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

Haputhanthirige Don Anurasiri Gunasekara

(138256 F)

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

Department of Chemical & Process Engineering

University of Moratuwa Sri Lanka

April 2017

DECLARATION

"I declare that this is my own work and this dissertation does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

Also, I hereby grant to University of Moratuwa the non-exclusive right to reproduce and distribute my dissertation, in whole or in part in print, electronic or other medium. I retain the right to use this content in whole or part in future works (such as articles or books).

Signature:	Date:
The above candidate has carried out resea supervision.	rch for the Master's dissertation under my
Signature of the co supervisor:	Date
Signature of the supervisor:	Date
Signature of the internal supervisor:	Date

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

ii

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.

TABLE OF CONTENT

DECLARA	TION	I	
ABSTRAC	Т	III	
TABLE OF	F CONTENT	IV	
LIST OF F	IGURES	VII	
LIST OF T	ABLES	IX	
ABBREVI	ATIONS	X	
1 INTRODI	UCTION	1	
1.1 Ol	bjectives	4	
2LITERAT	TURE REVIEW	5	
2.1 Cł	nemistry of Polymer Degradation	5	
2.2 De	egradative factors and effect of degradation	6	
2.3 Ro	ole of Anti-Degradants	7	
2.4 Pr	operties of Antioxidants /Anti Degradants	8	
2.5 Pc	olymer Degradation Process	10	
2.6 Pl	ant based antioxidants	10	
2.6.1	Lignin	10	
2.6.2	Characterization of lignin	14	
2.6.3	Lignin isolation	16	
2.7 A _I	pplications of lignin	18	
2.7.1	Advantages of lignin as an antioxidant	19	
2.7.2	Lignin as an antioxidant in thermoplastics	21	
2.7.3	Lignin in Rubber Compounds	22	
2.8 Sc	2.8 Solid Tire		
2.8.1	Solid tire tread compound	25	
3 EYDED IV	/ENT A I	27	

	3.1 Mat	terials	. 27
	3.2 Cor	npound Formulation	. 28
	3.3 Met	thodology	. 28
	3.4 Cor	npound Processing and Sample Preparation	. 30
	3.4.1	Mixing in internal mixer	. 30
	3.4.2	Mixing on mill	. 30
	3.5 Det	ermination of properties	.31
	3.5.1	Mooney viscometer	.31
	3.5.2	Cure characteristics	.31
	3.5.3	Preparation of test specimens	. 32
	3.5.4	Specific gravity (Density)	. 32
	3.5.5	Hardness	. 32
	3.5.6	Tensile properties	. 32
	3.5.7	Tear Strength	. 33
	3.5.8	Abrasion Resistance	. 34
	3.5.9	De Mattia Flexing	. 34
	3.5.10	Aging properties	. 35
4RI	ESULTS	AND DISCUSSION	. 36
	4.1 Vise	cosity	. 36
	4.2 Cur	e charcateristics	. 38
	4.3 Spe	cific Gravity	. 39
	4.4 Har	dness	. 40
	4.5 Ten	sile Streangth	. 41
	4.6 Elo	ngation at Break	. 45
	4.7 Effe	ect of Different Antioxidant Combinations on 300% Modulus	. 46
	4.8 Tea	r Strength	. 50

4	4.9 Abr	asion Resistance	. 52
4	4.10De	Mattia Flexing	. 55
5CO	NCLUS	ION	. 59
:	5.1 Sug	gestions	. 59
REF	ERENC:	ES	. 60
ANN	NEX 1		. 63
	A1.1	Antioxidants	. 63
	A1.2	Natural rubber	. 64
	A1.3	Carbon black	. 64
	A1.4	Activator	. 65
	A1.5	Stearic acid	. 66
	A1.6	Rubber processing oil (Low PAH oils)	. 66
	A1.7	Sulphur	. 67
	A1.8	Retarder (Pre vulcanization inhibitor, PVI)	. 67
	A1.9	Accelerator	. 67

LIST OF FIGURES

Figure 2.1 Schematic diagram of polymer degradation process
Figure 2.2 Three standard monolignol monomers
Figure 2.3 A suggested structure of softwood lignin
Figure 2.4 Position of lignin within lignocellulosic matrix
Figure 2.5 Lignin isolation process
Figure 2.6 Cross section of a solid tire
Figure 3.1 Process flow diagram of the research
Figure 4.1 SG of vulcanizates with three AO and their combinations
Figure 4.2 % Change of hardness of vulcaniztes with three AO and their combinations after aging 41
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 44
Figure 4.5 Dependence of elongation at break before aging with different AO loadings before aging
Figure 4.6 Dependence of elongation change % with different AO combinations before and after aging
Figure 4.7 Dependence of 300% modulus with different AO combinations before aging
Figure 4.8 Dependence of 300% modulus change with different AO loadings after
aging

Figure 4.9 Dependence of tear of the vulcanizatess with different loadings of AO
before aging
Figure 4.10 Tearing change % with different AO loadings after aging51
Figure 4.11 Dependence of abrasion loss of the vulcanizatess with different loadings
of AO before aging53
Figure 4.12 Abrasion loss % with different AO loadings after aging
Figure 4.13 Dependence of cycles for the first pin hole of the vulcanizates with
different loadings of AO before aging
Figure 4.14 Cycles for the first pin hole, change % with different AO loadings after aging
Figure 4.15 Dependence of cycles for full crack of the vulcanizates with different
loadings of AO before aging
Figure 4.16 cycles for the full crack, change % with different AO loadings after aging

LIST OF TABLES

Table 2.1 : Degradative factors and effect of degradation
Table 2.2 Properties of antioxidants and their effects
Table 2.3 Chemical comparison of various wood species
Table 3.1 Raw materials used in the rubber formulation
Table 3.2 Compound formulation28
Table 3.3 Mixing cycle 1 st stage
Table 3.4 Mixing cycle 2 nd stage
Table 3.5 Conditions at Mooney viscosity test
Table 4.1 Effect of three AO and their combinations on hardness, before 41
Table 4.2 Effect of three AO and their combinations on TS of vulcanizates before and after aging
Table 4.3 Effect of different AO loadings on elongation at break before and after aging
Table 4.4 Effect of different AO combinations on 300% modulus before and after aging
Table 4.5 Effect of different AO loadings on tear strength before and after aging 50
Table 4.6 Effect of different AO loadings on abrasion lose before and after aging 52
Table 4.7 Effect of different AO loadings on cycles for the first pin hole before and after aging
Table 4.9 Effect of different AO loadings on cycles for the full crack before and after
aging57

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

t₉₀ 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