EPDM/CIIR Blends: Compatibility, Morphology and Physical Properties

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by

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Certificate

Certified that, the thesis entitled **'EPDM/CIIR Blends: Compatibility, Morphology and Physical Properties'** submitted to Cochin University of Science and Technology under the Faculty of Technology, by Mr. Sunil Jose T, is an authentic record of the original research carried out by him under my supervision and guidance. The thesis has fulfilled all the requirements as per regulations and no part of the results embodied has been submitted to any other institution for any other degree/diploma.

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DECLARATION

I hereby declare that, the thesis entitled **'EPDM/CIIR Blends: Compatibility, Morphology and Physical Properties'** submitted to Cochin University of Science and Technology, under the Faculty of Technology, is based on the original research carried out by me under the supervision of Dr. Rani Joseph, Professor, Dept. of Polymer Science and Rubber Technology, and further, no part of the results presented has been submitted to any other institution for any other degree/diploma.

Cochin
20th Nov 2006

Sunil Jose T

. . . to my Parents,

Wife and loving Children

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PREFACE

Polymer blends are gaining technological importance due to their compromise set of properties, advantages in processing and reduction in cost. One polymer may possess a particular set of properties, while the other may have another set of properties. By blending two such polymers, a desired set of properties can be achieved. In the case of elastomers, blends are used in tires, belts, cables etc. For the successful applications of such blends, component elastomers must be miscible and compatible. The curing method adopted and the distribution of compounding ingredients has a vital role on the ultimate properties. The distribution depends mainly on the nature of the elastomers and the blending process. Therefore, knowledge of these parameters will facilitate in obtaining a successful elastomer blend.

In the present work, investigation has been carried out on the compatibility and mechanical properties of blends consisting of ethylene propylene diene rubber (EPDM) and chlorobutyl rubber (CIIR). This blend finds application in the manufacture of curing envelope and other high temperature performances.

This thesis is presented in seven chapters.

The various factors affecting the blend compatibility, the methods of blend preparation and the advantages of blends are explained in chapter I. A review of the earlier works in this field and the scope and objective of the present investigation is also presented.

The specifications of the materials used in the study and the different experimental techniques employed are described in the second chapter.

A detailed study of the compatibility behaviour of blends of EPDM with CIIR has been reported in the third chapter. The extent of compatibility has been evaluated based on mechanical, thermal and morphological studies. The effect of compatibiliser on the blend properties is also studied.

The fourth chapter deals with extensive study on the physical properties of sulphur cured EPDM/CIIR blends with respect to blend ratio and ageing.

The effect of precuring on the physical properties of sulphur cured blends of EPDM with CIIR has been discussed in chapter five.

Chapter six explains the property studies of resin cured EPDM/CIIR blends with special reference to their ageing resistance.

Finally, more technical features of the blends such as thermal diffusivity, thermal degradation resistance, air permeability and rheological behaviour are presented in the seventh chapter.

A summary of the whole investigation results is presented as the last chapter.

Chapter I

Introduction

The field of polymer science and technology has undergone an enormous expansion over the last several decades primarily through chemical diversity. First, there was the development of new polymers from a seemingly endless variety of monomers. Next, random copolymerization was used as an effective technique for tailoring or modifying polymers. Later, more controlled block and graft copolymerization was introduced. The list of new concepts in polymer synthesis has not been exhausted. Development of new molecules and chemical modifications of existing ones have been the most common ways of facing new challenges in this field. These routes have become increasingly complex and expensive over the years and thus alternative ones have become interesting and attractive.

In recent years, polymer blends are gaining technological importance due to their great regulatable variability of properties despite the limited number of initial components.[1-8] By blending two or more elastomers, it is possible to attain properties, that are not available with a single elastomer. The most important concept in polymer blends is additivity of properties. By this we mean that when a polymer is mixed with another polymer, the resulting blend has a property which is the weighted average of the properties of the individual polymers. Modulus is one of such properties that are expected to obey some additivity relationship.[9]

The success of a new material depends on several factors such as combination of properties and cost dilution. For example, when we blend a high thermal resistant polymer having poor processability with another polymer having good processability and poor thermal stability, the resulting blend may be useful for certain applications for which both the individual polymers are unsuitable. By blending of polymers several properties can be improved, mostly without sacrificing the others. For this, it is necessary to know which polymers can be successfully blended and what undergoing factors influence the results.[10-16]

1.1 Basic theory of polymer blends

A successful polymer blend is a cost effective mixture of two or more polymers with a better combination of different properties. Processability and mechanical properties of polymer blends depend mainly on their compatibility and miscibility. Miscible blends are those which are homogenous throughout in microscopic scale. Depending on the polymer miscibility, the blends can be classified as miscible, partially miscible and immiscible, or in a technological sense as compatible, semicompatible and incompatible. A large number of compatible polymer blends and alloys have been investigated and successfully commercialized.[17-20] Alloys are a class of polymer blends in which a large interpenetration of domains is secured by physical and/or chemical means. Although the terms alloys and blends are often used synonymously, they differ in the level of thermodynamic compatibilities and resulting properties. On the high end of the compatibility spectrum are the alloys. Alloys are synergistic polymer systems. Alloys give a tighter, denser molecular structure than blends.[21]

1.2 Properties of blends

A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compatibility is the fundamental property deciding the practical utility of a polymer blend.[22-24] Two-component polymer blends, in general, can be described by the following equation:[22,25]

$$P = P_1C_1 + P_2C_2 + I\,P_1P_2 \qquad (1.1)$$

where P is the property value of the blend, P_1 and P_2 are the properties of the individual components and C_1 and C_2 are their respective concentrations. I, is a term for the system which defines the level of synergism created by the combination of the two components.[26]

For $I > 0$, the property is synergistic,
$I = 0$, the property is additive,
$I < 0$, the property is nonsynergistic

The improved ozone resistance of blends of styrene-butadiene rubber (SBR) and ethylene-propylene-diene rubber (EPDM), increased electrical conductivity for blends of natural rubber (NR) and polychloroprene (CR) and improved tensile strength obtained for blends of polystyrene and poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) are few examples of synergistic blends. Figure 1.1 illustrates, for two component blend systems, the ideas of additive, synergistic and nonsynergistic properties.

The most important factor governing the ultimate properties of a polymer blend is the intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). The poor adhesion between the molecules at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface leading to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialized, the applicability of such polymer blends is limited because of the inferior macroscopic properties. Modification of incompatible polymer systems for developing useful materials has become an active field of research both in the industrial and academic level.

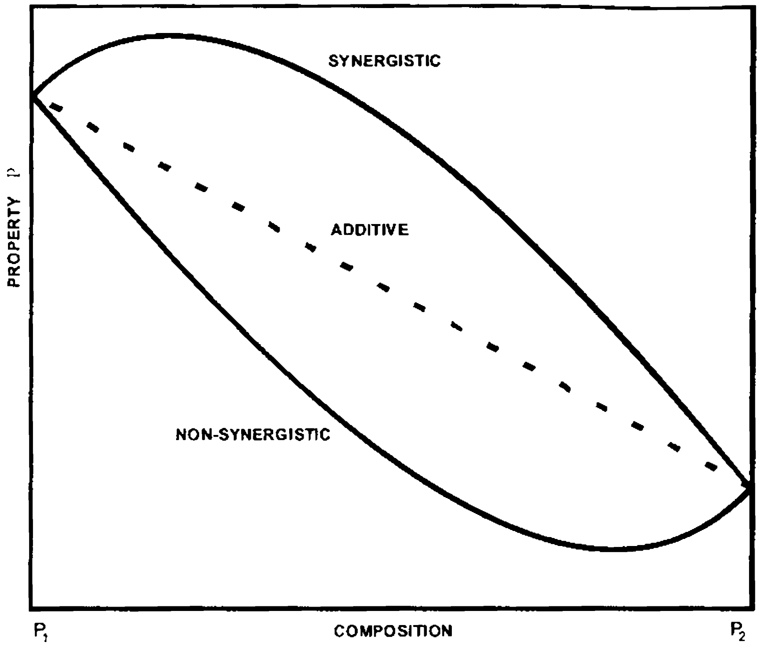

Figure 1.1 Variation of property with composition for a binary polymer blend

Several investigators have tried to correlate the morphology as revealed by electron microscopic studies with the mechanical properties of the blends.[27-30] It is convenient to divide the variables of a blend system into two categories viz. direct and indirect variables.[31]

1.2.1 Direct/Fundamental variables

The direct variables can be further subdivided into those which are important because the pure component properties depend on them and those that are unique to the blend systems. The direct variables are the fundamental ones and can be controlled by the indirect or processing variables. The direct variables are the following:

- Glass transition temperature
- Molecular weight
- Crosslink density
- Blend ratio
- Morphology

- Interfacial adhesion
- Relative stiffness
- Miscibility between polymers
- Compatibility between polymers
- Viscosity ratio between polymers

The first three fundamental variables are those that also affect the pure components. In general, the mutual solubility of two polymers decreases as the molecular weight of either component increases. In order to achieve a single T_g which controls blend properties such as resilience, some covulcanization between the different phases in the blend is needed. This explains the use of chlorobutyl in place of butyl rubber for blending with diene elastomers which give better general physical properties. Among the rubbery materials, a higher T_g or molecular weight generally increases toughness for a given crosslink density.[32] In addition, it is well known that the mechanical properties of elastomers depend very strongly on crosslink density.[33] Specifically, the energy required to rupture an elastomer in simple tension generally passes through a maximum as a function of crosslink density.

The next four direct variables are unique to blends. The properties obviously depend on the properties of each component in the blend. One of the major areas of studies on polymer blends is the dependence of the mechanical properties on blend ratio.[34-36] This is due to the fact that these complex systems exhibit a behaviour which does not simply follow the sum of the properties of the components. Bulk morphology is another important consideration which determines the physical properties of rubber blends. The process of blending, the phase viscosity and other processing conditions influence the morphology of the blend.[37-39] Two methods have been reported in literature. (1) Solutions of rubbers are stirred together, then dried or precipitated. (2) The bulk rubbers are co-masticated in a Brabender or similar high shearing mixer. Most investigators have used the latter method. With this technique, the mixing time, temperature, and/or speed can be varied to obtain different morphologies. Another means of changing the morphology is by annealing after mixing. This can cause an increase in dispersed particle size or phase inversion.

The interfacial adhesion between the two phases may determine the path that a growing crack takes in a deformed rubber blend and also determines the extent to which stresses can be transferred between the matrix and particle phases. If interfacial adhesion is sufficiently low, small cavities may be opened up between the dispersed domains and the matrix, when the blend is stressed leading to premature failure under stress. Thus the interfacial adhesion plays a key role in determining the mechanical properties. The interphase crosslinking is influenced by the type of curative system used, including its solubility in each phase and the response of the individual elastomers to the curatives.

The relative stiffness between the two phases is a function of molecular weight, glass transition temperature and rate of crosslinking of the two rubber phases. The micro-deformation of the blend will depend in part on this property. It is found in many blends that the relative stiffness also affects the mechanical properties.

1.2.1.1 Polymer – polymer miscibility

From a thermodynamic point of view, every polymer has same solubility in every other polymer, but the magnitude in most cases is exceedingly low.[3] For example, if polystyrene is fluxed in an internal mixer with poly (methyl methacrylate) (PMMA), a two-phase mixture results, no matter how long or intensive is the mixing. On the other hand, if one fluxes polystyrene with PPO as the second component, one phase results. It is thermodynamically stable because no matter how slowly the mixer turns or how long one waits there is still only one phase. The first represents an example of an immiscible blend, the second a miscible blend. The primary advantage of a miscible blend over its immiscible counterparts is the assurance of mechanical compatibility. The simplified average of ultimate mechanical properties is not always the observed or expected case, due to the importance of the position of the glass transition temperature (T_g) and/or brittle-ductile behaviour.

The structure and stability of polymer blends depends primarily on the miscibility of polymers used in its preparation. Miscibility is governed by the Gibbs free energy of mixing ($\triangle G_m$). The thermodynamic condition for obtaining miscible blend is that the free energy of mixing must be negative.

$$\triangle G_m = \triangle H_m - T\triangle S_m \qquad (1.2)$$

where $\triangle H_m$ is the change in enthalpy on mixing, $\triangle S_m$, the change in entropy on mixing and T, the absolute temperature. Since the entropy term is negligible for polymers, the heat of mixing, $\triangle H_m$, is the key factor deciding the polymer-polymer miscibility.[40,41] In the case of purely dispersive forces, $\triangle H_m$ is always positive. Consequently, high molecular weight systems with this type of interaction are rarely miscible. Miscibility drops significantly with growing chain length. However, if there exists the so-called specific interactions (ion–dipole interactions, hydrogen bond etc.) between the components, then $\triangle H_m$ can be negative and the polymers can be miscible. In other words, two polymers can be expected to be miscible when a very close match in cohesive energy density or in specific interactions, which produce a favourable enthalpy of mixing is involved.[42-45] The ability to co-crystallize can provide an additional driving force for polymer miscibility. Knowledge of solubility parameters of component polymers will be helpful in predicting miscibility. In the case of non-polar polymers, miscible blends can be prepared if they have same solubility parameters (δ's).[46] Compilation of the solubility parameters of the polymers is presented elsewhere.[47] For non-polar liquids the internal energy change on mixing is given by:

$$\triangle E_m = \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2 \qquad (1.3)$$

where φ_1 and φ_2 are volume fractions of the components. Realising that amorphous polymers are essentially liquids and assuming that the volume change on mixing is negligible, equation 1.3 is an expression for the change in enthalpy of mixing since $\triangle E_m = \triangle H_m$ for constant volume, constant pressure process. Thus equation 1.3 always results in a positive $\triangle H_m$, indicating that for non-polar high polymers, where the $T\triangle S_m$ term is small, true solution will not occur unless the δ's are almost perfectly matched. Thus, in order to achieve a homogeneous blend, it is necessary to choose polymer components that are capable of specific interactions among each other, leading to negative heats of mixing.

1.2.1.2 Blend compatibility

Compatibility is often used to describe whether a desired or beneficial result occurs when two polymers are combined together.[48-54] Compatible rubber blends are miscible only in a technological sense i.e., they can be covulcanised after blending and the properties are improved. In most cases either of the two components (in the case of a two-component blend system) forms the continuous phase in the matrix with the other phase dispersed in it. Generally the component with lower viscosity forms the continuous phase. The influence of structure on compatibility has been discussed by Marsh *et al.*[55] Although homogeneity at a fairly fine level is necessary for optimum performance, but certain degree of micro-heterogeneity is desirable to preserve the individual properties of the respective polymer components. Based on microscopic studies, it has been realized that almost all elastomer blends are micro-heterogeneous to varying degrees.[56]

Compatibility of a low unsaturation elastomer with a high unsaturation one can be improved by controlled interphase crosslinking of the blends. Compatibility of EPDM with high diene elastomers has been improved by this technique.[57] It has been found that better compatibility is possible if the component elastomers have virtually identical cure rate.[58] Baranwal *et al.* have shown that by grafting accelerators into EPDM, the co-curing ability of EPDM with a highly unsaturated diene can be improved, thus leading to good vulcanizate properties.[59] A few workers have investigated the dynamic mechanical properties of SBR/BR blends.[60]

It has been reported that interphase crosslinking causes a merging of the dynamic mechanical loss peaks that are characteristics of the individual polymers.

1.2.1.3 Compatibilisation

The addition of an interfacial agent called compatibiliser to immiscible blends is found to increase interfacial adhesion, provide stability of morphology against gross phase segregation and reduce the interfacial tension.[61] Several strategies of compatibilisation have been proposed. Normally, block or graft polymers, functionalized polymers, and low molecular weight materials are added as compatibilisers.[62] It has been found that block copolymers are usually better interfacial agents than graft copolymers because, in the latter, multiple branches will restrict the penetration into similar homopolymer phases. For the same reason diblocks are more effective than triblocks. Chlorinated polyethylene acts as a compatibilising agent in NBR/EPM or CR/EPDM blends.[63] Chloroprene rubber acts as a compatibiliser in NR/NBR blends.[64] The addition of some polyfunctional monomers in presence of peroxide is reported to be effective in blends of PVC with polyethylene.[65,66] Reactive compatibilisaton by compounding blends in presence of chemical reactants that leads to the modification of one of the components, results in the formation of an *in-situ* compatibiliser. Formation of maleic anhydride grafted polypropylene in polypropylene/nylon-6 blend was reported by Ide and Hasegawa.[67] Carboxyl terminated acrylonitrile-butadiene rubber (NBR) has been utilised for the successful blending with epoxies. Mechano-chemical blending that may lead chain break-up and recombination, thus generation of copolymer. Blends of polystyrene and polyethylene lead to the formation of styrene/ethylene graft copolymers.[68]

1.2.1.4 Viscosity considerations

In addition to thermodynamic factors, viscosity and cure rate of the component polymers must be taken into consideration. Tokita and Avergopoulos have thoroughly investigated the mixing parameters required for the optimum blending of elastomers and found that if there is considerable difference in the viscosities of component polymers, they will exist as separate domains.[69,70] The shape of the domains is more nearly spherical when the high viscosity component is the disperse phase. A softer disperse phase typically gives elongated domains. Extremely large domain size of the polybutadiene (BR) phase in NR/BR and SBR/BR blends were related to significantly higher viscosity for the BR phase.[71] In a blend of EPDM/NR, it was concluded that smaller domain size was achieved through a higher stress field during mixing, lower interfacial tension between the phases, and diminishing concentration of the disperse phase. Higher mixing temperature appeared to reduce domain size by diminishing the interfacial tension. Since the temperature normally goes up during mixing, the high shear blending of polymers with similar viscosities will give the most homogenous mixtures. Furthur studies in EPDM/BR blends indicated that the driving force for blend homogeneity was related to a similarity in the viscosities of the two phases under the specific conditions of mixing. Because of the large difference in T_g between EPDM and BR, it was possible to vary their relative viscosities simply by changing the shear rate and/or mixing temperature; the domain size of the disperse phase could thus be altered for the same blend. It was also possible to shift the disperse phase from one polymer to another even though that polymer is the minor component. In this case, the comparatively low viscous phase actually encapsulates the high viscous component and then become continuous.

The viscosity mismatch between the component polymers also affects the distribution of compounding ingredients in the blend. For example, when filler is added to a two-component elastomer blend, it preferably migrates to the less viscous polymer and when the viscosity becomes equal to that of the more viscous polymer it would be taken up by both the polymers. So often the low viscosity polymer gets highly loaded. It is evident that the distribution of fillers can profoundly influence the modulus in elastomer blends. At lower strains, where the filler network structure dominates the stiffness properties, an increase in the non-uniformity of this filler distribution results in a lower stock modulus. Hess *et al.*

demonstrated that carbon black normally locates preferentially in the BR component of 50/50 NR/BR blend.[72] The viscosity mismatch which prevents or greatly delays the formation of intimate mixture can be overcome by improving the blending process either by adjusting oil or filler concentration in the two elastomers or by adjusting the individual raw polymer viscosities, so that, the effective viscosities of the phases will no longer be mismatched.[73]

1.2.2 Indirect/Processing variables

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

- Distribution of filler between elastomers
- Distribution of plasticizers
- Distribution of crosslinking agents
- Crosslink type and network structure of vulcanized elastomer blend

1.2.2.1 Distribution of filler between elastomers

A general question which comes up in the case of elastomer blends is regarding the distribution of filler particles between the separate zones and how performace characteristics are affected. The effect of an appreciable volume loading of filler on the properties of cured elastomeric vulcanizates depends on whether the elastomer is stress crystallizing or not. Dinsmore *et al.* reported that the ratios of the tensile strengths of black filled to that of gum vulcanizates is 1 to 1.5 for NR vulcanizates and 5 to 10 for vulcanizates for SBR and similar elastomers.[74] Thus appreciable improvements in strength properties may be obtained for non-stress-crystallizing rubbers by incorporation of carbon black. Further, certain elastomers have optimum filler loadings for particular properties such as wear and tear resistance.[75] As different rubbers have different responses to filler loadings for certain properties, control of filler distribution in elastomer blends could have corresponding specific effects.

The distribution of filler particles between the separate phases of an elastomer blend is affected by a number of factors like unsaturation, viscosity, polarity, molecular weight etc.[76] Carbon black has a tendency to migrate to the more unsaturated polymers. Butadiene rubber has the greatest affinity towards carbon black and it follows the order: BR>SBR>CR>NBR>NR>EPDM>IIR.[77] Many authors have shown that the properties of a blend can be improved by preferential addition of carbon black in the blend.[78,79] Methods of assessing the reinforcing ability of the fillers have also been discussed elsewhere.[80-82] In addition, black transfer during blending was observed from a mechanically mixed IIR masterbatch to a high unsaturation gum rubber but not from a NR masterbatch.

It is apparent that the surface polarity of carbon black influences its distribution in elastomer blends. Basic furnace blacks locate in the cis BR phase in cis BR/NR blends but acidic channel blacks locate in the more polar NR phase. Inorganic fillers also behave differently, e.g. in cis BR/NR blends, silica tends to accumulate in the NR phase.[55] Filler distribution is also influenced by the point of addition of filler, the viscosity levels of the elastomers, and the blending methods. The ability of rubbers to accept black and other fillers is said to be an important factor in attaining good dispersion which in turn affects reinforcement and ultimate performance properties. The reinforcing ability of a filler in an elastomer can be assessed by bound rubber determination.[83]

The compounding of carbon black is greatly dependent on the method of mixing used.[84] The location of 40 phr GPF black in 50/50 NR/BR blends has been controlled by mixing separate motherstocks and blending these. The normal mix is one in which the two rubbers are blended in a Banbury before adding the black and the rest of the compounding ingredients. Tensile and tear properties showed improvement as more black located in the BR phase. 50/50 blends of BR and a high styrene SBR containing 50 phr black overall were prepared by blending a 50/50 BR/HAF black masterbatch and SBR gum. The blends were found to exhibit higher abrasion resistance than identical compounds mixed conventionally. It would hence be possible that by correct filler distribution in rubber blends, vulcanizate properties can be improved.

1.2.2.2 Distribution of plasticizers

In the normal rubber vulcanizate the concentration of plasticizer 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 rubber blends.

1.2.2.3 Distribution of crosslinking agents

It is of paramount importance in a binary elastomer blend that both the constituents cure to an optimum level. Results of dynamic mechanical studies and thermal analysis suggest that a two phase system is liable to change to a more homogeneous one with curing. Blends of BR and SBR display two dynamic mechanical loss peaks in the uncured state which are characteristic of the individual rubbers. These peaks merge quickly to form an intermediate loss peak on vulcanization of the blend probably due to interphase crosslinking.[85,86] Hence in a two-component elastomer blend, formation of interphase crosslinking when the two rubber phases undergo crosslinking is a necessary criterion for developing good mechanical properties.[87] Formation of interphase crosslinks is in competition with intraphase crosslinking. So interphase crosslinking is possible only when the cure rates in the two rubbers are comparable.[88] The different possibilities of crosslinking in a binary elastomer blend are shown in figure 1.2.

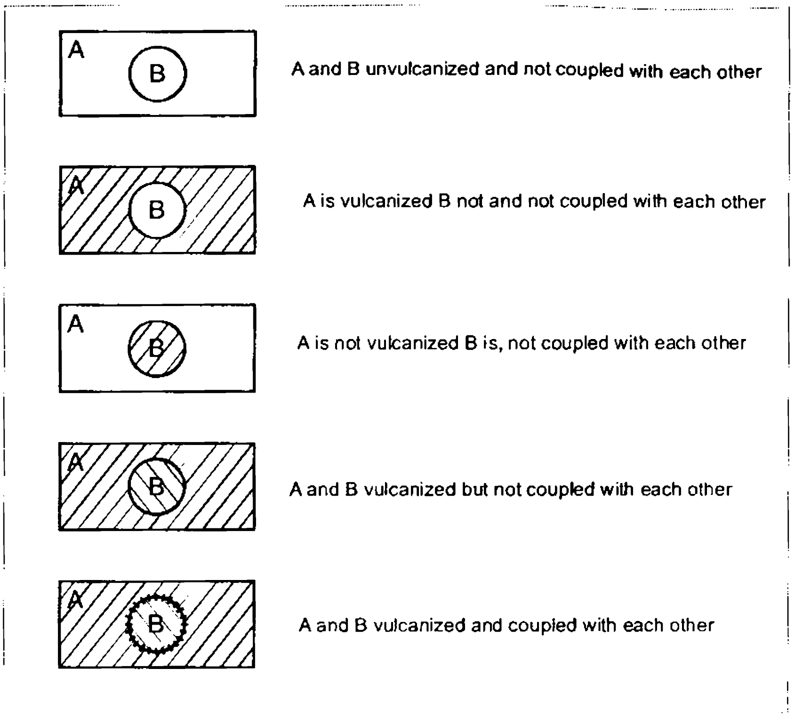

Figure 1.2 Various modes of crosslinking in a binary elastomer blend

The most prominent factor which leads to the mismatch of cure rate in two rubbers is the non proportional division of the curatives, since the solubility of the compounding ingredients is different in the constituents of an elastomer blend. This leads to diffusion of compounding ingredients before, during and after vulcanization and this is recognized as an important factor in the overall properties of the rubber article.[89] In certain cases it can be of benefit since waxes and p-phenylene diamine rely heavily on diffusion to provide optimum protection against degradation by ozone.[90,91]

Curative migration should be of particular concern in an uncured tire since it contains many interfaces between different rubber compounds with differing cure systems. It is an established fact that several commonly used curatives such as sulphur, CBS, TMTD and DPG will diffuse quite readily across a rubber to rubber interphase.[92-95] As solubility of the curatives is greater in highly unsaturated rubbers than in the less unsaturated rubbers, migration will occur to the former. As the cure rate is also faster in the highly unsaturated rubbers, the imbalance will be accentuated. In view of the associated under- and over-cure of the phases, the vulcanizate properties of blends of high and low unsaturation rubbers may not attain the desired levels. Attempts have been made, particularly with blends of EPDM and high unsaturation rubbers, to improve compatibility and co-crosslinking. These include grafting of accelerators on to EPDM, conversion of EPDM into a macromolecular retarder by the addition of certain N-chlorothioamides etc.[59,96] Similar attempts have been made successfully to make the crosslinking agent chemically bind to the elastomer in which it has the lowest solubility and then blend it with another elastomer, and also to use vulcanizing system that perform independently of polymer unsaturation in elastomer combinations.[97]

Gardiner showed that the inferior properties of rubber blends result from the difference in the migration of curatives from the less polar to more polar elastomer phases.[24,98] This diffusion was shown to occur very quickly during both the mixing and the vulcanization phases of compound processing. Gardiner further noted that the very polar thiuramdisulphide accelerators showed the greatest tendency to migrate because of their much greater solubility in the polar elastomer phase of a blend. Guillaumond determined the comparative solubilities of conventional curatives in several rubbers. It was shown that sulphur is 1.5 times soluble in SBR as in BR or EPDM, MBT is 4.5 times soluble in SBR as in EPDM and BR, TMTD is 3 times soluble in SBR as in BR or EPDM etc.[99-101] It appears that the solubility of the compounding ingredients exercise a profound influence on the properties of the vulcanizates especially when the constituents are incompatible.

Several investigators have tried to improve covulcanisation of elastomer blends and thereby improve the properties of the blends closely along the additive line with respect to the properties of the two individual elastomers. Improved covulcanisation of EPDM/NR blends was achieved by Woods and Davidson by using a TETD accelerator-lead oxide activator combination. The lead salts of TETD are insoluble in both polar and non-polar elastomers, which eliminate the thermodynamic driving force for curative diffusion.[102] Coran achieved better cure compatibility for EPDM/NR blends by modifying the EPDM with maleic anhydride which permits EPDM to be crosslinked independently with Zinc oxide in the accelerated sulphur vulcanising system. An ionic crosslink network is produced in the EPDM phase. This type of crosslinking is not competitive with the accelerated sulphur system, which reacts rapidly with NR. Compared to conventional NR/EPDM blends, those with the modified EPDM exhibited higher tensile strength and the fatigue life along with reduced hysteresis and permanent set, all of which reflect better covulcanisation. The maleic anhydride treatment has also been applied to IIR and EPDM by Suma and coworkers for improved blending with NR.[103] Zapp obtained interfacial bonding in the CIIR/SBR and CIIR/BR blends through the use of very active thiuram and thiuram tetrasulphide curative systems, and also with bis alkyl phenol polysulphide as sulphur donor.[104]

Apart from the migration of curing agents and fillers, the migration of other ingredients has also been reported. Corman *et al.* demonstrated that migration of oil on the elastomer surface takes place depending on the structure of both elastomer and oil.[105] In another study, Lewis *et al.* have shown that migration of antiozonant takes place preferentially from EPDM to SBR during curing.[106] Such diffusion across the rubber to rubber interphase can cause a change in the distribution of materials, which may result in a change in physical properties, a loss in adhesion or antidegradant protection and staining of light coloured compounds.[68]

1.2.2.4 Crosslink type and network structure of vulcanized elastomer blends

The most important factor in determining the physical properties of rubber vulcanizates is the degree of crosslinking. In the case of sulphur vulcanization, the nature of crosslinks and the presence of other rubber bound side products of vulcanization may also influence physical properties. In the general case, diene rubbers form not only mono-, di- and polysulphidic crosslinks but also, pendent sulphide groups terminated by an accelerator residue, cyclo sulphides, conjugated diene and triene units, cis-trans isomerized olefin units and vicinal crosslinks (figure 1.3).[107-109]

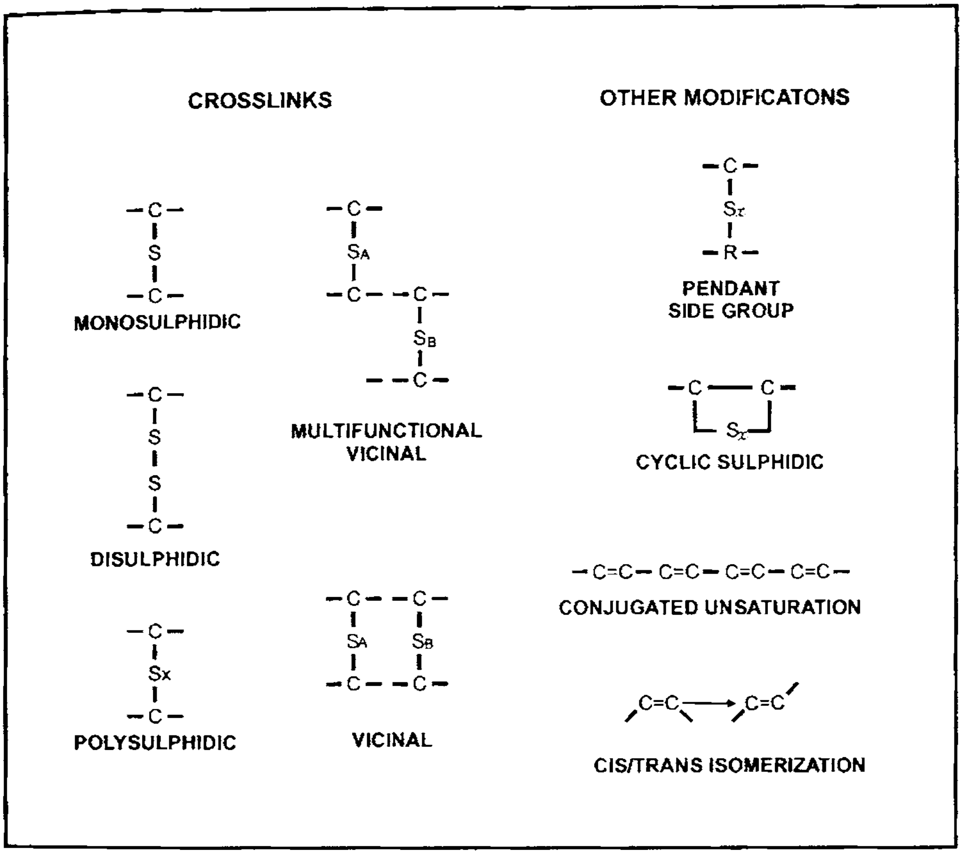

Figure 1.3 Structural features of sulphur vulcanized diene rubbers

Polysulphidic crosslinks display poor thermal ageing resistance as a consequence of their high chemical reactivity. Their enhancement of relaxation and swelling processes is almost certainly due to their reaction ability to undergo rapid interchange which allows crosslink breakage and reformation to occur.[110, 111] The networks formed with high proportions of polysulphidic crosslinks display higher tensile strength and tear strength than networks prepared with monosulphidic or carbon-carbon crosslinks.[112-114] There is also some evidence that resilience and resistance to fatigue failure are enhanced.[80] The main chain modifications formed by side reactions also appear to affect some properties.

Some of these are probably a consequence of an increase in polarity and/or an increase in the glass transition temperature of the rubber. Others are a result of interruptions in the stereo-regularity of the elastomeric backbone as a consequence of which the tendency to crystallize is reduced. Thus the physical properties of sulphur vulcanizates of diene rubbers depend on the network structure which is composed of the degree of crosslinking, crosslink structure and main chain modifications. Hence the primary objective of the rubber compounder must be to select a mix composition and vulcanizing conditions to achieve an appropriate network structure which will give and maintain optimum physical properties. Achieving a desired network structure in vulcanizates of elastomer blends is far too difficult than in individual rubbers due to the unproportional migration of the curatives between the constituents and the varied response of the rubbers towards them. However, arriving at optimum network structures in the constituent rubbers of an elastomer blend is important since almost every property of the blend vulcanizate depends upon the network structure.

1.3 Blending procedure

The general mixing methods for preparing elastomer blends include latex mixing, solution mixing, mechanical mixing and mechanochemical mixing.[63] These methods may be further divided into two general categories of preblending and phase mixing. In the first case, the compounding ingredients are generally added to the premixed polymers in a manner similar to the mixing of a single elastomer. The phase mixing method is generally accomplished by the preparation of separate masterbatches which are then blended mechanically.

1.3.1 Preblending

1.3.1.1 Mechanical blending

The simplest preblending method is mechanical blending.[115,116] This is accomplished either on a two roll mill or in an internal mixer, e.g. Banbury. Evans and Partridge have showed that a single stage preblending procedure was a most cost effective method for preparing blends of NBR and chlorobutyl (CIIR).[117] For best results, the polymer components of a blend are usually mixed for a short period prior to the addition of filler and rest of the compounding ingredients.[118] Bristow compared the properties of NR/BR blends as a function of blending method. Firstly, by the addition of ingredients with no preblending, and secondly by the blending of separate masterbatches which contained proportionate amounts of the compounding ingredients.[119] No major differences in final compound properties were observed. However, no studies were carried out with uneven proportions of compounding ingredients added to the separate masterbatches. The nature of the resulting dispersion depends on the period of mixing, temperature of mixing, rheological properties of the component polymers etc.

1.3.1.2 Latex blending

When the individual components are available in latex form, they may be conveniently combined by blending the latices.[120,121] The blend is then recovered by coagulation or spray drying. This method results in an intimate and uniform dispersion of the components. However one drawback is the difficulty in completely removing the non polymeric materials (emulsifier etc.) that are present in the latices.

1.3.1.3 Solution blending

Mixing of polymer solutions is mainly used for coatings, because it allows rapid and easy mixing of the components at low energy costs, leads to simple applications at normal temperatures and neither causes degradative colour changes nor premature crosslinking reactions.[122,123] But for the preparation of the solid polymer blends, this method requires removal of the solvent which usually leads to phase separation. Furthermore, the use of solvents implies problems connected with their price, toxicity, flammability, pollution and the economics of the whole process. Usually only laboratory samples of solid polymer blends are prepared by this method.

1.3.1.4 Reactive blending

Blends may also be prepared by dissolving a polymer in the monomer of the other component and then polymerizing the second component. This may result in appreciable grafting of the polymer in addition to good dispersion.

1.3.1.5 Dynamic vulcanization

Dynamic vulcanization is a comparatively new method of blending. This concept was originally developed by Gessler for blends of CIIR and polypropylene. With this mixing technique, the elastomer phase was crosslinked to provide a vulcanizate within a thermoplastic matrix. Dynamically vulcanized blends have been defined as elastomeric alloys (EA) which represent a synergistic combination of an elastomer and thermoplastic. The resultant properties are found to be superior than that would be expected for a simple blend of the component polymers.

1.3.2 Phase mixing

Separate master batches are employed with this type of mixing in order to locate specific types and amounts of curing agents or fillers in the separate polymer phases.[51,54,84,124-127] In one of the earlier studies of this type, solution mixing was used to prepare NR and BR master batches at different carbon black loading.[51,128] This is a convenient method for difficult-to-mix polymers such as cis-1,4 BR. The master batches were subsequently blended in a Banbury to produce tread compounds with variation in carbon black phase distributions. The phase mixing procedure assumes that the carbon black (or other ingredients) will remain in the polymer to which it has been added. But this is not always true since there are specific conditions under which carbon black has been observed to migrate from one polymer to another during mixing.

Characterization of rubber blends

Homogeneous or miscible blends are characterized by one value of any physical parameter, whereas several values of the same parameters (corresponding to the number of components) are characteristic of immiscible or heterogeneous systems.[129] For example, blends of two incompatible materials show two or multiple glass-transition temperatures. At the same time a homogeneous polymer blend has only one glass transition temperature that lies in between those of the two polymers. Thus many of the current methods employed to determine polymer-polymer miscibility depend on the transitional behaviour of polymer blends. In mechanical methods, the polymer blend is subjected to small amplitude cyclic deformations and the variations of elastic and the viscoelastic properties at the transition point will yield necessary information.[130,131] Data obtained over a broad temperature range can be used to ascertain the miscibility behaviour. In a highly phase-separated polymer blend, the transitional behaviour of the individual components will be unchanged. Likewise in a miscible blend a single and unique transition will appear. In dielectric methods the transition data is obtained from electrical measurements rather than dynamic mechanical testing.[64] The advantage is the ease with which the frequency can be changed. However, determination of transitions of non-polar polymers is difficult. The variation of dielectric constant at transition is measured in these methods. Dilatometric methods capitalize on the discontinuity in the rate of volume change with temperature in the region of the glass transition, while the calorimetric methods observe the change in specific heat of polymers when passing through the glass transition.[132-134]

Various types of energy absorption or fluorescence spectroscopies have been proven immensely useful for understanding the structure and dynamics of organic molecules. These methods can also be applied to the structural studies of polymer blends. NMR spectroscopy, infrared spectroscopy, energy dispersive X-ray analysis etc. have seen wide application in blend studies.[39,135-137]

For the detailed characterization of the phase morphology in blends, microscopy is unmatched by any other technique.[138] In bulk, compatible polymers form transparent films and fibers that exhibit no heterogeneity under considerable magnification in the phase contrast microscope or in the electron microscope, no matter what staining methods are employed. It should be noted that the films prepared from two incompatible polymers can be transparent if the two component polymers have equal refractive indices. Bohn *et al.* has indicated that, for transparency the critical difference between refractive indices cannot be greater than 0.01.[139] For example, Platzer reported that transparent vinyl bottle compounds prepared from blends of polyvinyl chloride (PVC) and methyl methacrylate-butadiene-styrene graft copolymers had matching refractive indices.[140] Optical contrast can arise from a number of sources such as colour, opacity, refractive index, orientation, absorption etc.[141,142] With transmission election microscope (TEM), electron scattering differences are the primary source of contrast. The scanning electron microscope (SEM) on the other hand, depends primarily on surface texture for contrast. SEM was used by O' Conner to observe the fracture surface of short fiber reinforced rubber composite with a view to find out the degree of alignment, the uniformity of fiber dispersion and the extent of fiber-rubber adhesion.[143] Bascom investigated fracture mechanism of rubber by using SEM.[144] The fracture surface of a series of gum and filled rubber vulcanizates under different modes of failure had been studied by Bhowmick *et al.*[145-147] Murty *et al.* and Chakraborty *et al.* had used the SEM technique to study the fracture surface of short fiber-rubber composites showing the fiber pull-out failure resulting from poor fiber-rubber adhesion, the role of silica in promoting adhesion, the alignment of fibers in the matrix and the nature of the fracture surfaces obtained in different types of failure tests.[148-150] Akhtar *et al.* had predicted the extrusion characteristics of natural rubber/polyethylene blend by observing the extrudate surface morphology using SEM.[151] Mathew *et al.* had reported the fracture mechanism at different modes of fracture and the effect of thermo-oxidative ageing of fracture surfaces of NR vulcanizate.[152-154] The fracture surface of unfilled NR vulcanizates showed a rough zone followed by a comparatively smooth region. The presence of antioxidant or the change in vulcanizing system does not show any change in the mode of fracture as shown by their SEM studies. Deuri *et al.* had studied the fracture surfaces of unaged and aged EPDM vulcanizates at different modes of failure.[155,156] They correlated the tensile strength with the distance between crack lines and tear lines.

Scattering methods depend on the principle that a stable homogeneous mixture is transparent, whereas unstable non-homogeneous mixture is turbid unless the components have identical refractive indices.[157] Probably the oldest and most used method for determining polymer-polymer miscibility is the mutual-solvent approach (ternary method).[158] It consists of dissolving and thoroughly mixing a 50/50 mixture of two polymers at low to medium concentrations in a mutual solvent. Miscibility is said to prevail if phase separation does not occur for a few days. Other methods like inverse gas chromatography, solution viscosity, melt rheology, melting point depression, sorption probes, spectroscopic techniques are also employed for the study of blends.[39,98,159,160]

1.5 Applications of rubber blends

Rubber-rubber blends are widely used for the manufacture of both small and large rubber products. Examples include tire, belt, cable etc. Tire industry is consuming almost more than half of the total consumption of rubber. It is interesting to note that the major components of tire except tread ply have been successfully compounded using rubber blends of two or three elastomers as shown below.[161]

Typical elastomers used in passenger and truck tires

	Passenger	Truck
Tread	SBR-BR	NR-BR or SBR-BR
Carcass	NR-SBR-BR	NR-BR
Black Sidewall	NR-SBR or NR-BR	NR-BR
Liner	NR-SBR or NR-SBR-IIR	NR-IIR

In cable industry, the insulating cover is made mostly from elastomer-elastomer or elastomer-thermoplastic blends for better resistance to abrasion, weathering, heat, chemicals etc. Conveyor belts are another area in rubber industry using elastomer blends. For top cover EPDM is blended with natural rubber (NR), chloroprene rubber (CR), chlorobutyl rubber (CIIR), bromobutyl rubber (BIIR) etc.

1.6 Some useful rubber blends

The abrasion resistance and elasticity of natural rubber (NR) has been improved by blending with polybutadiene (BR), finding application in tire tread.[34] The processing characteristics of car and truck tire tread recipes based on blends of BR and SBR have also been reported. EPDM blended with SBR has shown improvements in ozone and chemical resistance with better compression set properties.[162] The poor processing properties of cis BR were improved by the use of specific black and/or blending with NR or SBR.[163,164] One particular advantage of blending BR with NR is the effect of high curing temperatures on physical properties. This heat stability is conveyed by cis BR when blended with NR or SBR.[33] Butyl rubber is blended with NR for use as the inner liner of tubeless tires for its good resistance to mechanical damping and permeability. Blends of EPDM and nitrile rubber (NBR) have been cited as a compromise for obtaining moderate oil and ozone resistance with improved low temperature properties.[165] Blends of EPDM and chloroprene rubber are used in tire side wall. The blending of EPDM with butyl rubber imparts enhanced heat resistant property.[53] A blend of silicone and fluorosilicone polymers bonds easily with fluorosilicone adhesives and has better physical properties, better processing and is cheaper than the unblended polymer.[166]

1.7 Objectives and scope of the present work

The use of blends of elastomers in place of single elastomer is increasing day-by-day due to several technical reasons. It is evident from the foregoing discussion that the choice of elastomers depends on several factors. They must be cure compatible and allow covulcanization. After blending, their processing characteristics should be very good and product performance better over the component elastomers. All these properties must be understood fully to exploit various rubber blends.

A detailed study of the blends of ethylene-propylene-diene rubber (EPDM) and chlorobutyl rubber (CIIR) is proposed in this study. These blends may find application in the manufacture of curing diaphragms/curing envelopes for tire curing applications. EPDM possesses better physical properties such as high heat resistance, ozone resistance, cold and moisture resistance, high resistance to permanent deformation, very good resistance to flex cracking and impact. Because of the low gas and moisture permeability, good weathering resistance and high thermal stability of CIIR, blends of EPDM with CIIR may be attractive, if sufficient mechanical strength can be developed. Although a lot of work has been done on elastomer blends, studies on the blends of EPDM and CIIR rubbers are meagre. Hence in this investigation it is proposed to make a systematic study on the characteristics of EPDM and CIIR rubber blends.

The mechanical and physical properties of an elastomer blend depend mainly on the blend compatibility. So in the first part of the study, it is proposed to develop compatible blends of EPDM with CIIR. Various commercial grades of ethylene-propylene-diene rubber are proposed to be blended with a specific grade of chlorobutyl rubber at varying proportions. The extent of compatibility in these blends is proposed to be evaluated based on their mechanical properties such as tensile strength, tear strength and ageing resistance. In addition to the physical property measurements, blend compatibility is also proposed to be studied based on the glass transition behaviour of the blends in relation to the T_g's of the individual components using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). The phase morphology of the blends is also proposed to be investigated by Scanning Electron Microscopy (SEM) studies of the tensile fracture surfaces. In the case of incompatible blends, the effect of addition of chlorosulfonated polyethylene as a compatibiliser is also proposed to be investigated.

In the second part of the study, the effect of sulphur curing and resin curing on the curing behaviour and the vulcanizate properties of EPDM/CIIR blends are planned to be evaluated. Since the properties of rubber vulcanizates are determined by their network structures, it is proposed to determine the network structure of the vulcanizates by chemical probes so as to correlate it with the mechanical properties.

In the third part of the work, the effect of partial precuring of one of the components prior to blending as a possible means of improving the properties of the blend is proposed to be investigated. This procedure may also help to bring down the viscosity mismatch between the constituent elastomers and provide covulcanization of the blend.

The rheological characteristics and processability of the blends are proposed to be investigated in the last part of the study. To explore their possible applications, the air permeability of the blend samples at varying temperatures is proposed to be measured. The thermal diffusivity behaviour of EPDM/CIIR blends is also proposed to be investigated using novel laser technique. The thermal diffusivity of the blends along with the thermal degradation resistance may help to determine whether the blends are suitable for high temperature applications such as in the manufacturing of curing envelope.

This thesis is divided into the following eight chapters:

Chapter I	Introduction
Chapter II	Experimental techniques
Chapter III	Compatibility studies on EPDM/CIIR blends
Chapter IV	Studies on sulphur cured EPDM/CIIR blends

Chapter V	EPDM/CIIR blends: Improved mechanical properties through precuring
Chapter VI	Effect of resin curing on the mechanical properties of EPDM/CIIR blends
Chapter VII	Rheology, air permeability, thermal stability and thermal diffusivity studies on EPDM/CIIR blends
Chapter VIII	Summary and Conclusions

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Chapter II

Experimental Techniques

The materials used and the experimental procedures adopted in the present investigation are given in this chapter.

2.1 Materials

2.1.1 Ethylene-propylene-diene rubber (EPDM)

Four grades of EPDM were used. (1) Herline 301-T, manufactured by Herdilia Unimers Limited, Mumbai, (2) NDR-4640, manufactured by Nordel Dupont, Beaumont, USA, (3) Royalene MRD-10, manufactured by Uniroyal, Inc., Geismar, USA and JSR EP-96, manufactured by Japan EPR Company, Yokkaichi, Japan. The specifications of the four different grades of EPDM used are given in table 2.1.

Table 2.1 Specifications of EPDM grades

EPDM grade	301-T	NDR-4640	EP-96	MRD-10
Mooney viscosity [ML (1+8) @ 100°C]	47.8	53.4	74	14
E/P ratio	68/32	55/45	63/27	64/36
Diene type	*DCPD	#ENB	#ENB	#ENB
Iodine value	10.5	16.0	19.0	7.2

* Dicyclopentadiene

\# Ethylidene norbornene

2.1.2 Chlorobutyl rubber (CIIR)

Exxon Chlorobutyl (1066) manufactured by Exxon Chemical Company, Baton Rouge, USA having the following specifications was used.

Table 2.2 Specifications of chlorobutyl

Raw Polymer viscosity [ML (1+8) @ 100°C]	56.3
Volatile matter (%)	0.20
Chlorine content (%)	1.20
Iodine value	8.4

2.1.3 Chlorosulfonated polyethylene (CSPE)

Chlorosulfonated polyethylene used was manufactured by Aldrich Chemicals, USA. The CSPE was obtained as white chips and had a specific gravity of 1.12, sulphur content of 1.4 % and chlorine content of 26 %.

2.1.4 Polychloroprene rubber (Neoprene-W)

Polychloroprene rubber used was MC 30 Butachlor, manufactured by Enichem Elastomers, GRE Noble, France. The light cream flakes had a specific gravity 1.23, volatile matter 1.3 % and Mooney viscosity [ML (1+8) @ 100 °C] 46.

2.1.5 Zinc Oxide

Zinc oxide (ZnO) was supplied by Meta Zinc Ltd., Mumbai. It had the following specifications.

Specific gravity	5.5
ZnO content	98 %
Acid content	0.4 % max.
Heat loss (2 hrs at 100 °C)	0.5 % max.

2.1.6 Stearic acid

Stearic acid used was supplied by Godrej Soaps Pvt. Ltd., Mumbai and had the following specifications.

Melting point	50-69 °C
Acid value	185-210
Iodine value	95 max.
Specific gravity	0.85 ± 0.01
Ash	0.1 % max.

2.1.7 Mercapto benzthiazole

Mercapto benzthiazole (MBT) having the following specifications was supplied by Bayer India Ltd., Mumbai.

Specific gravity	1.50
Melting point	161 °C

2.1.8 Tetra methyl thiuram disulphide

Tetra methyl thiuram disulphide (TMTD) used was supplied by polyolefin Industries Ltd., Mumbai. It had the following specifications.

Melting point	136 °C
Specific gravity	1.4

2.1.9 Zinc diethyl dithiocarbamate

Zinc diethyl dithiocarbamate (ZDC) was supplied by ICI India Ltd., Kolkata as a creamy white powder, soluble in chloroform, CS_2 and benzene and had the following specifications.

Melting point	178 °C
Specific gravity	1.47

2.1.10 N-cyclohexyl-2-benzthiazyl sulphenamide

N-cyclohexyl-2-benzthiazyl sulphenamide (CBS) used in the study was Santocure CBS supplied by Polyolefin Industries Ltd., Mumbai, having the following specifications.

Ash	0.5 % max.
Moisture	0.5 % max.
Specific Gravity	1.27

2.1.11 Sulphur

Sulphur was supplied by Standard Chemical Company Pvt. Ltd., Chennai and had the following specifications.

Specific gravity	2.05
Acidity	0.01 % max.
Ash	0.01 % max.
Solubility in CS_2	98 % max.

2.1.12 Accinox ZC

Accinox ZC was supplied by ICI India Ltd., Kolkata as dark brown granules. It had the following specifications.

Specific gravity	1.02
Melting point	48 °C

2.1.13 Methylol phenol resin

Methylol phenol resin was supplied by Apollo Tyres Limited, Cochin. It had the following specifications

Specific gravity	1.04
Softening point	87.5 °C
Methylol content	9 %

2.1.14 High abrasion furnace black

High abrasion furnace black (HAF N 330) was supplied by Carbon and Chemicals (India) Ltd., Cochin. It had the following specifications.

Iodine adsorption number	80 mg/g
DBP absorption	105 cm^3/100 g
Mean particle diameter	32 nm

2.1.15 Paraffinic oil

Paraffinic oil was supplied by Hindustan Petroleum Ltd. It had the following specifications

Colour	Light Yellow
Aniline point	198 °C
Viscosity gravity constant	0.857
Density	0.861 g/cm^3

2.2 Preparation and moulding of specimens

2.2.1 Mixing and homogenisation

Mixing and homogenisation of elastomers and compounding ingredients were done on a laboratory size (16 × 33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip of (0.002 × 100)". Then it was given 2 passes through the nip of (0.002 × 10)" and allowed to band at the nip of (0.002 × 55)". After smooth band formation on the mill, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order: activators, fillers, accelerators and curing agents. Before the addition of accelerators and sulphur, the batch was thoroughly cooled to prevent scorching of the compound on the mill.

After incorporating all the ingredients, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. Blending of elastomers was done by banding EPDM first on the roll followed by the addition of chlorobutyl and blending continued till visual homogenization. The additives were then added as described above.

Properties of some partially pre-vulcanized EPDM/CIIR blends were also studied. For this, CIIR was compounded first with the required additives and precured to a low level. These precured samples were blended with EPDM on the mill and then compounding ingredients for EPDM were added. The mixing process was continued till visual homogenization to get the final mix.

2.2.2 Cure characteristics

Cure characteristics have been studied using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) as per ASTM D 1646 (1981). The die type used was biconical and the die gap was 0.487. It is a microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogenous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle of 0.20 degree. The optimum cure time of the samples was determined at 170 °C at a frequency of 50.0 cpm. The torque is measured on the lower oscillating die half. A typical elastograph cure curve is shown in figure 2.1 and the following data can be taken from the torque - time graph.

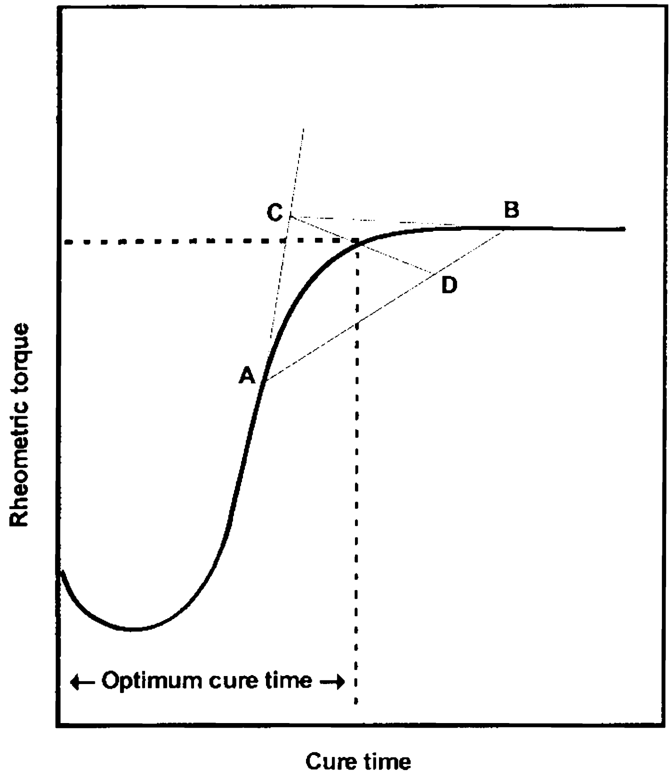

Figure 2.1 A typical cure graph

(1). Minimum torque: Torque obtained by the mix after homogenising at the test temperature before the onset of cure

(2). Maximum torque: Torque recorded after the complete curing of the mix

(3). Scorch time (t_{10}): Time taken for attaining 10 % of the maximum torque

(4). Optimum cure time (t_{90}): Time taken for attaining 90 % of the maximum torque

(5). Cure rate: Cure rate was determined from the following equation

$$\text{Cure rate (Nm/min)} = \frac{L_{\max} - L_{\min}}{t_{90} - t_{10}} \qquad (2.1)$$

where L_{max} and L_{min} are the maximum torque and minimum torque respectively and t_{90} and t_{10} are the times corresponding to the optimum cure time and scorch time respectively. The Rubber Process Analyzer evaluates the vulcanization curve and prints out the data after each measurement.

2.2.2.1 Cure time

On examination of the graph of torque vs. time (figure 2.1), one can observe that the torque decreases initially with time due to reduction in viscosity and thixotropic effect, but increases, steadily as vulcanization starts. As vulcanization proceeds this torque shows a steady increase, attains a maximum value and then slowly decreases due to polymer degradation. For practical purposes cure time is taken as the time for the development of 90 % of maximum torque and is denoted as t_{90}. But in the case of rheographs showing marching modulus, optimum cure time was calculated as follows. Two tangents AC and BC were drawn on the rheographs as shown in figure 2.1. They meet each other at point C. The points of contact (A and B) of the tangents and the rheograph were connected by a straight line AB. The middle point O of the straight line was connected with point C (point of intersection of the two tangents). The line CO cuts the rheograph at point T. The time corresponding to the torque at point T of the rheograph was taken as the optimum cure time. A similar procedure was adopted by Chakraborty and De.[1]

2.2.2.2 Mooney viscosity measurements

The Mooney viscosities of the raw rubbers were measured on the Mooney viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc rotating (2 rev/min) in a cylindrical cavity set at 100 °C and filled with rubber under test. In running a viscosity test, the sample was allowed to warm up for one minute after the platens were closed and the motor was then started. Reading taken after 8 minutes was reported as the Mooney viscosity of rubber [ML(1+8) @ 100 °C]. The procedure given in ASTM D 1646 (1981) was followed.

2.2.3 Compression moulding

The test specimens for determining the physical properties were prepared by vulcanizing the blanks cut from unvulcanized sheets marked with the machine direction at a temperature of 170 ± 1 °C in standard moulds by compression moulding on an electrically heated hydraulic press (Santosh model SMP- 50), having 30 × 30 cm platens at a pressure of 200 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times. Mouldings were cooled quickly in water at the end of each curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physicals tests. For samples having thickness more than 4 mm (heat build-up, compression set, abrasion resistance etc.) additional time based on the sample thickness was given to obtain satisfactory mouldings.

2.3 Physical test methods

For the tests described below at least three specimens per sample were tested for each property and mean values are reported.

2.3.1 Modulus, Tensile strength and Elongation at break

Tensile properties of the elastomer blends were determined according to ASTM D 412 (1980) using dumbbell specimens on a Shimadzu Universal Testing Machine (model-AG1) with a load cell of 10 kN capacity. All the tests were carried out at ambient temperature. Samples were punched out from compression moulded sheets along the mill direction using a dumbbell die. A bench thickness gauge was used to measure the thickness of the narrow portion. The sample was held tight by the two grips, the upper grip of which was fixed. The gauge length between the jaws at the start of each test was adjusted to 30 mm and the rate of separation of the power actuated upper grip was fixed at 500 mm/min for elastomeric specimens. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor. The modulus and tensile strength are reported in mega pascal (MPa) unit and elongation at break in percentage (%).

2.3.2 Tear strength

The tear strength of the samples was tested as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on a Shimadzu Universal Testing Machine (model-AG1). The speed of extension was 500 mm/min and the test temperature 28 ± 2 °C. The tear strength values are reported in Newton per millimeter (N/mm).

2.3.3 Hardness

The hardness of the moulded samples was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples of 12 mm diameter and minimum 6 mm thickness. A load of 12.5 Newton was applied and the readings were taken 10 seconds after the intender made a firm contact with the specimen. The mean value of three measurements is reported. The hardness values are reported in Shore A unit.

2.3.4 Compression set

The samples (6.5 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25 %) were kept 22 hours in an air oven at 70 °C. After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set (\%)} = \frac{(t_i - t_f)}{(t_i - t_s)} \times 100 \qquad (2.2)$$

where t_i and t_f are the initial and final thickness of the specimen respectively and t_s, thickness of the spacer bar used. The procedure used was ASTM D 395 (1982) method B.

2.3.5 Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader. Sample having a diameter of 15 mm and a length 20 mm was kept on a rotating sample holder and 10 Newton load was applied. Initially a pre-run was given for the sample and its weight was taken. The sample was then given a complete run and weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the weight of the test piece getting abraded away by its travel through 42 cm on a standard abrasive surface and expressed as weight loss in gram (g).

2.3.6 Thermal and Steam ageing studies

Dumbbell and angular test specimens for the evaluation of physical properties were prepared and kept in a multi cell ageing oven at 100 °C temperature for specified periods viz. 24, 48 and 72 hours. After taking out from the oven, the samples were conditioned at 28 ± 2 °C and 50 % relative humidity for 24 hours. After conditioning physical properties like tensile strength, tear strength, elongation at break etc. were measured. The percentage retention of these properties was evaluated for assessing the ageing resistance. The procedure given in ASTM D 573 was followed.

Steam ageing is also done at a steam temperature of 160 °C for 6, 18 and 36 hours. After taking out from the steam chamber, the samples were conditioned at 28 ± 2 °C and 50 % relative humidity for 24 hours and various properties were tested.

2.3.7 Rebound resilience

The rebound resilience of the samples was tested as per ASTM D 1054 (1979) using Scott Rebound Pendulum. This test is used for the determination of impact resilience of solid rubber from measurement of vertical rebound of a dropped mass. Resilience is determined as the ratio of rebound height to drop height of a metal plunger of prescribed weight and shape, which is allowed to fall on the rubber specimen. Resilience is a function of both dynamic modulus and internal friction of rubber. The test specimen should have a thickness of 12.5 mm and the standard temperature is 23 ± 2 °C. Resilience is tested as follows. The instrument is leveled and the plunger is raised to the top of the guide rod. The resilience scale is positioned so that its full weight rests upon the specimen. It is locked in that position. The plunger is then released making sure that it slides freely on its guide. The first three values are avoided. Recorded the next three values. Since the resilience scale is divided into 100 parts, the rebound height is equal to the resilience in percentage.

2.3.8 Tension set

Tension set properties of the elastomer blends were determined using dumbbell specimens. Samples were punched out from the compression moulded sheets along the mill direction using a dumbbell die. The sample was held tight by the two grips, the left grip of which was fixed. The specimens were stretched to 300 % by moving the right grip and clamped. The entire arrangement was kept in a multi cell ageing oven at 100 °C temperature for specified periods viz. 24, 48 and 72 hours. After taking out from the oven, the samples were conditioned at 28 ± 2 °C and 50 % relative humidity for 24 hours. After conditioning, the final length was measured. The tension set was calculated as follows

$$\text{Tension Set (\%)} = \frac{(Final\ length - Initial\ length)}{Initial\ length} \times 100 \qquad (2.3)$$

2.3.9 Flex crack resistance

Resistance to flex crack of the vulcanizates was measured using De-Mattia flexing machine as per ASTM D 430 (1973) test method. The machine operated at a constant speed under load at 300 ± 1 flexing cycles per minute. The sample was 6" long, 1" wide and 0.25" thick with a groove moulded across the width with grain direction perpendicular to the length of the specimen. The samples were held in a special jig and a chisel cut was being applied exactly at the center of the groove by a piercing tool of 2 mm width. The flexing is such that the specimen is bent almost double at the groove then straightened out without extension. Crack growth is measured at regular intervals with the point being the number of cycles required to extend the crack to 20 mm. The test was conducted at room temperature and was reported as the increment in cut length in millimeter.

2.3.10 Air permeability

The instrument consists of a gas cell divided into two chambers by the membrane to be tested. The gas under test is admitted at known pressure from one side. The permeability can be studied either by measuring the pressure decrease at the high pressure side or the pressure increase at the low pressure side. A highly sensitive heat conductivity cell with temperature compensation of the signal to standard conditions, a chart recorder, a water cooling/heating thermostat for maintaining constant temperature in the measuring chamber and a rotatory two stage vacuum pump are the remaining portions of the measuring instrument. Permeability measurements were carried out according to ASTM D 1434 (1982). Test specimens of thickness 0.25 mm were moulded and used for measurements. The equipment used was Lyssy Manometric Gas Permeability Tester L 100-2402.

The prepared film was used to divide the cell of the apparatus into two chambers and air at a flow rate of 500 ml/min was admitted from the upper compartment. The lower compartment was connected to a suction pump through a capillary

U tube. The conditioning of the test specimen for a definite period is calculated from the equation

$$T = b^2 / 2D \qquad (2.4)$$

where b is the thickness of test piece in meter and D, the diffusion coefficient in meter square per second. The preconditioning times will vary from few minutes to several hours and even days depending on the type of the sample. In practice the preconditioning time is the time taken for attaining 10^{-4} torr pressure in the lower compartment. Then mercury is poured into the capillary to a fixed mark. The level of mercury in the capillary steadily decreases as air permeates through the membrane. This change is recorded in a chart moving at a speed of 180 cm/hour. From the distance traveled by the pointer in the chart, the time taken for the permeance of the sample (t_s) is determined. Permeability of the sample is then calculated by substituting the time taken by the standard PET sample (t_r) in the above chamber and under similar conditions using the equation;

$$\text{Permeability of the sample,} \quad P_m = \frac{t_r \times P_r}{t_m} \qquad (2.5)$$

where P_r is the permeability of the standard PET sample. If air is used the value of P_r is 30 ml/m^2.day.

2.3.11 Thermal diffusivity

Photo thermal deflection (PTD) technique is defined as the field in which the thermal diffusivity of the material is probed using optical excitation of the material and optical probing of thermal energy, which results from this excitation. It is a non-destructive technique that can be used for any kind of sample. The photothermal method has a number of merits compared with other conventional techniques for thermal diffusivity measurement using thermocouple or thermistor. It is highly sensitive and absolute calibration is readily available i.e.; the observed temperature rise can be directly measured and related to physical parameters like thermal diffusivity. It is applicable to different types of materials (gas, liquid, liquid crystal and solid), transparent and opaque. It can be used in vacuum and in air, and with samples of arbitrary shape.[2-4] Radiation of any wavelength can be used (radio frequency, microwave, IR, visible, UV, X-ray, etc.). Thermal diffusivity (D) of the material is directly proportional to its thermal conductivity (k) and are related as $D = k/\rho C$ where ρ is the density of the material and C is the specific heat capacity.[5]

Photo thermal deflection technique depends on the detection of variations in the infrared thermal radiation emitted from a sample that is excited by an electromagnetic pump beam of varying intensity or wavelength[6]. A laser beam (pump beam) passes through the material of interest. The material absorbs the laser energy and in the presence of quenching collisions, some of this energy appears in the translational or lattice modes (heating) of the molecules of the material. The change in the refractive index of the medium in a thin layer adjacent to the sample surface, which is produced as a result of heat emission from the sample, is detected by a second laser beam (probe beam) passing perpendicular to the pump beam axis.[7-9] Here the refractive index change is measured directly by placing the sample in a Fabry-Perot cavity. The refractive index change produces a change in the optical path length, which is detected as a fringe shift.

The main components of photo thermal deflection technique are:[10]

(1) Pump beam, which produces the refractive index change in the sample. The excitation source should be a light source with sufficient power density to produce the refractive index change. Here, He-Ne laser of wavelength 6320 A° with output power 10 mW is used.

(2) Mechanical chopper, which modulates the pump beam. A variable frequency chopper, which can be used in the range 0-4 kHz is used for the purpose. The chopped light beam must be focused upon the sample.

(3) A probe laser beam to detect the refractive index change. A weak source must be used as the probe beam because it should not cause any heating in the sample. In the present case a He-Ne laser of power 1 mW is used as the probe beam. The probe beam is arranged so that it just grazes through the sample surface, perpendicular to the pump beam axis. Using a convex lens such that its focal spot is at the point where the pump beam is incident on the sample, the signal amplitude can be considerably increased.

(4) A closed sample cell, which can be rotated for correct alignment and is usually made of materials like quartz, so that the probe beam after passing through the cell is not absorbed or scattered by the cell wall. By placing the sample in the cell the noise due to room vibrations can be reduced to a considerable extent. The cell is placed at an exact position so that the pump and the probe beams fall at the correct position.

(5) A detector assembly and the associated electronics to measure the deflection of the signal. The probe beam passing through the region of varying index of refraction gets deflected and is detected using a position sensor. A bicell detector is used for the purpose. There are two photodiodes, which acts as the position sensors. The position sensor converts deflection into a varying output voltage depending upon the deflection of the beam. The output of the sensor is fed into a lock in amplifier, which extract the signal. The output of the lock in amplifier can be recorded on an x-y recorder. All the above optical components are placed on an optical bread board placed on a vibration free table. The alignment is made carefully and the detection is done.

The thermal diffusivity of the material is determined at a low frequency region, between 2.5 Hz to 20 Hz using the equation,[11]

$$ln\left|\frac{\partial n}{\partial x}\right| = \text{constant} - \frac{x\sqrt{\omega}}{\sqrt{2}\,D} \qquad (2.6)$$

where $\partial n/\partial x$ is the time dependent deflection of a narrow probe beam propagating through a non-homogeneous medium of refractive index n and temperature T. This term is recorded by the detector as the amplitude signal. Through out the experiment, the value of x remains the same as it represents the distance between the probe source and the sample. ω is the chopping frequency and D, the thermal diffusivity. By measuring the slope of the graph plotted between logarithms of amplitude against square root of frequency, the thermal diffusivity of the material can be calculated.

2.3.12 Differential scanning calorimeter

Direct calorimetric measurements, characterization and analysis of thermal properties of the samples were made using a Differential Scanning Calorimeter (DSC Q 100, TA instruments). About 20 mg of samples were used for the studies. Samples were encapsulated in standard aluminium pans and sealed by crimping. For purging the sample holders, pure dry nitrogen gas was used. The inlet gas pressure was adjusted at 2 kg/cm^2 to attain a flow rate of about 25 ml/min. Sub-ambient operation was carried out by cooling the specimen and the specimen holder with liquid nitrogen. Samples were cooled to -80 °C, maintained at that temperature for 10 minutes and then heated at a constant rate of 10 °C/min in nitrogen atmosphere.

2.3.13 Dynamic mechanical properties

The dynamic mechanical properties of EPDM/CIIR blends were measured using a Dynamic Mechanical Analyzer (DMA Q-800, TA Instruments), which consist of a temperature programmer and a controller. It measures dynamic modulii (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 1 Hz. Liquid nitrogen was used to achieve subambient temperature and a programmed heating rate of 3 °C min^{-1} was used. Mechanical loss factor, tan δ and the dynamic moduli (E'and E") were calculated using a microcomputer. Moulded samples of dimension 20 × 4 × 2 mm were prepared for testing. The complex modulus E* was calculated using the following equation:

$$E^* = \frac{(L+\Delta L)}{8\times S\times A_f\,(D_v - K)}\times 10^{12} \qquad (2.7)$$

where L = length of the sample between the clamps, ΔL = oscillating displacement, S = cross-sectional area of the sample, A_f = amplitude factor, D_v = values of dynamic force dial and K = error constant.

The storage modulus E' and loss modulus E" were calculated using the following equations:

$$E' = E^* \sin\delta \text{ and} \qquad (2.8)$$

$$E'' = E^* \cos\delta \qquad (2.9)$$

where δ = loss angle.

$$\text{Loss tangent, } \tan\delta = E''/E' \qquad (2.10)$$

indicates the damping characteristics of the material.

2.3.14 Thermogravimetric analysis

The thermogravimetric analyzer used for the studies was TGA Q-50 (TA Instruments). 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 has two components, an ultra sensitive microbalance and a furnace element. The balance is sensitive to 0.1 microgram and the furnace could be heated from ambient to 800 °C at rates of 0.1 to 200 °C per minute. For purging platinum the sample holder, nitrogen gas is used 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.

2.3.15 Rheological measurements

2.3.15.1 Equipment details

The rheological measurements were carried out using a capillary rheometer MCR 3210 attached to the Shimadzu Universal Testing Machine (model-AG1). The extrusion assembly consists of a barrel, made of hardened steel, mounted on a special support underneath the moving crosshead of the UTM. The capillary made of tungsten carbide material is inserted at the bottom of the barrel and locked using a clamping unit. The material is fed in the barrel and is carried to the capillary by a hardened steel plunger which is accurately ground to fit inside the barrel. The plunger is driven by the movement of the cross-head of the UTM and is held to the load cell extension with the help of a latch assembly. The barrel is mounted on a ball and socket system on the support so that the system will be self-aligning. The leakage of the material through the clearance between the barrel inner wall and the plunger is prevented by inserting a Teflon O-ring and a split ring on the plunger. Two identical Teflon rings are used in the capillary to prevent the leakage of the material through the gap between the barrel and the capillary. The barrel was heated electrically using a three zone temperature control system. The difference between the successive temperature zones in the barrel was kept at 5 °C and the temperature of the lower zone, where the capillary is located, is taken as the test temperature.

The moving cross-head of the UTM runs the plunger at a constant speed irrespective of the load on the material, maintaining a constant volumetric flow rate through the capillary. Using the UTM machine, the cross-head speed can be varied from 1 mm min^{-1} to 500 mm min^{-1}, giving a shear rate of 10 sec^{-1} to 5010 sec^{-1} for a capillary of length to diameter ratio 40 ($I_c = 2.0066 \pm 0.0001$ inch and $d_c = 0.0495 \pm 0.005$ inch) with 90° conical entry. Force corresponding to specific plunger speed was recorded on a strip chart recorder and the shear stress was calculated from the knowledge of capillary dimensions.

2.3.15.2 Test procedure

The whole capillary assembly was first heated to the desired temperature. The sample was placed inside the barrel and forced down to the capillary using the plunger attached to the moving cross-head. The samples were preheated to attain uniform temperature. The volume of the sample for each run was maintained constant. The machine was programmed to give six to nine different plunger speeds, with a single charge of the material. Each plunger speed was continued until the recorded force stabilized, before changing to the next speed. Force corresponding to the specific plunger speeds was recorded. Considering the geometry of the capillary and the plunger, the force and the cross-head speed were converted into shear stress (τ_w) and shear rate (γ_w) at the wall by using the following equations:[12]

$$\tau_w = \frac{F}{4\,A_p\,(\,I_c\,/\,d_c\,)} \qquad (2.11)$$

$$\gamma_w = \left(\frac{3n'+1}{4n'}\right)\frac{32q}{\pi d_c^3} \qquad (2.12)$$

where,

F = force applied at a particular shear rate.

A_p= cross sectional area of the plunger

I_c = length of the capillary

d_c = diameter of the capillary

n' = flow behaviour index, as defined in equation 2.4

q = volumetric flow rate = A_p x velocity of plunger.

The flow behaviour index n' was calculated by using the equation:

$$n' = \frac{d(\log \tau_w)}{d(\log \gamma_{w,a})} \qquad (2.13)$$

n' was determined by the regression analysis of the values of τ_w and $\gamma_{w,a}$, obtained from the experimental data. $\gamma_{w,a}$ is the apparent shear rate at wall and was calculated from the relation

$$\gamma_{w,a} = \frac{32\,q}{\pi\, d_c^3} \qquad (2.14)$$

The shear viscosity η was calculated from τ_w and γ_w by using the equation:

$$\eta = \frac{\tau_w}{\gamma_w} \qquad (2.15)$$

The Bagley correction for the entry losses is assumed to be negligible for the capillary used ($l_c/d_c = 40$ with 90° conical entry).[13] The temperatures of testing were 90 °C, 100 °C, 110 °C and 120 °C. The following assumptions were made for the analysis of the data:

a) The flow of the material was parallel to the axis

b) The viscosity of any fluid element was a function of radius only, giving axial symmetry

c) The fluid was incompressible

d) The fluid velocity was zero at the wall. i.e., there was no slip at the wall

e) All energy was consumed within the capillary and the flow was isothermal.

2.3.15.3 Measurement of extrudate die swell

The extrudate was collected for measurement of die-swell, taking care to avoid any further deformation. The diameter of the extrudate (d_e) was measured after 48 hrs of extrusion. For measuring the diameter of an extrudate, a fixed length of the most uniform portion of the extrudate was cut and its weight was taken as accurate as possible. By measurement of the density of the sample, the diameter was calculated using the following relations:

$$\text{Volume of the extrudate } (V_e) = \frac{\pi d_c^2 . l_e}{4} \tag{2.16}$$

$$\text{Density } (D_e) = \frac{M_e}{V_e} = M_e \Big/ \frac{\pi d_e^2 . l_e}{4} \tag{2.17}$$

$$\text{Diameter of the extrudate, } d_e = (4\, M_e \,/\, \pi\, l_e\, D_e)\ ½ \tag{2.18}$$

where l_e and M_e are length and mass of the extrudate respectively. At least three readings were taken for each extrudate diameter. The extrudate swelling index (die-swell) was determined by using the following relation:

$$\text{Extrudate swelling index} = \frac{\text{diameter of the extrudate } (d_e)}{\text{diameter of the capillary } (d_c)} \tag{2.19}$$

2.3.16 Scanning electron microscope

Scanning electron microscope (SEM) was used to investigate the morphology of fractured surfaces.[14,15] In SEM, electrons from an emission source or filament are accelerated by voltage usually in the range of 1 to 30 kV and are directed down to the centre of an electron optical column consisting of two or three magnetic lenses. These lenses cause a fine electron beam to be focused on to the specimen surface. Scanning coils placed before the final lens cause the electron spot to be scanned across the specimen surface in the form of a square raster, similar to that of a television screen. The current passing through the scanning coils is made to pass through the corresponding deflection coils of a cathode ray tube, so as to produce a similar but larger raster on the viewing screen in a synchronous manner.

The electron beam incident on the specimen surface causes various phenomena, of which the emission of secondary electrons is used in SEM. The emitted electrons strike the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. The time for the emission and collection of the secondary electrons is negligibly small compared with the time for the scanning of the incident electron beams across the specimen surface. Hence, there is one to one correspondence between the number of secondary electrons collected from any particular point of the specimen surface and the brightness of the analogous point on the screen and thus an image of the surface is progressively built up on the screen. In SEM, the large image magnification is determined by the ratio of the size of the rasters on the screen and on the specimen surface. In order to increase the magnification, it is only necessary to reduce the current in the SEM scanning coils.

The SEM observations reported in the present investigation were made using a JEOL JSM 35C model scanning electron microscope. The fractured surfaces of the tensile samples were carefully cut out without disturbing the surface. Care was taken to keep the samples in dust and moisture free atmosphere. The surfaces were then sputter coated with gold within 24 hours of testing. The gold-coated samples were kept in desiccators before the SEM observations were made.[16] The acceleration voltage used for image acquisition was 15 kV. The operation conditions of SEM are given in table 2.3.

Table 2.3 Operation conditions of SEM

Specimen position tilt, degree	0
Maximum resolution, nm	0.5
Spot size, angstrom	640
Emission current, ampere	26
Aperature, microns	200
Depth of focus	High

2.4 Chemical test methods

2.4.1 Determination of iodine value

0.2 gm of sample was dissolved in 25 ml chloroform in a 500 ml conical flask. 20 ml of 0.1 N solution of iodine monochloride in glacial acetic acid was added. It was then stoppered and allowed to stand in darkness for 30 minutes. After that 100 ml 10 % potassium iodide solution was added. The resultant solution was titrated against thiosulphate using starch as indicator. Iodine value was calculated as;

$$\text{Iodine value} = \frac{(V_1 - V_2) \times 12.69 \times n}{m} \qquad (2.20)$$

where n = normality of thiosulphate, m = weight of polymer sample, V_1 and V_2 = volume of thiosulphate for the sample and blank.

2.4.2 Determination of chemical crosslink density

The concentration of chemical crosslink was estimated from the equilibrium swelling data as follows. Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.20 g weight were punched out from the vulcanizate and allowed to swell in toluene. The swollen sample was taken out of the solvent after 24 hours and weighed. Solvent was then removed in vacuum and the sample weighed again.

The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding[17,18] from the following equation:

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}} \qquad (2.21)$$

where T is the initial weight of the test specimen, D, the deswollen weight of the test specimen, F, the weight fraction of insoluble components and A_0, the weight of the absorbed solvent corrected for the swelling increment. ρ_r and ρ_s represents the density of rubber and solvent respectively. The densities of EPDM and CIIR obtained were 0.856 g/cm^3 and 0.917 g/cm^3 respectively and that of toluene was 0.886 g/cm^3. Densities of the blends were calculated by taking into consideration the weight fraction of each component and the density of that component.

In the case of vulcanizate containing HAF black, the values of V_r obtained as above, were converted into V_{r0} (the value of V_r in the absence of black) by means of the following equation which was derived by Porter:[19]

$$V_{r0} / V_r = 0.56\, e^{-Z} + 0.44 \qquad (2.22)$$

where z = weight fraction of filler.

The crosslink density (1/2 M_C) was then determined from V_{r0} using the Flory-Rehner equation:[20]

$$\frac{1}{2}Mc = \frac{-\left[\ln(1 - V_{ro} + V_{ro} + \chi V_{ro}^2)\right]}{2\rho_r V_s (V_{ro})^{1/3}} \qquad (2.23)$$

where V_s = molar volume of solvent. For toluene the value is 106.2 cm^3/mol and χ is the parameter characteristic of interaction between rubber and solvent which is given by Hildebrand equation as:[21]

$$\chi = \frac{\beta + V_s(\delta_s - \delta_p)^2}{RT} \qquad (2.24)$$

where β = lattice constant, R = universal gas constant, T = absolute temperature, δ_s = solubility parameter of solvent and δ_p = solubility parameter of polymer. Values of interaction parameters taken for calculations[22,23] were the following: For CIIR-toluene = 0.568, EPDM-toluene = 0.490.

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Chapter III

Compatibility Studies on EPDM/CIIR Blends

3.1 Introduction

Blending two or more elastomers is carried out for specific objectives such as enhancement of technical properties, improvement of ageing resistance and also processing characteristics. In the case of miscible blends, the overall physico-mechanical properties depend 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. Unfortunately, this is not the case for most polymer blends in which the components are found to be immiscible and incompatible resulting in poor mechanical properties.[1-6] Several attempts have been made to minimize phase separation and increase interfacial adhesion. These include addition of a compatibilising agent such as a third polymer, which is, a graft or block copolymer that reduces the interfacial tension between the two phases thereby developing satisfactory network structure in each of the phases and in the interphase.[7-13] Consequently, compatibility is a fundamental property in polymer blends, deciding their practical utility.

The main objective of this part of the work is to explore the compatibility of blends of EPDM with CIIR without any compatibilisers. Four commercial grades of ethylene-propylene-diene rubber (EPDM) are proposed to be blended with a specific grade of chlorobutyl (CIIR) at various proportions. The cure characteristics and mechanical properties such as tensile strength, tear strength and ageing resistance of the blends are planned to be studied for all the four grades of EPDM blended with CIIR at various compositions. 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. In addition to the above mentioned physical property measurements, the extent of compatibility of these rubber blends is also proposed to be studied with different methods, such as glass transition measurements using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analyzer (DMA).[14] The determination of glass transition temperature of elastomer blends has been widely used to assess compatibility, since individual thermal responses are expected from each component in heterogeneous blends. The morphological characterization of the blends is proposed to be studied using scanning electron microscopy (SEM).[15-17] Due to differences in viscosity and unsaturation between EPDM and CIIR, the amount of curatives may not be optimum in the two rubbers resulting in inferior mechanical properties.[18-21] It is now well established that the phase morphology of immiscible polymer blends can be controlled by the addition of compatibilisers.[22-25] The effect of chlorosulfonated polyethylene (CSPE) as a compatibiliser in EPDM/CIIR blends is also proposed to be investigated.

3.2 Experimental

The four different grades of EPDM selected for the study are 301-T, EP-96, MRD-10 and NDR-4640. The specifications of these four different grades of EPDM are given in table 2.1 and those of CIIR in table 2.2. Firstly, EPDM was thoroughly masticated on a laboratory size two-roll mixing mill at a friction ratio of 1:1.25 and was blended with CIIR at different compositions. The blends were compounded according to ASTM-D 3182 (1982) as per formulations given in table 3.1. The samples were kept overnight for maturation.

Table 3.1 Compounding recipe

Ingredients	Concentration (phr)
EPDM Rubber	100
ZnO	4.0
Stearic acid	1.5
MBT	1.0
TMTD	0.5
ZDC	0.5
Carbon black	40
Paraffinic oil	7.0
Sulphur	1.0
Antioxidant	1.0

Ingredients	Concentration (phr)
CIIR Rubber	100
ZnO	4.0
Stearic acid	1.5
CBS	1.0
Carbon black	40
Paraffinic oil	5.0
Sulphur	1.5
Antioxidant	1.0

Cure characteristics have been investigated using Rubber Process Analyzer (RPA 2000, Alpha Technologies). The optimum cure time of the samples was determined at 170 °C at a frequency of 50.0 cpm and a strain of 0.20 degree. The compounds were vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 170 °C. Dumb bell shaped tensile specimens and angular tear specimens were punched out from the vulcanized sheets and the mechanical properties were studied using a Shimadzu Universal Testing Machine (model- AG1). Ageing resistance of the samples was studied by keeping the tensile and tear specimens at 100 °C for 24, 48 and 72 hours in a multicell air oven and then measuring the retention in these properties. The glass transition temperatures of the pure elastomers and the blends were determined by DSC and DMA. Samples for DMA were cut from the compression moulded sheet with a size of 20 × 4 × 2 mm, and the measurements were conducted on a Dynamic Mechanical Analyzer (DMA Q-800, TA Instruments) at a heating rate of 3 °C min^{-1} and a frequency of 1 Hz. The thermal analysis measurements with Differential Scanning Calorimeter were carried out using DSC Q-100, TA Instruments.

Samples with a weight of about 20 mg were sealed in aluminum pans, equilibrated at -80 °C, and then heated at a constant rate of 10 °C/min in nitrogen atmosphere to 20 °C. This allowed the identification of the glass transition temperatures (T_g's) of CIIR, EPDM and their blends.

The microstructure of tensile fracture surfaces of the blends at varying compositions were studied using a Scanning Electron Microscope (JEOL JSM 35C). The fracture surfaces of the test specimens were carefully cut from the test pieces and were then sputter coated with gold before they were examined through the SEM. The acceleration voltage used for image acquisition was 15 kV.

To improve the properties of blends of EP-96 and MRD-10 grades of EPDM with CIIR, chlorosulfonated polyethylene (CSPE) was added at varying amounts as compatibiliser. The compatibilisation effect was studied based on the improvement in mechanical properties (such as tensile strength, tear strength, ageing resistance) as well as surface morphology.

3.3 Results and discussion

3.3.1 Cure characteristics

The cure characteristics of the blends are given in table 3.2. The optimum cure time of blends of 301-T and NDR-4640 with CIIR increases as the EPDM content of the blend increases. But beyond 60 % EPDM in the blend, the trend reverses. This may be due to the unequal distribution of ingredients in the blend components.[26,27] In the blends containing upto 60 % EPDM, it can be assumed that preferential curative migration occurs to the EPDM phase, so that the formation of greater number of interface crosslinks gets prolonged. As the EPDM content increases further, it forms the continuous phase and the effect of preferential migration is not so significant.[28,29] The homogeneous distribution of curatives enhances the extent of crosslinking thereby causing a decrease in optimum cure time. For blends of EP-96 and MRD-10 grades of EPDM with CIIR there is no regular variation in optimum cure time which itself indicates the inhomogenity in these blends.

Table 3.2 Cure characteristics of EPDM/CIIR blends

Elastomer specification	Blend percentage of EPDM	Cure time (min)	Scorch time (min)	Maximum torque (Nm)	Minimum torque (Nm)
EPDM-NDR 4640	20	11.6	1.2	0.324	0.0386
	40	14.4	1.3	0.329	0.0394
	60	15.6	1.3	0.332	0.0386
	80	12.4	1.2	0.327	0.0412
	100	10.2	1.2	0.334	0.0412
EPDM-EP 96	20	9.8	1.0	0.293	0.0384
	40	9.1	1.0	0.287	0.0453
	60	11.6	1.2	0.307	0.0333
	80	12.4	1.4	0.287	0.0387
	100	8.6	1.1	0.286	0.0365
EPDM-MRD 10	20	13.4	1.4	0.336	0.0352
	40	12.9	1.1	0.317	0.0452
	60	16.9	1.4	0.333	0.0463
	80	15.2	1.5	0.325	0.0332
	100	18.1	1.7	0.339	0.0312
EPDM - 301 T	20	12.2	1.0	0.339	0.0420
	40	14.6	1.3	0.302	0.0361
	60	18.8	1.4	0.335	0.0337
	80	13.0	1.2	0.324	0.0376
	100	11.0	1.2	0.346	0.0413
CIIR	0	11.8	1.2	0.349	0.0460

3.3.2 Mechanical properties

Figure 3.1 shows the variation in tensile strength of the blends of different grades of EPDM with CIIR at various proportions. It is evident that the tensile strength under unaged conditions shows a synergistic behaviour for the grade NDR-4640 and an additive behaviour for 301-T. Hence these two grades of EPDM may be considered as compatible with CIIR as it is known that compatible systems exhibit tensile strengths as a function of blend composition that are at least a weighted average of the values corresponding to the two components.[30,31] Better co-curing might be taking place in the case of NDR-4640/CIIR blends as the viscosity of NDR-4640 is comparable with CIIR (table 2.1 and 2.2) leading to better molecular packing and resulting in synergistic behaviour of mechanical properties.[32] The viscosity of 301-T is slightly lower than that of CIIR so that a perfect co-vulcanization probably is not taking place, which results only in an additive behaviour in mechanical properties. For the remaining two different grades (EP-96 and MRD-10), the tensile properties show non-uniformity with respect to composition or in other words a non-additive behaviour is observed. Hence these are considered as incompatible with CIIR.[33,34] Since both EPDM and CIIR are non-polar rubbers, the main reason for the incompatibility of these grades might be the viscosity mismatch, which results in curative migration, so that co-curing of the two phases of the blend is not taking place. Based upon these observations, it is possible to correlate tensile strength versus composition plots with blend homogeneity.

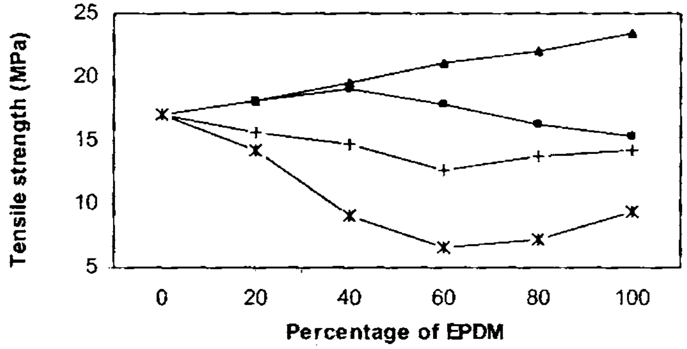


Figure 3.1 Variation of tensile strength of EPDM/CIIR blends with percentage of different grades of EPDM. ▲, 301-T/CIIR, ■, NDR-4640/CIIR, ж, MRD-10/CIIR and +, EP-96/CIIR

Figure 3.2 shows the variation of tear strength of the blends of different grades of EPDM with CIIR at various proportions under unaged conditions. It is evident that tear resistance is the maximum for blends of CIIR with 301-T and NDR-4640. This also confirms a rather increased compatibility between the two phases of the blends of these two grades. For the EPDM grades, EP-96 and MRD-10, a gradual variation in tear properties is not observed indicating their non-compatibility with CIIR.

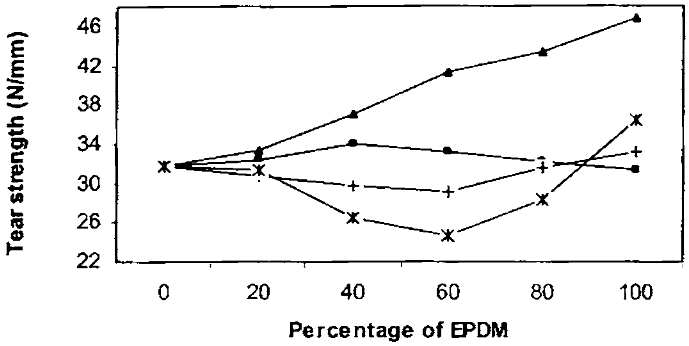


Figure 3.2 Variation of tear strength of EPDM/CIIR blends with percentage of different grades of EPDM. ▲, 301-T/CIIR, ■, NDR-4640/CIIR, ✱, MRD-10/CIIR and +, EP-96/CIIR

Figure 3.3 is a plot of tensile strength against the composition of blends of different grades of EPDM with CIIR after ageing the samples at 100 °C for 24 hours. As expected, the ageing resistance is found to be superior for blends containing higher percentage of EPDM. For blends of NDR-4640, it seems to have inferior ageing properties even though it shows synergistic behaviour in mechanical properties under unaged conditions. Better ageing resistance is observed for blends of 301-T, since it is a highly saturated rubber when compared with the other grades of EPDM (table 2.1). For the rest of the blends of two grades of EPDM (EP-96 and MRD-10), poor ageing resistance is observed. A similar effect in tear strength is also observed after ageing the samples at 100 °C for 24 hours. The results are given in figure 3.4.

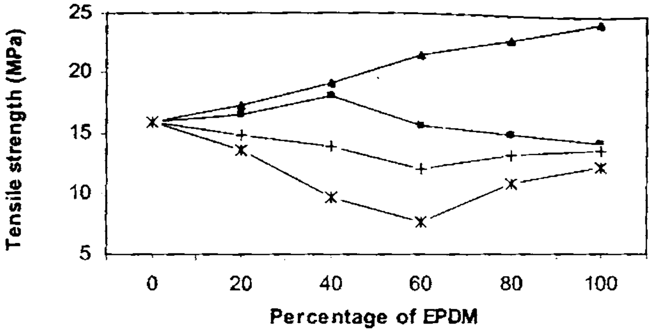


Figure 3.3 Variation of tensile strength of EPDM/CIIR blends with percentage of different grades of EPDM under aged conditions ▲, 301-T/CIIR, ■, NDR-4640/CIIR, ⋇, MRD-10/CIIR and +, EP-96/CIIR

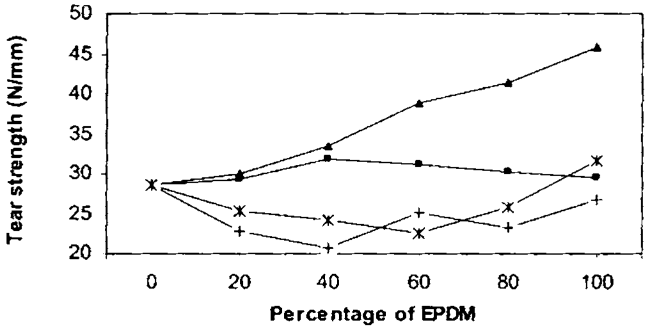


Figure 3.4 Variation of tear strength of EPDM/CIIR blends with percentage of different grades of EPDM under aged conditions ▲, 301-T/CIIR, ■, NDR-4640/CIIR, ⋇, MRD-10/CIIR and +, EP-96/CIIR

3.3.3 Thermal analysis

Figure 3.5 shows DSC thermograms for CIIR and four grades of EPDM and figure 3.6 shows the DSC thermograms of their 50/50 blends. For all the 50/50 CIIR/EPDM blends, there is only single T_g indicating molecular level homogeneity. Although the occurrence of a single T_g may be a definitive test of blend compatibility, there are certain circumstances under which the T_g criterion may be inapplicable or misleading. One such criterion requires that the T_g's of the components be sufficiently displaced from each other so that resolution is possible. The resolution of T_g's of the components less than about 20 °C apart is poor.[35,36] For all the 50/50 CIIR/ EPDM blends, the difference between the component T_g's is less than 15° and therefore appear as a single transition irrespective of the fact that whether they are compatible or not. Also if there is significant amount of intermixing of both the components in the interfacial regions, the individual transitions are significantly reduced in intensity resulting in a single transition.[37,38] This may be due to the molecular migration from well defined phases into broad variable composition interfacial regions, whose detection, because of the broad dispersion of the transition, may not be evident. The glass transition temperatures obtained for the pure elastomers and their 50/50 blends are shown in table 3.3.

Table 3.3 T_g values of pure elastomers and their 50/50 blends

Elastomers	T_g (°C)	50/50 blends of EPDM/CIIR	T_g (°C)
CIIR	-61.84	301-T/CIIR	-58.87
301-T	-54.46	NDR-4640/CIIR	-56.97
NDR-4640	-49.44	EP-96/CIIR	-60.82
EP-96	-58.15	MRD-10/CIIR	-58.41
MRD-10	-54.41		

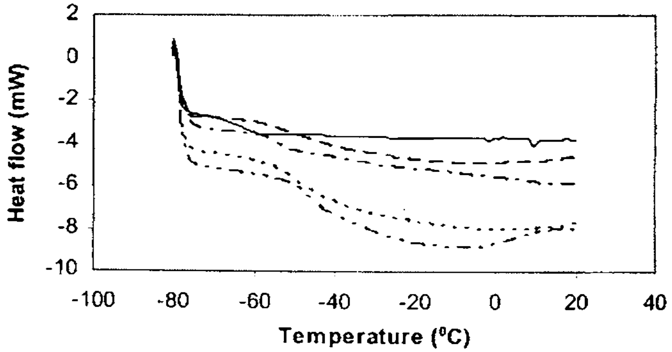


Figure 3.5 DSC plots of CIIR and various grades of EPDM. ———, CIIR; — — —, EP-96; — - — -, MRD-10; -------, 301-T; — -- — --, NDR-4640

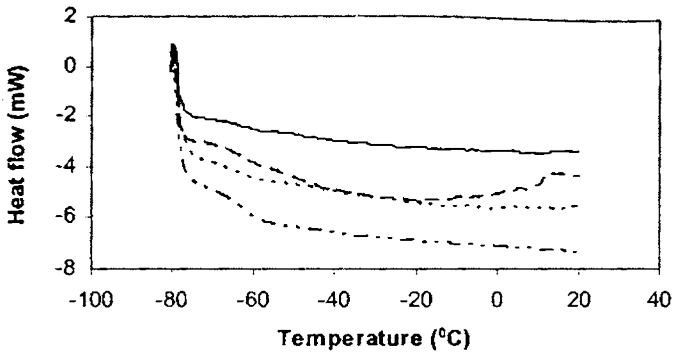


Figure 3.6 DSC plots for 50/50 blends of CIIR with various grades of EPDM. ———, 301-T/CIIR; — — —, NDR-4640/CIIR; ------, EP-96/CIIR; — -- — --, MRD-10/CIIR

Figures 3.7 and 3.8 shows the temperature dependence of the loss tangent (tan δ) at 1 Hz for EPDM, CIIR and their blends. The loss tangent (tan δ), which indicates the damping ability of the material, is the ratio of the mechanical dissipation energy to the storage energy. Thus, a high tan δ value is essential for good damping materials. CIIR shows a broad tan δ peak, in which the efficient damping (tan δ > 0.5) has a wide temperature range. But it should be noted that the effective damping range of CIIR is at relatively low temperature. The different values of tan δ maximum in CIIR/EPDM blends may be attributed to the dissimilar interactions between the chains of CIIR and EPDM molecules. As shown in the figures, the damping efficiency decreases with increase in EPDM content in the blends. The peak area under the tan δ - temperature curves, can be considered to be the damping index, which is a measure of the energy dissipation during a transition process.[39] These values are also higher for CIIR and decreases with decrease in the chlorobutyl content in the blends. In measurements of dynamic mechanical properties over a temperature range, the apperance of intermediate tan δ peaks and the concomitant decrease of the tan δ peaks of the individual polymers in a blend is a useful criterion of blend compatibility.[40] It can be seen from the figures that blending of EPDM with chlorobutyl causes a shift in the position of T_g. Further more; increasing the CIIR percentage in the blend gradually causes a corresponding continuous shift in the position of T_g and a change in the half peak width. The presence of single tan δ peak coupled with the intermediate tan δ value of the blends points towards the compatibility between EPDM and CIIR.[41] Similar observations are obtained with respect to storage modulus and loss modulus confirming compatibility between the two elastomers.

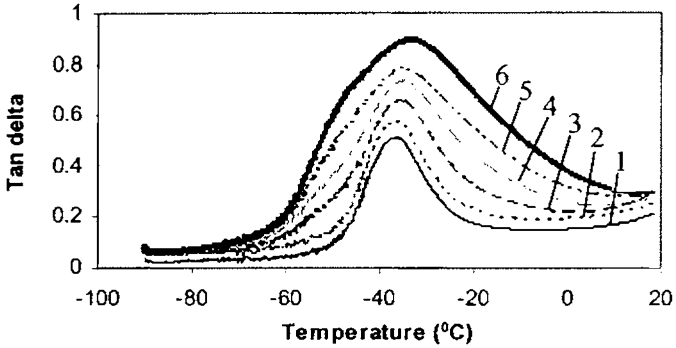


Figure 3.7 Variation of tan δ with temperature for CIIR, 301-T grade EPDM and their blends. EPDM/CIIR (1), 100/0; (2), 80/20; (3), 60/40; (4), 40/60; (5), 20/80; (6), 0/100

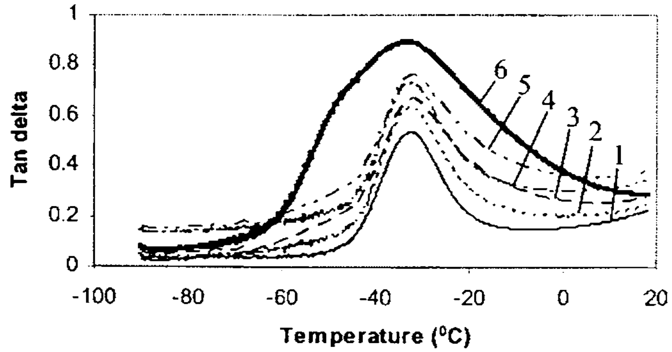
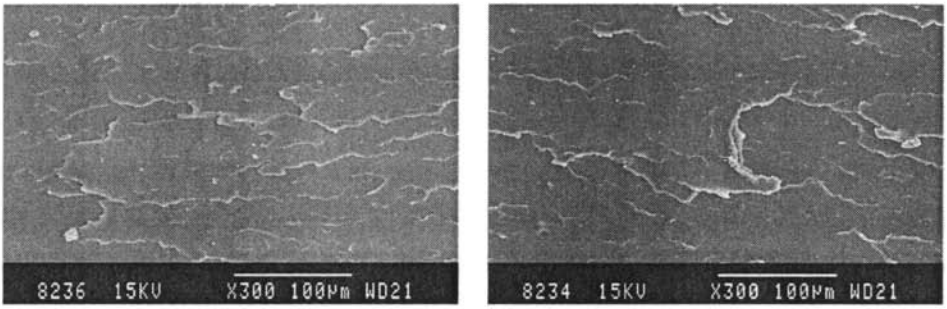


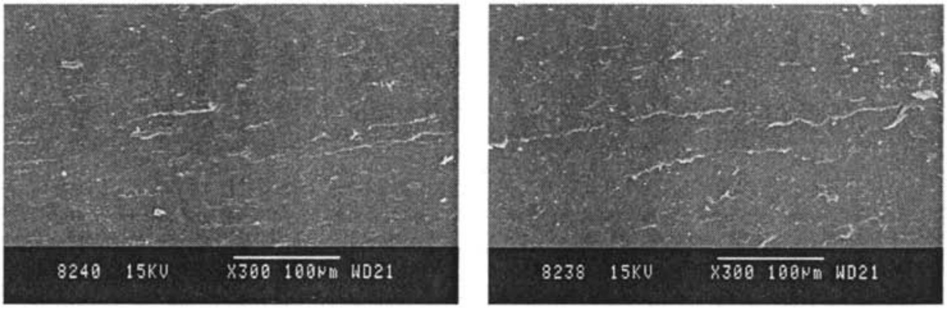
Figure 3.8 Variation of tan δ with temperature for blends of CIIR, NDR-4640 grade EPDM and their blends. EPDM/CIIR (1), 100/0; (2), 80/20; (3), 60/40; (4), 40/60; (5), 20/80; (6), 0/100

3.3.4 Morphological studies

Figures 3.9 – 3.12 show the SEM photographs of the fractured surfaces of blends of CIIR with various grades of EPDM. The fractured surfaces of 301-T and NDR-4640 show a more smooth and homogeneous pattern, justifying their higher tensile strength and other mechanical properties. The inspection of the micrographs of EP-96 and MRD-10 blends confirms two phases with irregular domain sizes and shapes. This means that these blends were completely immiscible, large EPDM domains being dispersed in CIIR matrix.

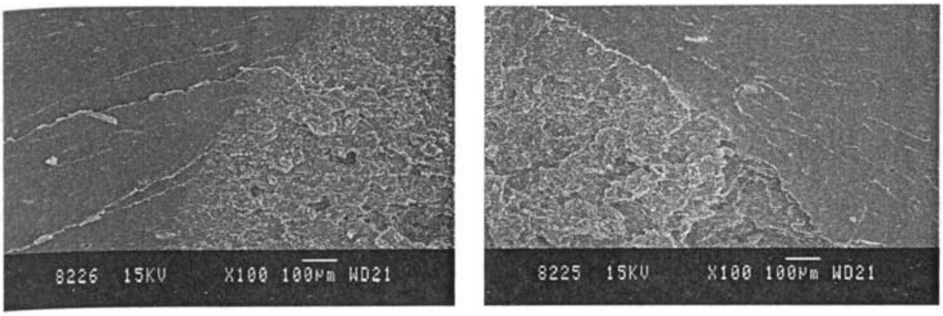


EPDM/CIIR-20/80 (a) EPDM/CIIR-40/60 (b)



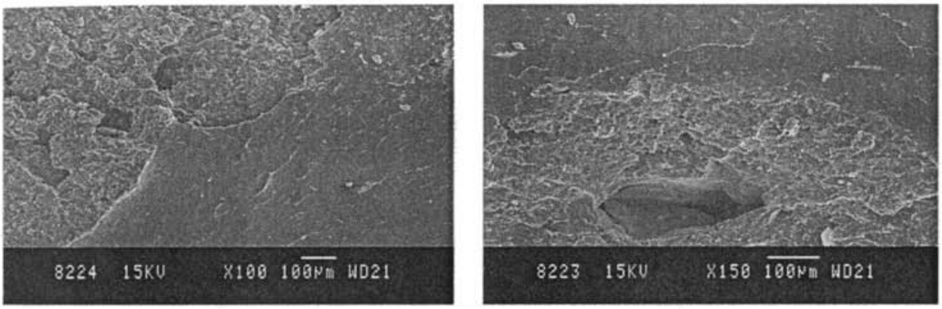
EPDM/CIIR-60/40 (c) EPDM/CIIR-80/20 (d)

Figure 3.9 [a-d] SEM photographs of 301-T grade EPDM/CIIR blends



EPDM/CIIR-20/80 (a)

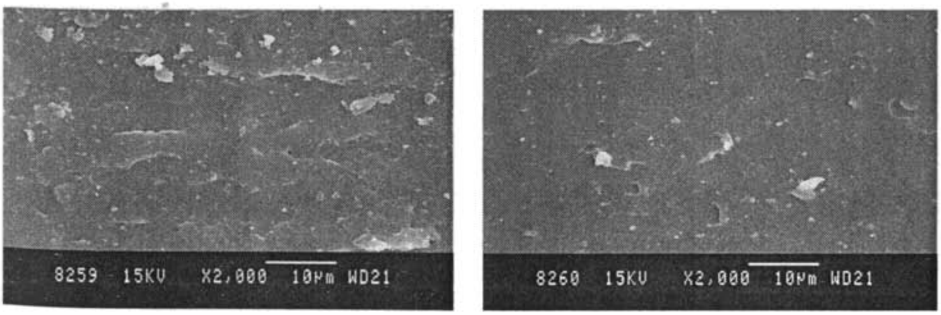
EPDM/CIIR-40/60 (b)



EPDM/CIIR-60/40 (c)

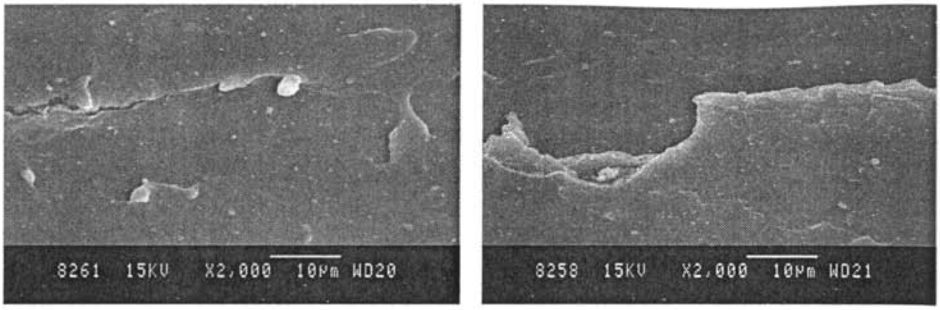
EPDM/CIIR-80/20 (d)

Figure 3.10 [a-d] SEM photographs of MRD-10 grade EPDM/CIIR blends



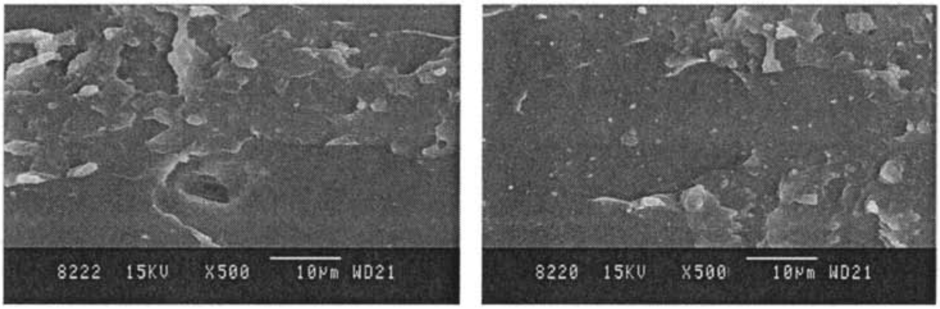
EPDM/CIIR-20/80 (a)

EPDM/CIIR-40/60 (b)

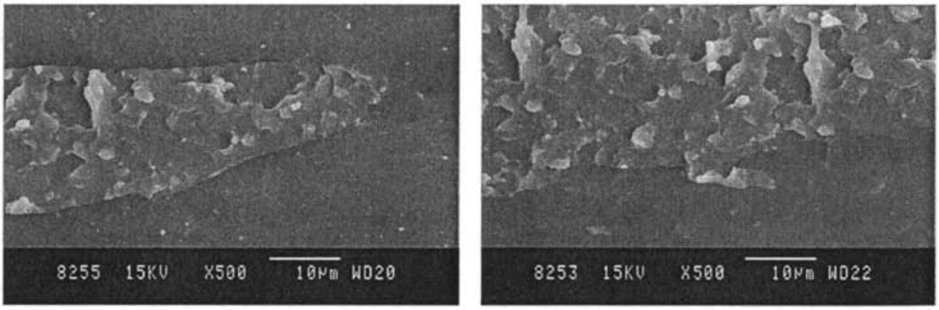


EPDM/CIIR-60/40 (c) EPDM/CIIR-80/20 (d)

Figure 3.11 [a-d] SEM photographs of NDR-4640 grade EPDM/CIIR blends



EPDM/CIIR-20/80 (a) EPDM/CIIR-40/60 (b)



EPDM/CIIR-60/40 (c) EPDM/CIIR-80/20 (d)

Figure 3.12 [a-d] SEM photographs of EP-96 grade EPDM/CIIR blends

3.3.5 Effect of compatibiliser

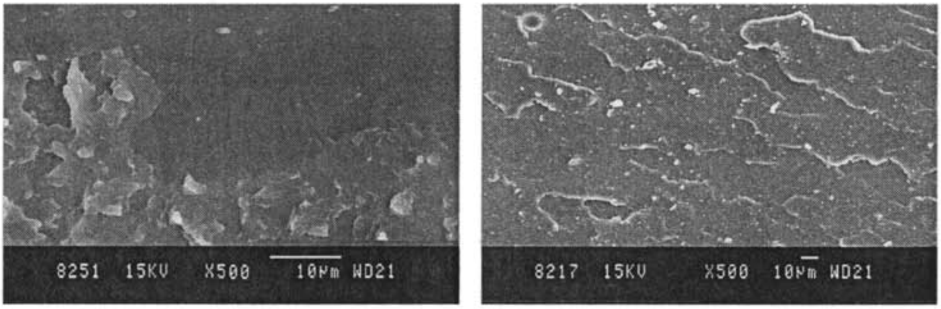
The variation of mechanical properties with varying dosage of chlorosulfonated polyethylene (CSPE) on 50/50 EPDM/CIIR blends is presented in table 3.4. It is evident that the compatibiliser has no significant effect in the case of MRD-10/CIIR blends. In the compatibilised blends of EP-96, tensile strength increases with increase in concentration of compatibiliser, upto a concentration of 10 phr, drops beyond this concentration. 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 agglomerate forming bigger aggregates.

As in the case of tensile strength, tear resistance also improves with the addition of chlorosulfonated polyethylene. The value gets maximized at a concentration of 10 phr of the compatibiliser. Formation of uniformly distributed finer domains tends to elongate to higher strain and effectively prevents tear propagation. With increase in the concentration of compatibiliser above 10 phr, the tear strength decreases. Modulus and elongation at break also follow the same trend.

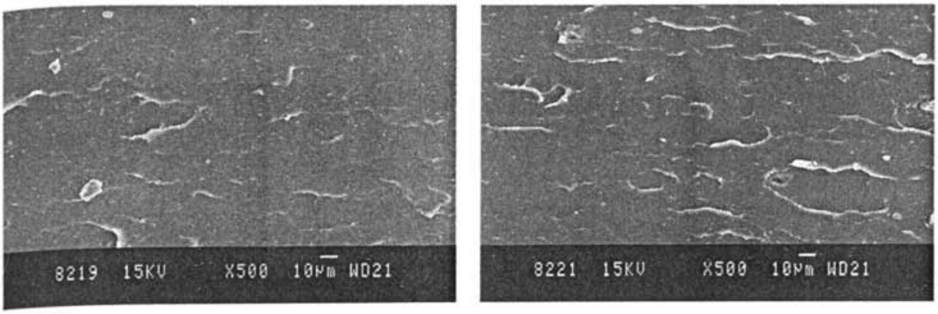
Table 3.4 Physical properties of EPDM/CIIR blends containing varying amounts of chlorosulfonated polyethylene

Blend ratio	50/50 EP-96/CIIR blend				50/50 MRD-10/CIIR blend			
Chlorosulfonated polyethylene (phr)	0	5	10	15	0	5	10	15
Tensile strength (MPa)	13.8	14.7	15.3	14.5	8	8.4	7.8	6.2
Tear strength (N/mm)	29.4	31.8	33.4	32.1	25.8	27.1	26	22.3
Modulus, 300% (MPa)	6.6	7.2	7.9	6.8	4.7	5.2	4.8	3.2
Elongation at break (%)	680	696	718	702	524	602	586	512

The effect of concentration of compatibiliser (CSPE) on the morphology of 50/50 EP-96 grade EPDM/CIIR blend is shown in figure 3.13. These SEM photographs show changes in the phase morphology of blends containing 0, 5, 10 and 15 phr compatibiliser, respectively. It is seen that with the addition of compatibiliser, more homogeneous surface texture is observed upto 10 phr and afterwards the homogeneity decreases. This is due to the reduction of interfacial tension between CIIR and EPDM phase. The equilibrium concentration at which the dispersed EPDM domain size levels off is called critical micelle concentration (CMC). The estimation of CMC from the plot of domain size vs. concentration is reported elsewhere.[42] 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 CIIR phase. Several reports are available from the literature regarding the linear decrease of dispersed domain size with increasing compatibiliser concentration.[43-45] Therefore it can be confirmed that a concentration of 15 phr of compatibiliser is much above CMC and comparatively very good reduction of interfacial tension is achieved at a concentration of 10 phr. This is in good agreement with the overall improvement in mechanical properties observed.



(a) (b)



(c) (d)

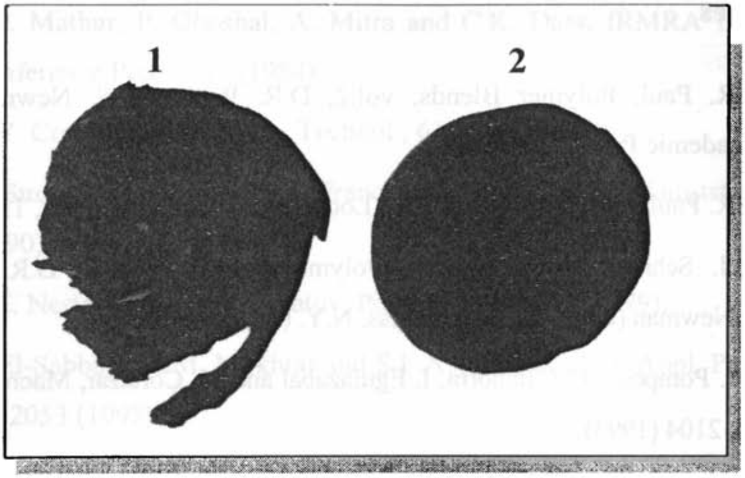
Figure 3.13 Scanning electron photographs of 50/50 EP-96 grade EPDM/CIIR blends (a) without compatibiliser (b) with 5 phr CSPE (c) with 10 phr CSPE (d) with 15 phr CSPE

Based on the above results, 10 phr chlorosulfonated polyethylene is taken as the optimum amount of compatibiliser required and is used for further studies of EP-96 grade EPDM blended with CIIR. The variation in mechanical properties with blend composition for the compatibilised blends is given in table 3.5. Compared to the uncompatibilised blends, the compatibilised sample shows an increase in the overall mechanical properties. If the segments of the added compatibiliser are chemically identical with those in the respective phases or adhered to one of the phases, then they act as efficient compatibilisers.[46-51] A comparatively higher percentage increase in tensile strength is observed for 20/80 and 40/60 EPDM/CIIR blends showing that compatibilising action is efficient in these compositions. The compatibilising action is due to the interaction of chlorine of CIIR with chlorosulfonated domain of compatibiliser. There is structural similarity between some segments of compatibiliser and EPDM. This also promotes compatabilising action of chlorosulfonated polyethylene in the blends. As the concentration of CIIR in the blend decreases, the probable interaction between the blend component and compatibiliser decreases. The mechanical properties, especially tensile strength are not governed by overall crosslinking alone, it depends on crosslink distribution and phase size as well. There is higher homogeneity of mixing of the rubbers in presence of compatiblisers as the CIIR content in the blend is higher or equal to that of EPDM.

Table 3.5 Comparison of physical properties of compatibilised and uncompatibilised EP-96/CIIR blends

	Uncompatibilised blend				Compatibilised blend			
Percentage of EPDM/CIIR blend	20/80	40/60	60/40	80/20	20/80	40/60	60/40	80/20
Tensile strength (MPa)	15.6	14.7	12.6	13.8	16.8	16.4	14.6	14.2
Tear strength (N/mm)	30.8	29.8	29.1	31.6	34.2	33.6	32.9	32.4
Modulus, 300 % (MPa)	7.6	6.9	5.21	6.4	9.2	8.6	7.2	6.6
Elongation at break (%)	664	686	672	654	734	726	709	682
Ageing resistance at 100°C, 24 hrs (MPa)	14.7	13.8	11.9	13.1	15.8	15.6	13.8	13.5

Circular specimen of 6.5 mm thickness of uncompatibilised and compatibilised blends were moulded and allowed to swell in n-hexane solvent for 120 hours and the resulting changes in appearances are shown in Figure 3.16. In uncompatibilised blends due to lack of interphase crosslinks, phase separation occurs while for compatibilised blends uniform curing and presence of interphase crosslinks prevents phase separation.



(1) Uncompatibilised (2) Compatibilised

Figure 3.14 Photographs of swollen samples of 50/50 EP-96 grade EPDM/CIIR vulcanizates

3.4 Conclusions

The compatibility of different grades of EPDM with a particular grade of CIIR was studied. The analysis of mechanical properties and ageing resistance revealed that two grades of EPDM (301-T and NDR-4640) were compatible with CIIR. The thermal analysis and morphological characterisation justifies the results. This is explained on the basis of their viscosities and unsaturation matching, so that covulcanisation between the two components upto certain extent is possible in these two cases. As far as the mechanical properties after ageing are concerned, they are superior for blends of 301-T than that with NDR-4640. This may be attributed to the less unsaturation of 301-T compared to that of NDR-4640. They also possess promising ageing résistance. It may be concluded that a molecular level homogeneity may be resulted with the constituents of comparable viscosity and unsaturation as is noticed with the blends of CIIR with EPDM's of different extents of unsaturation and different viscosities. The incorporation of compatibilisers into incompatible EPDM/CIIR blends greatly enhanced their compatibility and improved the properties.

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Chapter IV

Studies on Sulphur Cured EPDM/CIIR Blends

4.1 Introduction

It has been recognized for some time that prospects of continued synthesis of new rubbers with practical utility are limited. Efforts to develop blends for diverse applications have continued to burgeon for several decades. Several reviews on rubber-rubber blends are available in literature.[1-4] Tires probably represent the largest use of rubber blends. In non-tire industries, blends have been introduced for critical applications. When compared with other blending methods, blending of polymers by mechanical means is more important as this produces, in a short time, macroscopically homogeneous blend which is desired for better vulcanizate properties.[5] Shundo *et al.* has reported that for NR-SBR blend, mill mixing gives more homogeneous blend than Banbury mixing.[6] In the previous chapter of this thesis, the compatibility between the blends of EPDM and CIIR has been discussed. The compatibility study shows that, of the four grades of EPDM used, only two grades, viz; 301-T and NDR-4640 are compatible with CIIR. They have comparable unsaturation and viscosity which results in the covulcanization and uniform mixing of the two components. This covulcanization offers an effective molecular level mixing or compatibility between the two phases without the help of any compatibilisers. The mechanical properties of these two types of EPDM/CIIR blends are proposed to be investigated in this chapter.

4.2 Experimental

The compounding recipe is given in table 3.1. The compounds were prepared according to ASTM-D 3182 on a laboratory mixing mill (16 × 33 cm) at a friction ratio of 1: 1.25. The cure curves of the mixes were taken at 170 °C using a Rubber Process Analyzer (RPA 2000, Alpha Technologies). The compounds were vulcanized upto their respective optimum cure times in an electrically heated laboratory hydraulic press at 170°C. The total crosslink density was determined from the swelling data in toluene as per the procedures outlined in chapter 2. The individual crosslink densities of the EPDM and CIIR phases could not be measured because both had only common true solvents.[7]

The tensile properties of the vulcanizates were determined as per ASTM D 412 using dumbbell specimens at a cross head speed of 500 mm/min on a Shimadzu Universal Testing Machine (model-AG1). The ageing resistance and tension set of the vulcanizates were determined after ageing the samples at 100 °C for 24, 48 and 72 hours in a laboratory air oven. The steam ageing resistance of the vulcanizates was also studied using a steam chamber maintained at a pressure of one atmosphere and temperature 100 °C for different time intervals of 6, 18 and 36 hours. Angular test specimens were punched out of the compression moulded sheets and tear resistance of the unaged and aged samples were measured on the UTM according to ASTM D 624.

The hardness of the vulcanizates was determined according to ASTM 2240 and expressed in shore A units. Samples for abrasion resistance were moulded and weight loss/h was determined on a DIN abrader according to DIN 53514. Samples for compression set, flex crack resistance and rebound resilience were moulded and tested as per relevant ASTM standards.

4.3 Results and discussion

4.3.1 Cure rate and crosslink density

The cure rates of the blends of 301-T and NDR-4640 grades of EPDM with CIIR corresponding to various compositions are shown in figure 4.1. When compared with 301-T/CIIR blends, cure rate is higher for NDR-4640/CIIR blends which may be due to the higher unsaturation of NDR-4640 as well as the presence of the diene, ethylidene norbornene (ENB). In the case of 301-T grade EPDM, the diene is dicylopentadiene (DCPD) which has the slowest cure rate among the termonomers of EPDM. Also the unsaturation percentage of 301-T is lower than that of NDR-4640. The cure rates of pure EPDM and CIIR compounds were in the same range. The cure rate decreased with increase in EPDM content in the blends up to 60 % of EPDM and then increased. This may be attributed to the non-uniform distribution of curatives in the blend components.[8] The distribution of curatives enhances the extent of crosslinking. As longer time is needed for forming larger number of crosslinks, cure time increases, resulting in decreased cure rate.

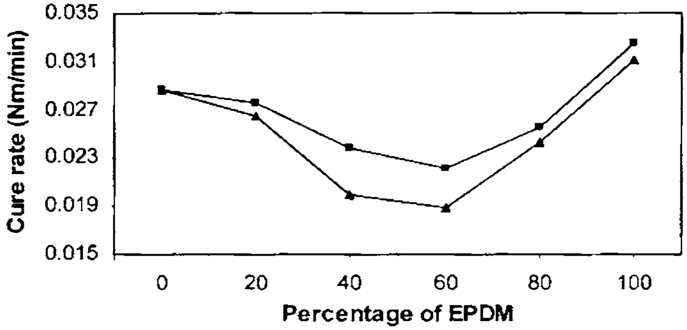

Figure 4.1 Variation of cure rate of EPDM/CIIR blends with EPDM content. ■, NDR-4640/CIIR and ▲, 301-T/CIIR blends

Figure 4.2 shows the variation of crosslink density of the vulcanizates. The total crosslink density increases with increase in EPDM content in the blend. In the 20/80 and 40/60 EPDM/CIIR blends, major component is chlorobutyl and the crosslink density shown is largely that of chlorobutyl, which is low due to curative migration. In 60/40 EPDM/CIIR blend even though EPDM phase gets a higher share of curatives, chlorobutyl phase also sufficiently gets cured.[9-11] In 80/20 EPDM/CIIR blend, EPDM forms the continuous phase and the effect of preferential migration is not so significant.[12,13]

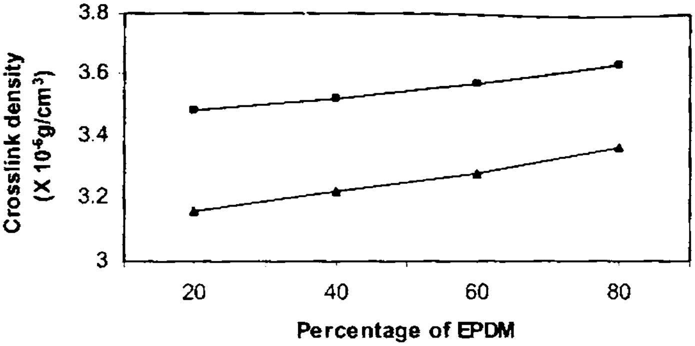

Figure 4.2 Variation of crosslink density of EPDM/CIIR blends with EPDM content. ■, NDR-4640/CIIR and ▲, 301-T/CIIR blends

4.3.2 Mechanical properties

The variation in tensile strength and elongation at break with percentage of EPDM is shown in figures 4.3, 4.4 and 4.5. The tensile strength of the unaged samples of 301-T/CIIR blends show additive behaviour while NDR-4640/CIIR blends are exhibiting a synergistic behaviour indicating that NDR-4640/CIIR blends are more compatible than 301-T/CIIR blends. The elongation at break is also close to the arithmetic average for 301-T/CIIR blends and synergistic behaviour for NDR-4640/CIIR blends. As the rate of vulcanization of the two phases is comparable, significant amount of interphase crosslinking may take place and this might be the reason for the better values of tensile strength and elongation at break.[14]

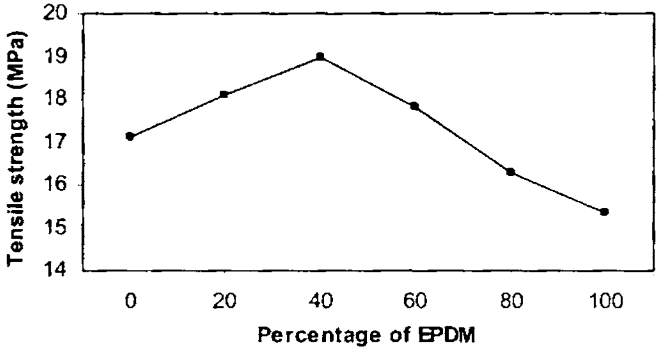

Figure 4.3 Variation of tensile strength of NDR-4640/CIIR blends with EPDM content

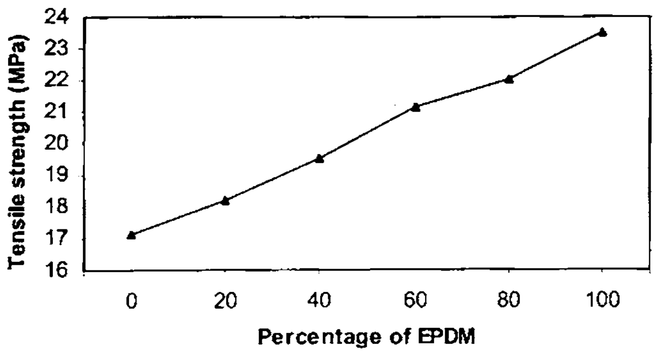

Figure 4.4 Variation of tensile strength of 301-T/CIIR blends with EPDM content

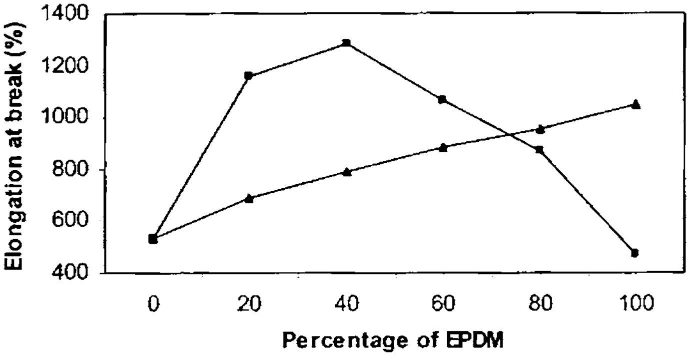

Figure 4.5 Variation of elongation at break of EPDM/CIIR blends with EPDM content. ▲, 301-T/CIIR and ■, NDR-4640/CIIR blends

The tensile strength and elongation at break of the vulcanizates after thermal ageing are shown in tables 4.1 and 4.2 respectively. The drop in tensile strength and elongation at break with ageing is observed more for NDR-4640/CIIR blends compared to 301-T/CIIR blends. This may be due to the higher unsaturation of NDR-4640 compared to 301-T, so that, in addition to the usual breakage of sulphur crosslinks during ageing, main chain scission may also occur more in NDR-4640.[15] Hot air ageing resistance is found to be superior for blends containing higher percentage of EPDM in both blends. This may be due to the increase in crosslink density with ageing because of the continuing marching cure of EPDM. CIIR attains maximum torque faster than EPDM and then it reverts. As ageing continues, the tensile strength values decrease. The tensile strength values of the vulcanizates are found to depend on the proportions of poly-, di- and mono-sulphidic linkages in addition to the crosslink density. A higher percentage of polysulphidic crosslinks is found to result in higher tensile strength. The decrease in values on continued ageing might be due to the decrease in the concentration of polysulphidic crosslinks.[16-18] The deterioration in the tensile strength of the vulcanizates with ageing may be principally due to main chain scission.[19-22] The chain shortening of polysulphidic crosslinks may also contribute to this effect.

Table 4.1 Variation of tensile strength with ageing for 301-T/CIIR and NDR-4640/CIIR blends

Percentage of EPDM in the blend	Tensile strength of 301-T/CIIR blends (MPa)			Tensile strength of NDR-4640/CIIR blends (MPa)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
100	24.4	23.2	21.8	14.2	13.0	11.6
80	22.8	21.3	20.5	14.8	13.4	12.1
60	21.4	20.6	19.8	15.6	14.8	13.7
40	19.1	18.2	17.2	18.0	16.8	14.8
20	17.2	16.0	14.6	16.5	15.2	13.6
0	15.9	14.5	12.9	15.9	14.5	12.9

Table 4.2 Variation of elongation at break with ageing for 301-T/CIIR and NDR-4640/CIIR blends

Percentage of EPDM in the blend	Elongation at Break for 301-T/CIIR blends (%)			Elongation at Break for NDR-4640/CIIR blends (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
100	928	860	812	412	356	278
80	864	786	708	528	343	242
60	812	718	654	582	396	316
40	676	584	532	608	412	338
20	570	472	418	520	406	326
0	474	397	306	474	397	306

Tables 4.3 and 4.4 show the steam ageing resistance of 301-T/CIIR and NDR-4640/CIIR blends respectively. As in the case of hot air ageing, the steam ageing resistance is also higher for blends with higher percentage of EPDM probably due to the post vulcanization reaction strengthening the network. Among the blends with two grades of EPDM, 301-T/CIIR blend is exhibiting better retention in properties owing to its more saturated nature. A comparison of tensile strength values of the vulcanizates of varying compositions subjected to hot air ageing and steam ageing show a drastic loss in property during steam ageing and the loss was higher for 100 % CIIR and blends containing higher percentage of CIIR. The comparative result points to the fact that dehydrohalogenation, which is the main problem for halogenated butyl compounds, is severe during steam ageing than during thermal ageing.[23,24]

Table 4.3 Effect of steam ageing on tensile strength and elongation at break for 301-T/CIIR blends

Percentage of EPDM in the blend	Tensile Strength after steam ageing (MPa)			Elongation at Break after steam ageing (%)		
	6 hrs	18 hrs	36 hrs	6 hrs	18 hrs	36 hrs
0	16.1	14.1	11.4	488	412	334
20	17.4	16.1	14.2	576	516	443
40	18.3	17.3	16.1	690	645	584
60	19.6	18.8	17.5	822	786	710
80	21.3	20.8	19.7	895	823	786
100	23.6	23.4	22.6	910	886	854

Table 4.4 Effect of steam ageing on tensile strength and elongation at break for NDR-4640/CIIR blends

Percentage of EPDM in the blend	Tensile Strength after steam ageing (MPa)			Elongation at Break after steam ageing (%)		
	6 hrs	18 hrs	36 hrs	6 hrs	18 hrs	36 hrs
0	16.1	14.1	11.4	488	412	334
20	16.7	14.5	12.0	526	459	376
40	17.4	16.1	14.3	580	492	422
60	16.5	15.4	13.8	485	426	368
80	14.6	13.8	12.5	432	362	302
100	13.8	13.1	12.2	388	331	314

Tear strength is an important property which contributes towards resistance to crack growth. It can be seen from the table 4.5 that the variation of tear strength with the addition of EPDM is very similar to that observed in the case of tensile strength. That is, tear strength increases gradually with an increase in percentage of EPDM in the vulcanizate. This observation is associated with the ability of EPDM phase to transfer the tearing force and also probably because of the optimum crosslink densities in the two rubber phases and at the interphase. The variation of tear strength followed an additive behaviour which points towards partial miscibility. Furthur reasons for the improved strength may be uniform filler distribution due to the similarity in the viscosities between EPDM and CIIR phases. Upon ageing, the tear strength values decrease primarily due to the crosslink scission.

Table 4.5 Variation of tear strength for 301-T/CIIR and NDR-4640/CIIR blends under unaged and aged conditions

Percentage of EPDM in the blend	Tear strength of 301-T/CIIR blends (N/mm)				Tear strength of NDR-4640/CIIR blends (N/mm)			
	Unaged	24 hrs	48 hrs	72 hrs	Unaged	24 hrs	48 hrs	72 hrs
0	31.8	28.6	24.1	21.2	31.8	28.6	24.1	21.2
20	33.4	30.1	28.5	24.8	32.4	29.4	25.7	22.0
40	37.0	33.6	30.7	28.0	34.0	31.8	29.4	23.6
60	41.2	38.8	35.0	32.1	33.2	31.1	29.0	25.9
80	43.4	41.4	40.8	37.2	32.1	30.2	28.7	26.7
100	46.7	45.8	43.6	40.8	31.3	29.6	28.8	27.3

Compression set and tension set values depend strongly on the elastic recovery of the sample. Figure 4.6 shows the variation of compression set with percentage of EPDM and table 4.6 shows the variation of tension set properties with blend composition for 301-T/CIIR and NDR-4640/CIIR blends. In general, the compression set and tension set values decrease with increase in CIIR content in the blend. This is due to the more elastic nature of CIIR so that even after stress-relaxation process, there is no significant change in dimensions resulting in lower set values. When compared with 301-T/CIIR blends, the compression set values are low for NDR-4640/CIIR blends due to its more compatible nature, but tension set values show a drastic fall probably due to the highly unsaturated nature of NDR-4640.

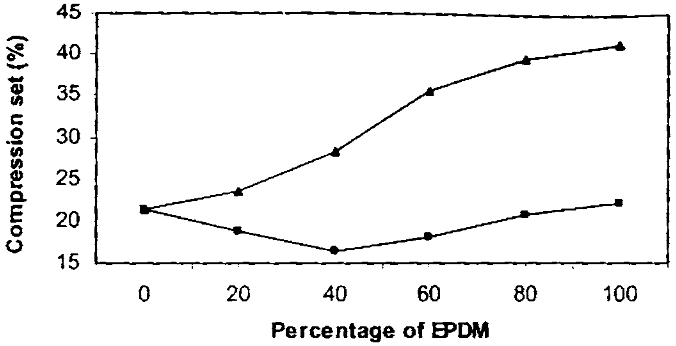

Figure 4.6 Variation of compression set of EPDM/CIIR blends with EPDM content. ■, NDR-4640/CIIR and ▲, 301-T/CIIR blends

Table 4.6 Variation of tension set for NDR-4640/CIIR and 301-T/CIIR blends

Percentage of EPDM in the blend	Tension set for 301-T/CIIR blends (%)			Tension set for NDR-4640/CIIR blends (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
0	-	-	-	-	-	-
20	76	-	-	97.5	-	-
40	102	-	-	117	-	-
60	116	125	-	128	-	-
80	123	131	144	136	-	-
100	130	136	141	141	158	-

Figure 4.7 shows the variation of hardness on increasing concentration of EPDM. It is evident from the figure that the rubber vulcanizates become stiffer and harder as the EPDM content increases. This is expected because, as more EPDM get into the blend matrix, the elasticity of the rubber blend is reduced, resulting in more rigid vulcanizates. Hardness values are higher for NDR-4640/CIIR blends probably due to their higher crosslink density.

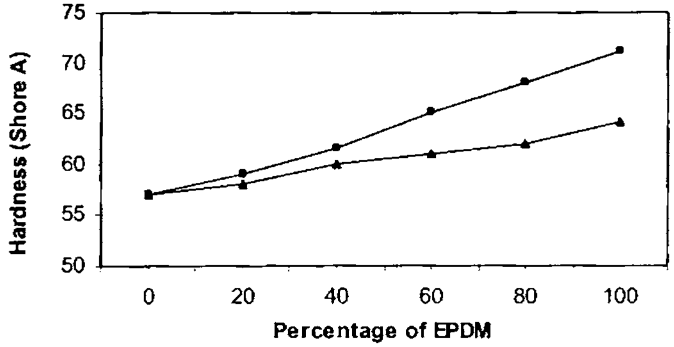

Figure 4.7 Variation of hardness of EPDM/CIIR blends with EPDM content. ▲, 301-T/CIIR and ■, NDR-4640/CIIR blends

Abrasion is another important factor leading to the failure of a number of rubber products.[25] The results in figure 4.8 reveal that EPDM as well as the samples containing higher percentage of EPDM exhibit higher abrasion resistance. It has been reported that crosslink density, hardness and modulus of the vulcanizate are important factors controlling the abrasion resistance.[26-30] The increased crosslink density which results in increased hardness and modulus ultimately give rise to the enhancement of abrasion resistance. On the contrary, lower the friction coefficient, higher the abrasion resistance. From the results obtained, the greater abrasion resistance of NDR-4640/CIIR blend vulcanizates when compared with 301-T/CIIR blends can be attributed to their higher crosslink density.

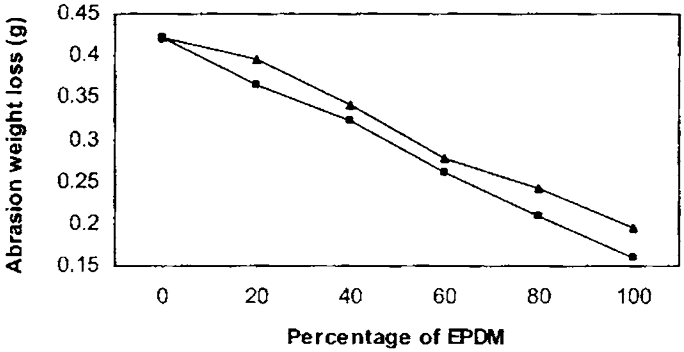

Figure 4.8 Variation of abrasion resistance of EPDM/CIIR blends with EPDM content . ▲, 301-T/CIIR and ■, NDR/CIIR blends

Figure 4.9 shows the variation of rebound resilience with percentage of EPDM. The rebound resilience decreases gradually with chlorobutyl content in the blends. The reason can be explained on the basis of morphological features and high strain energy density of chlorobutyl.[31,32] Due to the low viscosity of 301-T compared with NDR-4640, black loading is higher in the former. This result in an increased filler matrix interaction in the case of 301-T compared to NDR-4640 so that the resilience is lower for 301-T/CIIR blends when compared with NDR-4640/CIIR blends.

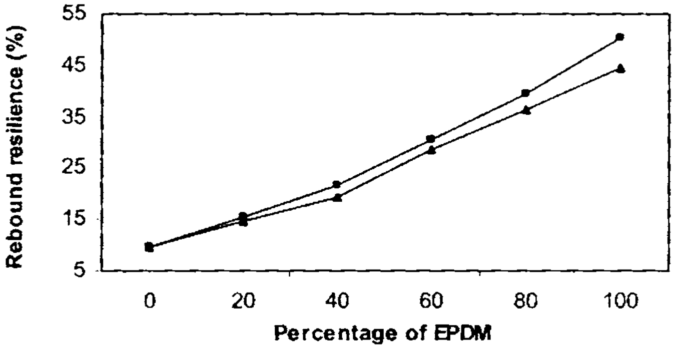

Figure 4.9 Variation of rebound resilience of EPDM/CIIR blends with EPDM content. ▲, 301-T/CIIR and ■, NDR-4640/CIIR blends

During service, the rubber goods pass through repeated stress conditions. It is desired that under these severe conditions the crack propagation should be minimum or negligible to have better service life. Increment in cut length against number of flexing cycles is shown in figures 4.10 and 4.11 for 301-T/CIIR blends and NDR-4640/CIIR blends respectively. The samples were tested at room temperature. It has been observed that, with the increase in chlorobutyl content in the blends, the rate of crack growth decreased which is due to the inherently superior viscoelastic nature of the CIIR.[33-35] This same trend is observed for both 301-T/CIIR and NDR-4640/CIIR blends containing higher percentage of chlorobutyl. The resistance to cut growth is better for 301-T/CIIR blends. This may be due to different extent of filler distribution in the two grades of EPDM. It is expected that reinforcing fillers like carbon black will get distributed more in the

EPDM phase in the case of 301-T/CIIR as compared with NDR-4640/CIIR, due to the low viscosity of 301-T.[36] This results in the formation of more active sites on 301-T surface when compared to NDR-4640 with the incorporation of the filler. When the two surfaces are brought into molecular contact, adsorption takes place in addition to the bonds formed by crosslinking. These bonds can absorb more stress before rupture leading to better flex crack resistance for 301-T/CIIR blends.

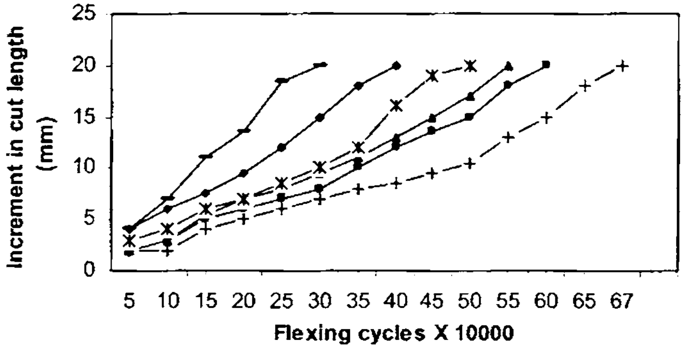

Figure 4.10 Plot of increment in cut length against flexing cycles for 301-T/CIIR blends at a precut of 2.0 mm. -, 100/0; ♦, 80/20; ж, 60/40; ▲, 40/60; ■, 20/80; +, 0/100

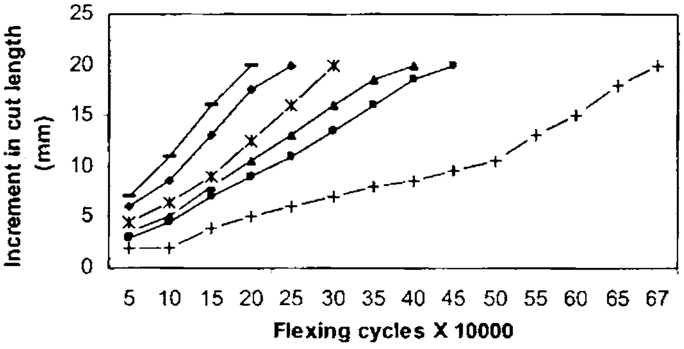

Figure 4.11 Plot of increment in cut length against flexing cycles for NDR-4640/CIIR blends at a precut of 2.0 mm. -, 100/0; ♦, 80/20; ж, 60/40; ▲, 40/60; ■, 20/80; +, 0/100

4.4 Conclusions

The sulphur cured EPDM/CIIR vulcanizates at varying blend compositions were found to exhibit good physical properties at all compositions. The properties are found to be weighted average of the properties of component elastomers. Although better mechanical properties are exhibited by NDR-4640/CIIR blends, they show a drastic drop under severe conditions of thermal and steam ageing. On the other hand, resilience, flex crack resistance and ageing resistances are better for 301-T/CIIR blends which is probably due to the low viscosity and saturated nature of 301-T. Based on the physical property studies, it is inferred that 301-T/CIIR blends can be used for high temperature applications such as curing bladder, conveyor belts etc.

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Chapter V

EPDM/CIIR Blends: Improved Mechanical Properties through Precuring

5.1 Introduction

More than ever before, today, there is increased technological interest in the use of blends of dissimilar rubbers.[1-3] However such blends generally show inferior mechanical properties compared to the average properties of the components. This can be attributed to three types of incompatibility which exist between dissimilar elastomers: viscosity mismatch, thermodynamic incompatibility and cure mismatch.[4] As a result of incompatibility, after mixing, the curatives migrate to the more unsaturated or more polar rubber which cures faster than the slow curing rubber causing the latter remaining undercured.[5-9] This phenomenon leads to poor mechanical properties of the blends. Such migration can also occur due to the difference between the reactivities of the elastomers or due to the difference between the solubilities of curatives in elastomers.[10-13] Several methods have been suggested to improve the mechanical behaviour of elastomer blends. Lead oxide activated curing and the use of long chain hydrocarbon dithiocarbamate accelerator is beneficial in sulphur cure of EPDM's with highly unsaturated or more polar rubbers like nitrile (NBR) rubber.[14]

Another approach is the chemical modification of the slow curing phase or binding of accelerators to the polymer backbone.[15] Preblending of curatives into respective elastomers at optimal concentrations prior to blending can improve the blend crosslink distribution, although the usual practice is to incorporate the curatives at the last stage inorder to avoid scorch problems.[16] Inorder to reduce the diffusion of curatives from one phase to the other, thereby improving the adhesion between the components, a novel method is to partially prevulcanise one of the blend components and then mixing the prevulcanised elastomer with the other component.[17-19]

In this part of the study, to improve the co-curing and hence the blend properties of chlorobutyl rubber (CIIR) with ethylene-propylene-diene rubber (EPDM), one of the component elastomers in the EPDM/CIIR blend is partially precured prior to blending. The mechanical properties of the blends prepared by this novel route are compared with those of conventional blends.

5.2 Experimental

5.2.1 Determination of optimum level of precuring

The optimum precuring required for the slow curing CIIR phase for making successful blends with EPDM was determined by measuring the tensile properties of 50/50 blends of EPDM/CIIR with CIIR phase precured to different levels. CIIR was compounded according to ASTM-D 3182 on a laboratory mixing mill at a friction ratio of 1: 1.25 as per the formulations given in table 3.1. The compound was sheeted out from the mill at a thickness of 3 mm and was precured for different periods viz. 10 %, 20 %, 30 % and 40 % of the optimum cure time at a temperature of 170 °C. These precured samples were blended with masticated EPDM on the mill and then compounding ingredients for EPDM were added. The compounds were cured upto their respective optimum cure time. The tensile properties of the blends were evaluated and the optimum precuring time was determined by comparing the tensile strength. In a similar manner, EPDM was compounded as per the formulation given in table 3.1, precured to different levels, blended with CIIR followed by the addition of its curatives, vulcanized and the tensile properties of the resulting blends were compared.

5.2.2 Swelling behaviour of precured EPDM/CIIR blends

Chlorobutyl rubber, precured upto the optimum level, was blended with EPDM rubber at various percentages. The compounding ingredients required for EPDM were then added. The optimum cure time was then determined at 170 °C using Rubber Process Analyzer. The compounds were then vulcanized upto their respective optimum cure times on an electrically heated laboratory hydraulic press at 170 °C. The total crosslink density was determined from the swelling data in toluene as per the procedures outlined in chapter 2.[20-22] The individual crosslink densities of the EPDM and CIIR phases could not be measured because both have common true solvents.[23]

5.2.3 Preparation of sample specimens

Dumbell shaped tensile test specimens were punched out from the compression moulded sheets along the mill direction. The tensile properties of the vulcanizates were measured as per ASTM D 412 at a cross head speed of 500 mm/min on a Shimadzu Universal Testing Machine (model-AG1). The ageing resistance and tension set of the vulcanizates were determined after ageing the samples at 100 °C for 24, 48 and 72 hours in a laboratory air oven. The steam ageing resistance of the vulcanizates were also studied after ageing in a steam chamber maintained at a pressure of one atmosphere and temperature 100 °C for the time intervals 6,18 and 36 hours. Angular test pieces were punched out of the compression moulded sheets and tear resistance of the unaged and aged samples were measured on the UTM as per ASTM D 624.

The hardness of the vulcanizate was determined according to ASTM 2240 and expressed in shore A units. Samples for abrasion resistance were moulded and weight loss/h was determined on a DIN abrader according to DIN 53514. Samples for compression set, flex crack resistance and rebound resilience were moulded and tested as per relevant ASTM standards.

5.3 Results and discussion

5.3.1 Optimization of precuring conditions

Figure 5.1 is a plot of tensile strength versus percentage curing time (various percentage of the optimum cure time) conditions for 50/50 EPDM/CIIR samples in which the EPDM phase is precured. The results indicate that, with increase in state of precuring, the tensile strength of the blend decreases. In the normal 50/50 EPDM/CIIR blend, owing to the low viscosity and more unsaturated nature of EPDM when compared with CIIR, the curatives and carbon black prefer to diffuse to the EPDM phase leading to slight overcuring. Hence in the case of the blend consisting of precured EPDM, the EPDM phase gets overcured leading to poor interfacial linking. Secondly, in the resulting blend, the CIIR phase remains undercured which also contribute to the inferior properties. Thus the method of precuring of EPDM followed by blending with CIIR was not found to be effective for improving the blend properties.

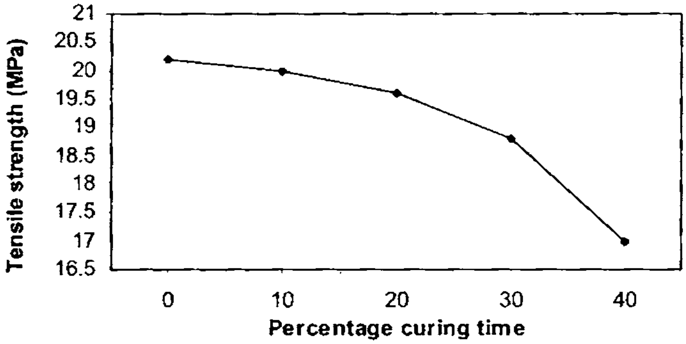

Figure 5.1 Variation of tensile strength for 50/50 EPDM/CIIR vulcanizates (partially precured EPDM with CIIR) with percentage curing time

Figure 5.2 shows the variation in tensile strength of 50/50 EPDM/CIIR blends at varying precuring conditions. The tensile strength of the blends is found to increase with the state of precuring of the CIIR phase initially, reach a maximum at 20 % precuring and then decreases. This behaviour shows that precuring the CIIR phase upto a certain degree of crosslinking assists co-crosslinking but nonhomogeneity develops in the blend at higher percentage precuring. This shows that, after the optimum level of precuring, chlorobutyl phase gets further cured and then it acts similar to an overcured or scorchy rubber leading to poor interfacial linking. Secondly, in the resulting blend one phase remains undercured. It also points towards the necessity for an optimum degree of precuring in the CIIR phase for preparing crosslinked blends with EPDM. Blends prepared by partially precuring the chlorobutyl rubber and then blending with EPDM are hereafter referred as 'modified' blends to distinguish from the blends prepared by blending chlorobutyl and EPDM by conventional method.

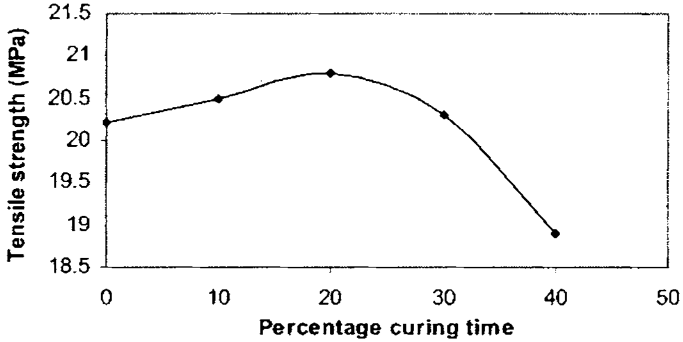

Figure 5.2 Variation of tensile strength of 50/50 EPDM/CIIR blends (EPDM with partially precured CIIR) with percentage curing time

5.3.2 Cure characteristics and crosslink density

Furthur studies on EPDM/CIIR blends were carried out by precuring the CIIR phase upto 20 % of the optimum cure time at 170 °C. The cure characteristics of the blends are shown in table 5.1 and cure rates corresponding to various compositions for conventional and modified blends are shown in figure 5.3. When EPDM forms the major constituent, there is no significant change in the cure time between the conventional and modified blends. As chlorobutyl content increases, cure time decreases for modified blends. This is expected, because the curing behaviour is likely to be more influenced by the major constituent.[24,25] Reduction in cure time for modified blends indicates that there is no significant curative migration to EPDM phase and curatives are trapped in the chlorobutyl phase itself due to precuring. The modified blends show marginally higher torque and cure rate which is related to the homogeneity of the modified blends. The processing safety of the modified compounds remains unaltered by the precuring step as there is not much variation in scorch time and cure time.

Table 5.1 Cure characteristics of conventional and modified EPDM/CIIR blends

EPDM (%)	20	40	60	80	20	40	60	80
CIIR (%)	80	60	40	20	–	–	–	–
Modified CIIR (%)	–	–	–	–	80	60	40	20
Cure time (min)	12.2	14.6	18.8	13.0	11.7	14.0	19.1	13.2
Scorch time (min)	1.0	1.3	1.4	1.2	1.0	1.3	1.4	1.2
Maximum torque (Nm)	0.34	0.30	0.33	0.32	0.39	0.35	0.38	0.36
Minimum torque (Nm)	0.042	0.036	0.034	0.038	0.082	0.064	0.048	0.041

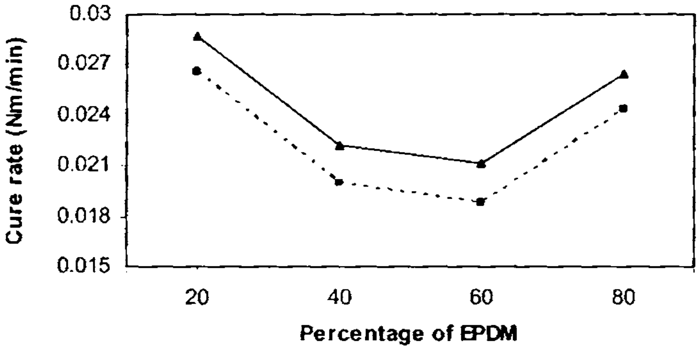

Figure 5.3 Variation of cure rate of EPDM/CIIR blends with EPDM content. ■, conventional and ▲, modified blends

Crosslink densities of the conventional and modified blends are shown in figure 5.4. The modified blends show a higher crosslink density than the corresponding conventional blends from swelling experiments in toluene. Higher crosslink density values on modification are due to the equal distribution of crosslinks owing to reduced curative migration. Improvement in values is more significant in the case of 80/20 EPDM/CIIR blend. In this case the crosslink density of chlorobutyl which is the major component is low due to curative migration. But on modification, curative imbalance is reduced resulting in uniform crosslinking in the component elastomers and at the interphase.

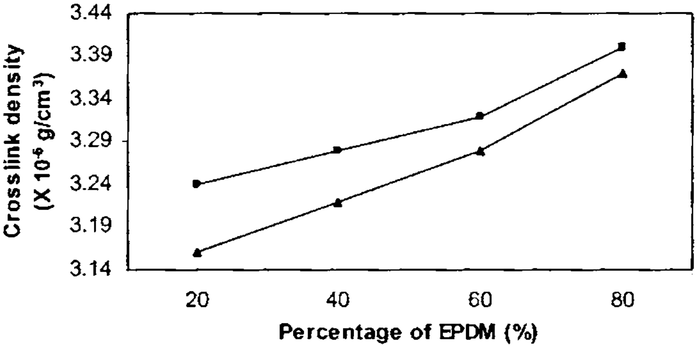

Figure 5.4 Variation of crosslink density of EPDM/CIIR blends with EPDM content. ■, modified and ▲, conventional blends

5.3.3 Comparison between conventionally cured and precured blend systems

Figure 5.5 shows the variation in tensile strength of the modified and conventional blends. The modified blends show better tensile strength compared to the conventional blends. This improvement in tensile strength is probably due to the optimum crosslink densities in both EPDM and CIIR phases and in the interphase.[26] Improvement is found to be more pronounced in the 20/80 EPDM/CIIR blend which shows that it was this composition that was comparatively most affected due to curative migration in conventional blending leading to the EPDM phase to get overcured whereas the CIIR phase remains undercured. The ageing resistance of the modified and conventional blends is given in table 5.2. The results reveal that the ageing resistance of the blends is also found to be better for the modified blends. This clearly shows the superiority of the precured CIIR in resisting curative migration and in getting optimally cured at the final curing stage along with EPDM.

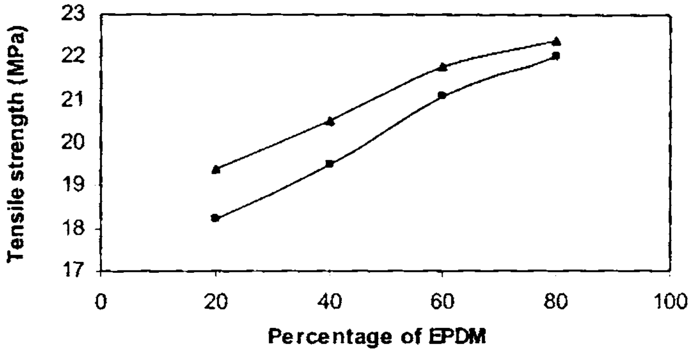

Figure 5.5 Variation of tensile strength of EPDM/CIIR blends with EPDM content. ■, conventional and ▲, modified blends

Table 5.2 Variation of tensile strength with ageing for conventional and modified EPDM/CIIR blends

Percentage of EPDM	Tensile strength of conventional blends (MPa)			Tensile strength of modified blends (MPa)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
20	17.2	16.0	14.6	17.8	16.3	14.8
40	19.1	18.2	17.2	19.6	18.4	17.4
60	21.4	20.6	19.8	21.7	20.8	19.8
80	22.8	21.3	20.5	23.0	21.4	20.5

Table 5.3 shows the elongation at break of the CIIR/EPDM blends. The modified CIIR/EPDM blends show higher elongation compared to the conventional blends

before and after ageing. Since the elongation is controlled by the continuous elastomer phase, the lower value in the case of conventional blends probably results from the overcure of the continuous elastomer phase. In the conventional curing method, EPDM gets a higher proportion of curing agents resulting in its overcure. The 20/80 EPDM/CIIR blend shows higher elongation at break since chlorobutyl rubber is the major component.

Tabel 5.3 Variation of elongation at break with blend composition for conventional and modified EPDM/CIIR blends

Blending method employed	Composition of EPDM/CIIR blend (%)	Elongation at break (%)			
		unaged	24 hrs ageing	48 hrs ageing	72 hrs ageing
Conventional	20/80	687	570	472	418
	40/60	788	676	584	532
	60/40	885	812	718	654
	80/20	958	864	786	708
Modified	20/80	712	582	480	422
	40/60	802	685	591	536
	60/40	896	818	722	659
	80/20	964	870	790	713

The variation in tear strength for conventional and modified blends under unaged and aged conditions are given in table 5.4. The modified blends show superior tear strength compared to conventional blends before and after ageing as observed in the case of tensile strength. The tear strength improvement with modification is more pronounced, since tear strength has stronger correlation with optimum crossslink densities in both rubber phases and in the interphase.[27] Furthur reasons for the improved strength may be attributed to the uniform filler distribution due to the reduction in the viscosity mismatch between EPDM and CIIR phases in the case of modified blends due to precuring.

Table 5.4 Variation of tear strength with blend composition for conventional and modified EPDM/CIIR blends under unaged and aged conditions

Blending method employed	Composition of EPDM/CIIR blend (%)	Tear strength (N/mm)			
		unaged	24 hrs ageing	48 hrs ageing	72 hrs ageing
Conventional	20/80	33.4	30.1	28.5	24.8
	40/60	37.0	33.6	30.7	28.0
	60/40	41.2	38.8	35.0	32.1
	80/20	43.4	41.4	40.8	37.2
Modified	20/80	39.2	36.8	31.1	26.4
	40/60	42.4	39.6	34.2	31.2
	60/40	45.6	43.2	38.9	36.4
	80/20	46.8	45.1	41.4	39.2

Figures 5.6 and 5.7 show the variation of abrasion loss and hardness with blend composition respectively. The modified blends show better abrasion resistance than the conventional blends. This is probably due to the uniform filler distribution in the two elastomer components which results from the better viscosity matching of the precured CIIR and EPDM.[28,29] Hardness is also found to be superior for modified blends due to uniform crosslinking and uniform filler distribution in both phases.

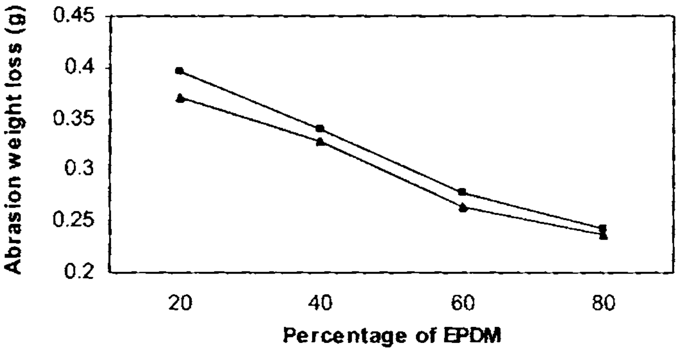

Figure 5.6 Variation of abrasion resistance of EPDM/CIIR blends with EPDM content. ■, conventional and ▲, modified blends

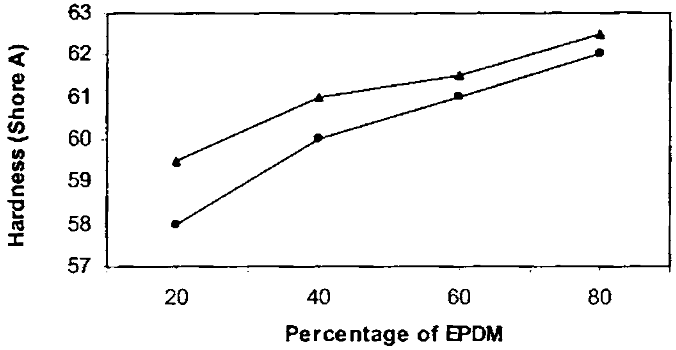

Figure 5.7 Variation of hardness of EPDM/CIIR blends with EPDM content. ■, conventional and ▲, modified blends

The steam ageing resistance of the conventional and modified vulcanizates is shown in table 5.5. The modified blends show only a marginal improvement in steam ageing resistance compared to the usual sulphur cured blends (discussed in chapter IV). This indicates that steam ageing resistance depends mainly on the nature of the component elastomers. Chlorobutyl rubber when exposed to steam, degrades easily due to the dehydrochlorination reaction resulting in inferior properties even after precuring.[30,31]

Table 5.5 Variation of steam ageing resistance with blend composition for conventional and modified EPDM/CIIR blends

Percentage of EPDM in the blend	Tensile strength of conventional blend (MPa)			Tensile strength of modified blend (MPa)		
	6 hrs	18 hrs	36 hrs	6 hrs	18 hrs	36 hrs
20	17.4	15.4	14.2	17.6	15.2	14.3
40	18.3	17.3	16.1	18.4	17.5	16.2
60	19.6	18.8	17.5	19.6	18.9	17.4
80	21.3	20.8	19.4	21.5	20.7	19.6

Figure 5.8 represents the variation of compression set properties and table 5.6 represents the variation of tension set properties with blend composition for conventional and modified blends. As the chlorobutyl content increases compression set and tension set decreases for both conventional and modified blends which is an inherent property of CIIR, but the modified blends, owing to the better homogeneity, display lower set values compared to conventional blends.

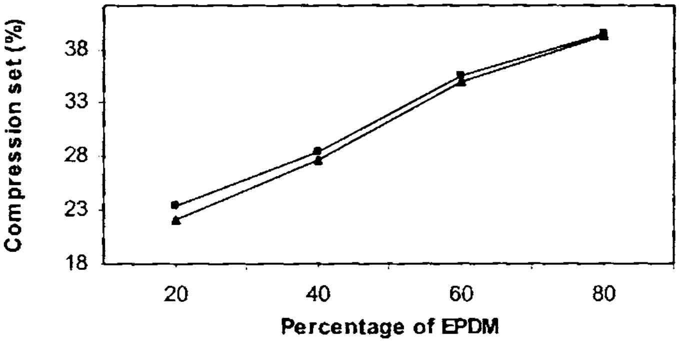

Figure 5.8 Variation of compression set of EPDM/CIIR blends with EPDM content. ■, conventional and ▲, modified blends

Table 5.6 Variation of tension set with ageing for conventional and modified EPDM/CIIR blends

Percentage of EPDM in the blend	Tension set values for conventional blend (%)			Tension set values for modified blend (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
20	76	-	-	64	-	-
40	102	-	-	95	118	-
60	116	125	-	109	121	138
80	123	131	144	118	127	142

Figures 5.9 and 5.10 represent the effect of precuring on the rebound resilience and flex crack resistance of blends. Precured blends show lower resilience compared to conventional blends. This is attributed to two reasons; one is higher crosslink

density of the vulcanizate and second is the uniform distribution of the filler in the matrix, both due to the partial precuring. Flex crack resistance also exhibits improvement with precuring, again due to the increased homogeneity in the blends because of precuring.[32]

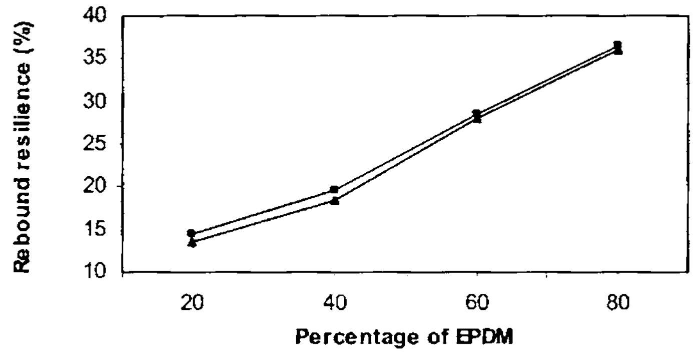

Figure 5.9 Variation of rebound resilience of EPDM/CIIR blends with EPDM content. ■, conventional blends and ▲, modified blends

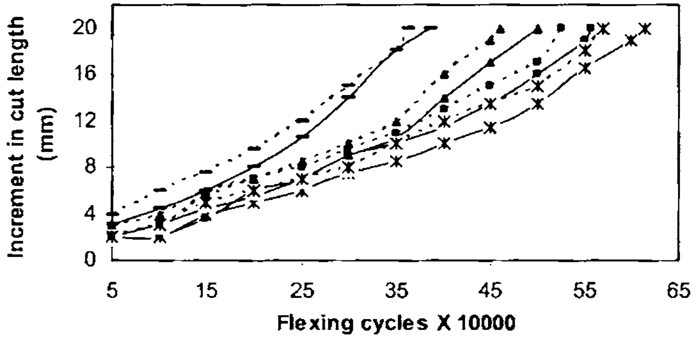

Figure 5.10 Increment in cut length Vs. flexing cycles for conventional (dotted lines) and modified (continuous lines) EPDM/CIIR blends at a precut of 2mm. –, 80/20; ▲, 60/40; ■, 40/60; ж, 20/80

5.4 Conclusions

Precuring chlorobutyl to a low level followed by blending with EPDM and then curing the blend is an efficient way of obtaining optimum crosslink density in both the elastomer phases and at the interphase. This may be due to the reduced curative migration from one phase to another. This novel route is found to improve the mechanical properties of EPDM/CIIR blends significantly over their conventional counterparts. The processing safety of the blend compounds is not affected by partial precuring.

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Chapter VI

Effect of Resin Curing on the Mechanical Properties of EPDM/CIIR Blends

6.1 Introduction

It has been a long term practice of the rubber technologist to find polymer compounds of desired processing and vulcanizate properties, as well as high performance. To achieve these objectives, rubber-rubber and rubber-plastic blends were studied by many researchers. A blend can offer a set of properties that may provide the potential of entering application areas not possible with either of the polymers comprising the blend. The effect of sulphur curing on the mechanical, thermal and steam ageing properties of ethylene-propylene-diene rubber (EPDM), chlorobutyl rubber (CIIR) and their various blends are reported in the earlier chapter. By chemical or physical processes, crosslinking forms a three-dimensional network structure which has a strong influence on the physical properties of polymers. Many scientists have established the factors which are important in determining the mechanical properties of blends.[1-4] It has been reported in the fourth chapter that for sulphur cured EPDM/CIIR blends under severe conditions, the properties, especially thermal ageing resistance and steam ageing resistance of NDR-4640 grade EPDM/CIIR blends is found to be inferior to that of 301-T grade EPDM/CIIR blends. This drop in properties may be due to the higher unsaturation of NDR-4640 grade EPDM. To use for high temperature applications such as curing bladder, conveyor belting for hot materials handling, high temperature service hoses etc. the hot air ageing resistance of these blends should be improved. It is known that, certain crosslinking systems, and specifically resin curing of NDR-4640/CIIR blends, provide vulcanized networks of outstanding heat resistance. It was not possible to vulcanize 301-T grade EPDM using resin, as it contains the diene, dicyclopentadiene. On the other hand, NDR-4640 grade EPDM contains the diene ethylidene norbornene and is resin curable. This chapter deals with the evaluation of properties of resin cured EPDM/CIIR blends before and after ageing, at various blend ratios and at various temperatures in comparison to sulphur cured vulcanizates.

6.2 Experimental

Mixing was done according to ASTM D 3182 (1982) as per the formulations given in tables 6.1. In this formulation neoprene serves as a halogen containing activator and zinc chloride is used as Friedel Craft catalyst for better resin curing in the case of EPDM.[5] The compounding was done on a laboratory two roll mixing mill at a friction ratio of 1:1.25 with cold water circulation. The optimum cure times of the compounds were determined at 170 °C using a Rubber Process Analyzer. The compounds were then vulcanized upto the respective optimum cure times in an electrically heated laboratory hydraulic press at 170 °C. The total crosslink density was determined by swelling in toluene as per the procedure outlined in chapter 2.[6,7]

Dumbbell shaped tensile test specimens and angular tear test specimens were punched out from the compression moulded sheets along the mill grain direction and their properties were measured at a cross head speed of 500 mm/min on a Shimadzu Universal Testing Machine (model-AG1) as per relevant ASTM standards. The ageing resistance and tension set of the vulcanizates were determined after ageing the samples at 100 °C for 24, 48, and 72 hours in a laboratory air oven. The steam ageing resistance of the vulcanizates was also studied using a steam chamber maintained at a pressure of one atmosphere and temperature of 100 °C for the time intervals 6, 18 and 36 hours.

Table 6.1. Compounding recipe

Ingredients	Concentration (phr)	Ingredients	Concentration (phr)
EPDM Rubber	95.0	CIIR Rubber	95.0
Neoprene	5.0	Neoprene	5.0
Reactive-		Reactive-	
Phenolic resin	10.5	Phenolic resin	10.5
Zinc chloride	2.0	ZnO	4.0
ZnO	4.0	Stearic acid	1.5
Stearic acid	1.5	Carbon black	40.0
Carbon black	40.0	Paraffinic oil	5.0
Paraffinic oil	7.0	Antioxidant	1.0
Antioxidant	1.0		

The hardness of the vulcanizate was determined according to ASTM 2240 and expressed in shore A units. Samples for abrasion resistance were moulded and weight loss/h was determined on a DIN abrader according to DIN 53514. Samples for compression set, flex crack resistance and rebound resilience were moulded and tested as per relevant ASTM standards.

6.3 Results and discussion

6.3.1 Cure characteristics and stress-strain properties

The cure characteristics and the physico-mechanical properties of resin cured NDR-4640/CIIR blends are given in table 6.2. It is evident that the maximum torque of resin cured blends is higher than those observed during sulphur curing. Also the cure times and scorch times of resin cured vulcanizates are longer than that of sulphur cured vulcanizates. It can be seen from table 6.2 that the maximum torque, cure time and scorch time increases with increase in NDR-4640 content of the blend while tensile strength, elongation at break and tear strength decreases with increase in NDR-4640 content. It is generally observed that the mechanical response of the blend is closely related to its compatibility and a synergistic effect is often obtained with miscible or partially compatible blends.[8,9] The tensile strength, elongation at break and tear strength values for resin cured vulcanizates show an additive variation indicating compatible behaviour. The tensile strength and tear strength of resin cured vulcanizates are remarkably higher than that of sulphur cured ones. When compared with sulphur cured blends, curative migration from one phase to another owing to viscosity and unsaturation differences is not significant in resin cured blends. This is probably due to the large size of phenolic resin molecules. This results in increased homogeneity of the blends leading to better properties.[5]

Table 6.2 Cure characteristics and stress-strain properties of resin cured and sulphur cured NDR-4640/CIIR blends

	Blend percentage of EPDM (%)	Cure time (min)	Scorch time (min)	Max. torque (Nm)	Min. torque (Nm)	Tensile strength (MPa)	Elong. at break (%)	Tear strength (N/mm)
Resin cured NDR/CIIR blends	0	17.4	2.7	0.380	0.048	20.1	596	37.1
	20	18.8	3.3	0.386	0.040	19.5	578	36.6
	40	19.6	3.8	0.395	0.042	18.9	562	35.8
	60	20.4	3.8	0.410	0.040	18.4	542	35.1
	80	21.3	4.2	0.421	0.042	17.9	530	34.6
	100	22.2	4.4	0.441	0.042	17.5	512	34.0
Sulphur cured NDR/CIIR blends	0	11.8	1.2	0.350	0.046	17.1	536	31.8
	20	11.6	1.2	0.324	0.039	18.1	1158	32.4
	40	14.4	1.3	0.329	0.039	19.0	1283	34.0
	60	15.6	1.3	0.332	0.040	17.8	1061	33.2
	80	12.4	1.2	0.327	0.041	16.3	868	32.1
	100	10.2	1.2	0.334	0.041	15.3	473	31.3

Figure 6.1 shows the variation of crosslink density of the vulcanizates with percentage of EPDM in the blends under sulphur cured and resin cured conditions. In both cases, the total crosslink density increases with increase in EPDM content in the blend. But compared to the sulphur cured vulcanizates, the extent of crosslinking is less for resin cured vulcanizates probably due to the decreased number of reactive sites in the case of phenolic resin curing.

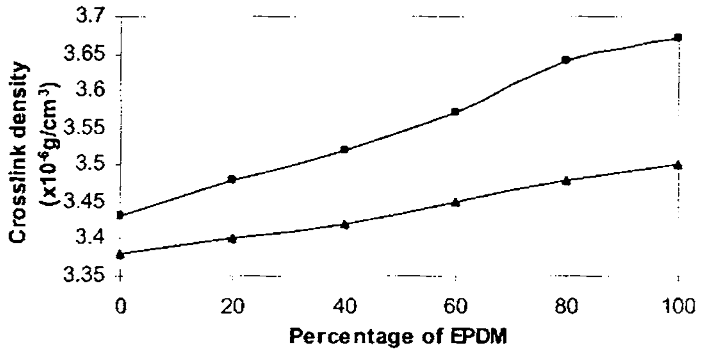

Figure 6.1 Variation of crosslink density of EPDM/CIIR blends with EPDM content. ▲, resin cured and ■, sulphur cured blends

6.3.2 Thermal and Steam ageing resistance

EPDM/CIIR vulcanizates, with various compositions, were subjected to thermal ageing at 100 °C for periods of upto 72 hours. The results from aged samples were plotted against percentage composition of EPDM as illustrated in figures 6.2-6.4 respectively. As expected, the resin cured blends exhibit outstanding heat resistance when compared with their sulphur cured counterparts.[10] It can be seen that the tensile strength and tear strength values of pure EPDM and blends containing higher percentage of EPDM exhibits better retention in properties than that of pure CIIR and blends containing higher percentage of chlorobutyl. This is because the resin curing system always shows a marching cure till it attains some saturation point. Chlorobutyl compound attains the saturation point faster than the EPDM compound and then it reverts.[11] The better retention in tensile strength and tear strength values of pure EPDM and vulcanizates containing higher percentage of EPDM can be explained on the basis of the increased crosslink density achieved because of the marching cure.[12] The elongation at break shows similar behaviour due to the increased crosslink density during ageing.

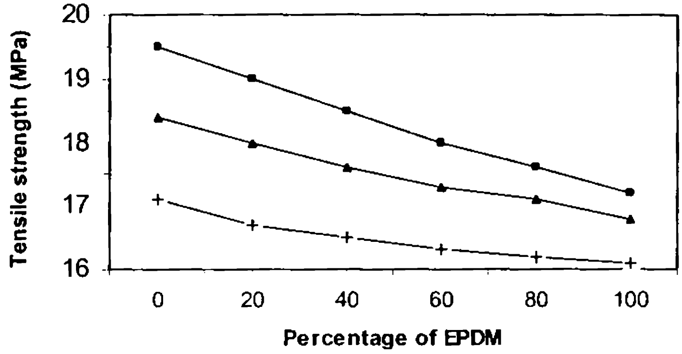

Figure 6.2 Variation of tensile strength with ageing for resin cured EPDM/CIIR blends. ■, 24 hours; ▲, 48 hours and +, 72 hours of ageing

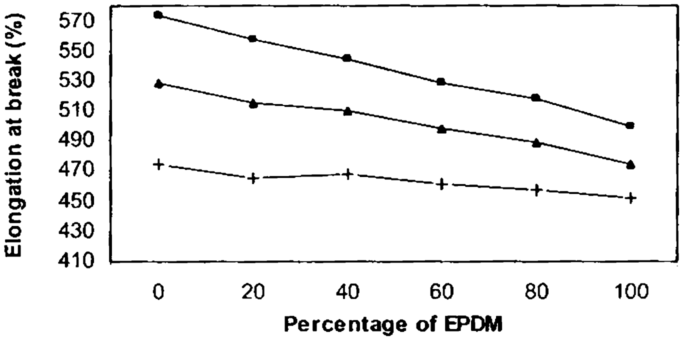

Figure 6.3 Variation of elongation at break with ageing for resin cured EPDM/CIIR blends. ■, 24 hours; ▲, 48 hours and +, 72 hours of ageing

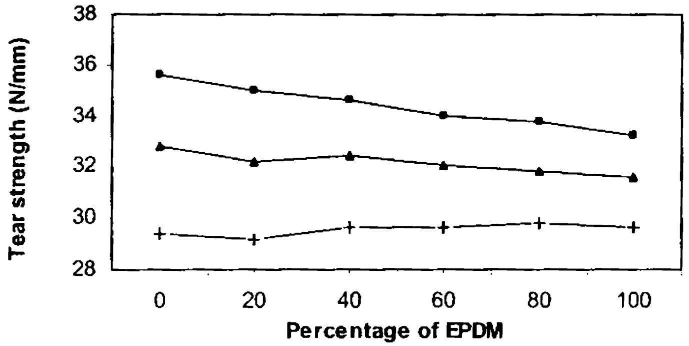

Figure 6.4 Variation of tear strength with ageing for resin cured EPDM/CIIR blends. ■, 24 hours; ▲, 48 hours and +, 72 hours of ageing

The effect of steam ageing on tensile and tear properties of the blends is shown in figures 6.5 and 6.6 respectively. As in the case of thermal ageing, the steam ageing resistance is higher for blends with higher percentage of EPDM. The resin cured blends exhibit improved properties compared to that of sulphur cured blends. As expected due to the elimination reaction occurring in halogenated compounds, which is severe during steam ageing, there is no significant improvement in the values for chlorobutyl and blends containing higher percentage of chlorobutyl even under resin curing conditions.[13-16]

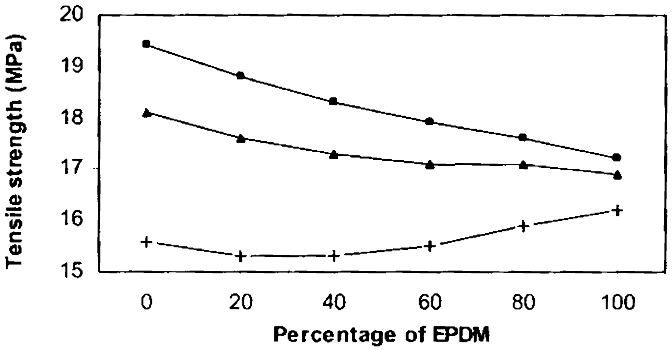

Figure 6.5 Effect of steam ageing on tensile strength for resin cured EPDM/CIIR blends. ■, 6 hours; ▲, 18 hours and +, 36 hours of steam ageing

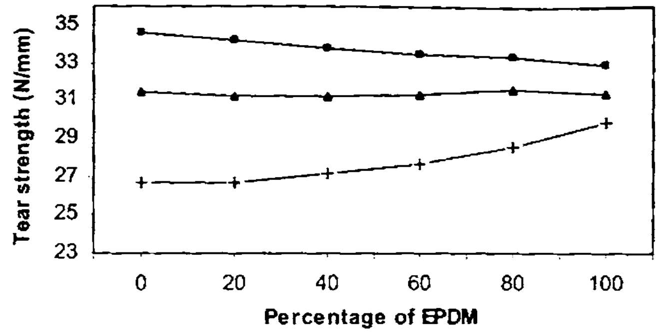

Figure 6.6 Effect of steam ageing on tear strength for resin cured EPDM/CIIR blends. ■, 6 hours, ▲, 18 hours and +, 36 hours of steam ageing

6.3.3 Physical properties

Figure 6.7 and table 6.3 shows, respectively, the compression set and tension set values of the resin cured blends with composition. As the chlorobutyl content increases, compression set decreases which is an inherent property of chlorobutyl rubber. The resin cured blends display higher compression set values compared to sulphur cured blends, probably due to the less extent of crosslinking in the resin cured blends. Although the resin cured blends exhibit inferior compression set properties, the low tension set which is a major property required for a good bladder compound is achieved by resin curing. The values are far better than that of sulphur cured blends which may be due to the better ageing resistance of resin cured vulcanizates strengthening the network by post curing.

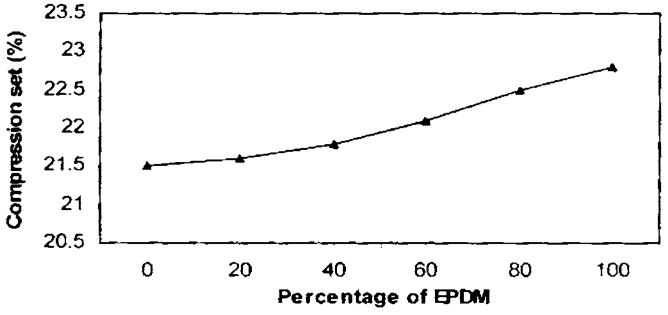

Figure 6.7 Variation of compression set with percentage of EPDM for resin cured EPDM/CIIR blends

Table 6.3 Variation of tension set with percentage of EPDM for sulphur cured and resin cured EPDM/CIIR blends

Percentage of EPDM (%)	Tension set values for sulphur cured blends (%)			Tension set values for resin cured blends (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
0	-	-	-	76	122	-
20	97.5	-	-	88	128	-
40	117	-	-	94	136	144
60	128	-	-	98	126	132
80	136	-	-	112	132	136
100	141	158	-	118	138	142

Hardness and abrasion resistance of the resin cured vulcanizates are higher than that of sulphur cured vulcanizates. Figure 6.8 shows the variation of hardness and figure 6.9 shows the variations of abrasion resistance with blend composition for sulphur cured and resin cured EPDM/CIIR blends. On increasing the concentration of EPDM, the elasticity of rubber chains get reduced leading to increased hardness. For a given rubber compound in addition to crosslink density, abrasion resistance is influenced by hardness of the vulcanizate.[17,18] Hence the abrasion resistance also increases with increase in EPDM content of the blend.

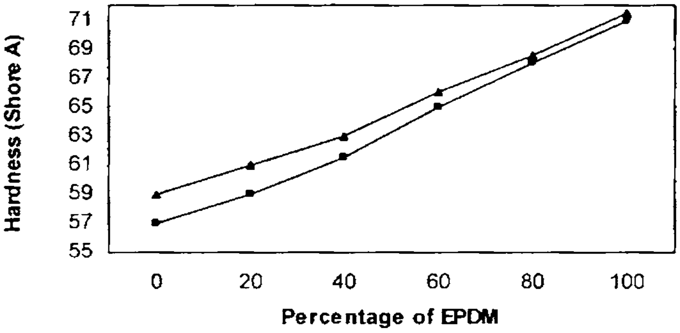

Figure 6.8 Variation of hardness with percentage of EPDM for EPDM/CIIR blends. ■, sulphur cured and ▲, resin cured blends

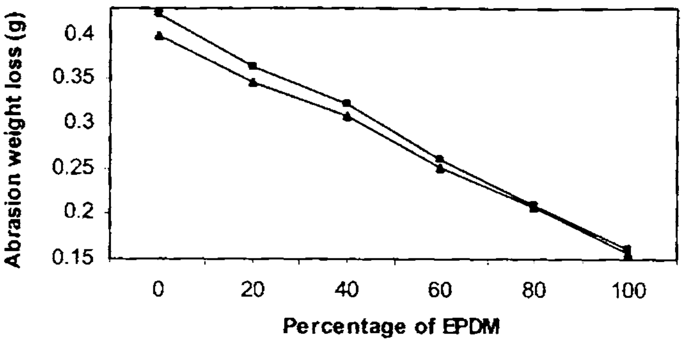

Figure 6.9 Variation of abrasion weight loss with percentage of EPDM for EPDM/CIIR blends. ■, sulphur cured and ▲, resin cured blends

The results of rebound resilience with blend composition for resin cured and sulphur cured blends are shown in figure 6.10. Compared with sulphur cured blends there is only slight variation for the resin cured blends because resilience is primarily an inherent property of the elastomer. As expected, the resilience value decreases with increase in chlorobutyl content related to the inherent high strain energy density of chlorobutyl. The viscoelastic properties of CIIR are a reflection of the molecular structure of the polyisobutylene chain. This molecular chain with two methyl side groups on every other chain carbon atom possesses greater delayed elastic response to deformation.[19,20]

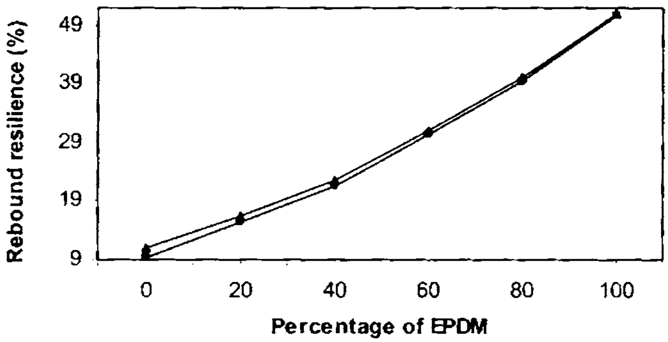

Figure 6.10 Variation of rebound resilience with percentage of EPDM for EPDM/CIIR blends. ■, sulphur cured and ▲, resin cured blends

The Increment in cut length against number of flexing cycles is given in figure 6.11. The results showed that the resin cured vulcanizates have a higher cut growth resistance than the sulphur cured ones. In addition to the improved interaction between the rubber matrices, the crosslinking in resin curing was by activated phenolic resin, so that the crosslinks formed are much flexible compared to the S-S bonds formed in the case of sulphur curing. With the increase in chlorobutyl content, the flex crack resistance increases which is due to its inherent high viscoelastic nature.[21,22]

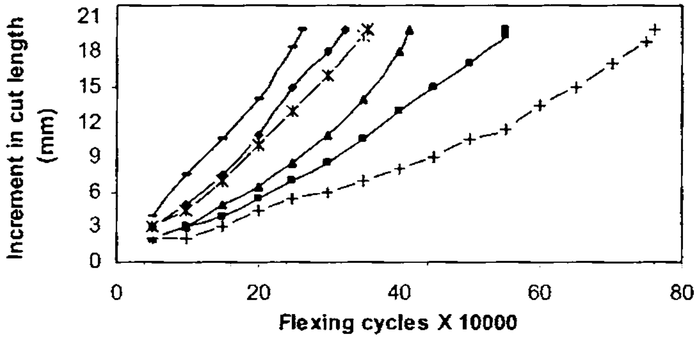

Figure 6.11 Plot of increment in cut length against flexing cycles for resin cured EPDM/CIIR blends at a precut of 2.0 mm. –, 100/0; ♦, 80/20; ⋇, 60/40; ▲, 40/60; ■, 20/80; +, 0/100

6.4 Conclusions

The mechanical properties of EPDM/CIIR blends, which are influenced by uniform crosslinking of both the phases and in the interphase were remarkably improved by resin curing. This is due to the reduced curative migration owing to the larger size of the phenolic resin molecules when compared with the curatives used in sulphur curing. The properties are found to be an average of the component elastomers. Of all the properties studied the best performance by resin cured vulcanizates over sulphur cured counterparts is in the outstanding thermal ageing resistance due to the superior thermal degradation resistance of phenolic resin linkages.

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Chapter VII

Rheology, Air Permeability, Thermal Stability and Thermal Diffusivity Studies on EPDM/CIIR Blends

7.1 Introduction

The processability and typical applications of the blends for use in envelope for precured retreading are investigated in this chapter. It has been reported that flow behaviour of polymer melts depends mainly on molecular characteristics, flow geometry and processing conditions such as temperature, shear rate or frequency.[1-18]

The basic requirement for a pneumatic tube or an envelope is that it must be highly impermeable to air. Several methods can be used for developing new materials for commercial applications; among these are the synthesis of new polymers, copolymerization and blending of miscible polymers etc.[19] Permeation properties are sensitive to changes in membrane structure such as crystallinity, crosslinking, additives and phase morphology.[20-26]

Thermal degradation resistance of polymers is another important parameter for testing the suitability of the material for retreading envelope. Fabrication of a variety of articles and their end uses need a detailed understanding of the thermal degradation of polymers.[27,28] For products like curing envelope, curing diaphram etc. the thermal conductivity is a significant parameter because it is the heat generated within the envelope/diaphram that is transferred to the tyre during vulcanization. In this study, photo thermal deflection (PTD) technique is used to determine the thermal diffusivity of compounds.[29-31]

In the first part of this chapter, the rheological characteristics of EPDM and chlorobutyl rubbers at different blend compositions over a wide range of temperatures, shear rates and various curing conditions are investigated. The extrudate die swell is also investigated to study the elastic behaviour of the blends. In the second part of the chapter, the air permeation characteristics of EPDM/CIIR blends under sulphur curing, pre-curing and resin curing conditions is investigated. In the third part, the thermal stability of EPDM/CIIR blends under varying curing conditions is investigated along with the effect of blending on thermal stability. In the concluding part, the thermal diffusivity of various blend compounds is evaluated and methods to improve the thermal diffusivity are also explored.

7.2 Experimental

The compounds for sulphur cured, precured and resin cured blends were prepared according to ASTM-D 3182 on a laboratory mixing mill (16 × 33 cm) at a friction ratio of 1:1.25. The rheological measurements were carried out using a capillary rheometer MCR 3210 attached to the Shimadzu Universal Testing Machine (model-AG1). From the recorded force and the cross head speed of the plunger, shear stress, shear rate and the shear viscosity were calculated. The diameter of the extrudate after 48 hours of extrusion and the swelling index were determined. The cure curves of the mixes were taken at 170 °C using a Rubber Process Analyzer. The compounds were then vulcanized up to the respective optimum cure times on an electrically heated laboratory hydraulic press at 170 °C. Permeability measurements were carried out according to ASTM D 1434 (1982) using air at a flow rate of 500 ml/minute. Test specimens of thickness 2 mm were moulded and used for measurements. The reading was taken at both 40 °C and 70 °C respectively. The equipment used was Lyssy Manometric Gas Permeability Tester (L 100-2402). The thermal stability of EPDM, chlorobutyl and their blends were studied by thermogravimetric analyzer (TGA Q-50, TA Instruments). The thermogravimetric analysis was carried out under nitrogen atmosphere and samples were scanned from 30-600 °C at a heating rate of 10 °C/minute. A constant sample weight was used in all cases. Thermal diffusivity of the material is determined by photo thermal deflection

(PTD) technique in which samples of 2 mm thickness and 1 cm diameter were used. Effect of thermal ageing at 100 °C for 24 hours and 48 hours on thermal diffusivity was also studied. To improve the thermal diffusivity of the blends, 1 phr of boron nitride was added and the effect of its addition on thermal diffusivity was also studied.

7.3 Results and discussion

7.3.1 Rheological characteristics

Figure 7.1 shows the plots of shear viscosity versus shear rate at 100 °C for filled 50/50 EPDM/CIIR blends under sulphur curable, partially precured and resin curable conditions. For all systems the shear viscosity falls sharply with increasing shear rate, confirming pseudoplastic flow behaviour of the systems. As expected, the partially precured blend exhibits highest shear viscosity as it contains partially cured chlorobutyl. The slightly higher value for resin curable blends when compared to the sulphur curable counterparts may be attributed to the presence of entangled long chain resin molecules.

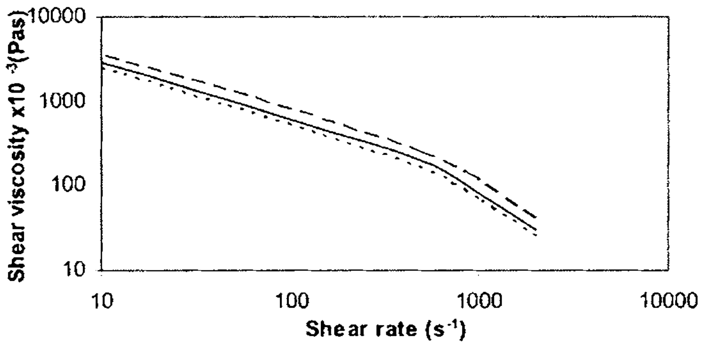

Figure 7.1 Variation of shear viscosity with shear rate for 50/50 EPDM/CIIR blends. ----, sulphur curable , ——, resin curable and — — —, partially precured blends

Figure 7.2 is a plot of shear viscosity against shear rate of sulphur curable 50/50 EPDM/CIIR blend at different temperatures. In all cases the viscosity drops with shear rate showing typical pseudoplastic behaviour of the systems. At high shear rates the temperature has little effect on viscosity and all the points converges to a small area. The convergence occurs at around 1000 s^{-1}. So it is clear that at high shear rate (above 1000 s^{-1}), temperature is not a critical parameter for controlling the flow properties of blends of EPDM and CIIR. This may be due to the fact that at higher shear rates, the stress alignment of the long and coiled chains occurs thereby reducing the resistance to flow and thus lowering down the viscosity. This shear effect is much higher than the temperature effect.

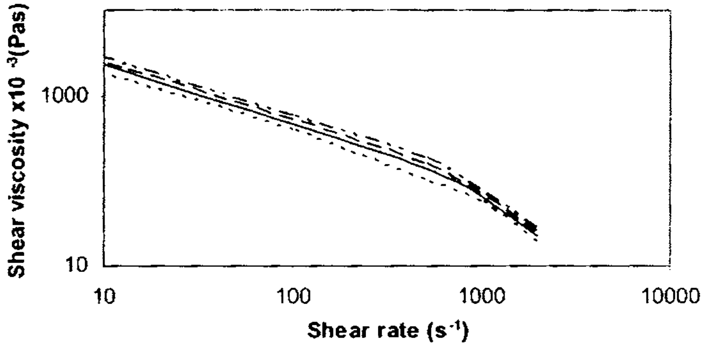

Figure 7.2 Shear viscosity against shear rate of sulphur curable 50/50 EPDM/CIIR blends. ----, 120 °C; ———, 110 °C; – – –, 100 °C; and – .. – .., 90 °C

Figure 7.3 shows the effect of blend ratio on shear viscosity of sulphur curable blends at two different shear rates. At both shear rates, the shear viscosity increases with EPDM content and show maximum value for 100 % EPDM. The viscosities of the blends fall in between that of pure components which further indicates the compatible behaviour of the blends. The change in viscosity with EPDM content is much higher at higher shear rate (501 s^{-1}) than that at lower shear rate (100 s^{-1}). Since EPDM possesses higher viscosity than CIIR, the drop in viscosity with shear rate is also high in the case of EPDM. This may be due to the severe wall slip mechanism in the case of EPDM.[8] At high shear rate, this wall slip is severe and hence the reduction in viscosity is more compared to that at low shear rate.

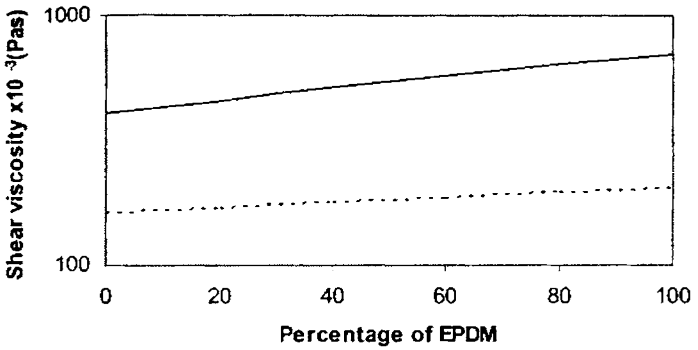

Figure 7.3 Variation of shear viscosity of EPDM/CIIR blends with percentage of EPDM at 100 °C. ----, shear rate of 501 s^{-1}; ——, shear rate of 100 s^{-1}

The extrudate swell characteristics at 100 °C for sulphur curable, resin curable and partially precured 50/50 EPDM/CIIR blends at varying shear rates are shown in figure 7.4. It is evident from the figure that die swell is maximum for sulphur curable and least for the partially precured blend. Due to the partial crosslinking of the CIIR phase, the partially precured blend exhibits better dimensional stability. The low value of resin curable blend when compared with that of sulphur curable may be due to the presence of entangled resin molecules which reduces the dimensional fluctuation thereby lowering the swelling index.

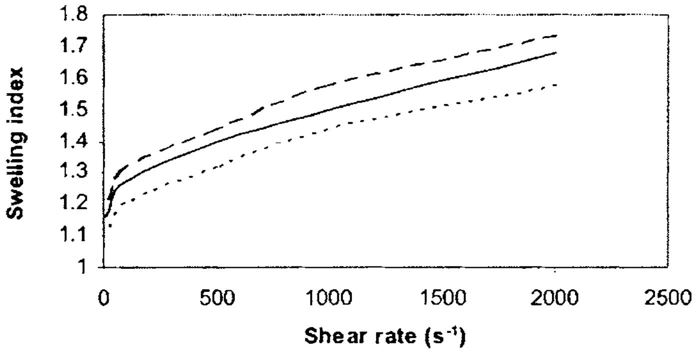

Figure 7.4 Plot of extrudate swelling index against shear rate of 50/50 EPDM/CIIR blends at 100 °C under varying curing conditions. ----, patially precured; ——, resin curable and — — —, sulphur curable blends

Figure 7.5 shows the variation of extrudate die swell for sulphur curable blends at 100 °C at different rates of extrusion. At low shear rates, the die swell decreases marginally with increase in CIIR content in the blends. But at high rate of extrusion, a reverse trend results; the die swell increases sharply with increasing CIIR content in the blends. This may be due to the fact that the elastic response of CIIR is much higher than that of EPDM. At high shear rates the behaviour is more significant as expected. This response gives rise to high die swell at high rate of extrusion for pure CIIR and blends containing higher amount of CIIR.

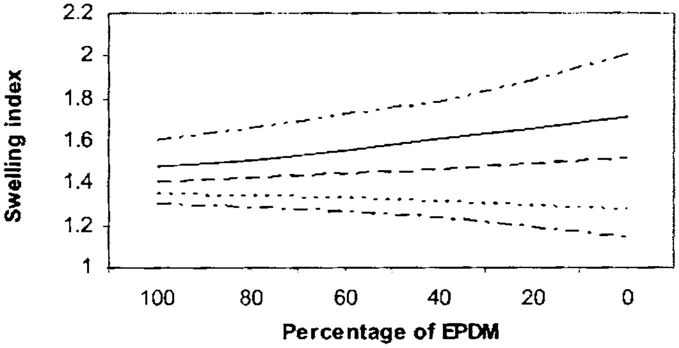

Figure 7.5 Plot of extrudate swelling index of EPDM/CIIR blends with percentage of EPDM at varying shear rates. — -, 10 s^{-1}; ---, 100 s^{-1}; — —, 500 s^{-1}; ——, 1000 s^{-1} and — - -, 2000 s^{-1}

7.3.2 Air permeability

The air permeabilities of sulphur cured, precured and resin cured EPDM/CIIR blends at 40 °C for varying blend compositions are given in figure 7.6. There is an almost linear variation in permeability with blend composition with highest permeability for resin cured vulcanizate and lowest for the precured one. The air permeation behaviour for the various vulcanizates follows the order resin cured > sulphur cured > precured. In both sulphur cured and precured vulcanizates, efficient vulcanizing system is used resulting in the formation of higher percentage of stable monosulphidic crosslinks. By precuring the curative migration is greatly reduced resulting in vulcanizates with increased crosslink density. This results in stable and compact structure when compared with the sulphur cured blends. For the resin cured vulcanizates, the crosslink density is comparatively low. Moreover the percentage free volume is more due to the bulkier phenolic resin linkages. As the number of crosslinks per unit volume of the polymer molecules increases, it becomes very difficult for the gas molecules to pass through the tightly crosslinked system. Therefore, crosslink density and partly, the nature of crosslinks, influence the gas permeation behaviour. The variation of permeability values of the blends at 70 °C with EPDM content are shown in figure 7.7. As expected, the permeability values increase for the three types of vulcanizates with EPDM content, the significant increase being for resin cured vulcanizate. With increase in temperature the flexibility of the chains increases resulting in an increased free volume. This effect is more pronounced in the resin cured vulcanizates as the chains are more flexible leading to an increased air permeability when compared with sulphur cured and precured blends.

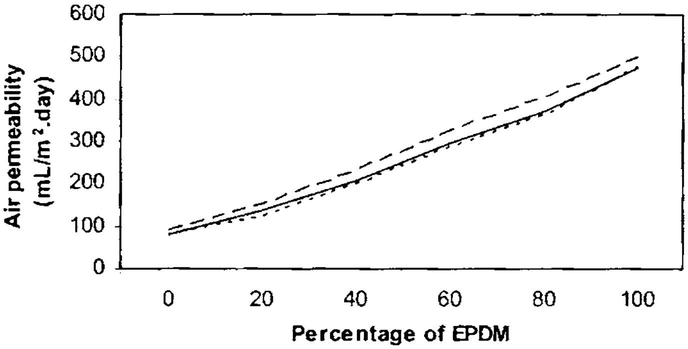

Figure 7.6 Variation of air permeability at 40 °C for EPDM/CIIR blends under varying curing conditions. -----, precured; ———, sulphur cured and — — —, resin cured blends

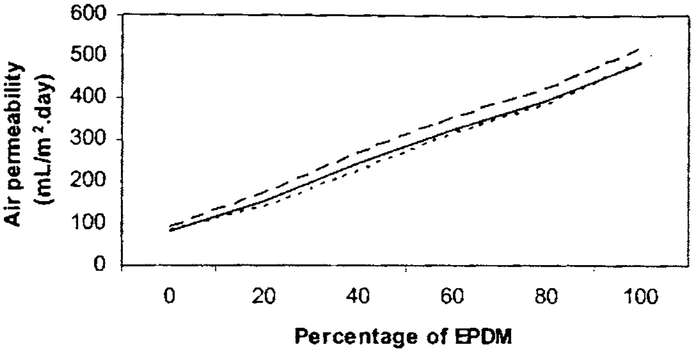

Figure 7.7 Variation of air permeability at 70 °C for EPDM/CIIR blends under varying curing conditions. -----, precured; ______ , sulphur cured and — — —, resin cured blends

7.3.3 Thermal stability

Thermogravimetric plots for sulphur cured EPDM, CIIR and their blends are given in Figure 7.8. The degradation behaviour of the blends is different from that of the individual components. The blends are found to possess superior stability compared to the components. It has been reported that improved stability can be achieved by the incorporation of a second polymer.[32] This is attributed to the fact that in the pyrolysis of EPDM/CIIR blends, each component degrades in a manner different from that observed when EPDM and CIIR are degraded individually. It can be explained by assuming that small radicals that are generated by chain scission in the first stage of degradation in one elastomer phase diffuse into the second elastomer phase, hydrogen abstraction takes place, and the radicals which would normally contribute to degradation of the elastomer phases are thus stabilized.[33] But the products of pyrolysis are identical both qualitatively and quantitatively.

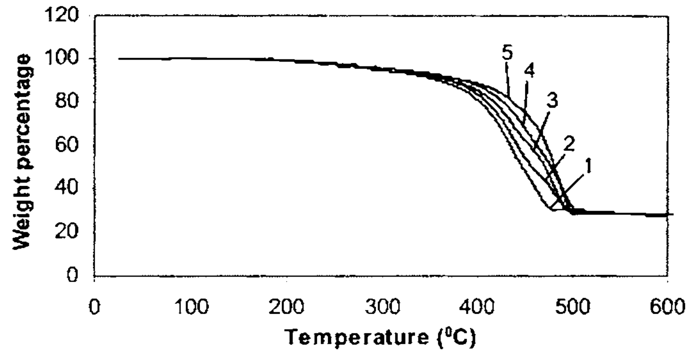

Figure 7.8 TGA curves of sulphur cured EPDM, CIIR and their blends. (1), 100 % CIIR; (2), 100 % EPDM; (3), 25/75 EPDM/CIIR blend; (4), 50/50 EPDM/CIIR blend and (5), 75/25 EPDM/CIIR blend

The onset decomposition temperatures (T_{10}), temperature corresponding to 50 % degradation (T_{50}) and peak decomposition temperatures corresponding to the peak value in the DTG curve (T_d) for sulphur cured EPDM, CIIR and their blends are given in figure 7.9. Both T_{10} and T_d of the blends increase with increase of percentage of EPDM in the blends. That is, the thermal stability of the various blends and elastomers can be ranked as follows: 75/25 EPDM/CIIR blend, 50/50 EPDM/CIIR blend, 25/75 EPDM/CIIR blend, EPDM, CIIR. This may be attributed to the high degree of thermal resistance of EPDM compared to that of pure CIIR.

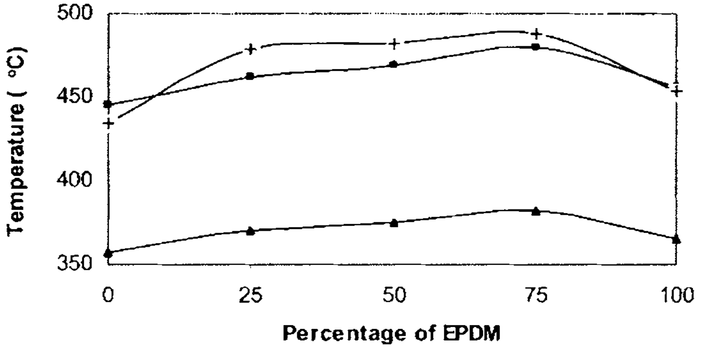

Figure 7.9 Decomposition temperatures of sulphur cured EPDM, CIIR and their blends. ▲, T_{10}; ■, T_{50} and +, T_d

Figure 7.10 shows the TGA curves of sulphur cured, precured and resin cured 50/50 EPDM/CIIR blends. The characteristic degradation temperatures obtained from TGA curves are summarized in table 7.1. The onset degradation temperature i.e. after 10 % of degradation and the degradation temperature obtained from the peak value of the DTG curve and temperature corresponding to 50 % of degradation are found to be highest for resin cured and lowest for sulphur cured vulcanizates. On comparing the decomposition pattern, resin cured blends exhibit the highest degradation resistance, followed by precured and finally for sulphur cured blends. The enhancement in thermal stability of precured blends than the conventional sulphur cured blends may be due to the improved compatibility of the component elastomers caused by the reduced curative migration. The superior thermal stability of resin crosslinked vulcanizates is due to the formation of C-O-C linkages, which are more thermally stable than C-S-C linkages in conventional sulphur cured and precured vulcanizates.

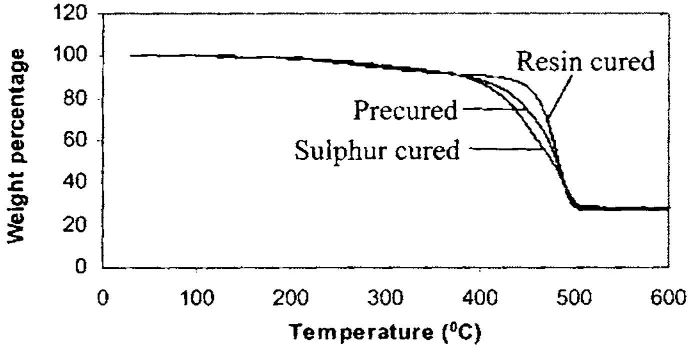

Figure 7.10 TGA curves for sulphur cured, precured and resin cured 50/50 EPDM/CIIR blends

Table 7.1 Decomposition temperatures of 50/50 EPDM/CIIR blends under varying curing conditions

Curing condition	Onset degradation temperature, T_{10} (°C)	Temperature corresponding to 50 % degradation, T_{50} (°C)	Peak decomposition temperature, T_d (°C)
Sulphur curing	374.63	468.39	479.28
Precuring	383.72	477.54	483.22
Resin curing	416.79	484.55	486.03

7.3.4 Thermal diffusivity

Figure 7.11 shows the variation of thermal diffusivity of EPDM/CIIR blends under unaged conditions and after 24 and 48 hours of ageing. Even though CIIR is slightly polar, the thermal conductivity value is maximum for EPDM and blends containing higher percentage of EPDM possibly due to the increased extent of interaction between EPDM and carbon black. The thermal diffusivity values increase marginally with ageing. This is probably due to the post vulcanization reaction which strengthens the network thereby making the structure more rigid and compact so that the thermal vibrations can more easily pass through the material.

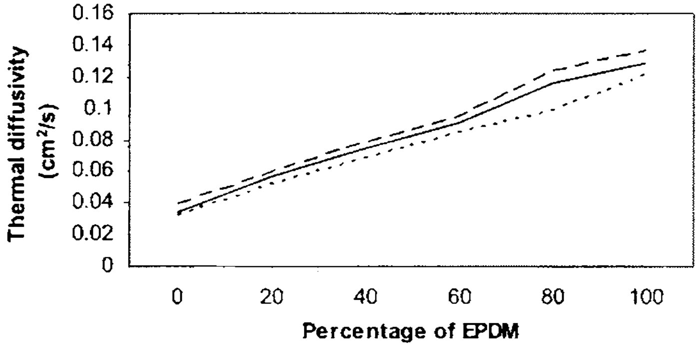

Figure 7.11 Variation of thermal diffusivity of EPDM/CIIR blends with percentage of EPDM. ----, unaged; ——, 24 hours of ageing and — — —, 48 hours of ageing

The effect of addition of one phr of boron nitride on thermal diffusivity of the blend compounds is shown in figure 7.12. As seen from the figure, the addition of boron nitride increases the thermal diffusivity of all the compounds abruptly. The highest fluctuation is shown by EPDM. Boron nitride resembles graphite in its structure and the presence of free electrons enhances the thermal diffusivity of the samples. These results are highly attractive, especially for products like curing diaphragms, envelopes etc. where the increased thermal diffusivity not only enhances the green tyre curing rate but also may reduce the extent of bladder degradation.

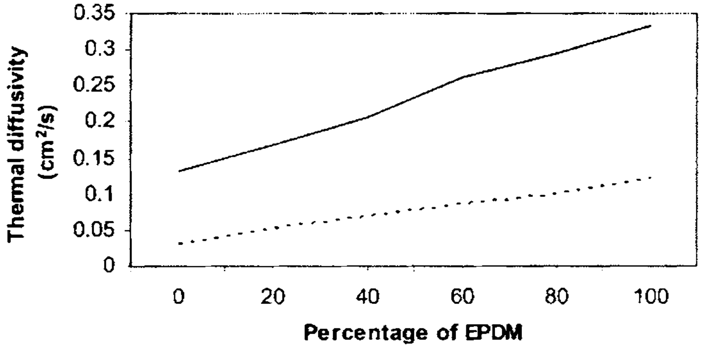

Figure 7.12 Effect of boron nitride on thermal diffusivity of EPDM/CIIR blends. ——, samples containing boron nitride and ----, samples without boron nitride

7.4 Conclusions

The study shows that, among the precured, sulphur cured and resin cured blends, highest shear viscosity, minimum die swell and lowest air permeability are observed for precured blends which indicate the superiority of the precured blends compared to the conventional blends while the thermal degradation resistance is maximum for resin cured vulcanizates. Thus, it can be concluded that the thermal degradation resistance of EPDM/CIIR blends can be improved by resin curing whereas better air impermeability and retention of dimensional stability can be achieved by precuring. Among the sulphur cured blends, lowest air permeability is for chlorobutyl whereas highest thermal degradation resistance, thermal diffusivity and shear viscosity is for EPDM. The thermal diffusivity can be improved by the addition of boron nitride. In general, the blends exhibit an additive behaviour and a compromise of properties can be attained by using a blend containing 60 % EPDM and 40 % CIIR.

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Chapter VIII

Summary and Conclusions

The main objective of this work has been to develop blends of EPDM and CIIR rubbers to utilize the high ageing resistance of EPDM and the air impermeability of CIIR. Compatibility, morphology and physical properties of the blends were investigated as a function of blend composition and curing systems. The major conclusions of the study are summarized below.

The degree of compatibility of different grades of EPDM with a particular grade of CIIR was investigated. From the analysis of mechanical properties and ageing resistance it was found that, out of the four grades used, two grades of EPDM (301-T and NDR-4640) are compatible with CIIR. The morphological studies justified this observation. This behaviour is explained on the basis of the comparable viscosities and extent of unsaturation of the components of these blends. Both these blends give rise to an additive behaviour of mechanical properties with blend composition suggesting covulcanisation. The effect of compatibiliser, chlorosulfonated polyethylene (CSPE), on the comparatively less compatible EPDM/CIIR blends was investigated. The resulting blends were characterized for their morphological and mechanical properties. The results obtained from the various analysis suggest that 10 phr of CSPE can be effectively used as a compatibiliser for certain incompatible EPDM/CIIR blends.

A detailed study on the physical properties of sulphur cured blends of EPDM and CIIR with respect to blend ratio, ageing resistance etc. have been conducted. The sulphur cured EPDM/CIIR vulcanizates are found to display linear or better variation in mechanical, physical and other properties with blend composition. Although good mechanical properties are exhibited by NDR-4640/CIIR blends, their thermal and steam ageing resistance is low. On the other hand, resilience, flex crack resistance and ageing resistances are better for 301-T/CIIR blends which is probably due to the comparatively low viscosity and more saturated nature of 301-T. Based on the physical property studies, 301-T/CIIR blends are found to be most promising for high temperature applications such as curing envelopes, conveyor belts etc.

Two methods have been tried to further improve the mechanical properties of compatible blends of EPDM with CIIR. Both the methods directed at developing a satisfactory network structure in each of the phases and at the interface.

First method investigated was precuring of the CIIR or EPDM phase to a low level prior to blending so that optimum crosslink densities can develop in both elastomer phases and at the interface after final curing. The distribution of curing agents and fillers in both the components of an elastomer blend plays a vital role in determining the curing behaviour and vulcanizate properties of the blend. The distribution of curatives and fillers largely depends on the nature of elastomers. It was found that precuring chlorobutyl to a low level followed by blending with EPDM and then curing the blend is an efficient way of obtaining optimum crosslink density in both the elastomer phases and in the interphase. Precuring possibly slowed down the migration of curatives from CIIR to EPDM. This novel route is found to improve the mechanical properties of EPDM/CIIR blends significantly over their conventional counterparts. The processing safety of the blend compounds was not affected by precuring.

Second method adopted was resin curing of NDR-4640/CIIR blends. It is known that resinous linkages provide vulcanized networks of outstanding heat resistance. It was found that in addition to the improved ageing resistance, the mechanical properties, which are influenced by uniform crosslinking of both the phases and in the interphase are remarkably improved by resin curing. This may be due to the reduced curative migration owing to the larger size of phenolic resin molecules when compared with the curatives used in sulphur curing. The properties are found to be a weighted average of the properties of the component elastomers. Considering the remarkable improvement in the ageing resistance during resin curing over sulphur cured counterparts, the resin cured blends form a very useful class of rubbers for high temperature applications.

In the concluding chapter, investigations on the processability and the specific requirements of the blends inorder to use them for fabrication of products such as curing envelope are discussed.

The rheological evaluation showed that among the precured, sulphur cured and resin cured blends, highest shear viscosity and minimum die swell are observed for precured blends and maximum for sulphur cured blends. The shear viscosities of both pure systems and blends decrease with increase in shear rate at all temperatures. At high shear rates the temperature has little effect on viscosity and all the points converges to a small area. This shows that effect of shear surpasses the effect of temperature for controlling the flow properties of blends of EPDM and CIIR. The viscosity of pure CIIR is lower than that of pure EPDM at higher shear rates and the viscosities of the blends were in between that of pure components. At low shear rate at 100 °C, the die swell decreased slowly with increase in CIIR content in the blends but at higher shear rate, the die swell increased with increase in both temperature and CIIR content in the blends.

The thermal degradation resistance is the maximum for resin cured EPDM/CIIR vulcanizates and highest thermal degradation resistance was for blends containing higher percentage of EPDM than that of pure EPDM. Thus blending improved the thermal degradation resistance of elastomers. Air permeability was found to be minimum for precured blends and among them, least air permeability was for blends containing higher percentage of chlorobutyl.

The thermal diffusivity was highest for EPDM and blends containing higher percentage of EPDM, possibly due to the increased extent of interaction between

EPDM and carbon black. The thermal diffusivity values increased slightly with ageing. The thermal diffusivity of elastomers and their blends can be improved significantly by the addition of small amounts of boron nitride. This is highly attractive, especially for products like curing diaphrams, envelopes etc. where the increased thermal diffusivity not only enhances the green tyre curing rate but also may reduce the extent of bladder degradation. In general, the blends exhibit an additive behaviour and an optimum compromise of properties can be attained by using a blend containing 60 % EPDM and 40 % CIIR.

It can be concluded that 60/40 EPDM/CIIR blend can be used for the high temperature applications especially for the manufacture of hot air curing envelopes as this particular blend composition satisfies the required envelope features in terms of tensile strength, tear strength, ageing resistance, flex crack resistance, thermal diffusivity and air permeability. Therefore it is possible to fabricate curing envelopes having attractive properties with this blend.

LIST OF ABBREVIATIONS AND SYMBOLS

ASTM	American society for testing and materials
BIIR	Bromobutyl rubber
BR	Polybutadiene rubber
CBS	N-cyclohexyl-2-benzthiazyl sulphenamide
CIIR	Chlorobutyl rubber
CR	Chloroprene rubber
CSPE	Chlorosulfonated polyethylene
DPG	Diphenyl guanidine
DCPD	Dicyclopentadiene
DMA	Dynamic mechanical analyzer
DSC	Differential scanning calorimeter
EA	Elastomeric alloys
EPDM	Ethylene-propylene-diene terpolymer
EPM	Ethylene-propylene copolymer
ENB	Ethylidene norbornene
HAF	High abrasion furnance
IIR	Butyl rubber
MBT	Mercapto benzthiazole
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
PET	Polyethylene terephalate
PTD	Photo thermal deflection
PMMA	Poly methyl methacrylate
PPO	Poly (2,6-dimethyl-1,4-phenylene oxide)
PVC	Polyvinyl chloride
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscope
TEM	Transmission electron microscope

TETD	Tetra ethyl thiuram disulphide
TGA	Thermogravimetric analyzer
TMTD	Tetramethyl thiuram disulphide
UTM	Universal testing machine
ZDC	Zinc diethyl dithiocarbamate

A_p	Cross-sectional area of plunger
A_o	Weight of the absorbed solvent
C	Specific heat capacity
D	Thermal diffusivity
d_c	Diameter of the capillary
d_e	Diameter of the extrudate
D_r	Deswollen weight
E'	Storage modulus
E"	Loss modulus
F	Force applied at a particular shear rate
l_c	Length of the capillary
k	Thermal conductivity
M_c	Number average molecular weight of rubber chains between crosslinks
phr	Parts per hundred rubber
P_m	Air permeability of sample
P_r	Air permeability of reference
q	Volumetric flow rate
rpm	Revolutions per minute
t_r	Air permeance time for the reference
t_s	Air permeance time for the sample
T_g	Glass transition temperature
V_e	Volume of extrudate
V_r	Volume fraction of rubber in the solvent swollen sample

V_{ro}	Value of V_r for filled vulcanizates
V_s	Molar volume of solvent
ΔE_m	Internal energy change during mixing
ΔG_m	Free energy change during mixing
ΔH_m	Enthalpy change during mixing
ΔS_m	Entropy change during mixing
τ_w	Shear stress at wall
γ_w	Shear rate at wall
n'	Flow behaviour index
γ_{wa}	Apparent shear rate at wall
η	Shear viscosity
$\tan \delta$	Loss tangent
φ	Volume fraction of component
χ	Polymer-solvent interaction parameter
ρ_r	Density of rubber
ρ_s	Density of solvent
δ_s	Solubility parameter

PUBLICATIONS AND PRESENTATIONS

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