

Utilization of Lignins in Rubber Compounding

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Synopsis

Lignin in the form of lignosulfonate containing about 33% moisture was found to be dispersible in natural rubber by dry mixing. Properties such as tear resistance, abrasion resistance, flex crack resistance, and crack growth resistance improved upon addition of lignin, irrespective of the nature of filler added. This lignin was found to have negative effects on modulus, tensile strength, resilience, heat buildup, and compression set, which showed, however, remarkable improvement upon aging.

INTRODUCTION

The major lignin derivatives are alkali lignin obtained by the sulfate process and lignosulfonic acids obtained by the sulfite process. Lignin derivatives are obtained as by-products in paper and pulp mills and are generally discarded into rivers, thus becoming environmental pollutants. The rubber industry represents the most important user of lignin. In 1949 Dawson¹ reviewed the use of lignin as a compounding ingredient with rubber. The influence of coprecipitation conditions on the properties of the product² and the problem of overcoming the slow rate of cure of lignin-rubber coprecipitates³ were also studied. In 1953 Sagajllo⁴ reported detailed investigations on the preparation and properties of natural rubber-lignin coprecipitates. Recently, a bibliography on "Lignin—Its Use in Rubber" has been compiled by the American Chemical Society.⁵ All these studies on lignin-rubber were carried out by the coprecipitation of alkali lignin with different elastomeric latices.

However, little work has been done on the effect of lignosulfonic acids on rubber. This lignin was mentioned in the literature as a processing aid only.⁶ It was also reported that coprecipitation of lignosulfonic acids with rubber latices was difficult because of its solubility in acid medium.⁷

The present paper deals with the effect of sodium lignosulfonate (hereafter referred to as lignin) on the processing, mechanical, and aging properties of both gum and filled natural rubber compounds. There is hardly any reference in the literature to an investigation in this regard. De et al. have recently reported results of preliminary investigations on compounding of natural rubber with lignins.^{8,9}

EXPERIMENTAL

The compositions of the mixes are shown in Table I. The materials used were of commercial grade. Lignin (sodium lignosulfonate powder) derived from bamboo was obtained from India Paper Pulp Co. Ltd., Calcutta. Natural rubber (RSS-1) was obtained from the Rubber Research Institute of India, Kerala.

TABLE I

	A	B	C	D	E	F
Natural rubber (RSS-1)	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5
CBS ^a	0.6	0.8	0.8	0.8	0.8	0.8
DPG ^b	0.1	—	—	—	—	—
HAF (N-330)	—	—	—	—	40	—
Spindle oil	—	—	—	—	5	—
Vulcasil S (silica)	—	—	—	40	—	—
Ethylene glycol	—	—	—	2	—	2
Whiting	—	80	—	—	—	—
Hard clay	—	—	80	—	—	—
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5
Lignin	0,5,10,15,20	0,5,10,15,20	0,10,20	0,5,10,15,20	0,5,10,15,20	0,10,20

^a N-Cyclohexylbenzothiazylsulfenamide.

^b Diphenylguanidine.

TABLE II
Effect of Lignin on Natural Rubber Gum Stock (Mix No. A)

Parameters	0 phr ^a	5 phr	10 phr	15 phr	20 phr
Mooney viscosity ML ₁₊₄ at 120°C	8	6	4	5	6
Mooney scorch time at 120°C, min	27	23	16	11	10
Optimum cure time at 140°C, min	25	24.5	25	25	25
Modulus, kg/cm ²	24 (32)	18 (22)	16 (22)	12 (23)	10 (23)
Elongation at break, %	650 (630)	680 (650)	690 (650)	710 (700)	690 (660)
Tensile strength, kg/cm ²	275 (300)	250 (300)	160 (300)	130 (270)	100 (200)
Tear resistance, kg/cm	35 (52)	38 (54)	44 (58)	37 (53)	29 (50)
Hardness (Shore A)	47 (50)	44 (46)	40 (44)	37 (43)	38 (42)
Resilience, %	85 (86)	77 (81)	72 (78)	68 (76)	63 (72)
Abrasion loss, cc/1000 rev	2.4 (2.7)	2.0 (2.2)	1.8 (2.0)	1.6 (1.9)	1.6 (1.9)
Compression set, %	55 (37)	65 (44)	68 (48)	73 (63)	78 (59)
Crack growth (0.5 in.), kilocycles	40 (23)	160 (50)	290 (150)	300 (150)	280 (130)
Flex cracking (grade C), kilocycles	280 (180)	330 (250)	390 (270)	370 (240)	290 (150)
Heat buildup, °C	6.5 (4.3)	9.3 (4.3)	15.3 (6.0)	22.0 (8.5)	30.0 (13.5)

^a Lignin content. Values in parentheses are those of samples aged for three days.

Mixing

The mixes were prepared on a laboratory-size two-roll mixing mill. Dry lignin powder did not mix properly with the rubber. When a lignin-water paste in the ratio of 2:1 by weight was mixed, the lignin was found to be easily dispersible in rubber. Possibly the lignin molecules coalesce into coarse aggregates owing to

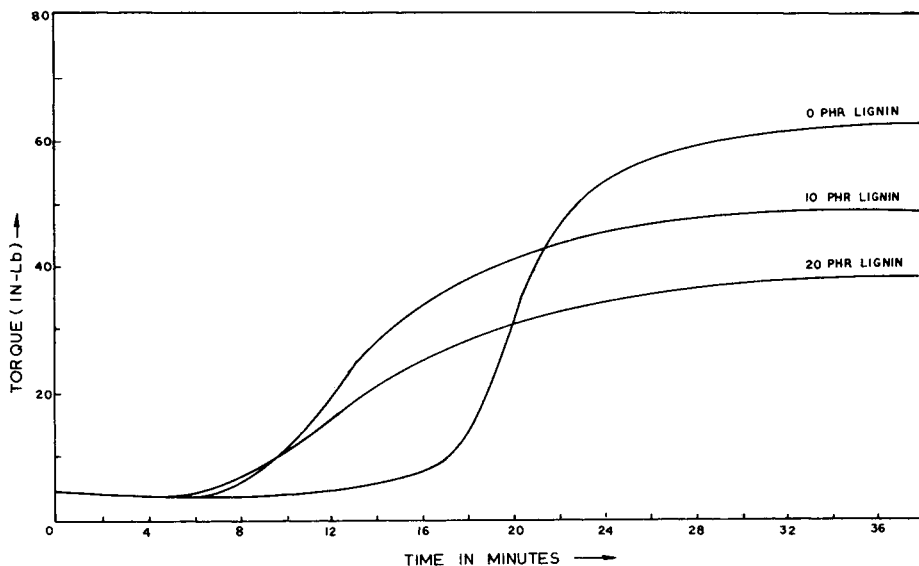


Fig. 1. Visurometer curves of lignin-filled compounds (mix A).

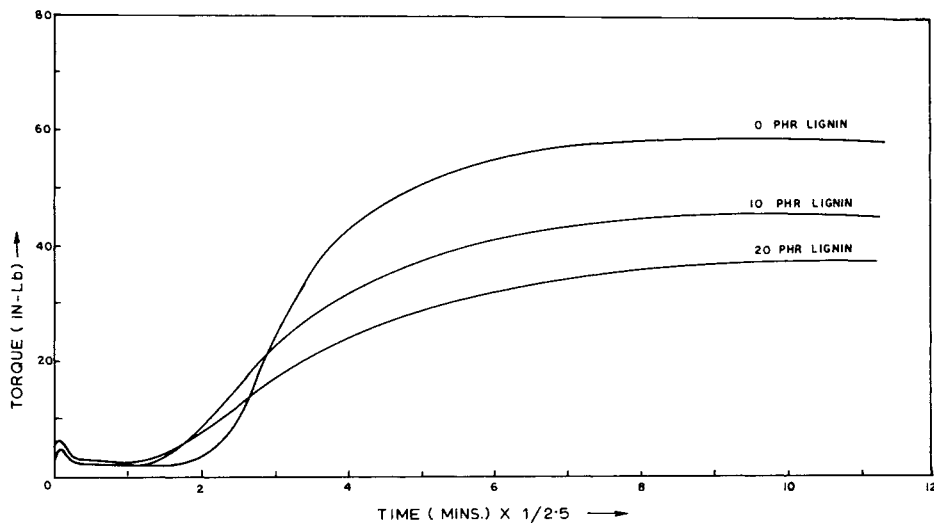


Fig. 2. Rheometer curves of lignin-filled compounds in presence of ethylene glycol (mix F).

intermolecular forces that cannot be readily broken by mechanical means. However, the addition of water weakens these intermolecular forces by forming new hydrogen bonds between the water and lignin molecules.⁴ Most of the water evaporated during mixing and the rest, during the overnight stay of the lignin-rubber masterbatch in thin-sheet form at room temperature. Further compounding with the necessary ingredients was possible without any difficulty.

TABLE III
Effect of Lignin on Whiting Filled Natural Rubber Stock (Mix No. B)

Parameters	0 phr ^a	5 phr	10 phr	15 phr	20 phr
Mooney viscosity ML ₁₊₄ at 120°C	6	6	6	8	9
Mooney scorch time at 120°C, min	32	26	17.5	9	9
Optimum cure time at 140°C, min	24.5	24.5	24.5	24.5	24.5
Modulus, kg/cm ²	29	22	23	26	27
	(32)	(26)	(29)	(32)	(33)
Elongation at break, %	610	630	640	650	650
	(590)	(600)	(630)	(600)	(600)
Tensile strength, kg/cm ²	160	115	125	135	105
	(170)	(150)	(150)	(150)	(150)
Tear resistance, kg/cm	29	30	35	29	30
	(30)	(32)	(35)	(35)	(32)
Hardness Shore A	61	56	54	51	53
	(63)	(59)	(58)	(57)	(56)
Resilience, %	76	69	65	62	60
	(78)	(72)	(70)	(70)	(67)
Abrasion loss, cc/500 rev	3.2	2.6	2.3	2.3	2.4
	(3.8)	(3.0)	(2.8)	(2.9)	(2.9)
Compression set, %	66	63	68	73	72
	(51)	(49)	(50)	(55)	(63)
Crack growth (0.5 in), kilocycles	10	30	45	50	30
	(5)	(10)	(15)	(25)	(20)
Flex cracking (grade C), kilocycles	20	35	40	35	25
	(15)	(20)	(25)	(10)	(10)
Heat buildup, °C	11.5	13.8	19.5	24.8	32.3
	(5)	(7.8)	(8.5)	(12)	(15.8)

^a Lignin content. Values in parentheses are those of samples aged for three days.

Test Procedures

The optimum cure times of the compounds (mixes A, B, C, D, and E) were determined by using a viscurometer (Model GSV, Scott Testers Inc.) at 140 ± 1°C. The time corresponding to 90% of the maximum torque was taken as the optimum cure time. Rheometer curves of mix F were obtained by using a Monsanto R-100 rheometer. Vulcanization was carried out at 140 ± 1°C and at a pressure of 600 psi on the cavity of the mold. Mooney viscosity and Mooney scorch time were determined according to ASTM D927-55T at 120°C. Tensile strength, modulus, and elongation at break were measured with a Zwick tensile testing machine according to ASTM D 412-51T and the tear resistance, according to ASTM D 624-48. Shore A hardness was determined according to ASTM D 676-55T. Impact resilience was measured at 35°C by using a Dunlop Tripsometer following BS 903, Pt. 2, 1950. Abrasion resistance was determined by using a Croydon-Akron abrasion tester and was expressed as volume loss in cc per 1000 or 500 revolutions of the grinding wheel. ASTM D395-52T (Method B) was used for measuring compression set. Both flex cracking and crack growth were measured according to ASTM D430-73 at 70°C. For the crack growth test an initial cut of 0.08 in. was made by using a Satra piercing tool. Heat buildup was measured by a Goodrich flexometer following ASTM D623-67. The initial temperature was 50°C, the load was 10.9 kg, and the stroke, 4.45 mm. The temperature rise at the end of 20 min of stroke was taken as the heat buildup. Aging was done in an air oven (Model No. FC 712, Blue M. Electric Co.) at 70 ± 1°C.

TABLE IV
Effect of Lignin on Hard Clay-Filled Natural Rubber Stock (Mix No. C)

Parameters	0 phr ^a	10 phr	20 phr
Mooney viscosity ML ₁₊₄ at 120°C	9	6	5
Mooney scorch time at 120°C, min	34	16	10
Optimum cure time at 140°C, min	24	25	26
Modulus, kg/cm ²	36	26	16
	(41)	(40)	(40)
Elongation at break, %	590	680	780
	(540)	(630)	(660)
Tensile strength, kg/cm ²	200	190	180
	(190)	(215)	(210)
Tear resistance, kg/cm	45	39	35
	(46)	(45)	(54)
Hardness (Shore A)	56	53	49
	(56)	(56)	(56)
Resilience, %	84	72	61
	(84)	(72)	(62)
Abrasion loss, cc/1000 rev	2.11	1.70	1.81
	(2.32)	(1.80)	(1.96)
Compression set, %	69	72	74
	(42)	(44)	(54)
Crack growth (0.5 in.), kilocycles	55	380	195
	(30)	(85)	(70)
Flex cracking (grade C), kilocycles	125	140	100
	(95)	(90)	(70)
Heat buildup, °C	5.8	11.0	22
	(3.0)	(6.0)	(12.3)

^a Lignin content. Values in parentheses are those of samples aged for three days.

Photomicrographs

Sample preparations and analyses of photomicrographs were done by Mr. James Brennick of Cabot Corporation, Billerica, Massachusetts 01821. The dispersions were characterised by the Cabot/Dunlop system.

RESULTS AND DISCUSSION

Effect of Lignin on Gum Stocks

Dispersion of lignin in natural rubber was found to be good.⁹ Table II shows the effect of lignin on different properties. Mooney viscosity decreased slightly and reached a minimum at 10 phr lignin loading, whereas the Mooney scorch time decreased continuously up to 15 phr lignin and then remained constant. Since hydroxylic groups accelerate vulcanization, the increased scorchiness may be due to the large number of hydroxylic groups present in the lignin structure. Optimum cure time, however, remained almost constant. Both tensile strength and modulus decreased and elongation at break increased due to the addition of lignin. These observations indicate that the lignin molecules reduce the elastic nature of the vulcanizate.

This assumption is further substantiated by the fact that lignin reduced hardness and resilience and increased compression set and heat buildup. But addition of lignin showed improvements in tear resistance, abrasion resistance, flex crack resistance, and crack growth resistance. It was observed that the

TABLE V
Effect of Lignin on Silica-Filled Natural Rubber Stock (Mix No. D)

Parameters	0 phr ^a	5 phr	10 phr	15 phr	20 phr
Mooney viscosity ML ₁₊₄ at 120°C	23	19.5	19	14	15
Mooney scorch time at 120°C, min	23.3	17.8	17	14	11.3
Optimum cure time at 140°C, min	37	26.3	27	32	32
Modulus, kg/cm ²	26	29	28	26	24
	(36)	(40)	(43)	(41)	(49)
Elongation at break, %	740	750	750	780	760
	(700)	(730)	(750)	(700)	(660)
Tensile strength, kg/cm ²	200	210	220	205	185
	(220)	(250)	(260)	(200)	(180)
Tear resistance, kg/cm	70	85	85	75	60
	(75)	(75)	(85)	(90)	(78)
Hardness (shore A)	64	63	62	63	64
	(68)	(66)	(70)	(74)	(76)
Resilience, %	40	38	37	35	35
	(42)	(40)	(40)	(38)	(41)
Abrasion loss, cc/1000 rev	1.26	1.23	1.22	1.29	1.29
	(1.57)	(1.38)	(1.33)	(1.30)	(1.43)
Compression set, %	64	83	78	72	69
	(55)	(60)	(57)	(54)	(55)
Crack growth (0.5 in), kilocycles	40	200	220	190	140
	(30)	(100)	(120)	(80)	(70)
Flex cracking (grade C), kilocycles	50	80	80	70	70
	(30)	(40)	(45)	(40)	(35)
Heat buildup, °C	24.5	27.3	28.8	30.8	32.5
	(20.8)	(21.5)	(22.8)	(23)	(26)

^a Lignin content. Values in parentheses are those of samples aged for three days.

tensile strength increased with the time period of aging in the case of lignin-loaded compounds and a maximum was reached after three days of aging. Aging also improved other properties of lignin-loaded compounds. The results after three days of aging are also included in Table II. Measurement of chemical crosslink density and free sulfur⁹ before and after aging indicated that lignin was responsible for reduction in the crosslink density. However, after aging the vulcanizates showed an increase in crosslink density. Sagajlo⁴ has reported formation of loose bonds between lignin and rubber during mixing. Lyubeshkina and coworkers¹⁰ have postulated similar bonding in lignin-modified polypropylene. Such bonds may block some of the vulcanization sites in the rubber chains, and they possibly break up at a slow rate during aging. Improved properties of the aged samples may be due to further crosslinking.

Figures 1 and 2 show the viscurometer/rheometer curves of lignin-filled compounds in the presence and absence of ethylene glycol. If lignosulfonate would behave as an acidic filler, reinforcement by a promoter such as ethylene glycol would have been observed. However, the viscurometer/rheometer curves indicate that the modulus did not change on addition of ethylene glycol.

Effect of Lignin on Filled Stocks

While studying the effect of lignin on filled stocks, we have included two non-reinforcing fillers (i.e., whiting and hard clay), one reinforcing nonblack filler

TABLE VI
Effect of Lignin on HAF Black-Filled Natural Rubber Stock (Mix No. E)

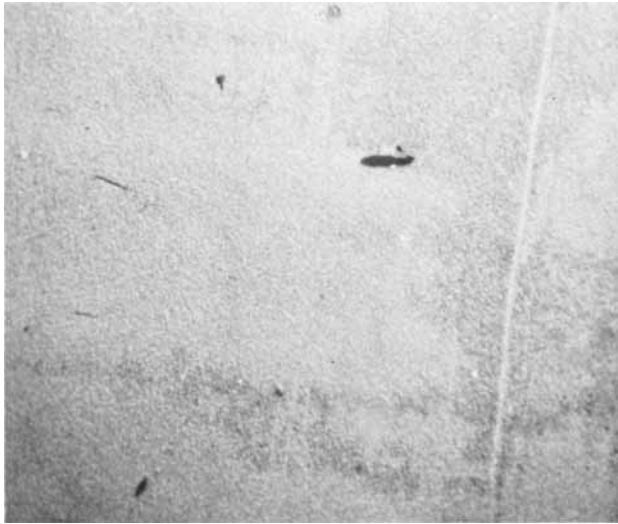
Parameters	0 phr ^a	5 phr	10 phr	15 phr	20 phr
Mooney viscosity ML ₁₊₄ at 120°C	19	17.5	16	16	14.5
Mooney scorch time at 120°C, min	19	17	13	13	14
Optimum cure time at 140°C, min	18.5	23	26	27.5	28
Modulus, kg/cm ²	135	100	85	70	65
	(160)	(130)	(120)	(105)	(100)
Elongation at break, %	530	540	540	550	580
	(440)	(460)	(490)	(460)	(450)
Tensile strength, kg/cm ²	280	220	210	195	175
	(255)	(225)	(220)	(185)	(170)
Tear resistance, kg/cm	80	85	95	85	80
	(75)	(80)	(90)	(70)	(65)
Hardness (Shore A)	66	67	66	66	66
	(70)	(71)	(75)	(76)	(79)
Resilience, %	61	54	49	45	41
	(65)	(55)	(52)	(50)	(46)
Abrasion loss, cc/1000 rev	0.79	0.78	0.77	0.83	0.92
	(0.96)	(0.95)	(0.93)	(1.00)	(1.20)
Compression set, %	55	58	63	65	70
	(38)	(44)	(46)	(55)	(61)
Crack growth (0.5 in.), kilocycles	150	160	170	190	145
	(20)	(40)	(40)	(50)	(50)
Flex cracking (grade C), kilocycles	70	85	90	120	150
	(40)	(50)	(55)	(90)	(115)
Heat buildup, °C	12.5	17.5	20.8	24.3	32.3
	(11.3)	(15.8)	(18.8)	(21.3)	(28.5)

^a Lignin content. Values in parentheses are those of samples aged for three days.

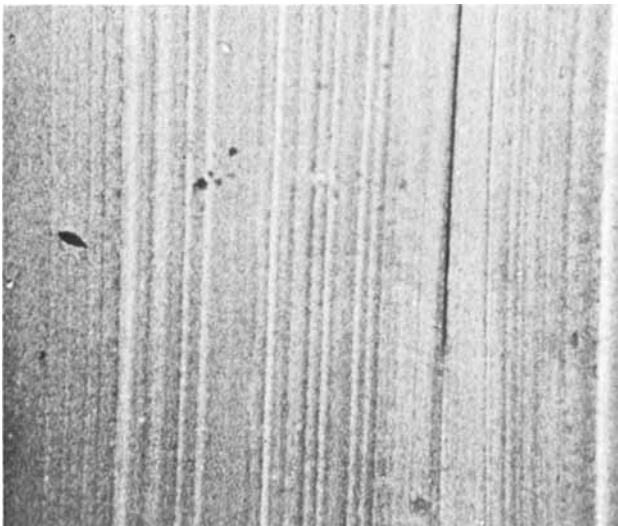
(i.e., vulcasil S) and one reinforcing black (i.e., HAF). Mooney viscosity of whiting filled compound remained constant up to 10 phr lignin, beyond which viscosity increased. However, in other fillers, viscosity decreased with addition of lignin. Mooney scorch time decreased with lignin content, irrespective of the nature of the filler. Optimum cure time of whiting and clay filled compounds remained almost constant. However, the optimum cure time of silica filled compound decreased while that of black filled stocks increased due to the addition of lignin.

Whiting-Filled and Hard Clay-Filled Stocks

Tables III and IV report results of studies on whiting- and hard clay-filled stocks, respectively. Since we observed improvement in the properties of the lignin-containing gum compound after aging, we repeated the aging experiments with filled stocks also. It is evident that the filled vulcanizates behave similar to the gum stock. Lignin imparts better abrasion resistance, crack growth resistance, and flex crack resistance. Tear resistance remains almost unchanged. Other properties such as tensile strength, modulus, compression set, and heat buildup, which generally deteriorated on addition of lignin, improved remarkably upon aging.



(a)



(b)

Fig. 3. (a) Photomicrograph showing dispersion of carbon black (40 phr) in natural rubber in absence of lignin (mix E). (b) Dispersion of carbon black (40 phr) in natural rubber in presence of lignin (20 phr) (mix E).

Silica-Filled Stocks

Table V summarizes results of various properties of silica-filled stocks. Lignin loading up to 20 phr did not significantly alter modulus, tensile strength, and abrasion loss. However, tear resistance, flex crack resistance, and crack growth resistance increased upon addition of lignin. As in the case of gum compounds, aging improved almost all properties including heat buildup.

Black-Filled Stocks

Table VI shows the results of HAF-filled stocks. Abrasion loss remained almost constant. But improvement in tear resistance, flex crack resistance, and crack growth resistance was noted. For example, flex crack resistance increased from 70 kilocycles (for grade C) at 0 phr to 150 kilocycles at 20 phr lignin. Aging studies of black-filled stocks indicated that properties such as tensile strength, modulus, resilience, and heat buildup did not show much improvement upon aging. It may be that lignin masks a portion of active sites of the filler. This phenomenon may be responsible for some deleterious effects. Photomicrographs (Fig. 3) indicated that addition of lignin did not alter the dispersion of filler. The dispersion ratings were A-2 both in the presence and absence of lignin.

CONCLUSIONS

Addition of lignin improved many properties of gum and filled natural rubber vulcanizates. It improved tear resistance, abrasion resistance, flex crack resistance, and crack growth resistance. Tensile strength, modulus, resilience, and compression set decreased while heat buildup increased upon addition of lignin. However, aging of the vulcanizates results in tremendous improvements in most of the properties.

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