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EVALUATION STUDY OF LIGNIN OBTAINED FROM PULP AND PAPER INDUSTRIES IN RUBBER COMPOUNDS

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Abstract:

Lignin is a byproduct derived from black liquor generated during pulping processes in pulp and paper mills. This lignin can be utilized for various applications in different industries. This paper investigates the potential of lignin as a substitute for hazardous/ carcinogenic carbon black in rubber industries. For this purpose, three lignin samples were mixed at 5 parts per hundred of rubber (Phr) and 10 Phr loading with different formulation compounds in two roll mixing mill. Formulated lignin filled vulcanizates were compared with 100% carbon black in terms of cure characteristics, rheometric and physico-mechanical properties. Reported results have shown that formulated lignin sample 3 was superior than other lignin samples in terms of higher initial torque (ML), higher maximum torque (MH), better tensile strength, break and abrasion resistance properties. It was concluded that lignin has good potential to completely/partially replace the carbon black in rubber industries which will certainly help to improve the environmental conditions in paper and rubber industries.

Keywords: Black liquor, Lignin, Carbon black, Pulp and Paper, Rubber Industry.

1. Introduction

In view of adoption and promotion of cleaner and greener technologies, the paper industries have been using oxygen delignification and low kappa pulping to reduce the generation of pollutant in the discharging effluent [1]. As a result, the chemical recovery system is likely to be overload making it difficult to manage the black liquor solids in the existing recovery systems. The capacity of the chemical recovery system can be enhanced by way of partial removal of lignin from the black liquor. This may address the above said issue of limitation of chemical recovery capacity and offer an opportunity to mill for marginal capacity expansion of the pulp mill. Further, the other emerging area is the production of bio-ethanol and value added chemicals from lingo-cellulosic biomass from paper industry where in after recovery of ethanol more than 40% of the biomass is recovered in the form of lignin in crude form.

Lignin, a complex natural polymer by virtue of its inherent nature having a wide range of functional groups like phenolic hydroxyl,

methyl, carboxyl group etc. maybe an excellent starting material for its conversion into industrially useful value added products that find use in various industrial applications including the rubber industry [2]. Among various industrial applications of lignin, application of lignin in rubber industry as an additive for replacement of carbon black offers a good potential for its utilization in rubber industry. Based on the preliminary research work undertaken, it has been observed that the partial replacement of lignin with carbon black may offer a large potential to improve quality and economics of both the paper and rubber industries. Rubber is normally used in auto tyres, cycle tyres, shoe and other miscellaneous uses. Automotive tyre sector is the major consumer of rubber (50% of total consumption) followed by cycle tyres and footwear. Styrene Butadiene Rubber (SBR) is a general purpose elastomer that is widely used in rubber industry. However, SBR is non-polar and non-crystalline with low gum tensile strength. Hence fillers like carbon black are added to improve the physico- mechanical properties of SBR [3].

During carbon black manufacturing hazardous air pollutants (HAP) like carbon di-sulphide, carbonyl sulphide and hydrogen cyanide are produced. These HAPs cause health hazards to human beings. Further carbon black after oxidation causes generation of carbon di-oxide which creates detrimental effect on environment and living organisms. Lignin is obtained as a byproduct from the paper industry. It possesses strong mechanical properties and is known to have a potential as a partial substitute for carbon black. The use of lignin as a partial or complete substitute of carbon black is known to reduce curing time and viscosity of rubber compound and thus reduces the energy requirement during masticate / compounding process. Lignin substitution also brings about improvement in properties of the rubber composites. Hence the substitution of carbon black with lignin will not only result in the substitution of hazardous / carcinogenic carbon black with a green and renewable product but will also reduce carbon di-oxide emissions and improve the environmental status of the rubber and paper industry.

A lot of research works and patents propose the use of lignin as a partial substitute of carbon black in rubber composites like Butadiene-Styrene-Butadiene, Isoprene-Styrene-Butadiene rubber, Styrene-Butadiene-Elastomer and natural rubber [4,5,6]. The uses of modified lignin treated with hexa-methylene-tetramine etc. have been explored to reduce the polarity of lignin that interferes with interaction of filler with elastomer resulting in its low performance [7]. The use of carbonized lignin as an alternative to carbon black has also been reported [8]. Work has also been reported on the use of lignin in development of bio-degradable nitrile butadiene rubber (NBR) composites [9]. However, no work has been reported on the use of crude lignin separated during production of bioethanol by bagasse pith. Also, no work has been reported on use of lignin partially isolated from black liquor or capacity enhancement of chemical recovery system.

Hence the objectives of this study are twofold. First to explore the utilization of lignin obtained as a byproduct from the paper industry from different sources like agro and wood waste mills for conversion into value added products for the rubber industry and second to improve the environmental status by way of providing a green product as well as to improve the economics of the paper and the rubber industry.

2. Material and Methods

Three powdered lignin samples of acidic nature, coded as Lig1, Lig2 and Lig3 were used for formulation with different compounds given in Table1. The rubber compounds were kept for maturation as per standard and curing characteristic was studied using Monsanto Rheometer R-100. The test slabs were cured using Hydraulic curing press. The vulcanized test specimens were tested for Hardness, tensile, modulus, elongation at break and tear strength. Fig.1 and Fig. 2 shows rheometer and hardness tester, used in this study.

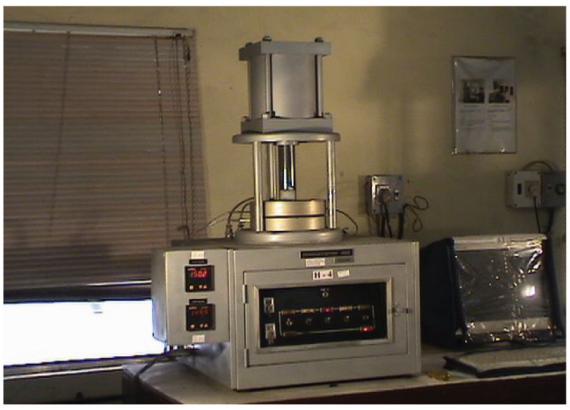

Fig-1 Rheometer

Fig-2 Hardness Tester

2.1 Preparation of different rubber compounds filled with lignin samples:

The 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 pmin 24 h before going for further testing.

Table 1: Lig-1, Lig-2 and Lig-3 formulations

Ingredients	100% Black	Lig1 5phr	Lig1 10phr	Lig2 5phr	Lig2 10phr	Lig3 5phr	Lig3 10hr
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
FEF black(N550)	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

BR: Butadiene Rubber, PPD: p-phenylenediamine, TMTD: Tetramethylthiuram disulfide

3. Result and Discussions

3.1 Rheometric Properties

The comparison of 100% carbon black and formulated compounds with lignin filled vulcanizates in terms of cure characteristics and rheometric properties are shown in Table 2. It can be seen that replacement of 05 Phr of the carbon black with Lig1 increases the optimum cure and scorch time which shows that Lig1 does not facilitate the used S curing process which may be attributed to the acidic character of the Lig1. The increased cure time after addition of the Lig1 will decrease the productivity. With increase in doses of Lig1, optimum cure and scorch time gets increases.

Table 2: Cure characteristics and physico-mechanical properties of Lin filled vulcanizates

Properties checked	Method	100% Black	Lig1 5phr	Lig1 10phr	Lig2 5 phr	Lig2 10 phr	Lig3 5 phr	Lig3 10 phr
Rheometric properties @ 160^{0}c								
MH(lbs. inch)	ASTMD-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

MH: Maximum torque, ML: Initial torque, Ts2: Scorch time, Tc90: Cure time, Phr: Parts per hundred rubber

Replacement of the 05 Phr of the carbon black with Lig1 increases the optimum cure and scorch time which shows that sample Lig1 does not facilitate the used S curing process which may be attributed to acidic character of the Lig2. The increased cure time after addition of the sample Lignin will decrease the productivity. With increase in doses of Lig2, optimum cure and scorch time gets increases.

Also, replacement of the 05 Phr of the carbon black with Lig1 increases the optimum cure and scorch time which shows that Lig1 does not facilitate the used S curing process which may be attributed to acidic character of the Lig3. The increased cure time after addition of the Lig1 will decrease the productivity. With increase in doses of Lig1, optimum cure and scorch time gets increases.

3.1 Rheometric Properties

Table 3: Physico-mechanical properties

Properties	Method	100% black	Lig1 5phr	Lig1 10phr	Lig 2 5phr	Lig 2 10phr	Lig 3 5phr	Lig 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
Change in Tensile Strength (after air ageing@70°C/72 hrs.)								
		+26%	+12%	-9%	-9%	-7%	-23%	-2%
Change in Elongation at Break (after air ageing@70°C/72 hrs.)								
		-30%	-20%	-27%	-18%	-20%	-33%	-21%
Change in Hardness after (air ageing@70°C/72 hrs.)								
		+2	+3	+2	+4	+2	+3	+3

The comparison of 100% carbon black filled compound with lignin filled vulcanizates in terms of physico-mechanical properties are shown in Table 3. It can be seen that addition of Lig1, 2 and 3 in carbon black filled compound decreases tensile strength and modulus while elongation at break gets increased with addition of the lignin samples in the carbon black filled compound. Lig3 shows better elongation at break properties compared to Lig1and Lig2 at the similar loading in the carbon black filled compounds; better tensile strength properties compared to Lig1 and Lig2 at the similar loading in the carbon black filled compounds; better abrasion resistance index properties compared to Lig1 and Lig2 at the similar loading in the carbon black filled compounds; better retention in physico-mechanical properties after aging compared to Lig1 and Lig2 at the similar loading in the carbon black filled compounds.

4. Conclusion

From cure characteristics results, it was concluded that replacement of the carbon black with supplied lignin samples at 05 and 10 Phr loading increases the optimum cure and scorch time which shows that all the three supplied lignin samples does not facilitate the used S curing process which may be attributed to acidic character of the lignin samples. Lig2 shows reduced scorch and optimum cure time than that of the Lig1 and Lig3 at the similar loading in the carbon black filled compounds.Lig3 showed higher values of initial and maximum torque than other lignin samples at the similar loading in the carbon filled compounds, which results in improved physico-mechanical properties in terms of better reinforcing behavior and cross-link density. Lig3 also exhibited better break, tensile strength and abrasion resistance index properties as compared to other lignin samples at similar loading in carbon black filled compounds.

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