

# Study On Use Of Lignin As An Antioxidant In SBR Based Tire Tread Compound

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**Abstract**—Next to cellulose, Lignin is the second most abundant plant based organic polymer in the world. Currently over 70 million of lignin is produced mainly through chemical pulping process. At present high amount of lignin use as inexpensive fuel or raw material to produce low added value products. The main aim of this study was investigation of potential of lignin to use as low cost, environmental friendly, high effective antioxidant for SBR based tire tread compound. Tread of a solid tire is degraded in static and dynamic conditions as it is exposed with the external environment. Oxygen is the principal environment factor, however, property deterioration are also supported by heat, light, humidity and radiation. Antioxidants hinder the oxidation of rubber and prevent property deterioration. Petroleum-based antioxidants are commonly used in tread compounds, though they have disadvantages like risk on health and adverse influence to environment. Therefore, this study aimed to investigate the possibility of replacing conventional antioxidants with a bio-based substitute. Kraft lignin (KL) is a naturally abundant and cost competitive wood-derivative and possesses antioxidant properties with Phenolic functionality. Lignin was compared with two conventional antioxidants, namely, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and sterically hindered styrenated phenol (SP). KL was varied from 2 to 3 phr at 0.5 phr intervals when it was used alone. When Lignin was combined with 6PPD and SP, each antioxidant was varied from 0 to 2 phr at 0.5 phr intervals, maintaining total loading at 2 phr. Mechanical Properties, Cure characteristics and other industrially important testing on rubber tread compound was investigated before and after thermo-oxidative aging. KL has reinforced the Vulcanizate, showing highest physical properties in tensile strength, tear strength, elongation at break, rebound resilience, hardness and abrasion resistance compared to Vulcanizate prepared incorporating commercially available antioxidants before the aging. After the aging cross linking density, abrasion resistance, rebound resilience and hardness have increased and other properties and their retentions have decreased in lignin alone than other Vulcanizate. Higher properties retention in tensile strength, tear strength, elongation at break and improvement in abrasion resistance except 6PPD and styrenated phenol alone show by Vulcanizate with lignin: 6PPD (1: 1) and lignin: Styrenated phenol (0.5: 1.5) ratios. Blend of KL and other antioxidants demonstrate better antioxidant effect than KL alone. The results obtained are shown that the KL exerts a stabilizing effect. Moreover KL blends with other selected antioxidants increased the stabilization effect.

**Index Terms**—Tire tread compound, Kraft Lignin, Antioxidant

## 1 INTRODUCTION

Polymers are widely used in everyday life. Polymers used for a variety of human needs, ranging from household appliances, auto parts, building materials up to the packaging for a variety of food and electronic components. Polymer degradation is an irreversible process in which useful polymer properties degenerate when exposed to the environment. In most instances degradation involves the rupture of primary chemical bonds and, secondary bonds can also be responsible for polymer degradation. There are several factors that affect this polymer degradation process. Those can be categorized under two main parts and those are external factors and internal factors of polymer. External factors are environment factors like heat, light and other radiations, oxygen, biological factors, water, chemicals, ozone and mechanical stress. Internal factors are chemical structure, physical structure,

impurities and added ingredients etc [1]. This polymer degradation is a chemical reaction which starts first at the polymer surface and then penetrates into the depth of polymer. This degradation takes place during two general periods in the life time of a polymer. The first occurs during the synthesizing, in this period polymer is exposed to relatively high temperature. Long term aging is the second important period of exposure. During this period the polymer is exposed to conditions of actual use, and degradation is more gradual.

Large amount of elastomers namely NR, SBR, Polybutadiene and EPDM are used in the tire industry. The tire industry can be divided into two main categories as solid tires and pneumatic tires. Basic components of normal pneumatic tires are tread, side walls, beads and carcass. Main components of resilience solid tires are tread, cushion rubber center and hard base [2-5]. The base component of every part of the tire is elastomers. Therefore in order to improve the durability of the tire, special attention should be given to control the natural degradation of elastomers. The main reason for tire aging is the oxidation of elastomers. Tire manufacturing companies use

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different type of antioxidants and antiozonants to protect tires from oxidation [6-8].

Lignin, due to the presence of Phenolic functionality, exhibits characteristics of an antioxidant agent in a similar way to the petroleum based organic antioxidants used for polymers [9-11]. Lignin has the capabilities of being used as a stabilizer and/or a dispersant in thermoplastics and thermosets and as a filler and/or a stabilizer in rubbers, but not a significant usage can be noticed in the rubber industry as a whole [12-15].

The focus of this study is to investigate the possibility of replacing the petroleum based organic antioxidants with Lignin in tire manufacturing industry. This paper presents a comparison of ageing properties of tire tread compounds prepared with Lignin and selected commercially available anti-oxidant, and their combinations.

## 2 EXPERIMENTAL SECTION

### 2.1 MATERIALS

Styrene Butadiene Rubber (SBR) was used as the rubber in the tread compound and was received from Rubber Research Institute of Sri Lanka. High abrasion furnace black (HAF, N 330) as the reinforcing filler, sulphur as the vulcanization agent, Tetramethylthiuramdisulfide (TMTD), N-Oxydiethylene-2-benzothiazole sulphonamide (MOR) as the accelerators, stearic acid and zinc oxide of 99.5% purity as the activators, and Naphthenic oil as the processing oil were used and were kindly supplied by the Samson International PLC of Sri Lanka. Two commercially available anti-oxidants N-(1,3-dimethylbutyl) -N'-phenyl-p-phenylenediamine (6PPD) and Sterically hindered polynuclear phenol, Vulkanox® SKF were purchased from Sinorghem, China while the Lignin antioxidant was supplied by Scion- New Zealand. All the ingredients were of industrial grade and were used without further purification

### 2.2 FORMULATION OF COMPOUND

The intentions of investigating to evaluate the effect of natural antioxidant in tread compound and different formulas were developed by changing the antioxidant contents, given in Table 1. 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 1. C01 and C02 were the control compounds.

### 2.3 PREPARATION OF COMPOUNDS

All materials were mixed according to the main formula in Table 1. Mixing and homogenization of elastomers and other compounding ingredients were carried out in a laboratory type internal mixture and two roll mill. One liter capacity internal mixture is used and rotor speeds are maintained at 30 and 35 rpm constant during the experiment. Internal temperature of compound was maintained 65 °C - 80 °C during the mixing. The friction ratio of two roll mill is 1: 1.14. During mixing two roll mill was cooled with normal water.

Mixing and homogenization done with two steps. In first step both internal mixture and two roll mill were used. During the first step SBR, High abrasion furnace (carbon black N330), Naphthenic oil, ZnO and Stearic acid were mixed and prepared eleven batches according to formula in Table 1. According to the mixing cycle in Table 2. All eleven batches were mixed together on two roll mill to homogenize the compound and finely homogenized compound divided into ten batches of 771.17g. Finally those batches were used in second stage of mixing. Second stage of mixing completed on two roll mill. During second stage all antioxidants, accelerators and Sulphur add to the each compounds according to the following formula. Finely from each compound 4mm thickness sheets were prepared separately.

TABLE 1  
COMPOUND FORMULATION

Item Number	Material	PHR									
		C-1	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8	C-2
1	SBR	100	100	100	100	100	100	100	100	100	100
2	Stearic acid	2	2	2	2	2	2	2	2	2	2
3	ZnO	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
4	N 330	47	47	47	47	47	47	47	47	47	47
5	6PPD	2	1.5	1	0.5	0	0	0	0	0	0
6	Kraft Lignin	0	0.5	1	1.5	2	3	1.5	1	0.5	0
7	Phynolic type A O	0	0	0	0	0	0	0.5	1	1.5	2
8	Napthanic Oil	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
9	Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
10	MOR	2	2	2	2	2	2	2	2	2	2
11	TMTD	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Total	164	164	164	164	164	165	164	164	164	164

## 2.4 DETERMINATION OF PROPERTIES

Cure characteristics such as minimum torque (ML - measure of Mooney viscosity and gives an indication of process ability), maximum torque (MH - gives an indication of state of cure), scorch time (TS2 - gives an indication of safe processing time), optimum cure time (T90), cure rate index (CRI) and extent of cure or delta cure (MH - ML, gives an indication of crosslink density) were obtained by an EKTRON (EKT-2000S) type Moving Die Rheometer at 150°C. Electrically heated ram press was used to prepare the rubber vulcanizates at specific thickness as required according to respective standards for test specimens. These sheets were vulcanized at a pressure of 4.5 bar (ASTM requirements is minimum 3.5 bar) and a temperature of 150 ± 20 °C. Optimum cure time, t90, was taken as the vulcanizing time for each compound. Hardness of the vulcanizate were measured according to ASTM D2240 using Shore-A durometer. Tensile properties such as tensile strength, elongation at break and modulus at 300% elongation were determined according to ASTM D412A using Gotech GT-7010-AE tensile testing machine. The dumbbell test specimens were punched out from the moulded 2 mm thick sheets. Gauge length was taken as 20 mm and the elongation was taken as the crosshead separation. Test was conducted at a strain rate of 500±50 mm/min. Tear strengths of the vulcanizates were determined according to ASTM D624 using the same tensile testing machine at the same strain rate. Test specimens were punched using Die C and a nick of depth 1±0.2 mm was made at the centre of its concave edge. Abrasion resistances of the vulcanizates were measured according to ASTM D5963 using a DIN abrader having a drum diameter 150 mm and length 500 mm. Results were expressed as percentage volume loss. Flex cracking was determined using De Mattia tester according to ASTM D623. All the

TABLE 2  
MIXING CYCLE IN INTERNAL MIXER

Stage	Material	Time/min
1	SBR	0
2	ZnO + Steric acid	2
3	HAF 1/2 + Oil 1/2	4
4	HAF 1/2 + Oil 1/2	7
5	Dumping	

specimens were conditioned 24 hours and the tests were performed at  $27 \pm 2$  °C.

Test specimens prepared for tensile, tear and hardness, flexing tests were kept in an aging oven at 70 °C and 100 °C for 70 hours according to ASTM D573 to observe property deterioration after aging period.

steric effect would retard the formation of active sulphurating agents, a reaction intermediate necessary for vulcanization. This may be the reason of increasing optimum cure time with combination of lignin and Phenolic type antioxidant. However, due to Phenolic bulky groups of lignin and SP increase TC90. CRI decreased due to increment of TC 90 values.

### 3 RESULTS AND DISCUSSION

#### 3.1 RHEOLOGICAL PROPERTIES

Effect of three antioxidants and their combinations in varying loadings on cure characteristics of compounds such as ML, MH, TS<sub>2</sub>, T<sub>90</sub> and CRI were determined as described experimental section and they are tabulated in Table 3.

The process ability of the compounds can be studied using M<sub>L</sub> and t<sub>s2</sub> values of rheographs. After attaining minimum torque, during cure phase scorch time T<sub>s2</sub> is recorded as the torque rises 2 units above M<sub>L</sub>. 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. This period before vulcanization starts is generally referred as T<sub>s2</sub>. T<sub>s2</sub> increase with the lignin concentration up to 3.10 minutes. Therefore use of lignin based antioxidant is not affected to curing safety of the compound.

The optimum cure time (T<sub>90</sub>) is usually taken to mean the time for vulcanization of the rubber compound at a definite temperature to obtain optimum physical properties. Usually, the optimum cure is taken at time for 90% or 95% rise in recorded torque for a rheograph. The rise in torque is considered to be proportional to the rise in crosslink density, thus this represent 90% or 95% completion of the cross linking reaction. The control compound C-1 with 6 PPD alone has shown 9.6 minutes for T<sub>90</sub> value and T<sub>90</sub> increase with concentration of lignin in combination of 6PPD and lignin up to 10.1 minutes. The presence of lignin only in the compound T-5 has shown 10.7 minutes for T<sub>90</sub> value. T<sub>90</sub> increase with concentration of SP in combination of SP and lignin up to 11.1 minutes However out of two control samples, Phenolic type antioxidant alone has shown the highest 11.8 minutes for T<sub>90</sub> values. Concentration of lignin and SP increase the T<sub>90</sub> by reducing the rate of vulcanization reaction but T<sub>90</sub> decrease with 6PPD concentration.

The cure rate index (CRI) is the measure of rate of vulcanization based on the difference between optimum vulcanization and the scorch time. Too long cure time may cause reduced network stability and a reduction on properties of vulcanized rubber. Ammine groups can increase the cure rate by catalyzing the formation of active sulphurating agent [15, 17]. The concentration of amine type 6PPD decrease and speed of formation of sulphurating agent decrease then T<sub>s2</sub> decrease. Phenolic type antioxidant decrease the cure rate, associated with the steric hindrance of the bulky groups. This

TABLE 3  
EFFECT OF ANTIOXIDANT ON CURE CHARACTERISTICS

Parameter	Results									
	C-1	T - 1	T - 2	T - 3	T - 4	T - 5	T - 6	T - 7	T - 8	C-2
M <sub>H</sub> (dNm)	83.66	83.75	83.91	84.88	84.92	85.22	85.15	85.96	84.75	84.07
M <sub>L</sub> (dNm)	9.48	9.57	9.81	9.95	9.57	9.97	10.22	8.65	8.64	8.51
T <sub>s2</sub> (min)	3.00	3.00	3.00	3.00	3.10	3.00	3.30	3.10	3.10	3.20
T <sub>c90</sub> (min)	9.60	9.60	9.90	10.10	10.40	10.70	11.40	11.20	11.10	11.80
CRI	15.00	15.31	14.46	14.02	13.82	13.04	12.27	12.37	12.53	11.63

### 3.2 AGEING PROPERTIES

Effect of three antioxidants and their combinations in varying loadings on Hardness were determined as described in chapter 3 and they are tabulated in Table 4. Hardness of vulcanisates before the aging were not influenced by lignin or ignin and other antioxidant combinations except C-1 and blend T-1. This is a positive indication that confirm the possibility of replacing lignin with SP antioxidant as combinations in industrial applications with minimum effect on Hardness.

TABLE 4  
EFFECT OF THREE AO AND THEIR COMBINATIONS ON HARDNESS OF VULCANIZATES BEFORE AND AFTER AGING AND IMPROVEMENT

Vulcaniztes	Hardness (Shore A)		Improvement %
	Before aging	After aging	
C-1	63.00	65.00	3.17
T-1	63.00	66.00	4.76
T-2	64.00	67.00	4.69
T-3	64.00	67.00	4.69
T-4	64.00	68.00	6.25
T-5	64.00	68.00	6.25
T-6	64.00	68.00	6.25
T-7	64.00	67.00	4.69
T-8	64.00	67.00	4.69
C-2	64.00	66.00	3.13

After accelerated aging, an increment in the Hardness was observed. The increase arises because the polymer chains cannot explore different configurations during constraint and are therefore less flexible. This can be also attributed to the formation of additional cross links via a post curing process and stabilizing of polymer network by lignin via forming inter molecular interactions between direct lignin-polymer matrix and lignin- polymer matrix via carbon black filler. This stabilization effect improve with polymeric nature of lignin [15].

Tensile strength which is given in table 5 shows that before aging, TS increase from C-1 to T-5 and from C-2 to C-5 with lignin concentration. Lignin alone, T-4 and T-5 showed higher, 14.93 MPa and 15.12 MPa TS than vulcanisates with C-1 and C-2. In literature, it is already shown that the incorporation of lignin into rubber matrix increased TS of SBR due to stabilization effect of lignin in SBR with formation of interactions between common functional groups on SBR and lignin structures [2, 16].

The TS of all vulcanisates decrease with thermal aging due to thermal oxidation degradation of polymer chains. There is a possibility of formation of cross-links during the thermal aging as well as degradation of the polymer chains. When the bond scission occurs at the branched part of the polymers, a linear free-polymer would be produced. Control samples show C-1 - 12.68 MPa and C-2 - 12.6 MPa. But lignin alone samples show lower TS values after aging, T-4- 12.52 MPa and T-5- 12.54 MPa. Vulcanizate with combination of 6PPD and lignin in T-2 have shown 12.96 MPa highest TS than other combinations and controlled samples due to synergistic effect lignin and 6PPD. T-4 and T-5 show lower retention 84% and 83% than vulcanisates with C-1, 88% and C-2, 89%. Highest retention, of 89% has shown by C-2 and SP shows highest antioxidant activity on the SBR compounds than lignin and other combinations [2].

Wear and tear properties of a tire tread are monitored through tear strength and abrasion resistance, in laboratoties. The two

property variations with the type, loading and composition of the antioxidants are given in Table 6. Highest tear strengths and lowest abrasion losses are exhibited by the vulcanizates with Lignin alone. Further, property enhancement was recorded with increase in Lignin loading when used alone and in combinations with 6PPD and SKF. Tear strength increase before aging with lignin loading. Lignin alone T-4 and T-5 vulcanizates have shown higher values respectively 41.59 N/m and 42.2 N/m than C-1 and C-2. Tear strength increase with lignin concentration from C-1 to T-5 and from C-2 to T-5. The lower wear and tear characteristics of the vulcanizates with Lignin are in agreement with the higher tensile properties obtained and confirms formation of bonds by Lignin with NR. Several simultaneous processes such as main chain scission, cross linking formations by joining of the free radicals, and crosslink scission occur during aging process. The change in tear strength depends on the extent of such reactions. Tear strength decrease in all vulcanizates due to thermal oxidation degradation of polymer chains with heat. There is a trend of decreasing tear strength with lignin concentration in all blends.

Vulcanizates with Lignin alone compared to vulcanizates with SKF and 6PPD alone showed higher elongation at break, and further both properties increased with Lignin loading when added alone or in combination. Lignin forms strong adhesion bond between lignin and SBR matrix. This attributes to the increasing elongation at break of rubber vulcanizates when lignin loading increases. The elongation at break of all vulcanizates decreased with thermal aging due to thermal oxidation degradation of polymer chains. There is no any linear variation of elongation shown in vulcanizates after aging. 6ppd 2phr (C-1) and SP 2phr (C-2) show higher elongation than lignin alone and blend of lignin after aging. The loss in elongation at break may be due to increase in crosslink density with ageing which leads to a restriction for chain extension and decrease in chain length between cross linking point and with formation of additional cross links, reducing the mobility of rubber chains.

Flex-fatigue life of rubber vulcanizates are monitored through time taken for crack initiation and crack growth of the vulcanizates, and these properties for vulcanizates with different types of antioxidant are shown in Table 6. Number of cycles taken for both crack initiation and full crack growth for the vulcanizates with Lignin alone is very low compared to those for vulcanizates with SKF and 6PPD, and their combinations with Lignin. When Lignin loading was increased, fatigue life decreased, and it could also be due to formation of additional interfacial bonds or cross links by Lignin with NR.

TABLE 5  
TENSILE PROPERTIES

Vulcanizate	Tensile Strength, MPa		Elongation at break%		300% Modulus, MPa	
	Unaged	Aged	Unaged	Aged	Unaged	Aged

	@ 70°C		@ 70°C		@ 70°C	
	C1	14.34	12.68	344	269	12.87
T1	14.58	12.64	349	244	12.90	14.96
T2	14.65	12.96	350	260	12.93	15.00
T3	14.73	12.73	355	238	12.95	15.01
T4	14.93	12.52	358	234	13.20	15.23
T5	15.12	12.48	362	253	13.21	15.31
T6	14.97	12.54	349	206	13.28	15.36
T7	14.71	12.55	345	238	12.82	14.87
T8	14.38	12.53	343	263	13.03	15.08
C2	14.21	12.60	337	263	13.05	15.18

TABLE 6  
TEAR STRENGTH, ABRASION LOSS, CRACK INITIATION

Vulcanizate	Tear Strength, N/mm	Abrasion Loss, mm <sup>3</sup>		Crack Initiation, Cycles		
		Unaged	Aged	Unaged	Aged	
		@ 70°C	@ 70°C	@ 70°C	@ 70°C	
C1	36.32	31.94	119.1	129.2	60000	45700
T1	37.33	29.2	118.8	128.2	60000	32500
T2	37.86	29.51	118.5	125.7	20000	32500
T3	39.3	27.23	117.6	125.2	17000	30000
T4	41.59	26.54	116.4	122.8	8000	7000
T5	42.2	24.87	116.3	124.0	7000	5000
T6	40.98	29.36	114.2	120.6	8000	5000
T7	38.32	28.25	118.1	124.5	8000	7000
T8	37.3	29.78	117.5	123.2	15000	4000
C2	36.26	30.62	116.2	122.5	11000	8500

## 6 CONCLUSION

Cure characteristics were more or less similar for all vulcanizates and confirms the possibility of substituting Lignin with 6PPD and SKF in industrial applications. Specific gravity of the vulcanizates were within a small variable range, so that Lignin will be a substitute to commercial antioxidants without variation of compound weight and the compound cost. Tensile properties, tear strength and abrasion resistance of the vulcanizates were enhanced with addition of Lignin alone or in combinations confirming its reinforcing or cross linking ability with NR. Further, being Lignin as an efficient antioxidant might prevent thermal oxidation of NR during processing and vulcanization. However, Lignin, compared to 6PPD and SKF showed reduced flex fatigue life of the vulcanizates. The aging properties of Lignin are more or less similar to those of other antioxidants. The overall results

revealed that Lignin could be used as an efficient antioxidant in tire tread compounds by substituting 6 PPD and SKF alone or in combination.

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