PROJECT REPORT

UTILIZATION OF LIGNIN BY-PRODUCT FROM PAPER INDUSTRY IN RUBBER INDUSTRY

Submitted by

CR & Biorefinery Division

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PROJECT EXECUTED BY:

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And

INDIAN RUBBER MANUFACTURERS RESEARCH ASSOCIATION (IRMRA), THANE - 400604 MAHARASHTRA

Project Investigating Team:

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OBJECTIVE

- To explore the utilization of lignin obtained as a by product from the paper industry from different sources like agro and wood based mills for conversion into value added product for the rubber industry
- To improve the environmental status by way of providing a green product as well as to improve the economics of the paper and Rubber Industry.

QUANTIFIED DELIVERABLES

- Improved process economics of paper mills which are either opting for marginal expansion of pulp mill and/or adopting ODL process thereby generating more black liquor by utilization of waste lignin in rubber industry
- Improved environmental & energy efficiency level of Paper and rubber industry by providing a green product to partly replace Carbon black, a petroleum product
- Utilization of lignin rich residual biomass obtained from emerging process for production of bio ethanol from lingo cellulosic waste biomass generated in paper mill like bagasse pith / rice straw waste etc in rubber industry

PREPARATION OF LIGNIN SAMPLES

- Four lignin samples marked Lignin 1, Lignin 2,Lignin 3 and Semi Solid Lignin were prepared from following black liquor samples:
    - ✓ Lignin 1 – Agro based packaging grade black liquor
    - ✓ Lignin 2 – Wood based Kraft black liquor
    - ✓ Lignin 3 – Agro based Soda black liquor
    - ✓ Semi Solid Lignin- Agro residue Alkaline sulphite lignin

- Lignin 1, Lignin 2,Lignin 3 samples were prepared by acid precipitation by addition of Sulphuric acid in black liquor.
- Separated lignin was dried, powdered and passed through 100 mesh
- Semi solid lignin is as such alkaline sulphite black liquor
- The powdered lignin as well as semi solid lignin samples were sent to IRMRA for utilization in rubber production.

PREPARATION OF DIFFERENT RUBBER COMPOUNDS FILLED WITH LIGNIN SAMPLE

The following compounds were mixed in two roll mill keeping the nip gap ,mixing temperature and mixing time constant, After the mixing the compound were sheeted out and allowed to mature for min 24 hrs before going further testing. The lignin samples were mixed at 5 Phr, 10 Phr loading as per Formulation.

Tyre Tread Formulation used for Lignin 1, Lignin 2 & Lignin 3

Ingredients	100% Black	Lignin 1 5phr	Lignin 1 10phr	Lignin 2 5phr	Lignin 2 10phr	Lignin 3 5phr	Lignin 3 10phr
SBR1502	80	80	80	80	80	80	80
BR1220	20	20	20	20	20	20	20
Zinc oxide	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2
HAF black(N330)	50	45	40	45	40	45	40
Lignin	0	5	10	5	10	5	10
Aromatic oil	5	5	5	5	5	5	5
TDQ	1	1	1	1	1	1	1
6PPD	1	1	1	1	1	1	1
CBS	1	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	2	2	2	2	2	2	2

Cure characteristics of Lignin filled vulcanizates

Properties checked	Method	100% Black1	Lignin 1 5phr	Lignin 1 10phr	Lignin 2 5 phr	Lignin 2 10 phr	Lignin 3 5 phr	Lignin 3 10 phr
Rheometric properties @ 160^0c								
MH(lbs.inch)	ASTM D -5289	18.71	16.32	13.13	17.58	14.92	17.91	16.25
ML(lbs.inch)	ASTMD -5289	1.54	1.37	1.28	1.42	1.24	1.61	1.55
Ts2(min)	ASTM D-5289	2.03	2.28	2.55	2.19	2.45	2.3	2.38
Tc90(min)	ASTM D-5289	4.13	4.86	6.33	4.38	5.32	4.59	5.54
Slab molded at 160^0 c for (min)		5	5	7	5	6	5	6
Surface finish Cured sample		Ok	Ok	Minor defect	Minor defect	Minor defect	Minor defect	Minor defect

Physico-mechanical properties

Properties	Method	100% black	Lignin 1 5phr	Lignin 1 10phr	Lignin 2 5phr	Lignin 2 10phr	Lignin 3 5phr	LIgnin 3 10phr
100% modulus (kg/cm^2)	ASTM D-412	41	35	22	34	28	32	30
After ageing (70C/72h)		48	37	29	42	31	39	36
200% modulus (kg/cm^2)	ASTM D-412	_	81	50	80	61	76	64
Tensile strength (kg/cm^2)	ASTM D-412	135	82	76	92	77	115	92
After ageing		101	91	69	83	71	88	90
Elongation@ break	ASTMD-412	180	200	290	220	250	300	320
After ageing		180	200	210	180	200	200	220
Hardness (shore-A)	ASTMD - 2240	67	63	60	63	61	66	63
After ageing		69	66	62	67	63	69	66
Relative Volume Loss RVL(mm^3)		127	152	154	157	177	138	158

RESULT AND DISCUSSION

Observation on sample Lignin 1

- From the cure characteristics results mentioned in the Table 3, it is seen that replacement of the 05 Phr of the carbon black with sample lignin 1 increases the optimum cure and scorch time which shows that sample Lignin 1 does not facilitate the used S curing process which may be attributed to acidic character of the sample lignin 1. The increased cure time after addition of the sample Lignin 1 will decrease the productivity. With increase of the doses of sample Lignin 1, optimum cure and scorch time gets increases.

Observation on sample Lignin 2

- From the cure characteristics results mentioned in the Table 3, it is seen that replacement of the 05 Phr of the carbon black with sample lignin 1 increases the optimum cure and scorch time which shows that sample Lignin 1 does not facilitate the used S curing process which may be attributed to acidic character of the sample lignin 2.
- The increased cure time after addition of the sample Lignin will decrease the productivity

Observation on sample Lignin-3

- Cure characteristics have shown that by addition of 10 Phr of Lignin 3, curing time is substantially reduced. It will improve productivity and reduce energy demand in curing.
- Lignin 3 shows better tensile strength properties compared to lignin sample-1 and lignin sample-2 at the similar loading in the carbon black filled compounds
- Lignin 3 shows better abrasion resistance index properties compared to lignin sample-1 and lignin sample-2 at the similar loading in the carbon black filled compounds

- It is seen that addition of sample lignin 1, 2 and sample lignin-3 in carbon black filled compound decreases Tensile strength and modulus while elongation at break gets increases with addition of the lignin samples in the carbon black filled compounds

- Lignin sample - 3 shows better elongation at break properties compared to lignin sample-1 and lignin sample-2 at the similar loading in the carbon black filled compounds
- Lignin sample - 3 shows better retention in physico-mechanical properties after aging compared to lignin sample-1 and lignin sample-2 at the similar loading in the carbon black filled compounds

PREPARATION OF DIFFERENT RUBBER COMPOUNDS FILLED WITH SAMPLE SEMI SOLID LIGNIN

The following compounds were mixed in two roll mill keeping the nip gap, mixing temperature and mixing time constant, after the mixing the compound were sheeted out and allowed to mature for 24 hrs before going further testing. The supplied lignin sample was mixed at 5 Phr, 10 Phr, as per following Formulation.

FORMULATION USED FOR SEMI--SOLID LIGNIN

Ingredients	Blank	100% Black	5phr semi solid	10phr semi solid
SBR1502	100	100	100	100
Zinc Oxide	3	3	3	3
Stearic Acid	2	2	2	2
SRF Black (N774)	0	50	45	40
Lignin	0	0	5	10
TDQ	1	1	1	1
CBS	1.5	1.5	1.5	1.5
TBBS	1.5	1.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5

CURE CHARACTERISTICS AND PHYSICO-MECHANICAL PROPERTIES OF SEMI - SOLID LIGNIN FILLED VULCANIZATE

Properties checked	Blank	100% Black	5phr powder form sample	10phr powder form sample
Rheometric Properties on rubber compound at 160°c				
MH (Lbs. inch)	59.75	86.39	80.77	78.21
ML(lbs. inch)	7.61	12.76	11.89	11.83
Ts2 (minutes)	8.83	3.58	3.54	3.56
Tc90 (minutes)	14.64	9.17	8.49	7.90
Slab Molded at 160°c for (mints.)	15	10	9	8
Surface finish of cured Sample	Free from visible defects			
Physical Properties observed on molded slab				
100% Modulus (kg/cm^2)	9	27	20	18
300% Modulus (kg/cm^2)	16	118	81	69
Tensile Strength (kg/cm^2)	18	159	110	134
Elongation@ Break	350	370	380	490
Hardness (Shore-A)	46	66	64	62
Tear Strength (kg/cm)	14	60	68	56

RESULT AND DISCUSSION

- From the cure characteristics results it is observed that addition of semi-solid lignin in the carbon black filled vulcanizate increases optimum cure at 05 phr loading while at 10 phr loading there is substantial decrease in optimum cure time which results in improved productivity and reduced energy demand.
- Physicomechanical properties after addition of semi-solid lignin up to 10 phr loading in carbon black filled compound marginally decreases modulus, tensile strength whereas it improves elongation and tear strength.

CONCLUSION ON EVALUATION OF THE VARIOUS UNMODIFIED LIGNIN SAMPLES

- All the three powder lignin samples being acidic in nature does not facilitate the S curing process resulting in higher optimum cure time in carbon black filled compound.
- Out of the 03 Powder lignin samples, Lignin sample 3 is found to show some better physico-mechanical and its retention properties
- Other two lignin samples do not show significant improvement on the physico-mechanical properties
- Addition of semi-solid lignin in the carbon black filled vulcanizate substantially decreases optimum cure at 10 phr loading which results in improved productivity and reduced energy demand.
- Lignin 3 and Semi solid Lignin sample can be evaluated further by way of increasing its surface area, its surface treatment, higher pH or by using any compatibilizer for its suitability as part replacement of carbon black for tyre and conveyor belt application

EFFECT OF SILANE MODIFIED LIGNIN ON THE PROPERTIES OF SBR/BR BLEND.

MODIFICATION OF LIGNIN

Si69

← Lignin dispersed in THF

Refluxed for 3 hours

In unmodified lignin the particle size is: Mean Diameter = 2165.2 nm

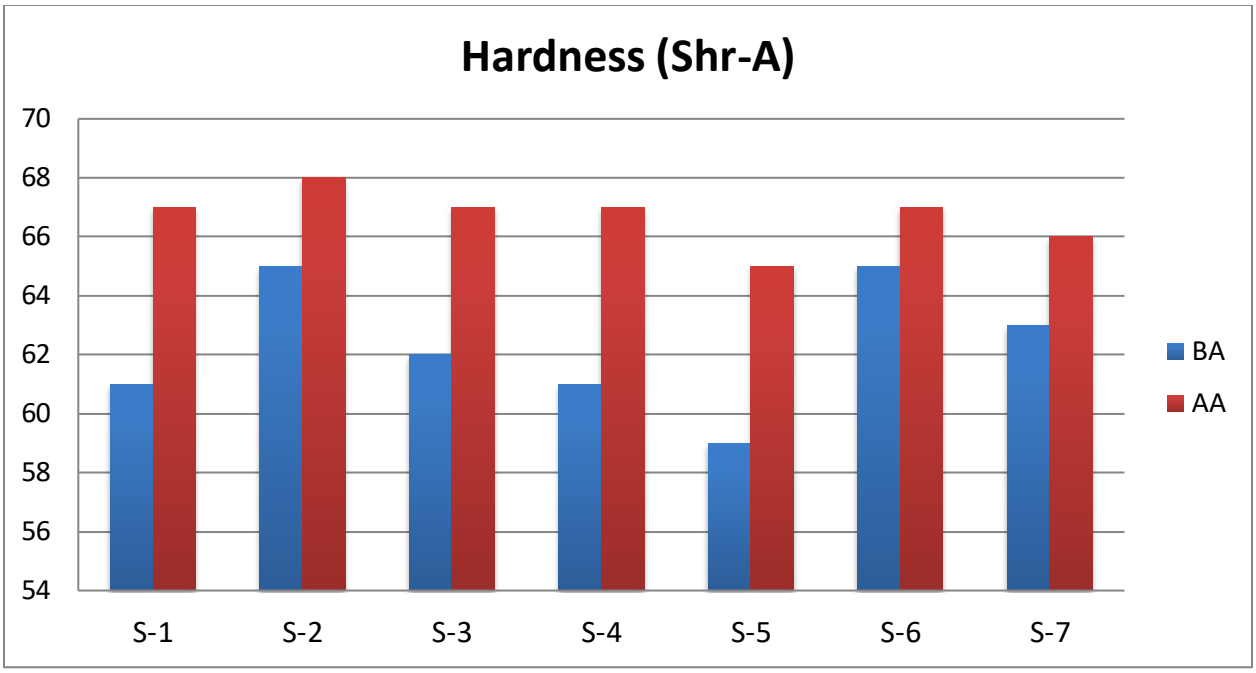
In modified lignin the particle size: Mean Diameter = 502.9 nm

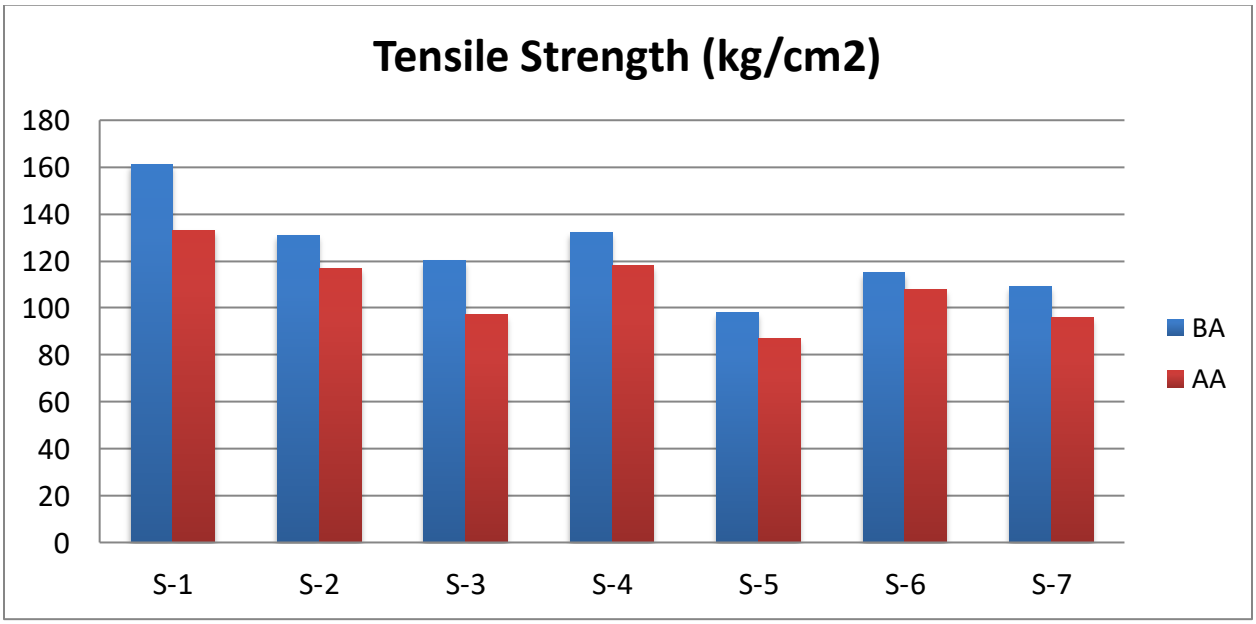
FORMULATION USED FOR MODIFIED LIGNIN

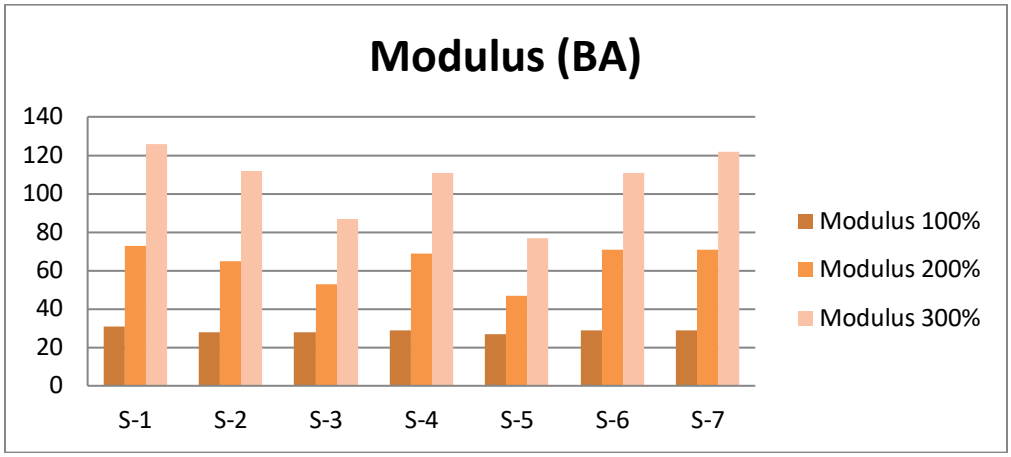
ingredients	100% black	Unmodified lignin	Unmodified lignin	Modified lignin	Modified lignin	Modified lignin	Modified lignin
SBR 1502	80	80	80	80	80	80	80
BR 1220	20	20	20	20	20	20	20
Zinc oxide	4	4	4	4	4	4	4
Steric acid	2	2	2	2	2	2	2
FEF black	50	45	40	45	40	45	45
lignin	0	5	10	5	10	5	5
Aromatic oil	5	5	5	5	5	5	5
TDQ	1	1	1	1	1	1	0
6PPD	1	1	1	1	1	0	1
CBS	1	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5
SULPHUR	2	2	2	2	2	2	2

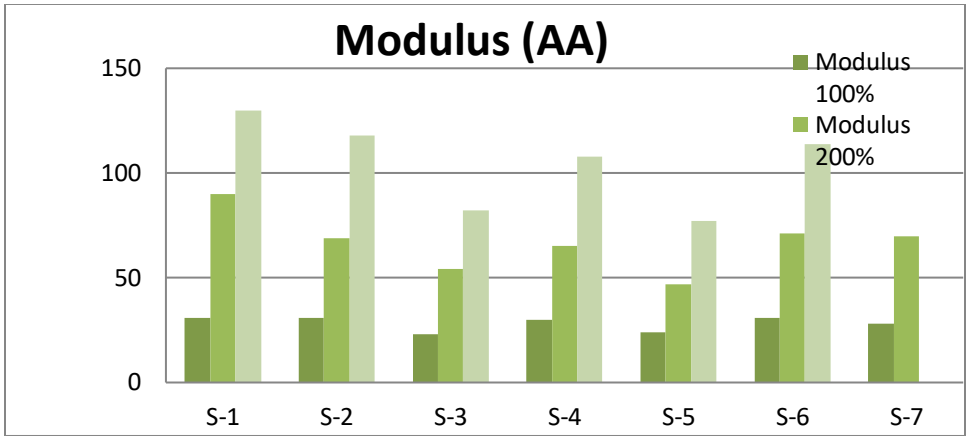
CURING PROPERTIES OF SILANE MODIFIED LIGNIN SAMPLE

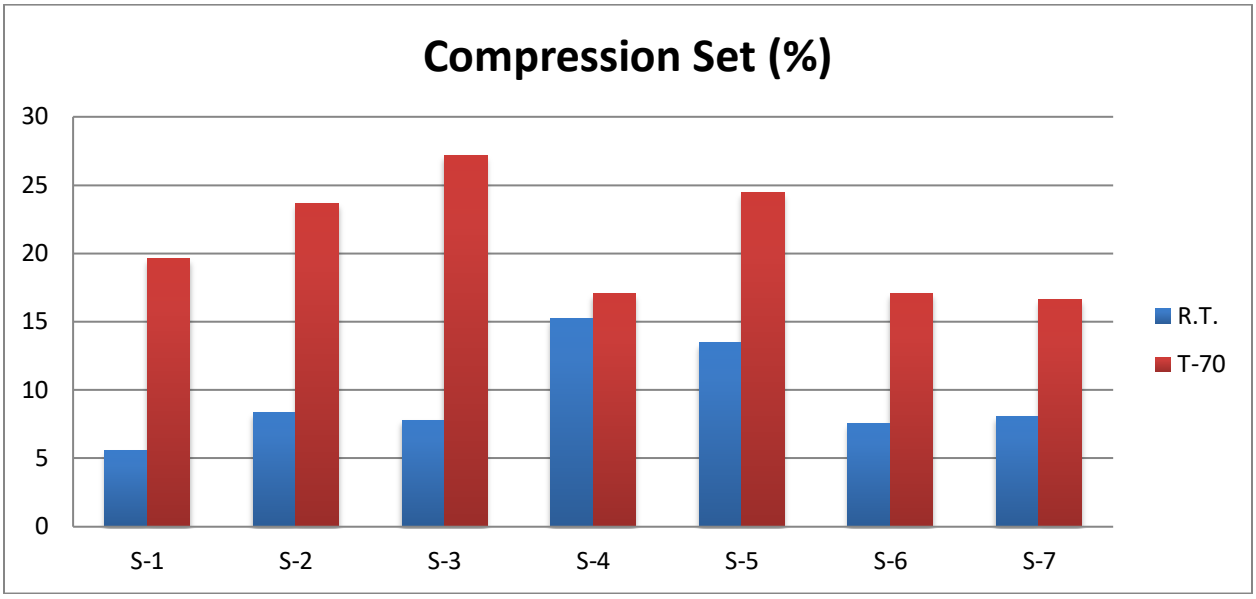
Batch no z	Temperature	ML	MH	Scorch time (TS1)	Scorch time (TS2)	Tc90
Unit	°C	Lbin	Lbin	minutes	minutes	minutes
100% black	160	1.20	16.23	1.44	1.56	3.38
Unmodified Lignin		1.26	15.34	1.85	2.00	3.85
Unmodified Lignin		1.31	13.62	1.87	2.02	3.87
Modified Lignin		1.29	15.75	1.87	2.02	3.93
Modified Lignin		1.21	12.98	2.07	2.26	4.59
Modified Lignin		1.37	17.00	2.01	2.23	4.56
Modified Lignin		1.42	16.71	1.87	2.02	3.75


Hardness (Shr-A)
70
68
66
64
62
60
58
56
54
S-1
S-2
S-3
S-4
S-5
S-6
S-7
BA
AA


Tensile Strength (kg/cm2)
180
160
140
120
100
80
60
40
20
0
S-1
S-2
S-3
S-4
S-5
S-6
S-7
BA
AA


Modulus (BA)
140
120
100
80
60
40
20
0
S-1
S-2
S-3
S-4
S-5
S-6
S-7
Modulus 100%
Modulus 200%
Modulus 300%


Modulus (AA)
150
100
50
0
S-1
S-2
S-3
S-4
S-5
S-6
S-7
Modulus 100%
Modulus 200%



CONCLUSION ON EVALUATION OF MODIFIED LIGNIN SAMPLES

- The silane modified lignin sample at the loading of 5 and 10 phr in the NR/BR based rubber compound shows comparative phyco-mechanical properties to that of 100 % carbon black filled compound
- The silane modified lignin sample was found to show better retention of physico-mechanical properties without addition of anti-oxidant and anti-ozonant which can be attributed to its anti-degradants characteristics.
- Silane modified lignin sample can be used as antidegradants (anti-oxidant and anti-ozonant) in the rubber based compounds at the 5-10 phr loading apart from its semi-reinforcing filler characteristics.