EFFECT OF LIGNIN BASE ANTIOXIDANT ON NATURAL RUBBER BASE SOLID TYRE TREAD COMPOUND

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Thesis submitted in partial fulfillment of the requirements for the degree Master of Science

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April 2017

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ACKNOWLEDGEMENT

First I would like to express my sincere gratitude to management of Camso Loadstar (Pvt) Ltd for providing me this opportunity and financial assistance to enhance my knowledge in polymer technology.

I would also like to extend my profound appreciation to my supervisor Dr. Renuka Nilmini for all the support and encouragement that she provides me during the master's degree program and I should specially mention co-supervisor, Dr. Karnika de Silva as well for her guidance and the support extended throughout the dissertation preparation.

I greatly appreciate the support received from Dr. Shantha Egodage, the internal supervisor; you have been an ever present beacon of support, encouragement, and advice.

Further, my special thanks go to the staff members of Camso Loadstar Research & Development Center for providing test and laboratory facilities.

Finally, I would like to acknowledge professors, lectures and staff of chemical and process engineering, University of Moratuwa, for coaching and support during the master's degree program.

H D A Gunasekara

ABSTRACT

The purpose of this research was to study the feasibility of lignin as an antioxidant for tire tread compounds. Lignin is naturally abundant and cost competitive wood derivatives possessing antioxidant properties and offering reactive functional groups on their surfaces. Further, lignin is a natural, non-hazardous and sufficiently bio degradable material.

The present study deals with a natural rubber based tire tread compound containing different antioxidant combinations.

Lignin as a bio polymer was combined with commercially available antioxidants (6PPD and SKF) to investigate from the view point of their thermo-oxidative aging. The research specifically focused on producing tire tread compound for industrial applications.

Physico-mechanical properties such as tensile properties tear strength, hardness, abrasion and flexing, and cure characteristics, on tire tread compound was investigated before and after thermo-oxidative aging. The results obtained are shown that the lignin exerts a stabilizing effect. Moreover lignin blends with the selected antioxidants increased the stabilization effect.

The conclusion extracted from this study demonstrates that the higher potential of using lignin as a natural antioxidant substitute for commercial tire tread compounds.

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
HDPE	High Density Poly Ethylene
KL	Kraft Lignin
NR	Natural Rubber
6PPD	N(1,3-dimethyl-butyl)-N'-phenyl-P-phenylenediamine
SKF	2, 2–Dicyclopentylene–bis–(4-methyl -6-tert –butyl – Phenolis
PAH	Polycyclic Aromatic Hydrocarbon
MI	Mooney Initial
MF	Mooney Final
ML	Minimum Torque
MH	Maximum Torque
t_{s2}	Scorch Time
t_{90}	Optimum Cure Time
Cu	Copper
Ni	Nickle
Mn	Manganese
UV	Ultra Violet Radiation
MOR	2 (Morpholinothio) benzothiazole
PVI	Pre-Vulcanization Inhibitor
RSS	Rib Smoked Sheet.
Tg	Glass Transition Temperature

Td	Decomposition Temperature
FTIR	Fourier Transform Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
TG	Thermogravimetry
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
SG	Specific Gravity
AO	Antioxidant

1 INTRODUCTION

All polymers and polymer products are subjected to degradation with time when they are exposed to degradative environments. It is distinct that most of physical and mechanical properties which originally possess are gradually diminished. The rate of property loss of a product is predominantly depended on factors such as chemical structure of base polymer, chemical ingredients used during mixing and curing system which applied for vulcanization (Hawkins, 1984).

Oxygen is the principal external environment factor, which causes adverse influence on the durability of the polymer and polymer products. The deterioration of properties are even supported by the other environment factors such as heat, light, humidity, Ultra Violet (UV) radiation and also tiny cracks or flaws that are present in the product (jialin, 2003). These flaws and cracks are usually originated during molding of the products where a chemical crosslinking reaction takes place with possible shrinking of the polymer matrix.

The impact of degradation is undesirable and creates a considerably important number of changes in the technical properties leading to reduction in durability and the service life and ultimate product failures during service (jialin, 2003).

These changes can be effectively controlled or minimized with the presence of certain materials in the formulations and which are commonly called as anti-degradants. Larger portion of anti-degradants are represented by antioxidants. Oxidation is basically a chemical reaction producing free radicals in creating chain reactions causing degradation (jialin, 2003). Antioxidants are types of molecules that hinders or restraints the oxidation of other molecules. The antioxidant bears the inherent ability of terminating these adverse reactions.

Effectiveness and the function of commercially available antioxidants are varied due to their chemical nature and the dosage use, hence, rubber formulations should be designed in such a way to get best performance at lowest cost benefits in exploring innovative solutions to meet the growing concerns in the manufacturing sector, it is important to pay attention to safety, health, the environment and sustainability (Yu and Jia, 2016).

In 2014, statistics explains that the current annual antioxidant consumption for polymer industry is around 120,000 tons and in which amines accounted for 54% of the total antioxidant consumption volume, followed by hindered phenols (28%) phosphites (12%) thioesters (2%) and nontoxic environmental friendly, plant and animal based natural products that currently contributes to a substantially low value of (4%) (Alonso, 2014).

When taking an insight to the tire industry it is evident that the automobile industry is one of the most dominant industries in the world as the economic benefits it carries are numerous. Tire industry alone creates revenue of around $200 billion, with around 6 million is employed in around 460 tire factories worldwide (Reynolds, 1938) . Tires consist of many types, passenger cars (PC), light trucks and buses (LTB), trucks and buses (TB), off the road applications (OTR), and agriculture.

Revenue of OTR tire business itself is $19 billion (Reynolds, 1938). This business sector mainly covers material handling, and construction applications. The solid industrial tire business which selected for this study is fallen under material handling business sector. The solid tire business has now become very competitive and in addition to worldwide small players, many multinationals are trying their best to consolidate their positions. Outcome of this type of innovative studies are vital in control cost structure and also able to offer environment friendly green product to the market. This novelty brings the competitive advantage not only to retain existing market share but also help to capture new markets.

The solid industrial tire is a composite, which made up of minimum two different rubbers mix and the steel components, part of the tire which contact with floor is called tread, it is compounded with specific rubber mix and carries important physical and mechanical properties to secure the performance of the product.

As tire tread is exposed and contact with external environment, it can be subjected to many degradation modes in static and dynamic conditions. These degradation modes can be described under, aging (storage, heat, light and weathering), loss of mechanical properties (T.S , elongation, modulus, tear strength and hardness) and cracking (flex fatigue and ozone cracking) (Reynolds, 1938).

Natural rubber (NR) as an unsaturated natural product with a chemical structure cis- 1,4 polyisoprene and due to its unsaturation, NR subjects to undergo degradation. Therefore the NR’s structure has to be protected with antioxidants.

Use of organic antioxidants such as is the most common industrial practice but it has disadvantages such as risk on health due to toxicity, and adverse influence to environment. New legislations are imposed to abolish use of health hazardous chemicals from the industry. One antioxidant namely N(1,3-dimethyl-butyl)-N'-phenyl-P-phenylenediamine suitable (IPPD) is also identified as hazardous and gradually being replaced with substitutes (Holmberg, 2009),

Lignin is the one of most abundant component in biosphere and estimated around 3×0^{11} tons occurs in the wood tissues of higher plants. It is a natural polymeric antioxidant with phenolic functionality. Commercial lignin is basically extracted in large amount as byproduct of pulp production during delignification (Li, 2001). It is evident that lignin has been used and identified as a reliable natural source over the years (Dizhbite and Viesturs, 2004). Lignin has the capabilities of being used as an antioxidant, and as a filler for rubber and can be used as a potential source of producing biodiesel (Gellerstedt, 2015). The specific features and characteristics of lignin can be highlighted as wide availability, natural non-hazardous and biodegradable therefore environmentally friendly and non-toxic unlike the organic antioxidants used in the prevailing industries. These tally along with its renewability, and the differences based on plant source.

As many researches unfold, it is imperative to take notice of the industries that lignin can be used in different sectors, such as; pharmaceutical, cosmetics, paper industry, plastics and rubber industry and even biodiesel industry (Kumaran el al, 1977).When the rubber industry is given the gravity, as per the present studies it is clear that lignin has already been used in natural rubber as filler (Frigerio and Castellani, 2014). but not a significant usage can be noticed in the rubber industry as a whole.

1.1 Objectives

Aim of this study was to investigate the possibility of replacing the petroleum based organic antioxidants with environment and health friendly natural substitutes in tire manufacturing industry. The focus was more specifically to study the effectiveness of lignin extracted from Kraft process to uses as an antioxidant. The specific objectives of this study are

- To prepare of NR compounds incorporating kraft lignin and commercially available antioxidants
- To analyze physical properties of prepared NR compounds at ageing and non-ageing conditions.
- To compare the degree of thermos-oxidation of prepared compounds

- To identify the optimum kraft lignin antioxidant loading which provide best ageing properties.

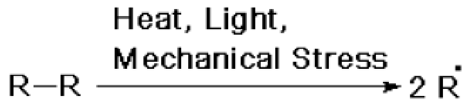
2 LITERATURE REVIEW

2.1 Chemistry of Polymer Degradation

The degradation process was taken place under 3 main stages (Nocil, 2010).

(i) Initiation process
(ii) Propagation process
(iii)Termination process

The formation of free radicals (R.) during polymerization, processing or service of the rubber product was the first stage of polymer degradation and was called as 'Initiation' of degradation process.



$$R{-}R \xrightarrow{\text{Heat, Light, Mechanical Stress}} 2\dot{R}$$

This process was enhanced through the 2nd stage, namely propagation process where the atmospheric oxygen reacts and couples with the free radicals forming "peroxy radicals" (Nocil, 2010). These proxy radicals can further react with hydrogen atoms and create unstable hydro peroxides. There will be immediate actions on degradation via hemolytic cleavage and form alkoxy and hydroxyl radicals to propagate the degradation further.

Below is considered as an autocatalytic oxidation reaction, which can be terminated at the termination process, with the use of an antioxidant.

$$R^{\cdot} + O_2 \longrightarrow RO\dot{O}$$

Termination reaction process composes of two stages (Nocil, 2010).

(i) Chain scission: this process exerts power and control over polymers, resulting in reduction in molecular weight and in the softening of over cured vulcanizates and reduces the tensile properties.

$$2\ R_2HCOO^{\cdot} \rightarrow R_2C{=}O + R_2CHOH + O_2$$

$$ROO^{\cdot} + {}^{\cdot}OH \rightarrow ROH + O_2$$

(ii) Cross linking: exerts control and power over polymers with less active double bonds. This results in gelation, reduction in elongation and brittleness.

$$2\ R^{\cdot} \rightarrow R-R$$

$$2\ R_3COO^{\cdot} \rightarrow R_3COOCR_3 + O_2$$

$$2\ RO^{\cdot} \rightarrow ROOR$$

$$R^{\cdot} + ROO^{\cdot} \rightarrow ROOR$$

2.2 Degradative factors and effect of degradation

The factors described in table below are degraded rubbers / rubber products causing substantial changes in their technical properties and ultimately lead to their failure during service or shorten the expected service life in the absence of antioxidants.

Table 2.1 : Degradative factors and effect of degradation

Degradative Factor	**Reaction Process**
I. Heat	• As the temperature increases the severity of the oxidation effects increases. • When natural rubber is considered, more cross links are formed at first with the absence of oxygen, whereas when the reversion follows, polymer chains will be broken. • This will lead to significant degradation, causing loss of T.S , elasticity and elongation defects.
II. Oxygen	• Oxidation is a complex process which renders as an outcome or the causative reactor for every degradative factor where a very small percentage ranging from 1-2% of combined oxygen can remove all the valuable properties of rubber. • This results in the loss of elastic properties of vulcanizates through simultaneous chain scissions and cross linking. • Cure systems are also subjected to oxidative degradation, conventional cure is highly prone than semi EV or EV curing

	systems.
II. UV light and weathering	• UV light and weathering renders in the action of frosting, where a film of oxidized rubber is formed on the surface of it. Colorized rubber is more prone to degradation, yet carbon black absorbs the UV lights in black color products. • Heat and humidity accelerates the actions and UV attacks are much severe for rubber products with thin cross sections.
V. Heavy metal ions	• Decomposition of hydro peroxides is generally accelerated by heat, light, fatty acids and salts of minerals (polymer soluble) Cu, Ni, Mn, (heavy metals) • These catalyze hydro peroxides and decompose to free radicals. • $ROOH + M(n)+ \rightarrow RO + M (n+1)+ + OH-$ • $ROOH + M(n+1)+ \rightarrow ROO + M(n)+ + H+$ • $2ROOH \rightarrow M(n)+ , M(n+1)+ \rightarrow RO. + ROO. + H2O$ • These may also result in free radicals ; • $R + Mx + Hx$ • $R + M + Hx$
V. Fatigue	• Mechanical ruptures can be caused due to continuous deformation of rubber where the stresses get accumulated in the cracks and grow rapidly. • This results in oxidation/ oxidative fatigue wearing off / degradation. • Antioxidants and anti-ozonants can be used to reduce the impacts of fatigue oxidation.

(Nocil, 2010).

2.3 Role of Anti-Degradants

Antioxidants and antiozonants are used against polymer degradation. In fact antioxidants are highly effective at low concentrations. It cannot take down restraint the entire degradation process, yet it can substantially reduce the radical propagation reaction (Hawkins, 1984).

Polymers can be protected throughout its life cycle based on the type and combination of antioxidants used.

Antioxidants;

- Primary/ chain termination → amines and phenols
- Secondary / peroxide decomposers → phosphites and thioesters

Antioxidants; scavengers the free radicals hindering its rapid growth and reduces the peroxide and hydro peroxides and inhibits from creating more radicals. Donation of reactive hydrogen atom to the free radical is commonly done by secondary aryl, amines, diaminies and sterically hindered phenolic antioxidants. Therefore the peroxy radicals gain more hydrogen through the added antioxidants (Nocil, 2010). Yet this doesn't harm the polymer until the antioxidant is consumed. Antioxidants converts/transforms into comparatively stable radicals which has no further propagation.

Antioxidants are grouped as (Nocil, 2010).

- H- donors
- Hydro peroxide decomposes
- Metal deactivators
- UV stabilizers

It is vital to notice the ability of amine class antioxidants to act as a chain terminator and peroxide decomposes. These are widely used in rubber compounds which require high protection.

2.4 Properties of Antioxidants /Anti Degradants

The choice of the antioxidant depends upon the requirement and the end results. Some key considerations when selecting type and dosage of antioxidant are listed in table below.

Table 2.2 Properties of antioxidants and their effects

<table>
<tr><td>I. Discoloring and staining</td><td>• Color imparted to the rubber
• Two types of staining can be seen ;
I. Contact stain: discoloration where it stains another surface which is in contact with rubber.
II. Migration stain: discoloration or stain which results in means the discoloration or stain which results in an object or article close by to the rubber compound.
• The discolorations occur mostly due to the oxidation products of antioxidants.
• In this case phenolic antioxidants are non-discoloring and the amines are discoloring.</td></tr>
<tr><td>II. Volatility</td><td>• This is based on molecular weight and type of molecule.
• Greater the molecular weight, the volatility is considered to be less.
• Yet the type of molecule carries greater importance.
• Reduction or loss of antioxidants can be caused due to low volatility of rubber during usage, curing and even while processing.</td></tr>
<tr><td>III. Solubility</td><td>• Poor solubility in rubber to specific antioxidants indirectly indicates that only smaller quantities can be used without causing any abnormal situations.
• Just as the other factors, solubility carries importance as it affects the performance, solvency and even on standard sets by food and drug administrations.</td></tr>
<tr><td>IV. Chemical Stability</td><td>• The effectiveness of antioxidants depends upon the stability withheld by itself to external factors such as heat, light, oxygen.
• The effects of external factors differ from one antioxidant to another.
<table>
<tr><td></td><td>Amine antioxidants</td><td>Affected by oxidative reactions</td></tr>
<tr><td>I.</td><td>Phenolic antioxidants</td><td>Affected by heat in the presence of acidic materials</td></tr>
<tr><td>II.</td><td>Dialkyl PPDs</td><td>Oxidizes fast
Effective for a shorter period</td></tr>
<tr><td>III.</td><td>Alkyl aryl PPDs</td><td>Effective for longer durations</td></tr>
<tr><td>IV.</td><td>Diaryl PPDs</td><td>Effective for longer durations</td></tr>
</table></td></tr>
<tr><td>V. Physical form</td><td>• Antioxidants are preferably solid due to ease of handling and weighing.
• Non dusty, free flowing antioxidants are also preferred over liquid antioxidants.</td></tr>
</table>

2.5 Polymer Degradation Process

The process of polymer degradation and effective antioxidant type to prevent further propagation is described as below.

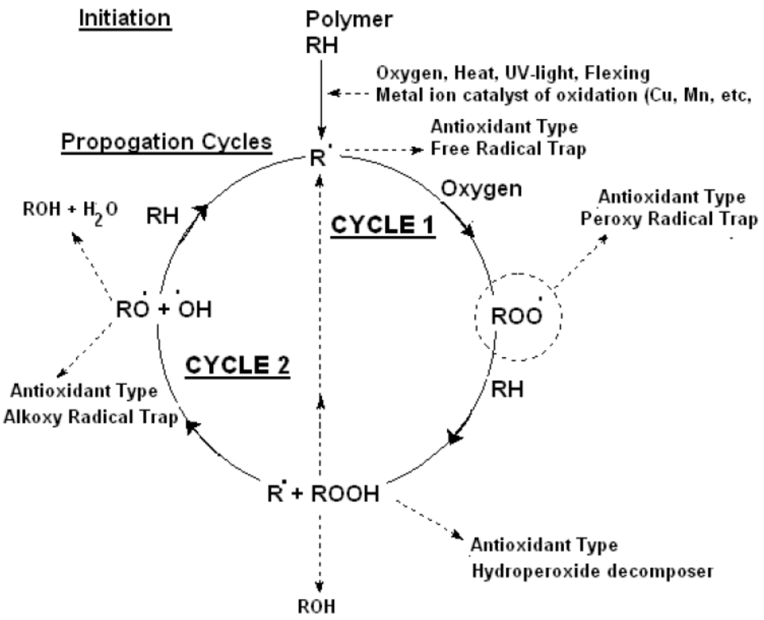


Figure 2.1 Schematic diagram of polymer degradation process

(Nocil, 2010)

2.6 Plant based antioxidants

In general the antioxidants of plants were phenolic. Some form complexes with metals. However, the major value is in their primary antioxidant activity, as free radical acceptors and as chain breakers. (Faustino and Duarte, 2010)

2.6.1 Lignin

Lignin, the most stable cell wall polymer of wood is one of the most abundant biopolymers in nature. It occurs in plants and act as a stabilizer against mechanical, biochemical and environmental stresses (Kumaran el al, 1977). The content of lignin in biosphere is around 3×10^{11} tons with annual increase of 2×10^{10} tons (Gregorova and Moravck, 2005). Lignin polymer is made up of phenyl propane monomers and many other functional groups such as carbonyl, hydroxyl, methoxyl and carboxylic present as substituents. Lignin is composed of three different cinnamyl alcoholmonomers: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol and are shown in Figure 2.2..

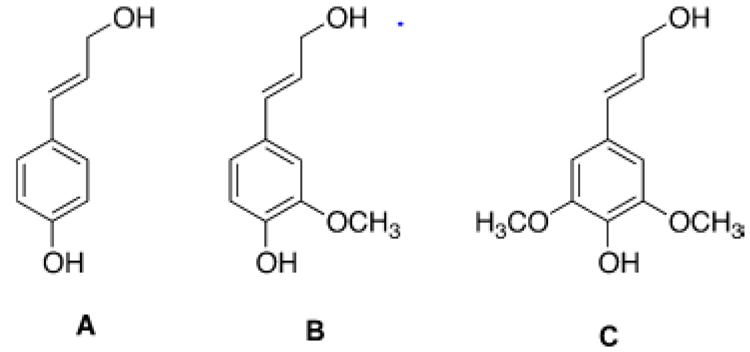


Figure 2.2 Three standard monolignol monomers.

A = p-coumaryl alcohol B = coniferyl alcohol C = sinapyl alcohol.

The physical property and the chemical characteristics of lignin are dependent on wood species and the method of isolation (Lin and Dence, 1992). Lignin exists in the wood tissues of higher plants. Most lignin byproducts in the pulping industry are consumed as fuel and as low as 2% by weight is used for other productive applications (McGraw, 1962).

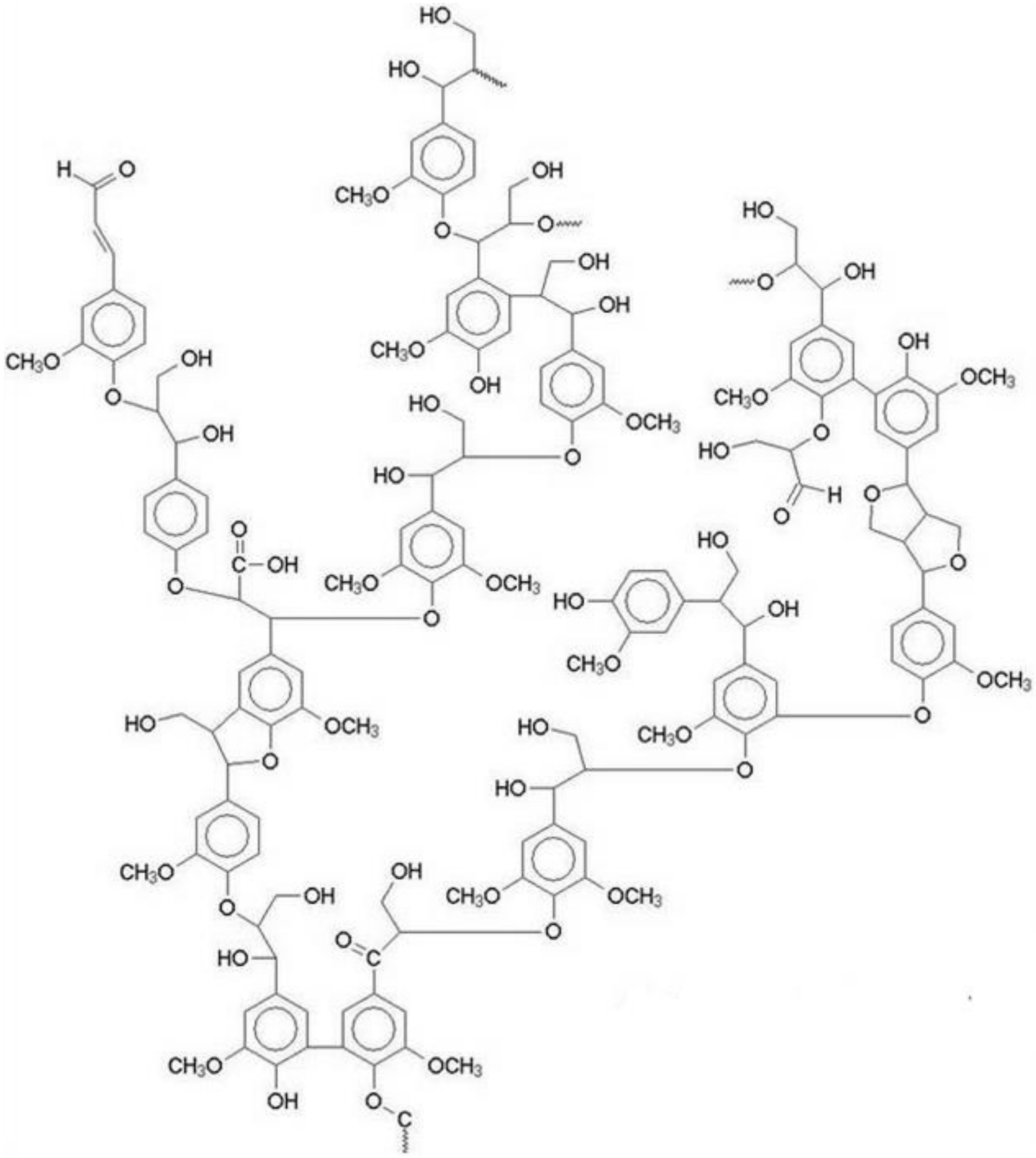


Figure 2.3 A suggested structure of softwood lignin

(Hata, 2006)

Wood is composed of polymers of lignin and carbohydrates that are physically and chemically bound together. Wood is composed with cellulose, hemicelluloses, lignin, and extractives (Li, 2001). Depending on the wood species their relative composition varies greatly. Table 2.3 shows chemical compositions of different wood species.
Lignin is having very complex chemical compound consisting with only aromatic polymer present in wood. The amount of lignin in normal wood is 20 to 35% depending on the different wood species (McGraw, 1962).

Table 2.3 Chemical comparison of various wood species

Constituent (%)	**Softwood**		**Hardwood**	
	Scots Pine (Pinus sylvestris)	**Spruce (Picea glauca)**	**Silver Birch (Betula verrucosa)**	**Eucalyptus (Eucalyptus camaldulensis)**
Cellulose	40.0	39.5	41.0	45.0
Hemicellulose				
-Glucomannan	16.0	17.2	2.3	3.1
-Glucuronoxylan	8.9	10.4	27.5	14.1
-other polysaccharides	3.6	3.0	2.6	2.0
Lignin	27.7	27.5	22.0	31.3
Total extractives	3.5	2.1	3.0	2.8

Figure 2.3 illustrates lignocellulosic matrix is a complex structure. Cellulose is surrounded by a monolayer of hemicellulose and embedded in a matrix of hemicellulose and lignin. Most isolated lignins are brown amorphous powders. Depending on the preparation method used and on the fraction represented of the total lignin, there are some changes correspondingly in color and shape.

The molecular weight, or average molecular weight, is a particularly important characteristic property of a lignin. Another important property of lignin is its capacity to absorb ultraviolet light. When the intensity of absorption is plotted against a given wavelength of ultraviolet light, an ultraviolet spectrum curve for the lignin is obtained. According to the type of lignin, the lignin solvent, and the pH of the solution and lignin structure, the shape of this curve may change (McGraw, 1962).

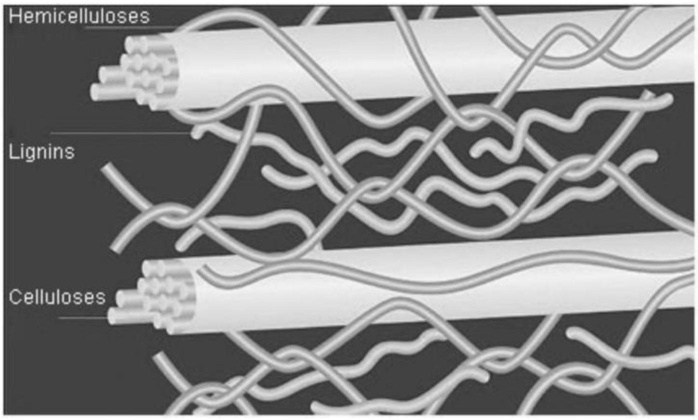


Figure 2.4 Position of lignin within lignocellulosic matrix

(Kuhad and Singh, 2007)

Through chemical linkages such as ethers and esters between lignin and the polysaccharide constituents, lignin carbohydrate networks are formed in the cell wall Making the direct separation of individual polymers impossible .In annual plants such as cereals, sugar cane or grasses, alkaline delignification is, however, much faster than in hardwood or softwood supporting the view that ester linkage is much more abundant in the former category (Epelde and Lindström, 1998)

2.6.2 Characterization of lignin

The solution-phase and solid-state characterization methods were used to measure, identify, and quantify the chemical and physical properties of lignin.

Hydrogen and carbon NMR spectroscopy or UV spectroscopy were widely being used in solution-phase characterization. These techniques were primarily used to determine hydroxyl and monolignol content in lignin. Characterization in solid phase was fairly simple when compared to solution phase characterization. The techniques indicated below were commonly used in solid state characterization.

FTIR spectroscopy, UV microscopy, interference microscopy, electron microscopy, cross-polarization/magic angle spinning (CP/MAS) NMR spectroscopy, Raman spectroscopy, gas chromatography mass spectrometry (GC−MS), thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). While all of the above methods provide important and diverse information, The thermal characterization techniques (TG, DSC, and DTA) as these were the most simple, accessible, and directly informative techniques regarding the physical properties of lignin and their potential use in commercial materials.

As lignin was an amorphous polymer, only Tg and decomposition temperature (T_d) was applicable. Tg results were varied with the measuring technique, for example, utilizing infrared spectrometry to determine molecular motion, measured the Tg of lignin to be 97−117 °C (Gregorova and Moravck, 2005). Where T_g of same sample was measured with differential scanning calorimetry, the results were quite different and value showed up between 92 and 142 °C. The large difference in the two methods as well as the broad range given demonstrates were not only the importance of sample handling and preparation but also the method used. T_g of lignin was typically reported to occur between 70−170 °C, depending on the structure and molecular weight of the fragments.

Similar inconsistencies could also be seen in the measurement of decomposition temperature with thermogravimetry. Lignin could be clearly identified from the other components of wood samples through its characteristic decomposition between 360−480 °C (Gregorova and Moravck, 2005). Well define single method for characterization of lignin was not available and the combination of several techniques had been successful in probing the physical property analysis.

Further work was devoted to studies of the radical scavenging properties of lignin, and was recognized as efficient antioxidants of natural origin. Radical scavenging efficiency of a series of lignin sample isolated from deciduous and coniferous wood species and lignin related monomeric compounds were examined against 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical in homogeneous conditions using ESR and spectrophotometry methods. Some structure activity relationships were proposed, pointing out the importance of the non-etherified OH phenolic groups, ortho-methoxy groups, hydroxyl groups and the double bond between the outermost carbon atoms in the side chain for increasing scavenger activity. Analysis of rate constants for the lignin–DPPH interaction revealed the contribution of polymer molecular weight and p-polyconjugation systems. The p-conjugation systems of lignin operated as catalysts/activators of the interaction with DPPH_. Heterogeneity in terms of component composition (carbohydrate admixtures) and polydispersity was the factor which could decrease drastically the antioxidant efficiency of isolated lignin samples. (Dizhbite and Viesturs, 2004)

2.6.3 Lignin isolation

As with all sourced materials, both industrial and lab-scaled processes for isolating lignins from lignocellulosic biomass were developed (Li, 2001). The isolation process was almost follows similar techniques, chemical degradation of the polymeric lignin structure until the resulting fragments become soluble in the pulping media. Depending on the method employed, the properties of the resulting isolated lignin differ. Key factors in the success of each process include: the pH of the entire system, the ability of the solvent and/or solute to participate in lignin fragmentation, the ability of the solvent and/or solute to prevent lignin recondensation, and the ability of the solvent to dissolve lignin fragments (Gregorova and Moravck, 2005).

The isolation process of pure lignin was categorized two by its content (Li, 2001).

- The resulting product contains sulfur- Lignin isolated from the sulfite and Kraft processes contain Sulphur
- The resulting products are free of Sulphur- Lignin isolated from the soda and organosolv process.

In addition to functionalization either with or without sulfur, the resulting products also differ in levels of purity, structure of the resulting fragments, and molecular weight (Upton and Kasko, 2016).

Lignin can be isolated from various raw materials i.e wood and black liquor. There are several methods for lignin isolation from wood. Generally, lignin is isolated either by removing of non-lignin or lignin from the rest of the components. Moreover, carbon dioxide or sulfuric acid is used to isolate lignin from black liquor, which is generated in the cooking process as the white liquor dissolves the lignin and other organic compounds in the wood.

The antioxidant activity of the phenolic compounds present in industrial black liquors obtained from the two cooking processes (kraft and sulphite) used in Portugal to produce Eucalyptus globulus pulp was evaluated (Faustino and Duarte, 2010). The black liquors treated at several pH values were extracted with ethyl acetate. Phenolic fractions were further separated by liquid chromatography of the crude extracts of kraft liquor at pH = 6 and sulphite liquor at the original pH. Total phenolic content was determined in terms of gallic acid equivalents (Folin-Ciocalteu colorimetric method), and the antioxidant activity in the crude extracts at several pH values and in the separated fractions was measured using the DPPH test for radical scavenging capacity. The fractions separated by column chromatography were submitted to mass spectrometry analysis and the results were compared to other similar studies in the literature of natural products, mainly from Eucalyptus, and the characteristic bands of functional groups were identified by 1H-NMR and FTIR.

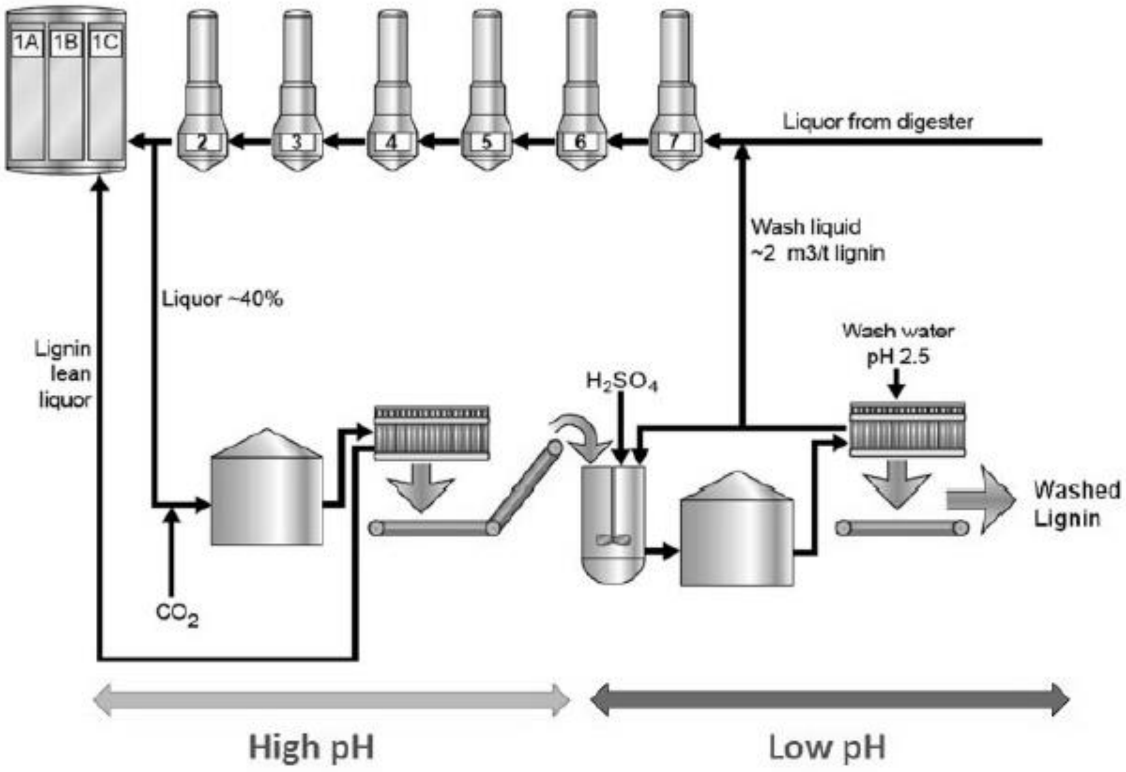


Figure 2.5 Lignin isolation process

Certain other in depth studies in relation to different lignin isolation methods from various wood species and black liquor is also reviewed. Accordingly the lignin obtained was identified by spectrophotometric methods which were UV and FTIR spectroscopy, to analyze and compare the physical and chemical properties of lignin, such as lignin content and color with different pH values, and their chemical structures, etc. Two different methods of lignin isolation were studied: one was isolation according to different pH values from the black liquor which was obtained from four wood species (pine, spruce, birch and aspen chips) in the batch digester by Kraft process, it was called Kraft lignin; another one was isolation from sawdust of four wood species in a flask reactor with reflux condenser, it was called Klason lignin. These lignins were characterized by UV and FTIR spectroscopy. According to the results, the lignin content and functional group were determined separately. The yields of lignin slightly increased with pH value decreasing, and the yields in softwood were higher than in hardwood. The UV absorption maximum of lignin revealed that lower pH value had a high purity level. In a comparison with Kraft and Klason lignin, they included different functional groups; there was a difference in chemical structure. In addition, the chemical structure was not similar between softwood and hardwood. (Li, 2001)

2.7 Applications of lignin

Lignin is second to cellulose as the most abundant natural polymer and in spite of this fact it is a vastly underutilized material. Major potion serves as fuel for thermal energy generation and only an insignificant part is used in specialty products.

- Use as a cement water reducer
- Cement grinding aids
- Bitumen emulsion
- Viscosity braking agent
- Surfactant and dye dispersant
- Composite material

Large quantities of kraft lignin are formed in the pulp industry. Although the vast majority is used for internal energy production at mill sites, modern pulping technology allows for a partial outtake of lignin without disturbance of the energy balance in the mill. At present, lignin from softwood pulping is available in commercial quantities and it can be assumed that this amount will rapidly increase in the future. Therefore, development of material systems based on softwood kraft lignin should be beneficial for the future sustainable society and add value to a renewable resource. In this review, the formation, structure, and properties of softwood kraft lignin is summarized and it is suggested that, depending on final use, an optimization of lignin properties is done through selected fractionation and purification (Gellerstedt, 2015).

2.7.1 Advantages of lignin as an antioxidant

Basic features of lignin to use in polymer industry are as follows (Gregorova and Moravck, 2005).

- Cross linked structure with tetra functional branch points
- Strong intra molecular interactions
- Better processing ability
- Stabilizing or antioxidant effect
- Reinforcing effect
- Biodegradability

Studies are shown that the antioxidant characteristics of lignin vary with their genetic origin, isolation method, and the molecular arrangement and its composition (Dizhbite and Viesturs, 2004). Therefore, it is important that the researches do have better understanding on type of wood used to source, extraction and purification methodology, molecular weight and molecular weight distribution.

Lignin acts as an antioxidant for natural rubber filled with carbon black during thermal aging (Dizhbite and Viesturs, 2004).

Moreover the effectiveness of the commercial rubber antioxidant IPPD can be enhanced by adding lignin (jialin, 2003).

Sulphur free lignin can be sourced from renewable sources and is widely available, a few of its characteristics include cost effectiveness, renewable, widely available non-volatile and non-toxic . (Hawkins, 1984)

Thermal, morphological and antioxidant properties of lignin irradiated with electron beam (EB) of doses 30, 60 and 90 kGy were investigated by Electron spin resonance (ESR), Fourier transform infrared spectroscopy, Differential scanning calorimetry, Scanning electron microscope and Spectrophotometer techniques. The presence of polyconjugated radicals in unirradiated lignin was confirmed by ESR studies; whereas irradiated lignin possesses both poly-conjugated and peroxy radicals. The peroxy radicals were decayed near the glass transition point on thermal heating while poly-conjugated radicals were stable even up to a temperature of 450K. Presence of conjugated structures was confirmed by the presence of 1604 cm-1 absorption band whose concentration was increased following radiation dose. Up to a radiation dose of 60 kGy the fall in glass transition temperature (Tg) was very slow, while at 90 kGy Tg decreased abruptly. The decrease in Tg was assigned to be due to intermolecular chain interactions or plasticization effect. Granular structure of lignin was found to be effected by EB irradiation. Cracks were generated on lignin granules on EB irradiation. Due to increase in poly-conjugation, amorphous nature and granular cracks the antioxidant property was observed to increase. The current research trends in lignin materials include modification of lignin, fabrication of biodegradable thermoset/thermoplastic and use of lignin as stabilizers and dispersants (Rao and Reddy, 2015)

Publications on antioxidant capability of lignin with their hydrothermal liquefaction products were also studied. Accordingly, black liquor alkaline lignin and magnesium lignosulfonate were liquefied at 320 C. The antioxidant abilities of the liquefaction products were compared with the raw materials. Results are shown that the total phenol content of both alkaline lignin liquefaction products (ALLP) and magnesium lignoslfonate liquefaction products (MLLP) were improved, and ALLP had a larger increase than MLLP. The influence of reaction time and temperature on oil yield, total phenol content was found to have certain relationships with the antioxidant abilities. These results explore a new approach for further studies and applications of liquid antioxidant from lignin (Kang and Fan, 2002).

The results of other study was shown that the lignins from a steam explosion process in crude and purified forms and modified Sulphur-free commercial lignin were characterized to establish their chemical composition. Then the lignins were tested again after treatment with hexamethylenetetramine. The resulting products were used to make rubber composites and their mechanical properties were compared to rubber composites made with carbon black to test the possibility of using HMT treated lignins as a partial replacement for carbon black in the production of rubber composites. In the crude lignin, a significant amount of impurities were detected, such as ash and residual polysaccharides and these substances interfered in filler-elastomer interactions. The purified lignin maintained a high content of strongly polarized hydroxyl groups that interfered with the interaction of the filler and elastomer, resulting in low performance. Improvements in the mechanical properties were observed using protobind 3000 lining or purified lignin with HMT added during with elastomers results in composites with higher reinforcement abilities compared to previously described rubber composites. However, in all samples, a poor and unsatisfactory dispersion of lignin in the polymeric matrix was observed. This is likely due to the incompatibility of lignin with the hydrophobic rubber, resulting in lower performances compared to the carbon black (Frigerio and Castellani, 2014).

2.7.2 Lignin as an antioxidant in thermoplastics

Polymers were subjected to oxidative degradation during all steps of their useful cycle. This degradative process was prevented using stabilizers like antioxidant of the type sterically hindered phenols or amines. Lignin, due to the presence of phenolic groups in their structure, can present characteristic as antioxidant agent, in a similar way to the additives used in polymers. A method based on non-isothermal differential scanning calorimetry (DSC) to evaluate this property was used to evaluate effect of KF antioxidant in high density polyethylene (HDPE). The HDPE compounds studied were subjected to heat treatment at different scan rates and in presence of oxygen to promote thermos oxidation of the material. The antioxidant capacity of different formulations of lignin and additives in HDPE was determined from the temperature of onset of oxidation at different heating rates and adjusting Arrhenius model prediction. The results indicated that the procedure can be used to predict the antioxidant capacity of antioxidant additives in HDPE with good reproducibility and accuracy, according to the Arrhenius model prediction (Pina and Lopez, 2015).

Lignin antioxidant properties in polypropylene (PP) were also evaluated in another study (Pouteaua and Boquillonb, 2002). Fifteen lignin samples from various botanical origins (wheat straw and wheat bran) were extracted and characterized using different processes of extraction and using industrial Kraft lignins fractions (Westaco). One percent by weight of the lignin was incorporated in PP. This study evaluated the effect of lignin solubility in PP on stabilization behavior. Polypropylene showed very low solubility ; as a consequence, classically important factors such as phenol content and intrinsic reactivity of the molecule are less important than factors making easier solubility. Solubility in PP could not be measured directly; a morphological criterion (average dimension of lignin aggregates in the blend) has been correlated to antioxidant activity and is thought indirectly to reflect solubility behaviour. Factors like low molecular weight, low total OH content (aliphatic+phenolic) tend to improve the compatibility (blend morphology) and consequently the antioxidant activity. The non-linear relation between Kraft lignin activity and its concentration in the blend has been explained by molecular weight polydispersity, and correlated to activities of Kraft fractions.

2.7.3 Lignin in Rubber Compounds

Lignin, as a renewable waste material of pulp and paper industries, was analyzed through Fourier-Transform Infrared Spectroscopy (FTIR) and found to be structurally similar to kraft lignin. Surface modification by addition of benzoyl peroxide and subsequent heating at 70 °C caused generation of new functional groups in lignin. Efficacy of the crude lignin as well as that of the modified variety as a filler in nitrile rubber (NBR) has been evaluated. Rubber vulcanizates were analyzed for physico-mechanical properties, oil and fuel resistance, and thermal stability, and compared with conventional fillers like phenolic resin and carbon black. Modified lignin has been found to produce superior elongation, hardness and compression set properties compared to phenolic resin but inferior to carbon black. Resistance to swelling, however, depends on the type of oil or fuel, and modified lignin always showed better properties than carbon black. Both thermo-gravimetric analysis (TGA) and thermo-mechanical analysis (TMA) showed highest thermal stability for the modified lignin followed by phenolic resin and carbon black (Setua, et al, 2000).

This study deals with the rice husk is used as filler in NR to observe its reinforcing effect on the rubber vulcanization. The effect of variation of particle size and of filler loading is investigated. The results of the study indicated that much reinforcement i~ not obtained by the incorporation of husk in different formulations. When used in smaller particle size, however, some reinforcement effect is noticed. This effect can further be increased by incorporation of resorcinol and hexamine in the compound recipe. In the next part of the study, the mixture of phenols consisting of ferulic, vanillic, pcoumaric, sinapic p-hydroxy benzoic, salicylic and indoleacetic acid extracted from rice husk has been tried as antioxidant in NR gum and filled vulcanizates. The results obtained were compared with those of control mixes containing stirenated phenol. The cure characteristics and vulcanizate properties were 'evaluated. The results indicated that there is not much variation in cure characteristics or tensile properties between control and experimental sets. Further, the antioxidant protection given by phenols from rice husk is comparable with that of stirenated phenol (Kuriakose et al, 1999).

A series of carbon black filled natural rubbers containing lignin was tested from the view point of their thermo-oxidative aging. Lignin is biopolymer that belongs to the main components of wood. Mechanical properties and crosslink density of lignin stabilized vulcanizates were measured before and after thermo-oxidative aging for 24, 72, 168, 240 and 408 h at 80 _C. The results were compared with those from NR vulcanisates stabilized with the commercial rubber antioxidant N-phenyl-N-isopropyl-p-phenylene diamine (IPPD). The results obtained show that lignin exerts a stabilizing effect in carbon black filled natural rubber. Its effect is comparable with that of conventional synthetic antioxidant. Moreover, the addition of lignin increased the stabilizing effect of IPPD (Gregorova and Moravck, 2005)

The stabilizing effect of natural filler, sulfur-free lignin, on the thermal degradation of natural rubber (NR) was examined. Lignin was incorporated into NR in amounts of 10–30 pphr (parts per hundred parts of rubber). It was shown that the lignin preparation used improved the physicomechanical properties of the rubber vulcanizates. Thermogravimetric analysis and differential scanning calorimetry were used to study the thermal degradation of unfilled and lignin-filled vulcanized natural rubber. Measurements were carried out under atmospheric conditions. It was revealed that lignin used as filler increased the resistance of NR vulcanizates to thermo oxidative degradation in air. (kova and ovicova, 2006).

2.8 Solid Tire

Solid tire is an important engineering product that is used for heavy load applications. High wear resistance and puncture proof characteristics force to use solid tires for some special applications such as in forklifts, ground support equipment and other material handling applications. Solid tire is a rubber composite structure which consists of several rubber compounds. By varying the compound types and their arrangement product designers keen to develop different features in a solid tire.

The main characteristics in a solid tire are.

- Reduced down time thanks to absolute puncture resistance.
- Less maintenance operations for fitting and removal thanks to the longer tire life.
- Higher maximum speed and maneuverability thanks to reduced tire heating
- Allowing for longer and more intensive use.
- Reduced requirement for maintenance thanks to less vibrations and shocks.
- Reduced downtime from refueling and recharging thanks to low energy consumption.
- Often best cost / hour.

Basically solid tire consist of four components; three 3 layers and a steel reinforcement, and are shown in Figure 2.6.

Figure 2.6 Cross section of a solid tire

Combination of high hardness, high compression set and high modulus, heel layer and steel rings provide extra reinforcement to ensure better grip in between rim and the rubber composite/tire (Reynolds, 1938). Middle layer with low heat buildup and high rebound resilience provide lower rolling resistance and thermal performance to the tire in application. Tread is the other part and it should better in abrasion, Low rolling resistance and low heat buildup provide extra performance for a solid tire.

Among the three layers, tread layer is the most exposed layer to external environment. Therefore compound developers always seeking new methods to protect tread layer from environment. Degradation is one of important phenomena that reduce performance of a tire. This research aimed to seek openings to use natural protector for degradation and their effects.

2.8.1 Solid tire tread compound

Tread is the upper most part of the any tire which comes in contact with running surface. The tread in the contact patch (The part of the tire that touches the road) must be resist to very significant stresses. The tread rubber compound must grip on all type of surfaces; resist wear and abrasion and heat up as little as possible.

Tread is made from pure natural rubber and or blend of synthetic rubbers, usually SBR/BR mixed with reinforcing fillers, carbon black or silica depending of the requirement. Generally non marking treads are filled with silica fillers. Other ingredients such as activators, oil and curatives are added as appropriate. Chemists are careful on selecting Antioxidant type, staining or none staining and dosages as it determines the color and performance of the product in application n.

In general all tread compounds demand on the following parameters.

- Wear resistance
- Low heat build up
- Low fuel consumption
- Resistance to cut and chip
- Excellent road grip (traction , both dry and wet conditions)

3 EXPERIMENTAL

The main aim of this investigation was to evaluate the performance of KL in NR as an antioxidant and to compare their performance with two conventional widely used antioxidants in solid tire manufacturing industry. It is known that oxidation of a polymer can occur at all stages, i.e. from synthesis to final use, causing undesirable changes in mechanical, aesthetic, and electrical properties and to protect the polymer from oxidation. Low molecular weight phenolic or amine antioxidants are widely used in all polymer based product manufacturing industries.

3.1 Materials

NR as the polymer, and rubber compounding ingredients, were used in this study and are given in Table 3.1. All the ingredients were of industrial grade and were used without further purification. Specifications of the rubber and the ingredients are given in Annex 1.

Table 3.1 Raw materials used in the rubber formulation

Name	**Category/function**	**Source**
Natural Rubber, RSS grade	Polymer	Rathnapura, Sri Lanka
Carbon Black, N220	Reinforcing filler	Phillips carbon, India
Stearic Acid	Organic Activator	Pan century petro chemical, Malaysia
Zinc Oxide 99.5% purity	Inorganic Activator	Agromax Asia , Sri Lanka
N-(1,3-dimethylbutyl) -N'-phenyl-p-phenylenediamine (6PPD)	Antioxidant	Sinorghem chemicals, China
Sterically hindered polynuclear phenol, Vulkanox® SKF	Antioxidant	Sinorghem chemicals, China
Kraft Lignin	Antioxidant	Scion- New Zealand
Low PAH oil (Polycyclic Aromatic Hydrocarbon)	Processing Oil	Nynas, Sweden
Sulphur	Vulcanization Agent	Mywon commercial Korea
2-(4-Morpholinothio) benzothiazole, Pilcure MOR	Accelerator	Flexsys , Malaysia
N-(cyclohexylthio)phthalimide, Santogard® PVI	Pre vulcanization Inhibitor	Flexsys , Malaysia

3.2 Compound Formulation

The intentions of investigating to evaluate the effect of natural antioxidant in tread compound and different formulas were developed by changing the antioxidant contents. A formulation used to manufacture tire treads by milling process was selected as a suitable formulation in this study. KL antioxidant was varied from 2 to 3 pphr at 0.5 pphr interval when it was used alone. When KL was combined with the commercially available antioxidants, 6PPD and SKF, each antioxidant was varied from 0 to 2 at 0.5 intervals while maintaining the total antioxidant content as 2 pphr, and the formulations for all eleven compounds are tabulated in Table 3.2. C01 and C02 were the control compounds.

Table 3.2 Compound formulation

	C 01	**S 01**	**S 02**	**S 03**	**S 04**	**S 05**	**S 06**	**C 02**	**S 07**	**S 08**	**S 09**
RSS	100										
N220	47										
Stearic Acid	2										
ZnO	3.5										
6PPD	2	1.5	1	0.5	0	0	0	0	0	0	0
KL	0	0.5	1	1.5	2	2.5	3	0	0.5	1	1.5
SKF	0	0	0	0	0	0	0	2	1.5	1	0.5
Oil	5.7										
Sulphur	1.5										
MOR	1.2										
PVI	0.1										

3.3 Methodology

NR and the other ingredients as per the formulations given in Table 3.2 were compounded. Processing characteristics and mechanical properties before and after ageing were compared with two commercially available antioxidants as controls. The flow of the basic steps is given below in Figure 3.1.

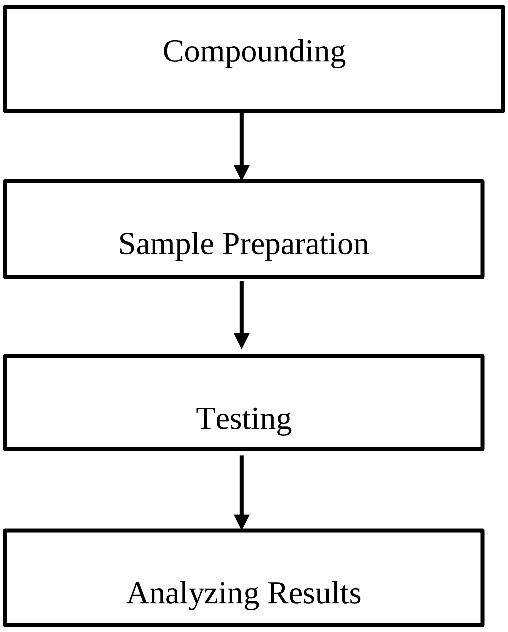


Figure 3.1 Process flow diagram of the research

3.4 Compound Processing and Sample Preparation

Laboratory scale internal mixer and mixing mill was used for the compounding stage.

3.4.1 Mixing in internal mixer

Farrel BR1600 Banbury mixer is used for compound mixing. It is a variable speed mixer, but rotor speeds are maintained at 30 and 35 rpm constant during the experiments, these rotor speeds generate the friction ratio of 1:1.16. The ingredients listed in Table 3.1 are sequentially added into the mixer at two mixing stages, and do mixing as per the times defined in the mixing cycles given in Table 3.3 and Table 3.4. In addition to mixing time, temperature raised was also a consideration to discharge compound from the mixer.

Table 3.3 Mixing cycle 1st stage

Time (sec)	Description
0	NR
+60	Carbon black + processing Oil
+60	All other ingredients
+45	Clean
+(30 – 40)	Dump (Compound temperature 150-155 ^{0}C)

Table 3.4 Mixing cycle 2nd stage

Time (sec)	Description
0	1st stage compound
+30	Second Stage Chemicals (MOR , PVI)
+60	Dump (Compound temperature 90-100 ^{0}C)

3.4.2 Mixing on mill

Mill mixing was done on two roll laboratory mixing mill of 200×400 mm in size. Mill roll speed can be adjusted independently to variable speed to provide different friction ratios. Friction ratio of 1:1.2 was used in the study. The lump taken from the internal mixer was passed five times through the tight nip to get a smooth band on mill rolls. Finally, the compound was sheeted out at a fixed nip gap and milling direction.

3.5 Determination of properties

3.5.1 Mooney viscometer

Viscosity of rubber compounds were measured by using Aktron Viscometer according to ASTM D-1646. A compound sample was introduced into the heated die cavity using knurled disc rotor subjected to rotational shear. Torque on which rotor measured and the reading on the scale was considered as viscosity of compound.

Variation of rheological behavior was studied using Mooney viscosity. The measuring conditions were defined such a way that the preheat time of 1.0 min and a set time of 4.0 min at 100 °C with the large rotor, which is expressed as ML(1+4)@100.In general, Mooney viscosity is measured at 100 °C. In this study same measuring temperature selected since initial viscosity is not a high value. Pre heat time and rotor size also acceptable for tested sample viscosity range.

The sample holder region of the viscometer is composed of the stator and rotor. Since the rotor is rotated during the measurement, shearing is applied to the compound sample and with applied heat viscosity of the compound decreased smoothly like and exponential decay.

Torque 84.6 kg cm = 100 Mooney units. Both 1st stage compounds and 2nd stage compounds were tested as test conditions given in Table 3.5.

Table 3.5 Conditions at Mooney viscosity test

Test Conditions	**Rotor Type**	
	Small	**Large**
Pre-heat time, min	1.5	1
Test time, min	4	4
Test temperature, ºC	120	100

3.5.2 Cure characteristics

Oscillating disc rheometer (ODR) was used to measure cure characteristics as per ASTM D2084. Unlike Mooney viscometer ODR consists of a bi-conical disc of diameter 35.5mm. This disc was oscillated at 1.7 Hz through rotary amplitude of 3 degree while keeping at 150 °C for 30 minutes in the mould cavity. Maximum

Torque (M_H), Minimum Torque (M_L), Scorch Time (t_{S2}), Cure Time (t_{90}) and t_{50} were measured.

3.5.3 Preparation of test specimens

Electrically heated ram press was used to prepare the rubber vulcanizates at specific thicknesses as required according to respective standards for test specimens. These sheets were vulcanized at a pressure of 4.5 bar (ASTM requirement is minimum 3.5 bar) and a temperature of 150±2 °C. Optimum cure time, t_{90}, was taken as the vulcanizing time for each compound.

3.5.4 Specific gravity (Density)

Densimeter based on Archimedes' principle was used to measure specific gravity directly according to the ASTM D297. Alfa Mirage MD 300S Electronic Densimeter was used for this test. Theoretical specific gravity of the formula and the actual specific gravity of the compound will indicate the accuracy of the mixing and quality of the compound.

3.5.5 Hardness

Hardness is officially defined as the resistance of a material to plastic deformation, usually by indentation. However, the term may also refer to stiffness or temper or to resistance to bending, scratching, abrasion or cutting. Within the field of engineering hardness is referred to as indentation hardness, which measures the resistance of a sample to material deformation due to a constant compression load from a sharp object. The tests work on the basic premise of measuring the critical dimensions of an indentation left by a specifically dimensioned and loaded indenter.

Resistance to indentation of rubber sample was measured by using a rubber hardness tester called Durometer as per ASTM D2240 standards. It is expressed as number referring to the scale of the instrument by which it is measured. It is an important property frequently used in rubber specifications along with tensile properties to which it is somewhat related.

3.5.6 Tensile properties

Tensile testing machine was used to determine the relationship between the applied force and the deformation produced. Dumbbell shaped test specimens were used.

Moulded sheets both along and across the fiber direction were used to prepare test pieces. Standard dimension test pieces prepared by die cut punching as per ASTM D412-A.

Test specimens were acclimatized at the test temperature 27±2 ºC for 24 hours before testing. The thickness was measured using a micrometer gauge. Three test specimens were used to get one test result. The dumbbell test specimen was placed at the center position of the grip and force and elongation were taken while the test piece is strained at a rate 500±50 mm/min.

T.S , elongation at break and modulus at 300% elongation (or modulus) were calculated according to Equation 3.1, Equation 3.2 and Equation 3.3, respectively.

$T.S = F/A$ ……………………….……………………..Equation 3.1

where, F Breaking Force,

A Initial cross sectional area

Elongation at Break % = $(L-L)_{\circ}/ L_{\circ}$ …………………………………..Equation 3.2

Where, $L_{\circ}$ Initial length

L Length at break

Modulus at 300% elongation = f / A …………………………………..Equation 3.3

where, f Force at 300% elongation

3.5.7 Tear Strength

Tear resistance is depended on different factors. The effect to tear resistance of different compounds are tested and analyzed to observe the effect. Crescent shaped specimens were prepared using ASTM D-624 die C, and specimens were cut from the vulcanized sheet of 2 mm thick. A nick of depth 1±0.2 mm was made at the center of the concave edge of the test specimen. Test specimen was then mounted in the testing machine and strained at a rate of separation of 500±50 mm/min until the test piece breaks. The maximum force at the break was recorded and the tear strength was calculated using Equation 3.4.

Tear Strength = F/d ……………………………….Equation 3.4

where F Maximum force

d Median thickness of each test specimen

3.5.8 Abrasion Resistance

Rubber products especially tires are usually subject for rubbing action during its application. Abrasion resistance is measured in order to compare its behavior under service condition. In otherwords if the labotory test show that trial compound gives less abression than the standard rubber, it is usually safe to expect a better in service for products.

DIN abresion tester was used for this study. The tester consists of a drum diameter 150 mm and length 500 mm and the outer surface of the drum is attached a specified abresive paper. Cylindrical test specimens having diameter 16 mm and thickness 6 - 16 mm was used and the abrasion resistance was determined according to ASTM D5963.

3.5.9 De Mattia Flexing

During this test rubber is repeatedly flexed and subject surface to a cyclic variation in strain. Cracks slowly develop or if a crack/cut already exists it will grow in a direction perpendicular to the strain. De Mattia tester measurses the spontaneous development of cracks by repeating flexing or the growth of a deliberately made cut through the test piece. The test specimens were inserted in the grips of the machine. The machince was then started and continued the test with frequent inspection until the first munute sign of cracking was detected. The number of flexing of cycles at this point was recorded and the tester was restarted. The tester was stoped after intervals in which the number of flexing cycles was increased in geometric pregression as per ASTM D623 standard.

3.5.10 Aging properties

Rubber and rubber products must resist the deterioration of physical properties with time caused by oxidative and thermal aging. This test method provides a way to assess these performance characteristics of rubber, under certain accelerated conditions as specified.

Specimens prepared for evaluations of mechanical properties mentioned in Section 3.5.1 to Section 3.5.9 were kept in an aging oven and heated at constant temperature. Minimum distance between samples was maintained at 10 mm from each other and 50 mm from sides of the oven. Specimens were aged at 70 ºC and 100 ºC for 70 hours according to ASTM D573 standard to observe property deterioration after aging period.

4 RESULTS AND DISCUSSION

This chapter provides viscosity, cure characteristics, hardness, specific gravity, T.S , elongation at break, modulus 300%, tear strength, abrasion resistance and Demattia flexing of rubber compounds or vulcanizates with KL, 6PPD and SKF antioxidants alone and their combinations at different compositions.

4.1 Viscosity

1st Stage compound

Effect of 3 AO and their combinations in varying loadings on viscosity of the 1st stage compounds are given in Table 4.1. Mooney viscosity of C 01, S 04 and C 02 consisted of individual antioxidants of 2 pphr loadings and showed similar viscosities. Among their combinations to total loading of 2 ppphr, S 01, which consisted of 1.5 ppphr of 6PPD and 0.5 ppphr of KL, has shown markedly increase in viscosity, compared to visicosity of compounds prepared with individual antioxidants. This increase is believed to be caused by a reduction in degree of chemical mastication during mixing. This could also be happened as a result of efficient antioxidant synergistic effect with the antioxidant combination in S 01. In general, efficient antioxidant is made its influence to stabilize rubber molecules during high shear mixing, resulting in relative high molecular weight and result with a high Mooney viscosity (jialin, 2003). KL with SKF antioxidant at similar combination (S 07), too, showed slightly higher viscosity compared to other combinations, however, synergitic effct in viscosity improvement is not dominant as with KL and 6PPD (S01).

When KL loaidng incresed from 0.5 to 1.5 ppphr and 6PPD loading decreased from 1.5 ppphr to 0.5 ppphr (S 01 to S 02 to S 03), visocisty decreased. KL with SKF at the same composition shows a similar variation (S 07 to S 08 to S 09). However, further researches are to be carried out to find the best optimized composition.

When the KL loading increased from 2 ppphr to 3 ppphr at 0.5 ppphr intervals (S 04, S 05, S 06) and KL used alone, viscosity further decreased. It is known that the high antioxident loading is influenced on vicosity reduction due to macromolecular lubricating phenomina (Kumaran el al, 1977).

Table 4.1 Variation of MI and MF of 1st stage compound with different AO

Compound	MI (MU)	MF (MU)
C 01	167.6	85.6
S 01	181. 6	92.8
S 02	169.7	86.4
S 03	167.7	85.8
S 04	167.5	85.6
S 05	165.6	84. 5
S 06	163.6	83.2
C 02	167.6	85.7
S 07	171.0	87.5
S 08	169.5	86.2
S 09	166.9	85.1

2nd stage Compound

Effect of the three antioxidants and their combinations in varying their loadings on 2nd stage compounds were studied and the viscosity variations are given in Table 4.2.

Table 4.2 Variation of MI and MF of 2nd stage compound with different AO

Compound	MI (MU)	MF(MU)
C 01	94.5	63.6
S 01	99.1	68.6
S 02	94.0	63.3
S 03	94.5	63.7
S 04	94.4	63.5
S 05	93.0	62.1
S 06	93.9	60.7
C 02	94.5	63.7
S 07	94.4	65.6
S 08	94.2	65.3
S 09	94.4	63.3

2nd stage compound follow the same pattern as of the 1st stage viscosity variation. This could be explained with the same reasons explained above. In general 1st stage compounds have high viscosity than 2nd stage compounds since the 2nd stage compounds are subjected to further cycle of mixing to the 1st stage compounds. This viscosity difference is reflected and proven by test results as well. However, in contrast to the visocity variation of the 1st stage compounds, 2nd stage compounds with KL and SKF combinations (S 04, S 05 and S 06) showed higher visocity compated to those with KL and 6PPD combinations (S 07, S 08 and S 09) at similar antioxidant loadings.

4.2 Cure charcateristics

Effect of the three antioxidants and their combinations in varing loadings on cure characteristics of compounds, such as M_L, M_H, t_{S2} and t_{90}, were determined as described in Section 3 and they are tabulated in Table 4.3.

Table 4.3 Effect of different loadings of AO on cure characteristics

Compound	**M_L (Mooney)**	**M_H (Mooney)**	**t_{s2} (min)**	**t_{90} (min)**
C 01	20.5	84.7	5.2	12.3
S 01	20.3	85.0	5.2	12.4
S 02	20.0	84.9	5.4	12.5
S 03	20.5	85.1	5.3	12.2
S 04	20.3	84.8	5.3	12.3
S 05	20.1	84.6	5.2	12.3
S 06	20.6	84.5	5.2	12.2
C 02	20.1	84.6	5.2	12.4
S 07	20.2	84.6	5.2	12.1
S 08	20.6	84.2	5.2	12.1
S 09	20.4	84.3	5.2	12.4

The processability of the compounds can be studied using M_L and t_{s2} values of rheographs, plots of torque generated with respect to time of curing. $M_{L,}$ the minimum torque of uncured rubber compound, corresponds to the viscosity or stiffness of the rubber compound. t_{s2}, scorch time, the period before vulcanization, is taken as the torque rise in 2 units above M_L during cure phase. Scorch is premature vulcanization in which the rubber becomes partly vulcanized before the product is in its final form and ready for vulcanization. This reduces plastic properties of the compound, therefore further processing of the compound is restricted. All the compounds did not show any significant variation of either M_L or t_{s2}. Therefore, it was evident that time required for the beginning of the process of crosslinking is not significantly influenced by the type and loading of antioxidant, and their combinations and compositions.

During the cure process, crosslinks are formed. It is found that $t_{90,}$ the optimum cure time, is not affected with type of antioxidant or their loadings. M_H, the maximum torque, which is an indication of the physical proprieties of the compound, too did not show a significant variation with type of loading of the antioxidant.

Cure charasteristics were reported as not influenced by Lignin or Lignin and other antioxidant combinations in another study (Gregorova and Moravck, 2005), confirming the findings of the present study. This is a positive indication and confirms the possibility of substituting KL with 6PPD and SKF antioxidant as combinations in industrial applications with minimum influence on cure characteristics (kova and ovicova, 2006).

4.3 Specific Gravity

Effect of three antioxidants and their combinations in varying loadings on specific gravity of the vulcanizates were determined as per the method given in Section 3 and the specific gravities are tabulated in Figure 4.1. Specific gravity of the vulcanizates were within the range 1.097 to 1.112, varying at 0.015. This variation is not significant, however, the vulcanizate contained KL alone showed the highest specific gravity. This implies that there is no correlation between antioxidant activity and specific gravity of rubber vulcanizates.

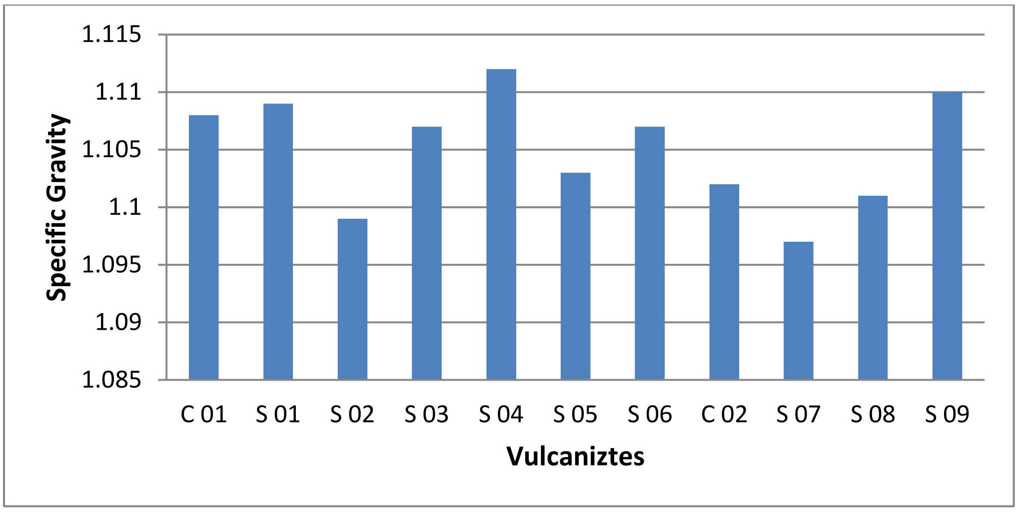


Figure 4.1 SG of vulcanizates with three AO and their combinations

4.4 Hardness

Effect of three antioxidants and their combinations in varying loadings on hardness before and after aging were determined as described in Section 3. The hardness values obtained are tabulated in Table 4.4, and the % change in hardness after aging is presented in Figure 4.2.

Hardness of the vulcanizates before aging were within the range of 64 to 66 Shore A. Vulcanizates with 6PPD (C 01) and SKF (C 02) showed hadness of 64 Shaore A, and that with KL (S 04) showed hardness of 1 Shore A unit greater. Further, increase of the KL loading, when used alone or combined with 6PPD and SKF, increased hardness slightly. This increase could be due to enhancement of crosslink development by KL or alternative interactions between KL and NR. However, it was reported in literature that the variation of hardness before aging was negligible with the type and loading of the anitoxidant (Gregorova and Moravck, 2005).

Hardness increased in all vulcanizates after aging at 70 °C by 2 to 3 Shaore A units and increased further by 2 to 3 Shore A units when aged at 100 °C. Moreover, the increase by approximatly 9% was high with increase of KL loading when used alone, compared to the increase in combinations with 6PPD (approximately 7%) and with SKF (approximatly 6%). This could be the reason of possible crosslinking of KL with NR during further heating at 70 °C and at 100 °C, thereby restricted to indentation.

Table 4.1 Effect of three AO and their combinations on hardness, before and after aging

Compound	Hardness (Shore A)		
	before aging	after aging at 70 ^{0}C	after aging at 100 ^{0}C
C 01	64	66	69
S 01	64	66	69
S 02	65	67	70
S 03	66	68	71
S 04	65	67	71
S 05	66	69	72
S 06	66	69	72
C 02	64	66	68
S 07	65	67	69
S 08	65	67	69
S 09	66	68	70

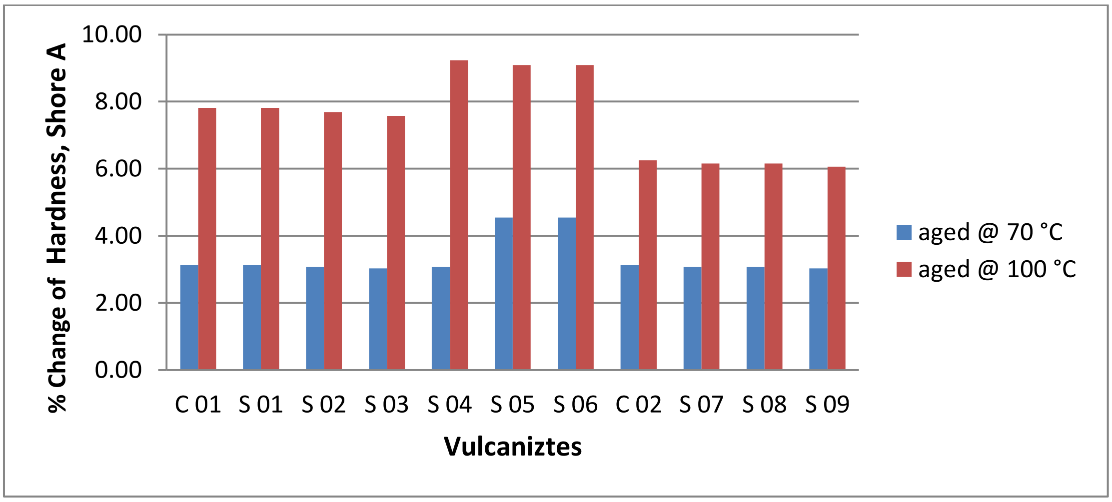


Figure 4.2 % Change of hardness of vulcaniztes with three AO and their combinations after aging

4.5 Tensile Streangth

Tesnisle properties were determined as per the method given in Section 3. Effect of three antioxidants and their combinations in different loadings on T.S before and after aging are presented in Table 4.4 and Figure 4..4. % Change of T.S of vulcanizates after aging at 70 °C and at 100 °C is shown in Figure 4.5.

Vulcanizates with 2 pphr of 6PPD (C 01) and SKF (C 02) before aging shows lower T.S when compared to the vulcanizates with 2 pphr of KL (S 04). Further, vulcanizates with KL alone (S 04, S 05 and S 06) or combined with 6 PPD (S 01, S02 and S03) and with SKF (S07, S08 and S 09) show increase of T.S with increase in KF loading. These increases are expected, since in another study (Gregorova and Moravck, 2005) had also indicated that the incorporation of lignin into rubber matrix increased T.S of NR due to stabilization effect of lignin in NR. Chemical functional groups present in lignin, namely carbonyl, hydroxyl, methoxyl and carboxyl have the ability to increase attraction among rubber molecules (Kumaran el al, 1977).Carbonyl is a polar functional group which has approximately 2/3rd potion of the dominant functional group present in lignin. Since those functional groups show polar and non-polar activities, the ability of lignin to incorporate with different ingredients of rubber compound is enhanced (Gregorova and Moravck, 2005). Interactions between molecules absorb more energy to breakdown molecules and hence when the loading is greater than 2 pphr, vulcanizates show greater T.S s. This is in agreement with the slight increase in hardness at higher KL loadings.

Table 4.2 Effect of three AO and their combinations on TS of vulcanizates before and after aging

Vulcaniztes	**Tensile Strength (MPa)**		
	Before aging	**After aging at 70 °C**	**After aging at 100 °C**
C 01	27.9	27.0	21.0
S 01	28.0	27.3	21.4
S 02	28.2	27.6	22.1
S 03	28.3	27.7	21.8
S 04	28.7	28.1	22.2
S 05	29.1	28.4	22.7
S 06	29.3	28.8	22.8
C 02	28.0	27.2	21.1
S 07	28.0	27.5	21.8
S 08	28.1	27.3	21.8
S 09	28.3	27.2	21.2

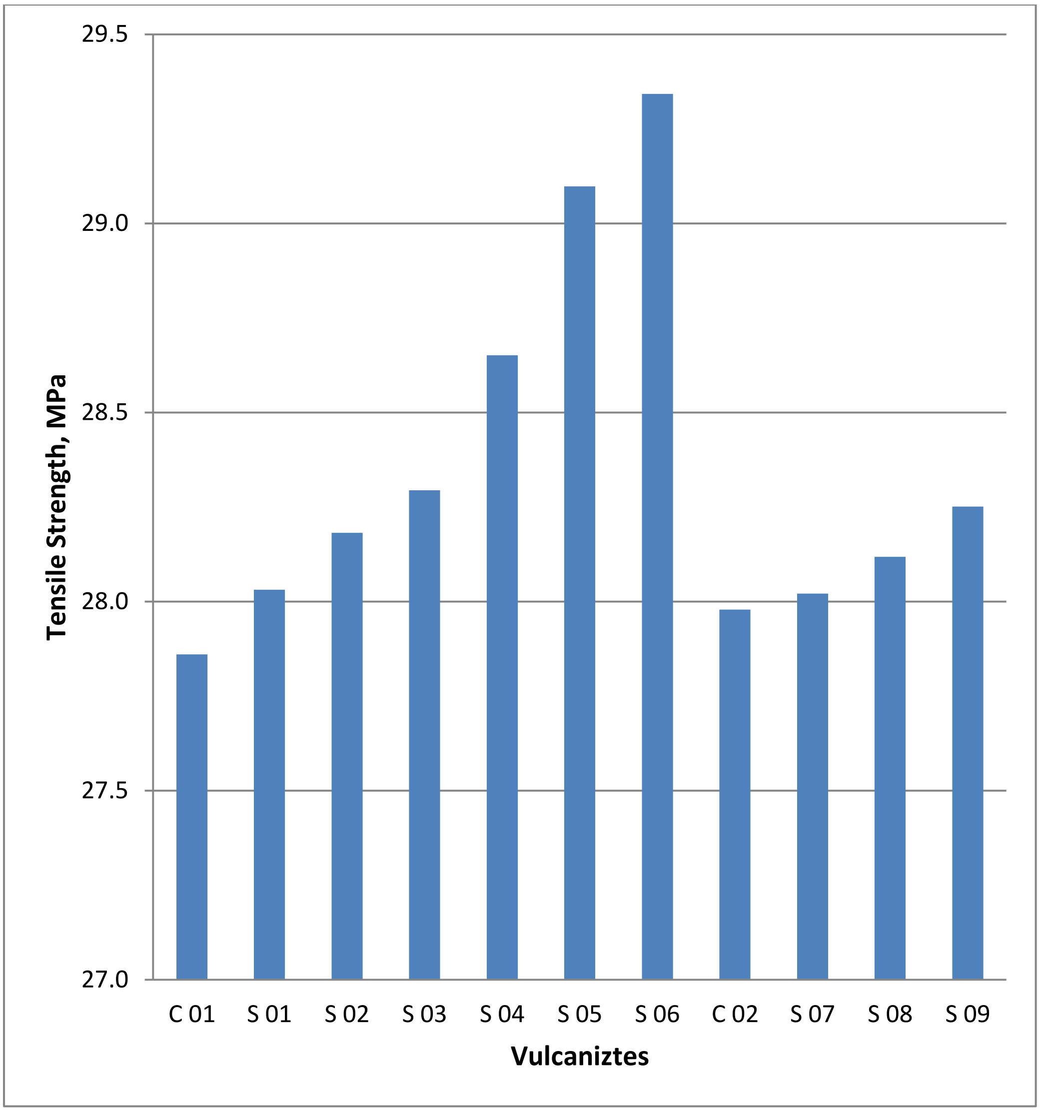


Figure 4.3 T.S of rubber vulcanizates with three AO and combinations before aging

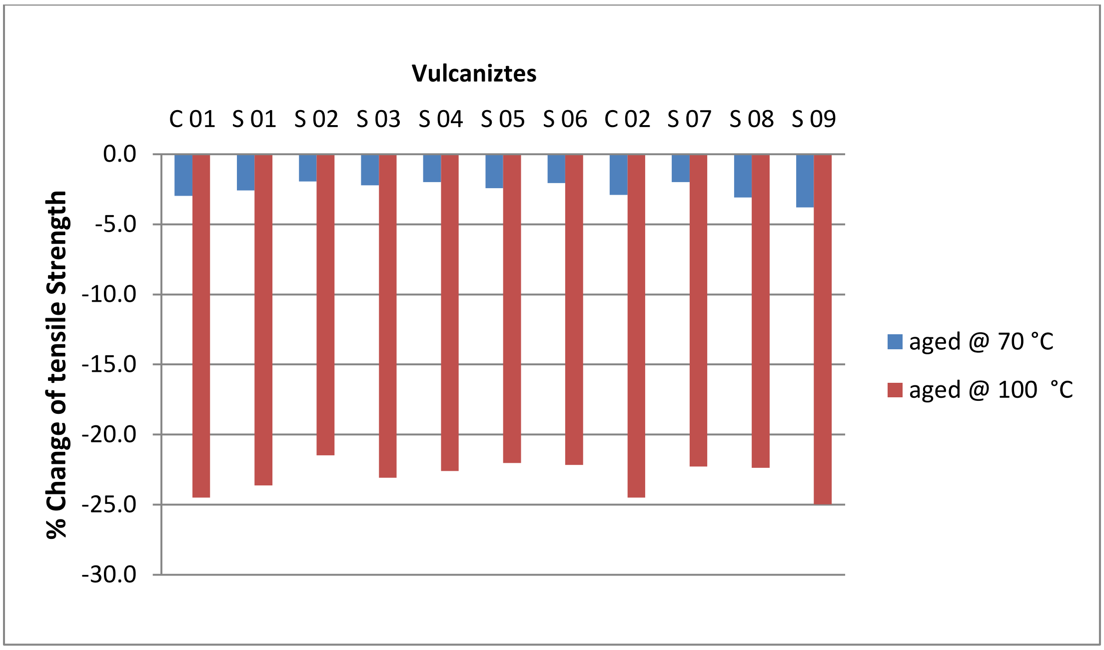


Figure 4.4 Percentage variation in TS with different AO combinations after aging

The T.S of the aged vulcanizates are reduced due to aging and the intensity of the drop is prominent at 100 °C. Breakdown of NR chain is led by oxidation reactions during aging process, which influence the T.S reduction. It is clear that at higher temperatures the tendency to degradation is significant. However, vulcanizates stabilized in the presence of antioxidants are rather stable towards thermo-oxidation process and the maximum reduction of strength was 24%. Vulcanizate with 1 pphr of 6PPD and 1 pphr of KL have shown slightly better thermal stability on tensile properties than with other combinations. This could be a synergistic effect of both 6PPD and KL.

The reasons for improved T.S during aging can be explained with several possible explanations. The phenolic structure of KL contains reactive free radicals. These free radicals are influenced to stabilize NR free radicals generated due to thermo-oxidation reaction in the NR compounds. On the other hand, the tensile retention can also be explained by strong intramolecular attractions between NR chain and the various substitute groups in KL (Gregorova and Moravck, 2005)

4.6 Elongation at Break

Effect of 3 AO and their combinations in varying loadings on elongation at break before and after aging were measured.The results obtained are tabulated as shown below.

Table 4.3 Effect of different AO loadings on elongation at break before and after aging

Vulcaniztes	**Elongation at break**		
	Before aging	**After aging at 70 °C**	**After aging at 100 °C**
C 01	505	492	365
S 01	508	496	363
S 02	511	500	368
S 03	514	500	366
S 04	516	503	368
S 05	519	507	369
S 06	521	509	367
C 02	507	494	357
S 07	507	495	360
S 08	510	496	361
S 09	513	500	364

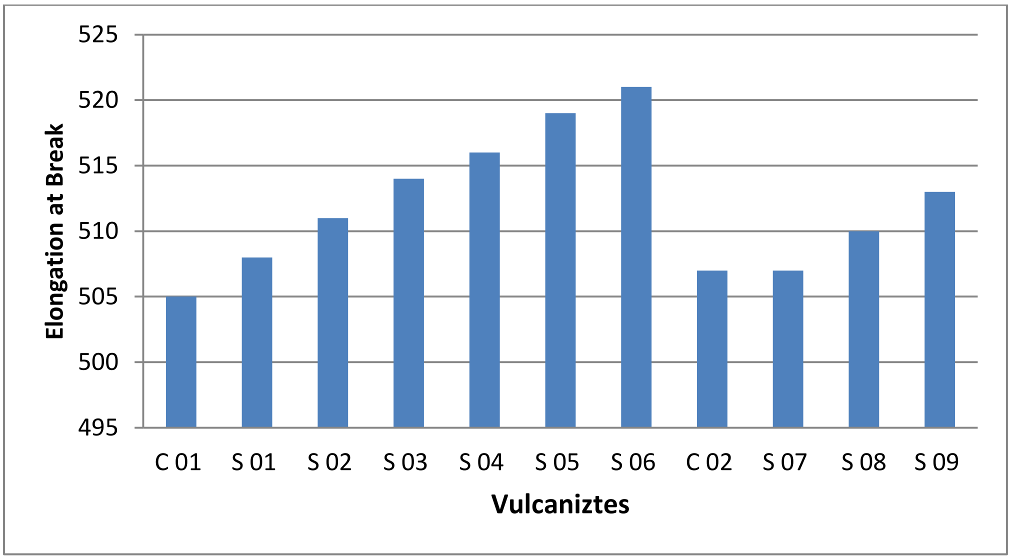


Figure 4.5 Dependence of elongation at break before aging with different AO loadings before aging

Vlucanixates with 6PPD (C 01) and SKF (C 02) before aging show lower Elongation at break when compared to the vulcanizates with 2 pphr of KL (S 04).As KL loading increase Elongation at break also increase with KL alone and KL + 6PPD or KL+SKF Vlucanixates. This implies that KL loading has positive impact on elongation at break before aging .

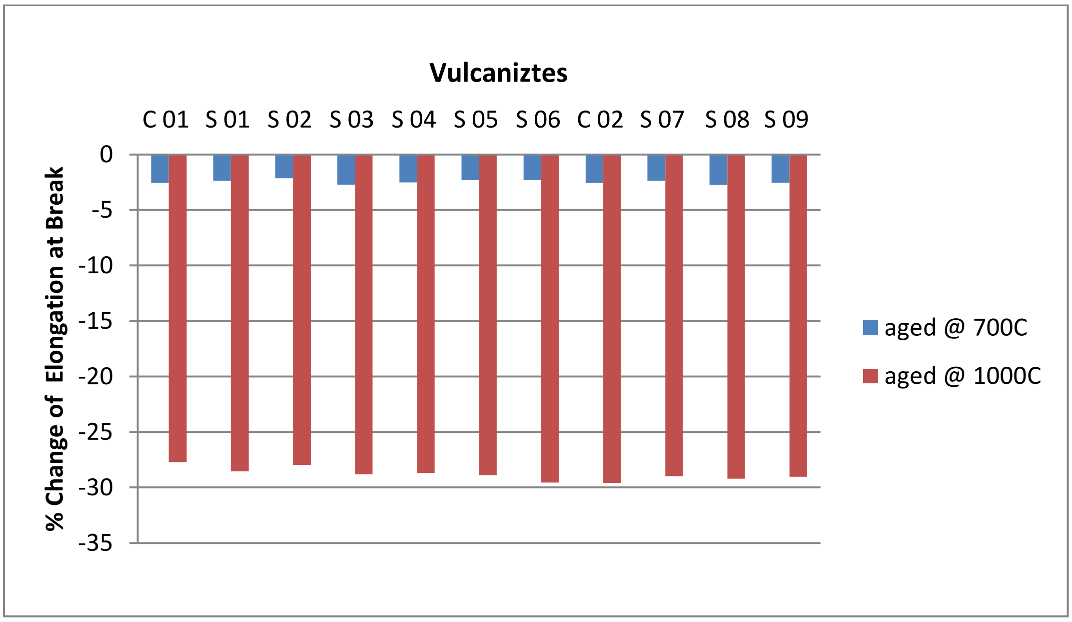


Figure 4.6 Dependence of elongation change % with different AO combinations before and after aging

Results indicate that elongation at break before and after aging also follow the same pattern of T.S results. Lignin attraction cause to increase of initial elongation at break (Kumaran el al, 1977). Elongation reduction is not much significant at 70 ºC aging condition. But at 100 ºC vulcanizates S 01 2 has shown slight improvement of retention of physical properties. This could be due to enhance thermal stability of the vulcanizates due to active contribution of antioxidant activity at considerable higher temperature.

4.7 Effect of Different Antioxidant Combinations on 300% Modulus

Effect of 3 AO and their combinations in varying loadings on 300% modulus before and after aging were measured.The results obtained are tabulated as shown below.

Table 4.4 Effect of different AO combinations on 300% modulus before and after aging

Vulcaniztes	**Modulus 300% (MPa)**		
	Before aging	**After aging at 70 °C**	**After aging at 100 °C**
C 01	12.9	14.5	17.0
S 01	12.9	15.0	17.4
S 02	12.9	15.0	17.5
S 03	13.0	15.0	17.4
S 04	13.2	15.2	17.8
S 05	13.2	15.3	17.9
S 06	13.3	15.4	18.0
C 02	12.8	14.9	17.2
S 07	13.0	15.1	17.5
S 08	13.1	15.2	17.5
S 09	13.1	15.2	17.7

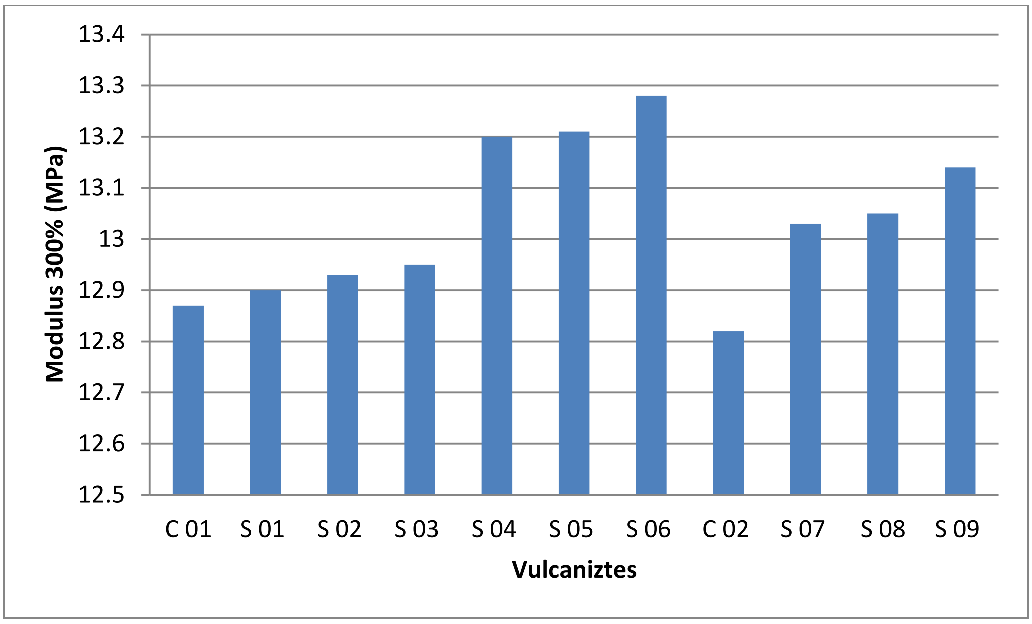


Figure 4.7 Dependence of 300% modulus with different AO combinations before aging

300% Modulus of vulcanizates C 01 ,C 02 before aging at the range of 12.8-12.9. while S 04 sample show 13.2 which is a comparative higher value. Property increase with KL loading for Vulcanizates of KL alone, KL+SKF and KL+ 6PPD. These results indicate that KL loading increase improve the property 300% modulus.

Even the variation of modulus before aging and after aging are not much significant, however slight improvement of modules is exhibited with increasing K.L loading. The reason to display this trend could be due to better incorporation of K.L in rubber matrix.As K.L increases the immobilized rubber molecule proportion in the matrix, it would result less elasticity of the composite. This could be the reason for positive trend of modulus with increasing K.L dosage (Gregorova and Moravck, 2005).

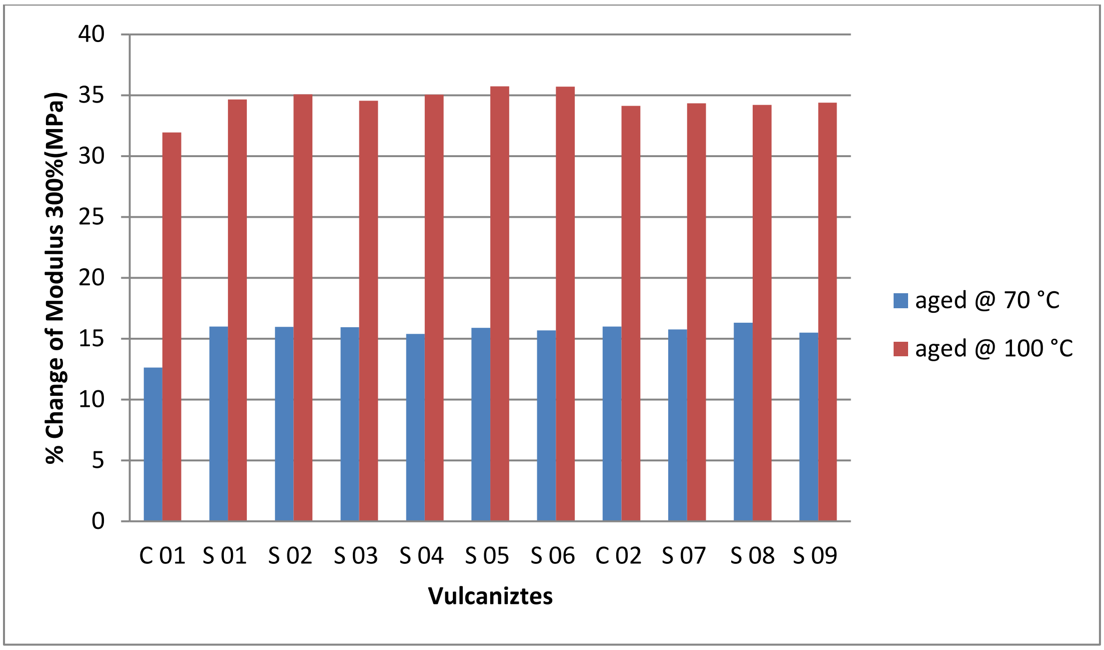


Figure 4.8 Dependence of 300% modulus change with different AO loadings after aging

After aging the modulus are increased as expected. It is clear that this is happened with cross links formation. It is also observed that the modulus is gradually increased for K.L/6PPD combination than 6PPD control. This could be explained as a result of high compatibility of K.L in rubber matrix.

4.8 Tear Strength

Effect of 3 AO and their combinations in varying loadings on tear strength before and after aging were measured.The results obtained are tabulated as shown below.

Table 4.5 Effect of different AO loadings on tear strength before and after aging

Vulcaniztes	**Tear Strength (kN/m)**		
	Before aging	**After aging at 70 °C**	**After aging at 100 °C**
C 01	62.62	60.10	54.86
S 01	63.80	61.16	55.89
S 02	65.31	63.62	59.33
S 03	65.59	63.01	58.24
S 04	68.09	65.83	61.20
S 05	66.74	65.08	59.35
S 06	69.68	67.62	62.48
C 02	60.54	60.04	55.70
S 07	61.92	59.68	54.82
S 08	63.48	61.28	56.72
S 09	65.72	63.15	58.97

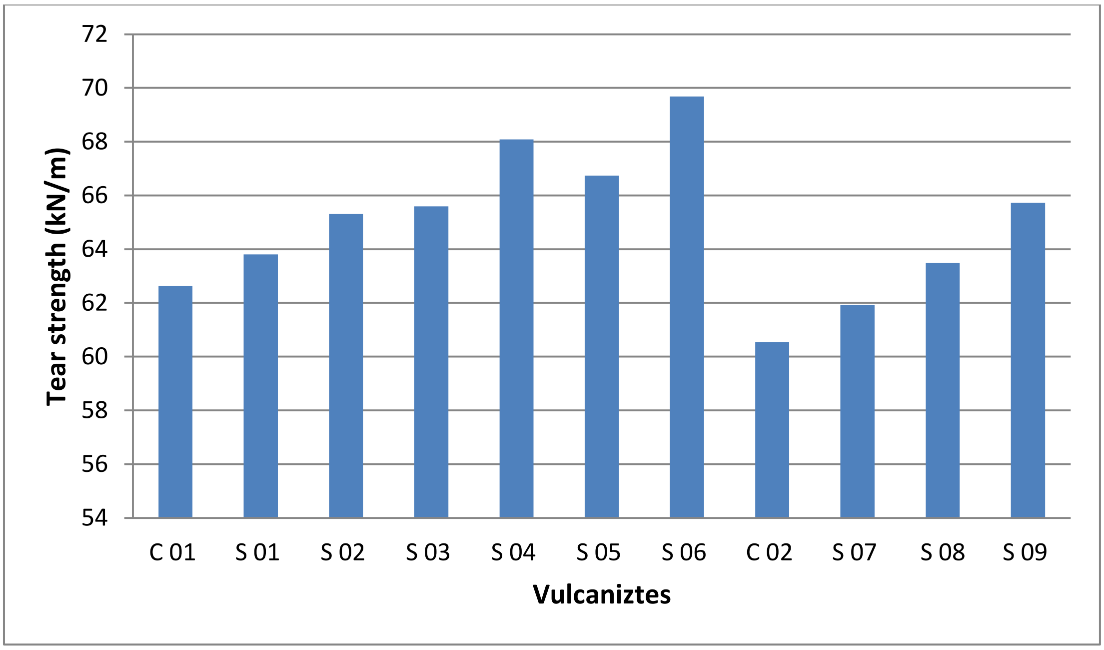


Figure 4.9 Dependence of tear of the vulcanizatess with different loadings of AO before aging

Vulcanizates with 2 pphr of 6PPD (C 01) and SKF (C 02) before aging show lower tear strength when compared to the vulcanizates with 2 pphr of KL (S 04). KL loading for the vulcanizates with 6PPD, SKF show improvement of the property. Vulcanizates with KL alone as AO improved tear strength with KL loading. Therefore KL loading shows a positive impact on tear strength improvement.

The effect on tear strength was tested and results presented in Table 4.9. Initial tear strength variation also followed the same pattern of T.S with a slight variation. It is explained by greater intermolecular attraction of lignin in its higher loadings (Kumaran el al, 1977) .It is also explained that lignin molecules are act as a binder for rubber molecules. It is responsible to form a strong structure and require more energy to brake or tear.

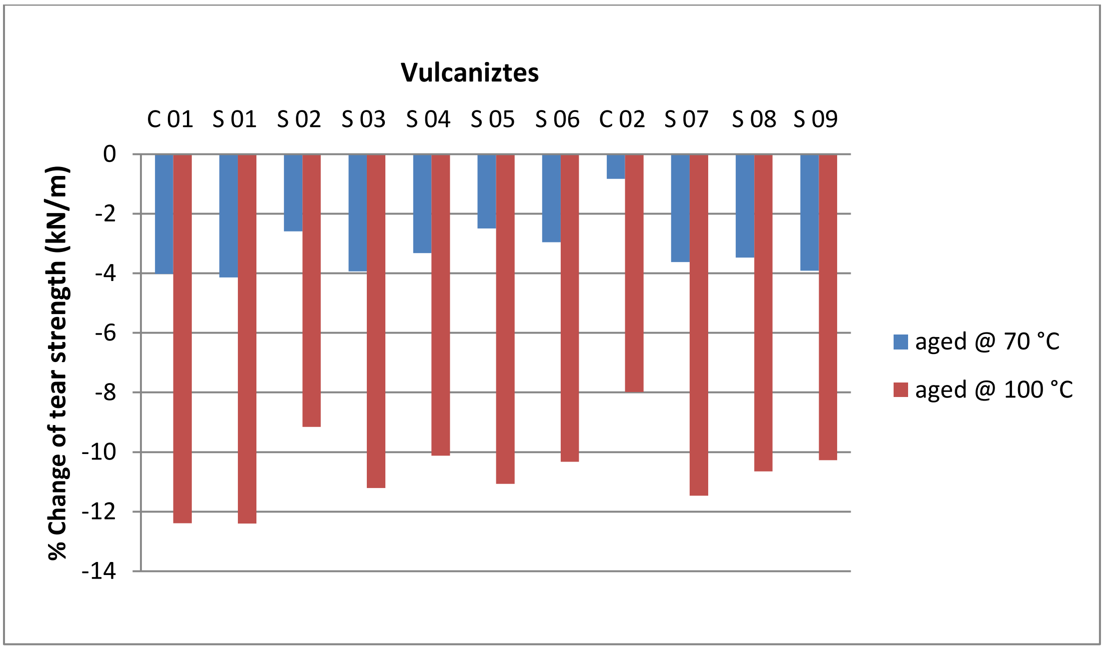


Figure 4.10 Tearing change % with different AO loadings after aging

Results show that the tearing retention reduced at high temperature. This happens because of degredation process. S 02 shows high thermal stability compared to other vulcanizates. It could be due to synergic effect of two antioxidants. Efficient antioxident activity and strong crosslinking are the probable explanation for this . Results indicate that SKF along as an antioxidant shows abnormal increase of thermal stability (Yu and Jia, 2016).

4.9 Abrasion Resistance

Effect of 3 AO and their combinations in varying loadings on abrasion Lose before and after aging were measured.The results obtained are tabulated as shown below.

Table 4.6 Effect of different AO loadings on abrasion lose before and after aging

Vulcaniztes	**Abrasion Loss (mm^3)**		
	Before aging	**After aging at 70 °C**	**After aging at 100 °C**
C 01	119.1	129.2	170.7
S 01	118.8	128.2	168.8
S 02	118.5	125.7	167.1
S 03	117.6	125.2	166.2
S 04	116.4	122.8	165.0
S 05	116.3	124.0	163.7
S 06	114.2	120.6	161.7
C 02	118.1	124.5	170.3
S 07	117.5	123.2	169.7
S 08	116.2	122.5	164.3
S 09	115.5	121.5	163.9

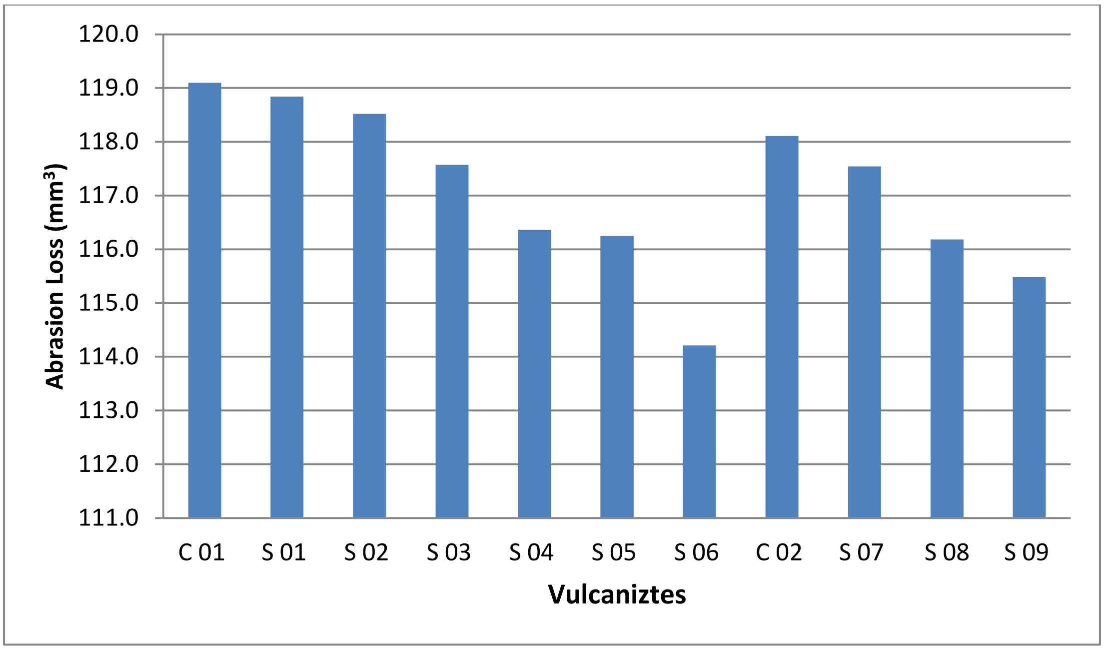


Figure 4.11 Dependence of abrasion loss of the vulcanizatess with different loadings of AO before aging

The results indicate the effect on abrasion loss is very less for vulcanizate except S 6. The vulcanizate of S 6 (3 pphr K.L loading) is displayed a slight reduction of abrasion loss. The property of improved inter molecular interaction of lignin might be the reason for this observation.

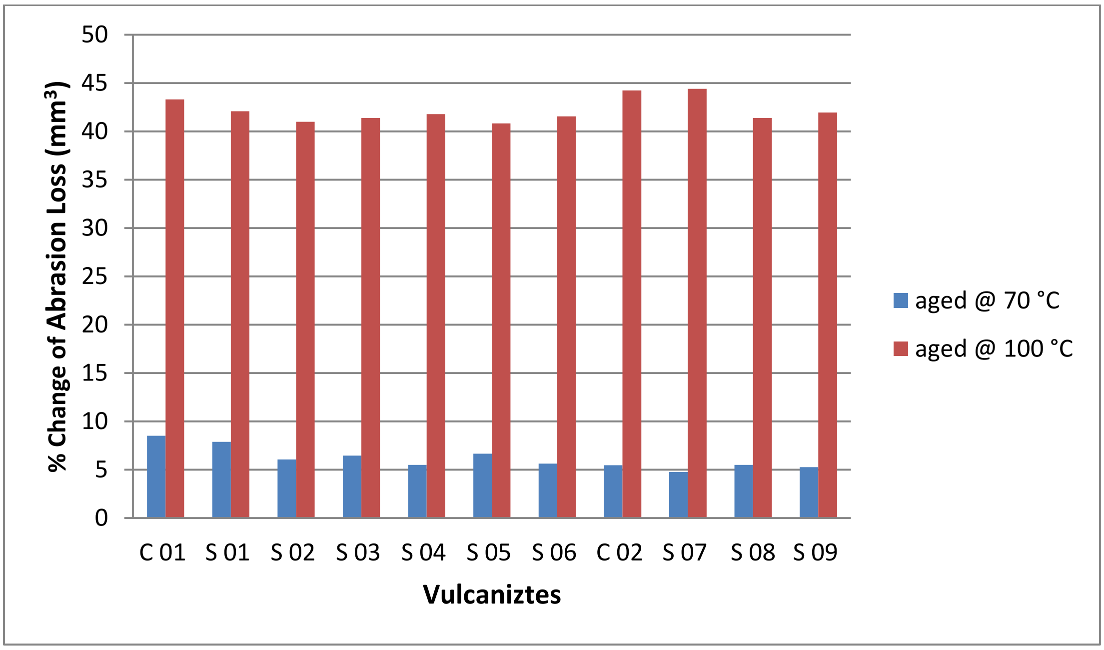


Figure 4.12 Abrasion loss % with different AO loadings after aging

The results indicate that abrasion loss at higher temperature is higher than the low temperature aging due to aggravated thermal decomposition.Abrasion resistance after aging showed a slight improvement and constant trend over 1pphr up to 3 pphr K.L loading for K.L/6PPD blend .it is also shown that after 1 pphr of K.L, the abrasion resistance is improved for K.L/SKF blend as well. It can be explained that the abrasion resistance improvement for S 2 vulcanizate is because of efficient antioxidant effect. But for S 07 vulcanizate the abrasion resistance at higher temperature is not improved as other mechanical properties. This is an unexplainable observation as the other unknown factor irrespective of antioxidant is influenced on this (Yu and Jia, 2016).

4.10 De Mattia Flexing

Effect of 3 AO and their combinations in varying loadings on cycles for the first pin hole before and after aging were measured.The results obtained are tabulated as shown below.

Table 4.7 Effect of different AO loadings on cycles for the first pin hole before and after aging

Vulcaniztes	**Cycles for first pin hole**		
	Before aging	**After aging at 70 °C**	**After aging at 100 °C**
C 01	60000	45700	28500
S 01	60000	32500	55200
S 02	20000	32500	28500
S 03	17000	30000	17000
S 04	8000	7000	4000
S 05	7000	5000	4000
S 06	8000	5000	4000
C 02	8000	7000	17000
S 07	15000	4000	17000
S 08	11000	8500	11000
S 09	15000	7000	11000

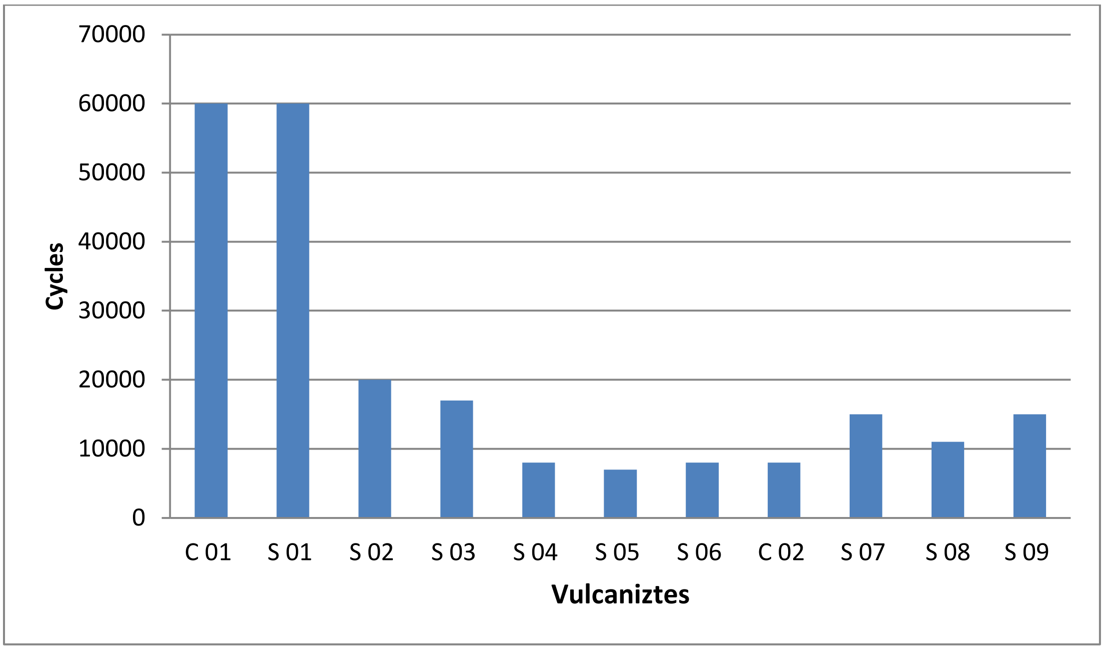


Figure 4.13 Dependence of cycles for the first pin hole of the vulcanizates with different loadings of AO before aging

Vulcanizates with 2 pphr of KL (S 04) and SKF (C 02) before aging show lower cycles to reach for first pin hole when compared to the vulcanizates with 2 pphr of 6PPD (C 01). As the KL loading increases S 02 , S 03, S 04 , S 05 samples show the reduction of cycles to first pin hole. High resistance to flex fatigue of vulcanizates with high loading of 6PPD can be explained by its anti cracking ability. 6PPD itself possesses an anti cracking property in addition to AO property. Which helps to increase cycles for first pin hole.

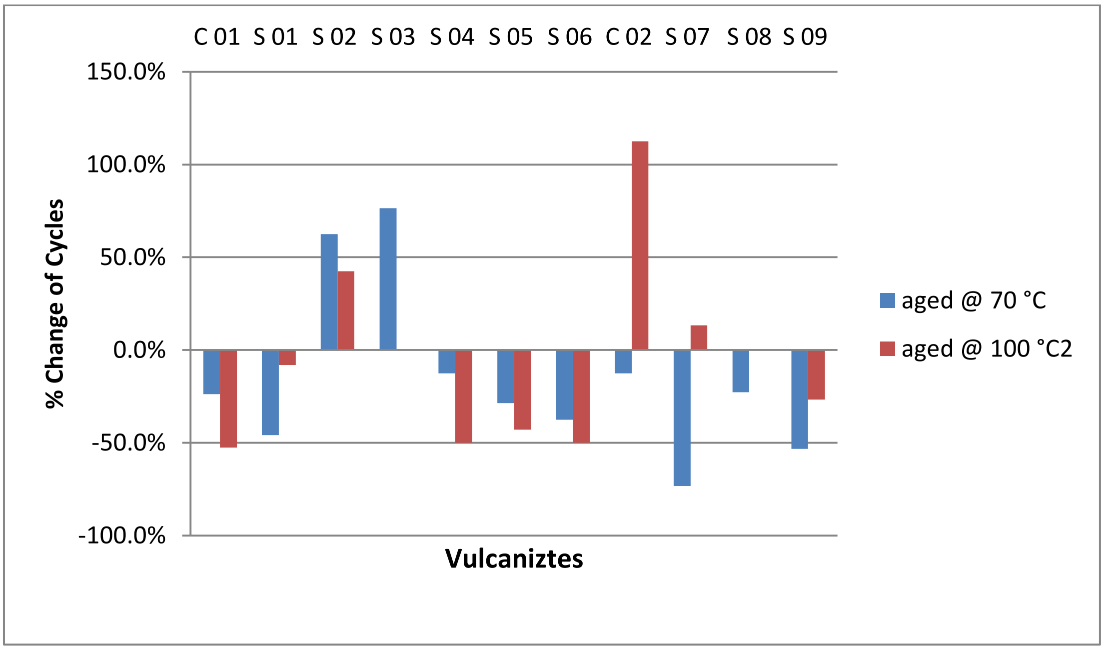


Figure 4.14 Cycles for the first pin hole, change % with different AO loadings after aging

Effect of 3 AO and their combinations in varying loadings on cycles for the full crack before and after aging were measured.The results obtained are tabulated as shown below.

Table 4.8 Effect of different AO loadings on cycles for the full crack before and after aging

Vulcaniztes	**Cycles for full crack**		
	before aging	**after aging at 70 °C**	**after aging at 100 °C**
C 01	315000	203900	135000
S 01	315000	185876	130500
S 02	232000	150000	127056
S 03	200000	125609	75000
S 04	42000	32500	62000
S 05	27000	32500	62000
S 06	29000	32500	62000
C 02	180000	70000	89999
S 07	83000	70000	89999
S 08	56000	50000	75000
S 09	60000	40000	90000

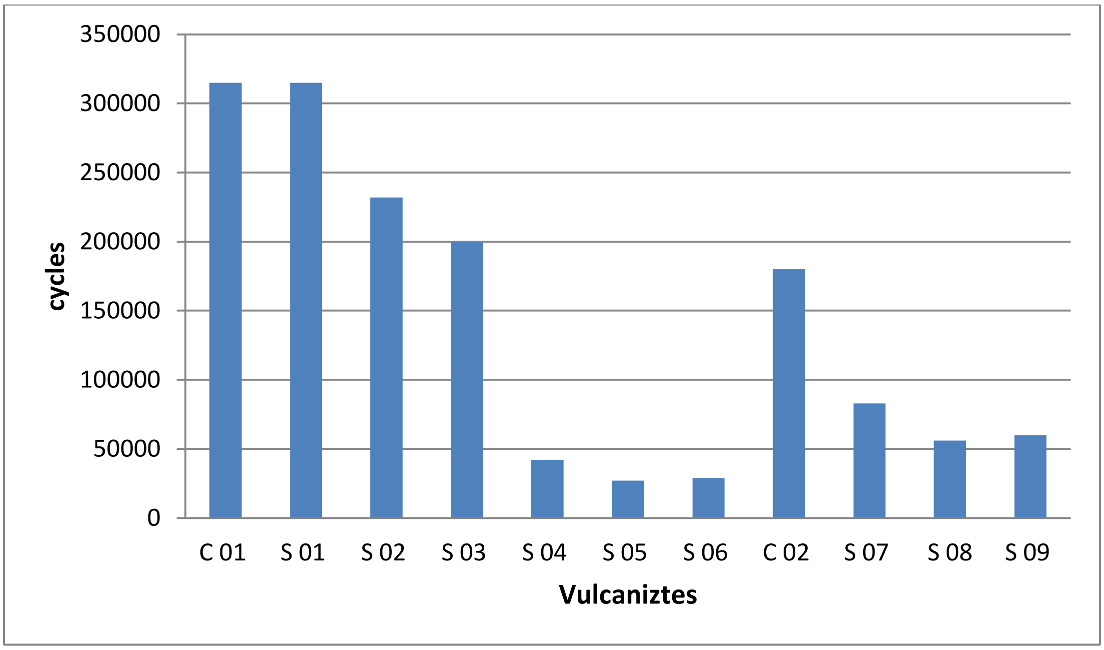


Figure 4.15 Dependence of cycles for full crack of the vulcanizates with different loadings of AO before aging

Flex fatigue life of vulcanizates with 6PPD is higher than vulcanizates with SKF or KF which can explained by 6PPD’s anticracking property.

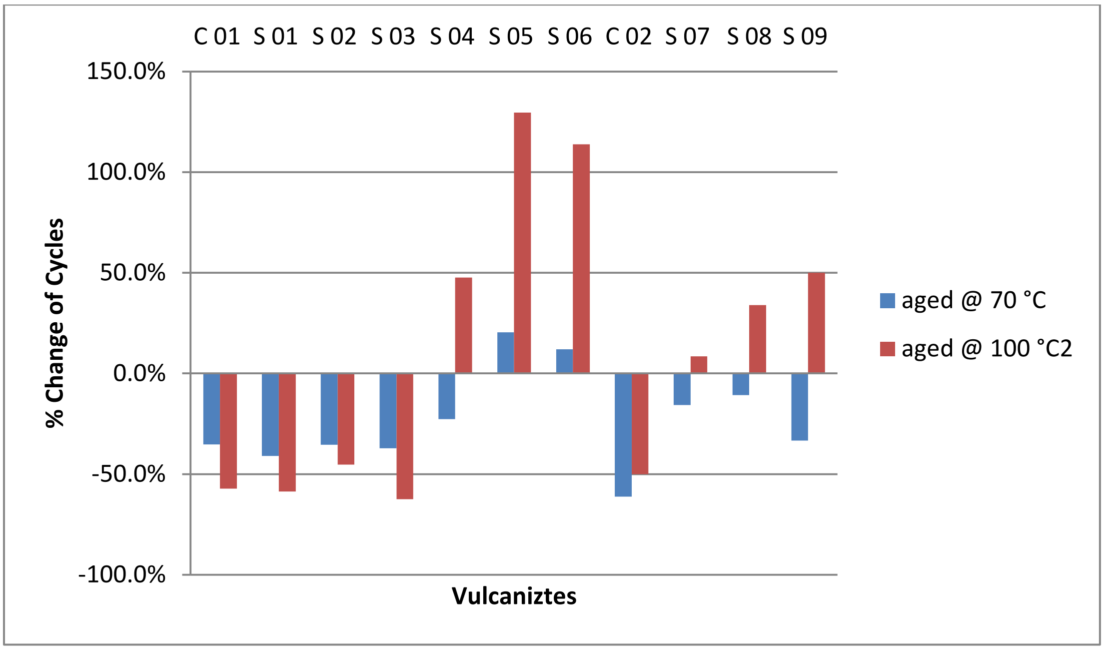


Figure 4.16 cycles for the full crack , change % with different AO loadings after aging

The flex-fatigue life of rubber compounds with different amounts of antioxidant is shown in Figure 4.15. The results are shown that the flex-fatigue life of rubber compounds are dramatically decreased with increasing K.L amount, especially when the K.L amount increased from 2 pphr to 3 pphr of K.L loading. As the K.L content is increased the flex-fatigue life is decreased for K.L/SKF blend as well.

There are many other factors influencing the fatigue life, such as the degree of crosslinking, the type of polymer matrix, antioxidant ability and so on. High cross linking density could result to lower the flex fatigue life. (Wu and Zhang, 2006) Reason for the reduction of fatigue life with high pphr of lignin could be the high interaction ability of lignin. Since lignin has attractive functional groups it has the ability to act as a crosslinking agent. This could result a reduction of flex-fatigue life with increasing lignin loading.

It is interesting to observe that the flex-fatigue life is enhanced with at 100^0C aging condition. This abnormal behavior is yet to be discovered. On the other hand improved flex fatigue life at higher temperature is indicated where lignin loading are higher than 2 pphr of 6 PPD blend, SKF itself and lignin SKF blends

5 CONCLUSION

- Blend of lignin and other antioxidants demonstrate better antioxidant effect rather than lignin alone.
- Incorporation of Lignin or Lignin and other antioxidant blends did not affect significantly for the cure characteristics. Minimum influence on cure characteristics confirms the possibility of substituting lignin with tested commertial antioxidant as blends in industrial applications.
- Mooney Viscosity was influenced by addition of Lignin or Lignin and other antioxidant blends. Lubricating or antioxident phenomina are decisive on this scenario
- Addition of Lignin increases the Initial T.S , initial elongation at break and slightly modulus, Tear Strength, abrasion resistance due to increase inter molecular attractions.
- Incorporation of Lignin exhibit minor effect on hardness and Specific Gravity
- Increased Lignin content has affected the flex fatigue life adversely due to enhanced intermolecular attractions

5.1 Suggestions

There are some suggestions to investigate and improve the several areas in this project further. Those suggestions are,

- This research can carry out further to study and optimize the percentage for the best antioxidant effect of Lignin and 6PPD / SKF blend
- Industrial scale test run should be done for the polymer blends in order to address the issues in manufacturing.
- This study was carried with black tread compound. Further work must be done with Non Marking Tread compounds for better evaluations.
- The study can be extended to other compounds in Solid industrial tire (middle, heel, bead and bonding compounds.)
- Study is widely open to evaluate effectiveness of lignin from different wood origin and different extraction technologies.

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ANNEX 1

A1.1 Antioxidants

There are chemicals which can delay the aging process of rubber and increases the durability of the product and such product are called protective chemicals or protective agents.

Major portions of these chemicals are categorized under antioxidants. These chemicals are good against oxygen attack to prevent polymer deterioration.

6PPD is generally recognized as the most effective and widely used all purpose antioxidant. In addition to oxygen protection, it imparts a high degree of protection against flex cracking.

Specification of antioxidant 6PPD is given as follows:

% of Ash Content (max)	0.2 (ASTM D 4574)
Melting point (min) °C	44 (ASTM D 1519)
% of Active Ingredient (min)	97 (ASTM D 4937)
% of Heat loss (max)	0.5 (ASTM D 4571)

The other antioxidant used during the study is SKF and its specification is given below.

% of Ash Content (max)	1 (Bayer 17 B)
% Evaporation loss	0.5 (Bayer 18 A)
Melting point (C)	105

Kraft lignin is experimented as third antioxidant. Among various natural polymers lignin is one of the richest natural polymers in the biosphere. It is a natural phenolic polymer composing up to one third of the material found in plant cell walls. Lignin is available mostly in abundant and renewable resources such as trees, plants and agricultural crops and shown antioxidant properties while keeping non-toxic and extremely versatile in performance. The advantages are obvious lignin as an antioxidant has important potential in tire industrial applications. Therefore kraft lignin was selected as the natural antioxidant for this research.

Lignin is identified as amorphous polymer, it composed of three different cinnamyl alcohol monomers, such as p-coumaryl alcohol, coniferyl alcohol, and Sinapyl alcohol in varying compositions. The diversity in both monomer content and chemical bonds makes the determination of the exact chemical structure of each isolated lignin extremely difficult.

A1.2 Natural rubber

NR is selected as base polymer since it provides intended properties for tread compounds, these properties can be listed as T.S , green tackiness and tear resistance. Micro structure of polymer is supported to achieve these tasks as polymer molecules tend to crystalline at low temperature and also during stretching. Natural rubber was sourced from one specific supplier of Sri Lanka. Principal intension of this action is to control viscosity of the base polymer.

Mooney viscosity [ML(1+4) at 100 °C]	75 +/-15
% Dirt content by mass (Max.)	0.05 (ISO249)
% of Volatile material by mass (Max.)	0.8 (ISO248)
% of Nitrogen content (Max)	0.6 (ISO1656)
% of Ash by mass (Max.)	0.5 (ISO 247)
Initial Wallace Plasticity (Po) * Range (Min.)	30 (ISO 2007)
Plastic Retention Index (PRL) (Min.)	70 (ISO 2930)

A1.3 Carbon black

Carbon black is the organic filler widely used worldwide. Filler with high surface area (Partial size up to 50 nm) is used to obtain required physical property of tread compounds.

N220 carbon black from Phillip India was selected as reinforcing filler and material specification is described below.

DBP absorption (cm3/100g	110 - 120 (ASTM D 2414)
Iodine adsorption number (g/Kg)	118 – 126 (ASTM D 1510)
Nitrogen adsorption (m2/gm)	119 (ASTM D 4028)
STSA surface area (m2/gm)	106 (ASTM D5816)
Compressed DBP absorption (ml/100/g	98 (ASTM D3493)
Tint strength, % ITRB	116 (ASTM D3265)
Pore density (gm/Lit)	320-370 (ASTM D1513)
Moisture (%)	1.2 Max. (ASTM1509)
Pellet hardness (gf)	15-45 Avg. (ASTM 5230)

A1.4 Activator

Zinc oxide, (inorganic activator) and stearic acid, (organic activator) will be formulated in almost all type of recipe. They are known as activators to accelerators. Activators are activating the process of cross linking formation and produce uniform state of cure in the compound. Modules of the rubber vulcanizates is improved by activators.

High purity Zinc oxide is used for the study. It is known that tracers of metals such as Copper, Manganese, and Ferrous can be present as impurity in Zinc oxide. These metals can cause degradation of polymer. This interference may lead to affect final results of the study.

Zinc oxide used for the study complies with following specification.

% of Moisture (Max)	0.5 (D 280)
% of Pbo (Max)	0.15 (D4075)
% of Purity (Min)	99.5 (D 3280)
% of Sieve Residue (max) 45 Micron (325 mesh)	0.25 (D 4315)
% of Loss on Ignition (Max)	0.6

A1.5 Stearic acid

Rubber grade stearic acid is not pure compound of stearic acid but it is normally a mixture of stearic acid (60%) Pulmitic acid (20%) and oleic acid (20%)
Steric Acid used for the study carries following specification:

Acid Value (mg, KOH/g)	190-215
Iodine Value (Max) (g, 100g)	5
% of Fatty acid C18 (Min)	32

A1.6 Rubber processing oil (Low PAH oils)

In recent years the carcinogenicity of poly cyclic aromatic hydrocarbons comes to be regarded as important. Oils containing 3% or more of polycyclic aromatic compounds (PCA) are obliged to indicate that they are toxic and there is a trend towards regulation of their use. Accordingly, it becomes an urgent task to reduce the content of PCA in rubber process oil to less than 3% these oils are called Low PAH oils.

Kinematic viscosity @ 100 °C	20-32 (ASTM D 445)
Aniline point °C	86-94 (ASTM D611)
Density @ 15.0 cg/ml	0.930-0.950 (ASTM D 1298)
Benzo (a) pyrene (BaP) (Max. ppm)	1
Sum 8 PAH's (Max. ppm)	10
Flash Point (Min.),°C	210 (ASTM D 92)

A1.7 Sulphur

Sulphur is commonly used because of its easy availability and affordable price. Tire industry consumes almost 80% of elastomers and all tires worldwide conventionally getting cured with Sulphur accelerator system.

% of Sieve Residue (325mesh), (Max.)	10 (D 4572-89)
% of Moisture (Max.)	0.5 (2 Hrs @ 105 C)
% of Purity (Min.)	99.5

A1.8 Retarder (Pre vulcanization inhibitor, PVI)

Faster the accelerator, higher is the productivity but it has some disadvantage in processing as well. With faster accelerators the cross linking process may begin in the heat history during the milling and mixing etc. and is often termed premature vulcanization. Precise weighing of this chemical is very important as it is used fairly low amount.

% of Active ingredient content (Min)	95
% of Ash Content (Max.)	0.2
% Drying loss (Heat loss)	0.4 2 hrs /105 °C
Melting point °C	88
% of Volatile matter (Max.)	0.5 Bayer K 234

A1.9 Accelerator

There are wide varieties of accelerators available to the rubber compounds. Sulphenamide is types of accelerators are widely used for tread compounds.

MOR is used as an accelerator and its specification is described below.

% Moisture content (Max.)	0.5 (ASTM D 4571)
% Purity (Max.)	96 (ASTM D 4936)
% Insoluble methanol (Max)	0.5 (ASTM D 4934)
% Ash content (Max.)	0.3 (ASTM 4574)
% Volatile matter (Max.)	0.3 (ASTM D 4571 (15-23)
% Free amine (Max.)	0.4 (ASTM D 4936)
Melting point (C)	75-90