Effect of Lignin on the Network Structure and Properties of Natural Rubber Mixes Vulcanized by Conventional, Semiefficient and Efficient Vulcanization Systems

INTRODUCTION

Recently, De and co-workers[1-4] have studied the effect of addition of lignin on the technical properties of rubbers. However, not much is known about the network structure of the lignin-modified rubbers.[5] In the present paper we have made a systematic investigation on the network structure of lignin-modified rubber. Previously,[5] it was demonstrated that addition of lignin reduces the concentration of polysulfidic crosslinks and does not influence the mono- and disulfidic crosslinks. It was presumed, therefore, that lignin might not influence the crosslink density of efficient vulcanization systems. With this objective in mind, the present work has been undertaken. The different mixes varying from conventional to efficient vulcanization have been chosen so that the total crosslink density in all cases is almost the same.[8] We have studied how lignin affects the network structure of natural rubber vulcanizates with different types of vulcanizing systems. The network structure has been determined in terms of total crosslink density, types of crosslinks, and sulfur inefficiency parameters.

EXPERIMENTAL

Compositions of the different mixes are shown in Table I. Details of mixing and testing procedures are the same as described by Kumaran and De.[1,2] The rheometer curves were taken at 150°C using the Monsanto rheometer R-100. Samples for determination of properties and chemical analyses were prepared by curing the stocks at the respective optimum cure times determined from rheographs. Aging of the samples was carried on in an air aging oven at 100°C for 36 hr.

Determination of chemical crosslink densities and types of crosslinks are the same as described earlier.[6,7] Methods of determination of network combined sulfur ($[S_c]$) and sulfur inefficiency parameter (E) are the same as described in a recent publication.[9] Network combined sulfur ($[S_c]$) was determined from compounded sulfur available for crosslinks minus (zinc sulfide sulfur plus free sulfur). The sulfur inefficiency (E) was defined as

$$E = \frac{[S_c]}{[2 \text{ Mc. chem.}]^{-1}}$$

where $[2 \text{ Mc. chem.}]^{-1}$ is the density of chemical crosslinks.

TABLE I
Composition of Mixes

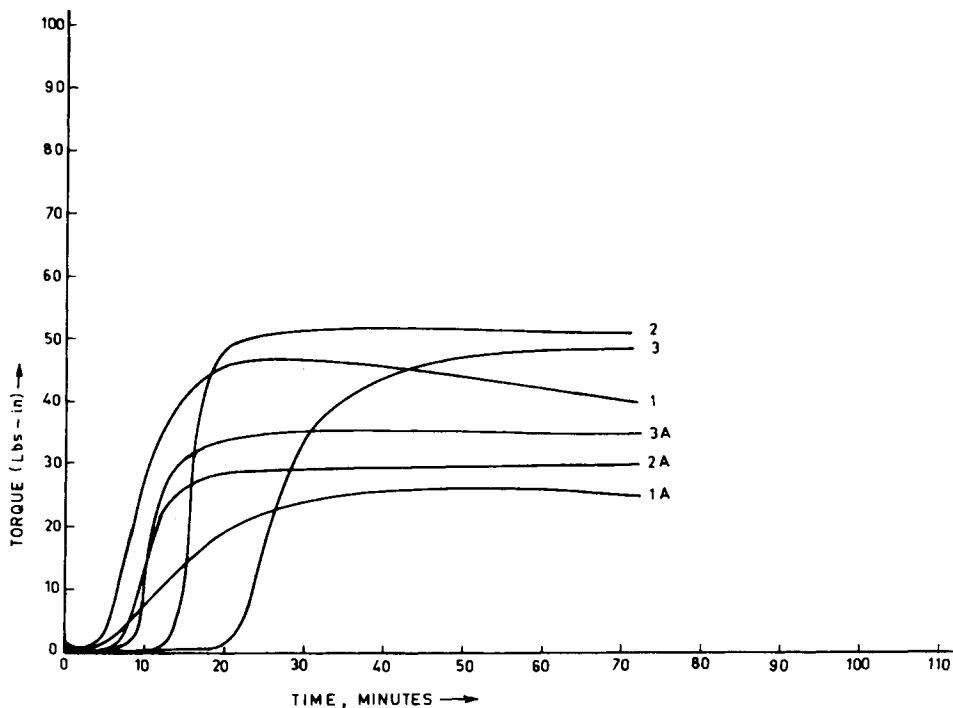| Ingredients	Mix no.					
	1	1A	2	2A	3	3A
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
MOR[a]	0.5	0.5	2	2	6	6
Sulfur	2.5	2.5	1.0	1.0	0.4	0.4
Lignin	0	10	0	10	0	10

[a] N-Morpholinothio-2-benzothiazole.

Fig. 1. Rheographs of different mixes at 150°C.

RESULTS AND DISCUSSION

It has been shown earlier by Kumaran and De[2] that lignin disperses well in natural rubber. Rheographs of different mixes are shown in Figure 1. The results of rheometer studies and Mooney scorch time of the different mixes at 150°C are shown in Table II. As expected, Mooney scorch time and optimum cure time increase as the vulcanization system passes from conventional to efficient vulcanization. However, addition of lignin changes this picture. Lignin makes the stocks more scorchy, and the effect becomes pronounced as one moves toward the efficient vulcanization system. Optimum cure time of the conventional system is delayed in the presence of lignin, while the opposite effect is observed in the case of semiefficient and efficient vulcanization (EV) systems. Addition of lignin increases the cure rate in the case of the EV system and decreases the same in conventional and semi-EV systems. As expected, the reversion time increases as we pass from the conventional to EV system. However, addition of lignin increases the reversion time of the conventional system and reduces the reversion time of the EV system. The reversion time of the semi-EV system remains almost unaffected because of the addition of lignin. As discussed below, the reversion resistance of the different stocks can be explained on the basis of the distribution of different types of crosslinks

TABLE II
Results of Rheometer Studies and Mooney Scorch Time

	Mix no. 1	1A	2	2A	3	3A
Mooney Scorch time at 120°C, min	40	35	75	60	98	52
Optimum cure time at 150°C, t_{90}, min	16	27	19	16	40	15
Maximum torque, lb. in.	46	25	51	30	49	35
Cure rate, $\dfrac{100}{t_{90} - t_2}$, %/min	7.7	4.9	16.7	11.1	5.4	15.3
Reversion time (time to reach 98% maximum torque after passing maximum), min	34	65	88	81	152	71

TABLE III
Effect of Lignin on Properties of Natural Rubber Stock

	Mix no. 1	1A	2	2A	3	3A
Modulus at 300%, kg/cm^2	7.6	0.5	8.9	0.7	6.1	4.2
Elongation at break, %	770	860	730	920	680	880
Tensile strength, kg/cm^2	224	97	216	139	198	210
Tear resistance, kg/cm	23	14	26	14	22	19
Hardness, Shore A	39	30	39	30	41	35
Resilience, %	75	51	78	57	77	65

(Table V). It is apparent, therefore, that lignin actually takes part in the vulcanization process and the vulcanization mechanism depends on the curing system used. An examination of Table III indicates that lignin has a deleterious effect on the technical properties, but the effect is less pronounced in the case of the efficient vulcanization system.

Table IV shows the percentage retention of properties after aging at 100°C for 36 hr in an air oven. As expected, the retention of properties is best in the EV system, followed by the semi-EV and conventional systems. Lignin generally enhances the aging resistance of the vulcanizates, and the effect is most pronounced in the case of the EV system.

Attempts have been made to correlate the results of the technical properties with the network of the vulcanizates. Table V shows the distribution of different types of crosslinks and summarizes the chemical characterization of vulcanizate networks. We have chosen the recipes in such a way that the total crosslink density is the same. However, addition of lignin lowers the crosslink density, and the decrease is least in the case of the efficient vulcanization system. As expected, the concentration of crosslinks of lower sulfidity increases at the expense of polysulfidic crosslinks as we move from the conventional to the efficient vulcanization system. In the lignin-modified conventional system, the decrease in total number of crosslinks is primarily due to a fall in concentration of polysulfidic crosslink. In the semi-EV system, however, the decrease is due to reduction of polysulfidic crosslinks and complete absence of monosulfidic crosslinks. In the EV-system, addition of lignin causes an increase in polysulfidic crosslinks and a decrease in both disulfidic and monosulfidic crosslinks.

TABLE IV
Percentage Retention of Properties after Aging at 100°C for 36 Hr in Air Oven

Properties	Mix no. 1	1A	2	2A	3	3A
Modulus, kg/cm^2	26	40	84	514	108	133
Elongation at break, %	57	71	85	71	97	78
Tensile strength, kg/cm^2	6	33	33	48	86	76
Tear resistance, kg/cm	61	83	103	137	96	118
Hardness, Shore A	82	73	105	98	90	106
Resilience, %	77	59	99	94	92	101

TABLE V
Distribution of Different Types of Crosslinks

Types of crosslinks	Mix no. 1	1A	2	2A	3	3A
Total crosslinks × 10^5, mol/g RH[a]	2.22	1.24	2.35	1.34	2.22	1.55
Polysulfidic crosslinks × 10^5, mol/g RH	1.15	0.33	0.89	0.41	0.17	0.31
Disulfidic crosslinks × 10^5, mol/g RH	1.07	0.91	0.66	0.93	0.58	0.46
Monosulfidic crosslinks × 10^5, mol/g RH	—	—	0.80	—	1.47	0.78
Network combined sulfur × 10^4, [S_c], mol S/g RH	7.23	6.85	2.68	2.72	1.10	1.11
Sulfur inefficiency parameter E, atoms/ chem crosslink	32.6	55.3	11.4	20.3	4.9	7.2

[a] RH = rubber hydrocarbon.

The higher proportion of mono- and disulfidic crosslinks in the lignin-modified vulcanizates is responsible for the better aging resistance of the vulcanizates and reversion resistance of the stocks.

In the presence of lignin, E values increase and crosslink density decreases. These factors are responsible for the drop in technical properties of the lignin-modified compounds. However, as we move from the conventional to the EV-system, the detrimental effect of lignin on the technical properties is less pronounced (Table III). The E value of the lignin-modified EV system is much smaller than the E values of conventional and semi-EV systems (Table V), and accordingly, the technical properties of the EV system do not drop, even in presence of lignin. It is evident, therefore, that the deleterious effect of lignin on the technical properties of natural rubber vulcanizate depends on the vulcanizing system, and the effect is not pronounced in the case of EV system.

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