

Role of Lignin Filler in Stabilization of Natural Rubber-Based Composites

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ABSTRACT: The stabilizing effect of a natural filler, sulfur-free lignin, on the thermal degradation of natural rubber (NR) was examined. Lignin was incorporated into NR in amounts of 10–30 phr (parts per hundred parts of rubber). It was shown that the lignin preparation used improved the physicochemical properties of the rubber vulcanizates. Thermogravimetric analysis and differential scanning calorimetry were used to study the thermal degradation of unfilled and lignin-filled vulcanized natural

rubber. Measurements were carried out under atmospheric conditions. It was revealed that lignin used as filler increased the resistance of NR vulcanizates to thermooxidative degradation in air. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1226–1231, 2007

Key words: rubber; mechanical properties; thermogravimetric analysis (TGA); differential scanning calorimetry (DSC)

INTRODUCTION

Natural rubber (NR) (*cis*-1,4-polyisoprene) is a versatile raw material with unique chemical and physico-mechanical properties that make it ideal for many dynamic applications such as tires, hoses, and belts. For most applications natural rubber is mixed with a variety of compounding ingredients to modify its characteristics. NR is highly unsaturated, a prerequisite for poor resistance to oxidation.¹ Therefore, the degradation process has to be inhibited by the addition of various kinds of stabilizers. Fillers, vulcanizing system, and processing aids are other important ingredients for obtaining the desired properties of vulcanizates. The fillers are primarily classified as carbon black or non-carbon black fillers. They are secondarily classified according to the filler's reinforcing effect. Good compounding involves the development of materials that are environmentally safe, factory processable, cost competitive, and applicable. Therefore, biopolymers such as starch and cellulose have been tested as fillers for rubber.^{2–4} So far, most studies of lignin as an additive to rubber compounds have investigated carbon black replacement in order to achieve similar reinforcement of rubber composites.^{5–8}

However, another important problem is producing rubber composites with sufficient stability. Lignin, as the most stable cell-wall polymer of wood, may have great potential to be a filler with a stabilizing effect.

Lignins are three-dimensional amorphous natural phenolic polymers with predominantly hydroxyl, methoxyl, carbonyl, and carboxyl substitutions. They occur in higher plants, mainly in woody tissues. The biosphere contains 3.10¹¹ tons of lignin, with an annual increase of about 2.10¹⁰ tons.⁹ However, most lignin byproducts in the pulping industry are used as fuel, and only about 2 wt % is utilized in any other way.¹⁰ Lignins are predominantly obtained in larger amounts as byproducts of pulp production during delignification, which occurs under various conditions, for example, acidic, neutral, or alkaline conditions. The most widespread delignification pulping processes are sulfite and kraft processes, which provide the basis for sulfite and kraft lignin production. There are also known sulfur-free delignification processes, for example, the Organocell and Alcell processes. Lignins vary in their chemical and physical properties depending on isolation methods used and plant origin.^{11–13} In the past decades, there has been extensive research into the use of multiple lignin properties in various applications.^{14–21} Lignins can be used as a source of low-molecular-weight chemicals, or they can be applied as dispersants, emulsifiers, and additives for polymeric materials.

Recently, we reported the results of a study of the positive influence of a lignin additive on the me-

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TABLE I
Formulation of NR Rubber Compounds

Ingredients (phr) ^a	Compound code			
	A	B	C	D
NR	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulfur	2.5	2.5	2.5	2.5
CBS	2.5	2.5	2.5	2.5
Lignin	0	10	20	30

^a Parts per hundred parts of rubber (special concentration used in rubber industry).

chanical properties of natural rubber vulcanizates filled with carbon black before and after thermooxidative aging.²² The present study was an extension of this work and examined lignin as a filler with a stabilizing effect. The thermal stability of NR vulcanizates was investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Compounding ingredients and formulation

The sulfur-free lignin powder sample [weight average molecular weight $M_w = 2 \times 10^3$; polydispersity $M_w/M_n = 1.2$; ρ (23°C) = 1.312 ± 0.001 g/cm³] was obtained by three 24-h extractions with a dioxane-water mixture (9:1) of lignin byproducts of beech wood prehydrolysis, followed by purification according to Björkman²³ in the Lignin Laboratory, Institute of Chemistry, Slovak Academy of Sciences Bratislava (Bratislava, Slovakia). Natural rubber (NR), ribbed smoked sheets (SMR 20) with ρ (23°C) = 0.914 ± 0.005 g/cm³ (Malaysian Rubber, Kuala Lumpur, Malaysia), zinc oxide (Slovzink, Košeca, Slovakia), stearic acid (Setuza, Ústí nad Labem, Czech Republic), sulfur (Siarkopol, Tarnobrzeg, Poland), and *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS; Istrochem, Bratislava, Slovakia) were used as obtained.

Compounding and testing

The formulation used in this study is given in Table I. Mixing of the rubber and compounding ingre-

dients apart from the vulcanization system was carried out in a BR 1600 mixer (Farrel intermesh rotor type, Farrel Corp., Ansonia, CT) at 70°C and 40 rpm for 6 min. Then the mixture of the first stage was dumped and calendered with rollers 200 × 400 mm in size, with a friction ratio of 1:1.14, a roller speed of 21 rpm, and a temperature of 70°C. During calendering the vulcanization system was added. Cure characteristics at 150°C were obtained with a Monsanto Rheometer 2000E. Test specimens were vulcanized in a hydraulic heated press at a temperature of 150°C and a pressure of 20 MPa at the respective optimum cure times. Vulcanizates were conditioned for 24 h prior to testing.

Tensile specimens were punched out from the molded sheet using a cut knife. Modulus of 100%, tensile strength, and elongation at break of dumbbell specimen type 1 were measured using Monsanto Tensometer T10, testing pieces type 1, at a 500 mm/min cross-head speed, according to STN ISO 37. Shore A hardness was determined by Zwick testing equipment (STN ISO 7619). A minimum of five samples were tested in each case.

The Tesla BS 300 scanning electron microscope was used for the observation of the cross section of NR vulcanizates coated with gold.

DT/TG analyses were carried out on a Mettler-Toledo TG 50 apparatus with samples of about 8 mg placed in alumina crucibles. An empty alumina crucible was used as a reference. The tests were performed in an air atmosphere at a flow rate of 200 mL/min and a heating rate of 10°C/min and at temperatures ranging from 35°C to 800°C.

DSC measurements were made with a Mettler-Toledo DSC 20 calorimeter. The temperature scale was calibrated using In, Sn, and Zn, and the enthalpy calibration was carried out to the heat of fusion of In. Samples of about 8 mg were placed in aluminum crucibles. An air atmosphere was used as the purge gas at a flow rate of 50 mL/min. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Cure characteristics

Table II shows that the addition of lignin had only a very slight effect on the cure characteristics of NR

TABLE II
Cure Characteristics of NR Compounds

Sample code	Minimum torque, M_{\min} (min)	Maximum torque, M_{\max} (min)	Extent of cure, ΔM (Nm)	Scorch time, t_2 (min)	Optimum cure time, t_{90} (min)	Cure rate index CRI (min ⁻¹)
A	0.32	3.55	3.23	5.8	9.5	27.0
B	0.36	3.18	2.82	6.0	8.6	38.4
C	0.38	3.22	2.84	5.5	8.3	34.5
D	0.40	3.28	2.88	5.3	8.5	31.3

TABLE III
Physicomechanical Properties of NR Vulcanizates

Sample code	Modulus 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
A	—	1.87 ± 0.33	89 ± 9	48 ± 1
B	2.29 ± 0.31	3.99 ± 0.25	187 ± 21	48 ± 1
C	2.46 ± 0.20	10.61 ± 2.31	267 ± 19	50 ± 1
D	2.48 ± 0.25	16.83 ± 4.21	357 ± 83	51 ± 1

compounds. The minimum torque and cure rate index of NR compounds moderately increased with an increasing lignin concentration. The increase in minimum torque indicates increased stiffness of the compound because of lignin loading. The maximum torque, scorch time, and optimum cure time of the lignin-filled NR composites were a bit lower than those of the control (compound A). The trend of maximum torque showed that lignin did not contribute to the increased shear modulus of the natural rubber composite during vulcanization. The increased scorching might have been a result of the acceleration of vulcanization by the large number of hydroxyl groups in the lignin structure. The mild decrease in the optimum cure time revealed interaction of lignin with the vulcanization system. Similar results were described in our previous article.²⁴

Physicomechanical properties

The physicomechanical properties of the vulcanizates are displayed in Table III. Properties such as 100% modulus, tensile strength at break, and elonga-

tion at break were improved on the addition of lignin in the whole range of concentrations tested; however, there was a negligible change in hardness. The observed positive effect of lignin on the mechanical properties of NR vulcanizates can be explained by its relatively low molecular mass and its polydispersity, which allowed good lignin miscibility in NR. Figure 1 shows the SEM micrographs of NR vulcanizates with and without lignin. It can be seen that lignin contributed to the dispersion of the other compounding ingredients.

Thermal stability of vulcanizates

Thermogravimetry was applied to measure the thermal stability of lignin-free and lignin-filled NR vulcanizates. In derivative thermogravimetric analysis change in mass is plotted against temperature (dm/dT). The beginning of the degradation signaled the onset temperature (T_0). The maximum rate of change in mass was indicated by the peak in the DTG curve and was characterized by the peak maximum temperature (T_{max}) and peak height. The mass change is

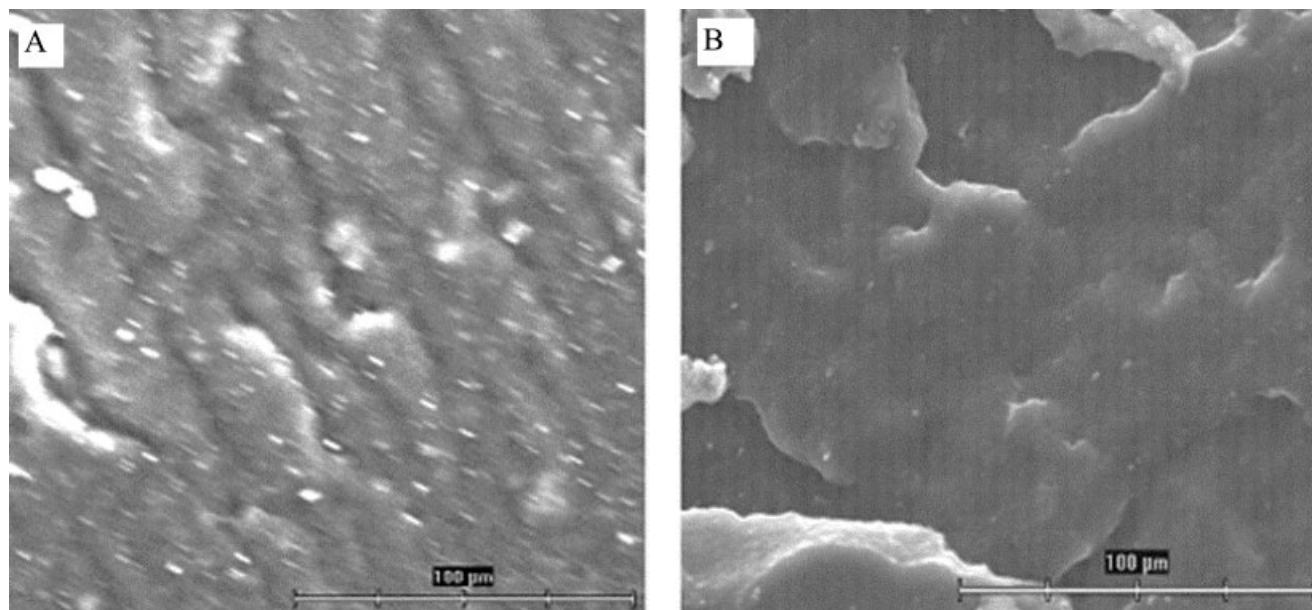


Figure 1 Scanning electron micrographs of NR vulcanizate containing compounding ingredients (A) without lignin and (B) with 30 phr lignin (magnification $\times 1000$).

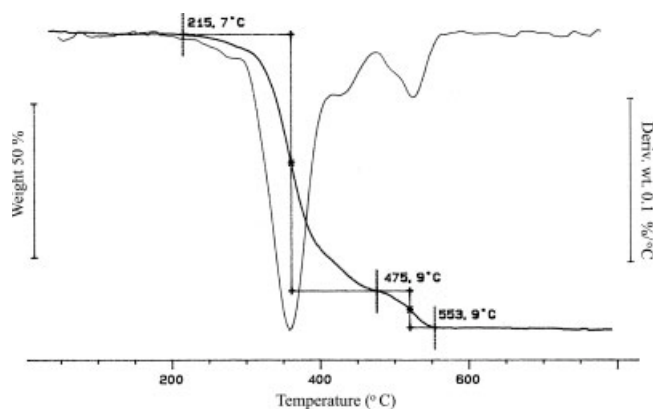


Figure 2 TG and DTG traces of unfilled NR vulcanizate (compound A).

marked by the area under a DTG curve. TG-DTG curves of the prepared vulcanizates in air are shown in Figures 2–5. It can be seen that all NR vulcanizates exhibited two prominent temperature regions; however, in the DTG curve of lignin-free NR vulcanizate (compound A) three peaks occurred, in contrast to lignin-filled NR vulcanizates (compounds B, C, and D). Lignin-free sample began to lose weight at 215.7°C, with an obvious mass change at 358.3°C resulting from the main oxidation of rubber. An additional two small peaks probably originated from degradation of compounding ingredients (418.5°C) and from the remaining part of the vulcanizate (525°C). The temperature range between 178°C and 475°C, where the major decomposition was significant (approximately 77%–83%), corresponds with data in the literature on the NR degradation region, 200°C–475°C.²⁵ It is known that vulcanizates with sulfur crosslinks oxidize more rapidly than the raw rubber. In our previous article we showed that sulfur-free lignin was able to interact with a sulfur vulcanization system during vulcanization of rubber

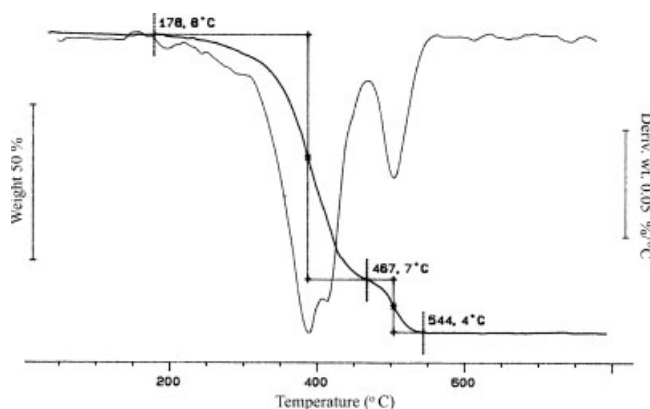


Figure 4 TG and DTG traces of NR vulcanizate filled with 20 phr lignin (compound C).

compound.²⁴ From Figures 2–4 it can be seen that lignin-filled samples did not show a peak at 418.5°C, probably because the formation of lignin–sulfur intermediates originated during vulcanization of lignin-containing NR compounds. The results given in Table IV show that in the presence of 10 phr (parts per hundred parts of rubber) lignin, the extent of mass reduction went from 83% to 79% in the temperature region 207.5°C–460.8°C. Also, there was a shift in the DTG peak (T_{max}) toward a higher temperature from 358°C to 365°C, which reflects the improved thermal stability of lignin-filled NR vulcanizate. Moreover, the additional increase in lignin concentration up to 30 phr in NR compounds caused further improvement in the thermal stability of NR vulcanizates. The thermal decomposition characteristics summarized in Table V were determined from the thermogram areas. The temperature at which 50% decomposition (T_{50}) occurs is considered an index of thermal stability.²⁶ Lignin-filled NR samples, especially with a 20-phr lignin concentration, showed evident increases in T_{50} decomposition val-

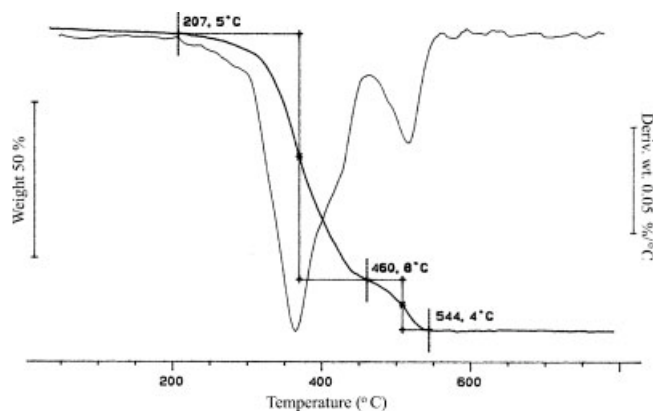


Figure 3 TG and DTG traces of NR vulcanizate filled with 10 phr lignin (cCompound B).

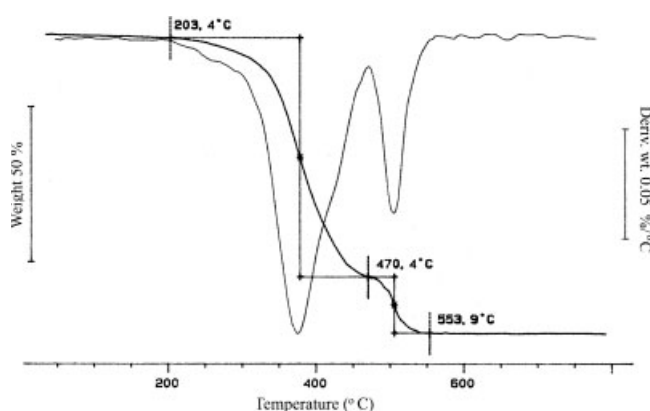


Figure 5 TG and DTG traces of NR vulcanizate filled with 30 phr lignin (compound D).

TABLE IV
Parameters Evaluated from TG and DTG of NR Vulcanizates

Sample code	Temperature range (°C)	Onset temperature, T_0 (°C)	Peak temperature, T_{max} (°C)	Decrease in mass (%)
A	215.7–475.9	215.7	358.3	83.30
	475.9–553.9		525.0	11.94
B	207.5–460.8	207.5	365.0	79.24
	460.8–544.4		515.0	16.14
C	178.8–467.7	178.8	388.3	77.17
	467.7–544.4		505.0	18.01
D	203.4–470.4	203.4	375.0	77.13
	470.4–553.9		505.0	18.08

TABLE V
Characteristics of Thermal Decomposition of NR Vulcanizates

Decomposition (%)	Decomposition temperature (°C)			
	A	B	C	D
10	321.4	322.6	327.0	326.9
20	338.7	343.4	357.6	352.4
30	349.1	357.1	374.0	366.2
50	366.4	380.2	397.7	389.8
75	407.1	426.4	433.4	437.2

ues. The observed improvement in the thermal stability of NR samples by the addition of lignin corresponded with radical scavenging efficacy of lignin. It is known that lignin's hindered phenolic hydroxyl groups can act as a stabilizer of reactions induced by oxygen and its radical species.²⁷

Further, the resistance of NR vulcanizates to thermooxidative decomposition has been studied by differential scanning calorimetric analysis. Data estimated from DSC thermograms such as the onset temperature, the peak temperature, and the enthalpy for two DSC peaks are summarized in Table VI. It can be seen from the values of the onset temperature that adding lignin into NR composites led to improvement in their resistance to thermooxidative degradation. Also, reduction in the enthalpy of oxidation (ΔH), which was calculated from the area under the exotherm plots obtained from DSC, indi-

cates the improvement of the resistance to thermooxidative decomposition when lignin was added. The highest thermal stability was observed for the vulcanizates containing 20 phr of lignin.

CONCLUSIONS

Novel NR composites filled with sulfur-free lignin were prepared under sulfur vulcanization. The addition of lignin in concentrations up to 30 phr into NR rubber composites caused significant improvement in the physicomachanical properties of the prepared vulcanizates such as 100% modulus and elongation and tensile strength at break. Lignin influenced the cure characteristics of NR compounds very softly. From the thermogravimetric and differential scanning calorimetric analyses, it could be concluded that the resistance to thermooxidative degradation of NR vulcanizates was considerably improved by the addition of lignin. Based on this, it may be suggested that lignin used as a filler for NR rubber would be able to subserve the role of thermal stabilizer during thermal degradation of NR vulcanizates. The greatest improvement in thermal stability was observed for NR vulcanizates filled with 20 phr of lignin. These results are in accordance with the observation of the chemical interaction between lignin and the sulfur vulcanization system up to 20 phr lignin loading in styrene-butadiene rubber.²⁴

TABLE VI
Parameters Evaluated from DSC Analysis of NR Vulcanizates

Sample code	Temperature range of exothermal effects	Onset temperature (°C)	Peak temperature (°C)	ΔH (J/g)
A	170.3–418.4	184.2	325.9	885.5
	418.4–600.0		569.5	2050.6
B	182.8–449.3	182.8	348.6	832.5
	449.3–600.0		588.6	1914.6
C	291.0–418.4	300.8	368.1	363.3
	418.4–600.0		555.6	3604.5
D	289.0–417.4	295.5	363.8	317.8
	417.4–600.0		567.2	4047.4

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