APPLICATIONS OF CARDANOL IN RUBBER PROCESSING

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Certificate

This is to certify that the thesis entitled "Applications of cardanol in rubber processing" which is being submitted by Mary Alexander in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22 is a record of the bonafide research work carried out by her under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Cochin-682 022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

Dr. Eby Thomas Thachil (Supervising Teacher)

DECLARATION

I hereby declare that the work presented in this thesis entitled "Applications of cardanol in rubber processing" is based on the original research work carried out by me under the guidance and supervision of Dr. Eby Thomas Thachil, Reader, Department of Polymer Science And Rubber Technology, Cochin University of Science and Technology, Cochin-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

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PREFACE

Cardanol is a substituted phenol obtained by the vacuum distillation of cashew nut shell liquid (CNSL). It is a feasible alternative to petrochemically derived phenol for many applications. This thesis is on the utilization of this substance for various rubber processing applications. It consists of six chapters. The first chapter consists of introduction and literature survey. The utilization of cardanol as plasticizer, co-activator, antioxidant and accelerator in natural rubber (NR) processing is dealt with in the second chapter. Cardanol in nitrile rubber (NBR) processing is the subject of the third chapter. Use of cardanol in processing ethylene propylene diene monomer (EPDM) is investigated in the fourth chapter. Applications of cardanol in chloroprene (CR) processing are given in the fifth chapter and the major findings are summarised in the sixth chapter.

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ABSTRACT

This research project explores the utilization of cardanol in various capacities for rubber processing. Cardanol is a phenol with a long side chain in the meta position of the benzene ring. It is obtained by the vacuum distillation of cashew nut shell liquid (CNSL) which is a cheap agro-byproduct. In this study, the plasticizer property of cardanol was investigated in silica filled and HAF black filled NR, NBR, EPDM and CR by comparing cure characteristics and mechanical properties of vulcanizates containing conventional plasticizer with those containing cardanol as plasticizer. The co-activator, antioxidant and accelerator properties were investigated in gum samples of NR, NBR, EPDM and CR by comparing the properties of vulcanizates which contain conventional co-activator, antioxidant and accelerator with those in which each of them was replaced by cardanol. The general effectiveness of cardanol was investigated by determination of cure time , measurement of physical and mechanical properties, ageing studies, crosslink density, extractability, FTIR spectra, TGA etc.

The results show that cardanol can be a substitute for aromatic oil in both silica filled and HAF black filled NR. Again, it can replace dioctyl phthalate in both silica filled and HAF black filled NBR. Similarly, cardanol can replace naphthenic oil in silica filled as well as HAF black filled EPDM and CR. The cure characteristics and mechanical properties are comparable in all the eight cases. The co-activator property of cardanol is comparable to stearic acid in all the four rubbers. The cure characteristics and mechanical properties in this case are also comparable. The antioxidant property of cardanol is comparable to TQ in all the four rubbers. The accelerator property of cardanol is comparable with CBS in the case of NBR and EPDM. No accelerator property is observed in the case of NR. The accelerator property of cardanol in CR is not negligible when compared with TMTD.

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1 Introduction

This research work investigates the use of cardanol, a substance occurring in cashew nut shell liquid (CNSL) for various rubber processing applications. The following sections give a summary of the chemistry and applications of cardanol followed by an account of important elastomers (rubbers), their processing techniques and a general survey of the field of rubber processing. Lastly, the scope and objectives of this study are spelt out.

1.1 Cashew nut shell liquid (CNSL)

Cashew nut shell liquid (CNSL) is one of the sources of naturally occurring substituted phenols (1). It is a dark viscous oil with a characteristic smell, quite unlike other vegetable oils. It is opaque and when applied as a thin film, reddish brown in colour. It is immiscible with water but miscible with most organic solvents. CNSL has germicidal and fungicidal properties. In Kerala, it is used traditionally as a cure for fungal attack of the feet.

CNSL is cheap and renewable. It is a by-product of the cashew nut processing industry. It occurs in the soft honeycomb of the shell of the cashew nut. Cashew nut is part of the cashew apple, the crop of the cashew tree (2) which is native to Brazil. The cashew tree is cultivated in tropical areas such as East Africa, South and Central America and the Far East. About 30-35% CNSL is present in the shell which accounts for approximately 67% of the weight of the nut. It is obtained during the process of separating the cashew kernel from the nut. The processes employed for this are mainly hot-oil bath and roasting during which CNSL oozes out of the shell. Cold processing of the shells after removing the nut by hand is becoming increasingly popular.

1.1.1 Composition

Table 1.1 Indian Standard (IS: 840 (1964)) Specifications for CNSL

Characteristic	Requirement
Specific gravity	0.95-0.97
Viscosity at 30°C,cp(max)	550
Moisture,% by wt.(max)	1.0
Matter insoluble in toluene, % by wt.(max)	1.0
Loss in wt. on heating, % by wt.(max)	1.0
Ash, % by wt.(max)	1.0
Iodine value (max)	
a.) Wij's method	250
b.) Catalytic method	375
Polymerisation	
a.) Time, min(max)	4
b.) Viscosity at 30 ^o C,cp (min)	30
c.) Viscosity after acid washing at	200
30°C,cp(min)	

The earliest work published concerning the composition of cashew nut oil was by Staedeler (3). Since then many researchers have investigated the constitution of the oil (4-6). CNSL is available in two types: natural and technical CNSL. (6, 7).

Natural CNSL consists of mainly anacardic acid, cardol, methyl cardol, cardanol and a mixture of polymeric substances. Technical CNSL is the oil subjected to heating either during the roasting or as a part of processing of the oil. Application of heat leads to decarboxylation of anacardic acid to cardanol. The components of CNSL are themselves mixtures of four constituents differing in side chain unsaturation, namely the saturated compound, monoene, diene, and triene. The structures of the side chains in anacardic acid, cardol, methyl cardol and cardanol are identical. Indian standards specification for CNSL is given in Table 1.1. Fig. 1.1 gives the structures of the main ingredients of CNSL. The composition of each is given in Table 1.2.



Fig.1. 1 The main ingredients of CNSL

Component	Natural CNSL	Technical CNSL	
Cardanol	1.2	62.86	
Cardol	11.31	11.25	
2-methyl cardol	2.04	2.08	
Polymer	20.3	23.8	
Anacardic acid	64.93	_	

Table 1.2 Compositions of natural and technical CNSL

Technical CNSL is often further processed by distillation at reduced pressure to remove the polymeric material. Crude CNSL is corrosive but becomes less so by decarboxylation and removal of H_2S during the refining process.

1.1.2 Applications

CNSL by itself is useful for insecticidal, fungicidal, anti-termite and medicinal applications (8). As an agro-byproduct it has the advantages of low cost and renewable supply (9-12). It can be used as a starting material for organic synthesis and replace phenol in many instances (10). Resins derived from CNSL are widely employed in the fields of friction materials, automobiles, surface coatings, adhesives, laminates, rubber compounding, and several miscellaneous applications (10). The most attractive reasons for use of CNSL in industry are its low cost, abundant availability and chemically reactive nature.

CNSL can be polymerised by a variety of techniques. The presence of an aliphatic side chain gives these resins pronounced hydrophobicity which is a valuable property for many applications. The unsaturation in the side chain can be the basis for addition polymerisation (13-15). The effect of processing parameters on the refining of CNSL has been studied (16). Cashew nut shell liquid and derivatives are reported to have other useful properties as rubber additives (17-18). Reactions of CNSL are of commercial importance because several useful industrial products can be produced starting from this substance. A few reviews have appeared

summerising the known reactions of CNSL (19-20). The properties of NR modified with phosphorylated cashewnut shell liquid (PCNL) have been compared with the performance of another plasticizer, 2-ethyl hexyl diphenyl phosphate (Santicizer 141) (21) by Pillai et al. The PCNSL modified NR vulcanizates showed higher tensile properties and resistance to thermo-oxidative decomposition and flame compared to those containing similar dosages of Santicizer 141.

1.2 Cardanol

It is a substituted phenol which can take part in a variety of reactions (22). Many workers have highlighted the potential of cardanol in rubber processing applications from time to time (23-30). As a derivative of an agro-byproduct it has the advantages of low cost and renewable supply (31-34). Cardanol is obtained by vacuum distillation of commercial grade CNSL conforming to Indian Standard, I S: 841-1964.

Symes and Dawson (35) and Cornelius (36) identified the components of cardanol as 3- pentadeca- anisole, 1- methoxy 3- (8', 11'- pentadeca dienyl) benzene, and 1- methoxy 3- (8', 11', 14' - pentadeca trienyl) benzene). Chemically it is an interesting reactive substance thanks to the double bonds in the alkyl chain and the phenolic character. The structure of cardanol is given in Fig.1. 1. The composition of the constituents of cardanol as determined by various techniques is given in Table 1.3

Table 1.3 Composition of the constituents of cardanol as determined by various techniques (values are in wt %) (37)

Constituents	Techniques employed			
of cardanol	Molecular distillation	Argentated column	TLC-GLC	TLC-mass spectrometry
Saturated	-	5.4	2.68 3.11	1.98 3.94 - 4.35
Monoene	60	48.5	29.5 36.1	31.31 21.64 - 32.2
Diene	10	16.8	16.6 20.1	15.23 15.36 - 18.22
Triene	30.6	29.3	51.2 40.6	51.47 45.23 - 58.9

1.2.1 Reactions

Cardanol can be reacted with formaldehyde or furfural to obtain resols or novolak resins (38-42) or with unsaturated acids like acrylic (43-45) and cinnamic (46) to form esters. Cardanol has been reported to possess antioxidant properties (47,48).The higher antioxidant activity of cardanol can be due to unsaturation in the long side chain. A possible mechanism for trapping free radicals by cardanol is given in Fig. 1.2. For simplicity sake, only one site of unsaturation is indicated in the cardanol structure. Steps II and IV are relatively difficult to occur considering the high molar mass of the rubber radical.



Figure 1.2 The mechanism of free radical trapping by cardanol (49)

1.2.2 Applications

The effect of cardanol formaldehyde polymer on the properties of natural rubber (NR) has been studied (49). Improvement in tensile strength, hardness and abrasion resistance was noticed. The effect of cardanol on the processing, curing, physical and mechanical properties and ageing of SBR has been investigated (50).Compounding of NR in the presence of black filler containing cardanol and vulcanization using various accelerator systems has been the subject of another study (51). The abrasion resistance, elongation and tear strength were higher compared to compounds not containing cardanol. The effect of cardanol on the processing, mechanical and electrical properties of nitrile rubber based compounds has also been studied (52). Tensile strength, modulus and hardness decreased with cardanol content whereas tear, ageing and solvent resistance improved. Modification of natural rubber by cardanol formaldehyde resins and epoxidised cardanol (53) has attracted the attention of another group. They found that cardanol-formaldehyde resin functions both as a reinforcing agent and a hardener. The adhesive property of blends of cardanol formaldehyde copolymer resin with polychloroprene is another recently explored subject (29).

The price of cardanol is low compared to similar synthetic phenolic substances. But it has the disadvantage that the actual composition often varies with the source of CNSL. Nevertheless cardanol is employed in several application areas (54) like fine chemicals and intermediates, additives for lubricants and diesel, flame retardants, antioxidants and stabilisers, insulating materials, adhesives, surface active agents, polymers etc.

Hindered phenolic compounds (Ar OH) represent the major family of both natural and synthetic antioxidants (55). They are excellent additives for polymers and lubricants (56). Despite not having substitution in the preferred ortho and /or para-position (57) antioxidant activity for cardanol or its derivatives has been reported (58-61) in the case of natural rubber vulcanizates. The presence of phosphate group (62), the formation of a network bound antioxidant (63) or the formation of phenolic sulfides in situ during the vulcanization (63) has been used to explain the antioxidant activity of cardanol derivatives in natural rubber vulcanizates. The steric effect due to the long tail substituent has also been reported as an important factor (64).

In spite of the general interest in the application of cardanol for rubber processing, no systematic study appears to have been undertaken to evaluate the effectiveness of cardanol in various capacities and for different rubbers. This study aims to fulfil this need.

1.3 Rubber processing

In general, rubber processing consists of mainly two steps namely compounding and vulcanization. Compounding or mixing is the process of incorporating various compounding ingredients including the vulcanization agents with the help of a mixing mill. The second step namely vulcanization or curing is the process of converting the linear rubber polymer into a crosslinked network. As is done with other thermoset materials, the moulding or shaping of the product is achieved during the curing process. Exceptions to this are the extrusion and calendaring techniques where vulcanization is completed by subsequently subjecting the extrudate or sheet to heat and pressure.

1.3.1 Compounding

Compounding is the process of incorporation of various ingredients into the virgin polymer. It is a necessary part of any rubber product manufacturing process. Compounding of elastomers involves milling down the raw rubber into pliable sheets and then incorporating compounding ingredients into it. The properties displayed by a particular rubber vulcanizate are determined by the compound composition. The various ingredients generally added to rubber during compounding include plasticizers, processing aids, vulcanizing agents, accelerators, activators, fillers, antidegradants etc. The main objectives of compounding are to facilitate processing and fabrication in order to achieve the required balance in vulcanizate properties and to provide durability at the lowest possible cost (65). The practical aspects of compounding vary from rubber to rubber depending on whether it is saturated or unsaturated, natural or synthetic etc. Compounding of dry elastomers is done either on a two roll mill or in a Banbury internal mixing mill. Compounding methods for natural rubber, synthetic rubbers and rubber blends vary greatly in details. Synthetic rubbers are slower curing than natural rubber and hence the quantity of the compounding ingredients will be different in their case.

Mixing and homogenisation of elastomers and compounding ingredients in this study were done on a laboratory size two roll mill. The two roll mill used has rolls of 160mm diameter and 330mm length. The mill is equipped with retaining guides. The speed of the slow roll is $24\pm$ 0.5 rpm and the ratio between slow and fast roll is 1 tol.4. The clearance between the rolls is adjustable from 0.2 to 8mm as a minimum range of adjustment and the temperature maintained at $70\pm$ 5°C. Rubber was initially masticated on a cold mill and the compounding ingredients were then incorporated. The mixing was done according to ASTMD 3182-3189.

Both natural and synthetic rubbers require mastication before compounding, but a longer mastication time is required for the former. For synthetic rubbers there is no need of viscosity reduction by mastication as they are tailor-made for processing. But in the case of NR, which has a high molecular weight, high temperature is produced during mixing due to chain scission. Scorch or premature vulcanization may occur during the processing of a compound due to the accumulated effects of heat and time. Natural rubber has relatively lower scorch safety. Further, natural rubber is more stress crystallisable than synthetic rubbers and the gum vulcanizates have good strength compared to synthetic rubber vulcanizates. The viscosity of a fully compounded stock held at elevated temperature will increase with time as a result of crosslinking (66).

1.3.2 Curing

For rubber to become truly useful, its chains must be permanently linked together for improving the strength and other properties. Vulcanization involves the conversion of linear raw rubber molecules into a network by the formation of crosslinks. By this process the rubber is transformed from a plastic substance of very low strength to a resilient highly elastic material of considerable strength, less sensitive to temperature changes (67). As more crosslinks are formed, the network becomes tighter and the forces necessary to achieve a given deformation increase. The discovery that rubber can be vulcanized or cured by heating with sulphur was a technological accomplishment of great importance.

A wide range of chemical reactions takes place more or less simultaneously during the vulcanization process, varying from reactions at the surface of metal oxides to radical chemistry. Superimposed there are physicochemical aspects such as dispersion and solubility of chemicals in the rubber. However, standard analytical and chemical methods are not suited to analyse vulcanized rubber because of the insolubility of the elastomer network, the low concentrations and the variety of possible crosslinked structures.

Many articles on different aspects of vulcanization have been published over the years (68-74). Sulphur vulcanization can only be applied to rubbers with unsaturation in the backbone or to rubbers with unsaturated side groups. The type of crosslinks formed in the case of sulphur vulcanization largely depends on the vulcanization system, i.e. curatives added to the rubber. Practical recipes for vulcanization contain different accelerators and activators in addition to sulphur to complete the cure in a reasonably short time and to give a strong vulcanizate.

Although the most common vulcanizing agent for diene rubbers is sulphur, natural rubber and most of the unsaturated synthetic rubbers can be vulcanized by a wide variety of non-sulphurated agents including organic peroxides, quinones and their oximes and imines, poly nitro benzenes, bizazodicarboxylic esters and by means of high energy radiations (75). Polychloroprene rubbers are usually vulcanized by metallic oxides (76) like MgO along with other ingredients. Non-olefenic elastomers are generally cured by peroxides or high energy radiations.

1.3.3 Mechanism of rubber vulcanization

Complex mechanisms are involved in the vulcanization process. A series of consecutive and competing reactions occurs during sulphuration of rubber under vulcanizing conditions and hence no single mechanism can be appropriate.

Sulphur may be incorporated into the vulcanization network in a number of ways. As crosslinks it may be present as monosulphide, disulphide or polysulphide. It may also be present as pendent sulphides or cyclic monosulphides and disulphides.For the study of reaction mechanism, sulphur vulcanization reactions can be broadly classified into two, the unaccelerated and accelerated types. Unaccelerated sulphur formulation consists of rubber and sulphur while the accelerated systems contain rubber, accelerator and sulphur. In addition to this, both types include a zinc oxide- stearic acid activator system also. There are also accelerator systems in which elemental sulphur is not present. Instead, the accelerator provides sulphur for vulcanization. This sulphur free vulcanization can be referred to as sulphur donor systems. The most widely used accelerator of this type is tetramethyl thiuram disulphide (TMTD).

Vulcanization with sulphur but without accelerators is an extremely slow process. Relatively large amounts of sulphur and long vulcanization times are necessary and the vulcanizates are not of high quality. They have strong tendency to revert and their resistance to ageing is poor. A problem of sulphur blooming is also found to occur. The yield of crosslinked polymer is low when sulphur is used alone which may be due to the formation of multivalent polysulphidic bridges, cyclic sulphidic and bridge links.

It is known that several reactions by different mechanisms may take place simultaneously or consecutively during vulcanization. These reactions range from double bond migration, isomerisation, chain cleavage, cyclisation and formation of vicinal crosslinks (77-83). The unaccelerated sulphur vulcanization follows a polar mechanism (84,85). The basic steps in accelerated sulphur vulcanization, proposed by Morrison and Porter (86) are illustrated in Figure 1.13.





S-S bond interchange

Final vulcanizate network

Figure 1.13 Out line of reaction scheme for the sulphur vulcanization of rubbers

(R represents the rubber chain; X, the accelerator residue).

The vulcanization can be characterised relatively easily by measuring the evolution of crosslinks as a function of time using an oscillating disc rheometer (ODR), moving die rheometer (MDR) or rubber process analyser (RPA). The result graphically expressed is commonly called the cure curve. With these torsional (dynamic) rheometers the torque or shear modulus as a function of time at a certain temperature is measured. It is assumed that the modulus is proportional to the evolving concentration of cross links. It is often desirable to increase the rate at which a rubber is vulcanized in order to minimise the length of time required to cure a rubber article. This leads to greater throughputs and decreased energy requirements in curing operations. Even a modest increase in vulcanization rate can result in greatly increased productivity and substantial cost savings in the curing of rubber articles.

A typical cure curve is given in Fig.1.14. It is a plot of the modulus or torque against time during the curing process. There are three main regions for the cure curve. The first region is the scorch delay period or the induction period and the extent of this period depends on the accelerator system. For example there is a very small scorch time for ultra accelerators like TMTD and very long scorch time for delayed action type accelerators. The second region is the crosslinking period wherein the initial network structures are formed and the accelerator intermediates are consumed. The final state is the over cure period, where maturation or reversion occurs.

All shaping and processing operations of rubber are done before scorching. In the curing region, permanent crosslinks are formed which depend on the amount of vulcanizing agent, its activity, the reaction time and temperature and the nature of the rubber and other ingredients. The slope of the line in the curing region gives the rate of the reaction. The cure time is determined as the time required to accomplish 90% of the total change in modulus/ torque due to cure.



VULCANIZATION TIME

Fig. 1.14 Typical cure curve for the accelerated sulphur system (67)

1.3.4 Moulding / shaping methods

The compounded rubber containing the curatives and other additives as well as the filler is crosslinked subsequently. Various aspects of the cure phenomenon have already been discussed in Section 1.3.2. The techniques adopted to make dry rubber products after the compounding step are compression moulding, extrusion, calendering, transfer moulding and to a much lesser extent injection moulding. Coating techniques for rubberzing textiles etc are not included here.

A) Compression moulding

Compression moulding is the operation of shaping and vulcanizing the rubber compound by means of heat and pressure in a mould of appropriate form. It is the oldest and still most universally used technique for rubber processing because of suitability for short runs and low mould costs.

Heat and pressure are applied to the rubber compound in a compression moulding operation most often by a hydraulic press. There are two types of compression presses in general use, the conventional parallel platen press and the automated hinged-platen type. The latter uses fixed moulds and because of reduced heat loss, reduces cure times by as much as 50% of those obtained in a conventional press with loose moulds. The opening action of the press provides the operator with readily accessible halves which are stripped and cleaned quickly.

The conventional press used for compression moulding is substantially constructed and has two or more platens which are heated either electrically or by saturated steam under pressure. The platens are brought together by pressure applied hydraulically, either by water or oil, to give a loading of 7.5 to 15MPa. Mould designs are generally based on the availability of such pressures which are necessary to achieve closure with an acceptably thin flash. Fundamentally, all processes of moulding are similar, only the ways of introducing the material into the mould being different. With compression moulding, to ensure dimensional stability, it is necessary to allow the excess material to move away from the edge of the cavity so that the 'lands' can contact with minimum thickness of rubber (flash) between them. Sprue grooves and channels are provided with sufficient dimensions to accommodate this excess and also to allow the escape of air from the mould cavity. In some cases where the shape is complex it may be necessary to provide extra venting to allow air to escape from a blind area where it is likely to be trapped. Compression moulding has been used in the present investigation to prepare vulcanized samples.

B) Other processing methods

Extrusion, calendering, injection moulding and transfer moulding are other processing methods (87).

a) Extrusion (88): Rubber is extruded to make solid or sponge tubing, rods, gaskets, seals, wire insulation and preforms used in compression moulding. With this process, the rubber is continuously forced through a die that forms it to the 16

desired cross-sectional size and shape before curing. The extruded compound is finally vulcanized continuously by liquid curing method (89). Formerly extrudates were nearly exclusively vulcanized in autoclaves, hot air or steam.

b) Calendering (90): Rubbers are calendered by compression in a multi-roll process to produce continuous solid or sponge sheets of uniform thickness. These sheets can be further fabricated into hoses, ducts and die cut seals. Calenders are used to manufacture sheets of varying thickness, to incorporate technical fabrics with rubber and to coat fabrics with rubber.

In most cases the calendered products are intermediate products and are taken unvulcanized. They are then finished to products and finally vulcanized. In some cases calendered sheets, impregnations or coatings are accelerated so rapidly that they vulcanize at ambient temperature. Most of the sheet products such as roof coverings, rain coat fabrics etc. are vulcanized pressure-less in hot air ie. heating chambers at 60-70°C (91).

c) Transfer moulding (67) Transfer moulding involves the distribution of the uncured stock from one part of the mould to the actual mould cavity. This process permits the moulding of complicated shapes or the imbedding of inserts in many products which are difficult with the usual compression moulds. Although the moulds are relatively more expensive than compression moulds, the actual process permits shorter cure times through the use of higher temperatures and better heat transfer obtained by the higher pressure applied to force the compound into the mould.

d) Injection moulding (67)In recent years, injection moulding processes which are normally used for the production of plastics, have been developed so that rubber compounds can be moulded and vulcanized by this method. By careful temperature control of the feed stock, items can be vulcanized in less than several minutes. This method can be completely, controlled by programmed feed, injection and demoulding cycles resulting in low rejection rates and lower finishing costs. The initial cost of both the moulds and equipment has hindered the wider adoption of this type of moulding.

Injection and transfer moulds do not require any provision for excess material flowing out of the mould; simply an escape route for air is sufficient. The mould is closed under pressure and held so while the rubber is forced into the cavities. Any problems of air entrapment in the mould arising from the product design can be overcome by applying a vacuum to the closed mould. These two methods give parts which carry little or no flash adhering to them at the parting lines of the mould.

1.3.4 Compounding ingredients

a) Vulcanizing (curing) agents

Substances that bring about the actual crosslinking process are called vulcanizing agents. Numerous and varied vulcanizing agents are now used in the rubber industry in addition to sulphur, viz. various organic peroxides, quinones, metal oxides, bifunctional oligomers, resins, amine derivatives etc. Vulcanization can also be achieved by using high energy radiation without any vulcanization chemicals.

The crosslinks formed by peroxides are purely carbon-carbon linkages. The significance of peroxides is that they are able to crosslink even saturated elastomers such as ethylene propylene rubber; silicone rubber etc. which cannot be crosslinked by other vulcanizing agents. Chloroprene rubbers are generally vulcanized by the action of metal oxides along with other chemicals.

Sulphur and non sulphur systems have advantages and disadvantages of their own, but sulphur systems are more versatile. There are several advantages for sulphur as the vulcanizing agent viz. (1) higher flexibility during compounding, (2) easier 18 adjustment of the balance between the vulcanizing stages, (3) possibility to control the length of crosslinks, (4) better mechanical properties of the vulcanizates and (5) economic reasons (92,93). However compared to peroxide curing, sulphur systems show lower heat and reversion resistance, higher compression set and higher possibility of corrosion in cable metal cores. Vulcanization reaction is determined by the type of vulcanizing agents, the type of process, temperature and time of cure. The degree of crosslinking has influence on the elastic and other properties of the vulcanizate. Therefore the type of vulcanization process is the important connecting link between the raw materials and finished product. Vulcanization with sulphur alone is of no technological importance at all. A major breakthrough came with the discovery of organic nitrogen compounds that function as accelerators (94) for vulcanization.

a) Accelerators

Substances that are added in small amounts during compounding to speed up the vulcanization reaction and to improve the physical and service properties of the finished products are called accelerators. These substances can reduce the cure time from days or hours to minutes or seconds at the vulcanization temperature. The decrease in vulcanization time is of tremendous economic importance because of increased turnover and consequent reduction in cost of production. Further the amount of sulphur required can be reduced considerably in the presence of an accelerator. The first accelerators used in rubber vulcanization were inorganic compounds (95). Magnesium oxide, litharge and zinc oxide were the most widely used inorganic accelerators.

Around 1920 it was discovered that thiuram disulphides enable vulcanization to proceed without sulphur. Later, more delayed-action and yet fast-curing vulcanization systems were made possible from thiazole derivatives of sulphenamides. With the discovery of ultra accelerators vulcanization could be achieved even at room temperature (96).

A common feature of some vulcanization accelerators is a tautomerisable double bond and many of them contain the -N = C - S- H functionality. The time to the onset of cure varies with the class of the accelerator used. Accelerators offer many advantages such as lowering the cure temperature and shortening the cure time, thus reducing thermal and oxidative degradation. Also optimum physical properties can be obtained at lower sulphur contents. A chemical classification of accelerators is given in Table 1.8. Substituted guanidines were the most widely used organic accelerators in the early 1920s (97). With the introduction of synthetic elastomers and the use of fine furnace blacks, accelerators with greater processing safety became necessary. The benzothiazole sulphenamides give processing safety and satisfactory cure rates (98).

b) Accelerator activators

The rate of vulcanization can be increased by the addition of activators which are often metal complexes. Activators enable an accelerator to exercise maximum effect. Organic accelerators usually require the presence of organic acid or inorganic activators. ZnO is probably the most important inorganic activator but magnesium and lead oxides also find use. Fatty acids (eg. stearic acid) are used as co-activators. Polyalcohols (eg. ethylene glycol) and amino alcohols are used to counteract the retarding effect of white fillers.

d) Activation by ZnO

A combination of ZnO and a long chain fatty acid like stearic acid used as coactivator forms an ideal activator system (100). Apart from reducing the curing time (101), ZnO also functions as a filler to reduce cost and has some reinforcing effect. The zinc cations from ZnO and / or zinc compounds react with organic accelerators to give an active zinc-accelerator complex, which is one of the main steps in the vulcanization scheme.

Туре	Example	Typical use	
Aldehyde- amine	Butyraldehyde-aniline	Self-curing	
reaction products	condensation product		
Amines	Hexamethylene tetramine	Delayed action for NR	
Guanidines	Diphenyl guanidine	Secondary accelerator	
Thioureas	Ethylene thiourea	Fast curing for CR	
Thiazoles	2-mercaptobenzothiazole	Fast curing, general purpose, w /	
		broad curing range	
		Safe processing, general	
	Benzothiazole disulphide	purpose, moderate cure rate	
Thiurams	Tetramethylthiuram	Safe, fast curing	
	disulphide		
Sulphenamides	N- cyclohexyl- 2-	Safe processing delayed action	
	benzothiazyll sulfonamide		
Dithiocarbamates	Zinc dimethyl	Fast, low temperature use.	
	dithiocarbamate		
Xanthates	Dibutyl xanthogen	General purpose , low	
	disulphide	temperature us Latex and	
	Zinc isopropyl Xanthate	adhesives room temperature	
		curing	

 Table 1.8 Chemical classification of accelerators (99)

The complexes react with sulphur, a sulphur donor and other activators to generate the active sulphurating agent. It has been suggested in many different studies that these active complexes of zinc ions with accelerators are more reactive than the free accelerator (102). This active sulphurating agent reacts at the allylic sites of the rubber polymer unsaturations to form a rubber bound intermediate which reacts with another rubber bound intermediate or with another polymer chain to generate a crosslink.

A number of papers has been published on the beneficial effects of ZnO on the curing of rubber (103-112). The high thermal conductivity of zinc oxide helps to dissipate local heat concentrations that might otherwise affect the properties of rubber. ZnO also helps to decrease shrinkage of moulded rubber products and maintain cleanliness of moulds. This aids productivity by increasing the number of moulding cycles between cleaning.

Nowadays there is an increasing concern regarding the ecological and health effects of release of zinc compounds into the environment during rubber processing (113). The requisite amount of ZnO can be reduced by using nano sized ZnO (114). Another route for reducing the amount of ZnO in formulations is to provide interaction between accelerators, stearic acid, and the zinc oxide before they are added to the rubber matrix (115). Results indicate the possibility of a considerable reduction of ZnO levels with retention of properties of vulcanizates.

e) Role of stearic acid

The acceleration system often needs some proportion of fatty acid for cure activation. In general, fatty acids as co-activators in rubber vulcanization increase the crosslink yield (116). It is assumed that stearic acid reacts with ZnO to form zinc stearate which is an essential cure activator (117). Stearic acid also functions as a mould release agent. In addition, it acts as an internal lubricant between polymer chains.

Several researchers (118) found that the fatty acid can be adequately substituted by other species having surfactant properties (quaternary ammonium and phosphonium salts, oligomeric polyethers and other non-ionic surfactants). Romanova et. al. (119) hypothesized that the influence of these substances on sulphur vulcanization is associated with their surface properties and their participation in the interphase transfer reactions

f) Fillers

Fillers are usually inorganic powders of small particle size incorporated during compounding for various purposes like improvement in strength and modulus, cheapening the product etc. Choice of the type and amount of the filler to be used depends on the hardness, tensile strength and other properties required in the product. Some fillers are incorporated primarily to reinforce the product and they are termed as reinforcing fillers. Carbon blacks, silicas, silicates etc are in this class. Others are included mainly to cheapen and stiffen the final product. China clay, barites etc. come under this type. Reinforcement by filler leads to the enhancement of one or more properties of an elastomer by making it more suitable for a given application (120,121). It is generally agreed that strong links exist between rubber chain and reinforcing filler particles (122-124).

The effect of filler on rubber vulcanizates depends on its physical properties such as particle size, surface area, surface reactivity, electrical charge on the particle and chemical properties such as pH and reactivity towards accelerators. Reinforcing fillers substantially improve the mechanical and dynamic properties of the rubber. As the filler dose increases the properties increase progressively and then decrease. This phenomenon also depends on the type of filler and rubber used.

The most common and effective reinforcing filler is carbon black. There are varieties of blacks characterised by the particle size, method of manufacture etc. A standard classification system for carbon blacks used in rubber is described in ASTM D1765. Some examples are given in Table 1.9. They are essentially elemental carbon and are composed of aggregated particles. During vulcanization carbon blacks enter into chemical reaction with sulphur, accelerator etc. participating in the formation of a vulcanized network. The modification of an elastomer by carbon black reinforcement and vulcanization generates a unique three dimentional visco-elastic network that transforms the soft elastomer into a strong, elastic product (125). Thus the filler will influence the degree of crosslinking also. Carbon black also interacts with the unsaturated hydrocarbon rubbers during milling and the rubber is adsorbed on to the

filler. This alters the stress-strain properties and reduces the extent of swelling of the product in solvents (126).

Porter has reported that the crosslink density of a black reinforced vulcanization system increased by about 25% compared to the corresponding unfilled ones (127). Carbon black generally increases the rate of vulcanization and improves the reversion resistance (128) However carbon blacks can be used in dark coloured products only.

ASTM D1765	Old name
N110	SAF (super-abrasion furnace)
N220	ISAF (intermediate super-abrasion furnace)
N330	HAF (high-abrasion furnace)
N358	SPF (Super processing furnace)
N660	GPF (general-purpose furnace)
N762	SRF (semireinforcing furnace)

Table 1.9 Current vs. previous nomenclature of carbon black (129)

Precipitated silica is the best non-black reinforcing filler so far developed and comes close to carbon black in reinforcing effect. They have particle size as fine as that of carbon black and have an extremely reactive surface. They are noted for their unique combination of tear strength, adhesion, abrasion resistance, age resistance, colour and economics in many applications. A comprehensive review of precipitated silicas and silicates in rubber was published in 1976 (127). These fillers are manufactured by the controlled precipitation from sodium silicate with acid or alkaline earth salt. The ultimate particle size is controlled closely by the conditions of precipitation. The properties of three products from one manufacturer (Table 1.10) (130) illustrate the range of available silicas. Silicas are produced by mainly twelve manufacturers throughout the world, and their products have been tabulated (127).

Filler type	HS-200	HS-500	HS-700
Particle size, nm	20	40	80
Surface area, m ² /g	150	60	35
pH	7	7.5	8.5
Loss at 105°C, %	6	6	7
Soluble salts, %	1.2	1.2	1.2

Table 1.10 Representative silica properties

Precipitated silica is highly adsorptive, and hence in formulations containing them, it is necessary to use more than the normal quantity of accelerator or a combination of accelerators which is more reactive. Proper choice of the accelerator and activator are essential to obtain appropriate scorch and cure times in silica filled mixes. Diethelene glycol (DEG) is added along with silica during compounding to prevent the adsorption of curatives by silica.

Contrary to the behaviour of most synthetic rubbers, natural rubber (NR) does not require the use of fillers to obtain high tensile strength. This is by virtue of its higher stress crystallisation. However the use of fillers is necessary in order to achieve the level and range of properties that are required for technical reasons. Reinforcing fillers enhance the already high tensile properties of gum natural rubber and they improve in particular the abrasion and tear resistances. Hardly any filler will enhance all properties to the same optimal degree. The choice of the reinforcing filler as well as the dosage required could be quite different for different elastomers. The activity of fillers in NBR, SBR, BR and EPDM is often more pronounced because of their lack of strain crystallisation than in NR and partially so in chloroprene rubber (CR) (131). The variation in the effectiveness of fillers in NR and synthetic rubbers can be explained by the theory of over stressed molecules (132-133).

g) Plasticizers

Besides fillers, plasticizers play the biggest quantitative role in building a rubber compound. The reasons for the use of plasticizers are manifold: 1) reduction of elasomer content by using high dosages of carbon black and plasticizer to lower the price of the blend, i.e. extending the rubber 2) improvement in flow of the rubber compound and energy savings during processing 3) improved filler dispersion in the rubber compound 4) improvement in tackiness of the rubber compounds 5) influence on the physical properties of the vulcanizate, especially its elongation and elasticity especially at low temperatures, lowering the glass transition temperature, elevating the electrical conductivity, increasing flame protection etc.

Physical modification of polymers with plasticizers has long been practised as a means to improve the processability of the compounds and the physicomechanical properties of the final products. One of the essential aspects to be looked at while using such plasticizers, is that along with improved processability, they should not affect the physico-mechanical properties of the final product adversely. Various organic esters, phosphates etc. are most often used as plasticizers for elastomers capable of polar interactions while natural rubber is plasticized by oils of petroleum origin like paraffinic oil, naphthenic oil and aromatic oil (134). These are crude oils which are complex mixtures containing thousands of different molecules. Since these complex mixtures are difficult to identify chemically, they are grouped according to the predominant type of hydrocarbon: paraffinic, naphthenic, or aromatic. SR is usually harder to process and less tacky than NR and needs larger additions of plasticizers. In comparison to NR, the larger amounts added to SR have less influence on the properties of the vulcanizate (135). Plasticizers are generally classified as mineral oils, natural products and synthetic plasticizers. To extend particularly the non-polar rubbers, relatively cheap mineral oils are used. The choice mineral oil type depends on its price, polymer type, and compatibility and has relatively little influence on the property spectrum of the

vulcanizate. Beyond that, a multitude of natural products can be used, like fatty

acids, vegetable oils, glue, rosin, as well as modified natural products like factice, in order to improve the processing properties, tackiness or filler dispersion of the rubber compound (134). Phosphatic plasticizers hold a place of great significance (136) as they are flame retardants. A wide variety of such plasticizers are being used for the modification of plastics and elastomers (137). An attempt to improve the flame retardancy of epoxidised liquid natural rubber by modification with dibutyl phosphate resulted in a decrease in the rate of cure and mechanical properties (138). All petroleum plasticizes are generally carcinogenic due to high level of poly cyclic aromatics (139,140).

Considerable improvement in the processability characteristics (141,142) and physico-mechanical properties (143,144) is noted for NR modified with 5 to 20 phr of phosphorylated cashew nut shell liquid (PCNSL) prepolymer. PCNSL (I) is an oligometric flame retardant plasticizer compatible with a variety of plastics and elastomers. The advantage of oligomeric flame retardants (145) over the low molecular weight counterparts with respect to permanence/durability in service well known. Thev have low volatility. is lower decomposition temperatures, lower viscosity and combine more readily with the polymer base (146).

Plasticizers are generally used in NBR compounds to improve processing and low temperature properties. Typically they are ester types, aromatic oils or polar derivatives and can be extractable or non extractable depending upon the end use applications (147). Examples are dibutyl phthalate, dibutyl sebacate, dioctyl phthalate, and trixylyl phosphate. Polyesters, polyester ethers, polyester polyethers etc are also used. In concentrations up to 30phr, typical plasticizers based on ethers, esters or polythioethers are very effective in increasing the rebound elasticity and low temperature flexibility of vulcanizates (148). For high temperature resistance of NBR, plasticizers of low volatility, such as butyl carbitol formal and poly ester polythioethers which simultaneously improve low temperature flexibility, should be used (149). 2-Ethyl hexyl diphenyl phosphate (Santicizer 141) (11) (150) has

been shown to be an ideal non-toxic flame retardant plasticizer for nitrile rubber (151).

Naphthenic oils have been the most widely used plasticizers for EPDM compounds because they provide the best compatibility at reasonable cost. For applications at higher temperatures or in coloured compounds, paraffinic oils are usually chosen because of their lower volatility and improved UV stability. Some paraffinic oils tend to bleed from cured, high ethylene EPDM compounds (152).

Plasticizers used in neoprene are low cost petroleum derivatives like naphthenic oil and aromatic oil. Naphthenic oils have the advantage over aromatic oils of not darkening light coloured vulcanizates or staining contacting surfaces. Petroleum plasticizers seldom improve the flexibility of a CR vulcanizate at low temperature. Dioctyl sebacate is excellent for this purpose.

h) Mechanism of plasticization

Even small quantities of plasticizer markedly reduce the T_g of the polymer. This effect is due to the reduction in cohesive forces of attraction between polymer chains. Plasticizer molecules penetrate the polymer matrix and reduce the cohesive forces between the polymer chains and increase the segmental mobility (153,154). This results in greater processability and reduced chances of degradation. Plasticizers assist micro and macro Brownian motion of the polymer chains and thereby also viscous flow (155). Plasticizers that solubilize rubber are called "primary plasticizers" which assist micro and macro Brownian motion of the polymer chains and thereby also viscous flow (155). They swell rubber, reduce the viscosity and confer generally good elastic properties on the vulcanizate at low hardness levels. Polar products in polar elastomers and non polar ones in non polar rubbers can function as primary plasticizers. Mineral oils, paraffin etc. belong to this category. They are rubber soluble at the processing temperature and reduce the tackiness of the compound. Plasticizers that solubilize very little or not at all are called "secondary plasticizers", which act as lubricants between the rubber chain
molecules and improve the formability without any appreciable effect on the viscosity of the compounds (155).

i) Antioxidants

These substances improve the resistance of elastomers to oxidative reactions which limit their use at higher temperatures and oxygen and ozone environments. The first antioxidants made their appearance in 1924 and slowly gained acceptance. Hydroquinone and pyrogallol were patented in 1901 (156), resorcinol and 2naphthol in 1920 (157), 1-naphthol and aldehyde condensation products in 1922 (158), and mercaptobenzimidazole in 1931(159). Currently, bound antioxidants, i.e. antioxidants bonded to polymers are being developed to give maximum resistance to losses by extraction and volatilisation (160,161).

All hydrocarbons are vulnerable to deterioration caused by heat, light and oxygen. Polymers vary widely in their susceptibility to oxidative degradation. It is well known that the relationship between polymer structure and ease of oxidation depends primarily on the relative C-H bond dissociation energies of various polymers. Polymers with C-H bonds of low dissociation energies are more readily oxidised than polymers with higher C-H bond dissociation energies. Similarly, a rubber with low olefin content such as EPDM, is more resistant to oxidation than the highly unsatuarated rubbers, such as SBR and NR (162). The chemical structure of the polymer not only determines the rate of oxidation but also the physical changes that can occur during oxidation. Hardening of the polymer occurs when oxidative crosslinking predominates in the degradation process. Most rubbers, such as SBR, NBR (nitrile-butadiene rubber) and BR (cis- polybutadiene), harden during oxidation, while rubbers derived from isoprene such as NR, IR (cispolyisoprene) and IIR (isobutylene isoprene rubber), soften on oxidation due to chain scission (163). An antioxidant which offers excellent protection in one rubber may not be the most effective one for another. Tyres account for the largest volume of antioxidants used each year (164). A wide variety of light coloured vulcanized products are protected with non-staining antioxidants.

Trimethyl diquinolines are materials primarily used to protect rubber articles from degradatrion by atmospheric oxygen at higher temperatures. They are moderately staining. Phenolic antidegradants represent a group of non-staining and non-discolouring additives used primarily in light coloured mechanical goods and tyres. They are weaker antioxidants than amine types. Commonly used example for amine and phenol type antioxidants are para phenylene diamine (PPD) and styrenated phenol (SP) respectively.

j) Mechanism of polymer degradation and action of antioxidants

Oxidation of polymers can lead to chain scission, cross-linking or formation of oxygen containing functional groups in the polymer or its degradation products. In order to understand the antioxidant inhibition mechanisms, a brief outline of the oxidation process is given below (165)

Initiation $RH + O_2 \rightarrow R^{-} + HO_2^{-}$ $AH + O_2 \rightarrow A^2 + HO_2^2$ $R' + O_2 \rightarrow ROO'$ Propagation $ROO^{-} + RH \rightarrow R^{-} + ROOH$ ROOH \rightarrow RO + OH ROOH + RH \rightarrow RO' + R' + H₂O 2ROOH \rightarrow RO + ROO + H₂O Chain transfer $ROO^{-} + AH \rightarrow A^{-} + ROOH$ $A' + RH \rightarrow R' + AH$ Termination $ROO + RO \rightarrow stable products$ ROO + 2A \rightarrow stable products $A^{++}ROO \rightarrow \text{stable products}$

RH – polymer molecule or portion thereof, AH – antioxidant, A- antioxidant radical, RO_2 –polymer peroxy radical, and ROOH – polymer peroxide.

It is expected that cardanol by virtue of its substituted phenol structure would show antioxidant properties in various rubber vulcanizates.

1.4 Important elastomers

Rubber is named after Joseph Priestley, who discovered in 1770 that dried latex of natural rubber rubbed out pencil marks. Rubbers are broadly classified into natural and synthetic. Synthetic rubbers are further classified into two categories, namely (1) general purpose rubbers like SBR, BR etc intended for the manufacture of tyres and general mechanical products and (2) special purpose rubbers like NBR, CR etc. which have properties suitable for specialized applications. The following reactions discuss important rubbers in use today based on their chemical structure.

A) Natural rubber (NR) (166,167)

Natural rubber is made up of cis 1,4 isoprene units arranged in a highly stereo regular manner. The molecular weight of the polymer is in the range of 500000 and varies widely (168). Due to the high structural regularity, NR tends to crystallise on stretching. This strain-induced crystallisation gives high tensile strength even in the absence of fillers. NR is preferred in many applications because of superior building tack, green stock strength, better processability, high resilience and excellent dynamic properties. It is the original rubber and in many ways an ideal polymer for dynamic or static engineering applications. It has excellent dynamic properties, with a low hysteresis loss and good low temperature properties. It can be bonded well to metal parts, has high resistance to tear, fatigue and abrasion and is relatively easy to process. It has excellent low temperature properties (with a T_g of approximately -70°C) also.

The major advantages of natural rubber which make it popular for many engineering applications are its dynamic performance and low level of damping. Its combined dynamic properties generally out-perform any synthetic rubbers or combinations available to date. Poor resistance to oil, ozone and fuels are the main drawbacks of NR. Despite proliferation of general and special purpose synthetics, natural rubber still holds a significant market share.

Over 99.99% of the hydrocarbon component of NR consists of linear cis 1,4 polyisoprene. NR has a relatively broad molecular weight distribution which is responsible for its excellent processing behaviour. In its relaxed state, rubber consists of long, coiled-up polymer chains that are interlinked at a few points. Between a pair of links, each monomer can rotate freely about its neighbour. This gives each section of the chain leeway to assume a large number of geometries, like a very loose rope attached to a pair of fixed points. At room temperature rubber stores enough kinetic energy so that each section of chain oscillates chaotically, like the above piece of rope when shaken violently.

Aside from a few natural impurities, natural rubber is essentially a polymer of isoprene units. Structures of (a) isoprene and (b) NR are given in Fig.1.3. Commercially, NR is available in two forms, latex and dry rubber.

i) Latex

Natural rubber latex occurs as a milky colloidal suspension in the sap of several varieties of plants notably the species *Hevea Brasiliensis* (Euphorbiaceae). In places like Kerala, where coconuts are in abundance, one half of a coconut shell is used as the collection pot for the latex from the tree. The shells are attached to the tree via a short sharp stick and the latex drips down into it. The latex can be concentrated by centrifuging to 60% rubber content and used for making latex based rubber products (gloves etc.). But the lion's share of field latex is coagulated and converted to dry rubber.

ii) Dry rubber

The latex from plantations is collected and mixed with formic acid which serves as a coagulant. The rubber coagulates and forms a separate layer. After a few hours, the wet sheets of rubber are wrung out by putting them through a press. Subsequently,

after drying, they are sent to factories where vulcanization and further processing are done.

The synthetic version of the rubber is the pure polymer of cis- isoprene. The material properties of natural rubber make it an elastomer and a thermoplastic. Products like tyres, conveyer belts, moulded goods etc are derived from dry rubber by compounding and curing.

(a) $CH_{2} = CH_{3}$ $CH_{2} = CH_{2}$ $CH_{3} = CH_{2}$ $CH_{3} = CH_{2} = CH_{2} - CH_{2$

Fig. 1.3 Structures of (a) isoprene and (b) NR

The use of natural rubber is widespread, ranging from household to industrial products, entering the production stream at the intermediate stage or as final products. Tyres and tubes constitute the largest share of the market, accounting for around 56% of total consumption. The remaining 44% are taken up by the general rubber goods (GRG) sector.

Other significant products from rubber are hoses, belts and dampeners for the automobile industry in what is known as the "under the bonnet" products. Gloves (medical, household and industrial) are also large consumers of rubber, although the type of rubber used is concentrated latex. A significant tonnage of rubber is used as adhesives in many manufacturing industries and products, although the two most noticeable are the paper and the carpet industries.

According to the Indian Rubber Board, the production of rubber during January 2007 increased to 96,450 tonnes compared with 93,510 tonnes in January 2006. Total

natural rubber production in India registered a growth of 6.3 per cent in 2006-07. A typical formulation for dry natural rubber compounding is given in Table 1.4.

 Table 1.4 Natural rubber recipe (169)

Ingredients	(phr)
Natural rubber	100
Zinc oxide	5
Stearic acid	3
Benzothiazyl disulphide	0.6
Carbon black	50
Sulphur	2.5

A detailed discussion of various compounding ingredients and their significance is provided later in Section 1.4.1

B) Synthetic rubbers

Although natural rubber with the benefit of modern compounding is sufficient for many applications, it is also a strategically important material; a natural crop only produced in tropical countries and has relatively poor ageing properties. Therefore synthetic materials have been developed to replace natural rubber in a wide range of applications. There is now a wide range of synthetics available to cope up with high and low temperatures, contact with fluids of various types (including at high pressures) and aggressive or corrosive environments.

1) Nitrile rubber (NBR)

Nitrile rubber is a co-polymer of butadiene and acrylonitrile. NBR has good resistance to a wide variety of oils and organic solvents (170) and hence is widely used in products like oil seals, fuel lines, pipe protectors, blow out preventers etc. The properties of NBR depend to a great extent on the acrylonitrile content (171). The structure of NBR is given in Fig.1.4



Fig. 1.4 Structure of (a) acrylonitrile (b) butadiene and (c) NBR

NBR is produced in an emulsion polymerisation system. The water, emulsifier /soap, monomers (butadiene and acrylonitrile), radical generating activator and other ingredients are charged into polymerisation vessels. The emulsion process yields a polymer latex that is coagulated using various materials (e.g. calcium chloride, aluminum sulfate) to form crumb rubber that is dried and compressed into bales.

Specialty NBR polymers contain a third monomer (e.g. divinyl benzene, methacrylic acid) (172,173). Some NBR elastomers are hydrogenated (174) to reduce the chemical reactivity of the polymer backbone, significantly improving heat resistance.

The ACN content is one of two primary criteria defining each specific NBR grade. The ACN level, by reason of polarity, determines several basic properties, such as oil and solvent resistance (175,176) low-temperature flexibility/glass transition temperature and abrasion resistance. Higher ACN content provides improved solvent, oil and abrasion resistance, along with higher glass transition temperature. Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients and further processing to make useful articles. Processing includes mixing, pre-forming to required shape and vulcanization to make the finished rubber article. Acrylonitrile content ranges from 15% to 51%. A typical NBR formulation is given in Table 1.5

Compounding ingredients	(phr)
Nitrle rubber	100
Sulphur	1.5
ZnO	4.5
Stearic acid	1.75
Carbon black	50
CBS	1
TMTD	0.5

Table 1.5 A typical nitrile rubber formulation

NBR is commonly considered the workhorse of the industrial and automotive rubber products industries. In the automotive area, NBR is used in fuel and oil handling hose, seals and grommets and water handling applications. With a temperature range of -40° C to $+125^{\circ}$ C, NBR materials can withstand all but the most severe automotive applications. On the industrial side NBR finds use in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications.

2) Ethylene-propylene rubbers (177-179)

Ethylene-propylene rubbers and elastomers (also called EPDM and EPM) continue to be one of the most widely used and fastest growing synthetic rubbers having both specialty and general-purpose applications. Polymerisation and catalyst technologies in use today permit the design of polymers to meet specific and demanding application and processing needs.

Ethylene-propylene rubbers are valuable for their excellent resistance to heat, oxidation, ozone and weather ageing by virtue of their stable, saturated polymer backbone structure. Properly pigmented black and non-black compounds are colour stable. As non-polar elastomers, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalies, phosphate esters, many ketones and alcohols. Amorphous or low crystalline grades have excellent low temperature flexibility with glass transition points of about - 60°C.

These polymers respond well to high filler and plasticizer loading, providing economical compounds. They can develop high tensile and tear properties, excellent abrasion resistance, as well as improved oil swell resistance and flame retardance.

Ethylene propylene rubbers contain only a few percent double bonds, just enough for sulphur vulcanization. They are copolymers of ethylene and propylene containing in addition a few percent of diene for unsaturation. Since the various chain units are randomly arranged in the chain, these elastomers do not crystallise on stretching and require a reinforcing filler to develop high strength. A third, nonconjugated diene monomer can be terpolymerised in a controlled manner to maintain a saturated backbone and place the reactive unsaturation in a side chain available for vulcanization or polymer modification chemistry. The terpolymers are referred to as EPDM (or ethylene propylene-diene with "M" referring to the saturated backbone structure). An EPDM polymer structure is illustrated in Fig. 1.5. The ethylene-propylene copolymers are called EPM. The two most widely used diene termonomers are ethylidene norbornene (ENB) followed by dicyclopentadiene (DCPD). Each diene incorporates with a different tendency for introducing long chain branching (LCB) or polymer side chains that influence processing and rates of vulcanization by sulphur or peroxide cures.



(a)

Fig. 1. 5 (a) Structure of EPDM containing ethylidene norbornene (ENB)



Fig.1. 5 (b) ethylidene norbornene (ENB) (c) dicyclopentadiene (DCPD)

The processing, vulcanization and physical properties of ethylene-propylene elastomers are largely controlled by the characteristics of ethylene content, diene content, molecular weight (or Mooney viscosity) and molecular weight distribution. For example, decreasing ethylene content decreases crystallinity and associated properties such as hardness and modulus. A typical EPDM formulation is given in Table 1.6.

EPDM has found wide acceptance in wire and cable applications because of its inherently excellent electrical properties combined with ozone, heat, cold and moisture resistance. The excellent resistance to heat, oxidation, ozone and weather aging are expected to provide continued value in demanding automotive, construction, and mechanical goods applications.

Ingredients	(phr)
EPDM	100
ZnO	5
Stearic acid	1
Carbon black	50
Naphthenic oil	12.0
S	1.5
MBT	0.5

Table 1.6 A typical EPDM formulation

3) Chloroprene rubber (Neoprene, CR)

Chloroprene monomer is 2- chlorobutadiene, the structure of which is given in Fig. 1.6. Since the polymer consists entirely of trans 1,4 units, the chains are sufficiently regular in structure to crystallise even in the absence of stretching. Hence neoprene exhibits high gum tensile strength and is used in the pure gum form in many applications. Crystallinity is an inherent property of all polychloroprene rubbers (180). But the degree of crystallinity is largely dependent upon the amount of trans configurations in the polymer (181).



Fig. 1.6 The structure chloroprene

The method of vulcanization of neoprene is quite different from the elastomers considered so far. Unlike the others, it is generally not vulcanized by sulphur. Metal oxides are an essential part of the curing system (182). They acceptors for trace amounts of hydrogen chloride that are released from the polymer during processing, curing and vulcanizate ageing. Combinations of magnesium oxide and zinc oxide produce the best balance of processability, cure rate and vulcanization performance. In this case, zinc oxide / magnesium oxide combination is used to combine with some of the chlorine and interlink the polymer chains at those sites (183). Sulphur vulcanization is also possible for CR (181).

Polychloroprene can be vulcanized using various accelerator systems over a wide temperature range. For practical cure rate and vulcanizate properties, an organic accelerator is required in addition to metal oxides for the W and T types of neoprenes. Amines, phenols, sulphenamides, thiazoles, thiurams, thioureas, guanidines and sulphur are common accelerators and/ or curing agents. There are different types of neoprenes. Dry neoprene is either of the speciality type or the widely used general purpose type. The special purpose types are designed primarily for a particular application, eg, adhesives, coatings, crepe soles etc. General purpose rubbers are classified as G, W, and T types. The G types are copolymerised with sulphur and contain thiuram disulphide stabilizer and hence cure rapidly without an accelerator whereas the W types require accelerators for acceptable curing rates and vulcanizate properties. T types have excellent storage stability, least nerve, best extrusion and calendering performance and properties similar to W types. Neoprene W type is used in the present study.

CR is important as a raw material for adhesives (solvent based and water based) and has different latex applications such as dipped articles (e.g. gloves), moulded foam. It is also employed for improvement of bitumen. Application areas in the elastomer field are numerous such as moulded goods, cables, transmission belts, conveyor belts, profiles etc. This multipurpose synthetic rubber has over half a century of proven performance in thousands of applications (182). It will continue to be one of the most important synthetic speciality elastomers because of its unique properties. A typical CR formulation is given in Table 1.7.

Ingredients	(phr)
Chloroprene rubber (W)	100
Magnesium oxide	4
Stearic acid	3
Carbon black	30
Naphthenic oil	3
Ethylene thiourea (NA 22)	1
Zinc oxide	5

Table 1.7 A typical CR formulation

4) Styrene butadiene rubber (SBR) (184)

SBR is a general purpose rubber which when compounded with carbon black, behaves similarly to NR (T_g is higher at about -55°C). They are copolymers obtained by polymerising a mixture of two monomers, butadiene and styrene. The basic structure of SBR is shown in Fig.1.7



Fig. 1.7 Styrene-butadiene rubber

The chains therefore contain random sequences of these two monomers, which give them rubber like behaviour but render them too irregular to crystallise on stretching. These rubbers do not develop high tensile strengths without the aid of carbon black or other reinforcing pigments (185). SBR contains 20-23% styrene.

Of all the SBR made, about 75% goes into tyres. The rest goes into shoes and other foot wear, mechanical goods, sponge and formed products, water proof materials, hose, belting, adhesives and other miscellaneous uses.

5) Butadiene rubber (BR) (186)

It is a non-polar rubber like NR and SBR, with a very low T_g (approximately - 80°C). BR is thus a very high resilience (very low loss) rubber used in 'superballs' and also commonly used in combination with NR and SBR in long life rubber tyre treads. It is difficult to process unless blended with another elastomer. The structure of butadiene is given in Fig. 1.8.

(a)
$$CH_2 = CH - CH = CH_2$$

$$-\left[CH_2 - CH = CH - CH_2 - \right]_n$$
(b)

Fig. 1.8 (a) Butadiene (b) Butadiene rubber

6) Isobutylene isoprene rubber (Butyl,IIR) (187)

The good regularity of the polymer chains helps this elastomer to crystallise on stretching, resulting in high gum tensile strength. Since it is a soft polymer it is compounded with carbon black to increase the modulus. This material has a low T_g but has very little 'bounce'. The viscoelastic properties of butyl rubber 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. The damping and absorption of shock have found wide application in automotive suspension bumpers (188).



Fig.1.9 (a)Isobutylene

(b) Isoprene

It has excellent ageing properties and has very low permeability to gases (187). So it is often used for tubeless tyre liner, as well as for reservoir linings and other membranes. Chemically modified forms are frequently used. Figs. 1.9 and 1.10 give the structures of isobutylene and isoprene

7) Silicone rubber (Q) (190)

Silicone rubber is unique in not having a carbon backbone, being-Si-O-Si-O-, and this extends the useful temperature range noticeably. It has a T_g as low as -127°C depending on type, and can be used in service at temperatures of 200°C or more for several years. Further modification with fluorine will give even better performance. The silicone rubbers represent a completely different type of polymer structure as their chain structure does not involve a long chain of carbon atoms but a sequence of silicon and oxygen atoms. The siloxane structure results in a very flexible chain with extremely weak interchain forces. Hence, silicon rubbers are noted for exhibiting very little change in physical properties over a range of temperature. They show no tendency to crystallise on stretching and must be reinforced by a pigment, usually a fine silica powder. Silicon rubber is customarily vulcanized by means of peroxides. These presumably are able to remove some of the hydrogen atoms from the methyl groups on the silicon atoms of two adjacent chains to couple and form crosslinks (191). The silicon-oxygen-silicon linkage in silicones is similar to the linkage in quartz and glass. Although the silicones are not as heat resistant as quartz, they have superior heat resistance compared to other

elastomers. One reason for this greater heat resistance of silicone rubber can be found in the bond energy of the silicone oxygen bond (192).

Silicon rubbers can be used for making gaskets, tubing, tape, wire and cable, seals, rods, channels and hose in a variety of sizes and shapes.



Fig. 1.11 Silicon rubber

8) Urethane rubbers (PUR) (193)

Urethanes are formed by a chain extension reaction rather than the usual polymerisation reaction. ie these systems are able to make "big" macromolecules from "small" macromolecules; rather than from the monomer itself. These systems have special advantages, since the properties of the final polymer depend both on the type of original short chain polymers used as well as on their chain length. Hence a wide variety of polymers can be synthesized ranging from rigid to elastic types.

The short-chain polymers used are generally two types, ie., polyethers and polyesters. The chain extension reaction, whereby these short chains are linked is accomplished by the use of a reactive agent, ie., a diisocynate. For this reaction, the short chain polymers must have terminal hydroxyl groups (194). In addition to this chain extension reaction the diisocynates can also react with some of the active hydrogen atoms attached to the polymer chain leading to a crosslinking, ie., vulcanization process. Thus the urethane polymers lend themselves to a one stage casting and curing process. Another reaction of diisocynate involves water, which reacts vigorously to form carbon dioxide gas. Hence, when a little water is mixed with the short chain polymer and diisocynate, a process of simultaneous foaming, polymerisation, and vulcanization results, leading to a rapid formation of foamed elastomers or plastics. As elastomers, the urethane polymers show some outstanding physical properties, including high gum tensile strength (194). The poly urethane reaction can be shown as



O = C = N - R' - N = C = O + n HO - R'' - OH

Fig. 1.12 Urethane reactions

The versatility of rigid polyurethane foam makes it suitable for an extensive range of thermal insulation applications like refrigerators and freezers for domestic use. The rigid polyurethane foam enhances the structural stability of a building. Flexible PU is employed in applications like apparel lining, upholstery etc.

Speciality rubbers like poly sulphide rubber, hypalon and flourocarbon elastomers are not included in this discussion.

1.5 Scope and objectives of the work

The scope of the investigation is limited to compounding studies using four different elastomers namely NR, NBR, EPDM and CR, wherein cardanol will be part of the formulation. The effect of including cardanol in various capacities will be investigated by determination of the physical properties of the vulcanizate. 46

Chemical changes undergone by the vulcanizates will be investigated by FTIR, crosslink density measurement and extraction studies.

The broad objective of the project is to explore the use of cardanol for rubber compounding. Specific objectives can be listed as given bellow.

- 1. Compounding and vulcanization of NR formulations so as to estimate the usefulness of cardanol as a compounding ingredient in different capacities.
- 2. To determine optimal levels of cardanol as plasticizer for black and silica filled NR compounds.
- 3. To investigate the suitability of cardanol as compounding ingredient for NBR in various capacities.
- 4. To determine optimal quantities of cardanol as plasticizer for black and silica filled NBR compounds.
- 5. To estimate the suitability of cardanol for EPDM compound formulation.
- 6. To optimize the cardanol content for plasticizing black and silica filled EPDM compounds.
- 7. To estimate the suitability of cardanol for CR formulations and to optimize its percentage for black filled CR compounds.
- 8. To determine the overall effectiveness of cardanol usage in rubber compounds by measurement of mechanical properties, crosslink density, extractability etc.

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Chapter II Utilization of Cardanol in NR Processing

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2.1 Introduction

In this chapter, possible uses of cardanol in natural rubber processing are investigated. The plasticizer property of cardanol is compared with that of a conventional plasticizer, aromatic oil, at various filler contents, viz. 10-50 phr HAF black and 5-25 phr precipitated silica (Section 2.2.3). The antioxidant property of cardanol was compared (Section 2.2.4) with that of trimethyl quinoline and styrenated phenol in gum samples. Ageing studies were done for evaluating the thermal resistance (Section 2.2.4). Co-activator and accelerator properties were compared with those of stearic acid and N-cyclohexyl-2-benzothiazole suphenamide (Sections 2.2.5 and 2.2.6) respectively.

2.2 Experimental work

2.2.1 Raw Materials

a) Elastomers

Natural rubber – ISNR – 5 (1) was obtained from Rubber Research Institute of India; Kottayam, Kerala. Specifications of ISNR-5 are given below.

Mooney viscosity ML (1+4) at 100°C	- 82
Dirt content, % by mass, max	- 0.05
Volatile matter, % by mass, max	- 1
Nitrogen, % by mass, max	- 0.07
Ash, % by mass, max	- 0.60
Initial plasticity, min	- 30
Plasticity retention index	- 60

1. Zinc Oxide (activator) was supplied by M/s Meta Zinc Ltd., Mumbai and Goderej Soaps Pvt Ltd., Mumbai. It had the following specifications.

Specific gravity	-5.5
ZnO content	- 98%

Acidity	- 0.4%
Heat loss, max (2hrs. at 100°C)	- 0.5%

2. Stearic acid (co-activator) used in the present study was supplied by Goderej Soaps Pvt Ltd., Mumbai and had the following specifications.

Specific gravity	-0.85 ± 0.01
Melting point	- 50-69 °C
Acid number	- 185 - 210
Iodine number	- 9.5
Ash content	- 0.1%

3. N-cyclo hexyl 2-benzothiazole sulphenamide (CBS) (accelerator) used in the present study was obtained from Polyolefine Industries, Mumbai.

4. Tetramethyl thiuram disulphide (TMTD) (accelerator) used in the present study was supplied by Flexys, Netherlands. It had the following specifications.

Melting point	- 108°C
Moisture content	- 0.12%
Ash content	- 0.03%

5. High Abrasion Furnace black (N330) used in the present study was supplied by M/s Philips Carbon Black India Ltd., Cochin, India. It had the following specifications

Appearance	- black granules
DBP absorption	- 102cc/ 100g
Pour density	- 376kg/m ³
Iodine number	- 82

6. Precipitated silica used was of commercial grade supplied by Sameera Chemicals, Kottayam. The specifications are given below

pH (5% aqueous solution)	- 6.3
Specific gravity	- 2.03
SiO ₂ in dried sample	- 90%
Loss on heating (105°C)	-5.5%

7. Aromatic oil obtained from Hindustan Organic Chemicals Ltd. Kochi, had the following specifications:

Specific gravity	- 0.98
Aniline point	- 43.00
Ash content % by mass	-0.01
Viscosity gravity constant	-0.96

8. Refined CNSL conforming to Indian Standard 1 S: 840 (1964) was supplied by Vijayalaksmi Cashew Exports, Kollam, India. Cardanol was separated from commercial grade CNSL by distillation under reduced pressure (1mmHg). The pale yellow fraction collected at 206-208°C was cardanol (2)

9. Sulphur (cross linking agent), was supplied by Standard Chemicals Co. Pvt. Ltd. Chennai. The sample used had the following specifications

Specific gravity	- 2.05
Acidity, max	- 0.01%
Ash, max	- 0.015

10. Styrenated phenol (SP) was supplied by Olympic Chemicals, Maharashtra, India

11. Diethylene glycol (DEG) was supplied by E. Merk Limited, India.

c) Solvents used for Soxhlet extraction

1. Toluene was supplied by Fine Chemicals Ltd., Mumbai and had the following specifications

Boiling Point	- 95°C
Acidity	- 0.012
Alkalinity	- 0.012
Non volatile matter	- 0.002%

2. Acetone (AR) was supplied by Qualigens Fine Chemicals, India. It had the following specifications

Minimum assay	- 99.5
Wt / ml at 20°C	- 0.789 - 0.791

- 1.35 - 1.36

2.2.2 Quality evaluation

Different evaluation methods employed for vulcanizate properties are the following:

a. Cure characteristics: The cure characteristics of the mixes were determined using Rubber Processing Analyser (RPA 2000) supplied by Alpha Technologies, USA, as per ASTM Standard, D 2084-01.

The instrument uses two directly heated opposing biconical dies with a die gap of 0.487 that are designed to achieve a constant shear gradient over the entire sample chamber. The lower die is oscillated at 50rpm and the torque transducer on the upper die senses the force being transmitted through the rubber. Rheometric scorch time (t_{s2}) is the time required for the torque value to increase by two units above the minimum torque. It is a measure of the scorch safety of the rubber compound. Rheometric induction time (t_{s1}) is the time required for the torque of the torque value to increase by one unit above the minimum torque. It indicates the minimum time required to start the cure reaction. The optimum cure time corresponds to the time to achieve 90 percent (t_{90}) of the cure. It is calculated using the equation 2.1 (3)

Optimum cure $(t_{90}) = 0.9 (M_h - M_0) + M_0$ (2.1)

where M_h and M_0 are the maximum and minimum torques respectively.

i) Cure rate index

Cure rate index which is a measure of the rate of cure, was calculated using the formula (4)

$$CRI = \frac{100}{t_{90} - t_{s2}} \tag{2.2}$$

where t_{90} and t_{s2} are cure time and scorch time respectively.

ii) Alpha value

Alpha (α) represents filler specific constant independent of the cure system and closely related to the morphology of the filler (5-7). This parameter has been used
to characterize the filler structure existing in vulcanizates, in particular for carbon blacks. A low value of α indicates good filler dispersion.

$$\frac{D_{\max} - D_{\min}}{D_{\max}^0 - D_{\min}^0} - 1 = \alpha \frac{m_{filler}}{m_{rubber}}$$
(2.3)

where, D_{max} and D_{min} , correspond to the maximum and minimum rheometric torques of compounds with filler, D^{θ}_{max} and D^{θ}_{min} that without filler and m_{filler} and m_{nubber} , mass of filler and mass of rubber respectively.

iii) Kinetics of vulcanization

The kinetics of vulcanization was studied from the rheographs by the method (8) given below. The general equation for the kinetics of a first order chemical reaction is $\ln(a - x) = -kt + \ln a$ (2.4)

where, a = initial reactant concentration, x = reacted quantity of reactant at time t, and k = first order rate constant.

For the vulcanization of rubber, the rate of crosslink formation is monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of rubber. So the following substitutions can be made

$$(\mathbf{a} - \mathbf{x}) = \mathbf{M}_{\mathbf{h}} - \mathbf{M}_{\mathbf{t}} \tag{2.5}$$

$$\mathbf{a} = \mathbf{M}_{\mathbf{h}} - \mathbf{M}_{\mathbf{0}} \tag{2.6}$$

 M_h and M_0 maximum and minimum rheometric torques, and M_t - Rheometric torque at time t. So the equation becomes

$$\ln(M_{h} - M_{t}) = -kt + \ln(M_{h} - M_{0})$$
(2.7)

This equation is of the general form of a straight line. Therefore, if the plot of

 $\ln (M_h - M_t)$ Vs. time t is a straight line graph, it means that the cure reaction follows first order kinetics. The cure reaction rate constant (k) is directly obtained from the slope of the respective straight lines.

The energy of activation E_{act} of curing was determined using Arrhenius equations (9) given below

$$k = A e^{-\frac{E_e}{RT}}$$
(2.8)

$$\log k = \log A - \frac{E_a}{2.303RT} \tag{2.9}$$

where, A is the Arrhenius constant, E_a , the activation energy, R, the universal gas constant and T, the absolute temperature.

The rubber compounds were subsequently vulcanized up to the optimum cure time in an electrically heated hydraulic press with 30cm x 30cm platens at the required temperature and 11.6 MPa. The mouldings were cooled quickly in water at the end of the curing and stored in a cool dark place for 24 h. prior to physical testing.

b. Tensile properties: The tensile tests were done on dumb-bell shaped specimens punched out from the vulcanized sheets. The measurements were carried out on a 'Shimadzu' Universal Testing Machine (10KN) model AG 50 kN with a grip separation of 40mm, using a crosshead speed of 500mm/min. as per ASTM D 412. The reinforcing index was calculated using the formula (30)

Reinforcing index =
$$\frac{N}{N_0} \times \frac{100}{m_{filler}}$$
 4.10

Where N and N₀ indicate any property of filled and gum samples respectively and m_{filler} the mass of filler per 100 g rubber. Reinforcing index is a measure of the reinforcing effect of filler on the rubber.

- c. Tear resistance: This test was carried out as per ASTM D 624 using type C, un-nicked test pieces with a 90° angle on one side and tab ends punched out from the vulcanized sheets parallel to the mill grain direction. The test was carried out on the 'Shimadzu' Universal Testing Machine (10KN) with a grip separation of 40mm, using a crosshead speed of 500mm/min.
- **d.** Hardness: The hardness (Shore A) of the moulded samples was determined using Zwick 3114 Hardness Tester in accordance with ASTM D 2240-05. The tests were performed on unstressed samples of 30mm diameter and 6mm

thickness. The readings were taken after 10s of indentation since firm contact had been established with the specimen.

e. Abrasion loss: The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53516). Samples having a diameter of 6 ± 0.2 mm and a thickness of 6mm were kept on a rotating sample holder and a 10N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The abrasion loss in cc/hr. was calculated using the formula

Abrasion loss = loss of weight / sp. gravity $\times \frac{60}{2.2}$ (2.20)

for an abrasion time of 2.2minutes.

f. Rebound resilience: Rebound resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. It is expressed as percentage and is measured using a Vertical Rebound Resilience Tester as per ASTM D 2632-01. A plunger weighing 28±0.5g is dropped from a height of 40cm to the sample of thickness 12.5mm and the rebound height is measured.

Resilience =
$$\frac{R_h}{D_h} \times 100$$
 (2.21)

where, R_h is the rebound height and D_h the drop height

- **g.** Soxhlet extraction: Known weights of different samples of vulcanized rubber were packed in Wattman I filter paper and extracted in a Soxhlet apparatus using toluene as solvent and the loss of weight (%) was noted.
- h. FTIR spectroscopy: FTIR spectra of the Soxhlet extract of the cardanol based vulcanizate and cardanol itself were taken on Fourier Transform Infrared Spectroscope Bruker-Tensor 27 (Netherlands) and compared.

Similar studies were made on a cardanol sample after reaction with sulphur in order to identify chemical changes if any. The sample was heated for half an hour with sulphur at 100° C and cooled prior to testing.

- Crosslink density : Crosslink density was determined on both aromatic oil based and cardanol based samples loaded with 30phr HAF using toluene as per ASTM D 6814-02^{€1}. The process was repeated for aged samples after varying periods of ageing.
- **j.** Free sulphur analysis: Free sulphur analysis was carried out as per ASTM D297 on both cardanol based and aromatic oil based vulcanizates each containing 30phr HAF black. The analysis was also carried out on samples aged up to 4 days.
- k. Thermo gravimetric analysis: Thermo gravimetric analysis was carried out on both cardanol based and aromatic oil based vulcanizates with 30phr HAF on a TGA Q50 V6.4 Build 193 instrument (Netherlands), at a heating rate of 20°C/minute over a range of 30-800°C
- I. Differential scanning calorimetric analysis: Differerential scanning calorimetric analysis was carried out on both cardanol based and aromatic oil based samples vulcanized with 30phr HAF on STAR^e SW 8.10 equipment at a heating rate of 10°C/ min. over a range of 100°C to +155°C.
- **m. Mooney viscosity:** Mooney viscosity was measured on a Model EKTRONTEK, TAIWAN Mooney Viscometer.
- n. Ageing tests: Oxidative ageing tests were carried out for ten days in accordance with ASTM D573-04, in an air oven at two temperatures, viz.70°C and 100°C. After 24 hours of conditioning at ambient temperature, tensile strength and tear resistance of the samples were determined as per ASTM D 412 and 624 respectively apart from other indicators like free sulphur content, extractable matter etc.

2.2.3 Compounding and curing of NR

The mixing of the ingredients was done according to ASTM D 3182-3189 at a friction ratio of 1:1.22. The mill opening was set at 0.2mm and NR was passed through the rolls twice without banding. This was then banded on the slow roll with the mill opening at 1.44mm and was increased to 1.9 mm as the band became smooth. The temperature of the rolls was maintained at $70\pm5^{\circ}$ C. The compounding ingredients were added as per procedure given in ASTM D3184-89 in the following order: activator, filler, plasticizer, accelerator and curing agents. Before the addition of accelerator and sulphur, the batch was thoroughly cooled.

After mixing, the compound was homogenised by passing the rolled stock endwise six times at a mill opening of 0.8mm. The mill was opened to give a minimum stock thickness of 6mm and the stock was passed through the rolls four times folding it back on itself each time.

The cure times of the mixes were determined as per ASTM Standard D 2084-01 using Rubber Processing Analyser, RPA 2000 supplied by Alpha Technologies, USA.

The rubber compounds were then vulcanized up to the optimum cure time in an electrically heated hydraulic press with 30cm x 30cm platens at 150°C and 11.6 MPa. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h prior to physical testing.

2.2.4 Cardanol as plasticizer in NR compounds

A) HAF black

In this study samples were prepared as per details given in Section 2.2.3. The formulations employed are given in Table 2.1. Initially specimens were prepared using aromatic oil as plasticizer. Subsequently all studies were repeated replacing aromatic oil by cardanol. All the samples were tested for different properties as per details mentioned in Section 1.13.

Sample	NR	ZnO	St.acid	HAF	Ar. oil/	TQ	CBS	S
4	(phr)	(phr)	(phr)	(phr)	cardanol	(phr)	(phr)	(phr)
					(phr)			
1	100	5	2	10	1	1	0.8	2.5
2	100	5	2	20	2	1	0.8	2.5
3	100	5	2	30	3	1	0.8	2.5
4	100	5	2	40	4	1	0.8	2.5
5	100	5	2	50	5	1	0.8	2.5

Table 2.1. - Formulations with varying HAF black content

B) Precipitated silica

In this study silica filled samples were prepared as per details given in Section 2.2.3 using formulations given in Table 2.2. Initially, specimens were prepared using aromatic oil as plasticizer and all studies were repeated replacing aromatic oil by cardanol. All the samples were tested for different properties as per details mentioned in Section 1.13.

Table 2.2 Formulations with varying silica content.

Sample	NR,	ZnO,	St.acid,	DEG,	Silica,	Ar. Oil	CBS,	TMTD,	S,
	phr	phr	phr	phr	phr	cardanol,	phr	phr	phr
	F					phr			
1	100	5	2	1	5	0.5	0.6	0.5	2.5
2	100	5	2	1	10	1.0	0.6	0.5	2.5
3	100	5	2	1	15	1.5	0.6	0.5	2.5
4	100	5	2	1	20	2.0	0.6	0.5	2.5
5	100	5	2	1	25	2.5	0.6	0.5	2.5

C) Ageing studies

Samples were prepared as described in Section 2.2.2 according to formulations given in Tables 2.1 and 2.2. Oxidative ageing was carried out as per ASTM D573-04 using an air oven at 100°C. Specimens were subjected to ageing for 1, 2, 3, 4 70

and 5 days. Physical properties of the specimens before and after ageing were determined after 24 hours of conditioning at ambient temperature. Graphs were plotted for property vs no. of days of ageing for both plasticizers.

D) Optimization of cardanol content

Optimization of cardanol percentage was done for both HAF black filled and silica filled samples. For the optimization of cardanol, samples containing optimum filler loadings, 30phr HAF black and 15 phr silica (Sections 2.5.1 and 2.5.2) were used. Different samples were moulded at a constant filler content and different cardanol percentages, viz. 0.25 to 15% of the filler content as given in Tables 2.3 and 2.4.

Sample	NR	ZnO	St.acid	HAF	Cardanol	TQ	CBS	S
	(phr)	(phr)	(phr)	black	(phr)	(phr)	(phr)	(phr)
				(phr)				
1	100	5	2	30	0.75	1	0.8	2.5
2	100	5	2	30	1.5	1	0.8	2.5
3	100	5	2	30	2.25	1	0.8	2.5
4	100	5	2	30	3	1	0.8	2.5
5	100	5	2	30	3.75	1	0.8	2.5
6	100	5	2	30	4.25	1	0.8	2.5

Table 2.3: HAF black formulations with varying cardanol content

Tahla	24	Silion	formulation	. with	varving	cardanal	content
I ante	2.4	Silica	101 mulations		, vai yiiig	caruanoi	content

Sample	NR	ZnO	St.acid	DEG	Silica	Cardanol	CBS	TMTD	S
	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
1	100	5	2	1	15	0.75	0.6	0.5	2.5
2	100	5	2	1	15	1.125	0.6	0.5	2.5
3	100	5	2	1	15	1.5	0.6	0.5	2.5
4	100	5	2	1	15	1.875	0.6	0.5	2.5
5	100	5	2	1	15	2.25	0.6	0.5	2.5

E) Comparative study of cardanol and CNSL as plasticizers

As in Section 2.2.3, mixes were prepared using formulations given in Table 2.5 and the properties of the vulcanizate were determined and compared with vulcanizates in which cardanol was used as plasticizer. Mechanical properties were determined as described in Section 1.13. Oxidative ageing tests were carried out as per ASTM D573-04 using an oven at 100°C. Specimens were subjected to ageing for 1, 2, 3, 4 and 5 days. Physical properties of the specimens before and after ageing were determined after 24 hours of conditioning at ambient temperature. Property vs days of ageing graphs were plotted and compared for samples using each of cardanol and CNSL as plasticizers.

Sample	NR	ZnO	St.acid	HAF	CNSL/	TQ	CBS	S
	(phr)	(phr)	(phr)	(phr)	cardanol	(phr)	(phr)	(phr)
					(phr)			
1	100	5	2	10	1	1	0.8	2.5
2	100	5	2	20	2	1	0.8	2.5
3	100	5	2	30	3	1	0.8	2.5
4	100	5	2	40	4	1	0.8	2.5
5	100	5	2	50	5	1	0.8	2.5

Table 2.5 Formulations with varying HAF black content

2.2.5 Cardanol as antioxidant

This study was conducted to investigate whether cardanol possesses any antioxidant property for NR. The study was conducted in gum and silica filled samples using the formulations given in Table 2.6 and 2.7.

A) Antioxidant property of cardanol for NR gum compound

Oxidative ageing studies were carried out as per ASTM D573-04 using an oven at 70°C both in the case of silica filled and gum samples. Specimens were subjected to ageing for 1, 2, 3, 4 and 5 days. Physical properties of the specimens before and 72

after ageing were determined after 24 hours of conditioning at ambient temperature. Graphs were plotted for property vs days of ageing for all the three cases where cardanol, SP and TQ were used as antioxidants.

TABLE 2.6 Formulation for gum samples

Ingredients	Quantity (phr)
NR	100
ZnO	4
Cardanol / SP / TQ	1
CBS	0.8
S	2.5

B) Antioxidant property of silica filled NR compounds

TABLE 2.7	Formulation	for silica	filled samples
------------------	-------------	------------	----------------

Sample	NR	ZnO	St.acid	DEG	Silica	A/B/C	CBS	TMTD	S
	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
1	100	5	2	1	5	0.5	0.6	0.5	2.5
2	100	5	2	1	10	1.0	0.6	0.5	2.5
3	100	5	2	1	15	1.5	0.6	0.5	2.5
4	100	5	2	1	20	2.0	0.6	0.5	2.5
5	100	5	2	1	25	2.5	0.6	0.5	2.5

A- Cardanol B- Aromatic oil C- {Cardanol as plasticizer + SP (1phr)}

2.2.6 Cardanol as co-activator for NR gum

This study was conducted to investigate whether cardanol possesses any coactivator property when used as a substitute for stearic acid in NR gum formulation. The formulation used for the co-activator study is given in Table 2.8. The cure characteristics and mechanical properties when stearic acid is replaced by cardanol or a combination of 1phr each of cardanol and stearic acid as co-activators were found out.

Ingredients	Quantity (phr)
NR	100
ZnO	4
Co-activator	2
CBS	0.8
S	2.5

Table 2.8 Formulation for cardanol as co-activator

2.2.7 Cardanol as accelerator for NR gum

The accelerator property of cardanol was investigated for curing NR gum samples using the formulation given in Table 2.9. The accelerator property was estimated by noting the cure characteristics.

Table 2.9 Formulation for cardanol as accelerator

Ingredients	Quantity (phr)
NR	100
ZnO	4
Stearic acid	2
Cardanol / CBS	0.8
S	2.5

2.2.8 Sulphurless curing

Table 2.10 Formulations for DCP curing of NR gum

	NR	Cardanol	DCP
	(phr)	(phr)	(phr)
1	100	5	2
2	100		2

NR was compounded with dicumyl peroxide as per formulation in Table 2.10 and vulcanized as per ASTM standard, D 2084-01 and physical properties of samples determined according to details given in Section 1.13. A similar study was done without cardanol and the properties compared.

2.3 Results and discussion

2.3.1 Performance of cardanol as plasticizer for NR

A) HAF black filler

1. Cure characteristics

The cure characteristics of the mixes were determined at 150°C and 11.6 MPa using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per ASTM Standard, D 2084-01.



Fig. 2.1 Cure curves of cardanol and aromatic oil based samples with 30phr HAF black loading.

Fig. 2.1. is a comparison of cure curves of 30phr HAF black filled compounds. Similar values of torque are attained for both plasticizers. The cure characteristics are given in Table 2.11

	t ₁₀ ,	t 50,	t 90,	ts_2 ,		CRI	Min.	Max.
Plasticizer	min	min	min	min	α	min- ¹	torque,	torque,
							dNm	dNm
Cardanol	2.25	3.81	7.41	3.6	1.23	26.53	0.016	4.38
Ar. oil	2.39	3.88	7.79	3.64	1.44	26.88	0.072	4.64

Table 2.11 Cure characteristics of 30 phr HAF black filled samples

The minimum torque value, which indicates viscosity of the compound, is much less for the cardanol based samples. Hence cardanol is a better plasticizer for NR. The scorch time, cure time, t_{10} and t_{50} are comparable for both samples. Even though the cure rate index is slightly lower for the cardanol based sample, the α -value which is a measure of filler agglomeration is lower for cardanol based sample and is indicative of better filler dispersion.

 Table 2. 12 Minimum and maximum torque values during cure for HAF black

 filled samples

Sample	Torque,	10phr	20phr	30phr	40phr	50phr
	dNm					
Cardanol	minimum	0.05	0.05	0.02	0.01	0.2
Aromatic oil	minimum	0.11	0.05	0.07	0.09	0.3
Cardanol	maximum	3.53	3.4	4.4	5.32	6.6
Aromatic oil	maximum	3.94	4.2	4.6	5.69	7.5

Table 2. 12 gives minimum and maximum torque values during cure for HAF black filled samples. It is seen that the minimum torque value, which is indicative of the viscosity of the compound is in general lower for cardanol based samples.



Fig. 2.2 Variation of cure time with HAF black content

Figure 2.2 shows the variation of cure time with HAF black content. A marginally lower cure time is obtained for the cardanol based sample. The latter can be the result of chemical interactions between cardanol and natural rubber/sulphur, which can accelerate the overall curing process. Various possibilities exist for cross-linking between the side chains of cardanol and also between these and natural rubber¹⁰ chains through sulphidic linkages and /or free radical mechanisms.



Fig. 2.3 Variation of a- value with HAF black content

Figures 2.3 and 2.4 give a comparison of α and scorch values of cardanol and aromatic oil based samples with varying HAF black content. Lower α values for cardanol based samples indicate that cardanol is a better medium for dispersing HAF black providing a higher degree of plasticization than aromatic oil. The lower α values also show that filler agglomeration takes place to a much smaller extent in cardanol based compounds resulting in better utilization of filler. The lower viscosity of cardanol, 45centipoise compared to 3400centipoise for aromatic oil, may lead to better flow properties and consequently better wetting of filler rubber interface compared to aromatic oil. A slight lowering of scorch values in the presence of cardanol points to a more reactive compound.



Fig 2.4 Variation of scorch value with HAF black loading





Cure rate index with HAF black loading (Fig 2.5) shows that CRI values of cardanol based samples are comparable to the values for aromatic oil. Kinetics of cure reactions of 30phr HAF black filled cardanol and aromatic oil based compounds show that they obey first order kinetics as $ln(M_h - M_t)$ vs t plot gives a straight line with rate constant k = 0.43935 and 0.43117 respectively.



Fig.2.6 ln($M_h - M_t$) vs t for cardanol based sample: k= 0.43935, where k is the first order rate constant



Fig.2.7 $\ln(M_h - M_t)$ vs t for aromatic oil based sample: k=0.43117

b) Tensile properties: Fig. 2.8 shows the variation of tensile strength of HAF reinforced natural rubber, for both cases. Both plasticizers show similar tensile strengths aromatic oil giving slightly higher values at 30phr black and above.



Fig. 2.8 Variation of tensile strength (MPa) with HAF black loading





Also comparative data on the effect of filler content on elongation at break (Fig. 2.9) show equivalent performance by both plasticizers. Fig. 2.10 shows that the variation of 300% modulus with HAF black content for both cases is similar up to 40phr filler content and at 50phr the cardanol based sample has a clear superiority. For the cardanol-based sample, the 300% modulus value increases linearly with increase in filler content. The tensile properties, in general, show that cardanol is equivalent to aromatic oil as plasticizer.



Fig. 2.10 Variation of modulus at 300 % elongation with HAF black content





c) Tear strength: The tear strength of samples employing both plasticizers has also been measured as a function of HAF black filler content (Fig. 2.11). The tear strength values of the cardanol based samples are marginally higher. This points to a better reinforcing action by the filler in the presence of cardanol. This can be the result of more effective wetting of the filler-rubber interface by cardanol or better dispersion of the filler in comparison with aromatic oil.



Fig. 2.12 Variation of reinforcing index on the basis of tensile strength with HAF black loading



Fig. 2.13 Variation of reinforcing index on the basis of tear strength with HAF black loading

Figs. 2.12 and 2.13 indicate the variation of reinforcing index with filler content on the basis of tensile and tear strength respectively. They are similar for both plasticizers.

d) Abrasion loss: Fig.2.14 shows the variation of abrasion loss with HAF black filler content for both cases. Both curves are close to each other.



Fig. 2.14 Variation of abrasion loss with HAF black content



Fig. 2.15 Variation of hardness (Shore A) with HAF black content



Fig. 2.16 Variation of resilience (%) with HAF black loading

e) Hardness: Surface hardness values (Fig.2.15) of specimens employing both plasticizers are also similar.

f) Resilience: Fig. 2.16 shows the variation of resilience with increase in HAF black filler loadings for both cases. Both curves are similar.



Fig. 2.17 Results of Soxhlet extraction of 30phr HAF black loaded samples using toluene as solvent

g) Soxhlet extraction: The data given in Fig. 2.17 after Soxhlet extraction of cured samples are also significant. Cardanol based samples contain very little extractable matter both before ageing and after an ageing period of three days. Even after ageing for three days, the cardanol based sample gives almost the original value.



Fig. 2.18 FT-IR spectrum of cardanol



Fig. 2.19 FT-IR spectrum of the extract of cardanol based vulcanizate (30 phrHAF black) in toluene



Fig. 2.20 FT-IR spectrum of sulphur treated cardanol

h) FT-IR spectra: Figs.2.18 and 2.19 show the IR spectra of cardanol and the Soxhlet extract of the cardanol based vulcanizate respectively. A comparison of the

two shows no sign of cardanol in the extract, as the –OH absorption peak of cardanol observed at 3338cm⁻¹ is absent in the spectrum of the extract. This shows that in the case of cardanol, loss of plasticizer during service is not likely. Fig.2.20 shows the FTIR spectrum of cardanol after heating with elemental sulphur. Comparison of Figs. 2.18 and 2.19 shows suppression of the peak at 3090cm⁻¹ resulting from the disappearance of =C-H stretch of the aliphatic side chain of cardanol. This points to a vulcanization type reaction cardanol has undergone with sulphur.

i) Crosslink density: Fig. 2.21 is a plot of crosslink density of both samples at various stages of ageing. Crosslink density is slightly less in cardanol based samples compared to aromatic oil based samples. The presence of cardanol molecules has led to a lower extent of crosslinking between the rubber chains. This can be viewed as an extreme case of plasticization or steric hindrance due to the bulky nature of cardanol molecules. But since properties of the cardanol based sample are similar or even better, this is not a matter of concern.





[#] Rubber hydrocarbon



Fig. 2.22 Variation of free sulphur content in 30phr HAF black loaded vulcanizate on ageing at 100°C

j) Free sulphur content: Variation of free sulphur content estimated at various stages of ageing shown in Fig.2.22 is supportive of this. Initially free sulphur content of the cardanol- based sample is much less than the aromatic oil based sample. But after the first day of ageing, there is a sharp increase in free sulphur content presumably due to the breakage of cardanol-sulphur linkages. It is likely that the sulphur is subsequently utilized by natural rubber to form more crosslinks. By the second day of ageing, both samples show practically the same free sulphur content after a sharp fall in the case of the cardanol- based samples. Both samples show almost equal free sulphur values for the rest of the ageing period.

k) Thermogravimetric analysis: Figs.2.23 and 2.24 show the thermograms of samples plasticized by cardanol and aromatic oil respectively. The onset point of degradation of the cardanol based sample is higher than that of aromatic oil based sample. 50% degradation temperature (T_{50}) is higher for aromatic oil based sample.



Fig. 2.23 Thermogram of 30 phr HAF black loaded cardanol based NR vulcanizate

The thermal properties are to some extent governed by the presence of the plasticizer. In this case, cardanol has a potential point of weakness in the linear aliphatic side chain. This may explain the lower amount of residue in the case of the cardanol based sample. The thermal data are given in Table 13.



Fig. 2.24 Thermogram of 30 phr HAF black loaded ar.oil based sample

Property	Cardanol	Aromatic oil
On set point of degradation	308.68	299.6
Temperature of 50% degradation	401.5	407.05
Maximum degradation temperature	389.96	389.26
Maximum rate of degradation (% / ° C)	1.207	1.094
Residue (%)	22.89	28.04

Table 2.13 Thermal data of 30 phr black loaded samples

I) Differential scanning calorimetric analysis: The DSC data (Table 2.14) show no difference in the T_g and T_m values when cardanol and aromatic oil are used as plasticizers whereas ΔH_m is slightly higher for the cardanol based sample. The differential scans of cardanol and aromatic oil based samples are given in Figs.2.25 and 2.26 respectively.

Table 2.14 DSC data of 30 phr HAF black filled samples

Property	Cardanol	Aromatic oil
Glass transition - onset (°C)	-63.39	-63.24
Glass transition - midpoint (°C)	-60.83	-60.49
T _{m -} onset (°C)	79.26	79.66
T _m peak(°C)	94.8	93.39
T_{m-} end set (°C)	103.94	102.43
ΔH _m (mJ/mg)	1.6414	1.417



Fig. 2.25 Differential scan of 30 phr HAF black loaded sample containing cardanol



Fig. 2.26 Differential scan of 30 phr HAF black loaded sample containing aromatic oil

B) Optimization of cardanol content for 30phr HAF black filled sample

a) Variation of cure characteristics with cardanol content (% of HAF black)

There is not much variation in cure time (Fig. 2.27) with cardanol content whereas α value (Fig. 2.28) which is a measure of filler agglomeration is a minimum when cardanol is 7.5% of HAF black. Again, the rate of cure as indicated by the cure rate index curve (Fig. 2.29) shows a somewhat steady but slow increase with cardanol content. The positive influence of cardanol on the curing process is indicated by this.



Fig. 2.27 Variation of cure time with cardanol content



Fig. 2.28 Variation of alpha value with cardanol content



Fig. 2.29 Variation of CRI with cardanol content

b) Variation of physical properties with cardanol content

Fig 2.30 shows that maximum tensile strength is obtained at 5% cardanol content (of HAF black weight). Fig. 2.31 shows that elongation at break increases roughly with increase in cardanol content. The variation of modulus at 300% elongation (MPa) is given in Fig 2.32. The modulus slightly decreases with cardanol content. Tear strength (N/mm) (Fig 2.33), also shows a prominent maximum value at 5% cardanol content. Tear strength is sharply influenced by the filler content and its dispersion.



Fig. 2.30 Variation of tensile strength (MPa) with cardanol content



Fig. 2.31 Variation of elongation at break (%) with cardanol content



Fig 2.32 Variation of modulus at 300% elongation (MPa) with cardanol content





Figures 2.30 and 2.33 indicate that the optimum amount of cardanol (plasticizer) based on tensile and tear properties of the vulcanizate is 5% of filler. The elongation at break shows a mild increasing tendency (Figure 2.31) at higher cardanol contents due to excessive plasticization. The lowering of tensile modulus (Figure 2.32) with increasing cardanol content is also based on this. A lower requirement of plasticizer (5% as against 10% for aromatic oil) improves the economic viability of the concept.



Fig. 2.34 Variation of abrasion loss (cc/hr.) with cardanol content

Abrasion loss (Fig 2.34) and resilience (Fig 2.36) increase with increase in cardanol content whereas hardness Fig 2.35 is almost steady.



Fig. 2.35 Variation of hardness (shore A) with cardanol content



Fig. 2.36 Variation of resilience (%) with cardanol content

C) Ageing at 100°C of HAF black filled samples

a) 10 phr HAF black filled NR



Fig.2.37 Variation of tensile strength with no. of days of ageing



Fig.2.38 Variation of elongation at break with no. of days



Fig.2.39 Variation of modulus at 300% elongation with no. of days



Fig. 2.40 Variation of tear strength with no. of days

b) 20phr HAF black filled NR



Fig.2.41 Variation of tensile strength with no. of days



Fig.2.42 Variation of elongation at break with no. of days



Fig.2.43 Variation of modulus at 300% elongation no. of days



Fig. 2.44 Variation of tear strength with no. of days
c) 30phr HAF black filled NR



Fig. 2.45 Variation of tensile strength with no. of days



Fig.2.46 Variation of elongation at break with no. of days



Fig.2.47 Variation of modulus at 300% elongation with no. of days



Fig.2.48 Variation of tear strength with no. of days

d) 40phr HAF black filled NR



Fig.2.49 Variation of tensile strength with no. of days



Fig. 2.50 Variation of modulus at 300% elongation with no. of days



Fig.2.51 Variation of elongation at break with no. of days



Fig.2.52 Variation of tear strength with no. of days

e) 50phr HAF black filled NR



Fig.2.53 Variation of tensile strength with no. of days



Fig.2.54 Variation of elongation at break (%) with no. of days



Fig.2.55 Variation of tear strength of with no. of days

Figures 2.37 to 2.55 indicate the ageing behaviour of samples containing different plasticizers and varying percentages of HAF black filler. The behaviour of all cardanol based samples show remarkable similarity in the case of tensile strength, tear strength, maximum strain and 300% modulus. These properties show a rapid fall after the first day of ageing to be followed by a rapid increase on the second day. With the exception of 300% modulus, all properties tend to fall beyond this point. In general, the properties measured are better for the cardanol based samples for almost the whole period of ageing. Since fairly rigorous conditions have been employed for ageing, the thermal age resistance of the cardanol based samples is seen to be remarkably good. The aromatic oil based samples show a rapid decline throughout the ageing period. The fall in properties after the first day of ageing, may be the result of reversal or modification of chemical reactions that had taken place between cardanol and sulphur during the curing process indicated by the FTIR spectra in Fig. 2.20 of Section 2.3.1. It can be hypothesized that the sulphur liberated by this process is utilized subsequently by the rubber, which is reflected by improved properties after the second day of ageing. Variation of free sulphur content estimated at various stages of ageing shown in Fig.2.22 of Section 2.3.1 is supportive of this.

D) Silica filled compounds

a) Curing studies

Fig. 2.56 is a comparison of typical cure curves for both cases. Higher torque values are attained for aromatic oil during cure. The lower values of torque attained during cure by the cardanol containing compound point to a lower shear modulus and a more effective plasticizing action.



Fig.2.56 Cure curves of cardanol and aromatic oil based samples with 15 phr silica loading.



Fig. 2.57 Variation of cure time with silica loading

Curing studies indicate that the variation of cure time (Fig.2.57) with silica content is similar for both processing oils.



Fig. 2.58 Variation of CRI with silica loading

Fig. 2.58 gives the variation of CRI with silica loading. The cure rate is slightly higher for cardanol based compounds indicating the possibility of a role for cardanol in the curing process. Fig. 2.59 shows a comparison of the variation of α value with silica content. Lower α values are obtained for cardanol based samples indicating that cardanol is a better medium for dispersing silica and it provides a higher degree of plasticization than aromatic oil. The lower α , values also show that filler agglomeration takes place to a much smaller extent in cardanol based vulcanizates resulting in better utilization of filler. The lower viscosity of cardanol may also lead to better flow properties and consequently better wetting of the filler rubber interface compared to aromatic oil.





Kinetics of cure reactions of 15phr silica filled cardanol and aromatic oil based compounds (Figs. 2.60 and 2.61) show that they obey first order kinetics as $\ln(M_h - M_t)$ vs t plot gives a straight line with rate constant k = 2.10 and 2.11 respectively. This shows that cardanol does not alter the kinetics of cure reactions when used as plasticizer.



Fig. 2.60 ln (M_h - M_t) vs t for cardanol based compound containing 15phr silica; k=2.10



Fig. 2.61 ln (M_{h} - M_{t}) vs t for aromatic oil based compound containing 15phr silica ; k=2.11

b. Tensile Strength: Fig. 2.62 shows the variation of tensile strength of silica reinforced natural rubber for both cases. The curves are similar and 15phr silica appears to be the optimal filler content for both cases. The performance of cardanol is almost equivalent to that of aromatic oil. But a deviation from the pattern is noticed beyond 20phr silica. At 20phr, there is a fall in tensile strength for the cardanol case. It is possible that there is a need to optimize the percentage of cardanol at higher filler contents. Fig. 2.63 shows the change in elongation at break on using cardanol in place of aromatic oil. Here also both plasticizers behave similarly although values for aromatic oil are higher for low silica content (5-10%). Similar values were obtained from 300% modulus (Fig.2.64) measurements on both samples. The tensile properties, in general, show that cardanol is not inferior to aromatic oil as plasticizer.



Fig. 2.62 Variation of tensile strength (MPa) with silica content



Fig. 2.63 Variation of elongation at break (%) with silica content



Fig. 2.64 Variation of modulus at 300% elongation (MPa) with silica content



Fig. 2.65 Variation of tear strength with silica content

c) Tear Strength: The tear strength of samples employing both plasticizers has been measured as a function of silica content (Fig. 2.65). Both cases show almost equivalent performance although at 25phr silica content aromatic oil has some superiority. Similar to the case of tensile strength (Fig.2.62)



Fig. 2.66 Variation of reinforcing index on the basis of tensile strength



Fig. 2.67 Variation of reinforcing index on the basis of tear strength

Figs. 2.66 and 2.67 indicate the variation of reinforcing index with filler content on the basis of tensile and tear strength respectively. They are similar for both plasticizers. On comparing Figs.2.12 and 2.13 with Figs. 2.66 and 2.67, the reinforcing effect of silica and HAF black are similar although very low percentages like 5% are not studied in the case of HAF black.

d) Resilience: The variation of resilience with silica content (Fig. 2.68) is similar for both plasticizers. A slight decrease in resilience with increase in silica content is observed in both cases.



Fig. 2.68 Variation of resilience with silica loading

e) Hardness: Surface hardness (Fig.2.69) of specimens employing both plasticizers also shows only minor variations.

f) Abrasion loss: Abrasion loss is slightly less when cardanol is used at higher silica contents. Fig. 2.70 shows the variation of abrasion loss with silica content.



Fig. 2.69 Variation of hardness with silica loading



Fig. 2.70 Variation of abrasion loss with silica loading

g) Soxhlet extraction: Fig.2.71 is a plot of the weight loss on Soxhlet extraction of NR samples plasticized by the two different materials. In general, cardanol gives less toluene soluble material in the vulcanizate for most of the range.





h) Thermogravimetric analysis: Thermogravimetric analysis (Table 2.15) shows that the thermal stability of both samples is similar.

Table 2.15	TGA	of 15	phr silica	filled	samples
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Property	Cardanol	Aromatic oil
On set point of degradation	320.07	311.92
Temperature of 50% degradation	391.84	392.92
Maximum degradation temperature	385.10	385.44
Maximum rate of degradation (% / ° C)	1.374	1.365
Residue (%)	13.37	14.10

E) Optimization of cardanol content in 15phr silica filled sample



a) Variation of cure characteristics with cardanol content (% of silica)

Fig. 2.72 Variation of cure time (min) with cardanol content



Fig. 2.73 Variation of cure rate index with cardanol content



Fig. 2.74 Variation of alpha value with cardanol content





Fig. 2.75 Variation of tensile strength (MPa) with cardanol content



Fig. 2.76 Variation of tear strength (N/mm) with cardanol content



Fig. 2.77 Variation of modulus at 300% elongation (MPa) with cardanol content



Fig. 2.78 Variation of elongation at break (%) with cardanol content



Fig. 2.79 Variation of resilience (%) with cardanol content





Figs 2.72 - 2.74 give the variation of cure characteristics with cardanol content. The CRI (Fig.2.73) shows a sharp increase from 5 - 10 % but remains steady for the rest of the range. There is not much difference in cure characteristics with increase in cardanol content. Figs 2.75- 2.80 give the variation of mechanical properties with cardanol content. The tensile strength and tear strength are not very sensitive to silica content. Still an optimal behaviour is noticed at 10phr. Modulus and elongation at break values are sharply influenced by cardanol content. Similarly resilience (Fig. 2.79) and abrasion loss (Fig. 2.80) are also affected by cardanol %.

F) Ageing of silica based vulcanizates at 100°C



i) 5phr silica based vulcanizates

Fig. 2.81 Variation of tensile strength (MPa) with no. of days



Fig. 2.82 Variation of elongation at break (%) with no. of days



Fig. 2.83 Variation of tear strength (N/mm) with no. of days

ii) 10phr silica based vulcanizates



Fig. 2.84 Variation of tensile strength (MPa) with no. of days



Fig. 2.85 Variation of elongation at break (%) with no. of days



Fig. 2.86 Variation of tear strength (N/mm) with no. of days





Fig. 2.87 Variation of tensile strength (MPa) with no. of days



Fig. 2.88 Variation of elongation at break (%) with no. of days



Fig. 2.89 Variation of tear strength (N/mm) with no. of days

iv) 20phr silica based vulcanizates



Fig. 2.90 Variation of tensile strength (MPa) with no. of days



Fig. 2.91 Variation of elongation at break (%) with no. of days



Fig. 2.92 Variation of tear strength (N/mm) with no. of days



v) 25phr silica based vulcanizates



Fig. 2.93 Variation of tensile strength (MPa) with no. of days



Fig. 2.94 Variation of elongation at break (%) with no. of days



Fig. 2.95 Variation of tear strength (N/mm) with no. of days

Figs. 2.81 to 2.95 indicate the ageing behaviour of samples containing different amounts of fillers and employing each plasticizer. After ageing for 10 days at 100°C, the cardanol-based vulcanizate shows superiority in tensile properties over the aromatic oil based samples. For the most part, especially in the case of tensile strength and tear strength, the cardanol based samples show better performance. Though the elongation at break is lower for cardanol based vulcanizates (all cases) after the first day of ageing, it is higher for the rest of the ageing period. Hence embrittlement during ageing is less likely in the case of cardanol. Crosslinking between cardanol and NR chains via sulphur linkages cannot be ruled out. But the sulphur–cardanol linkages may be sensitive to the prolonged ageing process, resulting in the liberation of sulphur. In almost all cases of tensile strength, tear strength and some cases of elongation at break, the graph for cardanol goes through a maximum on the third day of ageing. This makes an interesting comparison with the case of black filled samples when the maximum were most often noticed on the second day of ageing.



G) Ageing of 15phr silica based samples at 70°C

Fig. 2.96 Variation of tensile strength (MPa) with no. of days



Fig. 2.97 Variation of elongation at break (%) with no. of days



Fig. 2. 98 Variation of tear strength (N/mm) with no. of days

Figs. 2.96 to 2.98 indicate the ageing behaviour (70°C) of samples employing each plasticizer. After ageing for 10 days at 70°C, the cardanol-based vulcanizate shows a clear superiority in tensile properties over the aromatic oil based samples. Towards the end of the ageing period (10 days), the tear strength (Fig.2.98) of the aromatic oil based rubber shows rapid degradation whereas the cardanol based product shows an almost steady value.

Ageing at 70°C may not offer conditions rigorous enough to break any cardanol sulphur linkages already formed during cross linking. Hence the absence of ups and downs earlier observed in the case of 100°C ageing for black filled and silica filled samples.



H) Weathering studies on 30phr HAF black filled samples

Fig. 2.99 Variation of tensile strength (MPa) with no. of months



Fig. 2.100 Variation of elongation at break (%) with no. of months



Fig. 2.101 Variation of modulus at 300% elongation (MPa) with no. of months



Fig. 2.102 Variation of tear strength (N/mm) with no. of months

The tensile properties (Fig. 2.99 - 2.101) and tear strength (Fig. 2.102) values indicate the comparative performance of cardanol and aromatic oil as plasticizers after weathering 30phr HAF black filled samples in outdoor conditions for one year. The studies show that the comparative performance is similar for both cases. But the tear strength retention (Fig. 2.102) is noticeably better for cardanol based samples.

I) Comparative study of cardanol and CNSL as plasticizers for NR



Fig.2.103 Variation of tensile strength with HAF black content



Fig. 2.104 Variation of tensile strength with HAF black content



Fig. 2.105 Variation of elongation at break (%) with HAF black content



Fig.2.106 Variation of modulus at 300% elongation (MPa) with HAF black content





Fig.2.107 Variation of tear strength (N/mm) with HAF black content



Fig.2.108 Variation of hardness (Shore A) with HAF black content


Fig. 2.109 Variation of resilience (%) with HAF black content

This section reports results on plasticization by CNSL in place of aromatic oil. Cardanol is the main ingredient of CNSL which also contains cardol, methyl cardol and tarry materials. Since CNSL is cheaper and more readily available than cardanol, its performance in comparison with cardanol has been studied.

Figs.2.103-2.109 indicate the comparative performance of cardanol and CNSL at various filler contents. In general, the performance of CNSL is comparable to that of cardanol. However, CNSL, being a crude agro-byproduct, can have a varying composition depending on place of origin and method of processing. Hence cardanol is to be preferred. Moreover, CNSL can undergo changes during storage and has a much higher viscosity.

J) Ageing of cardanol and CNSL based samples at 100°C



Fig. 2.110 Variation of tensile strength (MPa) with no. of days



Fig. 2.111 Variation of elongation at break (%) with no. of days



Fig. 2.112 Variation of modulus at 300% elongation (MPa) with no. of days





Figs. 2.110-2.113 indicate the comparative ageing behaviour of cardanol and CNSL plasticized samples. 30phr HAF black filled samples were used in both cases. Even though the performance of samples plasticized by both plasticizers are comparable, CNSL is not favoured as a plasticizer because of inconsistency in composition. The marginally better tensile and tear strength after ageing in the case of CNSL based vulcanizates are attributed to the presence of a larger amount of polymeric matter.

2.3.2 Cardanol as antioxidant in NR

(a) Antioxidant property of cardanol in NR gum compounds

Cardanol being a substituted phenol, antioxidant activity can be expected from its use. It may function as a primary antioxidant whereby it can donate the phenolic proton and stabilize the phenoxyl radical by electron delocalization in the aromatic ring.



Fig. 2. 114 Cure curves of NR gum samples.

Table 2. 16 :	Cure characteristics with cardanol as antioxidant in gum
samples	

	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max. torque	Min. torque	CRI
	(min)	(min)	(min)	(min)	(dNm)	(dNm)	(min) ⁻¹
Cardanol	5.80	3.63	5.10	8.61	3.19	0.01	35.8
CD.	7.01	4 14	5.62	0.07	2.756	0.025	61
Sr	7.01	4.14	3.03	0.97	2.730	0.033	51
TQ	6.64	4.05	5.5	8.73	2.879	0.55	47.8

Fig. 2.114 gives the cure curves of NR gum samples containing 1) cardanol 2) TQ and 3) SP as antioxidant. Similar cure curves are obtained for all the three samples

with the cardanol based sample showing the maximum torque. From the measurement of cure characteristics of NR gum compounds containing 1) cardanol 2) TQ and 3) SP as antioxidant, it is seen that the minimum torque and cure rate index values (Table 2.16) are lowest for the cardanol based sample whereas the maximum torque is found to be highest for the cardanol based sample. The presence of SP leads to the highest CRI value.

b) Ageing of gum samples at 100° C

Figures 2.115-2.118 show the results of ageing tensile and tear samples containing different antioxidants, viz. cardanol, TQ and SP in NR gum compounds at 100° C for 48 hours.



Fig. 2.115 Tensile strengths of gum samples containing cardanol / SP / TQ as antioxidants before and after ageing.



Fig. 2.116 Elongation at break (%) of gum samples containing cardanol / SP / TQ as antioxidants before and after ageing.



Fig. 2.117 Modulus at 300% elongation of gum samples containing cardanol / SP / TQ as antioxidants before and after ageing





In the matter of retaining tensile and tear strengths on 48h ageing, all antioxidants give similar performance. But it must be remembered that usual amounts of cardanol will be more than this in the role of plasticizer. This leads to still better performance by cardanol.





Fig. 2.119 Variation of tensile strengths of NR gum samples containing cardanol / SP / TQ as antioxidants



Fig. 2.120 Variation of modulus at 300 % elongation of NR gum samples containing cardanol / SP / TQ as antioxidants





The tensile and tear properties (Figs. 2.119-2.121) of cardanol, TQ and SP based vulcanizates on ageing are similar after five days of ageing at 70°C. Thermal analysis of natural rubber gum vulcanizates (Table 2.17) with each of TQ, SP and cardanol as antioxidants gives similar thermal stability in all cases. Figs. 2.122-

2.124 give the thermograms of NR gum samples containing SP, cardanol and TQ as antioxidant respectively.

TO Cardanol SP Property Onset point of degradation (°C) 305.93 311.03 310.24 Temp at 50% degradation (°C) 385.43 386.12 386.31 Temp at maximum rate of degradation (°C) 382.15 383.22 382.39 Maximum rate of degradation $(\% / ^{\circ}C)$ 1.679 1.623 1.554 Residue (%) 4.401 4.218 4.376

Table 2. 17: TGA of NR gum samples with different antioxidants



Fig. 2.122 Thermogram of NR gum sample containing SP as antioxidant



Fig. 2.123 Thermogram of NR gum sample with cardanol as antioxidant



Fig. 2.124 Thermogram of NR gum sample with TQ as antioxidant d) Ageing of silica filled samples of varying filler contents at 100°C for 5 days Figs. 2.125 – 2.129 indicate results of tensile strength tests on samples containing a) cardanol as plasticizer without any added antioxidant. b) aromatic oil as plasticizer without any added antioxidant c) aromatic oil as plasticizer and SP as added antioxidant. The results indicate that in general after five days of ageing silica filled samples at 100° C, the antioxidant activity has not stopped the samples from loss of tensile strength. However, for most cases, cardanol still retains a

marginal superiority over the other two cases. The difference in behaviour is more noticeable as the filler content and consequently the cardanol content go up, say at 25phr (Fig.2.144).



Fig. 2.125 Variation of tensile strength (MPa) of 5phr silica filled samples with no. of days



Fig. 2.126 Variation of tensile strength (MPa) of 10phr silica filled samples with no. of days



Fig. 2.127 Variation of tensile strength (MPa) of 15phr silica filled samples with no. of days



Fig. 2.128 Variation of tensile strength (MPa) of 20phr silica filled samples with no. of days



Fig. 2.129 Variation of tensile strength (MPa) of 25phr silica filled samples with no. of days



Fig. 2.130 Variation of tear strength (N/mm) of 5phr silica filled samples with no. of days



Fig. 2.131 Variation of tear strength (N/mm) of 10phr silica filled samples with no. of days



Fig. 2.132 Variation of tear strength (N/mm) of 15phr silica filled samples with no. of days



Fig. 2.133 Variation of tear strength (N/mm) of 20phr silica filled samples with no. of days



Fig. 2.134 Variation of tear strength (N/mm) of 25phr silica filled samples with no. of days

Figs. 2.130 -2.134 indicate the tear strength values of similar samples on ageing. Generally the cardanol based samples show superior ageing behaviour with respect to tear strength. This effect becomes more apparent as the cardanol content goes up steadily with the silica filler content.

Figs. 2.135 - 2.139 indicate results of tensile strength tests on samples containing a) cardanol as plasticizer without any added antioxidant b) aromatic oil as plasticizer without any added antioxidant c) cardanol as plasticizer and SP as added antioxidant. The properties are found to be better when cardanol is used as plasticizer only. Styrenated phenol is found to reduce the antioxidant property of cardanol.



Fig. 2.135 Variation of tensile strength (MPa) of 5phr silica filled samples with no. of days



Fig. 2.136 Variation of tensile strength (MPa) of 10 phr silica filled samples with no. of days 152



Fig. 2.137 Variation of tensile strength (MPa) of 15 phr silica filled samples with no. of days



Fig. 2.138 Variation of tensile strength (MPa) of 20 phr silica filled samples with no. of days



Fig. 2.139 Variation of tensile strength (MPa) of 25 phr silica filled samples with no. of days

Figs. 2.140 -2.144 indicate the tear strength values of similar samples on ageing. Generally the cardanol based samples show superior ageing behaviour with respect to tear strength. For low levels of silica content, the quantity of cardanol used as plasticizer is proportionately less .Hence the effect is not pronounced at low levels of silica filler content.



Fig. 2.140 Variation of tear strength (MPa) of 5 phr silica filled samples with no. of days



Fig. 2.141 Variation of tear strength (MPa) of 10 phr silica filled samples with no. of days



Fig. 2.142 Variation of tear strength (MPa) of 15 phr silica filled samples with no. of days



Fig. 2.143 Variation of tear strength (MPa) of 20 phr silica filled samples with no. of days



Fig. 2.144 Variation of tear strength (MPa) of 25 phr silica filled samples with no. of days

2.3.3 Cardanol as co-activator

Co-activator property of cardanol in comparison with a conventional co-activator, stearic acid was determined by comparing cure characteristics and physical properties of the vulcanizates.

a) Cure characteristics

Figure 2.145 gives the cure curves when 1) cardanol 2) stearic acid and 3) (cardanol+stearic acid) are used as co-activators. Similar curves are obtained in all the three cases of which the highest torque is obtained when cardanol is used as co-activator.



Fig. 2.145 Cure curves for different co-activators in NR

The scorch time, cure time, t_{10} and t_{50} (Table 2.18) are found to be slightly higher for cardanol based samples. Similarly, the maximum and minimum torque values are also higher, whereas the CRI is found to be least when cardanol is used as coactivator. Hence, judging from cure characteristics, cardanol possesses only moderate co-activator property.

Table 2. 18 Cure characteristics of cardanol and / stearic acid as co-activator in gum compounds

	t ₁₀ ,	t ₅₀ ,	ts ₂ ,	t 90,	Max.	Min.	CRI,
Co- activator	min	min	min	min	torque,	torque,	Min-1
					dNm	dNm	
Stearic acid	3.28	4.29	5.5	7.03	2.64	0.032	64.93
Cardanol	3.92	5.41	6.7	8.76	2.82	0.059	48.54
(Cardanol+ Stearic acid)	4.02	5.43	6.83	8.55	2.72	0.045	58.1

Table 2. 19 Physical properties when	cardanol and / stearic acid is used as
co-activator in gum compounds	

Co- activator	Tensile strength, MPa	Tear strength, N/mm	Elongation at break, %	Modulus at 300% elongation, MPa	Resilience, %	Hardness, Shore A
Cardanol	24.8	41.6	1067	1.68	73	35
Stearic acid	24.71	37.25	1121	1.35	72	34
(Stearic acid + Cardanol)	21.89	35.9	1003	1.89	68	37

b) Physical properties

Table 2.19 gives a comparison of physical properties when 1) cardanol 2) stearic acid or 3) cardanol + stearic acid are used as co-activators in NR gum compounds. The physical properties of cardanol based samples are comparable to that of stearic acid based ones. Thus it can be concluded that cardanol possesses co-activator property.

In order to investigate interactions between cardanol and Zn^{++} ion, mixtures of 1) cardanol + ZnO and 2) Zn Cl₂ + cardanol were prepared and their IR spectra compared with the spectra of pure a) cardanol b) ZnO and c) Zn Cl₂. The IR spectra of the samples were taken on the same day. On comparison of 1) cardanol (Fig. 2.18) and 2) cardanol + ZnO (Fig. 2.146), it is seen that the O-H stretching frequency of cardanol is shifted from 3360.35 to 3350.66cm⁻¹ indicating an interaction between cardanol and Zn⁺⁺. As the d π - p π bond absorptions of Zn⁺⁺ and oxygen are in the region 500-400cm⁻¹ and as the absorptions in the region are subtle, the IR spectrum of Zn Cl₂ + cardanol (Fig. 2.147) is compared with the absorptions of 1) cardanol and 2) ZnCl₂. The O-H stretching frequency of cardanol is shifted from 3360.35 to 3398.78.It is also seen that the absorptions of ZnCl₂ in (Zn Cl₂+cardanol) in the region 500-400cm⁻¹ are shifted towards the absorptions of ZnO indicating that d π - p π bonding occurs between the oxygen of cardanol and Zn⁺⁺. Hence interaction between cardanol and ZnO is indicated. This can be the result of a complex formation between cardanol and Zn⁺⁺ ion.



Fig. 2.18 FTIR spectrum of cardanol



Fig. 2.146 FTIR spectrum of (cardanol + ZnO)

160



Fig. 2.147 FTIR spectrum of (cardanol + ZnCl₂)

c) Optimization of cardanol content for co- activator effect

Cure characteristics of gum compounds were determined (Table 2.20) for varying amounts of cardanol as co-activator. Minimum cure time is obtained when 1phr cardanol is used as co-activator.

Cardanol,	t _{s2,}	t _{10,}	t _{50,}	t _{90,}	Max.,	Min.,	CRI,
phr	min	min	min	min	torque	torque	min ⁻¹
İ				}	dNm	dNm	
2	5.5	3.28	4.29	7.04	2.64	0.032	69.93
1.5	4.62	2.87	3.89	6.05	2.785	0.006	69.9
1	4.57	2.91	3.85	6.01	2.86	0.039	69.44
0.5	5.56	3.67	4.55	7.02	2.678	0.094	68.49
0.25	5.05	3.07	4.09	6.48	2.677	0.035	69.9

Table 2. 20 Cure characteristics for different cardanol percentages

TGA shows (Table 2.21) that thermal stability when cardanol is used as coactivator is similar to that when stearic acid is used. The respective thermograms are given in Figs. 2.148 and 2.149.

Property	Cardanol	Stearic acid
Onset point of degradation (°C)	302.63	272.36
Temp at maximum rate of degradation (°C)	381.71	384.53
Temp of 50% degradation (°C)	387.5	389.6
Maximum rate of degradation (% / °C)	1.601	1.59
Residue (%)	4.254	4.571

Table 2. 21 : Thermal analysis when cardanol is used as co-activator



Fig. 2.148 Thermogram of NR gum vulcanizate containing stearic acid as coactivator.



Fig. 2.149Thermogram of NR gum vulcanizate containing cardanol as coactivator.



Fig. 2. 150 Variation of cure time (min) with cardanol content



Fig. 2. 151 Variation of maximum torque (dNm) with cardanol content



Fig. 2.152 Variation of cure rate index (min⁻¹) with cardanol

Figs. 2.150-2.152 indicate the variation of cure time, maximum torque and cure rate index respectively with cardanol content (co-activator). Cure time is found to be a minimum for 1-1.5phr cardanol, whereas maximum torque is obtained for 1 phr cardanol. The cure rate index is not much affected by cardanol content in this concentration range.

2.3.4 Cardanol as accelerator

	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻¹
Accelerator		1			(dNm)	(dNm)	
CBS	6.7	3.92	5.41	8.76	2.815	0.059	48.54
Cardanol	-	1.77	15.32	26.42	0.542	0.062	3.7

Table 2. 22 Cure Characteristics when cardanol is used as accelerator

Table 2.22 gives the cure characteristics when CBS is replaced by cardanol in gum compound. Cardanol does not show any accelerator property.

2.3.5 Sulphurless curing

When cardanol is used along with DCP for NR curing (Tables 2.23, 2.24 and Fig. 2.153), no positive effect is noticed.



Fig.2.153 Cure curves of sulphurless curing

Ingredients	t ₁₀ ,	t ₅₀ ,	t ₉₀ ,	t _{s1} ,	Min.torque,	Max.torque,
	min	min	min	min	dNm	dNm
DCP	1.24	5.33	18.75	8.11	0.13	1.653
DCP + cardanol	1.13	5.79	19.28	17.54	0.023	1.163

Table 2.23 Cure characteristics for DCP curing

Table 2.24 Mechanical properties for DCP curing

Ingredients	Tensile	Elongation	Modulus at	Tear
	strength,	at break (%)	300%,	strength,
	MPa		MPa	N/mm
DCP	5.6	995	0.79	15.8
DCP +	4.17	1129.9	0.66	12.21
cardanol				

2.4 Conclusions

Comparing the cure characteristics of HAF black filled NR for different plasticizers, the minimum torque values which indicate the viscosity are lower for cardanol plasticized compounds than aromatic oil plasticized compounds. The cure times of cardanol based samples are lower and the cure rate indices are higher. Similarly, the alpha value, which is a measure of filler agglomeration, is lower for cardanol based samples indicating better filler dispersion. The tensile properties in general show that cardanol is somewhat superior to aromatic oil as a plasticizer especially at higher filler contents. The tear strengths of cardanol based samples are marginally superior. The extractable matter in cardanol based samples is lower than that of aromatic oil based samples. The crosslink densities of cardanol based samples are somewhat lower. Optimization of cardanol content shows that optimum mechanical properties are obtained when cardanol is 5% of HAF black. Better ageing behaviour is observed for cardanol based samples on the basis of

ageing for five days in an air oven at 100°C. Kinetics of cure reactions of 30phr HAF Black filled compounds is similar for both cardanol and aromatic oil based samples with similar rate constants. Plasticization by CNSL is comparable to that of cardanol. Ageing behaviour of CNSL is somewhat superior to that of cardanol. The mechanical properties of cardanol based samples show a rapid fall after the first day of ageing to be followed up by rapid increase on the second day.

In the case of silica filled samples lower values of torque are attained during cure for cardanol based sample. Again cure times and alpha values are lower whereas the CRI values higher for the cardanol based samples. Kinetics of cure reactions of 15phr silica filled compounds are similar for both cardanol and aromatic oil based samples with equivalent rate constants. The mechanical properties and thermal stability are similar for both cardanol and aromatic oil based samples. The extractable matter in cardanol based samples is lower. Optimum amount of cardanol is about 10% of silica. Mechanical properties are superior for cardanol based samples after ageing 1) at 100°C for five days and 2) at 70°C for ten days.

Comparison of the antioxidant property of cardanol with TQ and SP in NR gum samples shows that thermal stability of the cardanol based sample is similar to that of TQ and SP based samples. The tensile and tear properties of cardanol, TQ and SP based vulcanizates after ageing at 70°C are similar after five days of ageing.

On comparing cure characteristics and mechanical properties the co-activator property of cardanol is comparable to stearic acid. Cardanol does not show any accelerator property.

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Chapter III Cardanol in NBR Processing

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3.1 Introduction

In this chapter, possible utilization of cardanol in nitrile rubber processing is investigated. The plasticizer property of cardanol is compared with that of a conventional plasticizer, dioctyl phthalate (1,2) for varying filler contents; ie. 10-50phr HAF black and 5-25phr silica. Antioxidant property of cardanol was compared with that of TQ using gum samples. Ageing studies were done on samples using cardanol as both plasticizer and antioxidant. Co-activator and accelerator properties were compared with that of stearic acid and CBS respectively.

3.2 Experimental

3.2.1 Raw materials

a) Elastomer

Acrylonitrile-butadiene rubber (Aparene N-50) and was supplied by Apar Polymers Ltd., Mumbai, India.

Acrylonitrile content	- 44%
Mooney viscosity	- 80-95 ML

b) Compounding ingredients

Dioctyl pthalate used in the present study was commercial grade supplied by Rubo-Synth Impex Pvt. Ltd., Mumbai. Other compounding ingredients and their details and suppliers are discussed in Section 2.2.1

3.2.2 Compounding and curing of NBR

Mixes were prepared and cured as already described in Section 2.2.2. Specific formulations are given under respective sections.

3.2.3 Evaluation methods

Evaluation methods employed for this study are the following:

a)	Cure characteristics (as per details provided i	n Section 2.2.2a)
b)	Tensile properties:	(Section 2.2.2 b)
c)	Tear resistance	(Section 2.2.2 b)
d)	Hardness:	(Section 2.2.2 c)
e)	Abrasion resistance:	(Section 2.2.2d)
f)	Rebound resilience:	(Section 2.2.2 e)
g)	Soxhlet extraction :	(Section 2.2.2 f)
h)	FTIR spectroscopy:	Section 2.2.2 g)
i)	Crosslink density:	(Section 2.2.2 h)
j)	Free sulphur analysis:	(Section 2.2.2 i)
k)	Thermo gravimetric analysis:	(Section 2.2.2j)
I)	Differerential scanning calorimetric analysis:	(Section 2.2.2 k)
m)	Ageing tests:	(Section 2.2.2n)

3.2.4 Cardanol as plasticizer in NBR

For this work, two types of fillers, viz. A) HAF black and B) silica were employed. Compounds were prepared as per formulations given in Tables 3.1 and 3.2 and each formulation was repeated with cardanol replacing dioctyl phthalate (DOP).

A) HAF black filled compounds

Table 3.1: NBR formulations for varying carbon black content

Sample	NBR	S	ZnO	St.acid	HAF	Cardanol/	TQ	CBS	TMTD
	(phr)	(phr)	(phr)	(phr)	(phr)	DOP	(phr)	(phr)	(phr)
						(phr)			
1	100	1.5	4.5	1.75	10	1	1	1	0.5
2	100	1.5	4.5	1.75	20	2	1	1	0.5
3	100	1.5	4.5	1.75	30	3	1	1	0.5
4	100	1.5	4.5	1.75	40	4	1	1	0.5
5	100	1.5	4.5	1.75	50	5	1	1	0.5

B) Precipitated silica

Sample	NBR	S	ZnO	St.acid	Silica	DEG	Cardanol/	TQ	CBS	TMTD
	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	DOP(phr)	(phr)	(phr)	(phr)
1	100	1.5	4.5	1.75	5	1	0.5	1	1	0.5
2	100	1.5	4.5	1.75	10	1	1	l	1	0.5
3	100	1.5	4.5	1.75	15	1	1.5	1	1	0.5
4	100	1.5	4.5	1.75	20	1	2	1	1	0.5
5	100	1.5	4.5	1.75	25	1	2.5	1	1	0.5

Table 3.2: NBR formulations for varying silica content

C) Optimization of cardanol content in black filled NBR

Optimization of cardanol content for plasticization was done using a constant filler percentage of 30phr HAF black. Cardanol content was varied from 5 to 15% of the filler weight. The formulations are given in Table 3.3.

Table 3.3: NBR formulations for optimization of cardanol (30phr HAF black)

Sample	NBR	S	ZnO	St.acid	HAF	Cardanol	TQ	CBS	TMTD
	(phr)	(phr)	(phr)	(phr)	black(phr)	(phr)	(phr)	(phr)	(phr)
1	100	1.5	4.5	1.75	30	1.5	1	1	0.5
2	100	1.5	4.5	1.75	30	3.0	1	1	0.5
3	100	1.5	4.5	1.75	30	4.5	1	1	0.5

D) Optimization of cardanol in 15phr silica filled samples

Optimization of cardanol as plasticizer (Table 3.4) was done using a constant filler content of 15phr silica. Cardanol content was varied from 2.5 to 15% of filler.
Sample	NBR	S	ZnO	St.acid	Silica	DEG	Cardanol	TQ	CBS	TMTD
	(phr)	(phr)	(phr)	(phr)	(phr)			(phr)	(phr)	(phr)
1	100	1.5	4.5	1.75	15	1	0.375	1	1	0.5
2	100	1.5	4.5	1.75	15	1	0.75	1	1	0.5
3	100	1.5	4.5	1.75	15	1	1.5	1	1	0.5
4	100	1.5	4.5	1.75	15	1	1.8	1	1	0.5
5	100	1.5	4.5	1.75	15	1	1.875	1	1	0.5
6	100	1.5	4.5	1.75	15	1	2.25	1	1	0.5

Table 3.4: NBR formulations for optimization of cardanol (15phr silica filler)

3.2.5 Cardanol as antioxidant

The antioxidant property of cardanol (Table 3.5) in NBR gum samples was studied by replacing conventional antioxidant TQ with cardanol and comparing properties of the vulcanizates.

Table 3.5: NBR formulation for antioxidant study

Antioxidant	NBR	S	ZnO	St.acid	Cardanol	TQ	CBS	TMTD
	(phr)	(phr)	(phr)	(phr)		(phr)	(phr)	(phr)
Nil	100	1.5	4.5	1.75			1	0.5
Cardanol	100	1.5	4.5	1.75	1		1	0.5
TQ	100	1.5	4.5	1.75		1	1	0.5

3.2.6 Cardanol as co-activator

The co-activator property of cardanol (Table 3.6) in NBR gum samples was studied by replacing stearic acid in the formulation and comparing the properties.

Co- activator	NBR	S	ZņO	St.acid	Cardanol	CBS (phr)	TMTD
	(phr)	(phr)	(phr)	(phr)			(phr)
Nil	100	1.5	4.5	1.75		1	0.5
Cardanol	100	1.5	4.5		1.75	1	0.5

Table 3.6: NBR formulation for cardanol as co-activator

3.2.7 Cardanol as accelerator

The accelerator property of cardanol was studied by replacing CBS in the formulation (Table 3.7) and comparing the cure characteristics and mechanical properties.

Table 3.7: NBR formulation for cardanol as accelerator

	NBR	S	ZnO	St.acid		CBS	TMTD
Accelerator	(phr)	(phr)	(phr)	(phr)	Cardanol	(phr)	(phr)
CBS	100	1.5	4.5	1.75	1		0.5
Cardanol	100	1.5	4.5	1.75		1	0.5

3.3 Results and discussion

3.3.1 Cardanol as plasticizer for NBR A) HAF black filled compounds

a) Cure Characteristics: Fig. 3.1 is a comparison of cure curves of 30phr HAF black filled compounds. Similar values of torque are attained for both plasticizers. The cure characteristics are given in Fig.3.2.



Fig. 3.1 Cure curves of cardanol and DOP based samples with 30phr HAF black loading.



Fig. 3.2 Variation of cure time with HAF black content

Both plasticizers give similar cure times for different filler contents. This shows that cardanol as a plasticizer does not interfere with the curing of NBR.

 Table 3.8: Minimum and maximum torque values during cure for cardanol

 and DOP based samples with varying filler content (HAF Black)

Sample	Torque	10(phr)	20(phr)	30(phr)	40(phr)	50(phr)
	(dNm)					
Cardanol	minimum	0.284	0.346	0.431	0.588	0.660
	minimum	0.280	0.350	0.403	0.555	0.600
DOF		0.200	0.559	0.495	0.555	0.099
Cardanol	maximum	5.230	6.534	7.162	7.93	8.096
DOP	maximum	4.423	7.106	7.333	7.851	8.368
				1	1	

The minimum torque values (Table 3.8), which indicate viscosity of the compound, are close for both plasticizers. The maximum torque values (Table 3.8) are also not much different for both plasticizers. Fig. 3.3 shows comparison of the variation of scorch time with HAF black content. Both curves are similar.





Fig. 3.3 Variation of scorch time (min) with HAF black content



Fig. 3.4 Variation of a-value with HAF black content

Fig. 3.4 shows comparison of the variation of α value with HAF black content. Similar α values for cardanol based samples indicate that cardanol is a good medium for dispersing HAF black.



Fig. 3. 5 Variation of cure rate index with HAF black loading

Variation of cure rate index (CRI) with HAF black loading (Fig 3.5) shows that CRI values of cardanol based samples are generally comparable to those of DOP based ones.



Fig. 3.6 ln $(M_h - M_t)$ vs t for cardanol based NBR vulcanizate containing 30phr HAF black: k = 0.7575 where k is the first order rate constant

Study of cure reactions of HAF black filled compounds plasticized by cardanol (Fig. 3.6) and DOP (Fig. 3.7) show that they obey first order kinetics as $\ln (M_h - M_t)$ vs t plot gives a straight line with rate constant k= 0.7575 and 0.74348 respectively.



Fig. 3. 7 $\ln(M_h - M_t)$ vs t for DOP based vulcanizate containing 30phr HAF black: k=0. 7435

b) Tensile properties: Fig. 3.8 shows the variation of tensile strength of HAF black reinforced nitrile rubber, for both cases. The tensile strength values of both samples are similar. Comparative data on the effect of filler content on elongation at break vs filler content (Fig. 3.9) show that the elongation at break (%) of cardanol based samples is slightly higher than that of DOP based ones. Fig. 3.10 shows the variation of 300% modulus with HAF black content. The cardanol based samples have slightly lower modulus values. The tensile properties in general show that cardanol is at least equivalent to DOP for plasticizing NBR.



Fig. 3.8 Variation of tensile strength of NBR samples (MPa) with HAF black content



Fig. 3.9 Variation of elongation at break (%) of NBR samples with HAF black content



Fig. 3.10 Variation of modulus at 300 % elongation of NBR samples with HAF black content



Fig. 3.11 Variation of tear strength (N/mm) of NBR samples with HAF black content

c)Tear strength: The tear strength of cardanol based samples is somewhat superior (Fig. 3.11) to that of DOP based samples and it increases with filler content.



Fig. 3.12 Variation of reinforcing index on the basis of tensile strength with HAF black content



Fig. 3.13 Variation of reinforcing index on the basis of tear strength with HAF black content

The reinforcing indices (Fig. 3.12 and Fig. 3.13) are similar for both plasticizers with a slightly better value for the cardanol based samples.



Fig. 3.14 Variation of resilience (%) of NBR samples with HAF black content



Fig. 3.15 Variation of hardness (Shore A) of NBR samples with HAF black content

d) Resilience: The resilience (Fig. 3.14) of cardanol based samples is similar to that of DOP based ones.

e) Hardness: The variation of hardness with HAF black (Fig. 3.15) is almost identical for both samples.

f) Abrasion loss: Variation of abrasion loss (cc/hr.) with HAF black content (Fig. 3.16) gives similar curves for both samples.



Fig. 3.16 Variation of abrasion loss (cc/hr.) of NBR samples with HAF black content



Fig 3.17 Variation of loss of weight (%) of NBR samples with HAF black content after Soxhlet extraction

g) Soxhlet extraction: Loss of weight (%) on Soxhlet extraction is plotted against HAF black content in Fig.3.17. The weight loss is comparable for both cardanol based and DOP based samples.



Fig 3.18 Variation of crosslink density of NBR samples with HAF black content

h) Crosslink density: It is seen from Fig. 3.18 that the crosslink density of cardanol based samples is similar to that of DOP based samples. This is some what different from what was observed in the case of NR (Section.2.3.1)



Fig. 3.19 FT-IR spectrum of the extract of cardanol based vulcanizate of NBR (30phr HAF black) in toluene

i) FT-IR spectra: Comparison of the FTIR spectrum of cardanol (Fig 2.18) and that of the extract of the vulcanizates (Fig. 3.19) show that there is no trace of cardanol in the extract. This shows that loss of plasticizer during service period is not likely because cardanol has been chemically incorporated into the rubber matrix.

j) Thermogravimetric analysis: Figures 3.20 and 3.21 give the thermograms of 30phr HAF black filled NBR vulcanizates and the thermal data are given in Table 3.9. Cardanol leaves a slightly higher amount of residue than DOP.

Table 3.9: Thermal analysis of 30phr HAF black filled NBR samples

Property	Cardanol	DOP
On set point of degradation (° C)	331.35	341.98
Maximum degradation temperature (° C)	463.14	468.57
Maximum rate of degradation (% / ° C)	0.9265	0.9032
Residue (%)	29.30	25.58



Fig. 3.20 Thermogram of 30 phr HAF black loaded cardanol based NBR vulcanizate



Fig. 3.21 Thermogram of 30 phr HAF black loaded DOP based NBR vulcanizate

k) DSC analysis: The data of the differential scanning analysis are given in Table 3.10. From the data it is seen that the glass transition temperatures are similar for both samples. This shows that the plasticization effect of cardanol is similar to that of DOP in NBR.



Fig. 3.22 Differential scan of 30 phr HAF black loaded NBR vulcanizate containing cardanol



Fig. 3.23 Differential scan of 30 phr HAF black NBR vulcanizate containing DOP

The integral heat ΔH_m and the melting points (onset, peak max. and end set) are found to be slightly higher in the case of cardanol based samples. The scans of 30phr HAF black filled NBR samples containing cardanol and DOP are given in Figs. 3.22 and 3.23 respectively.

Property	Cardanol	DOP
Glass transition - onset (°C)	-18.36	-17.37
Glass transition - midpoint (°C)	-14.95	-14.21
T _m -onset (°C)	101.41	98.96
T _{m-} peak(°C)	109.69	107.86
T_{m-} end set (°C)	115.04	113.77
Integral ΔH_m (mJ)	14.19	9.02

Table 3.10: DSC data of 30 phr HAF black filled samples

B) Optimization of cardanol % for 30phr HAF black filled NBR samples



Fig. 3. 24 Variation of minimum torque with cardanol content



Fig. 3.25 Variation of maximum torque with cardanol content

It is seen from (Figs.3.24 - 3.29) that the cure characteristics are not much affected by the cardanol content. Figs. 3.30 -3.33 show the mechanical properties of the vulcanizates for different cardanol contents. Tensile strength and modulus show some dependence on the cardanol content. On the basis of tensile strength and modulus an optimal behaviour can be noticed at 10phr cardanol.



Fig. 3. 26 Variation of scorch time (min) with cardanol content



Fig. 3. 27 Variation of t₁₀ with cardanol content



Fig. 3.28 Variation of cure time with cardanol content



Fig. 3. 29 Variation of cure rate index (min⁻¹) with cardanol content



Fig. 3.30 Variation of tensile strength (MPa) with cardanol content



Fig. 3.31 Elongation at break (%) with cardanol content



Fig. 3.32 Variation of modulus at 300% elongation (MPa) with cardanol content



Fig. 3.33 Variation of tear strength (N/mm) with cardanol content

Tear strength is somewhat negatively influenced by the cardanol content (Fig. 3.33).



C) Ageing of 30phr HAF black filled samples at 100°C

Fig. 3.34 Ageing at 100 °C; variation of tensile strength (MPa) of 30phr carbon black filled NBR vulcanizate with number of days

Figs. 3.34 - 3.37 indicate the ageing properties of samples based on both plasticizers in terms of some mechanical properties. By and large the behaviour of both the samples is similar.



Fig. 3.35 Ageing at 100°C; variation of elongation at break (%) of 30phr HAF black filled NBR vulcanizate with number of days



Fig. 3.36 Ageing at 100 °C; variation of modulus at 100% elongation (MPa) of 30phr carbon black filled NBR vulcanizate with number of days

Tensile strength, tear strength and elongation at break (%) show a sudden dip after the first day of ageing. Thereafter the decline is gradual. Only the modulus maintains a more or less steady value during the ageing period.



Fig. 3.37 Ageing at 100°C; variation of tear strength (N/mm) of 30phr HAF black filled NBR vulcanizate with number of days

The tear strength values (Fig.3.37) are slightly higher for cardanol-based samples for most of the ageing period. Modulus at 100% elongation (Fig.3.36) on the other hand, remains less for cardanol-based samples during the ageing period. This must be examined in the light of results of extraction studies on aged samples to be presented later. Higher modulus of DOP-based samples is probably the result of loss of plasticizer on ageing due to chemical decomposition or blooming. The fall in properties after the first day of ageing, may be the result of chemical reactions between cardanol and sulphur during the curing process. Many vulcanized vegetable oils (factices) customarily used for rubber processing are known to be unstable at temperatures normally employed for rubber vulcanization (1). It can be hypothesized that the sulphur liberated by decomposition of this product is utilized subsequently by the rubber which is reflected by improved properties after the second day of ageing. Considering that cardanol has several sites of unsaturation this is a definite possibility.



Fig. 3.38 Variation of free sulphur content of 30phr HAF black filled NBR vulcanizate on ageing

Variation of free sulphur estimated at various stages of ageing shown in Fig.3.38 is also supportive of this. Initially free sulphur content of the cardanol- based sample is much less than the DOP based sample. But after the first day of ageing, there is a

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sharp increase in free sulphur content presumably due to the breakage of cardanolsulphur linkages. It is likely that the sulphur is subsequently utilized by nitrile rubber to form more crosslinks. By the second day of ageing, both samples show practically the same free sulphur content after a sharp fall in the case of the cardanol- based samples. Both samples show almost equal free sulphur values for the rest of the ageing period. A similar behaviour has been noticed in the case of natural rubber plasticized by cardanol (Section 2.3.1). Crosslink densities (Fig. 3.39) of both cardanol and DOP based vulcanizates are similar.



Fig. 3.39 Variation of crosslink density of 30phr HAF black filled NBR sample on ageing



Fig. 3.40 Weight loss on Soxhlet extraction after 72h. ageing

Fig. 3.40 shows the comparative weight loss on Soxhlet extraction after ageing for 72h. The cardanol based samples give considerably less extractable matter after ageing.

D) Silica filled compounds

a) Cure characteristics: Curing studies indicate that cure characteristics do not vary much with plasticizer choice. Fig. 3.41 is a comparison of typical cure curves for both cases.



Fig. 3.41 Cure curves of NBR compounds with 15 phr silica content

Similar torque values are attained for cardanol and DOP during cure. The minimum torque values (Table 3.11), which indicate viscosity of the compound, are lower for cardanol-based samples. Hence cardanol is a better plasticizer for NBR. The lower values of maximum and minimum torques attained during cure by the cardanol-containing compound point to a lower shear modulus and a more effective plasticizing action.

Table 3.11Minimum and maximum torque values during cure for cardanoland DOP based samples with varying filler content

Sample	Torque(dNm)	5phr	10phr	15phr	20phr	25phr
Cardanol	minimum	0.251	0.219	0.268	0.287	0.317
DOP	minimum	0.271	0.245	0.275	0.330	0.343
Cardanol	maximum	4.847	5.256	6.429	6.348	6.466
DOP	maximum	4.968	5.465	6.459	7.534	6.953



Fig. 3.42 Variation of cure time (min) with silica loading for NBR samples

The cure time (Fig. 3.42) is largely unaffected by the filler content for both the plasticizers.



Fig. 3.43 Variation of alpha value with silica loading for NBR samples

Lower values of α indicate better filler dispersion in the case of cardanol (Fig. 3.43). From figure 3.44 it is seen that CRI values of DOP based compounds are higher than that of cardanol based ones suggesting that DOP plays a more active role in the curing process than cardanol.



Fig. 3.44 Variation of CRI (min⁻¹) with silica loading for NBR samples

b) Kinetics of cure reactions



Fig. 3.45 $\ln(M_h - M_t)$ vs t for 15phr silica filled NBR vulcanizate containing cardanol; k=0.85



Fig. 3.46 $\ln(M_h - M_t)$ vs t for 15phr silica filled NBR vulcanizate containing DOP; k = 1.1

Study of the kinetics of cure reactions of 15phr silica filled cardanol and DOP based compounds (Figs. 3.45 and 3.46) show that they obey first order kinetics as $ln(M_h - M_t)$ vs t plot gives approximate straight lines. DOP leads to a higher reaction rate constant.

c) Mechanical properties

Fig. 3.47 shows the variation of tensile strength of silica-reinforced nitrile rubber for both cases. The cardanol-based samples show somewhat better tensile values. More effective plasticization by cardanol gives a more homogeneous compound with better filler dispersion. About 20phr silica appears to be the optimal filler content for silica filled NBR. Modulus values at 300% elongation (Fig. 3.48) are similar for cardanol-based samples. Fig. 3.49 shows the change in elongation-at break on using cardanol in place of DOP. Cardanol shows somewhat higher elongation at break at higher filler contents which can be due to a higher level of plasticization. The tensile properties, in general, show that cardanol is the superior plasticizer.

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The tear strength of samples employing both plasticizers has been measured as a function of silica content (Fig.3.50). Although both cases show equivalent performance at 5phr silica content, the cardanol-based sample has a clear superiority at higher silica contents. This is an indication of better wetting of the filler by cardanol resulting in a more homogeneous product in comparison with DOP. The better wetting properties may be the result of lower viscosity, interactions with carbon black due to structural factors etc.



Fig. 3.47 Variation of tensile strength (MPa) of NBR vulcanizates with silica loading



Fig. 3.48 Variation of modulus at 300% elongation (MPa) of NBR vulcanizates with silica loading



Fig. 3.49 Variation of elongation at break (%) of NBR vulcanizates with silica loading



Fig. 3.50 Variation of tear strength of NBR vulcanizates with silica loading



Fig. 3.51 Variation of reinforcing index on the basis of tensile strength with silica loading



Fig. 3.52 Variation of reinforcing index on the basis of tear strength with silica loading

The reinforcing index values (Fig.3.51 and 3.52) are generally high for cardanol plasticized samples.



Fig. 3.53 Variation of resilience (%) of NBR vulcanizates with silica loading



Fig. 3.54 Variation of hardness (Shore A) of NBR vulcanizates with silica loading

Resilience and surface hardness (Figs.3.53 and 3.54) of specimens employing both plasticizers show similar behaviour.



Fig. 3.55 Variation of weight loss on Soxhlet extraction of 5-25 phr silica filled NBR vulcanizates using toluene.

Fig.3.55 is a plot of the weight loss on Soxhlet extraction of NBR samples plasticized by the two different materials. In general, the amounts of toluene-soluble material in the vulcanizate for both cases are similar.

Fig.3.56 shows the variation of abrasion loss with silica content. Abrasion loss is slightly less when cardanol is used as plasticizer. This again points to better homogeneity in the vulcanizate possibly due to more effective wetting of the filler by cardanol.



Fig. 3.56 Variation of abrasion loss with silica loading



Fig. 3. 57 Variation of crosslink density (mmol / kg RH) with silica loading

Fig. 3.57 shows the variation of crosslink density with silica content. Comparison of the two shows that both samples behave similarly. Table 3.12 gives the TGA of 15phr silica filled NBR samples. The onset point of degradation is higher for cardanol based sample compared to the DOP based sample, whereas the maximum degradation temperature and the maximum rate of degradation are lower for cardanol based samples. But the amount of residue is found to be marginally greater for DOP based samples.
Table 3.12: TGA data of 15phr silica filled samples

Property	Cardanol	DOP
On set point of degradation (° C)	334.14	304.64
Maximum degradation temperature (° C)	460.07	462.7
Maximum rate of degradation (% / ° C)	70.93	72.27
Residue (%)	20.92	22.48

Figs. 3.58 and 3.59 give the thermograms of 15phr silica filled NBR samples containing respectively cardanol and DOP as plasticizers. DOP has a slight superiority in the case of residue percentage.



Fig. 3.58 Thermogram of 15phr silica filled NBR samples containing cardanol



Fig. 3.59 Thermogram of 15phr silica filled NBR samples containing DOP

E) Optimization of cardanol percentage for 15phr silica based NBR compounds

The following Figs.3.60-3.64 indicate the results of variation of cure characteristics of 15phr silica filled NBR samples with cardanol content. 2.5- 15% of cardanol was used for the study as percentage of filler.



Fig. 3.60 Variation of minimum torque with cardanol content

The minimum torque value (Fig. 3.60) is found to increase slightly with increase in cardanol content; whereas the maximum torque value and cure time (Figs. 3.61-3.62) are not much affected.



Fig. 3.61 Variation of maximum torque with cardanol content



Fig. 3.62 Variation of cure time (min) with cardanol content



Fig.3.63 Variation of α - value with cardanol content





From alpha values (Fig. 3.63) and CRI (Fig. 3.64), it is seen that 5-7.5 % of cardanol is enough for plasticization of silica filled compounds.



Fig. 3.65 Variation of tensile strength with cardanol content



Fig. 3.66 Variation of elongation at break (%) with cardanol content



Fig. 3.67 Variation of modulus at 300% elongation with cardanol content





Figs. 3.65-3.68 indicate the variation of mechanical properties with cardanol content. The tensile strength and modulus (Figs. 3.65 and 3.67) are a maximum at 5% cardanol content, whereas tear strength is a maximum for 10% of cardanol. Generally, the properties of the vulcanizate are not very sensitive to cardanol content. About 5-7.5% cardanol appears to be necessary for an appreciable balance of properties.

F) Ageing at 100°C of 15phr silica filled samples containing each plasticizer

Figs. 3.69-3.73 indicate the ageing behaviour of samples employing each plasticizer. The mechanical properties have been estimated after ageing. The behaviour of the two sets of samples shows similarity in the case of tensile strength (Fig. 3.69), elongation at break (Fig.3.70) modulus at 300% elongation (Fig. 3.71) and tear strength (Fig. 3.72). Most of these properties show a more rapid fall after the first day of ageing in the case of cardanol-based vulcanizate. For the rest of the ageing period (3-10 days), the properties of cardanol and DOP based rubber show similar values.



Fig.3.69 Ageing at 100°C; variation of tensile strength of NBR with number of days with cardanol / DOP as plasticizer.

Fig.3.73 shows comparative weight loss of the vulcanizates on Soxhlet extraction after ageing for 72 hrs. The amount of extractables after ageing is substantially lower in the case of cardanol. This shows that cardanol is a more suitable candidate where extractability is of concern. The increase in extractables in the case of DOP might mean that the ester offers less protection to NBR from chain scission

reactions leading to the formation of extractable oligomers. Similar behaviour is observed in the case of HAF black filler (Fig. 3.40).



Fig.3.70 Ageing at 100° C; variation of elongation at break (%) of NBR with number of days with cardanol / DOP as plasticizer.



Fig. 3.71 Ageing at 100°C; variation of modulus at 300% of NBR with number of days with cardanol / DOP as plasticizer.



Fig. 3.72 Ageing at 100°C: variation of tear strength of NBR with number of days with cardanol / DOP as plasticizer.



Fig. 3.73 Weight loss on Soxhlet extraction after ageing for 72h.

3.3. 2 Cardanol as antioxidant

The following graphs (Figs. 3.74 -3.76) show the comparative performance of cardanol as an antioxidant for NBR gum compounds.

a) Cure characteristics:



Fig. 3. 74 Cure curves of NBR gum samples

Table 3. 13: Cure characterist	ics when o	cardanol is 🛙	used as	antioxidant
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	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
Antioxidant	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻¹
					(dNm)	(dNm)	
None	3.57	3.09	3.66	7.18	4.55	0.248	27.7
Cardanol	3.69	3.25	3.75	6.08	4.629	0.249	41.84
TQ	3.32	2.83	3.37	6.59	4.507	0.271	30.58

Similar cure curves (Fig. 3.74) are obtained for all the three gum samples. The scorch time, t_{10} , t_{50} and t_{90} (Table 3.13) are lower when cardanol is used as antioxidant. The cardanol based samples have higher maximum torque and cure rate index values whereas the minimum torque value which indicates the viscosity of the compound is low. Higher rates of cure are attained when cardanol is used as an antioxidant.

	Tensile strength	Elongation at	Modulus at 300%	Tear strength
AO	(MPa)	Break (%)	Elongation	(N/mm)
None	6.11	549.6	3.1	19.46
Cardanol	7.43	659.12	2.71	23.81
TQ	5.3	466.9	2.89	24.89

Table 3. 14 Mechanical properties when cardanol is used as antioxidant

b) Mechanical properties: Comparison of mechanical properties (Table 3.14) shows that the tensile strength, elongation at break, the tear strength and 300% modulus values are comparable or in some cases better for cardanol.

c) Thermal analysis: Thermal analysis (Table 3.15) indicates that the thermal stability of the cardanol based samples is comparable to that of TQ based ones. The thermograms are given in Figs. 3.75 and 3.76

Table 3.15 Thermal analysis of NBR gum samples with cardanol as AO

Property	Cardanol as AO	TQ as AO
Onset point of degradation (°C)	307.67	312.3
Maximum degradation temperature (°C)	458.03	461.24
Maximum rate of degradation (% / °C)	85.40	85.2
Residue (%)	10.55	11.62







Fig. 3.76 Thermogram of NBR gum sample with TQ as antioxidant

d) Ageing at 100°C of NBR gum samples



Fig. 3.77 Variation of tensile strength with no. of days



Fig. 3. 78 Variation of elongation at break (%) with no. of days

Figs. 3.77 - 3.80 show that on ageing 30phr HAF black filled NBR samples at 100°C for 5 days, initially (one day of aging) the tensile strength elongation at break values decrease to a greater extent for the cardanol based sample. But these values are similar to that of the TQ based sample for the rest of the ageing period.





The modulus at 300% elongation (Fig.3.79) and tear strength (Fig.3.80) values of cardanol based samples are similar to that when TQ is used as antioxidant.

Antioxidant properties of cardanol are comparable to that of TQ in NBR gum samples demonstrating the feasibility of using cardanol as an antioxidant in NBR.



Fig. 3.80 Variation of tear strength with no. of days



3.3.3 Cardanol as co-activator

Fig. 3.81 Cure curves of NBR gum samples with

Fig. 3.81 gives a comparison the cure curves A, B and C of NBR gum samples containing A) stearic acid co-activator and CBS accelerator B) cardanol co-activator and CBS accelerator and C) stearic acid co-activator and cardanol

accelerator respectively. On comparing A and B, it is seen that similar cure curves are obtained for both cases.

When stearic acid is replaced by cardanol for NBR compounding (B), similar values of ts_2 , t_{10} and t_{50} are obtained (Table 3.16). But t_{90} , the cure time is substantially lower compared to sample A. Similarly, minimum and maximum values of torque are comparable whereas cure rate index value, CRI is much higher for Case B. Hence cardanol can replace stearic acid in NBR compounds as co-activator.

The mechanical properties, tensile strength and tear strength (Table 3.17) are similar for both samples whereas the elongation at break is higher and the modulus at 300% elongation is slightly lower for Case B compared to Case A. Thermal analysis (Table 3.18) also shows that the thermal stability is equally good when cardanol is used as co-activator.

Table 3. 16 : Cure characteristics when cardanol is used as co- activator

NBR	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
gum	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻
samples					(dNm)	(dNm)	1
Α	3.57	3.09	3.66	7.18	4.55	0.248	27.7
В	3.51	3.08	3.50	5.46	4.19	0.258	51.28

Table 3. 17: Mechanical properties when cardanol is used as co- activator

NBR	gum	Tensile	Elongation at	Modulus at	Tear
samples		strength	break (%)	300%	strength
		(MPa)		Elongation	(N/mm)
A		6.11	549.6	3.1	19.46
В		5.48	590	2.52	19.9

Table	3.18:	Comparison	of TGA	of NBR	gum	samples	containing	1)	stearic
acid a	nd 2)	cardanol as co	o-activat	ors					

NBR gum samples	Α	B
Onset point of degradation (°C)	325.83	311.71
Maximum degradation temperature (°C)	460.88	461.35
Residue (%)	8.958	11.38

Similar thermal stability is observed when stearic acid is replaced by cardanol as co-activator (Table 3.18) in NBR gum samples. Interaction between cardanol and Zn^{2+} is explored in Section 2.3.3.

3.3.4 Cardanol as accelerator

A comparison of cure curves of NBR gum samples A and C is given in Fig. 3.81. Case A has CBS as accelerator and in C, CBS is replaced by cardanol. Similar cure curves with a lower torque are obtained for C.

On comparing the cure characteristics (Table 3.19) it is seen that t_{s_2} , t_{10} , t_{50} and t_{90} are slightly higher whereas maximum torque is slightly lower for the cardanol based sample. The minimum torque and cure rate index values are similar for both cases.

On comparing the mechanical properties of NBR gum samples A and C (Table 3.20), it is seen that the tensile strength, modulus at 300% elongation and tear strength are marginally lower for the cardanol based sample. Hence the use of cardanol in NBR gum compounds as accelerator is not fully justified.

Table	3.19	Cure char	racteristics	of NBR	gum s	samples	when	cardanol	is used
as acce	lerato	r							

NBR	gum	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max. torque	Min. torque	CRI
samples		(min)	(min)	(min)	(min)	(dNm)	(dNm)	(min) ⁻¹
A		3.57	3.09	3.66	7.18	4.55	0.248	27.7
c		4.6	3.18	4.38	8.32	3.88	0.248	26.88

Table 3. 20: Med	chanical	properties	of NBR	gum	samples	when	cardanol	is
used as accelerate	or							

NBR gum	Tensile	Elongation at	Modulus at 300%	Tear strength
samples	strength (MPa)	break (%)	elongation	(N/mm)
A	6.11	549.6	3.1	19.46
С	5.9	747	2.9	15.6

3.4 Conclusions

When cardanol is used as plasticizer in place of DOP for HAF black filled compounds, similar cure curves are obtained. The cure times, cure rate indices, α values (which indicate filler dispersion) and the minimum torque values (which indicate the viscosity of the compounds) are close for both plasticizers. On comparison of mechanical properties, viz. tensile strength, elongation at break, modulus and tear strength, similar values are obtained for both plasticizers. Other properties like resilience, abrasion loss and surface hardness are also comparable for both plasticizers.

Mechanical property measurements after ageing establish that cardanol leads to a vulcanizate of similar ageing behaviour. Free sulphur analysis and extraction using toluene suggest that cardanol undergoes chemical changes during cure / ageing which are generally beneficial. TGA results are similar for both cases with a slightly greater residue for the cardanol based sample. The crosslink density of cardanol based samples is similar to that of DOP based samples. Cardanol can hence be used as a plasticizer for black filled NBR compounds.

In the case of silica filled compounds, even though similar cure curves are obtained for both plasticizers, the minimum torque value as well as the α values are lower for cardanol based samples indicating a more effective plasticizing action. The tensile properties are slightly higher for the cardanol based samples at higher filler contents. The cardanol based samples have a clear superiority of tear strength at higher filler contents indicating better plasticization. The crosslink density of cardanol based samples is comparable to that of DOP based samples. Cardanol is hence a good plasticizer for silica filled NBR.

Optimization of cardanol content for 30phr HAF black filled compounds show that the cure characteristics are not much altered by increase in cardanol content. The mechanical properties are also a maximum at the same cardanol content. About 10% cardanol appears to be the optimal amount. But for silica filled compounds 5-7.5 % of cardanol is optimal.

The antioxidant property of cardanol is comparable to that of TQ for NBR gum samples. When cardanol is used as co-activator in place of stearic acid, cure time is lowered and CRI increased and the tensile properties and tear strength are comparable. When cardanol is used as accelerator in place of CBS, similar cure characteristics and slightly inferior mechanical properties are obtained. The study establishes the multifarious utility of cardanol, a renewable resource, for NBR processing.

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4.1 Introduction

In this chapter, methods of utilizing cardanol in EPDM rubber processing are investigated. The plasticizer property of cardanol is compared with that of a conventional plasticizer, naphthenic oil, (1,2) at various filler contents, ie. 10-50 phr HAF black and 5-25 phr precipitated silica (Section 4.3.1). Antioxidant property was compared with that of TQ in gum samples (Section 4.3.2). Ageing studies were done for both plasticizer and antioxidant applications (Section 4.3.1). Co-activator (Section 4.3.3) and accelerator (Section 4.3.4) properties were compared with that of the transformation of transformation of the transformation of transf

4.2 Experimental work

4.2.1 Raw Materials

a) Elastomer

EPDM (Dutral-TER 4038EP)) was obtained from Poland

Mooney viscosity	ML (1+8) 125°C	$-55 \pm 5 \text{ MV}$
Ash content		- ≤ 0.5%
Volatile matter		<i>-</i> ≤ 0.75%
Diene content		$-4.5 \pm 0.6\%$
Ethylene content		-68 ± 4%
Density		-0.86 g/cc

b) Compounding ingredients

Naphthenic oil

Naphthenic oil was supplied by Indian oil Corporation. It had the following specifications.

Colour - lightPour point (°CAniline point (°C)-78Viscosity gravity constant (VGC-0.85 -0.9

Aromaticity

-10-30

Other ingredients, their details and suppliers were already presented in Section 2.2.1

4.2.2 Compounding and curing of EPDM

Mixes were prepared on a laboratory size two roll mixing mill as per the procedure given in Section 2.2.2. The cure times of mixes were determined at 160°C using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per ASTM Standard, D 2084-01.

The rubber compounds were vulcanized to the optimum cure time at 160°C and 11.6 MPa. The moldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h. prior to testing.

4.2.3 Evaluation methods

Different evaluation methods employed for the present study are the following:-

a)	Cure characteristics (as per details given i	n Section 2.2.2 a)
b)	Tensile properties	(Section 2.2.2 b)
c)	Tear resistance:	(Section 2.2.2 c)
d)	Hardness:	(Section 2.2.2 d)
e)	Abrasion resistance:	(Section 2.2.2 e)
f)	Rebound resilience:	(Section 2.2.2 f)
g)	Soxhlet extraction:	(Section 2.2.2g)
h)	FTIR spectroscopy:	(Section 2.2.2h)
i)	Crosslink density:	(Section 2.2.2 i)
j)	Free sulphur analysis:	(Section 2.2.2 j)
k)	Thermo gravimetric analysis:	(Section 2.2.2 k)
I)	Differerential scanning calorimetric analys	is: (Section 2.2.2 l)
m)	Mooney viscosity:	(Section 2.2.2 l)
n)	Ageing tests:	(Section 2.2.2 n)

4.2.4 Cardanol as plasticizer in EPDM compounds

In this study mixes were prepared on a laboratory size two roll mixing mill.. The formulations employed are given in Tables 4.1, 4.2 and 4.3 and each formulation was repeated with cardanol replacing naphthenic oil. The cure characteristics of the compounds and properties of both cardanol and naphthenic oil based vulcanizates were compared using the evaluation methods given in Section 4.3.

A) HAF black filled compounds

Sample	EPDM	ZnO	St.acid	HAF	Naphthenic	CBS	TMTD	ZDC	S	TQ
:	(phr)	(phr)	(phr)	black	oil	(phr)	(phr)	(phr)	(phr)	(phr)
				(phr)	/cardanol					
					(phr)					
1	100	4	2	10	0.5	1	0.5	0.5	1	1
2	100	4	2	20	1.0	1	0.5	0.5	1	1
3	100	4	2	30	1.5	1	0.5	0.5	I	1
4	100	4	2	50	2.5	1	0.5	0.5	1	1
5	100	4	2	70	3.5	1	0.5	0.5	1	1

Table 4.1: EPDM formulations for varying HAF black content.

B) Silica filled compounds

i) Low silica content formulations

Mixes were prepared according to formulations in Table 4.2. The cure characteristics and mechanical properties of cardanol and naphthenic oil based samples were compared. As the properties showed a remarkable increasing trend at the maximum filler content studied, another study was also done covering a higher range of silica contents.

Sample	EPDM	ZnO	St.acid	Silica	DEG	Naphthenic	CBS	TMTD	ZDC	S	TQ
	(phr)	(phr)	(phr)	(phr)		oil (phr)	(phr)	(phr)	(phr)	(phr)	(phr)
1	100	4	2	5	1	0.25	1	0.5	0.5	1	1
2	100	4	2	10	1	0.5	1	0.5	0.5	1	1
3	100	4	2	15	1	0.75	1	0.5	0.5	1	1
4	100	4	2	20	1	1.0	1	0.5	0.5	1	I
5	100	4	2	25	1	1.25	1	0.5	0.5	1	1

Table 4.2: EPDM formulations for low silica content

Table 4.3 EPDM formulations for high silica content

Sample	EPDM	ZnO	St.acid	Silica	DEG	Naphthenic	CBS	TMTD	ZDC	S	TQ
	phr	phr	phr	phr		oil phr	phr	phr	phr	phr	phr
ł	100	4	2	30	1	1.5	1	0.5	0.5	1	1
2	100	4	2	40	1	2.0	1	0.5	0.5	1	1
3	100	4	2	50	1	2.5	1	0.5	0.5	1	1
4	100	4	2	70	1	3.5	1	0.5	0.5	1	1
5	100	4	2	90	1	4.5	1	0.5	0.5	1	1

ii) High silica content formulations

Compounds were prepared according to formulations in Table 4.3. The cure characteristics and mechanical properties of cardanol and naphthenic oil based samples were compared. Similarly, oxidative ageing tests were carried out for 120hrs.in accordance with ASTM D573-04, in an air oven at 100°C. After another 24 hours of conditioning at ambient temperature, tensile strength and tear resistance of the samples were determined as per ASTM D 412 and 624 respectively

C) Optimization of cardanol content

Optimization of cardanol content was done for 50phr HAF black loaded samples according to the formulations in Table 4.4. The cure characteristics and mechanical properties were compared.

Table 4.4 EPDM formulations for optimization of cardanol content in 50 phrHAF black filled compounds

Sample	EPDM	ZnO	St.acid	HAF	Cardanol	CBS	TMTD	ZDC	S	TQ
ļ	(phr)	(phr)	(phr)	black	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
				(phr)						
1	100	4	2	50	1.25	1	0.5	0.5	1	1
2	100	4	2	50	2.5	1	0.5	0.5	1	1
3	100	4	2	50	5	1	0.5	0.5	1	1

Similarly, optimization of cardanol content was done in the case of 50phr silica loaded samples according to the formulations in Table 4.5 and the cure characteristics and mechanical properties were compared to get the optimum value of cardanol percentage.

Table 4.5: EPDM formulation for optimization of cardanol content in silicafilled compounds

Sample	EPDM	ZnO	St.acid	Silica	DEG	Card-	CBS	TMTD	ZDC	S	TQ
	(phr)	(phr)	(phr)	(phr)	(phr)	anol	(phr)	(phr)	(phr)	(phr)	(phr)
						(phr)					
1	100	4	2	50	1	1.25	1	0.5	0.5	1	1
2	100	4	2	50	1	2.5	1	0.5	0.5	1	1
3	100	4	2	50	1	3.75	1	0.5	0.5	1	1
4	100	4	2	50	1	5	1	0.5	0.5	1	1

4.2.5 Cardanol as antioxidant

Compounds were prepared according to the formulation given in Table 4.6. The cure characteristics and mechanical properties (Section 2.2.2) of cardanol and TQ based samples were compared. Oxidative ageing tests were carried out for periods of 24, 48, 72, 96, and 120 h. in accordance with ASTM D573-04, in an air oven at

100°C. After 24 hours of conditioning at ambient temperature, tensile strength and tear resistance of the samples were determined as per ASTM D 412 and 624 respectively. The antioxidant property of cardanol was studied by replacing a conventional antioxidant TQ with cardanol in the formulation and comparing the cure characteristics, mechanical properties and ageing behavior.

Ingredients	Quantity (phr)
EPDM	100
ZnO	4
Stearic acid	2
TQ /cardanol	1
CBS	0.8
S	2.5

Table 4.6: EPDM gum formulation for antioxidant activity

4.2.6 Cardanol as co-activator in EPDM gum compounds

Compounds were prepared according to the formulation given in Table 4.7. The cure characteristics and mechanical properties (Section 2.2.2) of samples were determined. The co-activator property of cardanol was investigated comparing the cure characteristics and mechanical properties of the cardanol and stearic acid based samples.

Ingredients	Quantity (phr)
EPDM	100
ZnO	4
Stearic acid / cardanol	2
CBS	0.8
S	2.5

Table 4.7 EPDM gum formulation for co-activator property

4.2.7 Cardanol as accelerator

The accelerator property of cardanol was investigated by replacing CBS with cardanol in the formulation (Table 4.8). The cure characteristics and mechanical properties of both samples were compared.

Ingredients	Quantity (phr)
EPDM	100
ZnO	4
Stearic acid	2
CBS / cardanol	0.8
S	2.5

Table 4. 8: Formulation for cardanol as accelerator

4.3 Results and discussion

4.3.1 Plasticizer properties of cardanol in EPDM compounds A) HAF black filled compounds

a) Cure characteristics:



Fig. 4.1 Cure curves of 50 phr HAF black filled samples

Fig 4.1 is a comparison of cure curves of 50phr HAF black filled samples containing both plasticizers. Both curves are similar

Table 4.9 Cure characteristics of 50 phr HAF black filled samples

	ts ₁	ts ₂	t 10	t 50	t 90		CRI	Min.	Max.
Plasticizer	min	min	min	min	Min	α	min ⁻¹	torque,	torque,
								dNm	dNm
Cardanol	0.96	1.09	0.94	1.57	5.45	1.29	22.9	0.497	9.37
Naphthenic	1.0	1.27	1.08	1.68	5.08	1.44	26.3	0.486	9.754
oil									

The cure characteristics of 50 phr HAF black filled samples given in Table 4.9 are similar for both cardanol and naphthenic oil based samples. The naphthenic oil based sample shows a slightly higher CRI value.

ł	black filled samples										
		Torque	10	20	30	50	70	90			
	Sample	(dNm)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)			

Table 4.10: Minimum and maximum torque values during cure for HAF

	lorque	10	20	30	50	/0	90
Sample	(dNm)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
Cardanol	minimum	0.216	0.245	0.339	0.492	0.873	1.33
Naphthenic	minimum	0.182	0.278	0.324	0.486	0.987	1.42
oil							
Cardanol	maximum	5.86	5.887	7.871	9.37	13.09	14.06
Naphthenic	maximum	6.194	6.701	8.655	9.754	13.15	14.12
oil							

On comparing the minimum torque values (Table 4.10) for the two plasticizers, cardanol is seen to give lower values at higher filler loadings \geq 50phr. Again, the maximum torque values are found to be uniformly higher for naphthenic oil based samples. Though the cure times (Fig 4.2) of samples containing cardanol is slightly longer for lower filler contents, they are similar above 50phr HAF black. Similarly, cure rate index values (Fig 4.3) are slightly lower for cardanol based samples at low filler contents and are similar above 50phr HAF black content. The alpha values (Fig 4.4) are found to be somewhat lower for cardanol based sample indicating better filler dispersion.



Fig. 4.2 Variation of cure time with HAF black content



Fig. 4.3 Variation of CRI with HAF black content



Fig. 4.4 Variation of a value with HAF black content

Kinetics of cure reactions of 50phr HAF black filled cardanol (Fig 4.5) and naphthenic oil (Fig 4.6) based compounds show that they obey first order kinetics during cure as $\ln (M_h - M_t)$ vs t gives a straight line for each case; the rate constants of which are k = 0.32 and 0.33 respectively. M_h and M_t are the maximum torque and torque at time t respectively. This shows that cardanol does not affect the kinetics of cure reactions.



Fig.4.5 ln($M_h - M_t$) vs t for 50phr HAF black filled sample containing cardanol: k=0.323 where k is the first order rate constant



Fig.4.6 ln($M_h - M_t$) vs t for 50phr HAF black filled sample containing naphthenic oil: k=0.333

b) Tensile properties: Fig. 4.7 shows the variation of tensile strength of HAF reinforced EPDM rubber for both cases. Both curves are similar and the tensile strength falls gently above 50phr HAF black. Also comparative data on the effect of filler content on elongation at break (Fig. 4.8) shows equivalent performance by both plasticizers with a maximum at 50phr filler content. Fig. 4.9 shows that the variation of 100% modulus with HAF black content for both cases is similar up to 50phr filler content and at 70phr, the cardanol based sample has some superiority. For the cardanol-based sample, the 100% modulus value shows a maximum at 70phr filler content. The tensile properties, in general, show that cardanol is similar to naphthenic oil as a plasticizer.



Fig.4.7 Variation of tensile strength (MPa) with HAF black loading



Fig.4.8 Variation of elongation at break (%) with HAF black



Fig. 4.9 Variation of modulus at 100 % elongation with HAF black content

c) Tear strength: Tear strength values (Fig. 4.10) for both cases are similar, when each of cardanol and naphthenic oil is used as plasticizers for EPDM. The tear strength values increase with increase in filler content up to 50phr HAF black above which the values are somewhat steady.



Fig. 4.10 Variation of tear strength (N/mm) with HAF black loading (phr)







Fig.4.12 Variation of reinforcing index (RI) with filler content on the basis of tear strength

Figs. 4.11 and 4.12 show the variation of reinforcing indices on the basis of tensile strength and tear strength respectively with filler content. They are similar for both cases with minor differences. 50phr appears to be somewhat optimal for this case.



Fig. 4.13 Variation of abrasion loss with HAF black content

d) Abrasion loss: Similar abrasion loss (Fig. 4.13) is exhibited by both plasticizers.

e) Resilience: Similar resilience values are obtained (Fig. 4.14) for both cases.



Fig.4.14 Variation of resilience (%) with HAF black content



Fig. 4.15 Results of Soxhlet extraction of 50phr HAF black loaded samples using toluene as solvent

f) Soxhlet extraction: The data given in Fig. 4.15 after Soxhlet extraction of cured samples are also significant. Cardanol based samples contain less extractable matter compared to naphthenic oil based samples.



Fig.4.16 FT-IR spectrum of the Soxhlet extract of 50phr HAF black filled sample
On comparison of the IR spectrum of cardanol (Fig. 2.13) and that of the extract (Fig 4.16), it is seen that the OH absorption at 3368 cm⁻¹ is absent in the spectrum of the Soxhlet extract which shows that cardanol is not extractable from the sample. Hence loss of plasticizer during service period is not likely.

Property	Cardanol as plasticizer	Naphthenic oil as plasticizer
Onset point of degradation (°C)	395.46	394.45
Maximum degradation temperature (°C)	493.72	483.21
Maximum rate of degradation (% / °C)	1.715	1.947
Residue (%)	33.34	23.91

Table 4.11: TGA of 50phr HAF black filled samples

g) Thermogravimetric analysis: TGA of 50phr HAF black filled samples (Figs.4.17, 4.18 and Table 4.11) shows that the thermal stability of cardanol based sample is better than that of naphthenic oil based ones. The onset point of degradation, maximum degradation temperature and residue are found to be higher when cardanol is used as plasticizer for EPDM. The large difference in residue % is notable.



Fig.4.17 Thermogram of EPDM sample containing 50phr HAF black and cardanol



Fig.4.18 Thermogram of EPDM sample containing 50phr HAF black and naphthenic oil







Cure time (Fig. 4.19) is found to be a minimum for 5% of cardanol. The scorch time (Fig. 4.20) is only slightly affected by cardanol content there being a small increase in scorch time with increase in cardanol content.



Fig. 4.20 Variation of scorch time with increasing cardanol content

The minimum torque (Fig. 4.21), maximum torque (Fig. 4.22), and alpha value (Fig. 4.23) are found to decrease with increase in cardanol content. The tensile strength (Fig. 4.24) and tear strength (Fig. 4.27) are found to decrease with cardanol content above 5 % indicating excessive plasticization. Similarly the elongation at break (Fig. 4.25) is found to increase above 5 % which is also indicative of excessive plasticization. Modulus at 100% elongation (Fig. 4.26) is also found to decrease with increase in cardanol content.



Fig. 4.21 Variation of minimum torque with increasing cardanol content



Fig. 4.22 Variation of maximum torque with increasing cardanol content



Fig. 4.23 Variation of alpha value with increasing cardanol content



Fig. 4.24 Variation of tensile strength with increasing cardanol content



Fig. 4.25 Variation of elongation at break (%) with increasing cardanol content



Fig. 4.26 Variation of modulus at 100% elongation with increasing cardanol content



Fig. 4.27 Variation of tear strength with increasing cardanol content

Based on tensile strength (Fig. 4.24), tear strength (Fig. 4.27) and cure time, 5% cardanol of 50phr HAF black is found to be optimum for EPDM compounds.

C) Ageing at 100°C of 50phr HAF black filled compounds

Figs. 4.28-4.31 indicate the ageing behavior (based on tensile and tear properties) of 50phr HAF black filled NBR samples containing a) cardanol and b) naphthenic oil as plasticizers.



Fig. 4.28 Variation of tensile strength (MPa) with hours of ageing

The tensile strength (Fig. 4.28) remains almost steady on ageing for the cardanol based sample. Even though the modulus (Fig. 4.30) values of both samples are found to increase on ageing, the cardanol based samples are superior to that of naphthenic oil based ones.



Fig. 4.29 Variation of elongation at break (%) with ageing

The elongation at break values (Fig. 4.29) are similar for both samples. The elongation reduces for both samples on ageing in a similar fashion.



Fig. 4.30 Variation of modulus at 100% elongation with ageing





The tear strength values (Fig. 4.31) on ageing are found to be comparable as in the case of elongation at break. The tear strength falls on ageing.

The addition of cardanol has led to some interesting changes in the properties of the vulcanizate after ageing. The tensile strength remains steady for the cardanol based sample even after 5 days of ageing. The modulus values show a dramatic increase on ageing. In the case of elongation at break and tear strength both samples show a deterioration of properties in a strikingly similar pattern. The behaviour of cardanol in EPDM suggests chemical interactions between cardanol, the unsaturated components of EPDM and sulphur. It is possible that cardanol forms stable crosslinks with ENB and /or DCPD through sulphur chains. But unlike in the case of NR these crosslinks are not affected by ageing. This probably explains the excellent tensile strength and modulus of cardanol based samples on ageing.

D) Silica filled compoundsi) Low silica content (5-25phr)

Figures 4.32 - 4.36 indicate the variation of cure characteristics with silica content when each of a) cardanol and b) naphthenic oil are used as plasticizers for EPDM.

It is seen that t_{10} (Fig. 4.32), t_{50} (Fig. 4.33), cure time (Fig. 4.34), CRI (Fig. 4.35) and scorch time (Fig. 4.36) are comparable for both samples.



a) Cure characteristics

Fig. 4.32 Variation of t₁₀ with silica content in EPDM



Fig. 4.33 Variation of t₅₀ with silica content in EPDM





Fig.4.34 Variation of cure time with silica content in EPDM



Fig. 4.35 Variation of CRI with silica content in EPDM



Fig. 4.36 Variation of scorch time with silica content in EPDM

Table 4.12:	Maximum	and	minimum	torque	values	of	silica	filled	EPDM
compounds									

Sample	Torque(dNm)	5phr	10phr	15phr	20phr	25phr	
Cardanol	Minimum	0.196	0.182	0.238	0.157	0.196	
Naphthenic oil	Minimum	0.114	0.137	0.206	0.163	0.202	
Cardanol	Maximum	5.52	5.57	6.36	6.54	4.62	
Naphthenic oil	Maximum	5.36	4.406	6.4	6.59	5.6	

Table 4.12 gives the maximum and minimum torque values of EPDM compounds. The minimum torque values are lower for naphthenic oil based samples up to 15phr after which the trend reverses. This shows that cardanol is a better plasticizer than naphthenic oil above 20phr silica. Similarly eventhough the maximum torque is higher for cardanol based sample up to 15phr, the value is lower above 20phr.

b) Mechanical properties of EPDM vulcanizates of low silica content

The variation of tensile properties (Figs. 4.37-4.39) with silica content is comparable for both samples. Similarly the variation of tear strength (Fig. 4.40) is also comparable for both samples. The tensile strength shows substantial increase only after 20phr. Hence one more study was done subsequently for higher silica contents above 25 phr.



Fig. 4.37 Variation of tensile strength (MPa) with silica content in EPDM



Fig. 4.38 Variation of modulus at 100% elongation with silica content



Fig. 4.39 Variation of elongation at break (%) with silica content



Fig. 4.40 Variation of tear strength (N/mm) with silica content

The elongation at break (Fig. 4.39) and tear strength (Fig. 4.40) values increase with increase in filler content for both cases.

ii) High silica content (30phr -90phr)

a) Cure characteristics: Fig.4.41 gives the cure curves of 50 phr silica filled EPDM samples. The torque values are found to be lower for cardanol based

samples. Scorch time (Fig.4.42), t_{10} (Fig.4.43), and t_{50} (Fig.4.44) are found to be similar for both samples.



Fig.4.41 Cure curves of 50 phr silica filled EPDM samples

Table 4.15. Cult characteristics of Sophi sinca mica bi Dil compound	Table 4	4.13:	Cure	charac	teristics	of 5()phr	silica	filled	EPDM	comp	oun
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Plasticizer	t _{s1}	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
	(min)	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻¹
						(dNm)	(dNm)	
Cardanol	1.05	1.25	1.12	2.13	9.05	13.76	0.954	12.8
Naphthenic	0.71	1.24	1.13	2.91	12.08	18.26	1.167	10.84
oil								

Comparison of the cure characteristics of cardanol and naphthenic oil plasticized samples (Table 4.13), gives similar values of scorch time and t_{10} whereas t_{s1} is slightly higher for the cardanol based sample. The cure time, t_{50} , maximum torque and minimum torque of the cardanol based sample are lower whereas the CRI is higher. The minimum torque is indicative of the plasticizer property of cardanol. A higher value of CRI for cardanol suggests that it has a positive effect on the cure process.



Fig.4.42 Variation of scorch time (min) with silica content

Scorch time (Fig.4.42) is found to decrease with increase in filler content. This may be due to excessive heat of mixing at higher filler contents which can lead to partial crosslinking. Similar trends are observed for both plasticizers in Fig.4.43 (t_{10}) and Fig. 4.44 (t_{50})



Fig.4. 43 Variation of t_{10} (min) with silica content



Fig. 4. 44 Variation of t₅₀ (min) with silica content





Lower values of cure time (Fig.4.45) and higher values of cure rate index (Fig.4.46) are observed for cardanol based samples. This is again suggestive of a role for cardanol in the curing process.



Fig. 4.46 Variation of cure rate index with silica content





The α value (Fig. 4.47) is found to be a little lower for cardanol based sample and is a minimum at 50phr silica content. A low α value indicates better filler dispersion.

Table	4.14:	Maximum	and	minimum	torque	values	of	silica	filled	EPDM
compo	unds									

Sample	Torque	30phr	50phr	60phr	70phr	90phr
	(dNm)					
Cardanol	minimum	0.52	0.954	1.291	2.798	8.3
Naphthenic oil	minimum	0.58	1.167	2.27	2.837	8.4
Cardanol	maximum	11.05	13.76	20.98	20.06	32.9
Naphthenic oil	maximum	12.6	18.26	19.11	20.06	32.8

The maximum and minimum torque values of EPDM compounds are given in Table 4.14. The minimum torque values are lower for cardanol based compounds. Hence it is a better plasticizer for EPDM compared to naphthenic oil. The maximum torque values of naphthenic oil based samples are marginally higher than that of cardanol based samples up to 50phr above which the trend is reversed.

b) Variation of physical properties with silica content

Figs. 4.48 - 4.54 give the variation of physical properties with silica content for both plasticizers.



Fig. 4.48 Variation of tensile strength with silica content

The tensile strength values (Fig. 4.48) increase with increase in filler content to a maximum at 50phr silica content beyond which the values decrease.



Fig. 4.49 Variation of modulus at 100% elongation with silica content

Modulus at 100% elongation (Fig. 4.49) increases with increase in cardanol content up to 70phr and then decreases.



Fig. 4.50 Variation of elongation at break (%) with silica content



Fig. 4.51 Variation of tear strength (N/mm) with silica content

Generally, the mechanical properties are comparable for both samples. But the reinforcing index values on the basis of tensile strength (Fig. 4.52) and tear strength (Fig. 4.53) are superior for cardanol based samples. The reinforcing index shows the positive effect of filler on any property. The above two graphs show that cardanol is more effective in utilizing the properties of the filler.



Fig. 4.52 Variation of reinforcing index on the basis of tensile strength



Fig. 4.53 Variation of reinforcing index on the basis of tear strength



Fig. 4.54 Variation of abrasion loss (cc/hr) with silica content Similar values of abrasion loss (Fig. 4.54) are obtained for both samples.



Fig. 4.55 Loss of weight on soxhlet extraction

c) Soxhlet extraction: The Soxhlet extraction (Fig. 4.55) of silica filled EPDM vulcanizates shows that the loss of weight due to extraction is lower for cardanol based samples. Here again apparently cardanol undergoes chemical interactions with sulphur / unsaturated components of EPDM which prevents its extraction by toluene.

d) TGA: Table 4.15 gives the details of TGA of 50phr silica filled EPDM samples. The thermal stability of both samples is similar. Figs. 4.56 and 4.57 give the thermograms of 50phr HAF black filled samples with plasticizers cardanol and naphthenic oil respectively.

Table 4.15 TGA of 50phr silica filled EPDM samples

Property	Cardanol	Naphthenic oil
Onset point of degradation	403.53	392.43
Maximum degradation temperature	481.87	482.64
Maximum rate of degradation (% / ° C)	1.722	1.651
Residue (%)	27.78	28.64



Fig. 4.56 Thermogram of 50phr silica filled EPDM samples containing cardanol



Fig. 4.57 Thermogram of 50phr silica filled EPDM samples containing naphthenic oil

E) Optimization of cardanol content for 50phr silica filled EPDM

a) Cure characteristics: Figures 4.58 – 4.61 give the variation of cure characteristics with cardanol (% of silica) for EPDM.



Fig.4.58 Variation of minimum and maximum torque with increasing cardanol content





Minimum and maximum torque values (Fig.4.58) are not much altered by increasing cardanol content. Similarly there is only slight variation in scorch time and t_{10} (Fig.4.59) with increasing cardanol content. The cure time (Fig.4.60) is found to be least for 5% and less. The alpha value (Fig.4.61) shows a sharp decrease initially and reaches a minimum at 5%. Hence, on the basis of cure

characteristics, 5% of cardanol can be taken as optimum amount of plasticizer for silica filled EPDM.



Fig.4.60 Variation of cure time with increasing cardanol content





b) Mechanical properties: Figures 4.62 - 4.64 give the variation of mechanical properties with increase in cardanol content. The tensile strength (Fig. 4.62) is a maximum for 5% cardanol.



Fig.4.62 Variation of tensile strength with increasing cardanol content





The elongation at break (Fig. 4.63) as well as modulus (Fig.4.64) are not very sensitive to cardanol content.



Fig.4.64 Variation of modulus at 100% elongation with increasing cardanol content





The tear strength (Fig.4.65) shows very little variation in the range 2.5 - 7.5% of cardanol. It decreases with further increase of cardanol. The mechanical properties are almost optimal at about 5% cardanol on the basis of silica filler weight.

4.3.2 Antioxidant property of cardanol for EPDM gum samples

a) Cure characteristics

Figure 4.66 gives the cure curves of EPDM gum samples when 1) cardanol and 2) TQ are used as antioxidants and 3) there is no antioxidant. Both cardanol and TQ based curves are similar.



Fig. 4.66 Cure curves with different antioxidants in EPDM gum samples

Table 4.16:	Cure	characteristics	of EPDM	gum	samples	containing	various
antioxidant	S						

	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
Antioxidant	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻¹
					(dNm)	(dNm)	
None	3.6	2.04	4.77	8.32	5.541	0.157	13.31
Cardanol	4.15	3.25	4.22	12.10	5.495	0.182	12.57
TQ	3.41	2.81	3.88	11.11	5.612	0.114	12.9

The scorch time, cure time and t_{10} (Table 4. 16) are slightly higher for the cardanol based sample. CRI values are similar for all the three samples.

b) Mechanical properties of gum samples

The mechanical properties of EPDM gum samples containing 1) cardanol 2) TQ and 3) no antioxidant are given in Table 4.17. The tensile strength values of cardanol based samples are in between that without antioxidant and that with TQ. Tear strength on the other hand is lowest for cardanol.

Table 4. 17: Mechanical properties of cardanol as antioxidant in gum samples

Antioxidants	Tensile strength	Elongation at break	Tear strength		
	(%)	(%)	(%)		
None	68.4	70.6	88.54		
Cardanol	75.2	60	82.4		
TQ	83.4	71.9	86.5		
		l			

c) Ageing

The mechanical properties before and after ageing at 100°C for five days of EPDM gum samples containing 1) cardanol 2) TQ and 3) no antioxidant are given in Figs. 4.67-4.71.



Fig. 4.67 Variation of tensile strength of EPDM gum samples with and without antioxidant on ageing.

The tensile strength values (Fig. 4.67) of all the three samples are comparable. After ageing for 5 days the properties are found to be similar. The elongation at break values (Fig. 4.68) of all the three samples are comparable after ageing.







Fig. 4.69 Variation of modulus at 100% elongation of EPDM gum samples with and without antioxidant on ageing

The moduli at 100% elongation (Fig. 4.69) of all the three samples are comparable before and after ageing. Similar is the case of tear strength (Fig. 4.70). The

properties of the rubber at lower dosages of cardanol (as antioxidant) are not as impressive as when cardanol is used as plasticizer.



Fig. 4.70 Variation of tear strength (N/mm) on ageing of EPDM gum samples with and without antioxidant

d) Thermal analysis:

Table 4. 18 Thermogravimetric analysis of EPDM gum samples

	Antioxidant			
	None	Cardanol	TQ	
Onset point of degradation (°C)	411.6	412.61	406.56	
Temp at 50% degradation (°C)	474.7	476.57	475.29	
Temp at maximum rate of degradation (°C)	479.67	481.85	480.21	
Maximum rate of degradation (% / °C)	2.696	2.622	2.60	
Residue (%)	4.487	5.087	5.577	

Thermogravimetric analysis of all the three EPDM gum samples (Table 4.18) indicates that the thermal stability of all the three samples is similar. This is understandable in view of the sparse sites of unsaturation in EPDM and its generally good thermal resistance.



Fig. 4.71 Thermogram of EPDM gum sample without antioxidant



Fig. 4.72 Thermogram of EPDM gum sample with cardanol as antioxidant





Figs. 4.71- 4.73 give the thermograms of EPDM gum without antioxidant and also containing cardanol and TQ as antioxidants.

It is notable that when cardanol is used as plasticizer, ie. for higher percentages of added cardanol, the compound exhibits much better thermal stability and ageing characteristics.

4.3.3 Cardanol as co-activator

From a comparison of cure curves of EPDM gum samples (Fig.4.74) containing A) stearic acid co- activator and CBS accelerator B) cardanol co-activator and CBS accelerator C) cardanol accelerator and stearic acid co-activator, the t_{s1} , t_{s2} , t_{50} , minimum torque and cure rate index values are found to be higher (Table 4.19) whereas t_{90} is lower when cardanol is used as co-activator. The maximum torque value is found to be lower when cardanol is used as co-activator in place of stearic acid. From the high value of CRI and low cure time, it is clear that cardanol can be used as co-activator in EPDM gum compounds.



Fig. 4.74 Cure curves of EPDM gum samples A, B and C

A- stearic acid co- activator and CBS accelerator, B - cardanol co-activator and CBS accelerator C- cardanol accelerator and stearic acid co-activator

Table 4.19 Cure characteristics of EPDM gum compounds when cardanol is used as co-activator

EPDMgum	t _{s1}	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
samples	(min)	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻
						(dNm)	(dNm)	1
Α	2.53	3.6	2.04	4.22	11.11	5.54	0.16	13.3
В	5.01	5.83	4.11	5.92	10.16	4.43	0.231	23.4

The mechanical properties, viz. tensile strength, modulus at 300% elongation and tear strength (Table 4.20), are found to be similar whereas the elongation at break is found to be higher when cardanol is used as co-activator in place of stearic acid. Interaction between cardanol and Zn^{2+} ions has been suggested in Section 2.3.3.

Table 4. 20 Mechanical properties	of gum	samples	when	cardanol i	is u	ised	as
co-activator							

EPDMGum	Tensile	Elongation at	Modulus at	Tear	
samples	strength	break (%)	300%	strength	
	(%)		elongation	(%)	
A	2.5	368	1.92	12.68	
В	2.224	416.97	1.72	12.69	

4.3.4 Cardanol as accelerator

From the cure curves (Fig.4.74), it is clear that cardanol can be used as accelerator for EPDM gum compound. ts_1 , t_{s2} , t_{s10} and t_{50} are found to be higher (Table 4.21) when cardanol is used as accelerator in place of CBS. Higher CRI values and lower cure times are also obtained for this case. This behaviour is different from the case of NR. The maximum torque value and also t_{90} are found to be lower when cardanol is used as accelerator. The mechanical properties (Table 4.22) tensile strength, modulus at 100% elongation and the tear strength are found to be similar for all the three cases whereas elongation at break is found to be higher when cardanol is used as accelerator.

 Table 4.21: Cure characteristics of EPDM gum compounds when cardanol is used as accelerator

EPDM	t _{s1}	t _{s2}	t ₁₀	t ₅₀	t ₉₀	Max.	Min.	CRI
gum	(min)	(min)	(min)	(min)	(min)	torque	torque	(min) ⁻¹
samples						(dNm)	(dNm)	
Α	2.53	3.6	2.04	4.22	11.11	5.54	0.16	13.3
С	3.39	4.27	2.69	4.71	10.42	5.05	0.231	16.26
Table 4.22: Mechanical	properties	of gum	samples	when	cardanol	is	used	as
------------------------	------------	--------	---------	------	----------	----	------	----
accelerator								

EPDM gum	Tensile	Elongation at	Modulus at 100%	Tear	
samples	strength (%)	break (%)	elongation	strength (%)	
А	2.5	368	1.92	12.68	
С	2.278	403.95	1.75	13.37	

4.1 Conclusions

Cure times for black filled EPDM samples containing cardanol or naphthenic oil plasticizers are similar. The alpha values are found to be lower for cardanol based sample indicating better filler dispersion. Kinetics of cure reactions are similar for both cases with 50phr HAF black. Similar mechanical properties are obtained for both samples. Cardanol is nonextractable from the samples.

Thermal stability of both samples is also similar. The optimal amount of cardanol is 5% of HAF black filler. The tensile strength remains steady for the cardanol based sample even after 5 days of ageing at 100°C. Modulus values show a dramatic increase on ageing. For higher percentages of added cardanol, the compound exhibits much better thermal stability and ageing characteristics.

Cure times for both plasticizers in the case of silica are similar. This shows that cardanol is a better plasticizer than naphthenic oil above 20phr silica. The mechanical properties are similar for both samples. Reinforcing index (RI) values on the basis of tensile and tear strength are higher for cardanol based samples. On comparing mechanical properties and cure characteristics, the optimal amount of cardanol is about 5% on the basis of silica filler weight.

When cardanol is used as co-activator in place of stearic acid for EPDM gum compound, cure time is found to be lower where as the cure rate index is higher. Similarly when cardanol is used as accelerator in place of CBS, lower cure time and higher CRI are obtained. This demonstrates the accelerator property of cardanol in EPDM.

Hence cardanol can be used as plasticizer, co-activator and accelerator for EPDM compounds.

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Comparitive perform	nance of cardnol in different	
rubber components		

5.1 Introduction

In this chapter, the comparative performance of cardanol and naphthenic oil as plasticizers for CR containing i) HAF black (Section 5.2.1) and ii) precipitated silica (Section 5.2.2) has been studied by comparing the cure characteristics and physical, thermal and ageing properties. The antioxidant property (Section 5.2.3) of cardanol is investigated by comparing cure characteristics and physical, thermal and ageing properties of gum samples when TQ is replaced by cardanol. Similarly, the co-activator (Section 5.2.4) and accelerator (Section 5.2.5) properties are investigated by replacing stearic acid and CBS respectively by cardanol and comparing their cure characteristics and mechanical properties.

5.2 Compounding and curing of CR

The vulcanization chemistry of chloroprene rubbers is fundamentally different from those of other rubbers. The carbon - carbon double bonds in the polychloroprene chains are deactivated by the presence of chlorine atoms. It is assumed that the crosslinking of polychloprene molecules occur by way of ether formation accompanied by loss of chlorine atoms. The chlorine atoms which participate in the crosslinking reaction are believed to be those which are present in a small proportion of 1, 2 addition units (1, 2).

According to Pariser (3) the nature of crosslinking reaction in the presence of thiourea derivatives is such that the allyl bound chlorine atom takes part in the reaction during which it is substituted by an accelerator residue.

Contrary to the practice with other diene rubbers the vulcanization of CR compounds is carried out using metal oxides (4). The metal oxides most often used are zinc oxide as crosslinking agent and magnesium oxide mainly as an acid acceptor. As magnesium oxide serves as an acid acceptor, preventing premature crosslinking and cyclisation of polychloroprene compounds, it is usually the first compounding ingredient to be incorporated. Zinc oxide having a relatively strong

influence on the onset of vulcanization is added later. A typical combination of ZnO (5phr) and calcined MgO (4phr) is preferred for compounding. When used in conjunction with ZnO, MgO improves processing safety by removing the $ZnCl_2$ formed. Since $ZnCl_2$ also catalyses the crosslinking reaction, the vulcanization reaction is scorchy in the absence of MgO.

For practical cure rates and vulcanizate properties, an organic accelerator is also required in addition to metal oxides for W type neoprenes. The most widely used substance used for this purpose is a thiourea derivative, viz. ethylene thiourea (NA22) (5). This gives fast vulcanizing compounds and the vulcanizates are characterized by high modulus, good tensile strength, and low permanent set and high rebound resilience. The use of NA22 in combination with thiuram and guanidine accelerators in addition to suphur, gives vulcanizates with improved tear resistance and rebound resilience. However the compounds are less safe to process (6).

5.3 Evaluation methods

Different evaluation methods employed for compounds and vulcanizates in this part of study are the following.

- a) Cure characteristics: (Section 1.11a)
- b) Tensile properties: were measured as per details provided in Section1.11b and the reinforcing index calculated by the method described in Section 4.2.3 b).

c)	Tear strength:	(Section 1.11c)
d)	Hardness:	(Section 1.11d)
e)	Abrasion loss:	(Section 1.11e)
f)	Rebound resilience:	(Section 1.11f)
g)	Soxhlet extraction:	(Section 1.11g)
h)	FTIR spectroscopy:	(Section 1.11h)
i)	Thermo gravimetric analysis:	(Section 1.11k)

j) Ageing tests:

(Section 1.11m)

5.4 Experimental work

5.4.1 Raw materials

Chloroprene rubber used in this study was W type (CR B30) with Mooney viscosity [ML (1+4), 100°C] 47. Du Pont, USA supplied the rubber.

Other compounding ingredients, their suppliers and details are given in Section 2.2.1

5.4.2 Compounding

Mixes were prepared and cured as per details given in Sections 2.2.2 and 5.2. The formulations employed are given in Tables 5.1-5.6.

5.4.3 Cardanol as plasticizer for CR

For this work HAF black (10-50phr) and precipitated silica (5-15phr) were employed.

A) HAF black filled compounds

Table 5.1 gives the formulations employed. Cure characteristics of the compounds were determined. Moulding was completed and the mechanical and thermal properties and ageing behavior of vulcanizates were studied. Each formulation was repeated replacing naphthenic oil by cardanol. The properties of both types of vulcanizates were compared.

Sample	CR	MgO	St.acid	HAF	A/B	TQ	TMTD	S	ZnO
	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
1	100	4	1	10	1	1	0.6	1	5
2	100	4	1	20	2	1	0.6	1	5
3	100	4	1	30	3	1	0.6	1	5
4	100	4	1	40	4	1	0.6	1	5
5	100	4	1	50	5	1	0.6	1	5

Table 5.1: CR formulations for varying HAF black content.

A-cardanol B- naphthenic oil

B) Silica filled compounds

Mixes were prepared according to the formulation given in Table 5.2 and the properties were determined as given in Section 5.4.3A

Sample	CR	MgO	St.acid	silica	DEG	A/B	TQ	TMTD	S	ZnO
	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
1	100	4	1	5	1	0.5	1	0.6	1	5
2	100	4	1	10	1	1.0	1	0.6	1	5
3	100	4	1	15	1	1.5	1	0.6	1	5
4	100	4	1	20	1	2	1	0.6	1	5
5	100	4	1	50	1	5	1	0.6	1	5

Table 5.2: Formulation for varying silica content

A-cardanol B- naphthenic oil

C) Optimization of cardanol content

Optimization of cardanol percentage was done by preparing mixes based on formulations given in Table 5.3. The cure characteristics and the mechanical properties of vulcanizates were determined to identify the optimum cardanol percentage.

Table 5.3: Formulation for optimization of cardanol content

Sample	CR	MgO	St.acid	HAF	Cardanol	TQ	TMTD	S	ZnO
	phr	phr	phr	phr	phr	phr	phr	phr	phr
1	100	4	1	30	1.5	1	0.6	1	5
2	100	4	1	30	3	1	0.6	1	5
3	100	4	1	30	4.5	1	0.6	1	5

5.4.4 Cardanol as antioxidant

Antioxidant property of cardanol was investigated by preparing mixes according to the formulation given in Table 5.4 and determining the cure characteristics and the mechanical properties

CR	MgO	St.acid	Cardanol	TQ	S	TMTD	ZnO
(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
100	4	1	-	-	1	0.6	5
100	4	1	1	_	1	0.6	5
100	4	1	-	1	1	0.6	5

Table 5.4: Formulation of CR gum samples for antioxidant study

5. 4.5 Cardanol as co-activator

Co- activator property of cardanol was investigated by initially preparing mixes of gum CR samples according to the formulations given in Table 5.5. Subsequently, the cure characteristics and mechanical properties were determined and compared with the properties of gum samples containing a conventional co-activator, stearic acid.

Table 5. 5: Formulation of CR gum samples for co- activator study

CR	MgO	St.acid	Cardanol	TQ	S	TMTD	ZnO
(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
100	4	1		1	1	0.6	5
100	4	-	1	1	1	0.6	5

5.4.6 Cardanol as accelerator

Accelerator property of cardanol was investigated by preparing mixes of gum CR samples according to the formulation given in Table 5.6. Subsequently the cure characteristics and mechanical properties were determined. The properties were compared with those of conventional gum samples containing TMTD as accelerator.

CR	MgO	St.acid	Cardanol	TQ	S	TMTD	ZnO
(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)	(phr)
100	4	1	_	1	1	0.6	5
100	4	1	0.6	1	1	+	5

Table 5. 6: Formulation of CR gum samples for accelerator study

5.5 Results and discussion

5.5.1 Cardanol as plasticizer for CR

A) HAF black filled compounds

a) Cure characteristics: Fig. 5.1 is a comparison of cure curves of 30phr HAF black filled compounds. Lower values of torque are attained for the cardanol based sample which is indicative of lower viscosity. The cure characteristics are given in Table 5.7



Fig. 5.1 Cure curves of cardanol and naphthenic oil based samples

	t ₁₀ ,	t ₅₀ ,	t 90,	ts ₂ ,		CRI	Min.	Max.
Plasticizer	(min)	(min)	(min)	(min)	α	(min- ¹)	torque,	torque,
							(dNm)	(dNm)
Cardanol	1.08	6.16	19.98	2.73	0.6	5.8	0.24	8.19
Naphthenic oil	1.3	7.6	21.47	3.59	0.9	5.59	0.26	8.72

Table 5 .7 Cure characteristics of 30 phr HAF black filled samples

The scorch time, cure time, t_{10} and t_{50} are also found to be lower for cardanol based samples. The cure rate index is higher whereas the α -value which is a measure of filler agglomeration is somewhat lower for the 30phr cardanol based sample. As seen from Table 5.8, cardanol based samples show much lower minimum and maximum torques for various HAF black filler contents. So for these situations, cardanol is a better plasticizer for CR.

Table 5.	8 Minimum	and maximum	n torque	values	during	cure for	HAF	black
filled sa	mples							

	Torque	10(phr)	20(phr)	30(phr)	40(phr)	50(phr)
Sample	(dNm)					
Cardanol	Minimum	0.157	0.206	0.248	0.33	0.41
Naphtheniic oil	Minimum	0.169	0.226	0.265	0.356	0.535
Cardanol	Maximum	6.848	7.505	8.15	9.349	10.3
Naphthenic oil	Maximum	6.921	7.782	8.72	11.18	11.26



Fig. 5.2 Variation of scorch time (min) with HAF black content.

The scorch time (Fig. 5.2) and t_{10} (Fig. 5.3) of cardanol based samples are similar to those of naphthenic oil based samples.



Fig. 5.3 Variation of t₁₀ (min) with HAF black content



Fig. 5.4 Variation of cure time (min) with HAF black content

Similar values of cure time (Fig. 5.4) are obtained at low filler contents, where as at higher filler contents, the cure times of cardanol based samples are slightly lower.





The variation of α value with HAF black content (Fig. 5.5) shows that the values are lower for cardanol based samples for all filler contents. The lower α - values indicate that filler agglomeration takes place to a much smaller extent in cardanol based vulcanizates resulting in better utilization of filler.





Fig. 5.6 Variation of cure rate index with HAF black content.

The cure rate indices (Fig. 5.6) are similar for both plasticizers.



Fig. 5.7 Plot of $\ln (M_h - M_t)$ vs. time t of cardanol based compound containing 30phr HAF black ; k=0.11263



Fig. 5.8 Plot of $\ln (M_h - M_t)$ vs. time t of naphthenic oil based compound containing 30phr HAF black; k=0.10176

Kinetics of cure reactions of 30phr HAF black filled cardanol (Fig.5.7) and naphthenic oil (Fig.5.8) based compounds show that they obey first order kinetics as $ln(M_h - M_t)$ vs t gives straight lines with rate constants k = 0.1126 and 0.1018 respectively. The rate constant value is somewhat higher for the cardanol based sample.

b) Tensile properties: The tensile strength values (Fig. 5.9) are similar when both plasticizers are used.



Fig.5.9 Variation of tensile strength with HAF black content

The elongation at break (%) values (Fig. 5.10) of cardanol based samples is found to be higher than that for naphthenic oil based samples for all filler contents. This can be interpreted as due to a higher level of plasticization.



Fig. 5.10 Variation of elongation at break (%) with HAF black content

The modulus at 300% elongation values (Fig. 5.11) are found to be lower for cardanol based samples. This can be again the result of a higher extent of plasticization by cardanol.



Fig. 5.11 Variation of modulus at 300 % elongation with HAF black content c) Tear strength: Though the tear strength values are lower for cardanol based samples up to 40phr filler loading, there is a steady increase in tear strength values

with filler content (Fig. 5.8) and at 50 phr, it is higher for the cardanol based sample.



Fig. 5.12 Variation of tear strength with HAF black content





Reinforcing index on the basis of tensile strength (Fig. 5.13) is almost identical for both plasticizers. It decreases with increase in filler content especially after 20phr. Reinforcing index on the basis of tear strength (Fig. 5.14) also decreases with increase in filler content. In this case, the index is somewhat lower for the cardanol based sample.



Fig. 5.14 Reinforcing index on the basis of tear strength

d) Abrasion loss: The abrasion loss (Fig 5.15) is similar for both samples



Fig.5.15 Variation of abrasion resistance with HAF black content



Fig.5.16 Variation of resilience with HAF black content

e) Resilience: Variation of resilience (Fig 5.16) is also similar for both samples.



Fig.5.17 Variation of hardness (Shore A) with HAF black content

f) Hardness: Variation of hardness (Fig 5.17) follows a similar trend for both samples.

g) Thermal analysis: Thermal analysis of 30 phr HAF black filled CR samples (Table 5.9) shows that the thermal stability of both samples is somewhat similar. Even though the onset point of degradation is slightly lower for the cardanol based

sample, the residue is somewhat higher for the cardanol based sample. Figs. 5.18 and 5.19 are the thermograms of 30phr HAF black filled CR samples.

Property	Cardanol	Naphthenic oil
Onset point of degradation (°C)	289.51	293.55
Temp at maximum rate of degradation (°C)	318.05	318.28
Maximum rate of degradation (% / °C)	3.782	3.774
Residue (%)	43.51	42.56

Table 5.9:TGA of 30 phr HAF black filled CR samples



Fig.5.18 Thermogram of 30phr HAF black filled CR samples containing cardanol



Fig.5.19 Thermogram of 30phr HAF black filled CR samples containing naphthenic oil

B) Optimization of cardanol percentage for 30phr HAF black filled CR samples

a) Cure characteristics:



Fig. 5.20 Variation of scorch time (min) with cardanol content

The variation of cure characteristics with cardanol content is shown in Figs.5.20-5.22 and Table 5.10. The scorch time (Fig. 5.20) decreases with increase in cardanol content up to 10phr. Beyond this, the scorch time is almost constant.



Fig. 5.21 Variation of cure time (min) with cardanol content



Fig. 5.22 Variation of CRI (min⁻¹) with cardanol content

The falling cure time (Fig.5.21) and the increasing values of CRI (Fig.5.22) with cardanol content suggest that cardanol has some kind of role in the vulcanization reaction.

Cardanol	Min.	Max.	tsı	ts ₂	t ₁₀	t50	t90	CRI
(%)	torque	torque	min	min	min	min	min	min ⁻¹
	dNm	dNm						
5	0.235	6.91	1.56	4.27	1.08	7.86	21.98	5.646
10	0.265	7.39	1.33	2.74	1.08	6.16	19.98	5.8
15	0.278	7.44	1.48	2.7	1.09	5.58	17.98	6.67
20	0.282	7.56	1.52	2.62	1.10	5.48	16.8	7.1

Table 5.10: Cure characteristics vs cardanol content for 30phr HAF Black

Table 5.10 shows that the minimum and maximum torque values increase with increase in cardanol content.

b) Tensile properties: Variation of mechanical properties (Figs. 5.22-5.25) with cardanol content shows that cardanol content equivalent to 10% of filler is optimum for tensile strength (Fig.5.23) and almost so for elongation at break % (Fig.5. 24). The modulus (Fig.5. 25) is almost steady with increasing cardanol content.

c) Tear strength: The tear strength (Fig.5.26) is found to decrease only slightly with increase in cardanol content.



Fig. 5.23 Variation of tensile strength with cardanol content



Fig. 5.24 Variation of elongation at break (%) with cardanol content



Fig. 5.25 Variation of modulus at 300% elongation with cardanol content



Fig. 5.26 Variation of tear strength with cardanol content

C) Silica filled compounds

The silica filled CR compounds were difficult to mix at higher filler contents, say, 15phr and above. Moreover, the mouldings containing 10phr silica and more were extremely difficult to demould due to strong bonds formed between the mould and the cured compound. In such cases, the vulcanizate had to be demoulded with great difficulty and its properties were seen to be badly affected by the demoulding process.

a) Cure characteristics: On comparing the cure curves of 5phr silica based compounds, both curves are found to be similar (Fig. 5.27).



Fig. 5.27 Cure curves of cardanol and naphthenic oil based samples with 5phr silica loading.

On comparing Figures 5.28 and 5.29 it is seen that both cardanol and naphthenic oil based compounds obey first order kinetics during cure and the k values indicate that the rate of cure is slightly higher in the case of naphthenic oil based compound containing silica.



Fig. 5.28 Plot of ln (M_h - M_t) vs. time t for cardanol based CR compound containing 5 phr silica; k=0.12782 304



Fig. 5.29 Plot of ln (M_h - M_t) vs. time t for naphthenic oil based CR compound containing 5 phr silica ; k = 0 .13396



Fig. 5.30 Variation of scorch time (min) with silica content

The scorch time (Fig. 5.30) of the cardanol based compound increases with increase in filler content beyond 10phr whereas that of naphthenic oil based compounds does not change much.

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The variation of cure time (Fig.5.31) is similar for both samples and is a minimum at 15phr silica content for both.



Fig. 5.31 Variation of cure time (min) with silica content

Table 5. 11 Minimum and maximum	torque value	s during cur	e for silica	filled
samples				

	Torque	5(phr)	10(phr)	15(phr)	20(phr)
Sample	(dNm)				
Cardanol	Minimum	0.081	0.114	0.124	0.078
Naphthenic oil	Minimum	0.114	0.142	0.167	0.172
Cardanol	Maximum	12.2	12.6	13.2	13.6
Naphthenic oil	Maximum	11.7	11.5	11.8	12.2

Minimum and maximum torque values of silica filled compounds during cure are given in Table 5.11. The minimum torque values are lower for the cardanol based sample. But the maximum torque values are higher for the cardanol based sample. Again on comparing the cure characteristics of 15 phr silica filled compounds (Table 5.12), the alpha value is found to be somewhat higher for the cardanol based sample indicating a comparatively higher level of filler agglomeration.

The cure characteristics of 15phr silica filled samples (Table 5.12) show similar values for both cases.

	t 10,	t ₅₀ ,	t ₉₀ ,	ts2 ,	α	CRI	Min. torque,	Max. torque,
Plasticizer	min	min	min	min		min-	dNm	dNm
						1		
Cardanol	2.12	6.29	16.53	3.09	6.49	7.44	0.124	13.2
Naphthenic	0.93	3.66	15.55	1.61	4.9	7.17	0.167	11.8
oil								
				1				

Table 5.12: Cure characteristics of 15phr silica filled compounds



Fig. 5.32 Variation of CRI (min⁻¹) with silica content

Similarly the variation of cure rate index (Fig.5.32) is similar for both samples and is a maximum at 15phr silica content for both samples.



Fig. 5.33 Variation of tensile strength with silica content



Fig. 5.34 Variation of elongation at break (%) with silica content



Fig. 5.35 Variation of modulus at 300% elongation with silica content b) Tensile properties: The tensile strength (Fig.5.33) is found to be marginally superior in the case of cardanol based vulcanizates whereas the elongation at break values (Fig.5.34) are comparable and the modulus at 300% elongation values (Fig.5.35) slightly lower in the case of cardanol based samples. The slightly higher value of α for the cardanol based sample (Table 5.12) is immaterial as the tensile strength of the cardanol based compound is superior to that of the naphthenic oil based one.



Fig. 5.36 Variation of tear strength with silica content

c) Tear strength: Tear strength values (Fig.5.36) are also comparable for both cases.





Fig. 5.37 Thermogram of 15 phr silica based CR vulcanizate containing cardanol





Figs. 5.37 and 5.38 are the thermograms of 15phr silica filled CR samples. Thermal data given in Table 5.13 show that the onset point of degradation, temperature of 50% degradation, maximum degradation temperature and residue are considerably higher for the cardanol based sample. In general, thermal stability is much better for the cardanol based sample.

Plasticizer	Cardanol	Naphthenic oil
On set point of degradation	301.62	255.2
Temperature of 50% degradation	351.06	336.93
Maximum degradation temperature	327.21	323.92
Residue (%)	34.98	25.44

Table 5.13 Thermal analysis of 15phr silica based CR samples

D) Ageing at 100°C of 30phr HAF black filled CR samples



Fig. 5.39 Variation of tensile strength with time



Fig. 5.40 Variation of elongation at break (%) with time



Fig. 5.41 Variation of modulus at 300% elongation with time



Fig. 5.42 Variation of tear strength (N/mm) with time

Figs. 5.39-5.42 show the variation of some mechanical properties of 30phr HAF black filled samples on ageing. After ageing, the cardanol based samples show somewhat better properties in most cases. This is most notable in the case of modulus at 300% elongation.

5.5.2 Cardanol as antioxidant for CR

Antioxidant property of cardanol is studied by comparing cure characteristics and vulcanizate properties with that of TQ, a conventional antioxidant The lowest torque (Fig. 5.43). is observed when cardanol is used as antioxidant. From Table

5.14, it is clear that cure times and CRI for all the three cases are similar. Considering that cardanol is present only to the extent of 1%, this is not surprising. The mechanical properties

(Table 5.15) do not show much variation.



Fig. 5.43 Cure curves of gum samples

Table 5.14 Cure characteristics of CR gum samples

Antioxidant	t 10	t 50	ts ₁	ts ₂	t 90	Max.	Min.	CRI
	(min)	(min)	(min)	(min)	(min)	torque	torque	min ⁻¹
						(dNm)	(dNm)	
None	1.51	6.06	1.90	3.78	16.47	6.812	0.16	7.88
Cardanol	1.85	6.22	3.01	4.97	17.70	5.266	0.14	7.855
TQ	1.6	5.92	2.23	4.03	16.74	6.19	1.37	7.86

Table 5.15 Mechanical properties of CR gum samples with and without antioxidant

	Tensile strength	Elongation at	Modulus at 300%	Tear strength
	(MPa)	break (%)	elongation (MPa)	(N/mm)
None	16.2	1344	1.17	28.03
Cardanol	14.5	1301.5	1.04	28.9
TQ	15.9	1224	1.13	26.9

On ageing at 100°C (Figs. 5.44-5.47) the retention of mechanical properties in the case of cardanol based compounds are in general found to be either higher than or at least equal to those containing TQ / no antioxidant.



Fig. 5.44 Variation of tensile strength with time of ageing at 100°C

Neoprene rubber



Fig. 5.45 Variation of elongation at break (%) with time of ageing at 100°C



Fig. 5.46 Variation Modulus at 300% elongation with time of ageing at 100°C


Fig. 5.47 Variation of tear strength with time of ageing at 100°C

The TGA charts of CR gum samples with and without antioxidants are given in Table 5.16. Eventhough the onset point of degradation and the maximum degradation temperature are higher, the residue is found to be lower when cardanol is used as antioxidant for CR as against TQ. But as has been mentioned already, the thermal stability will be much better when larger amounts of cardanol is used, say, as plasticizer (Table 5.13).

Antioxidants	none	TQ	cardanol
Onset point of degradation (°C)	288.5	271.35	290.52
Maximum degradation temperature (°C)	315.35	316.93	321.47
Residue (%)	27.10	27.55	24.4

Table 5.16 TGA of CR gum samples with and without antioxidants

5.5.3 Cardanol as co-activator

The cure curves CR gum samples (Fig. 5.48) containing A) stearic acid coactivator and TMTD accelerator, B) cardanol co-activator TMTD accelerator and C) cardanol accelerator and stearic acid co-activator respectively. The cure curves A and B give a comparison when cardanol is used as co-activator in place of stearic acid. The cure time, scorch time, t_{s1} , t_{50} , and cure rate index (Table 5.17) are found to be somewhat higher when cardanol is used as co-activator. The maximum torque and t_{10} are lower.



Fig. 5.48 Cure curves of CR gum samples

A- stearic acid co- activator and TMTD accelerator, B- cardanol co-activator TMTD accelerator and C - cardanol accelerator and stearic acid co-activator respectively.

,um compo	unus							
Co-	t 10	t 50	ts ₁	ts ₂	t 90	Max.	Min.	CRI
activator	(min)	(min)	(min)	(min)	(min)	torque	torque	min ⁻¹
						(dNm)	(dNm)	
Stearic	1.51	6.06	1.9	3.7	16.47	6.8	0.16	7.8
acid								
Cardanol	1.04	6.19	3.17	6.3	18.5	4.08	0.248	8.19

Table 5.17 Cu	re characteristics	when cardanol	is used as c	o- activator	for CR
gum compoun	ds				

Table 5.18 Mechanical properties when cardanol is used as co- activator

Co-activator	Tensile strength	Elongation at break (%)	Modulus at 300% elongation (MPa)	Tear strength (N/mm)	
Stearic acid	(MPa) 16.2	1344	1.17	28.03	
Cardanol	17.6	1477.8	1.11	26.18	

The mechanical properties are (Table 5.18) also comparable. Hence cardanol possesses co-activator property in CR compounds.

5.3.4 Cardanol as accelerator

The cure curves A and C (Fig. 5.48) give a comparison when cardanol is used as accelerator in place of TMTD.

Table 5.19 Cure characteristics when cardanol is used as accelerator

Accelerator	t 10	t 50	ts ₁	ts ₂	t 90	Max.	Min.	CRI
	(min)	(min)	(min)	(min)	(min)	torque	torque	min ⁻¹
		}				(dNm)	(dNm)	
Cardanol	1.67	5.95	2.11	3.47	20.38	6.20	0.147	5.91
TMTD	1.51	6.06	1.9	3.72	16.47	6.812	0.16	7.8
			1					
	1			1		1		l

The maximum torque, minimum torque, CRI, ts_2 and t_{50} are found to be lower (Table 5.19) where as t_{10} , ts_1 and t_{90} are higher when cardanol is used as accelerator in place of TMTD. The mechanical properties are comparable (Table 5.20) in both cases. Though leading to somewhat longer cure times, cardanol is seen to have accelerator properties. It is worth noting that in this case the main crosslinking mechanism involving metal oxides has not been affected by the addition of cardanol.

Accelerator	Tensile	Elongation	Modulus at 300%	Tear strength
	strength	at break	elongation (MPa)	(%)
	(%)	(%)		
Cardanol	17.29	1325	1.45	26.16
TMTD	16.2	1344	1.17	28.03

Table 5.20 Mechanical properties when cardanol is used as accelerator

5.4 Conclusions

Kinetics of cure reactions of CR are similar for both samples with 30phr HAF Black.

The performance of cardanol as plasticizer for CR is similar to that of naphthenic oil when cure time, CRI and mechanical properties are comparable. Naphthenic oil has some advantage in the case of tear strength. Reinforcing index on the basis of tensile strength is similar for both samples.

Thermal analysis of 30 phr HAF black filled CR samples shows that the thermal stability of both samples is almost similar. Cardanol plasticized samples show superior ageing behavior when compared to naphthenic oil based samples.

The increasing values of CRI with cardanol content suggest that cardanol has some kind of role in the vulcanization reaction. 10% of HAF black filler is optimum for tensile strength and elongation at break % whereas modulus and tear strength decrease with increase in cardanol content. The cure time is a minimum at 15phr silica content for both samples. On comparing the cure characteristics of 15 phr silica filled compounds, the alpha value is found to be higher for cardanol based sample indicating greater filler agglomeration. Silica filled CR has a tendency to adhere to the mould surface which makes demoulding difficult.

When cardanol is used as antioxidant in place of TQ, the percentage retention of properties after ageing is higher for cardanol based samples except in the case of tear strength. When cardanol is used as co-activator in place of stearic acid, there is

improvement in scorch time and CRI. The mechanical properties are also comparable. Accelerator property of cardanol is not negligible as the CRI value is comparable with that when TMTD is used as accelerator. Mechanical properties are similar for both cases.

B. Comparative performance of cardanol in different rubber compounds.

This section presents comparative results of utilizing cardanol in different apacities for processing four rubbers viz, NR, NBR, EPDM and CR.

1) Performance of cardanol as plasticizer when compared with conventional plasticizers for different rubbers

Table	5.	21	Comparison	of cure	characteristics	when	cardanol	is used	as
plastic	ize	r in	place of conv	entional	plasticizer in H.	AF bla	ck filled co	ompoun	ds

Property	HAF b	HAF black filled samples for which maximum properties are										
		obtained										
Cure	NR 3	NR 30phr		EPDM 50phr		30phr	CR 30phr					
characteristics	HAF	black	HAFt	olack	HAF	black	HAF	black				
	Α	В	Α	С	A	D	Α	C				
Cure time												
(min)	7.41	7.79	5.45	5.08	4.21	4.47	19.98	21.47				
Minimum												
torque (dNm)	0.016	0.072	0.497	0.486	0.431	0.493	0.265	0.248				
Maximum												
torque (dNm)	4.38	4.64	9.37	9.754	7.162	7.875	8.72	8.185				
α –value	1.944	2.193	0.328	0.36	1.78	1.79	0.90	0.6139				
CRI /min	26.525 26.88		22.9	26.3	52.3	49.2	5.8	5.59				
Scorch time	3.64	3.6	1.09	1.27	2.31	1.023	2.74	2.17				

A-cardanol B-aromatic oil C-naphthenic oil D-dioctyl pthalate

Table 5.21 compares the cure characteristics for different rubbers. In general, cardanol leads to shorter cure times. This effect is most noticeable in the case of CR. The scorch times are some what higher for cardanol than conventional plasticizers with the exception of EPDM. The α - value which indicates filler agglomeration is less for cardanol, CR being an exception. Thus for the majority of rubbers, cardanol offers a better alternative from the view point of cure characteristics.

Table 5.22 Comparison of mechanical properties when cardanol is used as plasticizer in place of conventional plasticizer in HAF black filled compounds

Property	HAF black filled samples for which maximum properties								
		are obtained							
Mechanical	NR 30)phr	EPDM	EPDM 50phr		NBR 30phr		hr	
properties	HAF	olack	HAF b	lack	HAF black		HAF black		
	A	В	Α	C	A	D	A	С	
Tensile strength									
(MPa)	31.6	31.72	30.08	30.6	23.1	22.5	28	26.1	
Elongation at									
break (%)	766	1109	658	741	702	665	751	819	
Modulus at 300%									
elongation (MPa)	5.4	5.41	2.4	2.2	7.4	7.49	7.1	6.05	
Tear strength									
(N/mm)	91.6	82.16	76.33	83.39	70.7	67.9	71.35	82	
RI on tensile									
strength	4.2	4.3	22	22.4	12.6	12.2	4.59	4.39	
RI on tear			[
strength	8.2	6.6	11.4	12.4	12.1	11.6	8.48	9.75	

A -cardanol **B** – aromatic oil **C** – naphthenic oil **D**- dioctyl pthalate Referring to Table 5.22, marginal superiority in tensile strength is observed in the case of NBR and CR for cardanol plasticization. For NR and NBR, cardanol gives

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higher tear strength and for EPDM and CR, lower values. The performance of cardanol is in general good. The RI values on the basis of tensile strength and tear strength are remarkably similar for all rubbers and for both plasticizers.

Table 5.23 Comparison of cure characteristics when cardanol is used as
plasticizer in place of conventional plasticizer for silica filled samples

Property	Silica	filled	samples	for whic	h maxin	num proper	ties are ob	stained
	NR 1	5phr	EPDM	EPDM 50phr NBI		R 20phr	CR	5phr
Cure	silica		sil	ica		silica	sil	ica
characteristics					Ì		-	
	A	В	A	C	A	D	A	C
Cure time(min)	2.32	2.75	13.9	12.0	5.58	4.35	18.93	17.82
			6	8			Ŧ	
Mini. torque	0.06	0.15	1.45	1.16	0.28	0.330	0.081	0.114
(dNm)	5	7	7	7	7		ł	
Max. torque	3.77	4.02	16.1	18.2	6.34	7.534	12.26	11.70
(dNm)	6	7	1	6	8		-	
α-value	2.3	2.62	0.68	1.08	2.0	3.37	16.6	14.8
		4					1	
CRI /min	156.	125	12.8	10.8	30.4	46.5	6.16	6.3
	2			4	8			1
A -cardanol B -	- aromat	ic oil	C – na	phtheni	c oil	D- diocty	pthalate	:

Table 5.23 shows that cardanol in general leads to somewhat longer cure times when silica filler is used. This is not observed only in the case of NR. α - values are marginally lower for the majority of rubbers when cardanol is used. CRI values on the other hand show a mixed trend. The overall acceptability of cardanol is again evident.

Comparison of mechanical properties (Table 5.24) for silica filler shows that in the case of all the four rubbers, the tensile strength leads to better values when cardanol is used.

Property	Silica filled samples for which maximum properties are								
	obtained								
	N	R	EPDM	50phr	N	BR	C	R	
Mechanical	15phr	silica	sili	ca	20	phr	5phr silica		
properties					sil	ica		I	
	A	В	A	C	A	D	A	C	
Tensile strength	22.2	20.16	24.14	126	15 /	10.5	10 57	17 20	
(MPa)	32.2	29.10	27.17	15.0	15.4	10.5	10.57	17.50	
Elongation at	11123	1076	732	808	802	503	1031	1008	
break (%)	1112.5	10/0	132	000	002	575	1991		
Modulus at	28	2.69	2.55	3.29	3.4	39	1.35	1.58	
elongation(MPa)	2.0	2.07				5.5			
Tear strength	57 74	54 35	38.5	35.8	47.8	34 3	34.05	35.6	
(N/mm)		01.00	50.5	22.0	17.0	5	5 1.05	55.0	
RI on tensile	86	78	17.68	9.96	99	87	183	171	
strength	0.0	,.0	17.00	5.50	7.5	0.7	10.2		
RI on tear	10.2	9.8	5.75	5.35	13.6	9.4	13.1	12.2	
strength	10.2	2.0		3.33	13.0	9.4	13.1	12.2	

Table 5.24 Comparison of mechanical properties when cardanol is used as plasticizer in place of conventional plasticizer for silica filled samples

A -cardanol B - aromatic oil C - naphthenic oil D- dioctyl phthalate

The tear strength values are mostly favourable to cardanol with NBR giving much superior values for the cardanol case. Similar is the case with RI on the basis of tensile and tear strength. Hence, considering mechanical properties the improvement in performance of cardanol as plasticizer is better in the case of silica filled compounds than black filled compounds.

NR 3	0phr	EPDM	50phr	NBR	30phr	CR	30phr
HAF	black	HAF bl	ack	HAF t	lack	HAF black	
Α	В	Α	С	Α	D	A	C
33.1	31.7	30.08	30.06	24.6	22.5	28	26.5
**28	**5.8	29.07	21.5	14.9	3.9	23	21.3
85	18	97	70	61	17	82	80
766	1109	658	740	702	665	751	819
**670	**310	365	357	290	289	480	460
87	28	55	48	41	43	64	56
5.8	5.41	*4	*2.2	*3.2	*4	7.1	6.05
**6.09	**4.3	*4.8	*3.34	*3.71	*4.52	11.4	8.73
105	79	120	151	115	88	160	69
91.6	82.16	76.33	83.31	70.7	62.2	71.3	58.98
**101	**5.5	50.56	53.2	46.2	38.1	82	56.5
110	7	66	64	65	61	115	96
	NR 3 HAF A 33.1 **28 85 766 **670 87 5.8 **6.09 105 91.6 **101 110	NR 30phr HAF black A B 33.1 31.7 *28 *5.8 85 18 766 1109 **670 *310 87 28 5.8 5.41 **6.09 *4.3 105 79 91.6 82.16 **101 *5.5 110 7	NR 30 phr EPDM HAF black HAF black A B A 33.1 31.7 30.08 *28 *5.8 29.07 85 18 97 766 1109 658 **670 *310 365 87 28 55 5.8 5.41 *4 **6.09 *4.3 *4.8 105 79 120 91.6 82.16 76.33 **101 *5.5 50.56	NR 30 phrEPDM 50 phrHAF blackHAF blackABAC33.131.730.0830.06*28*5.829.0721.5851897707661109658740**670*'310365357872855485.85.41*4*2.2**6.09*'4.3*4.8*3.341057912015191.682.1676.3383.31**101*5.550.5653.211076664	NR 30 phrEPDM 50 phrNBRHAF blackHAF blackHAF blackHAF blackABACA33.131.730.0830.0624.6**28*5.829.0721.514.985189770617661109658740702**670**31036535729087285548415.85.41*4*2.2*3.2**6.09**4.3*4.8*3.34*3.711057912015111591.682.1676.3383.3170.7**101*5.550.5653.246.21107666465	NR 30 phrEPDM 50 phrNBR 30 phrHAF blackHAF blackHAF blackABACA33.131.730.0830.0624.622.5"28"5.829.0721.514.93.98518977061177661109658740702665"670"3103653572902898728554841435.85.41*4*2.2*3.2*4"6.09"4.3*4.8*3.34*3.71*4.52105791201511158891.682.1676.3383.3170.762.2"101"5.550.5653.246.238.1110766646561	NR 30 phrEPDM 50 phrNBR 30 phrCR 30 HAF blackHAF blackHAF blackHAF blackHAF blackABACAD33.131.730.0830.0624.622.528**28*5.829.0721.514.93.923851897706117827661109658740702665751**670**310365357290289480872855484143645.85.41*4*2.2*3.2*47.1**6.09**4.3*4.8*3.34*3.71*4.5211.4105791201511158816091.682.1676.3383.3170.762.271.3*101*5.550.5653.246.238.182

Table	5.25	Retention	of	mechanical	properties	before	and	after	ageing	at
100°C	for d	lifferent bla	ıck	filled rubber	s using botl	h plastic	zers			

A -cardanol **B** – aromatic oil TS- tensile strength (MPa) M– modulus at 300% elongatic

EB- elongation at break (%)

M- modulus at 300% elongation *modulus at 100% elongation TR- tear resistance R- retention (%)

[#] 120 h.ageing ^{**} 48h.ageing

Table 5.25 shows the % retention of some mechanical properties on ageing at 100°C. Maximum retention of tensile strength is observed in the case of EPDM plasticized by cardanol. The retention of tensile strength in the case of cardanol plasticized NR and NBR are much better than that when conventional plasticizer is

used. Generally cardanol plasticized samples have better retention of tensile strength than when conventional plasticizers are used. The retention of elongation at break values are also better for cardanol plasticized samples except in the case of cardanol plasticized NBR, which is slightly less. Retention of modulus is maximum in the case of CR plasticized by cardanol. Again it is favourable for all cardanol based samples except in the case of EPDM. Retention of tear strength is maximum in the case of NR plasticized by cardanol. Generally the retention of tear strength values are favourable for all the four rubbers plasticized by cardanol.

2) Performance of cardanol as antioxidant

Table 5.26 gives the retention of mechanical properties of gum samples on ageing at 100° C when cardanol or TQ is used as antioxidant. The retention of tensile strength on ageing is found to be better in the case of NR and CR when cardanol is used as antioxidant instead of TQ. In the case of EPDM and NBR, TQ is found to be a better antioxidant than cardanol. Retention of elongation at break values is found to be similar in the case of NR and CR for both antioxidants, whereas TQ based samples show better values in the case of EPDM and NBR. Retention of modulus values is advantageous in the case of NR, NBR and CR when cardanol is used as antioxidant whereas for EPDM, the values are comparable. Retention of tear strength values is comparable for both antioxidants in the case of NBR, EPDM and CR. In the case of NR, maximum advantage is obtained when cardanol is used as antioxidant.

Table 5.26 Retention of mechanical properties of gum samples on ageing at
100° C when cardanol /TQ is used as antioxidant

	NR		EPDI	М	NBR	ι	CR	
	Cardanol	TQ	Cardanol	TQ	Cardanol	TQ	Cardanol	TQ
TS	22.5	26.2	2.5	2.29	7.43	5.3	14.5	15.9
TS [#]	*26.6	29.16	1.88	1.91	4.2	4.6	8.7	7.3
R	118	111	75	83	57	87	60	46
TS								
EB	1077	1027	368	282	659	466	1301	1224
EB#	928	887.2	220	202	320	330	748	710
R	86	86	58	71	49	71	57	58
EB]		
М	1.68	1.85	1.92	1.82	2.7	3.2	1.04	1.13
M #	*2.46	2.54	1.88	1.91	3.6	3.8	2.18	2.06
R _M	146	137	98	105	133	118	210	182
TR	39.6	34.4	12.68	13.75	23.81	24.89	28.9	26.9
TR [#]	39.6	34.4	12.68	13.75	23.81	24.89	28.9	26.9
R	125	102	75	87	63	62	63	72
ŤR								

TS- tensile strength (MPa)

EB- elongation at break (%)

TR- tear resistance R- retention (%)

*96hrs of ageing at 70°C

M-modulus at 300% elongation

[#]120 hrs ageing

Retention of tensile strength is maximum beneficial in the case of NR.

3) Cardanol as co-activator

Table 5.27 Comparison of cure characteristics when cardanol is used as coactivator in place of stearic acid for different rubbers

Rubber	NR	gum	EPDN	1 gum	NBR	t gum	CR	gum
Co-activator	A	В	A	В	A	В	A	В
Scorch time (min)	6.7	5.5	5.83	3.60	3.51	3.57	6.25	3.72
Cure time (min)	8.76	7.03	10.16	11.11	5.46	7.18	18.45	16.47
CRI min ⁻¹	48.54	64.93	20.7	13.3	51.2	27.7	8.19	7.8
Tensile strength (MPa)	24.8	24.71	2.224	2.73	5.48	6.1	20.33	20.33
Tear strength (N/mm)	41.6	37.25	12.69	13.36	19.9	19.46	26.18	28.03

A-cardanol B- stearic acid

When cardanol is used as co-activator (Table 5.27), there is increase in scorch time for NR and CR where as there is decrease in cure time for NBR and EPDM. NBR is found to have a much higher cure rate index followed by EPDM when cardanol is used in place of stearic acid. For the other two rubbers, the cure characteristics are comparable.

Table 5.28 Comparison of mechanical properties when ca	rdanol is used as co-
activator in place of stearic acid	

	NR	gum	EPDN	l gum	NBR	gum	CR	gum
	A	В	A	В	A	В	В	A
Tensile	24.8	24 71	22	2 73	5 4 8	61	20.3	20.3
strength (MPa)	21.0	2	2.2	2.73	5.10	0.1	20.5	20.5
Elongation at	1067	1121	416.9	313.8	590	550	1477	1334
break (%)	1007	1121	110.5	515.0	550	550	1177	1551
Modulus at								
300%	1.68	1 35	17	2 74	22	29	1 1 1	1 17
elongation	1.00	1.50	,		2.2	2.9		,
(MPa)								

A-cardanol B- stearic acid

Similar values of mechanical properties (Table 5.28) are obtained for both coactivators for all the rubbers, except a better tear strength value for NR when cardanol is used as co-activator. Similarly elongation at break values are higher for all rubbers except NR.

4) Cardanol as accelerator

 Table 5.29 Comparison of cure characteristics when cardanol is used as

 accelerator in place of conventional accelerator

Rubber	NR	gum	EPDM	gum	NBR	gum	CR	gum
Accelerator	A	B	A	В	A	В	A	D
Scorch time		55	5.83	36	3 51	3 57	3 47	3 72
(min)		5.5	5.05	5.0	5.51	,	3.47	3.72
Cure time	26.4	7.03	10.16	11 11	5 46	718	20.38	16.47
(min)	20.1	1.05			0.10	1.10	20.50	
Minimum								
torque	0.02	0.03	0.231	0.16	0.26	0.248	0.15	0.16
(dNm)								
Maximum								
torque	0.54	2.64	4.43	5.54	4.19	4.55	6.2	6.81
(dNm)								
CRI (min ⁻¹)	3.7	64.9	20.7	13.3	51.28	27.7	5.91	7.8
A - cardanol	B-CE	BS I	D-TMTI)				

These values are found to be better for EPDM and NBR when cardanol is used as accelerator in place of CBS. Scorch time improvement is also observed for EPDM, where as these values are similar for NBR and CR. For CR cardanol is not as good as TMTD, as CRI is lower and cure time is slightly higher. On comparing the cure times, it is obvious that cardanol does not act as accelerator in the case of NR.

Chapter V

Rubber	EPDM	gum	NBR	gum	CR g	gum
Accelerator	A	В	A	В	A	D
Tensile strength (MPa)	2.27	2.73	5.9	6.1	17.29	20.33
Elongation at break (%)	403.9	313.8	645	550	1325	1334
Modulus at 300% elongation (MPa)	1.75	2.74	2.6	2.9	1.453	1.17
Tear strength (N/mm)	13.37	13.36	19.24	19.46	26.16	28.03

 Table 5. 30 Comparison of mechanical properties when cardanol is used as

 accelerator in place of conventional accelerator

The tensile strength (Table 5.30) of EPDM and NBR gums are comparable when cardanol and conventional accelerators are used. For CR cardanol gives slightly lower tensile strength. The same trend is followed by tear strength also. In the case of EPDM, the elongation at break is much higher when cardanol is used. Mechanical properties of NR accelerated by cardanol are not included as in this case the extent of acceleration is unsatisfactory.

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Conclusions

The important conclusions resulting from the this research work can be summarized as follows

Natural rubber

- When cardanol is used as plasticizer for HAF black filled NR in place of aromatic oil, lower cure time, compound viscosity and filler agglomeration result. Cardanol also leads to higher cure rate indices.
- 2) The mechanical properties are in general better than when aromatic oil is used.
- The percentage of cardanol needed for plasticizing HAF black filled NR is only 5% as against 10% for aromatic oil.
- 4) Cardanol leads to better ageing characteristics compared to aromatic oil.
- 5) In the case of silica filled NR, similarly, cure time and α values are lower for cardanol.
- 6) Mechanical properties and thermal stability are similar for both cardanol and aromatic oil based samples.
- The amount of cardanol needed for plasticizing silica filled NR is 10% of filler weight, same as that of aromatic oil.
- For both silica filled and black filled compounds, the ageing behaviour of the vulcanizates is better when cardanol is used as plasticizer.
- 9) Performance of cardanol is equivalent to that of TQ and SP when antioxidant properties are considered.
- 10) The co-activator properties of cardanol in NR are comparable to stearic acid.

11) The crosslinking density of cardanol plasticized NR is generally lower than when plasticized by atomatic oil.

NBR

- 1) For HAF black filled NBR, cure characteristics and α values are similar to those obtained when DOP is used as plasticizer.
- 2) Mechanical properties are also of comparable magnitude.
- 3) For silica filled NBR, compound viscosity and α values are lower for the case of cardanol.
- 4) The mechanical properties are superior when cardanol is used.
- 5) The crosslink densities are comparable for both DOP and cardanol for both fillers.
- 6) 10% cardanol is needed for plasticizing HAF black where as 5 7.5% is needed in the case of silica. The latter case compares well with DOP which is required to the extent of 10%.
- 7) Cardanol possesses antioxidant and co-activator properties in NBR comparable to conventional additives.
- 8) Cardanol has some activator property in NBR compounds.

EPDM

- 1) Cure characteristics and mechanical properties are similar for cardanol and naphthenic oil, the two plasticizers studied.
- 2) In the case of silica filled EPDM, cardanol shows superiority at high silica contents greater than 20phr.
- 3) The amount of cardanol required for plasticization is 5% for both fillers, which is the same as that used for conventional plasticizers.
- Cardanol possesses co-activator and accelerator properties comparable to conventional additives.

CR

- 1) For CR, cardanol gives similar cure characteristics and mechanical properties as naphthenic oil.
- Cardanol plasticized samples show better ageing behaviour compared to naphthenic oil based samples.
- 3) For black filled compounds, filler dispersion is more effective in the case of cardanol.
- 4) Silica filled CR has a tendency to adhere to the mould surface.
- 5) Optimal amount of cardanol in HAF black filled CR is 10%.
- Cardanol possesses antioxidant and co-activator properties in CR compounds. It has also some accelerator property.

Comparative performance

- 1) Lowering of cure time is maximum in the case of black filled CR when cardanol is used as plasticizer.
- Improvement in mechanical properties are comparatively better when cardanol is used for silica filled compounds rather than black filled compounds
- Maximum retention of tensile strength after ageing at 100°C is observed in the case of black filled EPDM followed by NR and CR when plasticized by cardanol.
- In general, cardanol shows much lower extractability compared to conventional plasticizers.
- 5) First order kinetics of rubber vulcanization is not altered by the presence of cardanol

ASTM	American Society for Testing and Materials
BP	Boiling point
BR	Butadiene rubber
CBS	N-cyclohexyl-2-benzothiazylsulfenamide
CNSL	Cashew Nut Shell Liquid
CR	Chloroprene rubber
CRI	Cure rate index
CS ₂	Carbon di sulphide
DEG	Diethylene glycol
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetic analysis
EPDM	Ethylene propylene diene monomer
FTIR	Fourier transform infra red
HAF	High Abrasion Furnace Black
HC1	Hydrochloric acid
HS	Hydrated silica
IIR	Isobutylene isoprene rubber
LR	Laboratory reagent
MgO	Magnesium oxide
Mn	Number average molecular weight
M w	Weight average molecular weight
Mz	Z average molecular weight
MP	Melting point
M.W	Molecular weight
N_2	Nitrogen

NA 22	Ethylene thiourea
NaOH	Sodium hydroxide
NBR	Acrylonitrile butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
PUR	Urethane rubber
Q	Silicone rubber
RH	Rubber hydrocarbon
SR	Synthetic rubber
SBR	Styrene butadiene rubber
TGA	Thermogravimetric analysis
TMTD	Tetramethyl thiuram disulphide
UV	Ultraviolet
VGC	Viscosity Gravity Constant
wt	Weight
w/v	Weight by volume
wpe	Weight per epoxy value
ZDC	Zinc Dithiocarbamate
ZnO	Zinc oxide

cm	Centimetre
cps	Centipoise
g	Gram
h	Hour
kg	Kilogram
kN	Kilo newton
m	Metre
min	Minute
ml	Millilitre
ML(1+4) at 100°C	Mooney viscosity number. L indicates the large rotor, 1 is
ML(1+4) at 100°C	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the
ML(1+4) at 100°C	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the
ML(1+4) at 100°C	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken and 100°C is the temperature of the test
ML(1+4) at 100°C	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken and 100°C is the temperature of the test Millimetre
ML(1+4) at 100°C mm MPa	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken and 100°C is the temperature of the test Millimetre Mega Pascal
ML(1+4) at 100°C mm MPa N	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken and 100°C is the temperature of the test Millimetre Mega Pascal Newton
ML(1+4) at 100°C mm MPa N nm	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken and 100°C is the temperature of the test Millimetre Mega Pascal Newton Nanometre

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