

## CHARACTERIZATION AND USE OF LIGNIN AS BIO ACCELERATOR FOR REPLACEMENT OF SYNTHETIC ACCELERATOR IN NITRILE RUBBER

Santosh C. Jagadale<sup>1,2,3a\*</sup>, Dr. Ganesh Bhagure<sup>1, b</sup>, Dr.K. Rajkumar<sup>2, c</sup>,  
Dr. Bhushan Langi<sup>1, d</sup>

1. Department of Chemistry, Satish Pradhan Dnyanasadhana College, Off Eastern Express Highway, Dnyanasadhana, Marg, Thane, Maharashtra 400604, India.
2. Indian Rubber Manufacturers Research Association, 254/1 B, Rd Number 16U, Wagle Industrial Estate, Thane West, Maharashtra 400604, India.
3. Department of Students Development, University of Mumbai, Mumbai- 400 020 Maharashtra, India

### Abstract

This work reports the use of bio-based lignin as greener accelerator in nitrile rubber compounds by partial replacement of hazardous, carcinogenic synthetic ingredients. Acrylonitrile butadiene rubber (commonly known as Nitrile or NBR is most widely used elastomer due to its superior chemical resistance. NBR's ability to resistance to various fuels and withstand a range of temperatures, makes it an ideal material for various applications like hose, seals, grommets, gaskets, tank linings and in various industries. During vulcanization process, various types of accelerators are used to enhance the curing rate and added into a rubber compound to increase the speed of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiency. Most of the conventional rubber accelerators used for curing of rubber, produce nitrosamine during and after processing. Accelerators like TMTD (Tetra methyl Thiuram Disulfide) are hazardous and carcinogenic, which creates harmful effect during rubber products manufacturing stage, application stage as well as after rubber product completes its usable life. Here experiments were done to see the effect of lignin addition by partial replacement of conventional Sulfenamide and Thiuram type Accelerator. We have investigated the effect of bio-based lignin as accelerator and it is evident that the lignin along with other conventional accelerator found to reduce the curing time, improves scorch safety and can replaces 75% accelerator without affecting much on mechanical properties. This is useful to rubber industry for minimizing the pollution along with cost reduction due to use of this low-cost byproduct of paper industry.

*Keywords:* greener, carcinogenic, hazardous, byproduct, lignin, accelerator

### 1.0 INTRODUCTION:

In rubber products several ingredients such as activators, accelerators, fillers, plasticizers, antidegradants are used, which make it very complex material. Most of them are non-renewable petroleum based materials such as carbon black as filler, plasticizers etc. [1]. Replacement of petroleum derived or synthetic materials with sustainable bio-based material from the point of view of economic and environmental concerns is the current need in rubber industry and has attracted much attention since last decades [2-4].

Lignin is the second most abundant source of biomass after cellulose in the world. Lignin has polyaromatic moieties and found to be potential bio based source for the replacement of fossil resources [5, 6]. The extensive research has been carried out to exploit lignin in polymer composites as reinforcing filler, as a coreactant for the production of thermosets, foams, resins

etc. [7, 8]. Several other attempts have been made in elastomeric composites towards the utilization of lignin as a partial replacement of conventional fillers like carbon black and silica [9-12]. From our earlier studies it was evident that the lignin can be utilized as a plasticizer in nitrile rubber compound as a partial replacement of DOP (Diethyl phthalate) with improved cure and after ageing properties [13]. Resistance to oxidative degradation of rubber is an important property which decides the service life of product. Oxidation of rubber chains results in the softening due to attack on unsaturated polymer backbone [14]. Various technical reports are available on the lignin based rubber composites where lignin showed a resistance towards thermo-oxidative degradation owing to the presence of sterically hindered phenolic groups in the structure in different polymeric systems, such as polypropylene, [15] sugar cane bagasse derived lignin in BR, SBR and NR [16, 17] and natural rubber [18, 19]. Lignin contains several functional chemical groups, such as hydroxyl (phenolic or alcoholic), methoxyl, carbonyl and carboxyl, in various amounts, depending on origin and the applied isolation process [20, 21]. The distinct network structure as well as the presence of the various chemical substituents confers unique functional properties to lignin. It has been shown that lignin is a versatile molecule that possesses multiple properties such as antioxidant (i.e. radical scavenger), UV-absorption, anti-fungal and antibiotic activity [22, 23, 24]. Also, anti-carcinogenic and antibiotic activities of lignin have been reported [23].

In the present work, lignin has been focused as an accelerator in nitrile rubber compounds. Here, effect of lignin combination with accelerator as well as partial replacement of conventional accelerators studied to see effect on curing kinetics, physico-mechanical properties. It is evident that the lignin along with other conventional accelerator found to reduce the curing time, replaces 75% conventional accelerator without affecting physico-mechanical properties. Instead, there is improvement in scorch safety of rubber compound.

## **2.0 MATERIAL:**

Sodium Lignosulfonate (Borresperse NA) is a modified sodium lignosulfonate derived from spruce (softwood), supplied by M/S Borregaard South Asia Pvt. Ltd., Navi Mumbai, Thane. Nitrile rubber grade, JSR230SL with medium acrylonitrile content (35% ACN) was sourced from JSR Corporation. Zinc oxide of Rubamin Limited and Stearic Acid of Godrej Industries used. Accelerator N-cyclohexyl-2-benzothiazole sulfenamide (CBS) and Tetra methyl Thiuram Disulfide (TMTD) were supplied by reputed manufacturers while Sulphur was supplied by Rubosynth Impex Pvt. Ltd.

## **3.0 CHARACTERIZATION / TEST METHOD**

### **3.1 SEM- EDX:**

The morphological feature of Sodium Lignosulfonate material and vulcanizates were investigated by using a scanning electron microscope ZEISS, INCA X-act model 51-ADD0048. The elemental analysis is also carried out by SEM EDX.

### **3.2 FT-IR:**

Spectra were recorded in the wavelength range  $500\text{ cm}^{-1}$  -  $4000\text{ cm}^{-1}$  by using Fourier transform infrared spectroscopy, Thermo Scientific make, Nicolet 6700 model.

### **3.3 Rubber Compounding and Experimental Formulations:**

The mixings were carried out in a conventional laboratory open roll mill of size (6 x 12 inch) as per ASTM D3182. The compounding ingredients were added in the order: polymer mastication followed by Sulfur, activator and lignin along with accelerators. To investigate

lignin's ability as accelerator, its optimum loading dosage as an accelerator and replacement of conventional accelerator by lignin, experiments were designed and given in table-1, 2, and 3.

**3.3.1 Lignin as Accelerator:** To check lignin's ability as accelerator experimental formulation is given in table-1

**Table 1 - Formulation of Rubber Compound – Lignin as Accelerator**

Ingredients	Control	CBS	TMTD	LI-5	LI-10	CLI-5	TLI-5
	phr	phr	phr	phr	phr	phr	phr
CBS	2	2	0	0	0	2	0
TMTD	1	0	1	0	0	0	1
Sodium Lignosulfonate	0	0	0	5	10	5	5

**3.3.2 Optimization of Lignin:** To see the optimum loading dose, in presence of conventional accelerator, experiments were done by loading sodium lignosulfonate up to 15phr and compared with control compound. All formulations contain Nitrile rubber (100phr), Zinc Oxide (4phr), Stearic Acid (1phr), Sulphur (1phr), while remaining ingredients are given in table-2.

**Table 2 - Formulation of Rubber Compound – Optimization of lignin loading**

**3.3.3 Replacement of Conventional synthetic Accelerator by Lignin:** To see the amount of

Ingredients	CONTROL	CTLI-5	CTLI-10	CTLI-15
	phr	phr	phr	phr
CBS	2	2	2	2
TMTD	1	1	1	1
Sodium Lignosulfonate	0	5	10	15

accelerator, lignin can replace, experiments were done. All formulations contain Nitrile rubber (100phr), Zinc Oxide (4phr), Stearic Acid (1phr), Sulphur (1phr), while remaining ingredients are given in table-3.

**Table 3 - Formulation of Rubber Compound – Replacement of Conventional accelerators**

Ingredients	CONTROL	NA-1	NA-2	NA-3	NA-4
	phr	phr	phr	phr	phr
CBS	2	1.5	1	0.5	2
TMTD	1	0.75	0.5	0.25	1
Sodium Lignosulfonate	0	10	10	10	10
	Control Compound	25%	50%	75%	Excess addition in control compound

### 3.4 Rheological properties:

The cure characteristics of these mixes were studied as per ASTM D5289, in a MonTech Rheometer (MDR-3000) at 150°C. The curing characteristics of the materials, expressed in terms of the scorch time (t<sub>S2</sub>), Induction time (t<sub>s1</sub>), optimum cure time (t<sub>90</sub>), the maximum (MH) and minimum (ML) values of the torque, delta torque (ΔT), and cure rate index (CRI). Cure rate index (CRI) is calculated by using following equation (1).

$$CRI = \frac{100}{(Cure\ time\ (t_{90}) - Scorch\ time\ (t_{s2}))} \quad (1)$$

### 3.5 Properties of Vulcanizates:

The modulus, tensile strength, elongation at break were measured on tensile testing machine (Tinius Olsen) as per ASTM D412 and hardness of the composites was tested by Shore A hardness tester as per ASTM D2240.

## 4.0 RESULTS AND DISCUSSION:

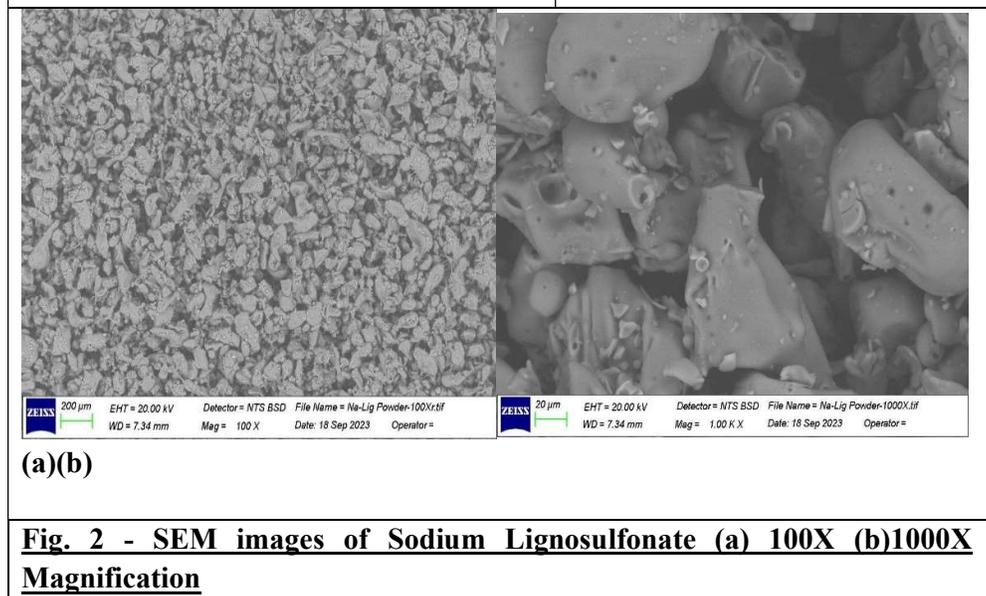
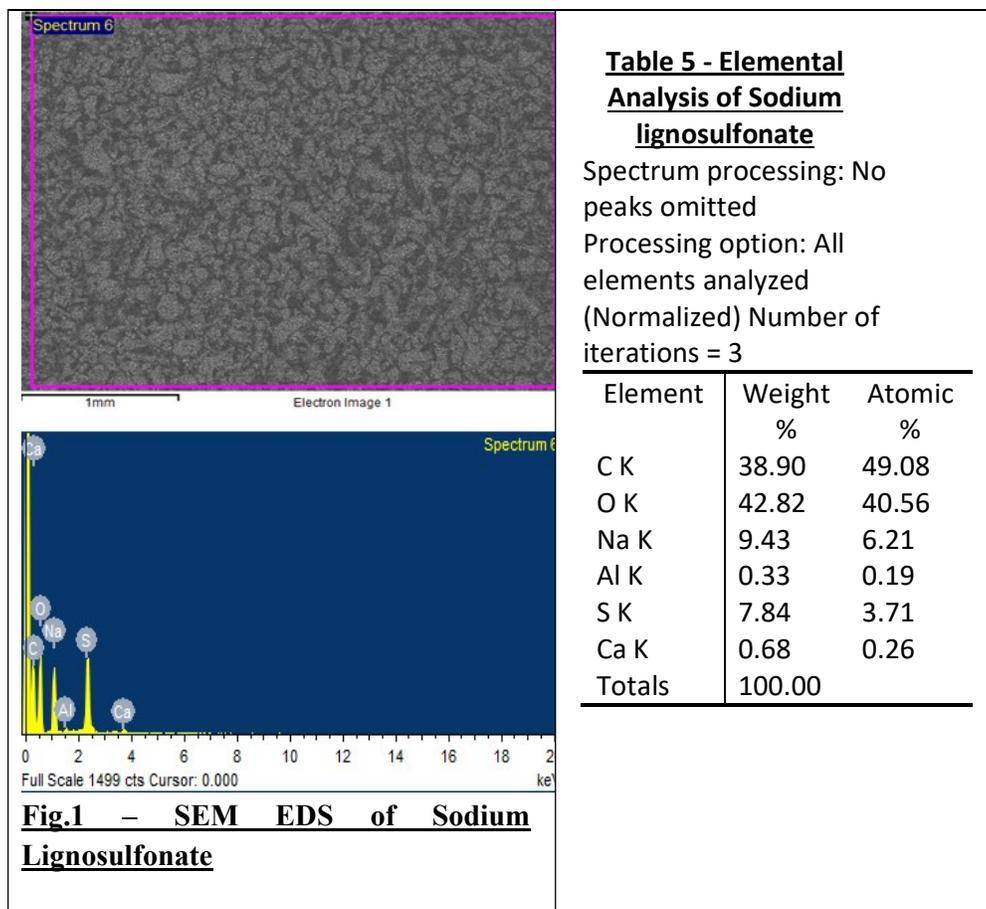
**4.1 Characterization of lignin:** The lignin used in this work is modified sodium lignosulfonate derived from spruce (softwood). The technical properties (given by the supplier) with material are given below:

**Table 4- Characteristics of lignin**

Parameters	Values
Colour	Brown
pH (10% Solution)	8.3±0.8
Dry matter (%)	Min.93
Insoluble (w/w %)	Max.0.3
Reducing Sugars (%)	1
Calcium (%)	Max 0.6
Na <sub>2</sub> SO <sub>4</sub> %	Max. 5.0
Sulfur content (%)	7
Sodium (%)	9

### 4.2 SEM-EDX:

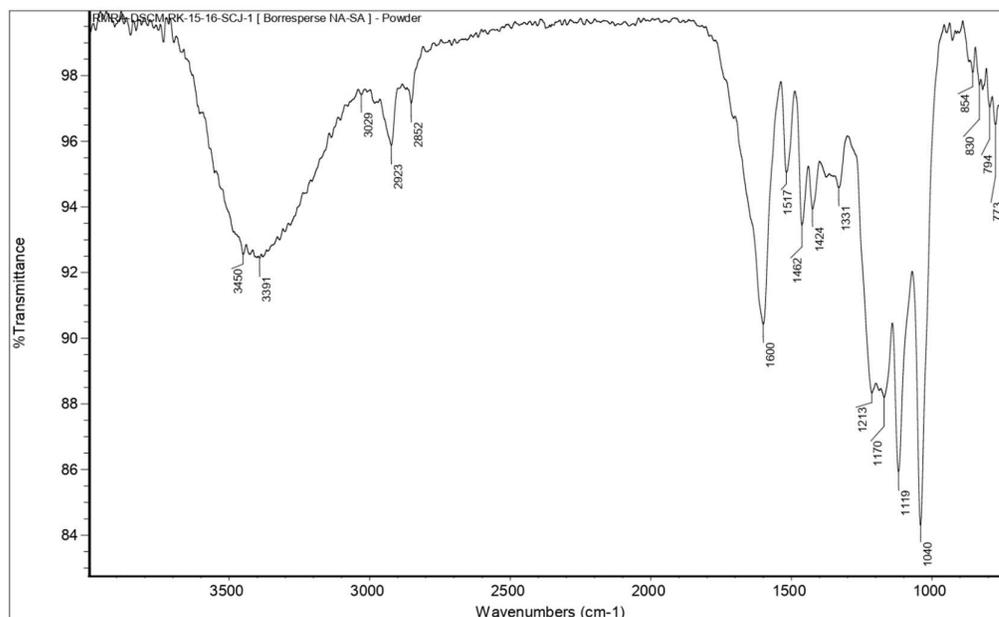
The morphology of lignosulfonate samples was studied by SEM and is shown in Fig. 2. Lignosulfonate particles size and shape is uneven as well as having some porosity. The elemental analysis related details given in table-5. It shows presence of Sulphur, from sulfonic group, sodium (Na) which comes from sodium bisulfite (NaHSO<sub>3</sub>) used during making of lignosulfonate process. Also, in small proportion Calcium (Ca), Aluminum (Al) detected.



#### 4.3 FT-IR Analysis of Sodium lignosulfonate:

Fourier-transform infrared spectroscopy (FT-IR) has been shown to be a powerful tool for the investigation of plant cell wall polymers, such as polysaccharides and lignin's [25, 26, 27, 28]

FTIR spectra of Sodium lignosulfonate showed typical bands corresponding to the functional groups expected to be found in lignin sample. Below we present an analysis of the recorded spectra of the lignin samples used in this study, based on the assignments given by Faix [25]. The broad wide band at 3391-3450 $\text{cm}^{-1}$  attributed to the hydroxyl groups in phenolic and aliphatic structures. Especially phenolic hydroxyl groups which mostly affect the antioxidant properties of lignin, and the bands around 2923 and 2852  $\text{cm}^{-1}$ , predominantly arising from CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains.



**Fig. 3 - FT-IR spectra of Sodium Lignosulfonate**

Aromatic skeleton vibrations at 1600, 1517 and 1424  $\text{cm}^{-1}$  and the C–H deformation combined with aromatic ring vibration at 1462  $\text{cm}^{-1}$  are found in sodium lignosulfonate grade which are generally common in various types of lignin's derived from various plant sources as well as lignin extraction methods, although the intensity of the bands may differ. Sharp peaks located at 1600 $\text{cm}^{-1}$  referred to vibration of aromatic rings [29]. Absorption peak at 1462 $\text{cm}^{-1}$  & 1424 $\text{cm}^{-1}$  is attributed to methoxyl groups and vibration of C-H in the aromatic ring respectively. The spectral region below 1400  $\text{cm}^{-1}$  is more difficult to analyze, since most bands are complex, with contribution from various vibration modes. However, this region contains vibrations that are specific to the different monolignol units and allows the structural characterization of lignin. Lignin samples are a weak band at around 1370–1375  $\text{cm}^{-1}$  originating from phenolic OH and aliphatic C–H in methyl groups and a strong vibration at 1213 $\text{cm}^{-1}$  that can be associated with C–C, C–O, C=O stretching. The aromatic C–H deformation at 1040  $\text{cm}^{-1}$  appears as a complex vibration associated with the C–O, C–C stretching and C–OH bending in polysaccharides. Carbohydrate originating vibrations are associated also with other vibrations in the spectral region 1000–1300  $\text{cm}^{-1}$ . There is influence of polysaccharide impurities on the spectral profile.

Also there is characteristic vibration at 1331 $\text{cm}^{-1}$  assigned to Syringyl Ring breathing with C-O, Sulfonic acid groups in lignosulfonates appeared at about 1213  $\text{cm}^{-1}$  in agreement with literature [29]. OH stretching vibration of secondary alcohols (around 1170  $\text{cm}^{-1}$ ), 1119 $\text{cm}^{-1}$

to ether group stretching vibration, 854 and 830cm<sup>-1</sup> (C-H out of plane vibration), the band appearing at 620-660cm<sup>-1</sup> is assigned to sulfonic groups (S-O stretching vibration) formed from the reaction of sodium sulphite with secondary OH of the aliphatic acid chains of the lignin.[27]

**4.4 Compounding and Rheological Properties:**

**4.5 Lignin as Accelerator:**

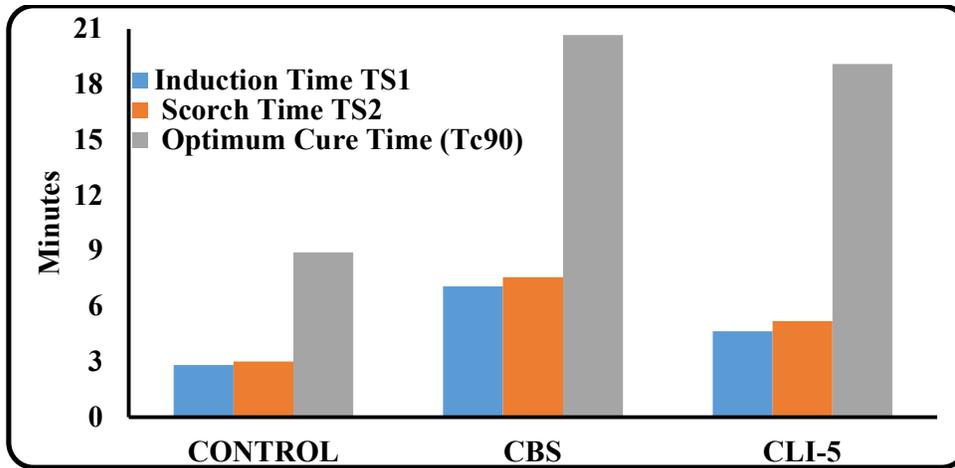
Rheometric analysis was carried out as per ASTM D5289 by using **MonTech Rheometer (MDR-3000) at 150°C. The observed properties were given in table-6.**

With increase in lignin loading (formulation LI-5 to LI-10), there is decrease in scorch time (ts<sub>2</sub>) and curing time, indicates its ability to enhance the crosslinking reaction and reduction in curing time. But Lignin, alone is not giving that effect compared to control compound or compared to alone CBS & TMTD filled compound.

**Table 6- Rheometric Properties @150°C**

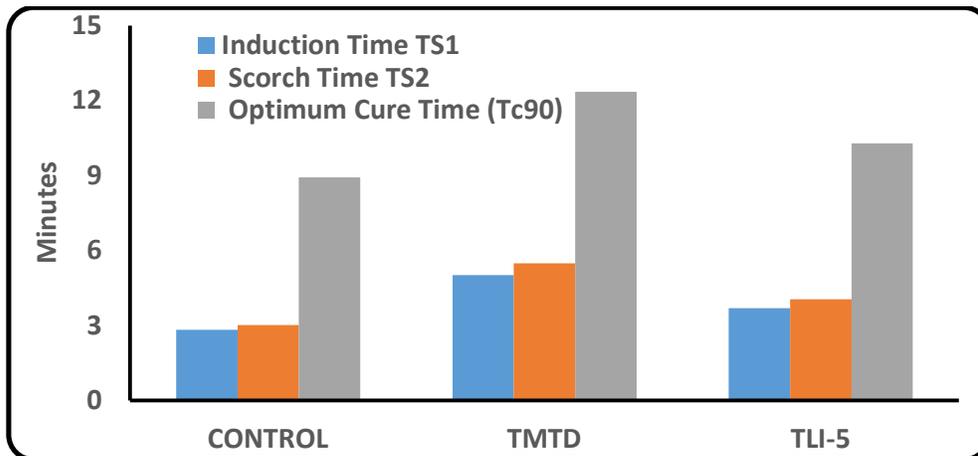
<b>Parameters</b>	<b>Control</b>	<b>CBS</b>	<b>TMTD</b>	<b>LI-5</b>	<b>LI-10</b>	<b>CLI-5</b>	<b>TLI-5</b>
Maximum Torque(lbs.in)	10.45	8.14	7.2	2.4	3.53	7.92	7.14
Minimum Torque (lbs.in)	0.37	0.38	0.4	0.37	0.4	0.36	0.38
Induction Time TS1 (minutes)	2.84	7.07	5.02	35.89	23.07	4.64	3.7
Scorch Time TS2 (minutes)	3.02	7.58	5.49	59.25	38.68	5.2	4.05
Optimum Cure Time (Tc90)	8.92	20.69	12.35	55	53.22	19.12	10.29
ΔT Torque (MH-ML)	10.08	7.76	6.8	2.0	3.1	7.6	6.8
Cure Rate Index (CRI)	16.9	7.6	14.6		6.9	7.2	16.0

But it shows synergetic effect along with conventional accelerators, even in presence of single conventional accelerator (can be seen in formulation CLI-5 & TLI-5). Compared to conventional accelerator (formulation marked as CBS & TMTD), when lignin added (formulation CLI-5 & TLI-5), drop in scorch and curing time observed, indicates synergetic effect, due to sulfonic groups present in lignin.



**Fig. 4 – Scorch & Curing time for Control, alone CBS filled compound and CBS + Lignin Filled compound.**

In case of  $\Delta T$ , in presence of conventional accelerator (formulation CLI-5 & TLI-5) value of  $\Delta T$  is almost same, while that of CRI, in presence of CBS its again almost same, while in presence of TMTD, its towards higher side. The CRI is a measurement of the cure rate. It indicates that the rate of curing increased with addition of the lignin loading in presence of TMTD accelerator. This indicates the accelerating nature of lignin in presence of conventional accelerators.



**Fig. 5 – Scorch & Curing time for Control, alone TMTD filled compound and TMTD+Lignin Filled compound.**

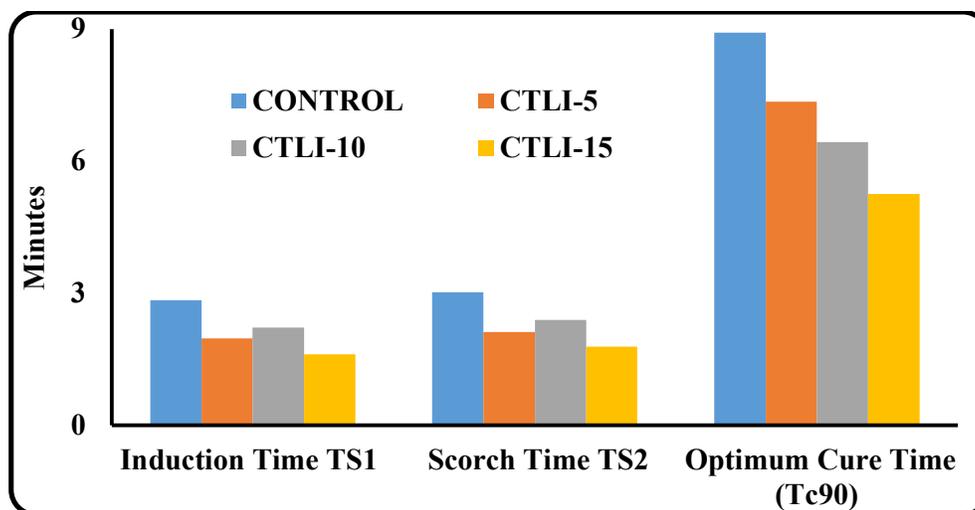
#### 4.6 Optimization of Lignin:

To see the optimum loading dose, in presence of conventional accelerator, experiments were done as per the formulation given in table-2, by loading sodium lignosulfonate up to 15phr and compared with control compound. **The rheometric properties of the compounds are tabulated in table-7**

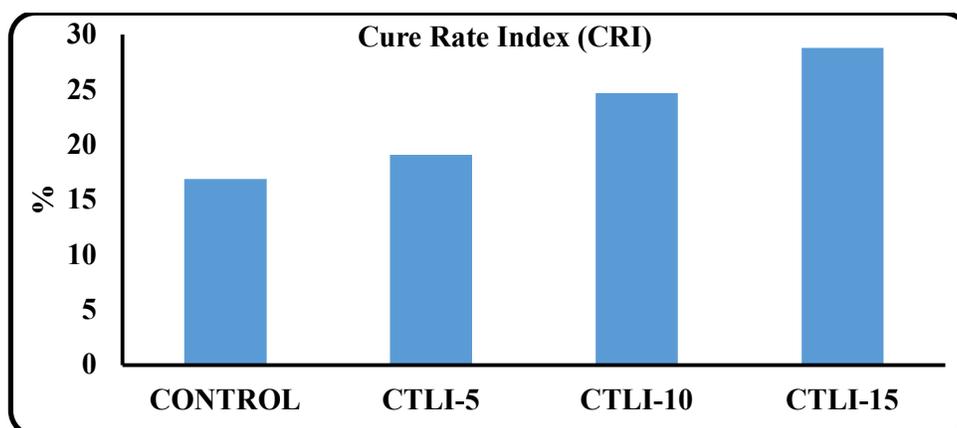
**Table 7- Rheometric Properties @150°C**

Parameters/Description	Control	CTLI-5	CTLI-10	CTLI-15

Maximum Torque (lbs.in)	10.45	11.01	8.63	6.59
Minimum Torque (lbs.in)	0.37	0.38	0.29	0.21
Induction Time TS1(minutes)	2.84	1.98	2.22	1.62
Scorch Time TS2 (minutes)	3.02	2.12	2.39	1.79
Optimum Cure Time (Tc90)	8.92	7.35	6.43	5.26
$\Delta T$ Torque (MH-ML)	10.1	10.6	8.3	6.4
Cure Rate Index (CRI)	16.9	19.1	24.7	28.8



**Fig. 6 – Scorch & Curing time with increase in lignin loading**



**Fig. 7 – Cure Rate Index (CRI) with increase in lignin loading**

Data shows, in presence of conventional accelerator, lignin filled compounds shows reduced scorch time, curing time, increase in CRI, suggesting that lignin accelerates the vulcanization of NBR. This was attributed to the sulphur bearing sulfonic group present in the lignin, which accelerates the reaction rate along with conventional accelerators synergistically.

At 15phr lignin loading, vulcanized slabs show very small size visible air bubbles, may be due to moisture content. Up to 10phr loading, sample surface is free from visible defects.

The values of minimum torque ML, maximum torque MH and  $\Delta T$  (MH - ML) drops at 10 and 15phr lignin loading, indicates along with accelerating nature, there is effect of polymeric

nature of lignin at high volume level, which drops the viscosity of the compound as well as modulus. While at 5phr loading, MH, ML and  $\Delta T$  are towards higher side, indicates dominating nature of lignin as accelerator over the polymeric nature. The CRI is a measurement of the cure rate based on the differences between the optimum cure time ( $t_{90}$ ) and incipient scorch time ( $t_{s2}$ ) [30]. The CRI of the compound with Lignin was higher than that of the Control compound. It indicates that the rate of curing increased with addition of the lignin loading as well as with increase in the lignin quantity.

**4.7 Replacement of Conventional synthetic Accelerator by Lignin:**

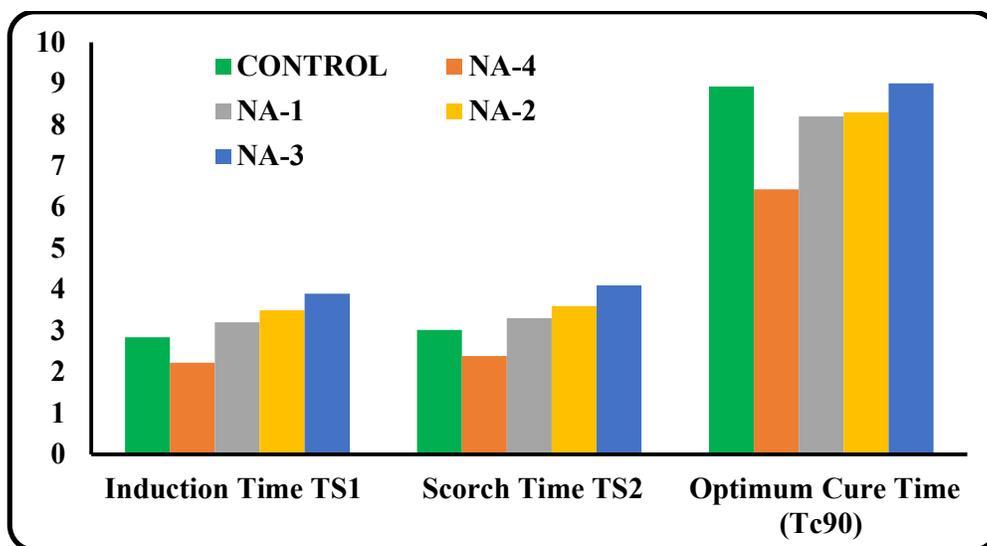
As the data show's ability of lignin as accelerator, experiments were done by taking 10phr sodium lignosulfonate as optimum loading dose and mixing was done as per the formulation given in table-3. Observed rheometric properties were given in table-8.

**Table 8 - Rheometric Properties @150°C**

Data

Parameters/Description	Control	NA-1	NA-2	NA-3	NA-4
Maximum Torque (lbs.in)	10.45	11.4	9.7	7.8	8.63
Minimum Torque (lbs.in)	0.37	0.5	0.5	0.5	0.29
Induction Time TS1(minutes)	2.84	3.2	3.5	3.9	2.22
Scorch Time TS2 (minutes)	3.02	3.3	3.6	4.1	2.39
Optimum Cure Time ( $T_{c90}$ )	8.92	8.2	8.3	9.0	6.43
$\Delta T$ Torque (MH-ML)	10.1	10.9	9.2	7.3	8.3
Cure Rate Index (CRI)	16.9	20.4	21.3	20.4	24.7
Slab molding time (minutes)	9	9	9	9	7

shows, with excess addition of lignin (NA-4) in control compound, there is drop in induction time, scorch time and curing time. While with accelerator replacement with lignin, it's giving the almost same curing time compared to control compound along with improved scorch safety. This indicates lignin's ability as accelerator and can replace the conventional carcinogenic accelerators. Due to replacement of conventional accelerator there will be reduction in compound cost, harmful Nitrosamine (here due to TMTD). Reduction in curing time, attributes to accelerating nature of lignin due to Sulphur donor sulfonic (-SO<sub>3</sub>) groups, which enhances the rate of crosslinking [18, 31, 32].



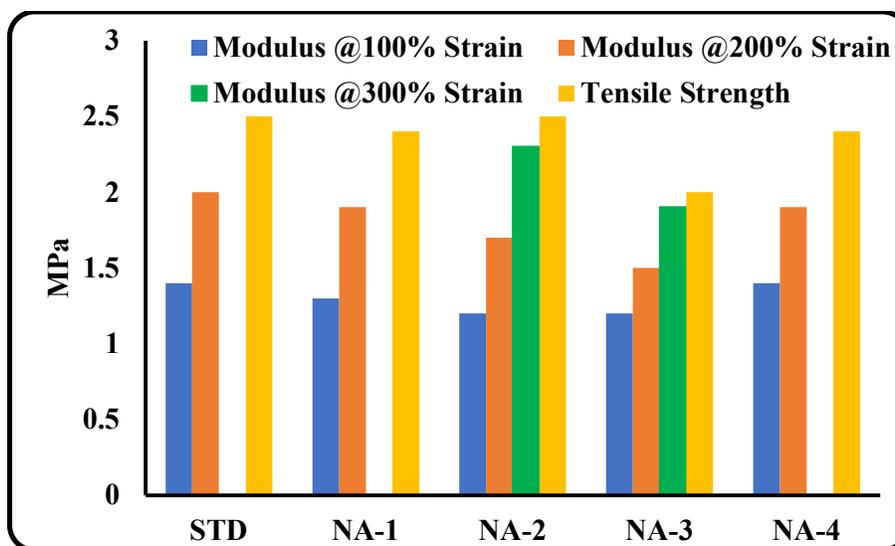
**Fig. 8 – Scorch & Curing time with excess addition of Lignin in Control compound & replacement of accelerator**

The values of minimum torque ML, is slightly towards higher side with accelerator replacement, and indicates slight increase in viscosity of compound. While at excess addition in control compound (NA-4), it slightly drops. MH and  $\Delta T$  (MH - ML) drops with reduction in quantity of accelerator from 50% onwards, while at 25% replacement, values are slightly higher one indicating slightly high viscosity, improved modulus than control compound. The CRI of the compound with Lignin was higher than that of the Control compound. It indicates that the rate of curing increased though there is reduction in quantity of conventional accelerators.

#### **4.8 Vulcanization of Rubber Composites:**

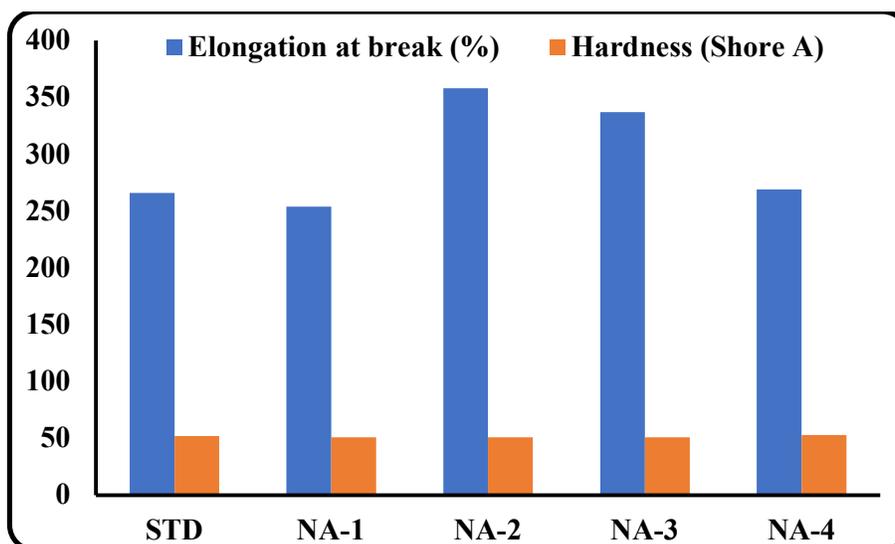
The physical properties of rubber composites are lot more dependent on the state of filler dispersion, surface chemistry, particle Size and rubber-filler interaction, curing system. The reinforcing capability of lignin in nitrile rubber compound is evaluated in terms of the extent of which modulus and tensile strength is improved with the addition of lignin.

The modulus, tensile strength, elongation at break were measured on tensile testing machine (Tinius Olsen) as per ASTM D412 and tear strength as per ASTM D624 die C. Hardness of the composites was tested by Shore A hardness tester as per ASTM D2240. Observed properties were given in Fig, -9 and 10.



**Fig. 9 – Modulus and Tensile Strength with excess addition of Lignin in Control compound & replacement of accelerator**

In case of mechanical properties, with reduction in conventional accelerators, slight drop in modulus observed. While tensile is almost same, up to 50% reduction in accelerator after that it drops.

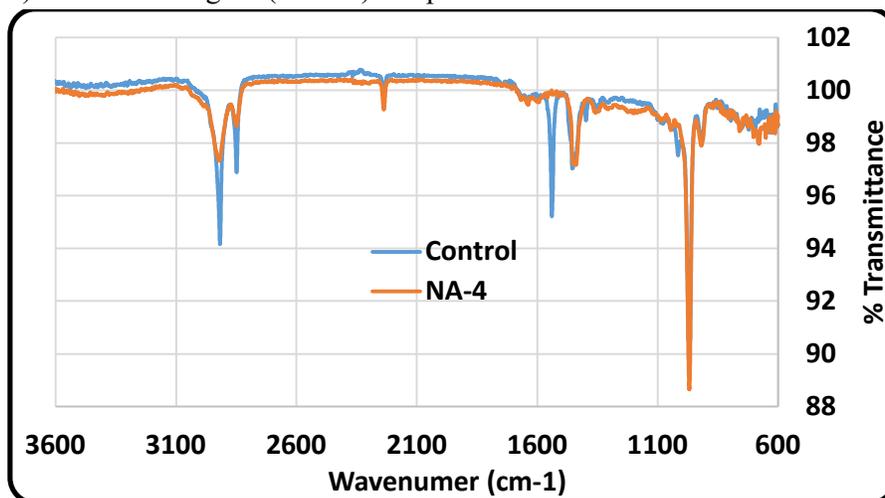


**Fig. 10 – Hardness & Elongation at break with excess addition of Lignin in Control compound & replacement of accelerator**

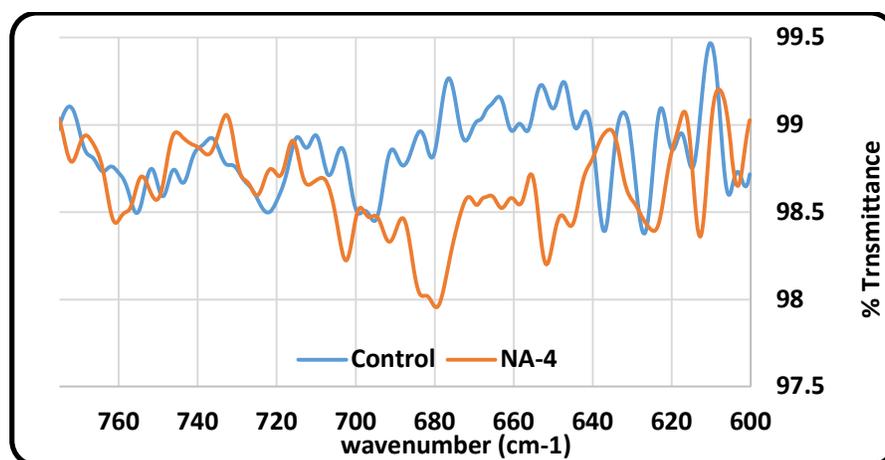
While in case of elongation at break, there is increase observed as the quantity of conventional accelerators drops. This observation attributes the fact that, with reduction in conventional accelerator quantity, polymeric nature of lignin dominates and that reduces the modulus and there is increase in elongation at break. While with excess addition of lignin in control compound (NA-4), there is not much change in modulus, tensile, elongation at break and hardness.

#### 4.9 FT-IR analysis of vulcanizate with and without lignin:

Here after mixing rubber materials are molded as per curing time and study done on vulcanized materials. Characterization was done for with (NA-4 with excess lignin in Control compound) and without lignin (control) sample.

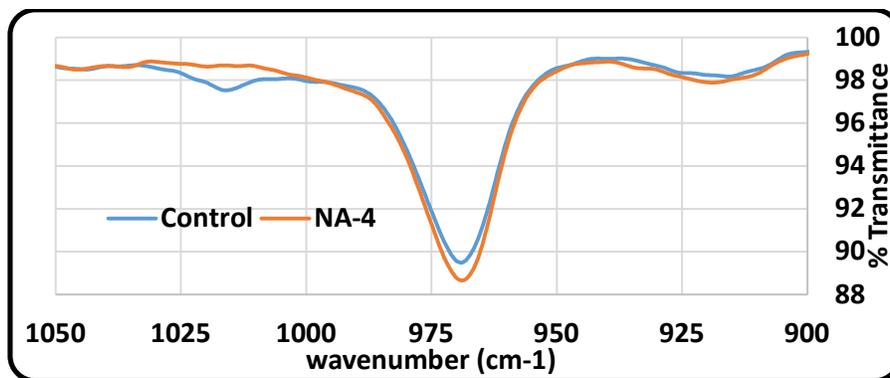


**Fig. 11 - FT-IR spectra of with (NA 4) and without (Control) lignin**



**Fig. 12 - FT-IR spectra of with (NA 4) and without (Control) lignin at 600-760 wavenumber (cm-1)**

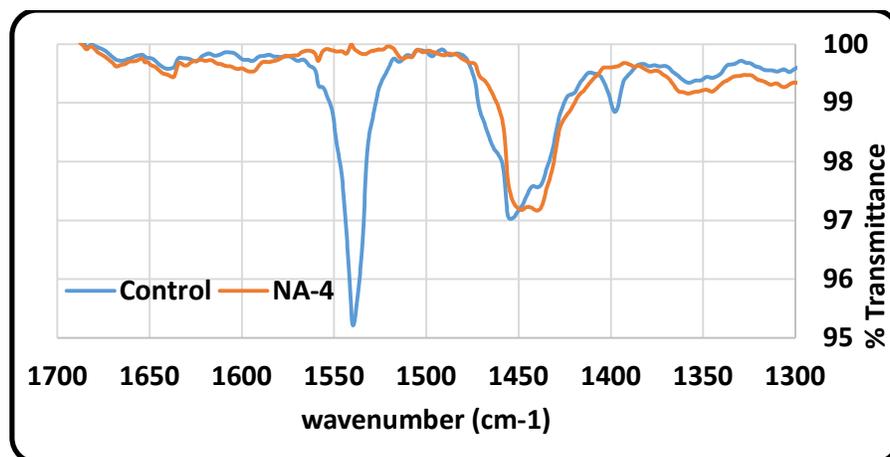
Compared to control, compound NA-4 (having excess addition of lignin in control compound) shows band appearing at 620-660cm<sup>-1</sup> is assigned to sulfonic groups (S-O stretching vibration) of lignin formed from the reaction of sodium sulphite with secondary OH of the aliphatic acid chains of the lignin [27] (Boeriu et al., 2004). After curing gets shifted to 645-680cm<sup>-1</sup> where in control its intensity is comparatively less, indicates participation of sulphur bearing sulfonate groups participation in reaction mechanism, as accelerator. While peaks around 750 in nitrile rubber is for C-H bonds in -CH=CH- butadiene monomer units, which gets shifted towards 760 cm<sup>-1</sup> after addition of accelerator.



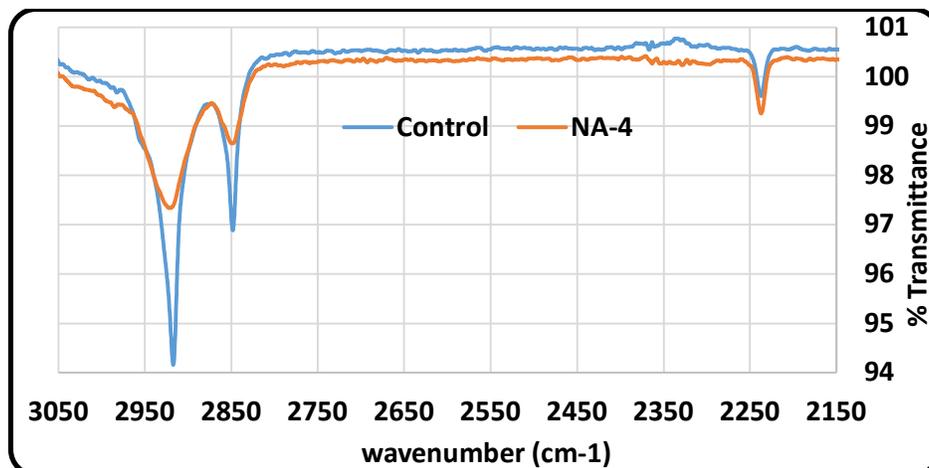
**Fig. 13 - FT-IR spectra of with (NA 4) and without (Control) lignin at region 900 -1100 wavenumber (cm-1)**

According to the standard and characterization of acrylonitrile butadiene rubber, the peak at wave numbers 915 and 970  $\text{cm}^{-1}$  originated from C-H groups, compared to control lignin filled compound shows more intensity. Peak 1015  $\text{cm}^{-1}$  in control compound, is not appearing in NA-4.

Figure-14 illustrates the FTIR spectrum for vulcanized NBR rubber with and without Sodium lignosulfonate at the wave range of 1300–1700  $\text{cm}^{-1}$ . The peak at wave numbers around 1540  $\text{cm}^{-1}$  are concerned with the chemical bond of  $\text{-C=C-}$ , in the structure of NBR rubber [33]. There is no any transmission value in NA-4, indicates lignin's reaction with Nitrile rubber. The peak at 1540  $\text{cm}^{-1}$   $\text{-C=C-}$  from butadiene decreases significantly, which indicates the reduction in this type of bonds in NBR after addition of lignin. Along with antioxidant (due to phenolic groups) properties, this (disappearing or minimization of butadiene double bonds due to reaction of lignin), may be the one of the reason for improved thermal stability for lignin filled polymeric composites. In control compound, 1450  $\text{cm}^{-1}$  is assigned to C-H group, which shows comparatively wide peak in NA-4. Also, there is no presence of peak 1397  $\text{cm}^{-1}$  in NA-4 which is available in Control compound. The peak at wave numbers 1595-1600  $\text{cm}^{-1}$  are concerned with chemical bond of  $\text{-C=C-}$  in the structure of NBR rubber [33].

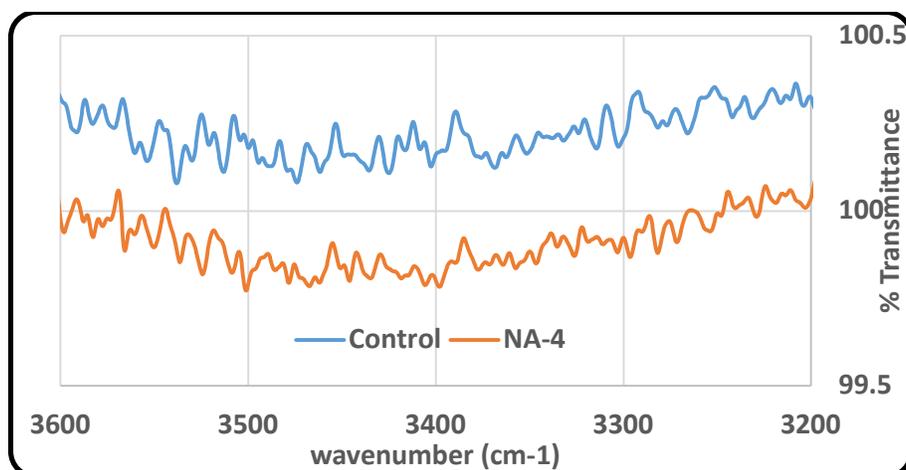


**Fig. 14 - FT-IR spectra of with (NA 4) and without (Control) lignin at region 1300-1700 wavenumber (cm-1)**



**Fig. 15 - FT-IR spectra of with (NA 4) and without (Control) lignin at region 2150-3050 wavenumber (cm-1)**

As it can be observed in this figure, molecule indexes of the NBR rubber are characterized in the format of peaks. Peak at the wave number of 2845-2850  $\text{cm}^{-1}$  is related to the functional group of  $\text{CH}_2$  and observed peak at the wave number of 2235-2240  $\text{cm}^{-1}$  is also regarded to the group of  $\text{CN}$  and connected bond of  $\text{C}\equiv\text{N}$  [34]. According to the standard of rubbers and characterization of acrylonitrile butadiene rubber, the peak at wave numbers of 2920, 2850  $\text{cm}^{-1}$  originated from C-H groups. Compared to control, the intensity of these peaks is low in lignin filled compounds.



**Fig. 16 - FT-IR spectra of with (NA 4) and without (Control) lignin at region 3100-3700 wavenumber (cm-1)**

The peak at wave numbers around 3500  $\text{cm}^{-1}$  are concerned with the functional group of  $\text{OH}$  in the structure of NBR rubber [33], while in case of lignin filled compound, NA- 4, the broad wide band at round 3400-3500  $\text{cm}^{-1}$  attributed to the hydroxyl groups in phenolic and aliphatic structures. Especially phenolic hydroxyl groups which mostly related to the antioxidant properties of lignin.

#### 4.10 SEM-EDS of Vulcanizate:

**CHARACTERIZATION AND USE OF LIGNIN AS BIO ACCELERATOR FOR REPLACEMENT OF SYNTHETIC ACCELERATOR IN NITRILE RUBBER**

Samples were studied by scanning electron microscopy using energy dispersive spectroscopy (SEM-EDS). The elemental analysis related details given in table-9a, b and c. With excess lignin as well as by replacement of conventional accelerator, shows presence of Sulphur, from sulfonic group, sodium (Na) which comes from sodium bisulfite (NaHSO<sub>3</sub>) used during making of lignosulfonate process.

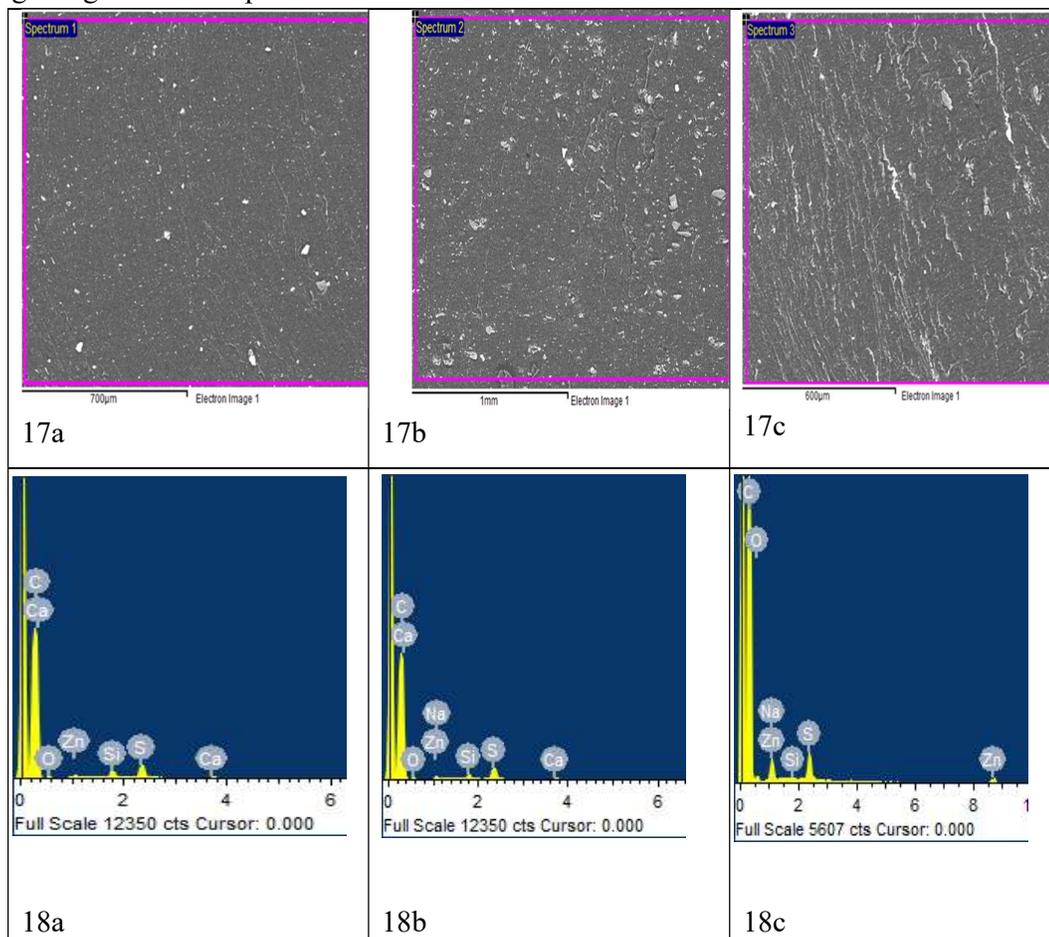


Fig. 17 & 18 SEM-EDX – Control (a), Excess addition of lignin in control (b) & 75% replacement of conventional accelerator by lignin (c)

Table -9a		Table -9b		Table -9c	
Element	Weight%	Element	Weight%	Element	Weight%
C K	89.41	C K	84.94	C K	85.10
O K	5.31	O K	9.52	O K	6.37
Si K	0.97	Na K	0.61	Na K	1.10
S K	2.72	Si K	0.70	Si K	0.02
Ca K	0.41	S K	2.85	S K	2.74
Zn K	1.19	Ca K	0.50	Zn K	4.68
Totals	100.00	Zn K	0.87	Totals	100.00
		Totals	100.00		

**Elemental Analysis by SEM-EDX – Control (a), Excess addition of lignin in control (b) & 75% replacement of conventional accelerator by lignin (c)**

Elemental analysis shows almost same weight % Sulphur (even after 75% replacement of conventional accelerators), compared to control compound.

### 5.0 Observation:

Data shows lignin has ability to enhance the curing reaction like conventional accelerator and gives synergetic effect in presence of conventional accelerator. As an accelerator, lignin reduces the curing time of the rubber compound, which is helpful to increase the productivity. As an accelerator, lignin can replace conventional accelerators up to 75%, without affecting much on curing time and viscoelastic properties, instead there will be reduction in curing time and increase in scorch safety of the rubber compound compared to control compound. After addition of lignin in control compound (i.e. in presence of conventional accelerators), there is drop in curing time, almost 20 to 25%, so it will increase more productivity. Also, as the cost of lignin is low than synthetic accelerators, there will be drop in product cost. Due to reduced accelerators (by replacing lignin), there will be comparatively less pollution, less use of synthetic materials required to make conventional accelerator.

### REFERENCE:

1. Rodgers, B. (Ed.). Rubber Compounding: Chemistry and Applications. CRC Press, 2015.
2. Z. S. Petrović, M. Ionescu, J. Milić, J. R. Halladay. Rubber Chem. Technol. 86 (2013) 233-249.
3. J. Li, A. I. Isayev, X. Ren, M. D. Soucek, Polymer 60 (2015) 144-156.
4. J. Li, A. I. Isayev, X. Ren, M. D. Soucek. Rubber Chem. Technol. 89 (2016) 608-630.
5. S. Laurichesse, L. Avérous, Prog. Polym. Sci. 39 (2014) 1266-1290.
6. D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, Green Chem. 18 (2016) 1175-1200.
7. V. K. Thakur, M. K. Thakur, P. Raghavan, M. R. Kessler, ACS Sustain. Chem. Eng. 2 (2014) 1072-1092.
8. D. Feldman, M. Lacasse, L. M. Beznaczk, Prog. Polym. Sci. 12 (1986) 271-299.
9. M. R. Snowdon, A. K. Mohanty, M. Misra, ACS Sustain. Chem. Eng. 2 (2014) 1257-1263.
10. P. Myllytie, M. Misra, A. K. Mohanty, ACS Sustain. Chem. Eng. 4 (2015) 102-110.
11. P. Yu, H. He, Y. Jia, S. Tian, J. Chen, D. Jia, Y. Luo, Polym. Test. 54 (2016) 176-185.
12. M. R. Snowdon, A. K. Mohanty, M. Misra, ACS Sustain. Chem. Eng. 2 (2014) 1257-1263.
13. S. C. Jagdale, K. Rajkumar, R. P. Chavan, D. N. Shinde, C. L. Patil, International Journal of Research in Engineering and Applied Sciences 6 (2016) 78-84.
14. R. W. Keller, Rubber Chem. Technol. 58 (1985) 637-652.
15. C. Pouteau, P. Dole, B. Cathala, L. Avérous, N. Boquillon, Polym. Degrad. Stab. 81 (2003) 9-18.
16. M. A. De Paoli, L. T. Furlan, Polym. Degrad. Stab. 13 (1985) 129-138.
17. L. T. Furlan, M. A. Rodrigues, M. A. De Paoli, Polym. Degrad. Stab. 13 (1985) 337-350.
18. M. G. Kumaran, S. K. De, J. Appl. Polym. Sci. 22 (1978) 1885-1893.
19. A. Gregorova, B. Košíková, R. Moravčík. Polym. Degrad. Stab. 91 (2006) 229-233. UPTO this OK.
20. Gosselink, R. J. A., Abächerli, A., Semke, H., Malherbe, R., Käuper, P., Nadif, A., van Dam, J. E. G., 2004. Analytical protocols for characterisation of sulphur-free lignin. Ind. Crops Prod.

- 19, 271–281
21. Sun, S., Tomkinson, J., Mao, F.C., Sun, X.F., 2001. Physicochemical characterisation of lignins from rice straw by hydrogen peroxide treatment. *J. Appl. Polym. Sci.* 79, 719– 732.
  22. Mai, C., Milsterin, O., Huttermann, A., 2000. Chemoenzymatical grafting of acrylamide onto lignin. *J. Biotechnol.* 79, 173– 183.
  23. Lu, F.J., Chu, L.H., Gau, R.J., 1998. Free radical-scavenging properties of lignin. *Nutr. Cancer* 30, 31–38.
  24. Barclay, L.R.C., Xi, F., Norris, J.Q., 1997. Antioxidant properties of phenolic lignin model compounds. *J. Wood Chem. Technol.* 17, 73–90.
  25. Faix, O., 1992. Fourier transformed infrared spectroscopy. In: Lin, S.Y., Dence, C.W. (Eds.), *Methods in Lignin Chemistry*. Springer-Verlag, Berlin-Heidelberg, pp. 458–464.
  26. Séné, C.F.B., McCann, M.C., Wilson, R.H., Grinter, R., 1995. Fourier-transform Raman and Fourier-transform infrared spectroscopy: an investigation of five higher plant cell walls and their components. *Plant Physiol.* 106, 1623– 1631.
  27. Boeriu, C.G., Stolle-Smits, T., van Dijk, C., 1998. Characterisation of cell wall pectins by vibrational spectroscopy. *Polish J. Food Nutr. Sci.* 7 (48), 257–266.
  28. Xiao, B., Sun, X.F., Sun, R.C., 2001. Chemical, structural and thermal characterisation of alkali-soluble lignins and hemicellulose from maize stems, rye straw and rice straw. *Polym. Degrad. Stab.* 74, 307–309
  29. K.V. Sarkanen, C.H. Ludwig (Eds.), *Lignins Occurrence, Formation, Structure and Reactions*, Wiley–Interscience, 1971, pp. 267–297.]
  30. Haixu Wang, Weifeng Liu, Jinhao Huang, Dongjie Yang and Xueqing Qiu, *Polymers* 2018, 10, 1033; *Bioinspired Engineering towards Tailoring Advanced Lignin/Rubber Elastomers*
  31. G. B. Nando, S. K. De, *J. Appl. Polym. Sci.* 25 (1980) 1249-1252.
  32. C. Jiang, H. He, H. Jiang, L. Ma, D. M. Jia, *Express Polym. Lett.* 7 (2013) 480-493.
  33. Poh BT, Ismail H, Quah EH, Chin PL (2001) Cure and mechanical properties of filled SMR L/ENR 25 and SMR L/SBR blends. *J Appl Polym Sci* 81:47–52. <https://doi.org/10.1002/app.1411>
  34. Zuiderduin WC, Westzaan C, Huétink J, Gaymans R (2003) Toughening of polypropylene with calcium carbonate particles. *Polymer (Guildf)* 44:261–275. [https://doi.org/10.1016/S0032-3861\(02\)00769-3](https://doi.org/10.1016/S0032-3861(02)00769-3)