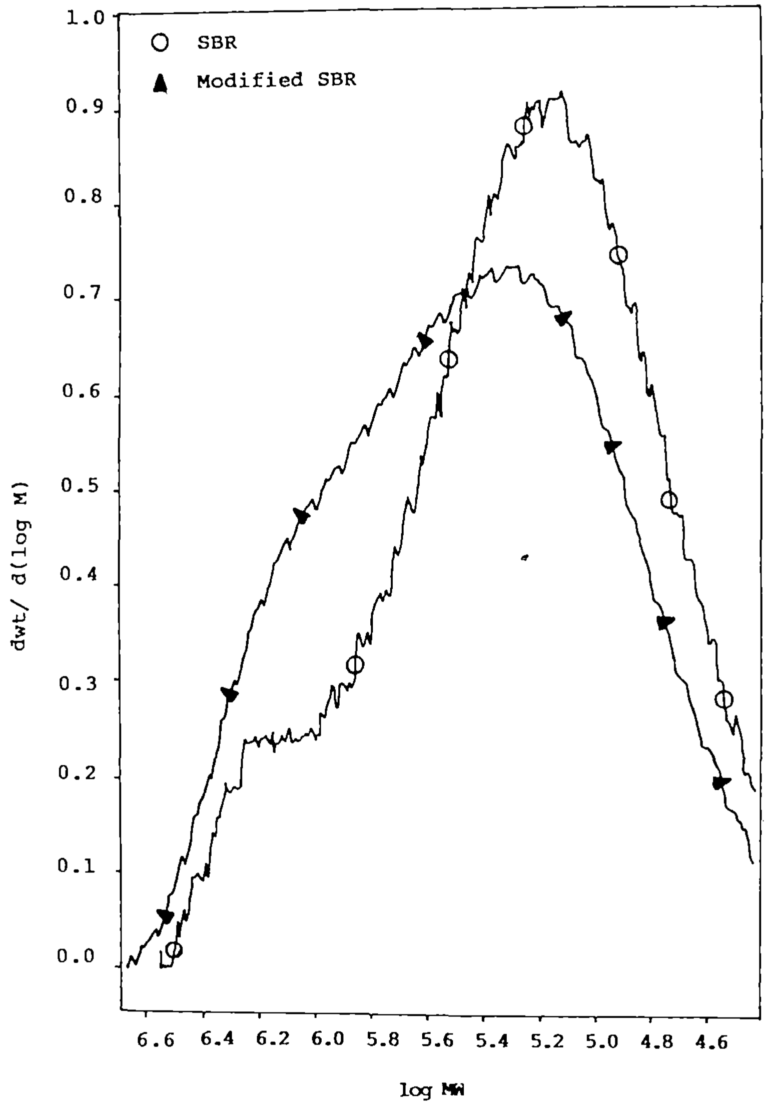


Figure 3 Molecular weight distribution curves of SBR and dichlorocarbene-modified SBR.

solution (5%) was directly cast onto a leveled glass plate.[19] Molecular weight determination was carried out by a Waters 510 gel permeation chromatography (GPC) instrument attached to a 410 diffraction refractometer. HPLC-grade toluene was used as a solvent with a flow rate set to 1 mL/min. The GPC columns were calibrated with polystyrene standards. TGA was carried out with a Shimadzu-50 thermogravimetric analyzer at a heating rate of 10°C/min in a dry nitrogen atmosphere.

The flame resistance was measured with a

Table III Molecular Weights of Modified SBR

Materials	$\bar{M}_n$ (Daltons)	$\bar{M}_w$ (Daltons)	$\bar{M}_z$ (Daltons)	Polydispersity
SBR	125,550	359,502	996,026	2.8634
6% Cl	142,260	421,251	1,225,600	2.9611
20% Cl	164,980	525,782	1,241,151	3.1869

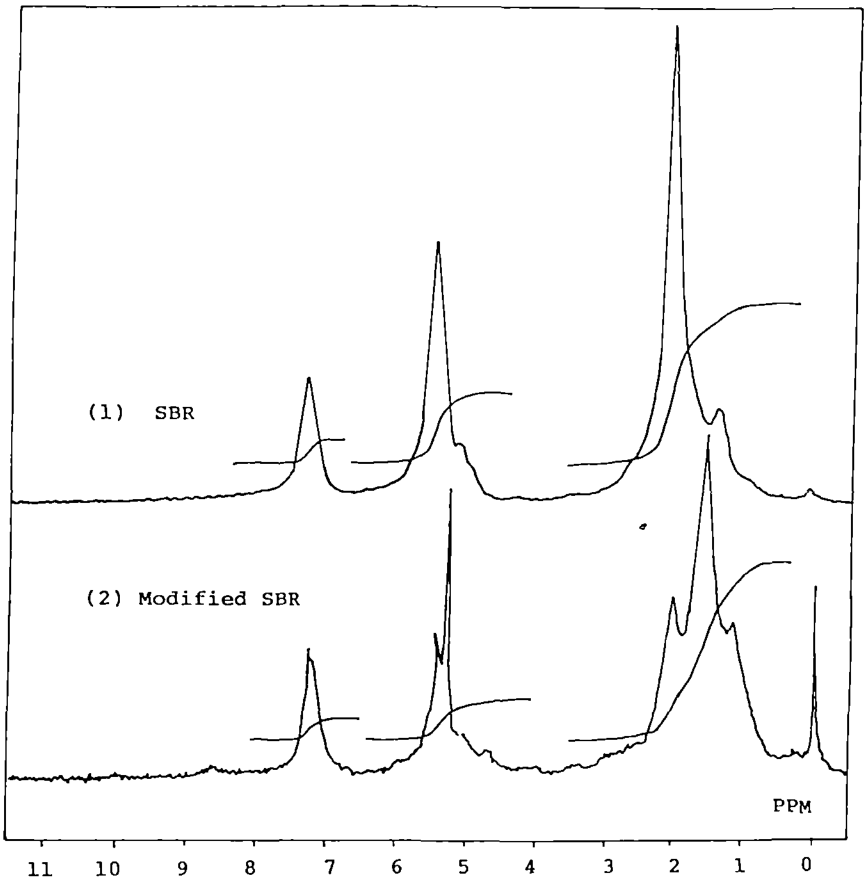


Figure 4 FT ^{1}H-NMR spectra of (1) pure SBR and (2) dichlorocarbene-modified SBR (representative polymer) 26% Cl.

Stanton Redcroft FTA flammability unit as per ASTMD-2863-77. Samples for tensile tests were prepared by pressing the modified rubber at 180°C for 5 min with a pressure of 50 kg/cm^2 in a hydraulic press so as to obtain sheets of 3 mm thickness. The tensile strength of the samples was tested with a Zwick universal testing machine (Model 1474) at a temperature of 25 ± 2°C and at a crosshead speed of 50 mm/min, according to ASTM D-412-80 using dumbbell-shaped test pieces. All other physical tests were carried as per relevant ASTM standards.

RESULTS AND DISCUSSION

Effect of Time and Temperature on Chlorination

Figure 1 shows the percentage of chlorine versus time at temperatures of 28, 40, and 60°C. The dichlorocarbene addition is fast in the initial stages but decreases at later stages of the reaction. The rate reaction almost levels off after 12 h of reaction. The rate of reaction and the chlorine content increases with the temperature of the reaction. As far as the first 15 min of the reaction are concerned, the reaction is extremely fast at 60°C.

Figure 2 shows the change in percentage of chlorine $\log(c_\infty - c_t)$ versus time, where c_∞ is the maximum chlorine percentage obtained at a particular temperature and c_t is the percentage of chlorine at any time t. Linearity of the plots shows that the modification reaction proceeds according to first-order kinetics. Rate constants (k) of the reactions calculated are 3.24×10^{-5} s^{-1}, 2.05×10^{-5} s^{-1}, and 1.23×10^{-5} s^{-1} at 28, 40, and 60°C, respectively. The activation energy of the reaction calculated from the linear plot of log k versus $1/T$ (where k is the rate constant and T is the temperature in K) is found to be 35.89 kJ/mol.

Gel Permeation Chromatography

The molecular weight distribution curves of SBR and modified SBR (<20%) determined by GPC

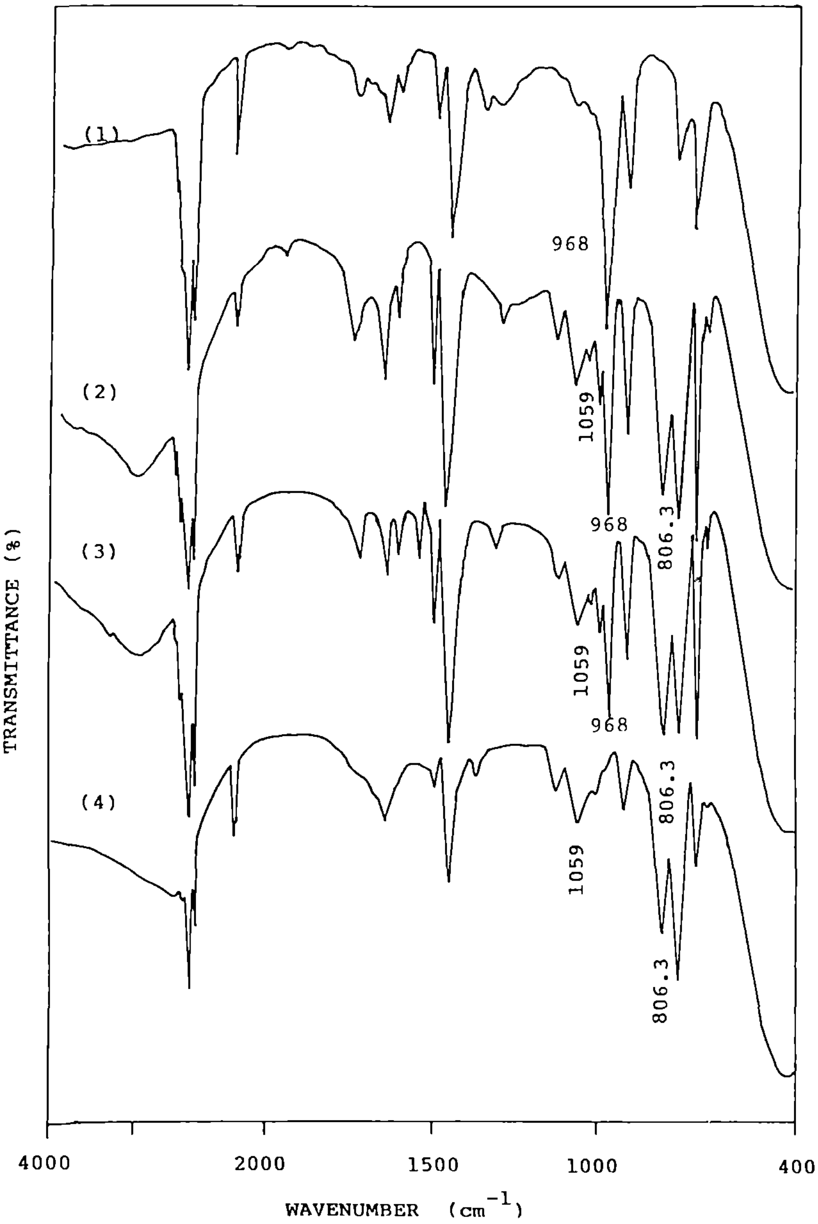


Figure 5 FTIR spectra of thin films of (1) pure SBR, (2) dichlorocarbene-modified SBR of 16%, (3) 26%, and (4) 36% chlorine.

are given in Figure 3. From the figure, it is evident that high molecular weight fractions are formed in modified SBR as a result of the modification. The molecular weight ranges from 2.5×10^4 to 5.01×10^6 in both modified and pure SBR. The high molecular weight fraction above a molecular weight of 10^6 is higher for the modified samples (as seen from the area under the molecular weight distribution curve). The increase in $\bar{M}_n$ (number-average molecular weight), $\bar{M}_w$ (weight-average molecular weight), and $\bar{M}_z$ (z-average or sedimentation-average molecular weight) with very little change in the polydispersity given in Table III shows that dichlorocarbene modification is accompanied by an increase in molecular weight due to the addition of chlorine through the cyclopropyl ring as a side chain.

FT ^{1}H-NMR Characterization

FT ^{1}H-NMR spectra recorded for SBR and dichlorocarbene-modified SBR are given in Figure 4. SBR and representative modified SBR exhibit signals for the hydrogen region of benzene at 7.3–7

Table IV IR Absorption Peak Height Ratios

Time (h)	Chlorine (%)	1653/806 cm^{-1}	968/806 cm^{-1}	910/806 cm^{-1}	698/806 cm^{-1}
1	16	0.307	1.199	0.631	1.78
12	26	0.115	0.957	0.620	1.75
24	36	1653 absent	968 absent	0.619	1.71

ppm. Pure SBR displays signals at 2 and 1.4 ppm due to the methylene hydrogens ($-CH_2-$) and at 5.6 ppm (s) due to the unsaturated methine hydrogen ($-CH=$) of butadiene. Modified SBR displays a triplet for methylene hydrogens, in the region of 1.1–2 ppm. These additional signals can be attributed to the cyclopropyl ring. The doublet in the region 5.8 to 5.2 ppm shown by the modified SBR can be due to the hydrogen of the carbene bearing carbon and the hydrogen of the carbon attached to the benzene ring.

FTIR Characterization

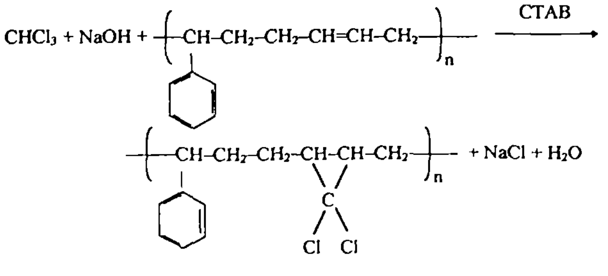
Figure 5 shows the IR spectra of the thin films (cast from $CHCl_3$) of SBR [Fig. 5(1)] and modified SBR at 1 h [Fig. 5(2)], 12 h [Fig. 5(3)], and 24 h [Fig. 5(4)]. The modified SBR shows characteristic C—Cl absorption peaks at 806 and 1059 cm^{-1} due to the cyclopropane ring.[20] It is likely that the *cis*-butadine takes part in the reaction initially, as $:CCl_2$ more readily attacks the *cis* double bond. As the reaction time increases, there is a reduction in the intensity of the absorption at 968 cm^{-1} which is due to the *trans* —CH= and at 1653 cm^{-1} which is due to *cis* —CH=. The absorption at 698 cm^{-1} is due to the presence of an aromatic ring, whose concentration remains unaffected with modification. The absorption at 910 cm^{-1} (vinyl 1,2 content) remains almost unaffected after modification. There is a shift of 698 cm^{-1} absorption to 702 cm^{-1} due to the increase in chlorination; this may be attributed to steric hindrance of the cyclopropane ring. The peak ratio of absorption at 1653/806 cm^{-1}, 968/806 cm^{-1}, 910/806 cm^{-1}, and 698/806 cm^{-1} is shown in Table IV. With increase in the duration of the chemical reaction, there is a progressive reduction in the double-bond concentration and corresponding increase in the concentration of C—Cl bonds, whereas the styrene concentration remains almost unchanged. Hence, it can be inferred that it is the double bond[4,21,22] of butadiene that takes part in the chemical reaction. The proposed reaction is shown in Scheme 1.

Thermogravimetric Analysis

The thermograms of SBR, modified SBR, and chloroprene rubber (Neoprene W) are given in Figure 6. The decomposition pattern is compared with a commercial chloroprene rubber. Pure SBR (curve 1) shows a single-stage decomposition at a temperature of initiation of 454°C. As the chlorination increases, there is a considerable change in the decomposition pattern. The decomposition of chlorinated SBR (at a higher percentage of Cl) takes place in two steps (curves 2 and 3): The first decomposition begins at 286°C, and the second, at 454°C. The time taken for a 50% weight drop for chloroprene rubber and chlorinated SBR are presented in Table V. It is clear from the table that the time taken for a commercial chloroprene rubber for a 50% weight drop is lower than that of dichlorocarbene-modified SBR. This indicates that the chlorinated SBR has a superior thermal stability to that of commercial chloroprene rubber.

Flammability Behavior

The limiting oxygen index (LOI) (which is a direct measure of the flame resistance of the materials) of pure SBR, modified SBR, and commercial chloroprene rubber are given in Table VI. When halogen-containing elastomers are ignited, they could



Scheme 1 Proposed pattern of dichlorocarbene modification.

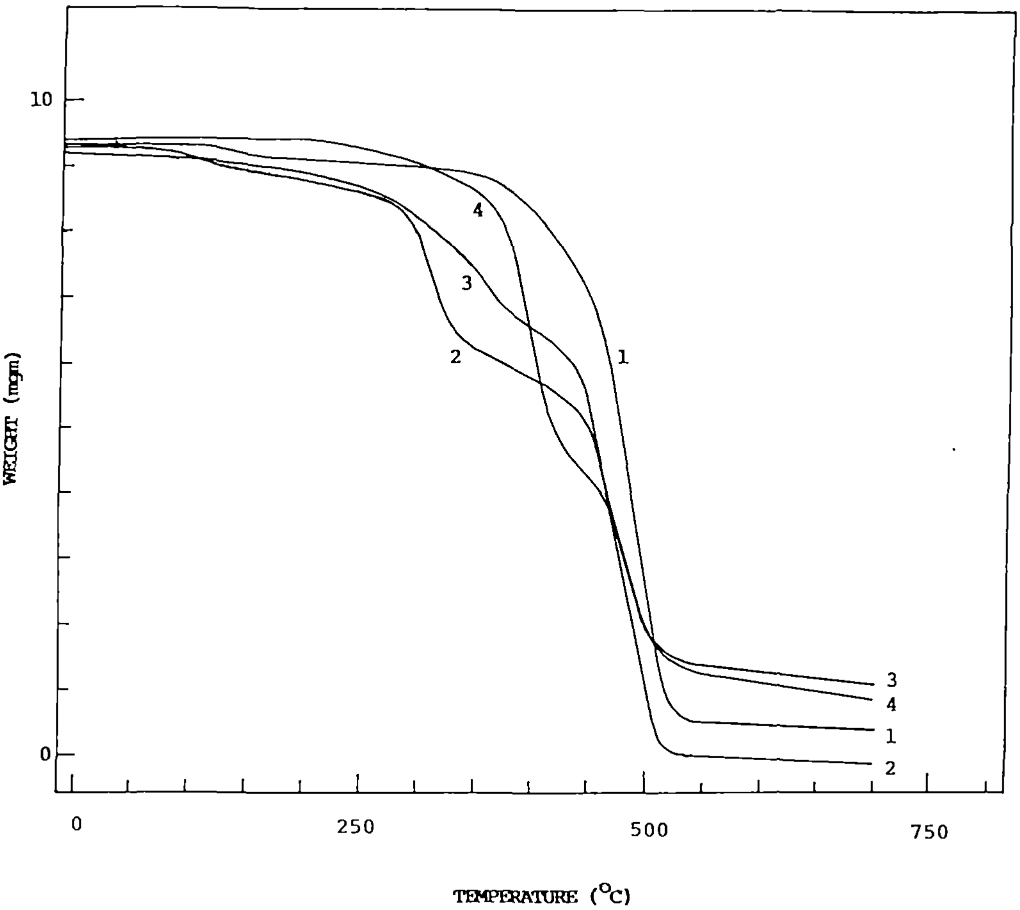


Figure 6 Thermograms of (1) pure SBR, (2) modified SBR of 16% chlorine, (3) modified SBR of 36% chlorine, and (4) commercial chloroprene rubber.

exhibit an intumescence effect, due to which the char formed thermally insulates the polymer from the flame and thus inhibits combustion. From the table, it is clear that modified SBR shows better flame resistance than does unmodified SBR. Moreover, the LOI value for SBR with a chlorine content of 36% is almost the same as that of commercial chloroprene rubber. Thus, modified SBR can be recommended as a substitute for building materials, since materials with an LOI value[2] greater than 20.8 are considered to be safe for indoor applications, because these materials wil be self-extinguishing even if ignited.

Physical Properties

Chemical modification changes SBR from a sof elastomeric material to a hard thermoplastic material. Modified SBRs with high percentage o chlorine (>20%) were insoluble in solvents including DMF and THF. Thus, at higher levels o chlorination, it is possible that there are side reactions involving crosslinking. The physical proper

Table V Time for 50% Weight Drop

Material	Curve	Time for 50% Weight Drop (min)
Chloroprene	1	39.8
Modified SBR (16% Cl)	2	44.8
Modified SBR (26% Cl)	3	43.3
Modified SBR (36% Cl)	4	43.3

Table VI Limiting Oxygen Index (LOI) Values

Materials	Chlorine (%)	LOI (%
SBR	—	19
Modified SBR	16	24
Modified SBR	26	28
Chloroprene	40	28.4

Table VII Physical Properties

Materials	Tensile Strength (MPa)	Elongation at Break (%)	Shore D Hardness
Modified SBR (16% Cl)	5.29	106.6	15
Modified SBR (26% Cl)	28.57	1.3	45
Modified SBR (36% Cl)	20.49	0.9	60

ties are shown in Table VII. At levels of chlorination of < 16%, the material shows comparatively low tensile strength and elongation. As chlorination increases, tensile strength increases to a maximum and then decreases at still higher levels of chlorination. The elongation at break decreases progressively, and at very high levels of chlorination, it behaves like a thermoplastic polymer.

CONCLUSIONS

The dichlorocarbene modification of SBR can be carried out by the alkaline hydrolysis of $CHCl_3$ using CTAB as a phase-transfer catalyst. The chlorine content increases with temperature of the reaction and the reaction follows first-order kinetics. The basic decomposition pattern and thermal stability of the samples are superior to those of commercial chloroprene rubber. The presence of chlorine in the samples enables them to be safely used as a flame-resistant material for indoor applications. The modified materials are thermoplastics with higher tensile strength and hardness than those of unmodified SBR. The modified SBRs have excellent solvent resistance compared to other chlorine-containing elastomers like chloroprene, even at low levels of chlorination (16–20%), where they exhibit rubbery properties. Further studies on more efficient chemical modifications of SBR are in progress.

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Dichlorocarbene Modified SBR – Vulcanization Behaviour and Physical Properties

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Dichlorocarbene modified SBR vulcanization · physical properties

Dichlorocarbene modification of SBR results in an enhancement in physical properties, improvement of air aging behaviour and excellent oil resistance as compared to SBR. This chemical modification changes SBR from a soft elastomeric to hard thermoplastic material. A satisfactory level of vulcanization with sulfur or metal oxide is only possible when the chlorine content of modified sample is $< 25\,\%$.

Dichlorcarbenmodifizierter SBR – Vulkanisationsverhalten und physikalische Eigenschaften

Dichlorcarbenmodifizierte SBR – Vulkanisation · physikalische Eigenschaften

Die Modifizierung von SBR durch Dichlorcarbon ergibt eine Verbesserung der physikalischen Eigenschaften, eine erhöhte Luftalterungsstabilität sowie ausgezeichnete Ölbeständigkeit im Vergleich zu SBR. Die chemische Modifizierung verändert SBR von einem weichen Elastomeren zu einem harten Thermoplasten. Ein zufriedenstellender Vulkanisationszustand mit S oder Metaloxiden wird nur erreicht, wenn der Cl-Gehalt $< 25\,\%$ liegt.

Introduction

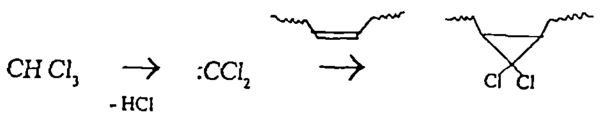
Modification of rubbers has been a growing interest in the dynamic field of research due to improvement in physical and chemical properties achieved through modification. Schultz discussed various method of chemical modification [1], among these halogenation is the most common and effective [2–5]. Compared to NR, SBR has slightly inferior physical properties, better heat resistance and more compatibility with polar synthetic rubbers like CR and NBR. A number of attempts have been made to increase the green strength of SBR and also to improve its oxidative and oil resistance. One attempt to increase the green strength was by introduction of carbonyl groups during the polymerization. Another method was by introduction of tertiary amine containing monomers during polymerization, followed by reaction with dihalides to form a small number of labile crosslinks [6, 7]. The technique of anionic polymerization using modified alkyl lithium initiators has been used to prepare high vinyl SBR [8, 9]. This material contains 90 % diene as 1,2 vinyl units and exhibit high green strength and hence of use in tyre industry. When 1, 4 trans-butadiene units were long enough in SBR, it was shown to have low temperature crystallization accompanied by good green strength [10, 11]. Dichlorocarbene addition to double bonds, an attempt to modify elastomers has been done earlier [12–15]. However, the product of dichlorocarbene modification has not found any commercial application. Dichlorocarbene modification of SBR results in a produc that has good green strength and mechanical properties, high oxidative and oil resistance as compared to SBR. This paper focuses on the vulcanization characteristics and on a correlation to the physical properties of the modified rubbers with the structural change occuring during modifications.

Experimental

Materials and methods

SBR (Synaprene 1502, 25 % bound styrene) was obtained from Synthetics and Chemicals Ltd. Bareilly U.P. India. Dichlorocarbene modified SBR prepared by the e alkaline hydrolysis of $CHCl_3$ using cetyl trimethyl ammonium bromide (CTAB) as phase transfer catalyst [16]. The modification was monitored by the determination of the chlorine percentage using chemical analysis Chlorine conten of DCSBR used in the study was varied from 15 to 30 %. The structural change taking place during modification is shown in eg. (1). Rubber additives were of reagent grade obtained from local rubber chemical suppliers.

Mixing was carried out on a laboratory size two roll-mixing mill at a frictional ratio of 1:1.25 at 40 °C and formulation of mixes is given in *Tab. 1*. Cure characteristics were studied using a Monsanto rheometer R100 at 150, 160, and 170 °C ac-



Scheme 1

Tab. 1. Formulation of mixes (phr)

Mix No.	1	2	3	4	5	6	7	8	9	10	11
SBR/50 %	100	–	–	–	–	–	–	–	–	–	–
DCSBR containing 15 % chlorine	–	100	–	–	–	–	–	100	–	–	–
DCSBR containing 20 % chlorine	–	–	100	–	–	–	–	–	100	–	–
DCSBR containing 25 % chlorine	–	–	–	100	100	100	100	–	–	100	–
DCSBR containing 30 % chlorine	–	–	–	–	–	–	–	–	–	–	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.0	–	–	–	–
Zinc oxide	5	5	5	5	5	5	5	–	–	–	–
MgO	–	–	–	–	–	–	4	–	–	–	–
CBS	1	1.5	1.5	1.5	1.0	1.5	–	–	–	–	–
TMTD	–	0.5	0.6	0.8	0.8	0.5	0.5	–	–	–	–
ETU (NA-22)	–	–	–	–	0.5	–	0.5	–	–	–	–
Sulfur	2.2	2.2	2.2	2.2	2.2	2.2	–	–	–	–	–
Dicumyl peroxide	–	–	–	–	–	–	–	4	4	4	4

cording to ASTM D 2705. The mechanical properties were determined as per relevant ASTM standards. Oil resistance of the samples was tested by ASTM oils No. 1, 2, and 3. Low temperature behaviour was studied by differential Scanning Calorimetry using a Perkin-Elmer DSC for a temperature range of – 80 to 30 °C, at a heating rate of 15 °C/min.

Results and discussion

Dichlorocarbene modified SBR (DCSBR) of chlorine content varying from 15 to 30 % does not undergo any appreciable level of cure by either metal oxides or sulfur (mix. No. 6 and 8 of *Fig. 1*) whereas a chlorine containing polymer like Chloroprene (CR) readily undergoes crosslinking by metal oxides [17]. CR undergoes crosslinking in presence of metal oxide and ethylene thiourea [ETU] producing crosslinks that are monosulphidic in nature and crosslinks occuring due to the presence of labile chlorine [18] CR is also known to undergo crosslinking by heat at 180 °C without the use of any crosslinking agent (thermal vulcanization) [19]. However, DCSBR is found to be less susceptible to thermal vulcanization as evidenced from *Fig. 2*. Thermal vulcanization of CR has been shown to be due to the liberation of chlorine from CR with the formation of HCl resulting in crosslinks. In the case of DCSBR the chlorine is attached to the main chain through a cyclopropyl ring [16]. In DCSBR reactive allylic or tertiary allylic chlorine which is responsible for crosslink formation by metal oxide [20] is absent and thus crosslink formation is prevented. Accelerated sulfur vulcanization is, however, possible for DCSBR (Mix No. 2, 3 and 4). At lower level of modification, comparatively lower amount of accelerators brings about vulcanization, but at a higher level of modification higher amounts of accelerator is required. A combination of accelerator CBS/TMTD/ETU at a dosage 1/0.8/0.5 also brings appreciable states of cure (mix No. 5 of Figure 1). A comparatively poor scorch safety is obtained by this combination. ETU is generally scorch and TMTD is used for CR along with ETU as a retarder for better scorch safety.

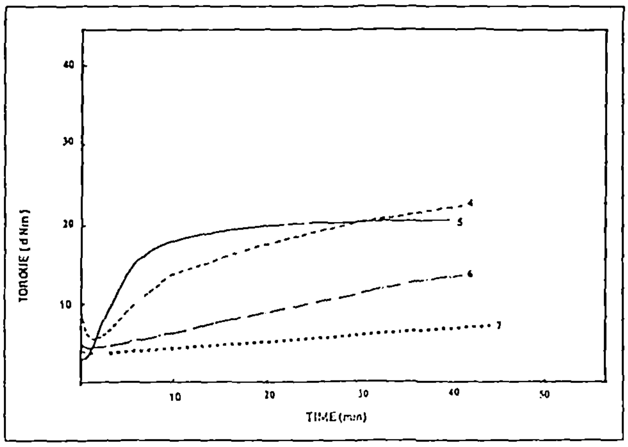


Fig. 1. Rheographs of DCSBR containing 25 % chlorine cured by sulfur and metal oxide vulcanization at 150 °C

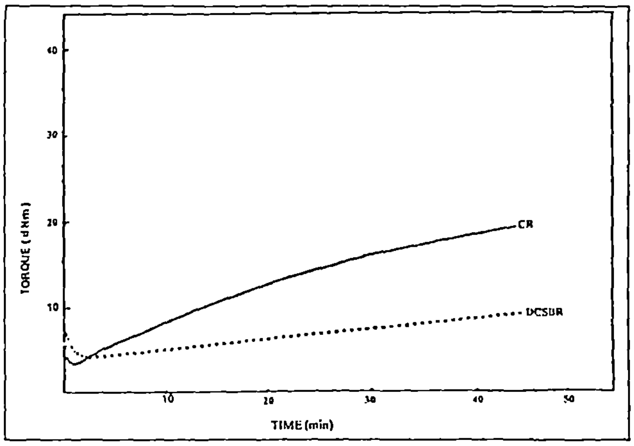


Fig. 2. Thermalvulcanization of CR and DCSBR (containing 25 % chlorine) at 180 °C

Due to lower unsaturation, SBR requires a higher dosage of accelerator as compared to NR. Dichlorocarbene modification occurs at the double bond, reducing the active sites of vulcanization, resulting in a requirement of higher dosage of accelerator to bring about satisfactory cure.

A higher level of crosslinking is obtained with peroxide cure (mixes No. 8–11 of *Fig. 3*). The state of cure attained for each modified compound is different and depends on the level chlorination. The curing efficiency decreases as modification increases. The diene structure of a polymer, its type and amount is shown to influence peroxide vulcanization of an elastomer like EPDM [21]. As the level of modification in DCSBR increases, the polymer chain becomes more and more saturated, and the availability of allylic hydrogen, which is a site for crosslinking reduces. Hence crosslinking efficiency with peroxide decreases as chlorine content of the modified sample increases.

The state of cure attained by peroxide vulcanization can be increased by temperature as seen from rheographs of DCSBR containing 25 % chlorine cured with 4 phr (*Fig. 4*). The level of crosslinking increases as dose of DCP increases which is evidenced from the increase in torque (*Fig. 5*). It is known that in the case of peroxide vulcanization, temperature is a controlling factor. Activators are known to affect very little the cure characteristics. The concentration of peroxide controls the total number of crosslinks produced during vulcanization process. Even though cure time does not change appreciably, the state of cure increases significantly with DCP concentration as indicated by larger change in net torque (*Tab. 2*).

The physical properties of modified SBR are given in *Tables 3* and *4*. The tensile strength and modulus of the sample increase progressively as the chlorine content increases. At very high levels of modification the sample becomes hard with low elongation at break as seen for mix No. 11 (DCP cured). The EB increases with modification of SBR up to 25 % of chlorination and then progressively decreases. The tensile strength of DCSBR containing 25 % chlorine is rather high (17 MPa, mix No. 4) with an EB of 520 %, a behavior similar to that of strain crystallizing polymer.

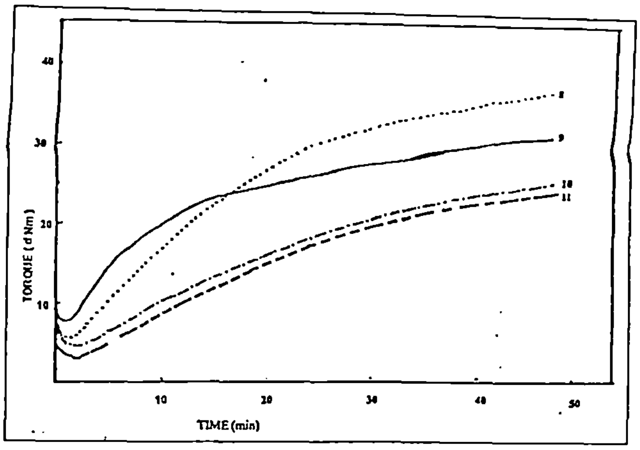


Fig. 3. **Rheographs of DCSBR containing varying percentage chlorine cured by DCP (4phr)**

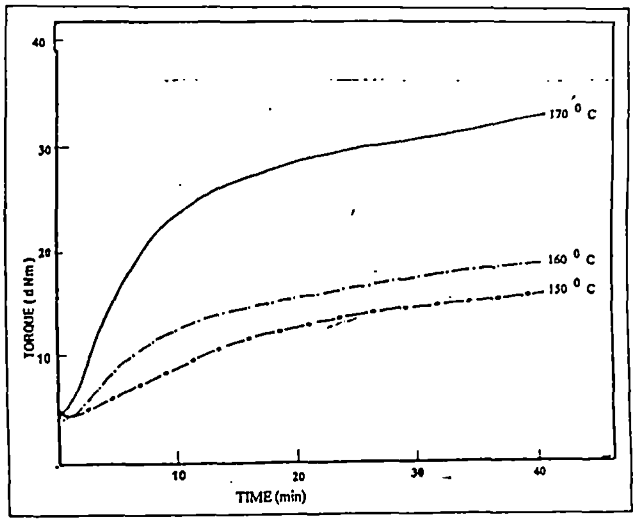


Fig. 4. **Rheographs of DCSBR containing 25 % chlorine cured by 4 phr DCP at 150, 160 and 170 °C**

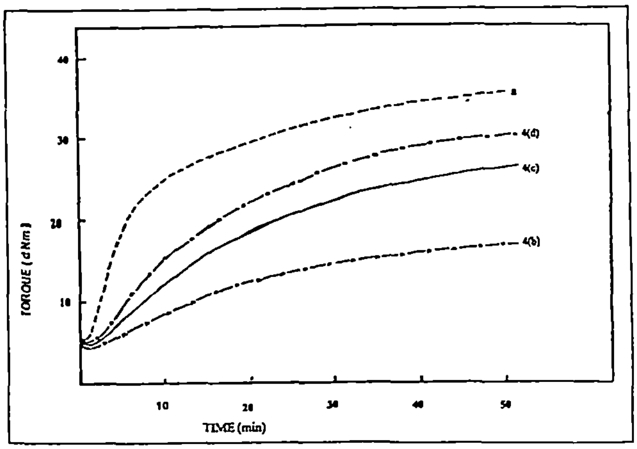


Fig. 5. **Rheographs of (a)-CR cured by 4 phr DCP, 4(b)-DCSBR containing 25 % chlorine cured by 2 phr DCP, 4(c)-DCSBR containing 25 % chlorine cured by 4 phr DCP, 4(d)-DCSBR containing 25 % chlorine cured by 6 phr DCP**

The stress strain curve for the samples shown (mix No. 1, 2 and 4) in *Fig. 6* revealed that up to chlorination of 25 % the modified samples are rubbery in nature and strain crystallizing. Resilience decreases with increasing level of chlorination whereas compression set, hardness and heat build-up incease. Tear strength increases with chlorine content of modified samples (*Tab. 4*). The physical properties of sulfur vulcanizates are superior to peroxide cured vulcanizate. It is well known that differences in technical properties are due to the type of bond formed during peroxide cure.

Mechanical properties of samples aged in air at 70 °C for 96 h are shown in *Tab. 5.* The materials show comparatively good mechanical properties and better resistance to oxidative degradation as seen from the change tensile strength. This is attributed to the decrease in double bonds during chemical modification. Dichlorocarbene modification also imparts considerable oil resistance, as seen from *Tab. 6.* Dichlorocarbene modification imparts excellent resistance to oil, superior to CR and approaching that of NBR (medium AN content). Oil resistance of DCSBR increase with increasing chlorine content of the samples. DCP cured DCSBR results in a much enhanced oil resistance, which is superior to conventionally cured NBR. The combined oil resistance with a low compression set enable DCSBR for use in oil-seal application.

DSC thermograms of the modified rubber shown in *Fig. 7*, readily demonstrate the presence of crystallinity with increasing chlorination. The DCSBR containing 15 % chlorine (mix No. 2) shows two thermal transitions one at − 56 °C, corresponding to Tg of SBR and another at − 37 °C corresponding to the to Tg of chlorinated segments. As chlorination proceeds samples show melting endotherms. For a sample containing 20 % chlorine, (mix No. 3) the melting endotherms are broadened and occur at − 22 and + 16 °C. The sample containing 30 % chlorine (mix No. 11) shows two sharp melting endotherms one at − 12 and other at + 16 °C. This observation reveals that during dichlorocarbene modification there are structural changes which can lead to crystallizations at low temperatures. Chemical modification had been used earlier to increase the green strength of synthetic rubbers.

Tab. 2. Cure characteristics of DCSBR containing 25 % chlorine cured by varying concentration of DCP

Concentration of DCP (phr)	2	4	6
Difference in torque, Δ torque (dN-m)	10	20	23
Optimum cure time, t_{90} (min)	34	40	32
Cure rate index (dN-m)	0.707	1.50	1.48

Tab. 3. Physical properties of accelerated S-cured DCSBR

Mix No.	1	2	3	4
Tensile strength (MPa)	2.88	9.68	12.52	17.05
Modulus 300 % (MPa)	1.86	2.51	2.99	3.9
Elongation at break (%)	340	410	480	520
Tear strength (kN/m)	24.4	37.8	43.65	58.1
Hardness (Shore A)	34	42	44	47
Resilience (%)	41	35	34	31
Heat build-up (°C)	12	11	10	9
Compression set (%)	11	12.6	13	13.5

Tab. 4. Physical properties of DCP cured DCSBR

Mix No.	8	9	10	11
Tensile strength (MPa)	6.6	9.12	15.01	22.0
Modulus 300 % (MPa)	1.98	2.11	2.48	1.34
Elongation at break (%)	325	300	242	96.0
Tear strength (MPa)	31.26	38.74	44.87	46.3
Resilience (%)	29	26	23	15.0
Heat build-up (°C)	10	9	8	8.0
Compression set (%)	11	12	12.5	13.5

Tab. 5. Effect of air ageing on mechanical properties of modified SBR at 70 °C for 96 h

Mix No.	Decrease in tensile strength (%)	Decrease in elongation at break (%)
1	38	19.8
2	26	7.3
3	22.6	21
4	12.3	14.4
8	19.7	17.1
9	12.1	13.3
10	6.1	9.4
11	5.8	9.0

Conclusions

Dichlorocarbene modification of SBR is accompanied by a reduction of double bonds which can be vulcanized with an accelerated sulfur system which impart excellent tensile strength and oxidative stability. The combination of a lower compression set and increased oil resistance to oil swell makes modified SBR of use in oil-seal application. The structural change that takes place during modification brings about crystallisation of the material at low temperature.

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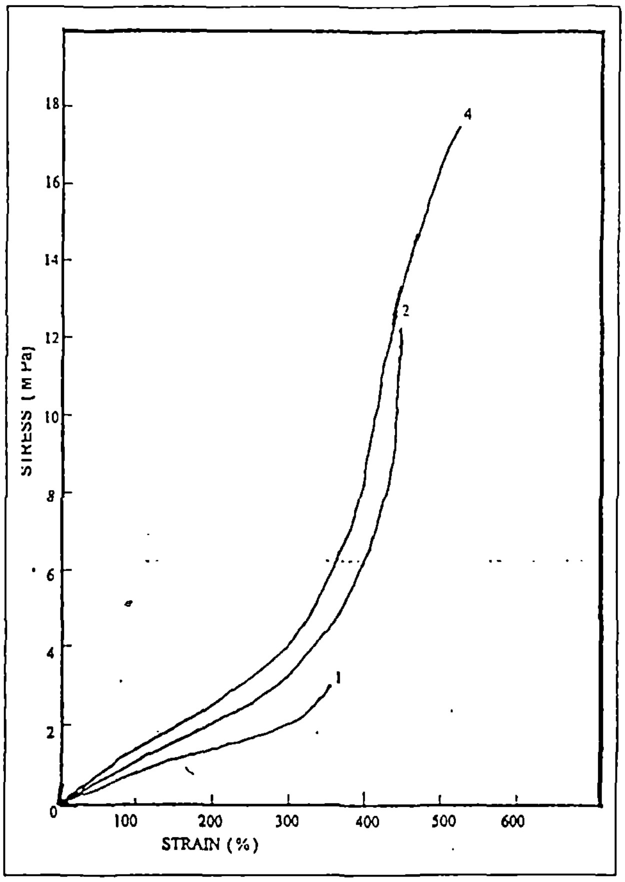

Fig. 6. Stress-strain curve of SBR and DCSBR containing 15 % and 25 % Cl

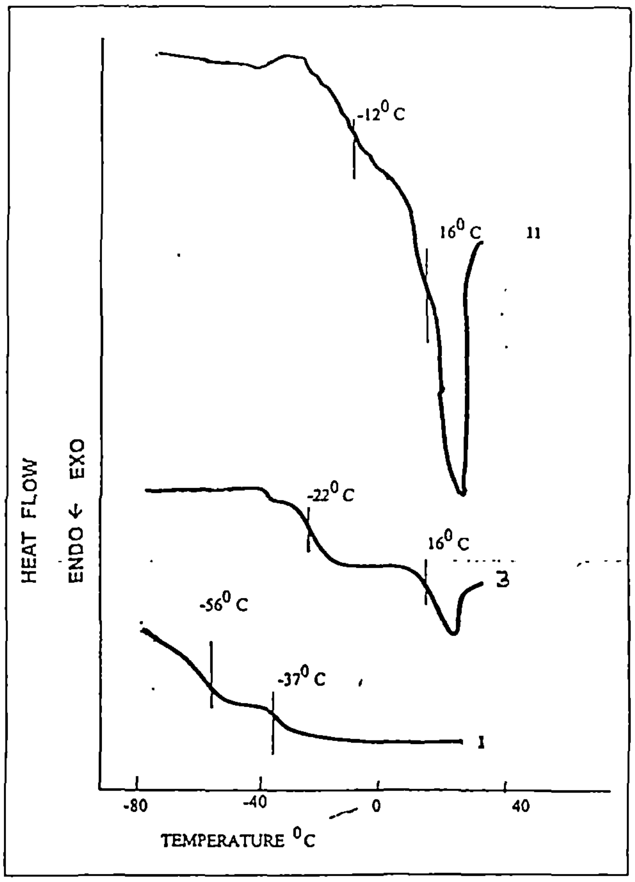

Fig. 7. DSC Thermograms of DCSBR of varying chlorine contents (15, 20 and 30 %)

Tab. 6. Swelling behaviour of DCSBR, SBR, CR and NBR

Mix No.	ASTM oil No. 1 (%)	ASTM oil No. 2 (%)	ASTM oil No. 3 (%)
CR^a	2.12	4.37	16.21
NBR^b	0.34	0.51	0.68
1	9.28	15.94	52.78
2	1.22	4.2	15.5
3	1.09	2.23	8.97
4	0.9	1.6	4.95
8	0.51	0.63	2.1
9	0.26	0.32	2.5
10	0.04	0.07	0.9
11	0.02	0.03	0.5

[a] CR – 100, stearic acid – 0.5, TMTD – 0.5, ETU – 0.5, MgO – 4, ZnO – 5.

[b] NBR – 100, stearic acid – 1, ZnO – 5, CBS – 1.5, TMTD – 1, Sulfur – 0.5.

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