Lignin As a Plasticizer

In Nitrile Rubber, It'sEffect on Properties

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1. Abstract:

Plasticizer is an additive that serves to increase the polymer flexibility, elongation or ease of processing, workability, reduction in viscosity, reduction in stiffness and improve certain properties such as low temperature flexibility, glass transition temperature (Tg). There is ban on phthalate plasticizers in many countries, due to health effects.Phthalates are often classified as endocrine disruptors or hormonally-active agents (HAAs) because of their ability to interfere with the endocrine system in the body.[1] But still plasticizers such as dioctyl phthalate (DOP) are used in nitrile rubber compound due to low cost, lack of knowledge of end user. Technical papers suggests.[2,3,4,5], there is improvement in flexibility, elongation, workability, viscosity reduction after addition of lignin, experiments are done to see the possibility of replacing completely and partially processing oil by lignin. It is observed that addition of sodium lignosulfonate (here in after called as lignin) in acrylonitrile rubber compound reduces viscosity like plasticizer, reduces curing rate like

accelerator and also increasing modulus and hardness like filler. Though for certain properties its not competing conventional plasticizer, it has a potential and can be used like plasticizer,if certain properties are not required in product such as low temperature resistance.

2. Introduction:

Wood is composed of many chemical components, which are distributed nonuniformly as the result of anatomical structure. Lignin is one of them. Next to cellulose, Lignin is the most abundant biopolymer in the world. It is found in almost all plant wall cells. Lignin is byproduct in papermaking industries and is removed by pulping and bleaching processes and generally used as a low-grade fuel for the pulp and paper industry.

Structure of lignin is very complex, amorphous, three-dimensional polymers that have in common a phenyl propane structure. Also there are some functional groups, which have an impact on its nature. It mostly contains methyl groups, phenolic hydroxyl groups, few terminal aldehyde groups, carbonyl and alcoholic hydroxyl groups. The phenyl propane (C9or C6C3) units in lignin are connected by C-C and ether (C-O-C) linkages. The frequency of such linkages is believed to have significant effect on the lignin's overall reactivity toward the delignification process. In case of sulfite pulping, the lignin molecule combines with strongly polar sulfonicacid groups.Due to all these groups ligninhas a unique and very complex structure.

3. Scope for Lignin : As lignin is very complex natural polymer with many random couplings, composed of different groups, there are many possible bonding patterns between individual units. This can be used in rubber industry either replacement or partial replacement for some ingredients. It is reported in various technical papers about the lignin's ability to reduce the compound viscosity and plasticizing nature. Perez-Guerrero et al.[2] reported torque reduction and improving ability to process the mixtures in presence of lignin during melt mixing of polystyrene-based materials. Kumaran et al.[3] also observed reduction in Natural rubber compound viscosity along with improved tear resistance, abrasion resistance, flex crack resistanceand crack growth resistance. Tensile strength, modulus, resilience, and compression set decreased while heat buildup increased upon addition of lignin. Aging of the vulcanizates results show tremendous improvements in most of the properties.J. Feranc et al.[4], reported decrease in both the scorch time as well as optimum cure torque of the blends with increasing concentration of lignin between 0 to 40 phr in natural rubber.Paolo Frigerio et al.[5] reported the application of Sulphur-free Lignin as a filler and has a potential application in the rubber industry, where along with different properties data shows decrease in torque value and reduction in hardness.D. K. Setua et al.[6] reported a detailed study of lignin reinforced nitrile rubber composites and concluded about the reinforcing characteristics of crude lignin and modified lignin. Also there are some more references given in literature reviewarticle by Santosh et al.[7]

4. Experimental:

4.1Raw Material: Here in this study Sodium lignosulfonate (Borresperse NA-SA) is used. It is supplied by M/S Borregaard South Asia Pvt. Ltd., Navi Mumbai, Thane. The source of Lignin is from Eucalyptus tree.Technical data sheet of this product shows pH of 5±1.5 (10% solution), Dry matter 93% (min.), Sodium Sulphate ≤ 5.0 %, Sodium 5.6%, Chloride content ≤ 0.1%, 6% moisture content, bulk density 600kg/m3. This product is also tested for total sulfur content its,5.2% Sulfur. FT-IR data shows presence of Phenyl Propane units (C6C3), C-C linkages, ether (C-O-C), phenolic groups, aldehyde groups, sulfonic group (-SO3), C=C and methyl (-CH3) group.

Nitrile rubber grade, JSR230SL with medium acrylonitrile content (35%) of JSR Corporation is used. Semi-reinforcing furnace black (SRF, N774) of Birla make is used as filler, while all other ingredients are taken from reputed suppliers.

4.2 Formulation: The composition of mixes is as per the table 1with different ingredients such as polymer, activators, fillers, accelerator and curing agent is taken. Experiment is done by replacing DOP partially and completely by lignin.

Table 1

Ingredients	Formulation Code Number					
	O -Std. [A]	O1[B]	O2[C]	O3 [A]	O11[B]	O4 [C]
	phr	phr	phr	phr	phr	phr
Nitrile Rubber (JSR230SL)	100	100	100	100	100	100
Zinc Oxide	4	4	4	4	4	4
Stearic Acid	1	1	1	1	1	1
SRF Black (N774)	**60**	**60**	**60**	**60**	**60**	**60**
Sodium Lignosulphonate	**0**	**10**	**5**	**0**	**20**	**10**
Dioctyl phthalate (DOP)	**10**	**0**	**5**	**20**	**0**	**10**
Accelerator MBTS[D]	1.5	1.5	1.5	1.5	1.5	1.5
Accelerator TMTD[E]	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1	1	1	1	**1**	1

A – Rubber compound with 100% DOP filled.
B – Rubber compound with 100% lignin filled.
C – Rubber compound with partial replacement of DOP by lignin.
D– 2,2' Dibenzothiazyl Disulfide
E– Tetramethylthiuram disulfide

4.3 Mixing: The mixings were carried out in a conventional laboratory open roll mill of size (6 x 12inch) as per ASTM D 3182. The compounding ingredients were added in the order: polymer mastication followed by curing agent, activator and filler along with lignin. In case of DOP, filler along with DOP is added. Before the addition of accelerator the batch was thoroughly cooled.

4.4 Rheological properties: Mooney viscosity and mooney scorch time is tested as per ASTM D 1646 by mooney viscometer. Rheometric properties are tested as per ASTM D 2084 by using Monsanto Rheometer. The properties observed are given in table 2

Table 2

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Compound viscosity ML (1+4)@100° C (MU)	34	55	44	30	53	34
2.	Mooney Scorch(min.) t5@125°C	12	4.85	6.6	11.7	4.57	5.95
3.	**Rheometric Properties @ 160°C**						
I)	MH (lbf.inch)	94.28	119.81	122.38	80.51	87.04	98.27
Ii)	ML (lbf.inch)	5.3	9.97	6.12	4.28	10	5.57
iii)	TS2 (minutes)	2.02	1.4	1.61	2.2	1.1	1.62
iv)	Tc90 (minutes)	7.86	4.96	7.78	8.35	4.5	7.53

Results and discussion - Compare to lignin filled compound, DOP filled compound shows less viscosity and improved scorch safety. Comparatively lignin filled compounds have higher viscosity but with good tackiness. High viscosity and reduction in curing and scorch time shows the reinforcing as well as accelerating nature of lignin. This reduction in curing time property is useful for industry to increase the productivity and reduction in energy consumption.
Also in case of partial replacement of DOP by lignin, shows intermediate value of mooney viscosity and mooney scorch along with good combination of processability, tackiness.

4.5 Molding: The rubber compounds are vulcanized in a hydraulic press having electrically heated platens as per temperature and timing given in table 3. All the samples are cured at 160°C except slab of compound O11. Above 10 phr loading and molding temperature above 135°C, for thin articles such as test slab, product shows roughness, small air bubbles, getting adhered to surface of mold. This is due to not proper dispersion, compatibility above optimum level, sticky nature of lignin to metal at high temperature. So the compound with 20phr loading (formulation O11), is cured at 130°C. At this temperature product is free from visible defects.

Table 3

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Rubber Slab	8	5	8	9	55*	8
2.	Compression set button	13	10	13	14	10	13
3.	Visual Observation	All the samples are free from visible defects and blooming					

Results and discussion - Rubber compound for testing different physico mechanical properties, cured as per temperature and time given in table 3. It is observed that 10phr is the optimum loading level of lignin, above that optimum level and temperature above 130°C product shows surface defects for thin vulcanizates.

4.6 Physical properties – Before Ageing: The results obtained on the slab are given in table 4Modulus, tensile strength, elongation at break is tested on Instron tensile testing machine model 3365 as per ASTM D 412, tear strength as per ASTM D 624 die C. Hardness tested by ShoreA hardness tester as per ASTM D 2240.

Table 4

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Vulcanizate Properties – Before Ageing						
i)	Hardness (Shore A)	68	74	71	62	78	68
ii)	100% Modulus (MPa)	4	5.5	4.6	3.1	6.7	3.4
iii)	200% Modulus (MPa)	10.5	12.8	11.8	7.9	13.1	7.8
iv)	Tensile Strength (MPa)	13.5	16.4	14.7	11.9	14	9.1
v)	Elongation at Break (%)	250	255	240	260	225	235
vi)	Tear Strength (Kg /Cm)	54	60	65	56	48	59

Results and Discussion: Data shows that, 100% DOP filled compound gives low values for hardness, tensile strength, modulus and elongation at break. While lignin filled compound with 10phr lignin loading, gives higher hardness, tensile strength, modulus and elongation at break. This is due to combined effect of lignin i.e. as a reinforcing agent and polymer with plasticizing nature. Also it is observed that DOP with lignin jointly gives vulcunizate with improved tear strength.Above 20phr lignin loading, there is drop in elongation at break, while hardness, modulus and tensile are towards higher side. While in case of partial replacement of plasticizer by lignin, properties for different parameters, are in between corresponding 100% DOP filled compound and 100% lignin filled compound properties.

4.7 Physical properties – After Air Ageing: Air ageing of samples was carried out in air circulating oven at 120°c for 72 hrs.as per ASTM D 573. The properties observed are given in table 5.

Table 5

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Change in Properties after ageing @ 120°c/ 3 days						
I)	Hardness change (points)	+10	+7	+8	+17	+4	+12
Ii)	100% Modulus (%)	+134	+86	+111	-NA-	+66	+134
iii)	Tensile Strength (%)	-14	-26	-19	-22	-8	+5.5
iv)	Elongation at Break (%)	-55	-57	-52	-65.5	-51	-53

Results and Discussion: After air ageing, 100% lignin filled compound shows much improved hardness properties, while in case of 100% DOP filled compounds hardening of the product observed. This hardening of rubber compound is due to volatilization of DOP during air ageing process. This reduces flexibility of product and makes it tough and hardened. This is also the reason for poor properties for air ageing tensile strength, modulus and elongation at break for 20phr DOP filled (formulation O11) compounds compare to corresponding 100% lignin filled compound. This is due to presence of phenolic hydroxyl group and its effect like antioxidant, which gives good stability at high temperature. While in case of partial replacement, properties for different parameters, are in between 100% DOP filled compound and 100% lignin filled compound properties.

4.8 Low Temperature Brittleness Point: In NBR rubber compound, low temperature resistance is mainly depends on acrylonitrile content of selected polymer, plasticizer nature and quantity used. Here low temperature brittleness properties are tested as per ASTM D 2137 by Cryochamber and reported in table 6

Table 6

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Low Temperature Brittleness Point (°C)	-38	-30	-35	-45	-30	-35

Result and Discussion: In case of low temperature brittleness test, 100% DOP filled compound shows, good flexibility at low temperature compare to 100% lignin filled compound. While partial replacement of DOP by lignin shows intermediate values.

4.9 Compression Set: This test is carriedon button samples of 12.5 ± 0.5 mm thickness, as per the ASTM D 395 method B. Data observed is given in table 7

.**Table 7**

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4 C
1.	Compression Set (%)						
i)	@R.T./70hrs/25% deflection.	4	3	4	3	12	5
ii)	@100°c/70hrs/25% deflection	20.5	34	27	16.5	55	40

Results and discussion: At room temperature, compression set values arealmost same for 10phr loading. But at 20phr lignin loading, values are towards higher side, due to less plasticizing nature compare to DOP filled compound. After air ageing, compression set values are towards higher side for lignin filled compound. This is due to presence of sulphur in lignin. With increase in lignin phr loading, it makes the compound with more polysulphidic bonds. Polysulphidic bonds are susceptible to break due to low bond energy under air ageing and compressed condition. Due to this, drop in compression set observed.While in case of partial replacement, compression set values are in between corresponding values of 100% lignin filled compound and 100% DOP filled compound.

4.10 Volumetric swelling Test: This test is done as per ASTM D 297 in IRM 903 oil at 100°C for 72 hrs. Results observed are given in table 8.

Table 8

Sr. No.	Properties	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Volume Swelling (%)						
i)	Volume Swelling (%) in IRM 903 oil/100°C/70hrs.	+6.7	+9.9	+7.4	-1.5	+10	+3.4

Results and Discussion: Swelling is the key property in case of Nitrile rubber. Mostly in oil medium, while selecting the polymer, nitrile is the main choice. At 10phr loading (formulation O-Std, O1 and O2), volume swell values are within the range of +7 to +10%. But at 20phr loading, lignin filled compound shows stable value compare to 10phr lignin filled compound. But in case of 20phr DOP filled compound, value is -1.5%. It shows that, material is getting extracted in the oil medium, so the volume loss observed at 20phr DOP filled compound. In case of partial replacement of DOP by lignin (formulation O4), value is quiet improved i.e. not extraction as well as no much increase in volume.

4.11 Specific gravity: This test is done as per ASTM D 297 by using Sartorius weighing balance. The observed data is given in table 9.

Table 9

Sr. No.	Properties on Rubber Compd.	Formulation code Numbers					
		O -Std.	O1	O2	O3	O11	O4
1.	Density (gm/cm3)	1.19	1.22	1.21	1.18	1.23	1.2

Results and discussion: Lignin filled compound shows high density than DOP filled compounds. Also with increase in lignin loading densityincreases.

5. Conclusion:

Above experimental data shows that DOP filled compound show more viscosity reduction than lignin filled compounds. While partial replacement of DOP by lignin gives intermediate values for mooney viscosity.In case of mooney scorch time and curing time lignin filled compound shows reduction in values due to accelerating nature of lignin. Before ageing hardness, tensile strengthand modulusoflignin filled compound is towards higher side, while tear strength and elongation at break is towards higher side up to 10phr lignin loading. This is due to comparatively less plasticizing nature of lignin.After air ageing, DOP filled samples shows more hardness change, while lignin filled and partial replacement of DOP by lignin shows improved results. Also at high DOP loading, this hardening effect is of more concern, while lignin filled samples are more stable. For tensile strength and elongation at break in100% lignin filled and partial lignin filled compounds, shows good recovery compare to 100% DOP filled compound.In 100% DOP filled compounds, improvement in low temperature brittleness point observed which is due to more plasticizing nature. For volume swelling in IRM903 oil at 100°c, lignin filled compound shows, good stability, while 100% DOP filled compound gets extracted in Oil at high loading (20phr DOP loading). But at the same time, combination of lignin and DOP, gives improved volume change. Lignin filled vulcanizates shows higher density than DOP filled vulcanizate.

So though the lignin has less plasticizing effect, it can be used partially or completely for replacing DOP, to improve properties like before ageing and after ageing modulus, tensile strength, improved hardness recovery, volume change in IRM903 oil.Also it has some other benefits also like improved productivity as it reduces curing time, and thus saving of energy. Also it will help to minimize the use of DOP, and thus its effect on environment and pollution.

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