STUDY OF CARDANOL AS ANTIOXIDANT IN TRUCK TYRE TREAD IN PLACE OF TMQ

A REPORT ON THE PROJECT WORK

Carried out
At

APOLLO TYRES LIMITED

PERAMBRA

By

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Cochin 682022

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APOLLO TYRES LTD.

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TO WHOMSOEVER IT MAY CONCERN

This is to certify that **Mr. SAMSON DAVID** B-Tech. 8th semester Polymer Science and Rubber Technology student of Cochin University of Science and Technology, Kochi, have successfully completed his factory training under the guidance of the undersigned, during the period from 8th January to 21st February 2007.

Mr. SAMSON DAVID showed good inquisitiveness and keenness in carrying out his project work successfully and I take this opportunity to wish him all the best.

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This is to certify that **Mr. SAMSON DAVID** B-Tech. 8th semester Polymer Science and Rubber Technology student of Cochin University of Science and Technology, Kochi, have successfully completed the project on ***"EFFECT OF CARDANOL AS ANTIOXIDANT IN TRUCK TYRE TREAD INSTEAD OF TMQ"*** under the guidance of the undersigned, during the period from 21st February 2007 to 11th May 2007.

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My debts of gratitude……

We thank almighty God for showering grace up on us, without his blessings we would not have achieved my goal. Whenever we started feeling low, He would fill us with new hope and determination.

It is my privilege to place on record my gratitude to ***Dr. Thomas Kurian,*** *Head of the department of polymer Science and Rubber technology, CUSAT Kochi, for granting me permission to work on this interesting project at* ***Apollo Tyres,*** *Perambra. His encouragement and support were invaluable for the completion of this project.*

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I thank all my friends at CUSAT Kalamassery, for extending their help in every possible way. Last but not least I would like to thank my dear classmates and family for their moral support.

Samson David

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1. INTRODUCTION

The technological performance of various types of rubber depends on their ability to withstand the effects of the service environment. The development of rubber for many modern uses would not have been possible without the discovery of chemicals to prevent their degradation during service.

The deterioration in the useful properties of rubber products with time is a serious problem involving the oxidation of polymers by the oxygen of the atmosphere. Natural and synthetic polymers deteriorate on ageing in varying degrees as a result of the combination of a number of factors like heat, light, oxygen and ozone. The irreversible nature of the oxidative processes to which industrial polymers are subjected during high temperature processing and under aggressive conditions during service has intensified the search for improved stabilizing systems. This has resulted in the development of Antioxidants, Anti-fatigue agents, Melt stabilizers, UV-stabilizers and Fire retardants.

Antioxidants - Historical Background

Natural rubber latex contains a small percentage of non-rubbery materials, which function as antioxidants. These materials effectively protect the rubber during coagulation and storage, but they are destroyed during the processing and curing operations. Thus, it is not surprising that the earliest manufacturers of rubber products, who knew nothing of oxidation, were plagued by the problem of deterioration. Hofmann in 1861 was credited with being the first to discover the oxygen absorption involved in this degradation, and the first patent, concerned with the use of phenol and cresol as antioxidants was issued to Murphy in 1870.Until about 1910 the materials chosen to reduce this oxidative degradation were natural products, such as coal tar resins, coumarone resins, paraffin, creosote and inorganic and organic reducing agents.

The stability of the rubber product was not greatly improved when these additives were used.

The first antioxidants made their appearance in 1924 and slowly gained acceptance. Within a few years, their true value in rubber industry became apparent and the resulting search for new antioxidants led to the patenting of hundreds of materials. The first two widely used antioxidants were the reaction product of aniline and acetaldehyde and aldol naphthylamine. Hydroquinone and pyrogallol were patented in1901, resorcinol and 2-naphthol in 1920, 1-naphthol and aldehyde condensation products in1922, and mercaptobenzimidazole in 1931. In 1957, a new way to manufacture 2,6-di-terf-butylphenol in high yield and purity was discovered. The attachment of methylene bridged groups to the para position of this phenol by condensation reactions with formaldehyde and acrylates led to the discovery and commercialization of a number of new antioxidants. Currently, bound antioxidants are being developed to give maximum resistance to losses by extraction and volatilization.

General Aspects of Polymer Degradation and Stabilization

All hydrocarbons are vulnerable to deterioration caused by heat, light and oxygen. These 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 the various polymers. Polymers with C-H bonds of low dissociation energies are more readily oxidized than polymers with higher C-H bond dissociation energies. Consequently, branching and un-saturation lower bond energies and increase the polymer's susceptibility to oxidation. The amount of un-saturation present in a polymer is also important. The rubber with low olefinic content, such as EPDM (ethylene propylene diene terpolymer), is more resistant to oxidation than the highly unsaturated rubbers, such as SBR (styrene

- butadiene rubber) and NR (natural rubber).

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 pre-dominates 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 (cis-polyisoprene) and IIR (isobutylene isoprene rubber), soften on oxidation due to chain scission. It is not surprising, then, that an antioxidant which affords excellent protection in one rubber is not the most effective stabilizer for another.

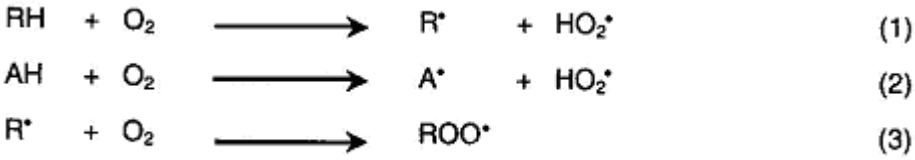
A broad distinction is generally made between materials, which can protect raw synthetic rubber, and those, which protect vulcanized rubber products. Synthetic rubbers are very susceptible to oxidation and must be protected with an antioxidant immediately after they are formed by polymerization in order to prevent oxidative degradation during the high temperature drying step and during the subsequent storage.

Tyres account for the largest volume of antioxidants used each year; they are primarily the amine staining antioxidants. A wide variety of light coloured vulcanized products are protected with non-staining antioxidants.

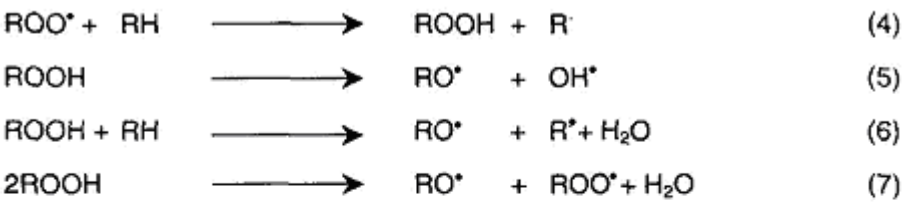
Mechanism of polymer oxidation

Oxidation of polymers can lead to chain scission, crosslinking 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.

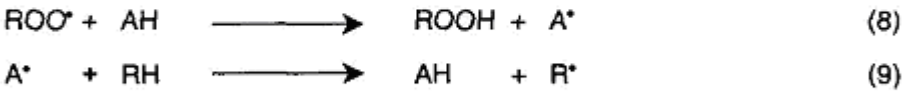
Initiation



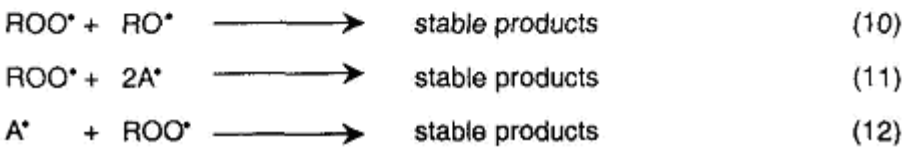
Propagation



Chain transfer



Termination



RH = polymer molecule or portion thereof,

AH = antioxidant,

A =antioxidant radical,

RO_2 =polymer peroxy radical, and

ROOH = polymer peroxide.

Basic classification of antioxidants

Rubber antidegradants included in this classification are divided into six classes as shown below. The classification in general is based on chemical structure and application on rubber.

a) Class 1. p-Phenylene diamines (PPDs) - This group of additives represents the primary materials used in tyres and other mechanical goods to

impart ozone protection. These additives are also used as antioxidants and antiflex agents in a number of applications but are considered to be strongly staining and thus limited to black rubber applications. They can also be used as raw polymer stabilizers.

b) Class 2. Trimethyl-diquinolines (TMQs) - These materials are primarily used to protect rubber articles from degradation by atmospheric oxygen at higher temperatures. They are moderately staining.

c) Class 3. Phenolics - Phenolic antidegradants represent a group of nonstaining and non discoloring additives used primarily in light colored mechanical goods and tyres. They can also be employed as raw polymer stabilisers. In general they are weaker antioxidants than amine types.

d) Class 4. Alkylated diphenylamines (DPAs) - This class of additives generally represents substituted amine antioxidants and it is used as raw polymer stabiliser in vulcanizate applications. These additives are moderately discoloring and staining.

e) Class 5. Aromatic phosphites - These are phosphorus containing fully non-staining, non-discoloring additives used as stabilzers for synthetic elastomers in 'white rubber' applications. They also have applications as peroxide decomposers and radical traps in polymer systems.

f) Class 6. Diphenylamine - ketone condensates - This group of additives is used primarily in carbon black loaded compounds to protect them against oxygen and heat deterioration.

Classification of antioxidants based on their mode of action

Two main groups of antioxidants are distinguished according to their mode of action: primary or chain breaking, and secondary or preventive antioxidants.

Chain breaking antioxidants

Chain breaking antioxidants interfere with the chain propagation steps of

polymer oxidation. These antioxidants can terminate the kinetic chain by,

a) Free radical traps which interact with chain propagating RO_2' radicals to form inactive products. Quinones and conjugated molecules (e.g. anthracene) can function as free radical traps.

b) Electron donors give electron to peroxy radical and thus stabilising the system.

c) Hydrogen donors are the most commonly used chain terminating antioxidants. Inhibitors of the aromatic amine (InH) type interfere with oxidative chain propagation by competing with the polymer for peroxy radicals:

Preventive antioxidants

a) Light absorbers

Processes operative in environmental ageing of hydrocarbon polymers include transformations induced by light. Commonly used photo-stabilizers are hydroxybenzophenone derivatives, substituted benzotriazole derivatives, metal complexes of different ligands and different metals etc. The oxidation mechanism developed by Bolland to explain the thermal oxidation of rubber has been applied successfully to thermal oxidation of other substrates and also to photo-oxidation.

b) Metal deactivators

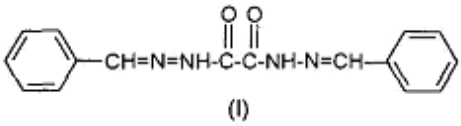
They are strong metal ion complexing agents that inhibit catalyzed initiation. The most effective groups are polydentate chelating agents capable of forming very stable chelates in which all the co-ordination sites are occupied. Examples are

oxalyl bis- benzylidene hydrazide (i),

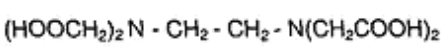
ethylene diamine tetra acetic acid (ii),

N,N^1-di-naphthyl-p-phenylene (iii),

$2,2^1$methylene-bis (4-methyl-6-tert-butylpheno!) (iv).



(I)



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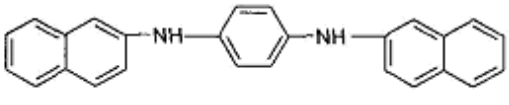

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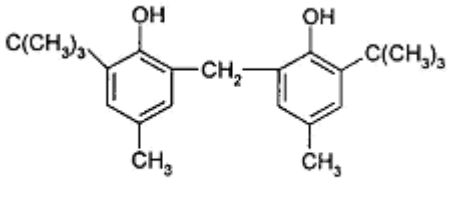
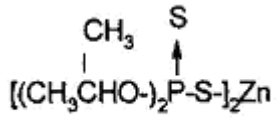


(IV)

c) Peroxide decomposers

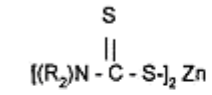
Peroxide decomposers have proved to be very important in rubber. The main requirement of compounds falling into this class is that they should substantially reduce hydroperoxides to alcohols without substantial formation of free radicals. Several organic sulphur compounds, including zinc dialkyl dithiophosphates (V) were found to decompose hydroperoxides and the mechanism of inhibition by the latter has been reviewed.



(V)

Compounds containing an imino group have also been found to be effective antioxidants. In certain cases peroxide decomposers decompose hydroperoxides through polar reactions, thereby inhibiting initiation. This class includes metallic salts of certain dithioacids such as zinc dithiocarbamates (VI),

xanthates(VII), di-tert - butyl sulphide (VIII), tert-butyl thio sulphoxylic acid(IX). etc.



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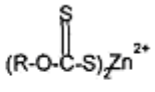

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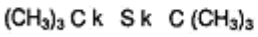

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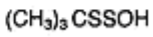


(IX)

Important characteristics of antioxidants

There are a number of properties that antioxidants must possess besides good antioxidant activity if they are to be widely used in rubber applications. They should be inexpensive and should not interfere with the cure characteristics of the rubber. They should be non - toxic, non-fugitive, handy, compatible with the rubber and for certain applications, non-discolouring and non-staining.

Service requirements placed on finished rubber products demand improved polymer stabilization. The effectiveness of antioxidant depends on two factors. (I) intrinsic activity of the antioxidant and (II) permanence of the antioxidant in the polymer.

I) Intrinsic activity of the antioxidant

This is the fundamental ability of the antioxidant and its transformation products to interfere with and retard the radical chain oxidation process, which in turn depend on the chemical structure of the antioxidant.

II) Permanence of the antioxidant in the polymer

The concentration of the antioxidant in a polymer decreases during long term use as a consequence of the following processes: (1) chemical loss of antioxidant and (2) physical loss of antioxidant from the polymers. Chemical loss of antioxidant as a result of their mechanism of stabilization is summarized by Vink. Physical loss of antioxidant mainly depends on (a) distribution of antioxidants in polymers, (b) compatibility of antioxidants in polymers, (c)

volatility of antioxidants, (d) diffusion of antioxidants in polymers and (e) extractability of antioxidants from polymers.

(a) Distribution of antioxidants in polymers

In general, it may be assumed that the distribution of antioxidants is uniform in amorphous polymers where the antioxidants form micro heterogeneous phases uniformly dispersed in a polymer according to their compatibility with the polymer. In semicrystalline polymers, the distribution of antioxidants is not uniform owing to the presence of crystalline and amorphous phases. The distribution of several types of low molecular weight compounds in different polymers was investigated by Billinghametal. They also ascertained that the distribution of stabilizers in spherulitic polymers depended on the conditions of crystallisation and on the total amount of the atactic polymer concentrated at the boundaries of spherulites.

Irrespective of the problems of solubility and migration of the antioxidants, such distribution of antioxidants in polymers appears to be advantageous because the amorphous portion of most of the polymers is the region most sensitive to degradation. The uneven distribution of an antioxidant raises the concentration in the amorphous phase thus protecting it more effectively against degradation.

(b) Compatibility of antioxidants in polymers

One of the factors which affect the effectiveness and permanence of antioxidants in polymers is compatibility, which represents the totality of effects which are involved in the polymer additive interaction. If polymers are modified by antioxidants, a physical mixture characterised by certain degree of homogeneity or heterogeneity arises. The degree to which this occurs depends mainly on the cohesion and adhesion forces between the components and their bulk or surface interactions.

The theory of solutions of macromolecular substances is most frequently applied to mixtures of polymers with low molecular weight substances or to

polymer —polymer mixtures. This theory predicts that the compatibility of components in mixing may be approximately estimated from the squared difference of the values of solubility parameters of the components (Ää). The solubility parameter 5 represents the density of cohesion energy and is numerically equal to the potential energy of a unit volume of a material,

$$\delta = \frac{E}{V} = \frac{N_0 v}{V}$$

where E is the potential energy, V is molar volume, N_0 is the Avogadro number and v is the potential energy of one molecule. The greatest difference between the solubility parameters of the polymer (δ_P) and the second component (δ_a) defines the critical value:

$$(\Delta\delta)_{max} = (\delta_p - \delta_a)_{max}$$

If the experimental or calculated value of (Ää) is less than the critical value $(Ää)^2_{max}$, the components are able to form a homogeneous mixture. If the value $(Ää)^2$ exceeds the maximum value, the formation of a heterogeneous mixture is to be expected.

c) Volatility of antioxidants

One of the causes of the physical loss of stabilizers in polymers is their volatility which in turn is a manifestation of thermal motion of molecules on the surface of a sample. It is related to the heat of evaporation of antioxidant in the sense of the Clausius Clapeyron equation (16) and dependent on the interactions in the polymer - stabilizer system.

$$d \ln p / dT = \Delta H / RT^2$$

The solubility of an additive in a polymer is a thermodynamic equilibrium property of the additive polymer combination and the diffusion coefficient is a kinetic parameter defined for closely controlled conditions. In contrast, the rate of evaporation of an additive is a kinetic quantity which is sensitive to the conditions of measurement. Spacht measured the vapour pressures of a series of phenolic and amine antioxidants by a direct manometric

measurement at temperatures above the melting points. Angert showed that the loss of amine antioxidant from a thick rubber sample follows the first order kinetics and concluded that the rate constant is related to the volatility of the pure additive. These authors showed that the presence of carbon black or chalk as fillers significantly reduces the loss rate although they did not interpret this result. The introduction of an amine or hydroxy group into the para position of diphenylamine reduces the volatility almost by an order of magnitude; the formations of intermolecular hydrogen bonds lead to an increase in the intermolecular attraction forces and thus lead to volatility.

(d) Diffusion of antioxidants in polymer

The diffusion of antioxidant in polymer does not itself produce any loss of antioxidant from the polymer. The diffusion processes play an important role in the evaporation and leaching of antioxidants from polymers. The diffusion of gases, solvents and hydrocarbons in rubber has been extensively studied.[31,,33]The nature of the polymer and the size of the diffusant appear to be the main factors that govern the rate of diffusion.

In most cases, the method employed for diffusion coefficient determination is a radio isotope labelling technique. The attempt to correlate the antioxidant diffusivity to rubber crosslink densities was done by N. C. Billingham et al. Carlsson et al. believe that the optimum stabilization may be achieved by using a very low concentration of the antioxidant in the bulk of the polymer but a higher concentration in the surface layer. Nevertheless, evaporation of the low molecular weight antioxidants washing with water or organic solvents and mechanical abrasive wear of the surface layers in long term use results in an overall decrease in stabilizer content in the polymer and hence a decrease in its resistance to degradation.

(e) Extractability of antioxidants from polymers

Another factor causing the physical loss of antioxidants in polymers is extraction. This plays a part wherever the polymer articles come into contact

with water or organic solvents. The extraction reduces the antioxidants in the polymers especially in the surface layers which are the most sensitive to degradation during ageing. The extractability can be estimated. (1) by determining the stabiliser concentration in the polymer after extraction, (2) according to the content of antioxidant in the extraction medium and (3) by comparing the stability of non-extracted and extracted samples. Cain et al. have observed that diethylaniline bound to rubber, although less effective than its low molecular weight analogue, N-phenyl-N'-isopropyl-p-phenylene diamine becomes more effective with water at 100°C and its antioxidant activity does not decrease.

Leachability decreases with increasing molecular weight of the stabilizer. Another factor which influences extractability is the relation among the interactions of stabilizer, extraction medium and polymer.

Accelerated solvent extraction of antioxidants in linear low density polyethylene was studied by M. Waldeback et al. A method for quantitative supercritical fluid extraction of Ethanox 330 antioxidant from high-density polyethylene was studied by A M Pinto.

As a result of the above processes, the decrease in concentration of the antioxidants in polymers affects the resistance to degradation. Basically there are two approaches in increasing the persistence of an antioxidant:

(1) To produce antioxidant of high molecular weight.

(2) To chemically attach the antioxidant to a polymer, thereby guaranteeing its persistence in the final product i.e. polymer-bound antioxidants.

Mechanism of antioxidant action

Oxidation inhibition processes have been classified into two main types: kinetic chain-breaking processes and initiation prevention mechanisms. The first type embraces the traditional rubber antioxidants, the aromatic amines and phenols, and the second includes the hydroperoxide decomposers, the transition

metal deactivators and UV-stabilizers acting by the light absorption mechanism.

Chain-Breaking (CB) mechanism

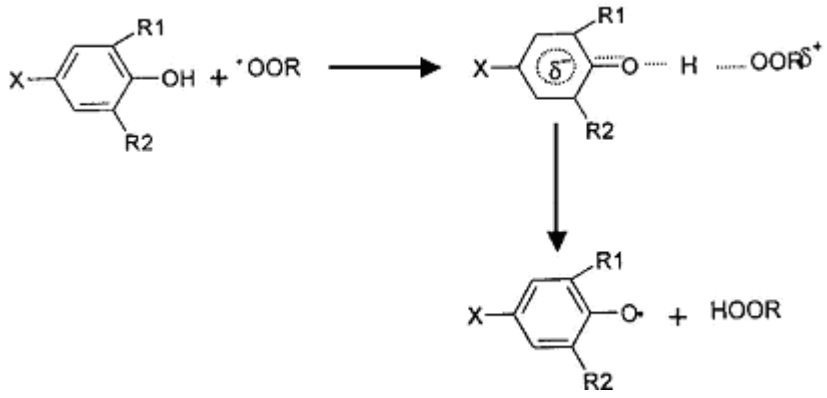
This was the first antioxidant mechanism to be investigated in detail. The free radical oxidation chain reaction indicates two ways in which the chain might be interrupted. These may be summarized below

Chain-Breaking Donor Mechanism (CB-D)

Chain breaking antioxidants act according to the following general reaction.

Where AH is the antioxidant. The chain breaking antioxidants are frequently called as primary antioxidants. The geometry of the reaction is influenced by the steric environment of the reaction site of the antioxidant {OH or NH). From a sterically hindered 'AH', H is transferred in a direction perpendicular to the plane of the aromatic ring. If at least one ortho substituent is not very bulky, the process is most likely a coplanar one, a longer life may be assumed for the resulting transition state. Depending on the nature of the AH, the radical A' may be either phenoxyl or amino radical. Transformation products of phenoxy and amino radical are summarised by Pospisil.

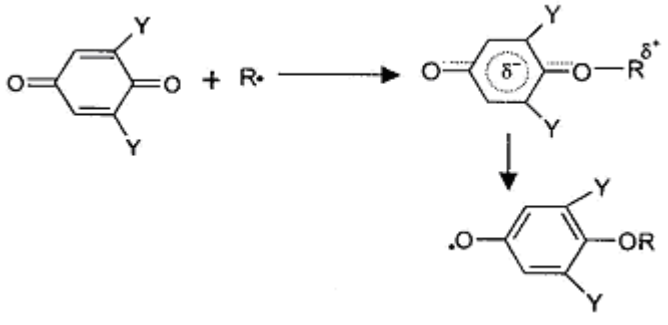
Both amine type and phenolic type antioxidants can donate hydrogen to an alkylperoxy radical. The effects of substituent groups in the aromatic rings are to reduce the energy of the transition state (II) which involves electron delocalisation in the aromatic ring.



The products formed by further reaction of the initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant activity.

Chain - Breaking (Acceptor) Mechanism (CB- A)

Macro-alkyl radicals, unlike alkylperoxyl radicals, are not powerful oxidizing agents, but they are themselves readily oxidized by electron acceptors. A variety of oxidising agents are capable of removing alkyl radicals from an auto-oxidising system and if they are able to do this in competition with alkyl peroxyl radicals, they have antioxidant activity. In general, the molecular requirements for a CB-A antioxidants are the same as for polymerization inhibitors. This class includesquinones, nitro compounds and stable free radicals of which nitroxyls and phenoxyls have been most studied.



Polymer-Bound Antioxidants

The antioxidant action depends mainly on three factors. The first is the intrinsic activity of the antioxidant itself. This is the fundamental ability of the antioxidant or its transformation products to interfere with and retard the radical chain oxidation process. The second factor is the compatibility or solubility of

the antioxidant in the polymer matrix. Polarity changes will result in aggregation of the stabilizer, insolubility in the matrix, spewing or blooming of the material, or preferential absorption on the filler. All these factors result in the stabilizer not being present uniformly in the polymer.

The third factor is the volatility or fugitive nature of the antioxidant. Losses due to extraction or volatility immediately affect the ultimate performance of the final product. Of the three factors, the third factor is the most important, since it affects the antioxidant's persistence directly. Basically, there are two approaches for increasing the persistence of an antioxidant. One is to produce antioxidants of high molecular weight and therefore, of low volatility or extractability. The other is to chemically bind the antioxidant to the polymer i.e. polymer-bound antioxidant, thereby guaranteeing its persistence in the final product.

One of the more exciting areas of research during the past decade was the preparation of polymer-bound antioxidant systems. The advantages of bound antioxidants in oil and fuel resistant nitrile rubber have been well documented.

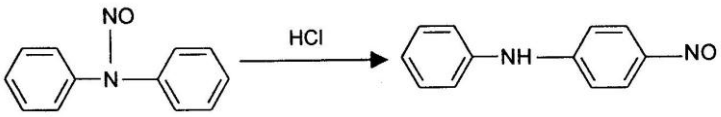
Considerable effort has been expended in the preparation and utilization of phenolic antioxidants which have pendant unsaturated groups. The utility of such a system was demonstrated by Davy and Williams, who co-vulcanised 2-allyl - 4 -alkoxy - phenols into natural and synthetic rubber recipes. Excellent nonstaining and anti-flex properties were claimed for the vulcanizates.

TJne preparation of nitrile rubber containing copolymerized N- (4-anilinophenyl) methacrylamide was reported by Meyer and coworkers. Several polymerisable amine and phenolic antioxidants were discussed in the literature.

Most versatile method of polymer modification is the direct introduction of an antioxidant function by the reaction of a conventional polymer with a suitable reactive adduct. The advantages of such modification are numerous. These include a multiplicity of polymer choices, a choice on ultimate level of stabiliser loading and the introduction of the stabilizer in a separate step from

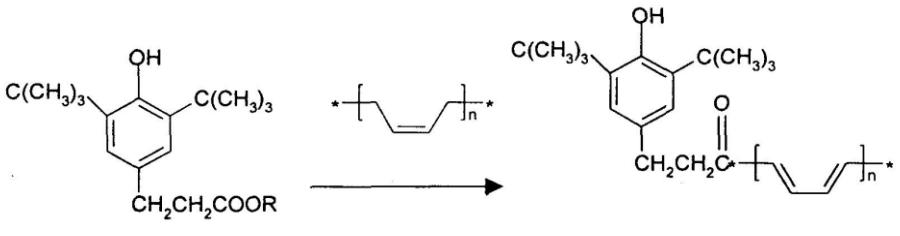
the production process. An existing commercial polymer is modified inexpensively by a chemical reaction with a polymer reactive antioxidant.

Cain and co workers found that "ene" addition of nitroso phenols or aniline derivatives produce polymer-bound stabilizers. A commercial preparation of p-nitrosodiphenylamine by hydrochloric acid catalyzed rearrangement of the N-nitrosodiphenylamine was described by Levy and Seif.



The preparation of polymer-bound antioxidants by 1,3 - Saltman first described cycloaddition reaction and Auerbach. They prepared a series of compounds related in structure to 1-(3,5-di-t-butyl-4-hydroxophenyl)-N-phenyl-nitrone. This material was found to add readily to unsaturated polymers to provide a bound antioxidant.

One novel process for introducing bound antioxidants was described by Farrar Living polymers, produced by lithium-catalyzed polymerization of diene monomers were reacted with a variety of commercial antioxidants, which contained ester functionality. Presumably, the polymer behaves as a normal alkyl lithium reagent, which adds to the carbonyl function. Neutralisation produces the bound antioxidants as a ketone.



Although synergism between sulphur compounds such as thiodipropionates and chain breaking antioxidants is well- known and reasonably well understood in polyolefin and in certain non vulcanized rubbers,

the synergistic effect is generally not noted in vulcanized rubber.[91,92] Shelton has attributed this lack of synergism as possibly being due to a masking effect from the presence of other sulphur compounds present in the vulcanizate such as crosslinks and vulcanization fragments. Other explanations centre on antagonism between the synergist and the curative system, other antioxidants or fillers. This antagonism leads to synergist destruction, trapping, or absorption.

An additional example of a system which binds into the polymer during cure was described by Dhami. This material is 2-mercapto-3-allyl-3,4 dihydroquinazoline-4-one. Oxidation-resistant polymers were produced, but no explanation was given as to its method of attachment.

Gregory prepared polymer-bound phenolic antioxidants by alkylation of various alkylated phenols by a variety of polydiene rubbers. M. S. Al-Mehadawe et al described the preparation of polymer-bound antioxidants by direct hot melt mixing of chlorine containing polymers and a commercial antioxidant. Scott et al have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position can react with natural rubber in the presence of oxidizing free radicals to yield polymer bound antioxidants. Antioxidants like styrenated phenol, diphenylamine etc bound to hydroxy terminated liquid natural rubber by modified Friedel Craft's reaction were also found to be effective in improving ageing resistance. Natural rubber bound diphenylamine antioxidants were reported by Avirah and Joseph. Syntheses of new polymeric antioxidants were reported in recent literature.

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2. Cardanol as Antioxidant

Cashew nut shell liquid (CNSL) is a unique natural source for unsaturated long-chain phenols. It is a cheap and renewable material, obtained as a by-product of the cashew industry. CSNL by itself is useful as insecticidal, fungicidal, anti-termite and medicinal applications. It can be used as starting material for organic synthesis and replaces phenol in many instances with equivalent or better results. Resins derived from CNSL are widely employed in the field of friction materials, automobiles, surface coating, adhesives, laminates, rubber compounding, and have several miscellaneous applications. The most attractive consideration for CNSL use as an industrial product can be its low cost, abundant availability, and its chemically reactive nature.

On the basis of the mode of extraction from cashew nut shell, CNSL is classified into two types: solvent-extracted CNSL and technical CNSL. A typical solvent-extracted material contains anacardic acid (60-65%), cardol (15-20%), cardanol (10%), and traces of 2-methyl cardanol. Technical CNSL is obtained by roasting shell at 180-200 °C. The anacardic acid is thermally unstable and is easily decarboxylated during the extraction process by heating and then transformed into cardanol. Technical CNSL contains mainly cardanol (60-65%), cardol (15-20%), polymeric material (10%), and traces of 2-methyl cardol.[3] Depending on the conditions of the roasting process, the composition of the technical CNSL can change and reach higher cardanol content (83-84%), less cardol (8-11%) and maintain polymeric material as 10% and 2-methyl cardol content as 2%.

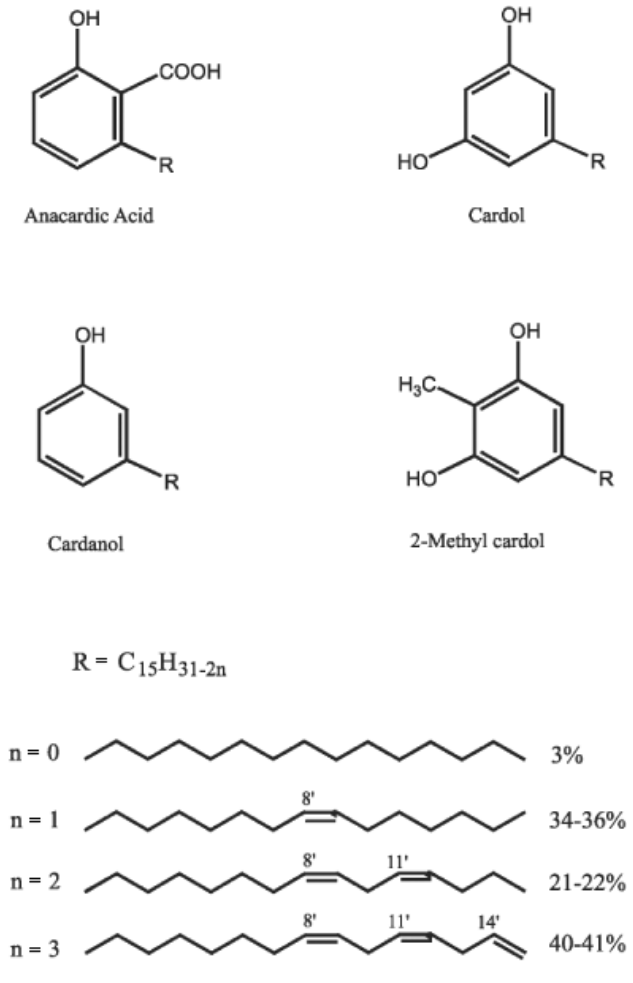
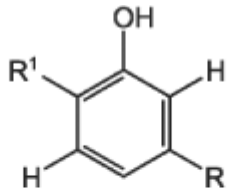


Figure 1. Structures of CNSL constituents.

The use of natural antioxidants is well established. Hindered phenolic compounds (ArOH) represent the major family of both natural and synthetic antioxidants. They are an excellent additive in polymers and lubricants. In general, efficient phenol antioxidants have substituents in *ortho*- and/or *para*-positions. The antioxidant effect is related to the electron donating nature and the steric effect of the substituent(s). The electron-donating effect can enhance the electron density at the oxygen of the phenol, resulting in a high radical-trapping rate. The steric effect prevents phenoxy radicals from coupling and to increase the number of trapped peroxy radicals. CNSL is a mixture of hindered phenols with a long alkyl substitution at the *meta*-position. Despite not displaying substitution in the preferential *ortho* and/or *para*-position, the antioxidant activity of CNSL or its derivatives, in special phosphorylated, in

natural rubber vulcanizates has been reported. The presence of phosphate group, the formation of a network bound antioxidant or the formation of phenolic sulfides *in situ* during the vulcanization have been used to explain the antioxidant activity of CNSL derivatives in natural rubber vulcanizates. The steric effect, due to long tail substituent, has been also reported as an important factor.



ArOH	R	R^1
Cardanol	$C_{15}H_{31-2n}$ n = 0, 1, 2, 3	H
Hydrogenated Cardanol	$C_{15}H_{31}$	H
Alkylated Hydrogenated Cardanol	$C_{15}H_{31}$	*t*-but

Figure 2. Structure of antioxidant species.

Basic Mechanism

The basic mechanism of autooxidation of polyisoprene (RH) includes four steps: initiation, propagation, chain branching and termination. One important reaction in the propagation step is the formation of $RO_2^{\bullet}$, also formed in chain branching step.[19] Phenolic compounds (ArOH) are chain breaking antioxidants (interrupt the chain reaction) well known as a radical scavengers that trap peroxy radicals ($RO_2^{\bullet}$). The manifested activity is due to their higher reactivity towards these radicals. While reducing the $RO_2^{\bullet}$ radicals in reaction (1), phenols convert themselves into resonance-stabilized phenoxy radicals

($ArO^{\bullet}$). To be effective the phenoxy radical must also reacts slowly with substrate RH and rapidly with $RO_2^{\bullet}$. In the oxidation chain termination reaction (2), $ArO^{\bullet}$ are generally consumed to produce non radical products:

$$RO_2^{\bullet} + ArOH \rightarrow RO_2H + ArO^{\bullet} \quad (1)$$

$$\left.\begin{array}{l} RO_2^{\bullet} + ArO^{\bullet} \\ ArO^{\bullet} + ArO^{\bullet} \end{array}\right| \text{---> non radical products} \quad (2)$$

One important parameter in the antioxidant activity is the molar mass. Low molar mass antioxidants are easily lost from polymer through migration, evaporation, and extraction. This physical loss of antioxidants constitutes a major concern in the long-term use of polymers or when high temperature is employed. The new tendency to prevent this problem and guarantee their performance is the production of polymer-bound antioxidants. The presence of about 10% of polymerized and compatible material, normally present in the technical CNSL, could decrease the migration of this antioxidant to the surface, reduce its volatilization and retain the antioxidant activity during heating.

EXTRACTION OF CNSL

Traditionally, a number of methods are employed to extract the oil from the nuts. Often a particular region follows a technique by convention rather than by deliberate choice. The following are the popular methods currently employed for the extraction of the oil.

1. Hot oil bath method

The raw nuts are passed through a bath of hot CNSL at 180 to 200°C. The outer part of the shell bursts open and releases CNSL. About 50% of the oil is thus recovered. This process makes the decortications of nuts easy, without adversely affecting the quality of the kernels. Improvements over this basic

technique include initial surface wetting and dipping in water at 20-25 °C and subsequent steam treatment prior to exposure to the hot CNSL bath. The excess moisture content of 7-10% of the weight of the nuts causes the cells to burst, with the result that the oil oozes into the bath. Another 20% could be extracted by passing the spent shells through an expeller and the rest by a solvent extraction technique. The expeller oil can be upgraded by acid washing followed by centrifugation and heating.

2. Roasting method

Sudden exposure to high temperature from ambient Is the basis of this method. The shells are charred during this process, producing an explosive pressure in the cellular structure which forces the liquid out of the shell. One variation of this method is abrading at 100-300°C for about 1 h and subsequent roasting at 400-700°C in an inert atmosphere. In yet another patent, the nuts are first abraded and then treated with moisture and heated in an infrared oven. Finally they pass through a high-frequency electric field, where the liquid flows out. Often this technique is employed in conjunction with an expeller, where the oil is expelled from the shells to an extent of 90%.

3. Miscellaneous methods

Heating by superheated steam to force out the oil and subsequent expulsion using an expeller, form the basis of a recently reported method. Extraction of the oil by solvents such as benzene, toluene, petroleum hydrocarbon solvents or alcohols or supercritical extraction using a mixture of CO2 and isopropyl alcohol are other reported techniques. Reports of a power-operated cashew nut sheller have also appeared.

REFINING

Sulfides, nitrogenous materials, and minerals contained in the crude

CNSL directly affects the quality of the oil. Hence CNSL is often subjected to chemical treatment with materials such as hydrocarbon sulfates and sulfuric acid before industrial use. Several acid treatment processes have been found to reduce the poisoning or vesicant action [1]. Aqueous solutions of acids such as hydrochloric acid, sulfuric acid, acetic acid, chloroacetic acid or phosphoric acid, or acid sulfates such as sodium hydrogen sulfate are employed for this purpose. This performs two important functions mineral oil of ammonium, calcium and potassium are precipitated and there is a reduction in the content of skin vesicant present in CNSL. The chemical treatment is accompanied by the evolution of hydrogen sulfide. The reduction in sulfur content has been found to correspond roughly to the removal of the agent responsible for the skin irritation. Treatment with amines or with hydroxides of the metals of Group IA or IIA has been found to reduce the cardol content.

The refined CNSL can be readily distilled under reduced pressure or hydrogenated, both processes leading to products with good color stability. Steam treatment of H_2SO_4-treated CNSL followed by distillation has been found to deodorize this oil to a substantial extent. Physical constants of CNSL before and after chemical treatment are summarized in appendix.

DISTILLATION

Cardanol is separated from commercial grade CNSL by Distillation under reduced pressure (1mm Hg). The pale yellow fraction collected at 206-208^{0}C was Cardanol.

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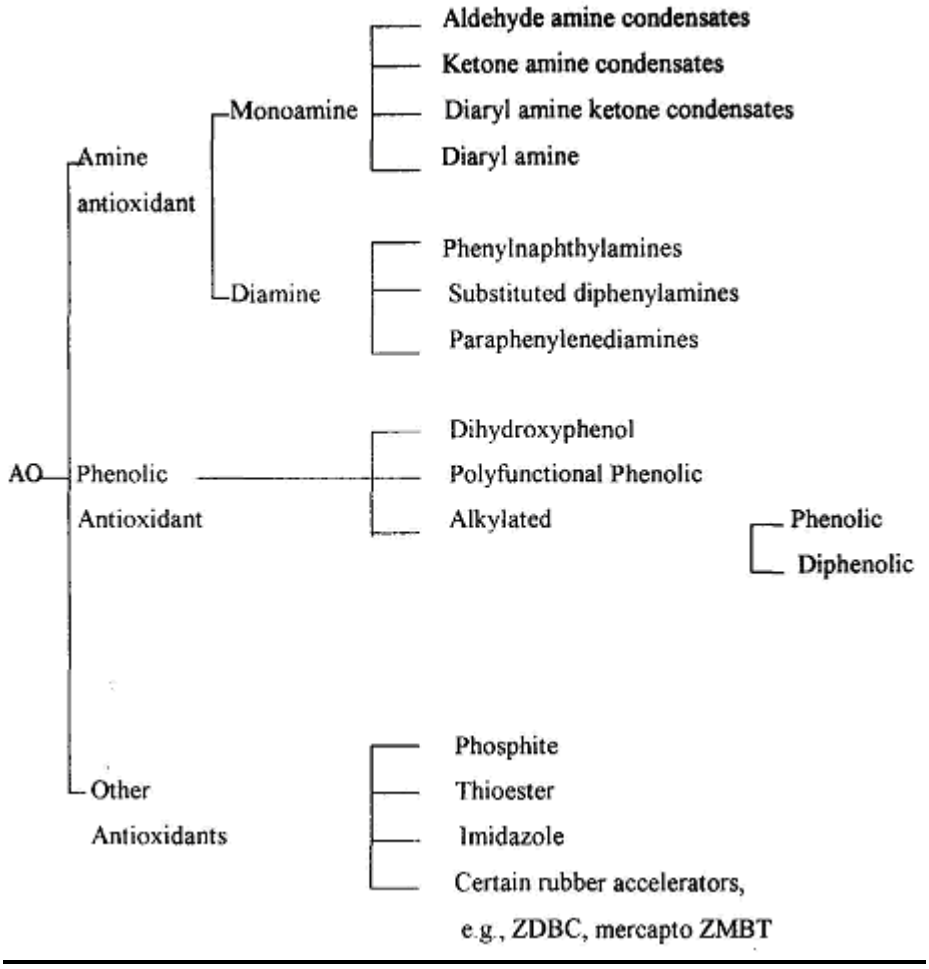
3. Common Rubber Antioxidant Types



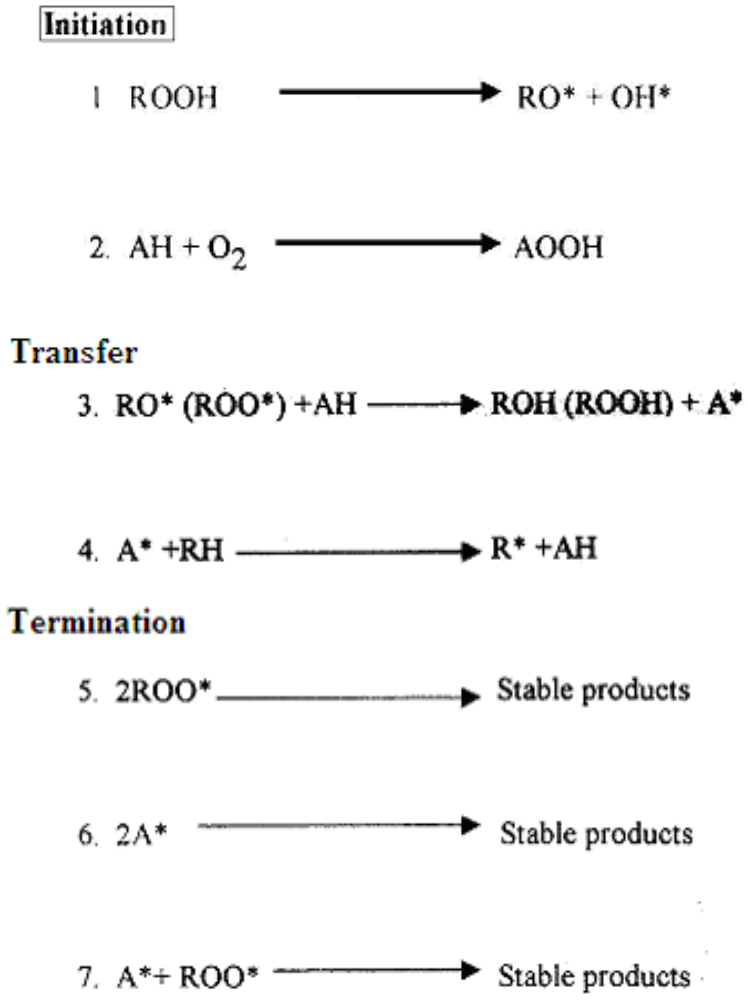
Four common ways of antioxidant action

1. As radical chain reaction stoppers (chain breaking or chain stopping mechanism)
2. As agents of decomposition of initiating peroxides to non radical products (preventive mechanism)
3. As agents of complexation and deactivation of catalytic metals (preventive mechanism)
4. As catalytic UV-light absorbers (preventive mechanism)

Radical chain reaction stoppers

Phenols and aromatic amines have readily abstractable hydrogen, and these compounds are often used as anti-oxidants due to their ability to act as efficient chain transfer agents.

The chain stopping mechanism is as follows:



The anti-oxidant AH, reacts with a peroxy radical resulting in the abstraction of a labile hydrogen from the anti-oxidant, The resulting anti-oxidant radical is more stable than the initial peroxy radical and becomes deactivated by reaction with another radical in the system (dimerization) or bond rearrangement. The steps 3 and 6 are most important for anti-oxidant action as they reduce the normal oxidative

degradation process by half excess anti-oxidant can result in a pro-oxidant effect if steps2 and 4 become important.

Anti-oxidants which interrupt the propagation step by reacting with ROO* Radicals and removing them from the medium are called chain stoppers or 'chain breakers.

Decomposition of initiating peroxides

Anti-oxidants accomplish the function of decomposition by reacting with the initiating peroxides to form non-radical products. Anti-oxidants which prevent or retard the decomposition of hydroperoxides into free radicals in the initiation step are referred to as "preventive antioxidants" They react with peroxides to form non-radical products.

Mercaptons, Thiophenols, Zinc dialkyl dithiocarbamates are believed to act in this way.

Complexation and deactivation of catalytic metals

Organic compounds such as EDTA and its various salts are metal chelating compounds These have multiple coordination sites and they form cyclic structures which trap the pro-oxidant metal ions by forming coordination complexes with metals. Inhibition of metal catalyzed reactions may be achieved by strongly complexing the ion to its maximum coordinating number and thereby inhibiting the further coordination of hydroperoxide. P-phenylene diamines are also effective as metal deactivators.

Absorption of catalytic UV light

Fillers which impart opacity to the compound e.g., carbon black, zinc oxide, as well as UV absorbers such as benzidine and hydroquinone tend to stabilize rubber against UV catalyzed oxidation. As the degradation takes place only at the surface, UV absorbers must bloom to the surface.

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4. SCOPE OF THE WORK

The main objective of this work is to compare the performance of the antioxidants TMQ (Dihydro trimethyl quinoline) & Cardanol in tread cap compound. The interesting part in this work is to see whether TMQ can be replaced with Cardanol in Tread cap compound without affecting performance and durability, while having a cost saving.

OUTLINE OF THE WORK

All the mixing was done in two stages - Masterbatch and Final mixing. Masterbatch mixing and final mixing was done in laboratory size two roll mill. Six compounds were mixed for Tread Cap. One with Cardanol at 0.75, 0.85, 1.0, 1.25, 1.50, phr and second with TMQ at 0.75 phr.

The compounds were evaluated for rheometer characteristics and the following vulcanizate properties were evaluated before and after ageing.

1. Tensile properties (Both Aged & Un-aged)
2. Tear strength (Both Aged & Un-aged)
3. Hardness (Both Aged & Un-aged)
4. Leaching Test
5. Thermo Gravimetric analysis (TGA)
6. IR Spectroscopy
7. Abrasion Resistance

5. EXPERIMENTAL TECHNIQUES

Tyre Tread compound

Ingredients	TMQ 00	CRDL 01	CRDL 02	CRDL 03	CRDL 04	CRDL 06
Natural Rubber	80.0	80.0	80.0	80.0	80.0	80.0
Poly Butadiene	20.0	20.0	20.0	20.0	20.0	20.0
Peptiser	0.10	0.10	0.10	0.10	0.10	0.10
Zinc Oxide	3.00	3.00	3.00	3.00	3.00	3.00
Stearic Acid	2.50	2.50	2.50	2.50	2.50	2.50
N 330	55.0	55.0	55.0	55.0	55.0	55.0
Aromatic Oil	11.0	11.0	11.0	11.0	11.0	11.0
6PPD	2.00	2.00	2.00	2.00	2.00	2.00
TMQ	0.75	-	-	-	-	-
Cardanol	-	0.75	0.85	1.00	1.25	1.50
MOR	0.60	0.60	0.60	0.60	0.60	0.60
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00

RAW MATERIALS USED FOR EXPERIMENT

Elastomer Ribbed Smoked Sheet (RSS 4)	Composition	HEVEA Rubber
	Appearance	Brown to Dark Brown ribbed sheets
	Specific gravity	0.92
Carbon Black HAF (N330)	Composition	Furnace process carbon black
	Appearance	Black pellets
	Specific gravity (25^0C)	1.80
	DBP Adsorption	1.02 cc/100gm
	Iodine Number	82
	Supplier	Philips Carbon Black Ltd, Karimugal
Process Oil Highly Aromatic oil	Composition	Blends of Petroleum fractions
	Appearance	Viscous greenish, Brown Oil
	Specific gravity	0.98
	Viscosity SVS (98^0C) Seconds	175
	Aniline Point(^{0}C)	10-54
	Supplier	APAR Ltd, Bombay

Activator System 1.Zinc Oxide	Composition	Zinc oxide
	Appearance	White densified powder
	Specific gravity (20^0C)	5.6
	ZnO content %)	99 (Minimum)
	Loss of heating at 105^0C	0.5 (Maximum)
	Supplier	Anban Chemicals industries, Mysore
2.Stearic Acid	Composition	Stearic Acid
	Appearance	White ,off white to light beads, flakes or powder
	Specific gravity (20^0C)	0.93
	Iodine Number No.GI/100G	9.0 Max
	Ash (residue on ignition at 950^0C) %	0.10 Max
	Supplier	Bripranil Pvt Ltd, Bombay
	Composition	N-1,3 -dimethylButyl

Anti Ozonants Alkyl-aryl P-Phenylene diamine(6PPD)		N'-Phenyl P-Phenylenediamine.
	Appearance	Dark, Purple flakes or pastilles
	Specific gravity (15.50^0C)	0.993
	Melting Point ^{0}C	46-52
	Freezing Point ^{0}C	44-50
	Supplier	Bayer ndia Ltd, Thane, Maharashtra
Anti Oxidants 1. Dihydro trimethyl quinoline (TMQ)	Composition	Polymerised 1,2-Dihydro 2,2,4-trimethyl quinoline
	Appearance	Ambar Brown Resinous Beads or flackes
	Specific gravity (25^0C)	1.08
	Softening Point ^{0}C	80-95
	Ash %	0.3 Max
	Supplier	Bayer India Ltd.Bombay
	Specific gravity	0.95-0.97

2. Cardanol		
	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 b) Catalytic method	 250 375
	Supplier	Satya Cashew Chemicals Pvt. Ltd. Chennai, T.N
Accelerator Sulphenamide acceleratator	Composition	2-(Morpholinothio) Benzothiazole Sulphenamide
	Appearance	Cream to Dark flacks or pellets
	Ash %	0.5 Max
	Specific Gravity	1.37

	(25^0C)	
	Methanol Insolubles %	0.5 Max
	Moisture %	0.5 Max
	Supplier	Bayer (India)Ltd, Bombay
Vulcanizing Agent sulfur	Composition	Ground Rhombic Sulphure
	Appearance	Pale Yellow powder
	Ash %	0.1 Max
	Specific Gravity (25^0C)	2.050
	Acidity %	0.01 Max
	Solubility in CS_2 %	98 Min
	Supplier	Standard chemical Co.Pvt.Ltd. Bombay

6. EXPERIMENTAL PROCEDURES

COMPOUNDING

The mixing was carried out in two stages for tread Cap compounds.

First stage mixing:

The first stage of compounding was master batch preparation. Here the black and the chemicals except curatives were mixed with rubber. It was done in a 6"xl2" laboratory mill having a friction ratio of 1:1.4 ordinary cooling water was used for circulation.

Second stage mixing:

The final batch mixing was one after 24 hrs ageing. This was carried out in a 6"xl2" laboratory mill having a friction ratio of 1:1.4. The stock was sheeted out and passed endwise 6 times through tight nip in order to get a good dispersion of accelerator and sulphur. Finally the stock was sheeted out. Mixing temperature and time were controlled for all the batches.

PROCESSABILITY STUDIES

Rheometer Studies (as per ASTM D 2084)

The rheometer study was done in oscillating disc rheometer (ODR) with the following specification.

Temperature ^{0}C	141.7
Range	100
Arc	1°

The sample is subjected to an oscillating shearing action of constant amplitude. The torque required to oscillate the rotor, which is confined in the die cavity under pressure and controlled at a desired vulcanization temperature, is noted. As the vulcanization proceeds the torque required to shear the rubber increases and a curve of Torque versus curing time can be generated. From the data, Tc90, ML, MH, Ts2 of compounds were found out.

From the plot of Torque Vs time, scorch time (Ts2), time for 90% cure (Tc90) and cure rate can be calculated.

i) Cure rate

$$\text{Cure Rate} = \frac{MH - ML}{Tc90 - Ts2}$$

Cure rate is the rate at which stiffness (modulus) develops after the scorch point. During this period, compound changes from a soft plastic to a tough elastic material, owing to the introduction of cross-links.

ii) Minimum Torque (ML)

It is a measure of the viscosity of the stock at the test temperature. The rheometer minimum Torque is proportional to the Mooney viscosity when both the tests are conducted at same temperature.

iii) Maximum torque (MH)

It is the measure of the stiffness or shear modulus of the test specimen at the test temperature. It is also an effective measure of the changes in tensile modulus and cross-link density.

iv) Induction time (Ts2)

It is the time corresponding to two units rise in torque about ML. It is a measure of the time available for mould flow. At lower temperatures Ts2 is a

processability measure similar to Mooney scorch.

v) Optimum cure (Tc90)

It is the time to achieve 90% of the maximum Torque

Tc90 = [(MH-ML) X 90/100] + ML

MOULDING OF TEST SPECIMENS

The molding of test specimens were done on a steam heated single day light press (INDEX PELL) with a platen size of 24" X 24". The molding specifications for the various test samples were as follows.

Type of test	Temperature(	Time (min)	Pressure
Physical	141	45	75
Abrasion	141	55	35

PHYSICAL TESTING OF CURED SAMPLES

Modulus, Tensile strength and Elongation at break.

These tests were carried out according to ASTM D 412-83 by using an INSTRON - 4301 tensile tester at a crosshead speed of 500 mm per minute.

Instron

The modulus of rubber compounds is very important because it is a measure of the shear stresses that will exist at the interface of two different compounds. It is also an indication of the deflection of the material under load. Here the modulus is the stress required to stretch the test specimen from 0% strain to a specified strain (100% and 300% elongation).

Tensile strength is the tensile stress per unit cross sectional area required to stretch the piece to breaking point. Elongation at break is the tensile strength

in the test piece at the breaking point. In the tyre industry, these tests are carried out in the area of identification and quality control.

Test pieces were punched out from vulcanised sheets, parallel to mill grain direction.

TEST PIECE SPECIFICATIONS

Total length	115 mm
Width of ends	25 ± 1.0 mm
Width of the narrow parallel portion	06 ± 0.4 mm
Length of the narrow parallel portion	33 ± 2.0 mm

Tear strength

The tear resistance is defined as the force required per unit thickness to initiate tearing in a direction normal to the direction of stress. Tear resistance of tyre compounds reflect not only their ability to resist cutting from foreign objects, but also reflects the compounds ability to resist the propagation of a cut once it is formed. Tear strength was tested as per ASTM D 624 using Instron 4301 at a crosshead speed of 500mm/min.

Hardness

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions that do not puncture the rubber The hardness was tested as per ASTM D 2240 standard using a Durometer of Type-A.

Shore-A Durometer Hardness

Introduction

Shore-A hardness is a measure of the resistance to the penetration of an indenter of specified size and shape forced in to the test specimen. The hardness is measured in Shore-A hardness units ranging from 0 to 100. This test method

permits hardness measurements based on either initial indentation or indentation after a specified period of time, or both.

Reference

ASTM D 2240

Equipment

Shore-A hardness tester with calibrated test spring or approved equipment.

Test Specimens

1. The minimum dimension of the specimen is 30mm (1.2inch) diameter and 6mm (0.25) thick. Tensile pads may be tested for hardness by stacking 3 pads of similar hardness.
2. Surface of specimens must be flat and as free of surface irregularities as possible.
3. Condition the specimen at 23°C ± 2°C (73.4 + 3.6°F) for a minimum of 16 hours before testing.

Procedure Summary

1. Test two test specimens for each sample
2. Test the specimens at room temperature, 23°C + 2°C (73.4 ± 3.6°F)
3. Take three measurements at different positions on each of the two specimens
4. Record the three second mean value reading of each specimen and report the average of the two median values.

Test procedure for shore type Durometer

1. Place the specimen on a hard, flat surface.
2. Position the Durometer such that the indentor is 12mm (0.5inch) from the edge of the specimen and at least 6mm (0.25") between measuring points.
3. Apply the pressure foot to the specimen rapidly without shock, with sufficient

pressure to obtain firm contact between pressure foot and the specimen

4. Read the indicator on the Durometer three seconds after firm contact has been made.

5. Take three measurements at different positions on each of the two specimens.

6. Record the two median values and report the average of the two median values.

Abrasion Resistance

This method is used to determine the abrasion resistance of cured rubber compound. Test should be carried out only 16 hrs after vulcanization.

Equipments:

DIN Abrader.

Sample preparation:

1. Prepare rubber compounds in accordance with ASTM D
2. Sheet out stock to obtain a thickness of 0.27"
3. Make out 16mmx 6mm cylindrical type samples.
4. Clearly identify each samples with silver lead or silver ink
5. Carefully place samples in the pre-heated mold with identification up.
6. Cure samples in accordance with instructions supplied.
7. Start timer when pressure has been fully applied. It is important to ensure that air is not trapped in samples or mold while curing. Apply full pressure and release three times to allow trapped air to escape.
8. Carefully remove samples from the mould using the brass screw driver,
9. Place all samples at room temperature or cooler water for 10 minutes.
10. Trim the edges of each specimen to remove any overflow.
11. Condition samples at room temperature for 24 hours prior to testing.
12. Weight the test piece prior to testing
13. Fit the sample in the sample holder of the Din abrader machinery.
14. "ON" the machinery and allow the sample to abrade.
15. Stop the machinery, when the sample get 20 meter run.
16. Remove the sample from the holder and remove the loose material then

weigh it again accurately.

17. Take the weight after 40 meter run.
18. Find the specific gravity of the sample.

$$\text{Specific Gravity} = \frac{\text{weight in air}}{\text{Loss of weight in water}}$$

$$\text{Abration Resistance} = \frac{\text{Mass loss}}{\text{Specific Gravity}}$$

Soxhlet Extraction

A Soxhlet extractor is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of a lipid from a solid material. However, a Soxhlet extractor is not limited to the extraction of lipids. Typically, a Soxhlet extraction is only required where the desired compound has only a limited solubility in a solvent, and the impurity is insoluble in that solvent. If the desired compound has a high solubility in a solvent then a simple filtration can be used to separate the compound from the insoluble substance.

Normally a solid material containing some of the desired compound is placed inside a "thimble" made from thick filter paper, which is loaded into the main chamber of the Soxhlet extractor. The Soxhlet extractor is placed onto a flask containing the extraction solvent. The Soxhlet is then equipped with a condenser.

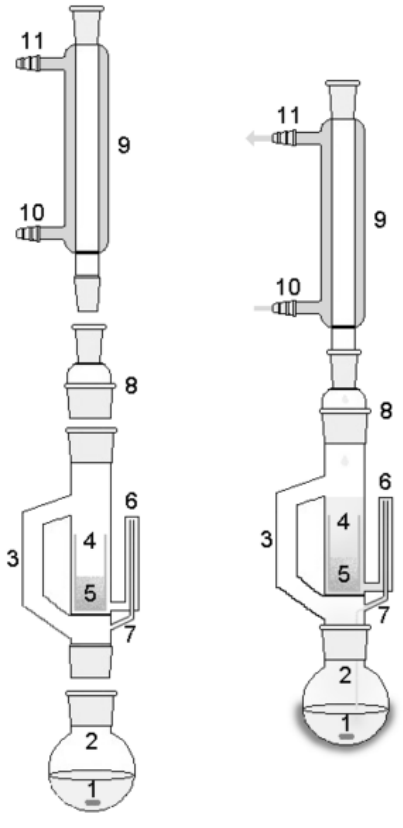
The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools and drips back down into the chamber housing the solid material.

The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound will then dissolve in the warm solvent. When the Soxhlet chamber is almost full, the chamber is automatically emptied by a

siphon side arm, with the solvent running back down to the distillation flask. This cycle may be allowed to repeat many times, over hours or days.

During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.



A schematic representation of a Soxhlet extractor

1: Stirrer bar 2: Still pot 3: Distillation path 4: Thimble 5: Solid 6: Siphon top 7: Siphon exit 8: Expansion adapter 9: Condenser 10: Cooling water in 11: Cooling water out

Thermal oxidative analysis by Thermogravimetric Analysis (TGA) Method

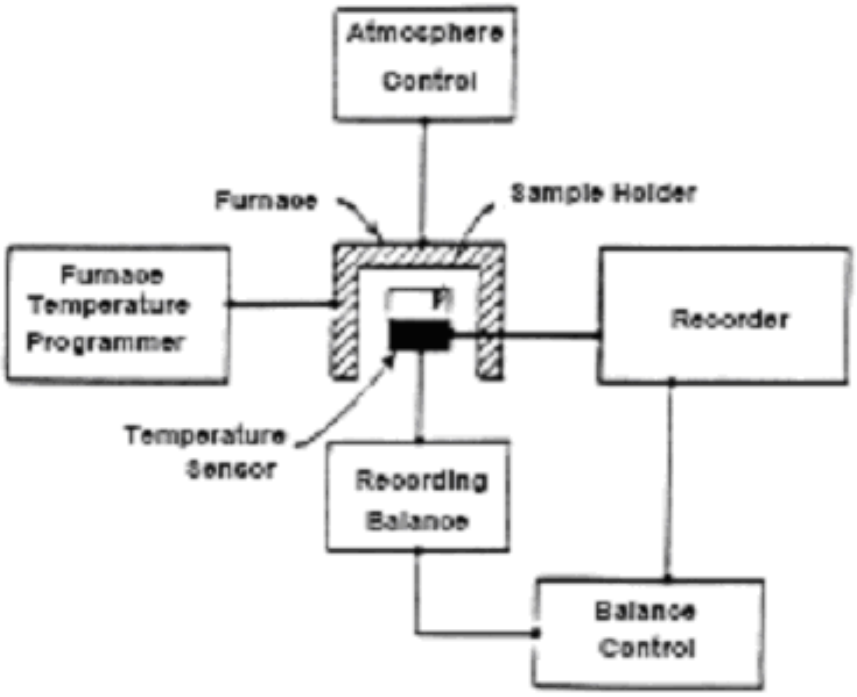
TGA makes a continuous weighing of a small sample (10 mg) in a controlled atmosphere (e.g., air or nitrogen) as the temperature is increased at a programmed linear rate. The thermogram illustrates weight losses due to desorption of gases (e.g., moisture) or decomposition (e.g., HBr loss from halobutyl, CO, from calcium carbonate filler).

TGA is commonly employed to determine characristics of polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

The analyser usually consists of a high-precision balance with a pan loaded with the sample. The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an air to assist oxidation .A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection.

In most cases, TGA analysis is performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature is selected so that the specimen weight is stable at the end of the experiment, implying that all chemical reactions are completed (i.e., all of the carbon is burnt off leaving behind metal oxides). This approach provides two important numerical pieces of information: ash content (residual mass, Mres) and oxidation temperature (To). Oxidation temperature can be defined in many ways, including the temperature of the maximum in the weight loss rate (dm/dTmax) and the weight loss onset temperature (Tonset).



Typical components of a TGA instrument.

The former refers to the temperature of the maximum rate of oxidation, while the latter refers to the temperature when oxidation just begins. The use of the former definition, To = dm/dTmax, is preferred for two reasons. Oxidation temperature, To; is basically a measure of the thermal stability of material in air and depends on a number of parameters.

INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption

measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

In order to measure a sample, a beam of infrared light is passed through the sample, and the amount of energy absorbed at each wavelength is recorded. This may be done by scanning through the spectrum with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum may be plotted, which shows at which wavelengths the sample absorbs the IR, and allows an interpretation of which bonds are present. This technique works almost exclusively on covalent bonds, and as such is of most use in organic chemistry. Clear spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures however

Sample preparation:

Liquid samples can be sandwiched between two plates of a high purity salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and will not introduce any lines onto the spectra. Some salt plates are highly soluble in water, and so the sample, washing reagents and the like must be anhydrous (without water).

Solid samples can be prepared in two major ways. The first is to crush the sample with a mulling agent (usually nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is applied onto salt plates and measured.

The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to the different physical states the sample is in.

Typical method

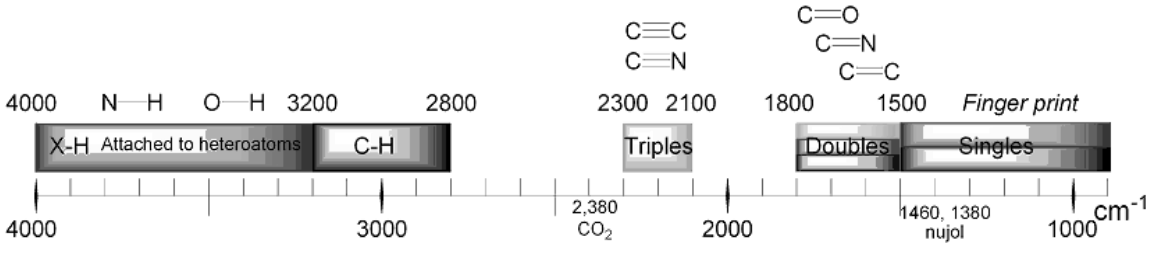
Apparatus

A beam of infra-red light is produced and split into two separate beams. One is passed through the sample, the other passed through a reference which is often the substance the sample is dissolved in. The beams are both reflected back towards a detector, however first they pass through a splitter which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained.

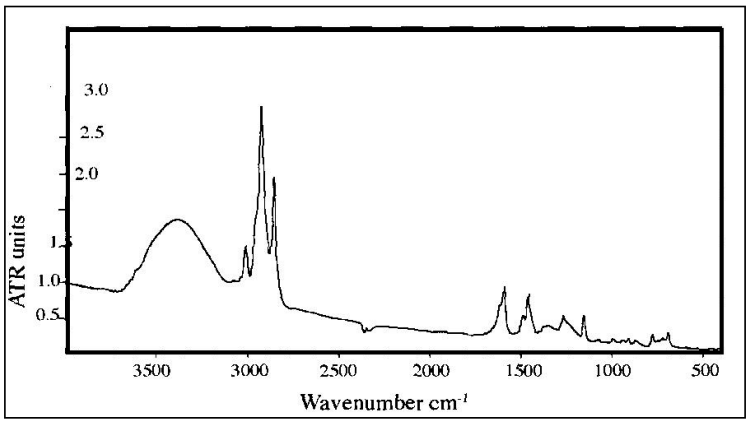
A reference is used for two reasons:

- This prevents fluctuations in the output of the source affecting the data
- This allows the effects of the solvent to be cancelled out (the reference is usually a pure form of the solvent the sample is in)

Summary of absorptions of bonds in organic molecules



Absorptions listed in cm^{-1}.



IR Spectrum of Cardanol

7. EXPERIMENTAL COMPARISON

1. Physical Properties for Un Aged Samples

Phr	Sample ID	Tensile Strength (psi)	Elongation @ Break(%)	Modulus @100% (psi)	Modulus @ 300% (psi)	Tear Strength (lb/in)
0.75	**TMQ00**	**3525**	**541**	**347**	**1662**	**586**
0.75	CRDL01	3518	523	346	1653	618
0.85	**CRDL02**	**3523**	**533**	**340**	**1697**	**614**
1.0	CRDL03	3524	541	336	1679	593
1.25	CRDL04	3548	537	345	1692	621
1.50	CRDL05	3520	539	336	1692	612

2. Abrasion Resistance and Hardness of Un Aged Samples

Phr	Sample ID	Abrasion loss Cc	Hardness (Shore A)
0.75	**TMQ00**	**0.157**	**61**
0.75	CRDL01	0.144	62
0.85	**CRDL02**	**0.135**	**62**
1.0	CRDL03	0.144	61
1.25	CRDL04	0.144	61
1.50	CRDL05	0.144	61

3. Tensile Properties for 48Hrs Aged(at 100^{O}C) Samples

Phr	Sample ID	Tensile Strength (psi)	Elongation @ Break(%)	Modulus @100% (psi)	Modulus @ 300% (psi)
0.75	**TMQ00**	**2273**	**354**	**450**	**1970**
0.75	CRDL01	2005	323	455	1928
0.85	**CRDL02**	**2201**	**337**	**452**	**2009**
1.0	CRDL03	2382	338	461	2027
1.25	CRDL04	2281	353	452	1963
1.50	CRDL05	2451	364	459	1959

4. Tear Strength and hardness

Phr	Sample ID	Tear Strength (lb/in)	Hardness (Shore A)
0.75	**TMQ00**	**263**	**66**
0.75	CRDL01	234	67
0.85	**CRDL02**	**235**	**67**
1.0	CRDL03	266	66
1.25	CRDL04	244	66
1.50	CRDL05	248	66

5. Physical Test for 96Hrs Aged(at $100^{O}C$) Samples

Phr	**Sample ID**	**Tensile Strength (psi)**	**Elongation @ Break(%)**	**Modulus @100% (psi)**	**Tear Strength (lb/in)**	**Hardness (Shore A)**
0.75	**TMQ00**	**1304**	**186**	**568**	**135**	**69**
0.75	CDL01	1196	171	557	128	69
0.85	**CDL02**	**1303**	**196**	**535**	**135**	**69**
1.0	CDL03	1303	177	547	133	69
1.25	CDL04	1100	173	527	122	68
1.50	CDL05	1302	184	500	124	68

Percentage change of Physical properties for 48HrsAged (at 100^{O}C) Samples with un aged samples

Phr	Sample ID	Tensile Strength (%)	Elongation @ Break(%)	Modulus @100% (%)	Modulus @ 300% (%)	Tear Strength (%)	Hardness (%)
0.75	**TMQ00**	**-36**	**-34**	**+30**	**+18**	**-55**	**+8**
0.75	CDL01	-43	-38	+31	+17	-62	+8
0.85	**CDL02**	**-37**	**-36**	**+33**	**+18**	**-57**	**+8**
1.0	CDL03	-32	-37	+37	+21	-55	+8
1.25	CDL04	-35	-34	+31	+16	-60	+8
1.50	CDL05	-30	-32	+36	+15	-59	+8

Percentage change of Physical properties for 96HrsAged (at 100^{O}C) Samples with un aged samples

Phr	Sample ID	Tensile Strength (psi)	Elongation @ Break(%)	Modulus @100% (psi)	Tear Strength (lb/in)	Hardness (Shore A)
0.75	**TMQ 00**	**-63**	**-65**	**+62**	**-77**	**+13**
0.75	CRDL 01	-66	-67	+61	-79	+11
0.85	**CRDL 02**	**-63**	**-63**	**+57**	**-78**	**+11**
1.0	CRDL 03	-63	-67	+50	-78	+13
1.25	CRDL 04	-69	-68	+52	-80	+12
1.50	CRDL 05	-63	-66	+49	-80	+12

Hot water Leaching at 80^0C for 4Hrs + Aging at 100^OC for 48Hrs

Phr	Sample ID	Tensile Strength (psi)	Elongation @ Break(%)	Modulus @100% (psi)	Modulus @ 300% (psi)	Tear Strength (lb/in)	Hardness (Shore A)
0.75	**TMQ00**	**2185**	**334**	**480**	**1981**	**246**	**66**
0.75	CDL01	1988	312	475	1938	224	67
0.85	**CDL02**	**2195**	**320**	**471**	**2012**	**226**	**67**
1.0	CDL03	2340	318	484	2030	254	66
1.25	CDL04	2200	339	479	1983	232	66
1.50	CDL05	2390	342	489	1974	234	66

Percentage change of Physical properties for 4Hrs Leached at 80^0C + 48HrsAged (at 100^OC) Samples with un aged samples

Phr	Sample ID	Tensile Strength (%)	Elongation @ Break(%)	Modulus @100% (%)	Modulus @ 300% (%)	Tear Strength (%)	Hardness (%)
0.75	**TMQ00**	**-38**	**-38**	**+38**	**+19**	**-58**	**+8**
0.75	CDL01	-44	-40	+37	+17	-64	+8
0.85	**CDL02**	**-38**	**-40**	**+38**	**+19**	**-60**	**+8**
1.0	CDL03	-34	-41	+44	+21	-57	+8
1.25	CDL04	-38	-37	+39	+17	-63	+8
1.50	CDL05	-33	-36	+45	+17	-62	+8

Cure Properties

SAMPLE CODE	ML	Ts1	Ts2	MH	Tc15	Tc25	Tc50	Tc90
TMQ 00	**5.02**	**5.75**	**6.98**	**31.50**	**8.32**	**9.57**	**12.63**	**23.65**
CRDL 01	4.95	5.78	6.70	32.39	7.82	8.93	11.85	23.02
CRDL02	**5.05**	**6.17**	**7.10**	**31.63**	**8.17**	**9.32**	**12.33**	**23.82**
CRDL 03	4.89	6.13	7.05	31.87	8.13	9.27	12.22	23.73
CRDL 04	4.98	5.92	6.88	31.79	8.00	9.15	12.20	24.07
CRDL 05	5.13	6.05	7.05	32.05	8.15	9.32	12.32	24.07

ΔT and Cure Rate

Sl No:	Phr	SAMPLE CODE	ΔT	Cure Rate
01	**0.75**	**TMQ 00**	**26.48**	**1.59**
02	0.75	CRDL 01	27.44	1.68
03	**0.85**	**CRDL 02**	**26.58**	**1.59**
04	1.0	CRDL 03	26.98	1.62
05	1.25	CRDL 04	26.81	1.56
06	1.50	CRDL 05	26.92	1.58

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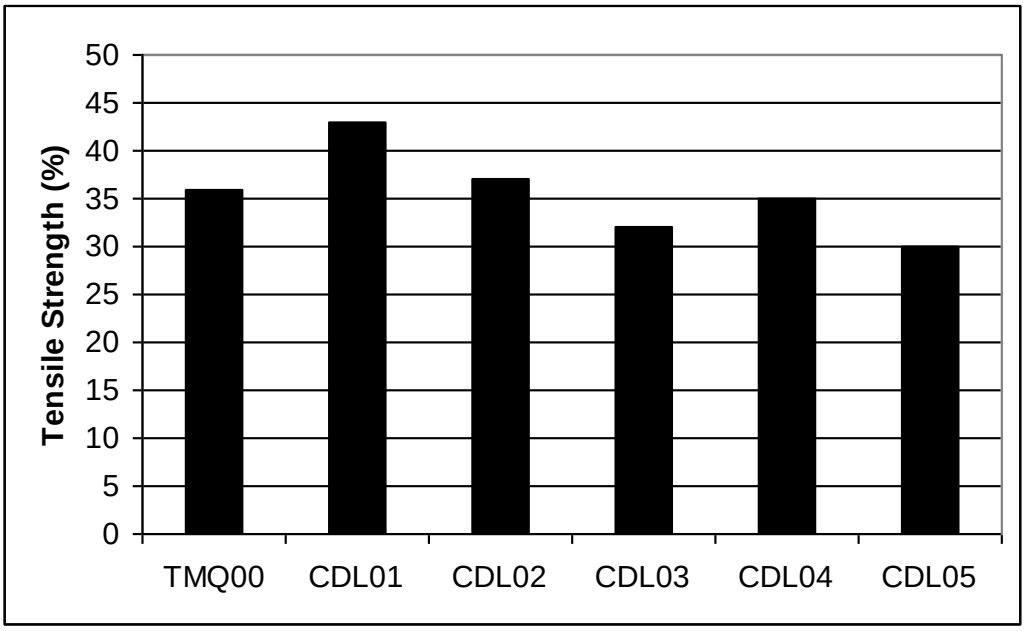
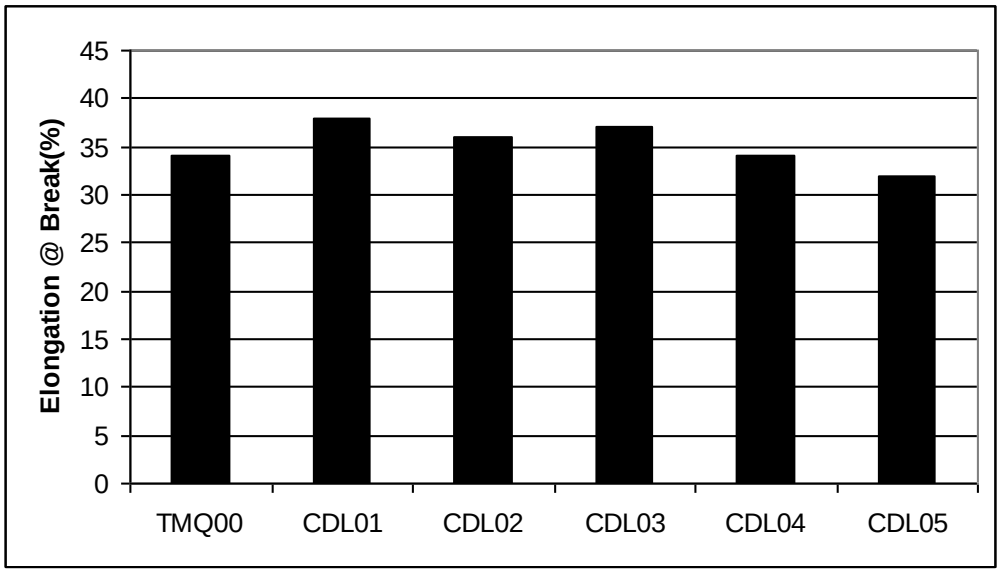
8. G R A P H S

RETENTION PROPERTIES AFTER AGEING AT 100^0C FOR 48HRS

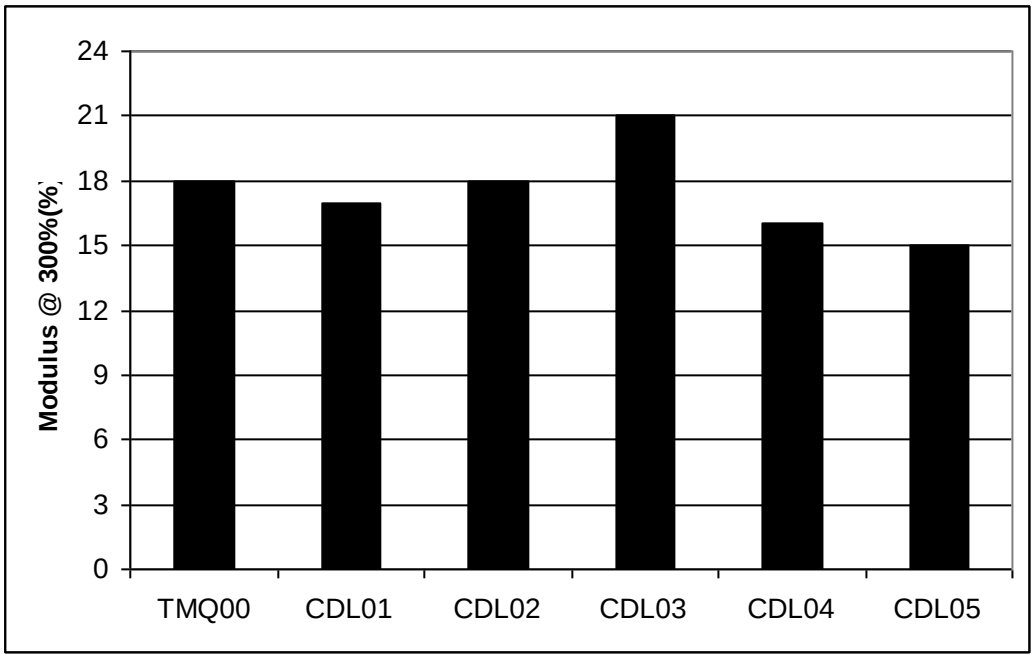
PERCENTAGE RETENTION OF TENSILE STRENGTH



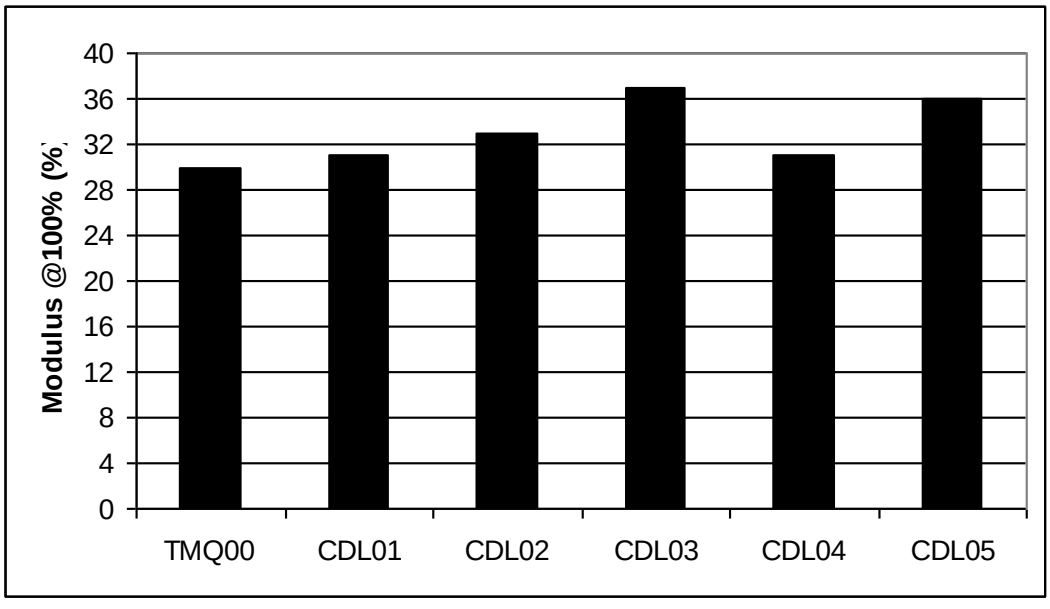
PERCENTAGE RETENTION OF ELONGATION AT BREAK



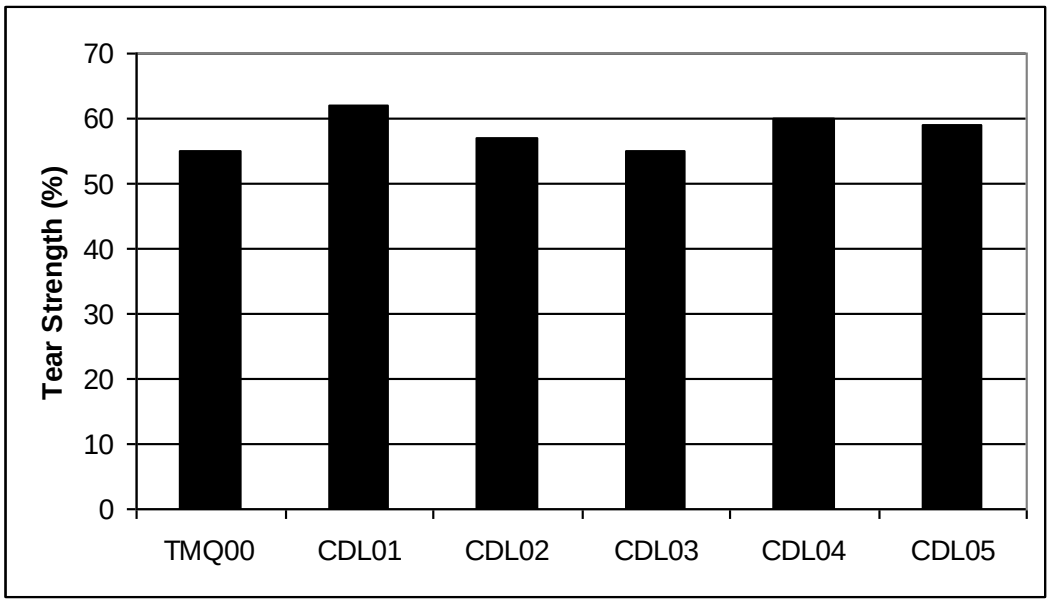
PERCENTAGE RETENTION OF MODULUS @ 300% ELONGATION



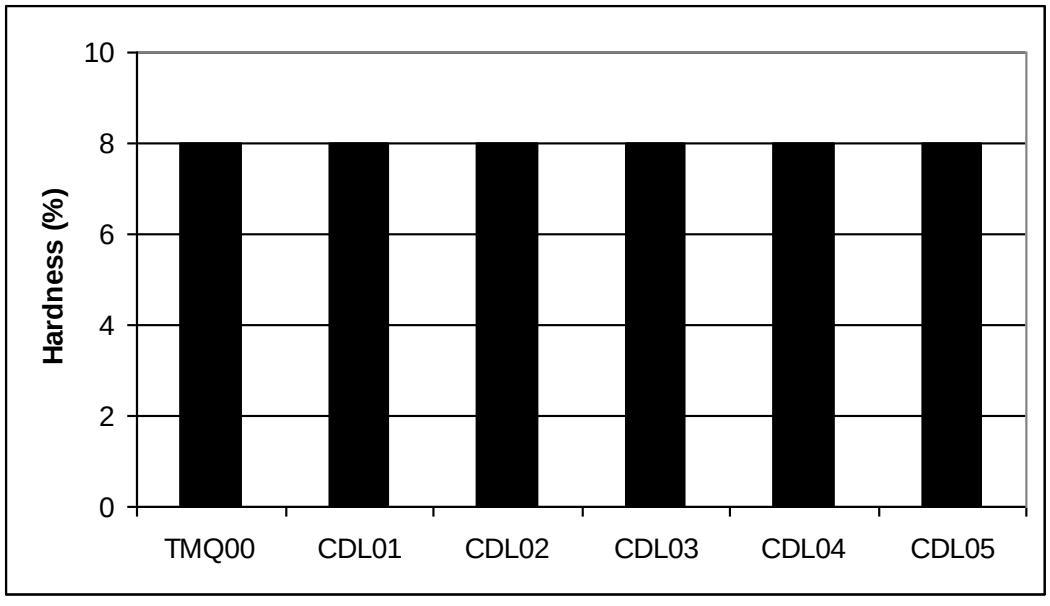
PERCENTAGE RETENTION OF MODULUS @ 100% ELONGATION



PERCENTAGE RETENTION OF TEAR STRENGTH

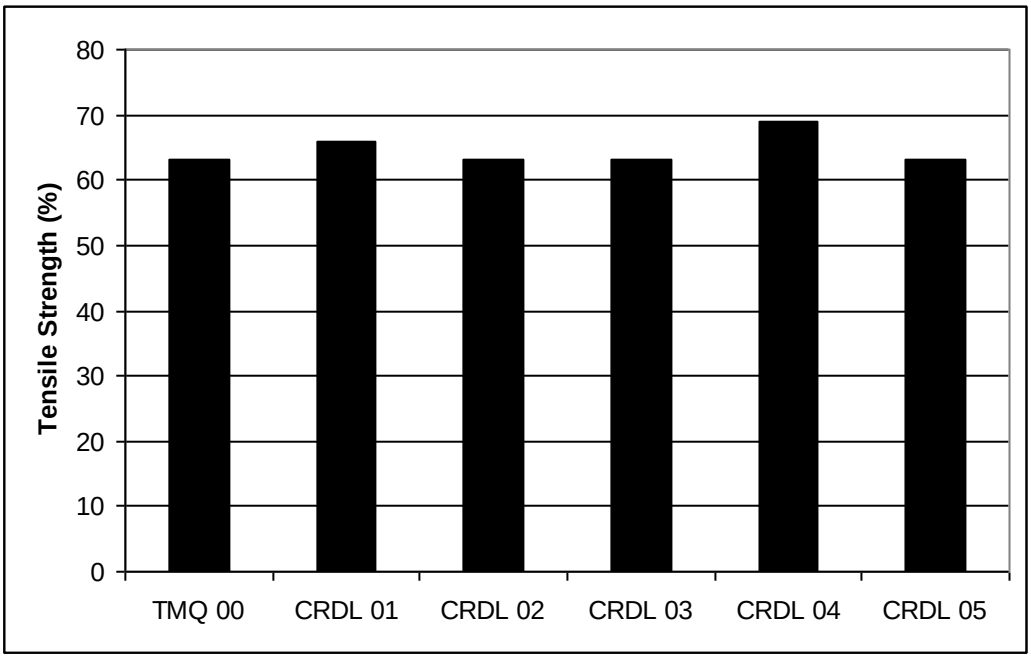


PERCENTAGE RETENTION OF HARDNESS

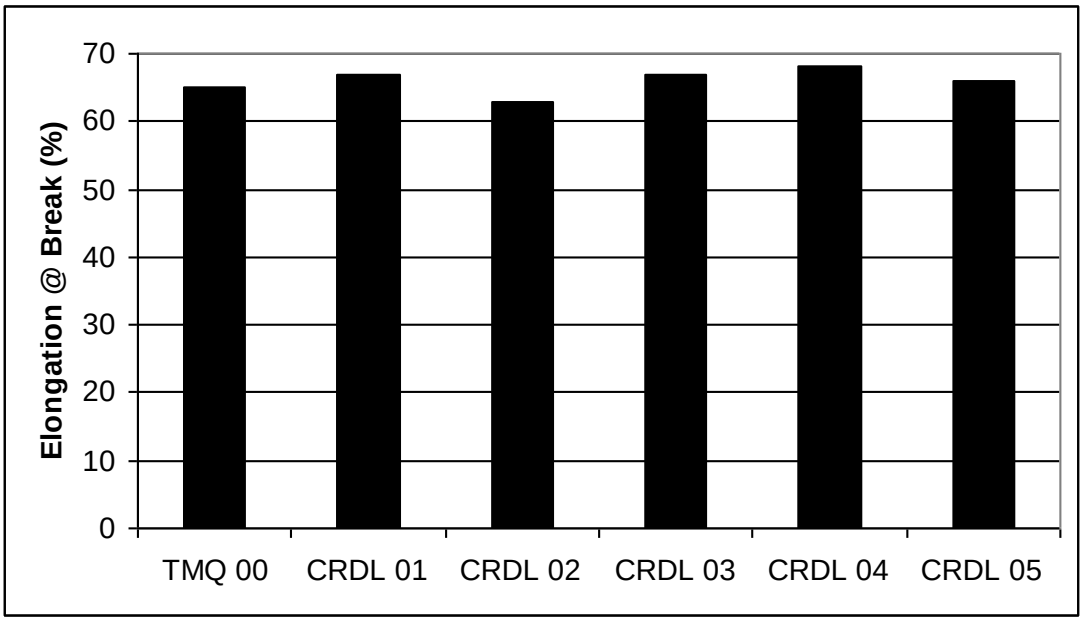


RETENTION PROPERTIES AFTER AGEING AT 100^0C FOR 96HRS

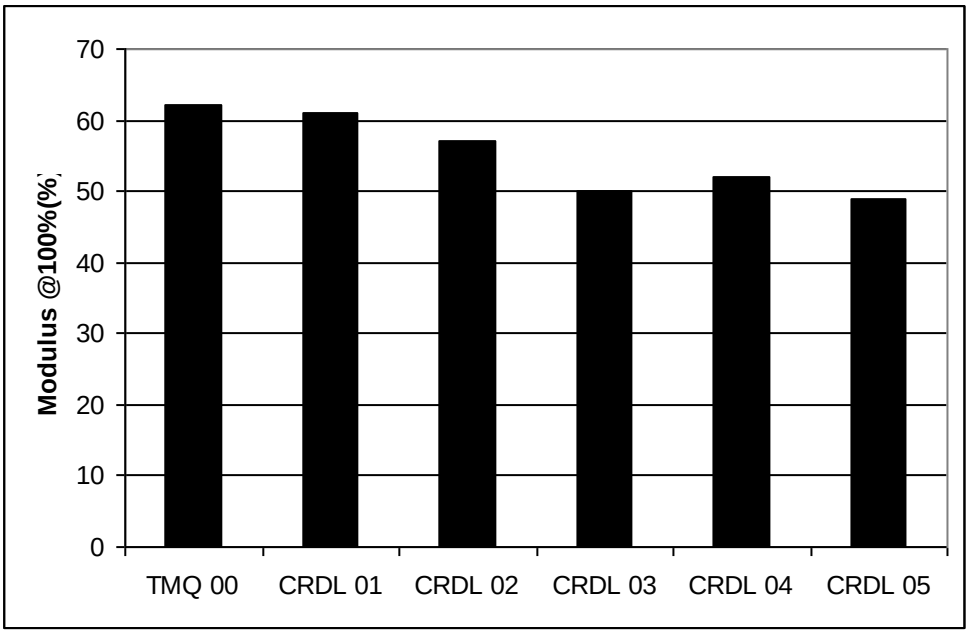
PERCENTAGE RETENTION OF TENSILE STRENGTH



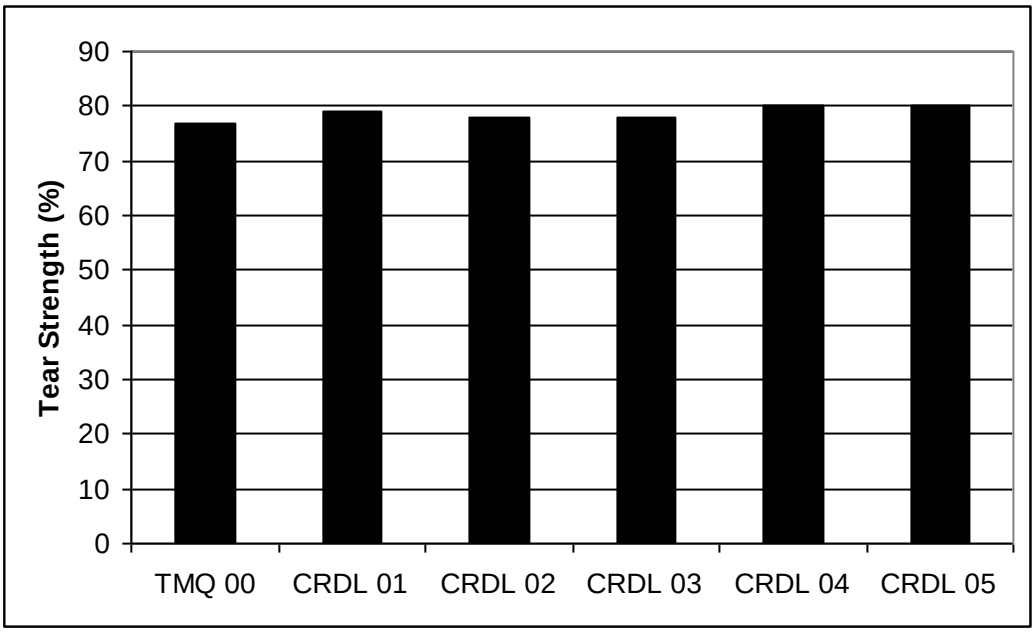
PERCENTAGE RETENTION OF ELONGATION AT BREAK



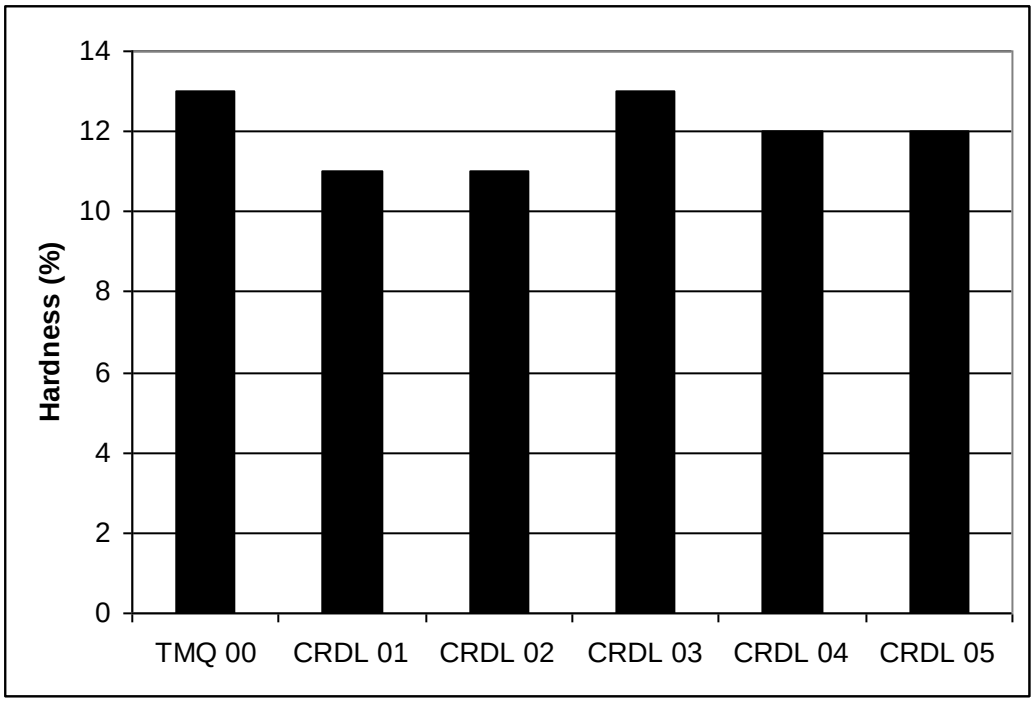
PERCENTAGE RETENTION OF MODULUS @ 100% ELONGATION



PERCENTAGE RETENTION OF TEAR STRENGTH

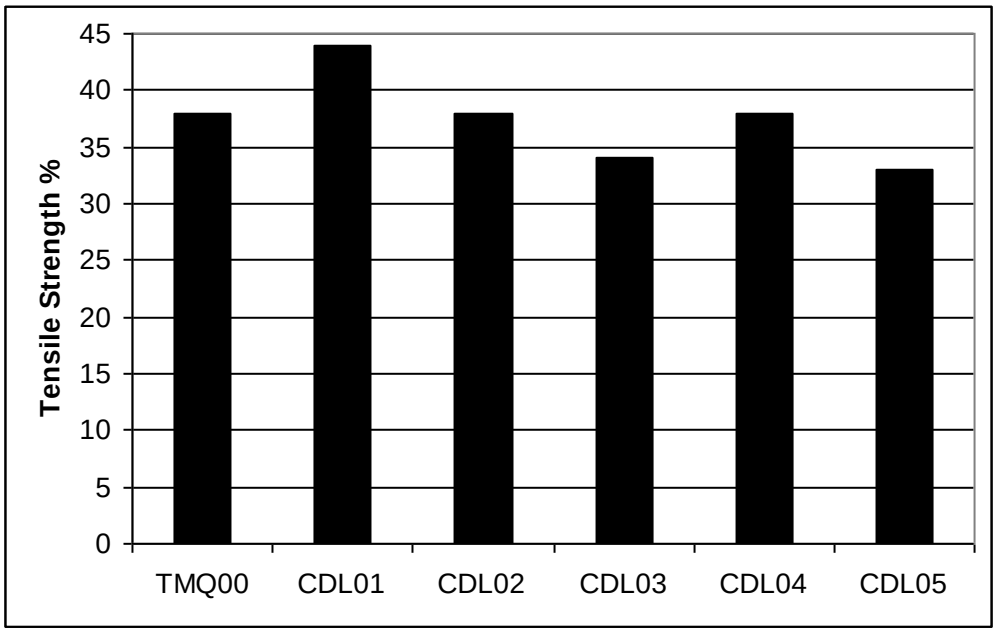


PERCENTAGE RETENTION OF HARDNESS

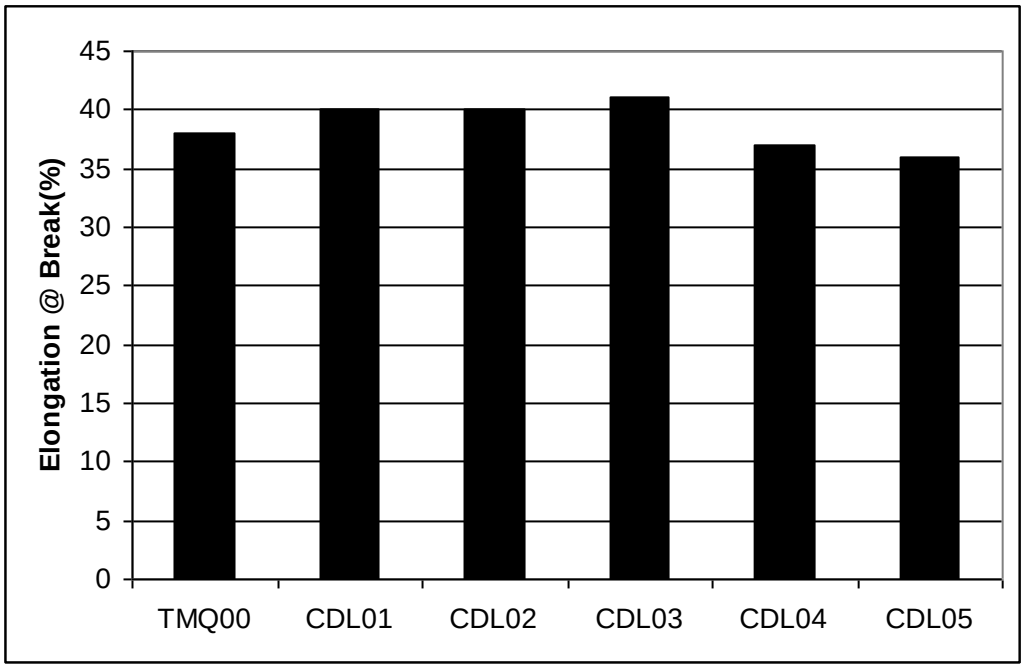


RETENTION PROPERTIES AFTER HOT WATER LEACHING + AGEING

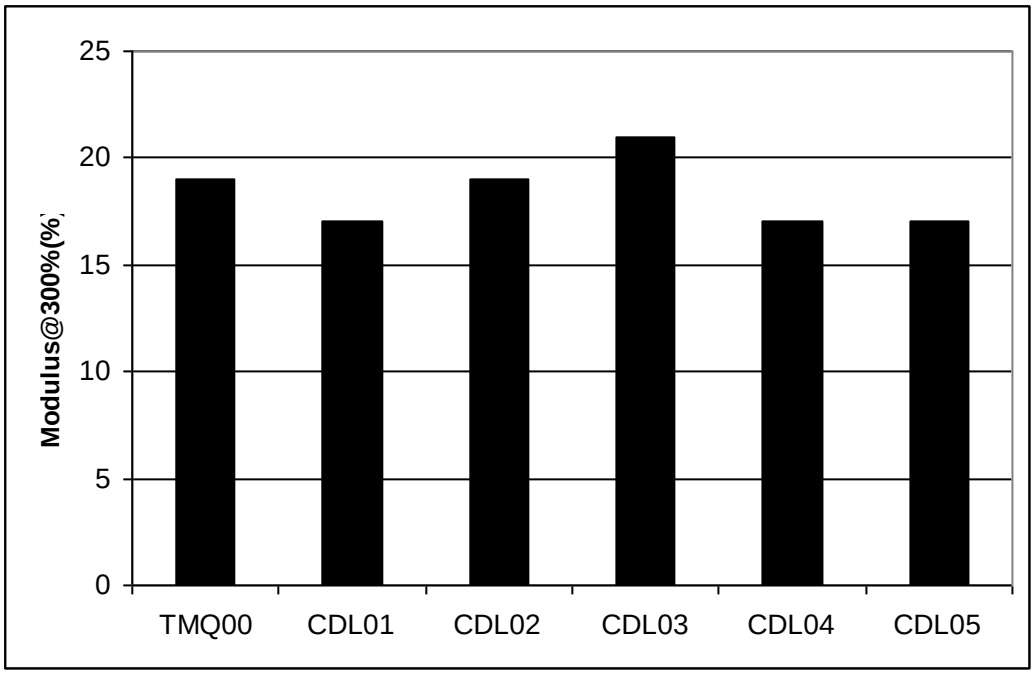
PERCENTAGE RETENTION OF TENSILE STRENGTH



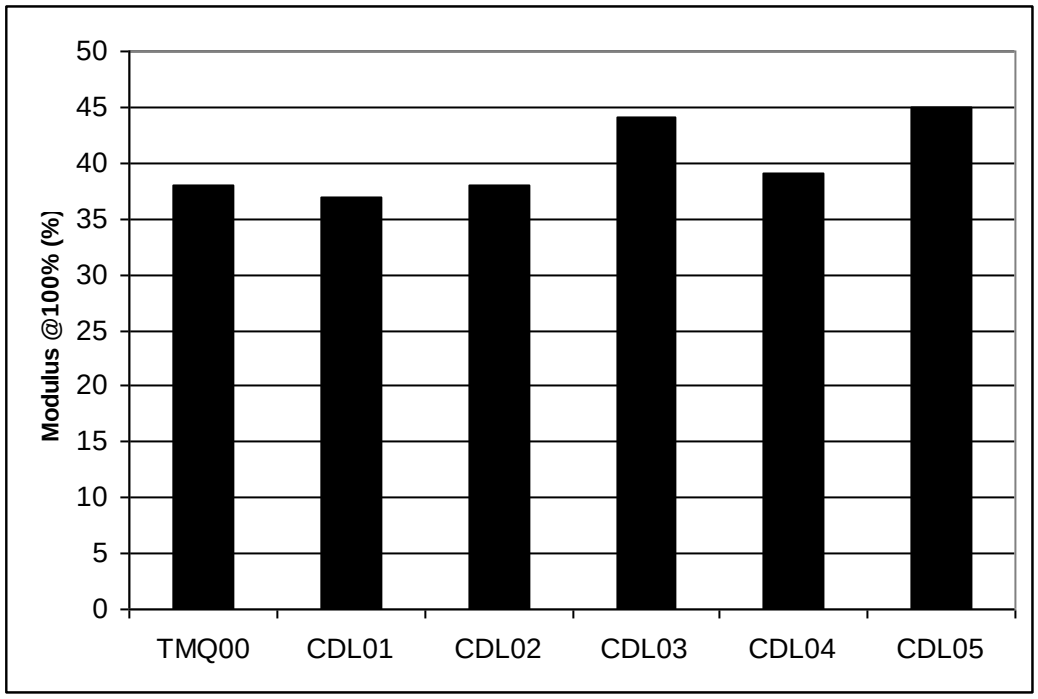
PERCENTAGE RETENTION OF ELONGATION AT BREAK



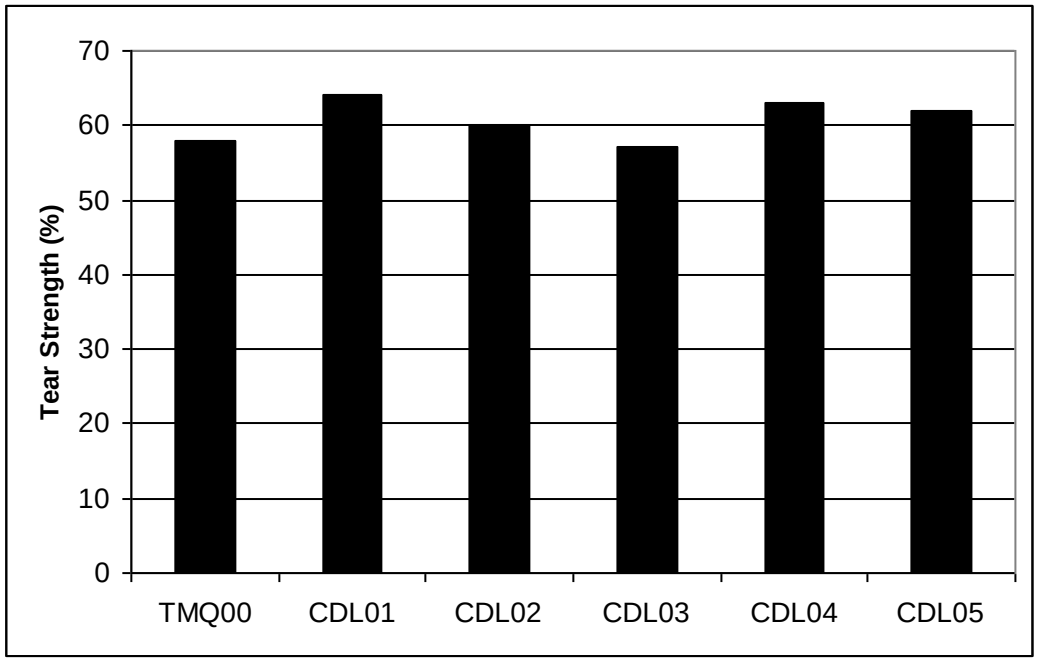
PERCENTAGE RETENTION OF MODULUS @ 300% ELONGATION



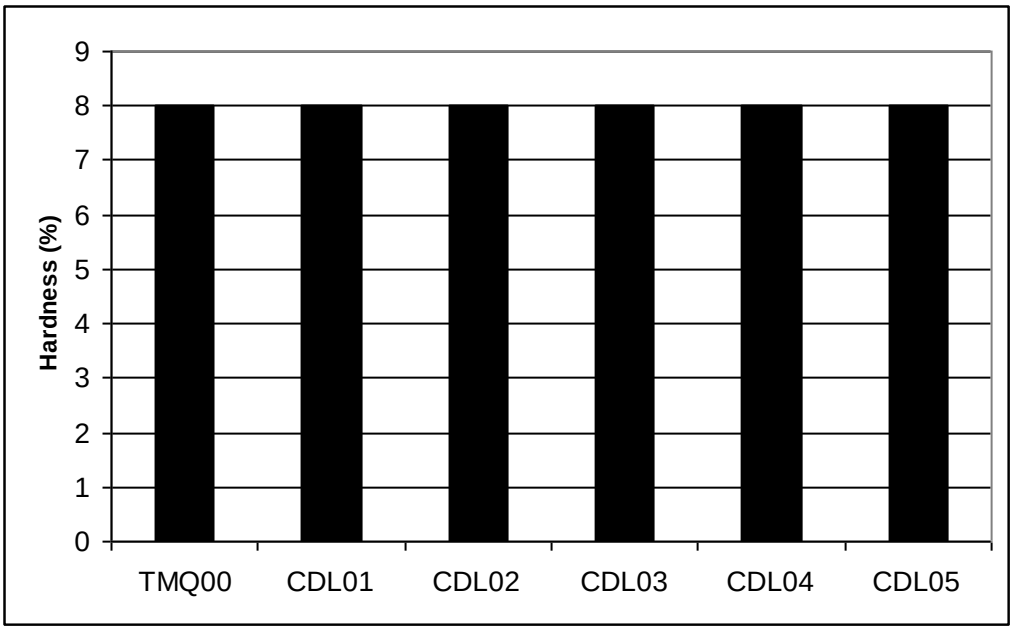
PERCENTAGE RETENTION OF MODULUS @ 100% ELONGATION



PERCENTAGE RETENTION OF TEAR STRENGTH

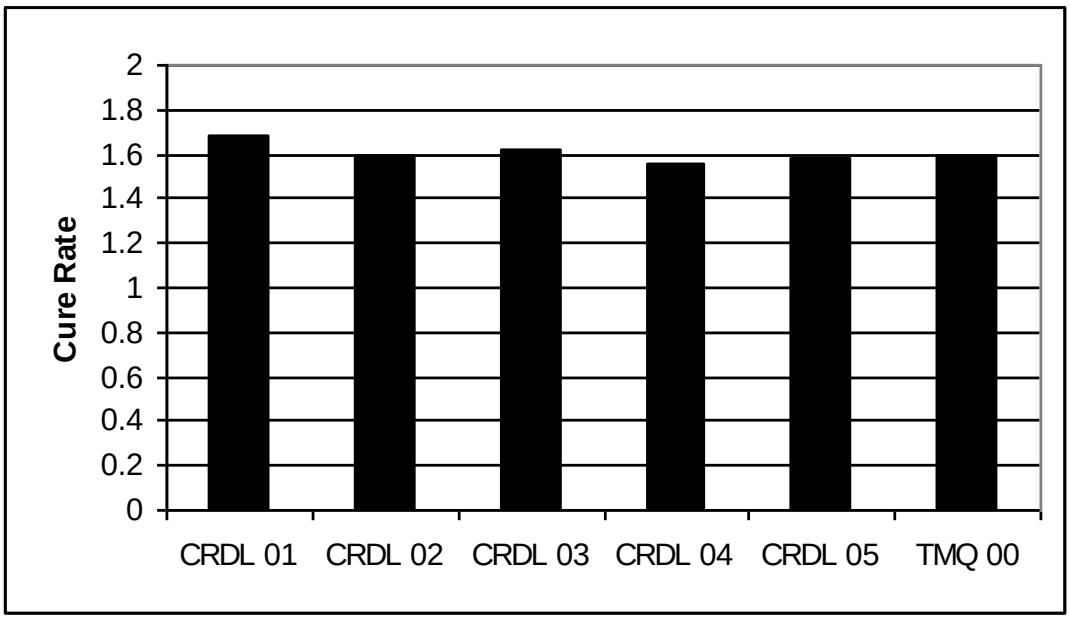


PERCENTAGE RETENTION OF HARDNESS

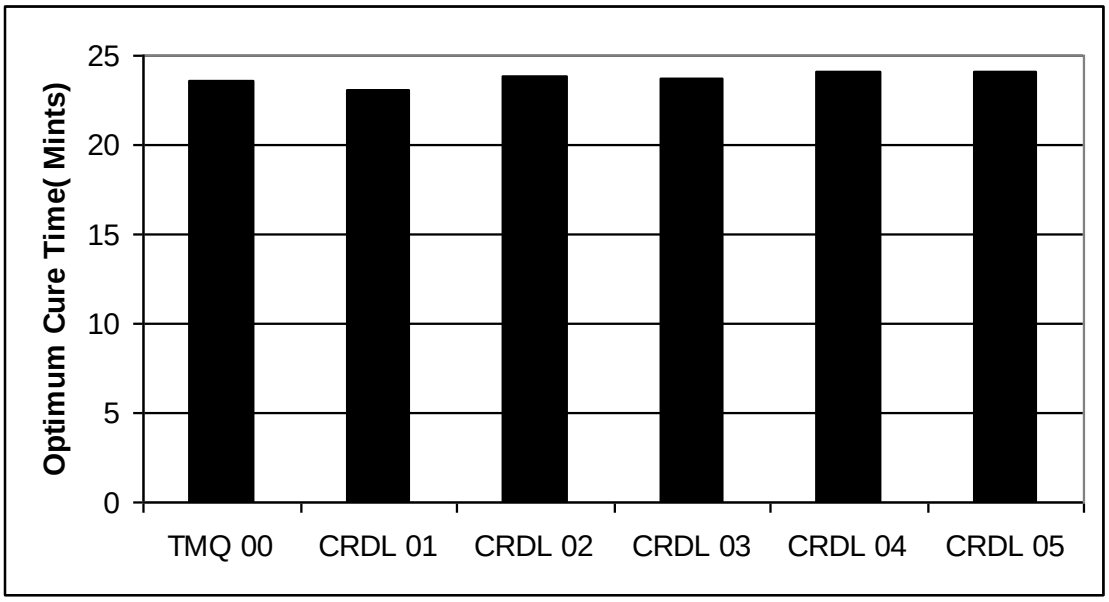


CURE PROPERTIES

CURE RATE



OPTIMUM CURE TIME



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9. RESULTS AND DISCUSSIONS

Rheometer Properties

Rheometer studies were done at 141.7°C for all the compounds to check whether cure characteristics are affected when TMQ is replaced with CARDANOL. The values are given in the tables. There is no significant variation in any of the cure characteristics for compounds with CARDANOL at 0.75 to 1.50 phr. However a slight variation is expected due to processing variation.

The minimum torque is a measure of the viscosity of uncured compound and the maximum torque is a measure of shear modulus or stiffness of the compound.

Tensile Properties

Tensile properties of both un-aged and aged samples were found using an INSTRON - 4301 tensile tester at a cross head speed of 500mm per minute. Samples were subjected to three types of ageing.

1. Ageing at 100°C for 48 hrs in a multi cell ageing oven.
2. Ageing at 100°C for 96 hrs in a multi cell ageing oven.
3. Hot water leaching at 80°C for 4 hrs +ageing at 100°C for 48 hrs in a multi cell ageing oven. The first two types of ageing were done to compare the effectiveness of antioxidants in accelerated conditions and the last type of ageing was aimed to compare the resistance to water extraction property of antioxidants.

From the first two types of ageing it can be seen that the performance of the these types of were almost comparable With Cardanol at 0.85 phr. When Cardanol takes 0.85 phr, Percentage retention of 100% and 300% moduli are almost comparable for TMQ and Cardanol compounds. Anyhow percentage retention of tensile strength and elongation at break are slightly (1-2%) less for Cardanol compounds at 0.85 phr. This will not affect the compound properties significantly and hence can be neglected.

There shows 18 % improvement in tensile property and 11% improvement in Eb when Cardanol takes 1.75 phr. But it shows 4 -7 % less in value in M_{100} and M_{300}. And also the un aged physical property values are less in the case of these Cardanol with 1.75 phr, Hence it is not recommended.

In the last type of ageing the samples were first subjected to hot water leaching in a hot water bath at 80°C for 4 hrs with occasional stirring. After leaching the samples were subjected to ageing at 100°C for 48 hrs in an ageing oven and tests were done to compare the retention of physical properties. Cardanol compounds showed similar percentage retention of tensile strength, elongation at break etc. This is an indication of better water extraction resistance of Cardanol. This is very important in the case of rubber products especially tyres which will be exposed to rain water during service.

Cardanol is considered as a low molar mass antioxidant. These antioxidants are easily lost from polymer through migration, evaporation, and extraction. This physical loss of antioxidants constitutes a major concern in the long-term use of polymers or when high temperature is employed. The new tendency to prevent this problem and guarantee their performance is the production of polymer-bound antioxidants. The presence of about 10% of polymerized and compatible material, normally present in the technical Cardanol, could decrease the migration of this antioxidant to the surface, reduce its volatilization and retain the antioxidant activity during heating.

Tear Strength

In the case of tear resistance, percentage retention was same as that in the case of tensile strength and elongation at break. Both TMQ and Cardanol compounds showed almost same percentage retention, when 0.85 phr Cardanol sample is used, After leaching 0.85 phr Cardanol compounds showed almost similar retention of tear strength.

Hardness

Hardness was almost same for both Cardanol and TMQ

Abrasion Resistance

Abrasion Resistance was almost same for both Cardanol and. TMQ.

▲▲▲

10. SUMMARY AND CONCLUSIONS

The effect of replacing the antioxidant TMQ with Cardanol in tread Cap compound has been studied by evaluating both compound and vulcanisate properties as discussed in the previous chapters. Based on these studies following conclusions can be drawn…

- No significant differences were observed with any of the properties when TMQ is replaced with Cardanol.
- It was found that there was no significant improvement in any of the properties when the phr of Cardanol was increased from .85 phr to 1.5 phr.
- Cardanol is more resistant to water extraction.
- The Cure characteristics are not altered when Cardanol is used as antioxidant.
- The Cardanol based samples shows remarkable similarity with conventional antioxidants when tensile strength, tear strength, elongation at break and 300% modulus are compared.
- By Comparing of the FTIR spectra of Soxhlet extract,it is found that Cardanol is not extractable from the vulcanizate.
- The Thermogravimetrtic analysis[TGA] of gum vulcanizates with TMQ and Cardanol as antioxidants gives similar thermal stability.
- Cardanol improves the ageing characteristics of NR with respect to retention of tensile strength, modulus, tear strength and elongation at break similar to that of TMQ.
- Cardanol based vulcanizates shows similar thermal stability when compared to TMQ based vulcanizates.
- Hence Cardanol can replace TMQ at 0.85 parts instead of 0.75 parts of TMQ in tyre tread cap compounds without significantly affecting performance and durability, while having a cost saving.

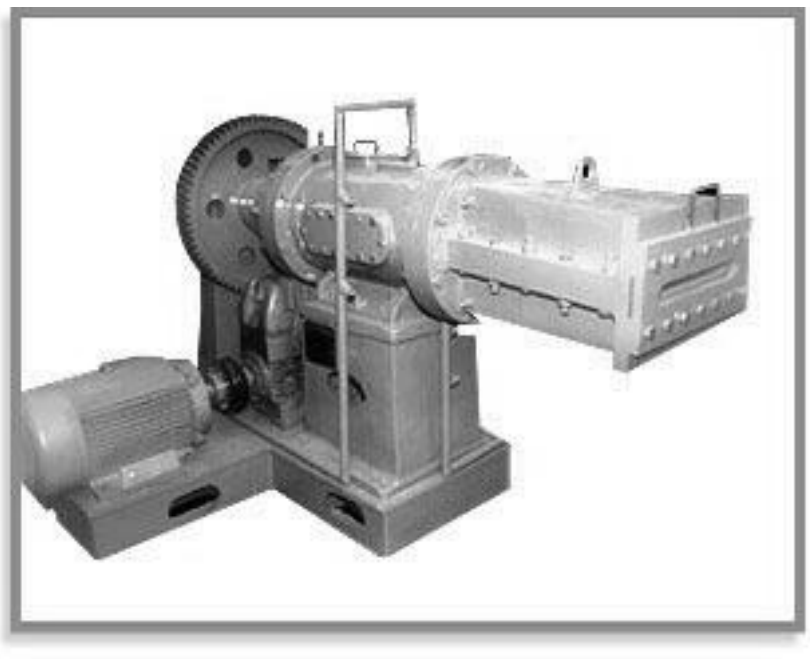
Appendix-1

Tread Extrusion

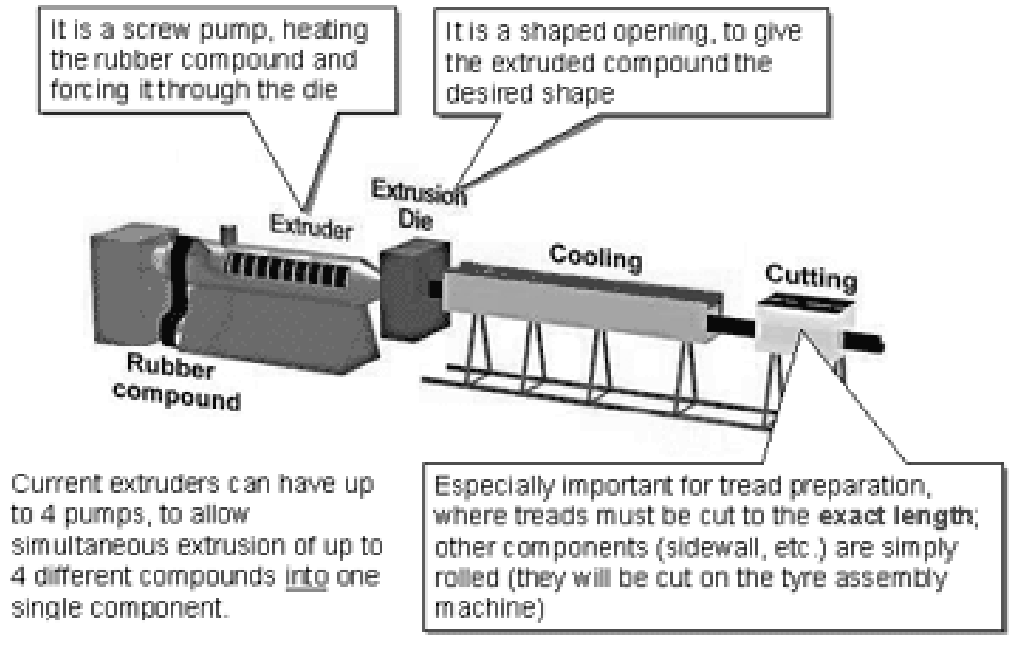
Dual Extruder

Extruders are machines, which forces the rubber through the nozzle or die to give a profiled strip of material. In a dual extruder, there are two extruders with a common 'y[1] shaped head, joins two stocks under high pressure and moderate temperature in to a single extrudate through the die. It is mainly used for the extrusion of tread, which consists of two compounds commonly referred to as cap and base. Cap forms the abrading surface and this is the compound to get good abrasion resistance and flex and tear resistance. But the base compound is designed to have less heat build up.

By changing the pre former and die, dual extruder can be used for sidewall reduction also. In this case, both extruders are fed with the same compound.



Extrusion



To start with, the head temperature controller is set to the temperature as per the specification. The steam line is switched on and also the cooling water for the barrel and the screw. The screw speed and the scale weight are set as per specification.

The desired pre former and die for the tread extrusion is fitted and the correct die clamping pressure is applied. The feed warmed to the appropriate temperature is fed to the feed mill. From the feed mill a slab at the correct width and thickness is cut and fed to the extruder through a conveyor.

The tread is extruded under pressure and taken by a take-away conveyor, under a smooth roller, which can route it along the conveyor and to the shrinkage conveyor. The speed difference between the shrinkage conveyor and the proceeding one are so arranged that it produce shrinkage of about 6.6%.

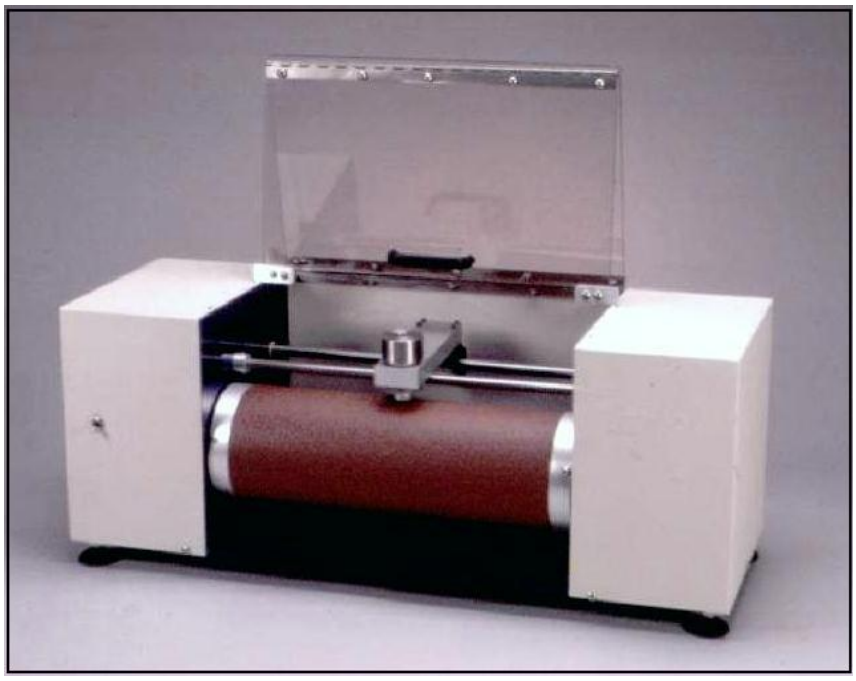
Before it passes to the second conveyor the cushion compound is applied under the tread by the cushion calender and the disc rollers. The disc roller consolidates the compound under the tread. After the shrinkage conveyor the extrudate passes over the running weight balance. The weight of tread is set on the balance as per the specification. And as the extrudate passes over the balance

it reads the weight. Noticing any slight difference the speed of the take away conveyor can be increased or decreased so that the balance reads the incorrect weight. After this the shift and code print as well as line marking is done for identification. Then conveyors take the tread to the cooling chamber where it is cooled by spraying chilled water. The tread coming out of the cooling chamber is cut using the skiver at the pre-set length. After skiving and water removal it is inspected for width and length. Too many variations in the above parameters as well as any visual defects like blisters, voids etc. may result in the rejection of the tread. The acceptable pieces are stored in a leaf truck.

Appendix-2

Testing Equipments

DIN ABRADER



THERMO GRAVEMETRIC ANALYSER

UNIVERSAL TESTING MACHINE

IR SPECRTOMETER

SAMPLE CUTTER 2000R

RHEOMETER

Appendix-3

Indian Standards (IS: 840(1964) specification 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) Wig's method b) Catalytic method	250 375

Physical constants of the oil before and after chemical treatment

	Raw oil	Treated oil
Iodine No.	269	254
Refractive index	1.5158 - 1.5162	1.5212 - 1.5218
Specific gravity	958	96
Saponification Value	19.6	29.7
Viscosity at 25 °C	400	435

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