Application of Sulphur-Free Lignins as a Filler for Elastomers: Effect of Hexamethylenetetramine Treatment

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Lignins from a steam explosion process in crude and purified forms and modified sulphur-free commercial lignin (Protobind 3000®) were characterised to establish their chemical compositions. Then, the lignins were tested again after treatment with hexamethylenetetramine (HMT). The resulting products were used to make rubber composites, and their mechanical properties were compared to rubber composites made with carbon black to test the possibility of using HMT-treated lignins as a partial replacement for carbon black in the production of rubber composites. In the crude lignin, a significant amount of impurities were detected, such as ash and residual polysaccharides, and these substances interfered in filler-elastomer interactions. The purified lignin maintained a high content of strongly polarised hydroxyl groups that interfered with the interaction of the filler and elastomer, resulting in low performance. Improvements in the mechanical properties were observed using Protobind 3000® lignin or purified lignin with HMT added during mixing with the rubber. Finally, the mixing of HMT-treated lignin with elastomers resulted in composites with higher reinforcement abilities compared to previously described rubber composites. However, in all samples, a poor and unsatisfactory dispersion of lignin in the polymeric matrix was observed. This is likely due to the incompatibility of lignin with the hydrophobic rubber, resulting in lower performances compared to the carbon black.

Keywords: Lignin; Hexamethylenetetramine; Rubber composites; Mechanical properties; Dispersion; Particle size

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INTRODUCTION

Lignin is the third most abundant natural polymer present in nature, after cellulose and hemicelluloses. The biosynthesis process consists primarily of the radical coupling of three alcohols (p-cumaryl, coniferyl, and sinapyl alcohols) that differ by their degree of methoxylation. The respective aromatic constituents of these alcohols in lignin are called p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) moieties (Lewis and Yamamoto 1990). The resulting amorphous and raceme biopolymer consists of phenylpropanoidic units linked with ether and C-C bonds that confer a complex three-dimensional structure.

Lignin has different functional groups, such as hydroxyl, carbonyl, carboxyl, and methoxyl in aromatic rings or in lateral chains. The presence of these groups affects the reactivity. Lignins vary in structure according to their plant source and their method of isolation (Lora *et al.* 2008; Lora and Glasser 2002). Wood lignins primarily contain guaiacyl and syringyl units, whereas the lignins from herbaceous plants contain all three units (H, G, and S) in significant amounts with different ratios (Lapierre *et al.* 1995; Billa *et al.* 1998). Lignins are obtained as by-products of different processes, such as papermaking and bioethanol production. Today, the majority of lignin is burned to produce electricity to feed these productions (Sarkanen and Ludwig 1971; Adler 1997; Northey 1992; Lin and Lebo 1995; Ciobanu *et al.* 2004). Lignins are characterised by a wide range of functional groups able to meet the needs of the industry, and their diversity and complexity can be a huge asset.

Sulphur-free lignins are receiving increasing attention because they offer greater versatility and can be heat-processed without the irritating odor release commonly observed with commercial kraft lignin. In addition to the cost advantages, the annual renewability and the wide availability are factors that could promote the use of sulphur-free lignin. Sulphur-free lignin can be used in many thermoplastic (Bertini *et al.* 2012) and thermosetting applications in conjunction with phenol, epoxy, or isocyanate resins.

A great amount of research (Setua *et al.* 2000; Griffith and MacGregor 1953; Kumaran and De 1978) and patents (Benko *et al.* 2010; Boutsicaris 1984; Davidson and Wunder 1977; Doughty 1967; Doughty and Charlestion 1966) have focused on lignin for its use as a filler that can be added to rubber composites for total or partial replacement of carbon black, while achieving similar reinforcement. Lignin has been applied as a filler in butadiene-styrene-butadiene (Furlan *et al*. 1985) and isoprene-styrene-butadiene rubbers for shoe soles (Savel'eva *et al.* 1983), in styrene-butadiene elastomers (Kosikova *et al.* 2003), and in natural rubber (Kramarova *et al.* 2007). It has been demonstrated that lignin affects the curing behavior. The scorch time decreases slightly and the optimum cure time increases significantly as lignin content increases in SBR rubber blends. This behaviour is due to the interaction of lignin with the vulcanisation system (Košíková and Gregorová 2005). Sugar cane bagasse lignin exerts a genuine antioxidant effect towards SBR and NR (Luis and De Paoli 1985). Lignin acts as an antioxidant for natural rubber filled with carbon black during thermal aging. The revealed antioxidant activity of lignin indicates the possibility of replacing commercial antioxidants in the thermo-oxidative aging of carbon black-filled natural rubber. Moreover, the activity of the commercial rubber antioxidant IPPD was enhanced by the addition of lignin (Gregorová *et al.* 2006). It has been demonstrated that lignin and lignin/antioxidant D composites are good antioxidants for SBR (Shusheng and Xiansu 2010).

Sulphur-free lignins come from renewable sources and are available in great amounts. Their price is favorable, and they have lower density than typical fillers such as carbon black or silica. Because of these observations, in this work, purified sulphur-free lignin obtained by a purification process and a modified commercial sulphur-free lignin (Protobind 3000®) were utilised as partial replacements for carbon black in rubber composites. The commercial lignin was obtained by a pre-blend step with HMT and treated in a pilot extruder (Bono *et al.* 2008).

EXPERIMENTAL

Reagents and Materials

All reagents were purchased from Sigma-Aldrich and used as received. The crude lignin used was a biomass waste material coming from a steam explosion process for biofuel production. Commercial lignin, Protobind 3000®, was purchased from Green

Value sas. The following materials were used in the rubber composites: natural rubber (NR) STR 20, styrene butadiene rubber (SBR) SBR 1500, N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine, 6PPD Santoflex-6PPD from Flexys, stearic acid Stearina TP8 from Undesa, carbon black N 375 from Cabot, sulphur Zolfoindustria, zinc oxide from Zincol Ossidi, Aromatic oil MES from ENI SPA, N-t-butyl-2-benzothiazyl-sulphenamide, TBBS Vulkacit NZ/EG-C from Lanxess, and HMT Rhenogran HEXA-80® (80% HMT and 20% elastomer binder and dispersing agent) from Rhein Chemie.

Lignin Characterization

Lignin content

The Klason lignin method gave a quantitative measure of the acid-insoluble lignin measured according to the procedure reported by Yeh *et al.* (2005). The lignin content is the sum of Klason lignin and acid-soluble lignin. The values reported are the average of 3 analyses ± 1.0% ($P = 0.05$, $n = 3$).

Ash

The ash content of lignins was defined as the residue remaining after ignition at 600 °C for 3 h, or longer if necessary to burn off all the carbon. This is a measure of mineral salts in the lignin (Sluiter *et al*. 2008).

GPC analysis: Distribution of molecular weight

The lignin samples were acetylated in an acetic anhydride pyridine solution (1:1, v/v). An evaluation of the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity index (I) was performed following the methodology reported by Salanti *et al*. (2010).

^{31}P NMR derivatisation

By derivatisation of the labile hydroxyl groups of lignin with a previously reported method (Salanti *et al*. 2010), it is possible to determine the amount of aliphatic hydroxyls, condensed and syringyl phenolic moieties (Cond PhOH + S-OH), guaiacyl units (G-OH), p-coumaryl alcohols (P-OH), and carboxylic acid functionalities (COOH). The ^{31}P NMR data reported in this paper are the average of three experiments. The maximum standard deviation was 2×10^{-2} mmol/g, while the maximum standard error was 1×10^{-2} mmol/g.

Elemental analysis

The quantitative determination of carbon, nitrogen, and hydrogen in the structure was made with a Perkin Elmer 2400 series II CHNS/O elemental analyser.

Purification of Biomass

To produce purified lignin, the starting material was subjected to alkaline cooking in 1% NaOH aqueous solution under continuous stirring for 30 min at 50 ºC. At the end of the extraction, the treated material was centrifuged to separate the liquid and solid fractions. This procedure was repeated twice. The solid fraction was eliminated, whereas the liquid ones were acidified with HCl until pH 1 allowing the lignin precipitation. The precipitated matter was then collected by centrifugation (4000 rpm, 15 min), washed with deionised water, and air dried. The yield of the reaction was 36% with respect to the starting material.

Reaction of Lignin with Hexamethylenetetramine (HMT)

The reaction was carried out using the following method (Falkehag 1972). Lignin was slurried in 5 mL of water. To this slurry, 10% NaOH (1.5 mol/1000 g lignin) and 33% NH_3 (6 mol/1000 g lignin) were added, and the mixture was stirred for 2 min. Then, hexamethylenetetramine was added. The flask was dipped into an oil bath fitted with a reflux condenser set at 100 ºC for 6 h. At the end of the reaction, the NH_3 was distilled, acetic acid was added, and the mixture was stirred for 2 min to form an emulsion and then air dried.

Preparation of Rubber Composite

The formulation of the rubber composite is shown in Table 1.

Table 1. Formulation of Rubber Composites

	Ingredients	A	B	C	D	E	F	G
1°step	STR 20	50	50	50	50	50	50	50
	SBR 1500	50	50	50	50	50	50	50
	Carbon black	65	50	50	50	50	50	50
	Biomass		15					
	Purified Lignin			15		15	15	
	Protobind 3000®				15			
	HMT pre-reacted Lignin							15
	Rhenogran HEXA-80®					1.125	1.5	
	Stearic acid	2	2	2	2	2	2	2
	Zinc oxide	3	3	3	3	3	3	3
	Aromatic oil	10	10	10	10	10	10	10
	6PPD	2	2	2	2	2	2	2
2°step	Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	TBBS	0.8	0.8	0.8	0.8	0.8	0.8	0.8

The mixtures were prepared in a Haake mixer with a 246-cm^3 chamber. The fill factor used in the mixing was 0.81. Rubber was kneaded with lignin and half of the carbon black at 90 °C and 40 rpm for 1 min. Later, oil and the other half of the carbon black were added. After 3 min of kneading, stearic acid, zinc oxide, and 6PPD were added to the rubber composites and mixed for 3 min. After the mixing step, the rubber composite was passed through a two-roll mill at 40 °C. The accelerators and sulphur were added during this step. Vulcanisation of samples was carried out at 170 °C using an electrically heated hydraulic press (BM Biraghi) at a pressure of 4.5 MPa for 10 min.

Curing Characteristics

Vulcanisation properties were measured with a Moving Die Rheometer (RPA2000, Alpha Technologies) under the following conditions: oscillating angle ±1°, temperature 170 °C, pressure 4.5 bar, and running time 20 min. The curing characteristics of the rubber composites were expressed in terms of the vulcanisation times, tS2 (scorch time), t90 (optimum cure time), and maximum and minimum values of the torque, MH[dN m] and ML[dN m], respectively.

Mechanical Properties

Tensile tests were performed according to ISO 37 (BS ISO 37, 2005) using a Zwick tensile machine. Ring specimens with working dimensions of 50 mm x 6 mm were cut from a vulcanised 2-mm-thick slab. The tensile strength, expressed as TS, was calculated as the force in MPa measured at the breakpoint divided by the original cross-sectional area. The modulus value is the force, expressed in MPa, corresponding to the original cross-sectional area measured at a certain elongation: modulus at 50% of elongation (M50), modulus at 100% of elongation (M100), and modulus at 300% of elongation (M300). Hardness measurements were obtained with an IRHD machine according to ISO 48 (ISO 48, 1994 AMD 1, 1999) at 23 °C and 100 °C. The values are the average of 5 analyses reported with the confidence interval ($P = 0.05$, $n = 5$).

Morphology of Rubber Composites

The determination of the dispersion of fillers with the Dispergrader® 1000 apparatus manufactured by Optigrade is based on the operating procedure given in ISO/DIS 11345 (ISO 11345, 2006). To determine the X value, a scale of reference pictures has to be chosen in a library and a value from 1 to 10 must be assigned to the image after numerical comparison to the reference scale. X value is a measure of the dispersion of filler in the polymeric matrix. To determine the Y value, a histogram of size distribution is calculated and a value from 1 to 10 is assigned to the image as a function of the quantity of agglomerates larger than 23 µm. This value is independent of the reference scales and indicates the distribution of filler in the rubber composite (Otto 2005). Morphological analyses were carried out using an optical microscope, the Leica DM L.

RESULTS AND DISCUSSION

Characterisation of Lignin

The starting materials were dried in an oven at 110 °C overnight and were then characterised to establish their composition by the determination of the lignin and ash content. The amount of polysaccharides was calculated by difference. Moreover, the materials were characterised by gel permeation chromatography (GPC) analyses to identify the molecular weight distribution. Quantitative ^{31}P-NMR spectroscopy was used to determine the amounts of aliphatic hydroxyls, condensed and syringyl (Cond. PhOH + S-OH), guaiacyl (G-OH) and p-coumaryl phenolic units (P-OH), and carboxylic acid functionalities (COOH). The results are reported in Table 2.

The starting biomass was composed of 16.5% ash, 58.1% lignin, and 25.4% polysaccharides. More than half of the by-product obtained by the steam explosion process was lignin, but it also contained a high percentage of residual polysaccharides and ash. The high polysaccharides content could be attributed to the partial cleavage of lignin-carbohydrate complexes naturally present in herbaceous lignocellulosic materials (Salanti *et al*. 2012) during the steam explosion process. The data reported after GPC and ^{31}P-NMR analysis (indicated with ^{a} in Table 2) are not reliable due to the incomplete solubility of the sample in the analysis solvent.

Table 2. Chemical Characterisation of Starting Materials

	Biomass	Purified lignin	Protobind 3000®
Ash (%)	16.5	0.2	0.89
Lignin content (%)	58.1	99.2	82.5
Polysaccharides (%)	25.4	0.6	16.6[b]
GPC			
M_n (g/mol)	2500[a]	4400	3200
M_w (g/mol)	7000[a]	12000	8600
I	2.8[a]	2.7	2.7
^{31}P NMR			
Aliphatic OH (mmol/g)	2.39[a]	1.84	1.88
Condensed PhOH + S-OH (mmol/g)	0.58[a]	0.79	1.51
G-OH (mmol/g)	0.46[a]	0.74	0.87
P-OH (mmol/g)	0.23[a]	0.24	0.28
COOH (mmol/g)	0.27[a]	0.51	0.86
Elemental analysis			
C (%)	49.3	59.2	60.8
H (%)	5.4	5.7	6.2
N (%)	1.9	1.6	3.2
O (%)	43.4	33.5	29.8

The data indicated with *a* are not reliable due to the incomplete solubility of the sample in the analysis solvent, and the value indicated with *b* was overestimated due to the presence of HMT in the specimen.

The dissolution of the biomass in alkaline solution and the recovery by acidification with HCl allowed attainment of pure lignin with all inorganic impurities and polysaccharides removed. The main evidence of the purification process was the increase of lignin content from 58.1% to 99.2%. Furthermore, the molecular weight of purified lignin increased as a consequence of the purification process, in which the lower molecular weight fractions were lost.

The lignin Protobind 3000® was composed of 0.89% ash, 82.5% lignin, and 16.6% polysaccharides. The value for polysaccharides content in Protobind 3000® (indicated with *b* in Table 2) was overestimated due to the presence of HMT in the specimen (Bono *et al.* 2008). This material was also characterised by GPC analysis to identify the molecular weight distribution. The data showed that the molecular weight was between 1000 and 10,000 g/mol, as observed for the purified lignin.

All samples were analysed by quantitative ^{31}P-NMR spectroscopy. By derivatisation of the labile hydroxyl groups of lignin with an opportune derivatising agent, 2-chloro-4,4,5,5-tetramethyl 1,3,2-dioxaphospholane, it was possible to quantify the amount of different -OH groups. The removal of polysaccharides during the purification process was confirmed by the decrease in aliphatic hydroxyl content while the phenolic and acid group content relatively increased. Most hydroxyl groups of purified lignin and lignin Protobind 3000® were aliphatic hydroxyl groups, while 30% were phenolic hydroxyl groups. Moreover, a considerable amount of carboxylic acid was detected for both the samples.

Elemental analyses showed that in the Protobind 3000® lignin sample, the percentage of nitrogen was higher in comparison to the purified lignin due to the pre-blend step with hexamethylenetetramine.

The samples were also analysed by IR spectroscopy (Fig. 1). The purification demonstrated by the increase of lignin content was also confirmed by the intensity decrease of the peaks relative to the C-O bonds, at 1121 and 1032 cm^{-1}, due to the removal of the carbohydrates (Fig. 1B). In the Protobind 3000®, the peak at 1363 cm^{-1} reflects the CH in-plane deformations due to the methylene group in HMT.

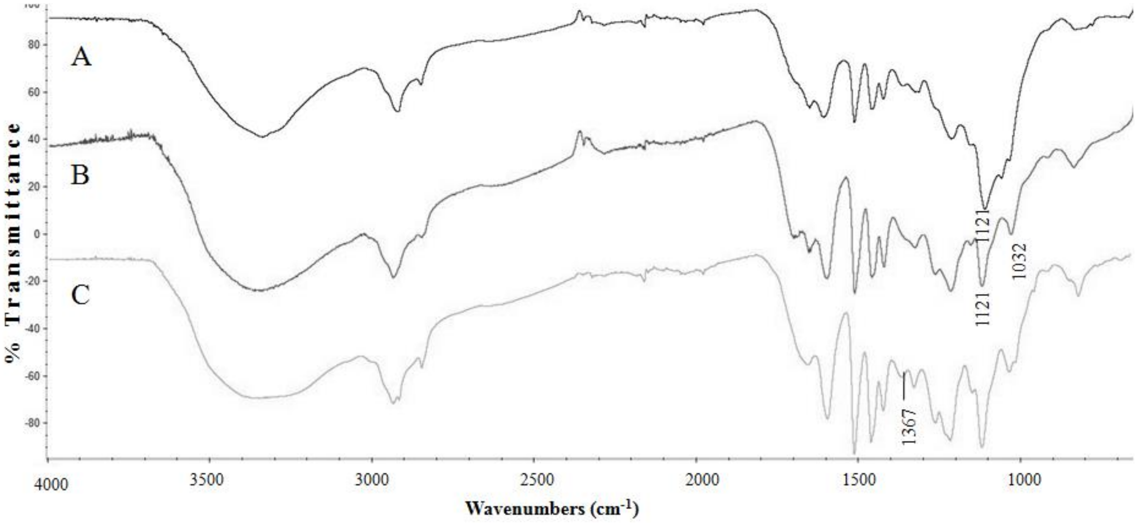

Fig. 1. IR spectra of biomass (A), purified lignin (B), and modified commercial lignin (C)

Overall, the purified lignin and Protobind 3000® were comparable according to the molecular weight, the functional group distribution, and the lignin content. This implies that they should have comparable performance as fillers for elastomers, excluding the presence of HMT.

All of the materials were also characterised by optical microscope (Fig. 2A). The characterisation highlighted the fibrous aspect of the starting biomass and the presence of large agglomerates. On the contrary, purified lignin and Protobind 3000® had granular natures, with the particle size around tenths of a micron (Fig. 2B and C).

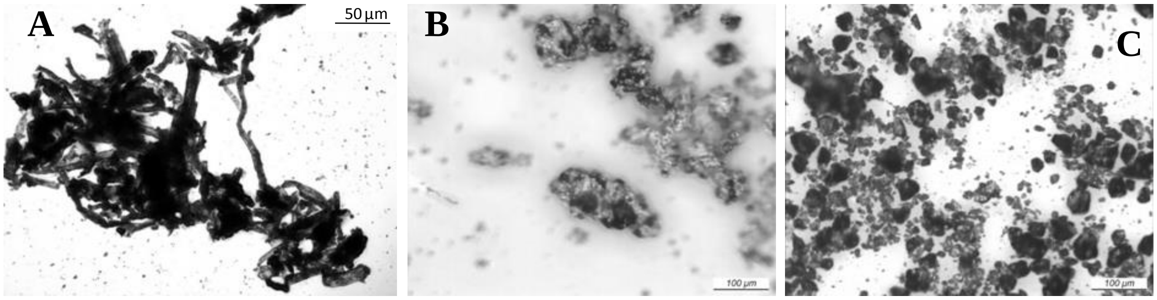

Fig. 2. Optical microscope images of biomass (A), purified lignin (B), and modified commercial lignin (C)

The elemental analysis of the HMT pre-reacted lignin (Table 3) showed an increased amount of nitrogen in comparison to the purified lignin, a value close to that obtained for Protobind 3000® (Table 2). Although the mechanism of the pre-reaction of lignin with HMT is still unknown, these results seem to confirm the mechanism described by Dargaville *et al.* (1996) for model phenols with HMT. In that paper, the authors describe the formation of di-benzylamine and tri-benzylamine from the reaction between phenols and HMT.

Table 3. Elemental Analysis of Purified Lignin and HMT Pre-Reacted Lignin

	C (%)	H (%)	N (%)	O (%)
Purified lignin	59.2	5.7	1.64	33.5
HMT pre-reacted lignin	50.9	5.67	3.03	40.4

The HMT pre-reacted lignin was not analysed by ^{31}P-NMR spectroscopy due to the sample insolubility in the analysis solvent. The GPC analysis does not show an increase in molecular weight after treatment with HMT.

In the IR spectra of HMT pre-reacted lignin (Fig. 3B), it is possible to observe the presence of a small peak at 1367 cm^{-1} due to CH in-plane deformations of the methylene group in HMT, as was previously described for Protobind 3000®.

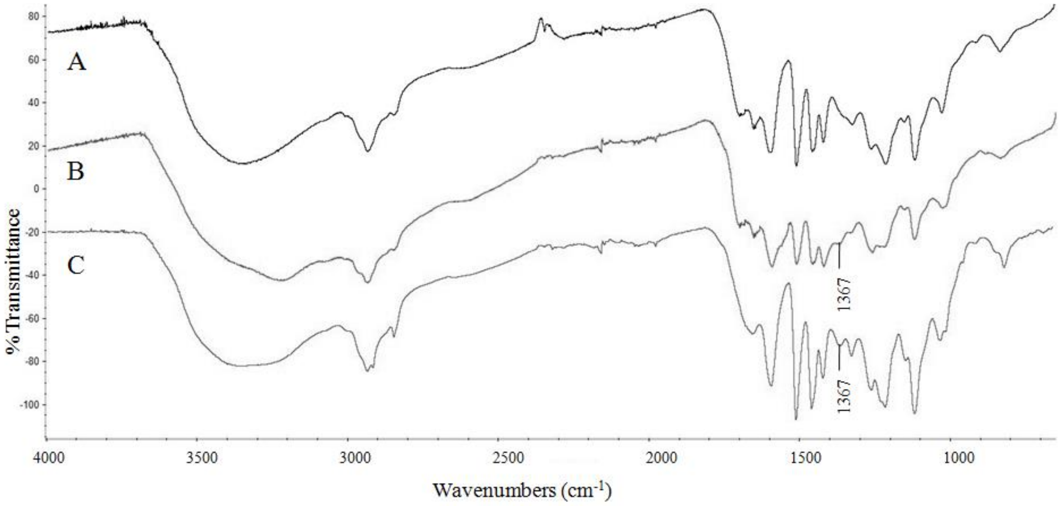

Fig. 3. IR spectra of purified lignin (A), HMT pre-reacted lignin (B), and modified commercial lignin (C)

Properties of Lignin-containing Rubber Composites

A rubber composite with 65 phr of carbon black was utilised as a reference (A). The partial replacement of carbon black with the starting biomass (B) strongly decreased the mechanical properties of rubber composites. High levels of impurities such as carbohydrates and ash and high contents of strongly polarised hydroxyl groups were identified as possible interferences for elastomer-biopolymer interactions. The purification process allowed the attainment of pure lignin, where all inorganic impurities and polysaccharides were removed. After mixing purified lignin (C) with elastomers, a slight improvement in the mechanical properties was observed in comparison to biomass (B), but overall, the results indicated a detrimental effect of lignin in the composite.

Protobind 3000® (D) was also tested in rubber composites as a partial replacement for 15 phr of carbon black. Comparing C and D, it can be seen that the lignin influenced the vulcanisation process. In general, the scorch time as well as the optimum vulcanisation time increased for the purified lignin. This could be attributed to the lignin phenolic group's reaction with the curing system, which led to the increase in the optimum cure time due to their acidity (Kumaran and De 1978; Nando and De 1980) and the presence of free carboxylic acid. On the other hand, the presence of HMT in the Protobind 3000® reduced the optimal cure time of the rubber composite. HMT is also used as a primary accelerator for NR and synthetic rubbers (Jung 2008). As reported in Table 4, an increase in the mechanical properties, particularly the hardness and tensile strength, was observed in the Protobind 3000® composite (D) compared to other compounds (B, C). Thus, the composite D showed a higher reinforcement ability compared to the purified lignin, but it did not achieve the performance of carbon black.

Following the results obtained from the use of Protobind 3000®, two different strategies were investigated to evaluate the influence of lignin and HMT on the rubber compound: the addition of lignin and HMT directly to the compound, and the pre-reaction of lignin with HMT.

Protobind 3000® can be easily reacted with purified lignin and HMT by direct addition during the mixing stage. This is confirmed by the results reported in Table 4 (E and F). Hardness, tensile strength, and tensile modulus measured at a certain elongation % were comparable. The best results were obtained in the range of 6 to 8% HMT, as reported in a patent application (Bono *et al.* 2008).

Table 4. Properties of the Rubber Composites: Kinetics of Curing, Tensile Test, Hardness, and Dispergrader Analysis

		A	B	C	D	E	F	G
MDR 20 min 170 °C	**ML [dN m]**	2.12	1.45	1.64	1.57	1.58	1.6	1.45
	MH [dN m]	12.46	9.52	10.35	11.59	11.54	11.83	12.72
	TS2 [min]	2.12	2.29	2.44	1.75	1.9	1.81	1.66
	T90 [min]	6.49	6.84	7.59	4.73	5.06	4.79	4.22
RING TENSILE TEST 23 °C	**M50 [MPa]**	1.01	0.91	0.88	1.07	0.98	0.99	1.07
	M100 [MPa]	1.6	1.39	1.36	1.74	1.62	1.64	1.77
	M300 [MPa]	8.57	4.98	5.5	7.09	6.96	7.11	7.78
	TS [MPa]	16.58	12.92	13.4	16.03	15.99	15.79	16.43
HARDNESS IRHD 23 °C	**Hardness [IRHD]**	61.5	53.6	55.6	58	60	59.3	63.7
HARDNESS IRHD 100 °C	**Hardness [IRHD]**	51.3	43.4	46.3	50.8	51.7	50.7	53
DISPERGRADER ANALYSIS	**Average (X) [-]**	5.2	0.5	0.5	0.5	0.7	0.5	0.5
	Average (Y) [-]	9.4	0.5	2.6	2.2	3.3	2.9	3

Another strategy could be to pre-react purified lignin with HMT before adding the material in the mixing stage.

This material, used as a partial replacement for carbon black, has given good reinforcement results (G). It was decided to use hardness and tensile strength as the mechanical properties to highlight the ability to reinforce the lignin in rubber composites. For clarity, the hardness at 23 °C and 100 °C is reported in Fig. 4. The hardness of rubber composites with biomass, purified lignin, and commercial lignin were lower in comparison to the reference, while HMT pre-reacted lignin (G) led to a higher value of hardness than the reference (A).

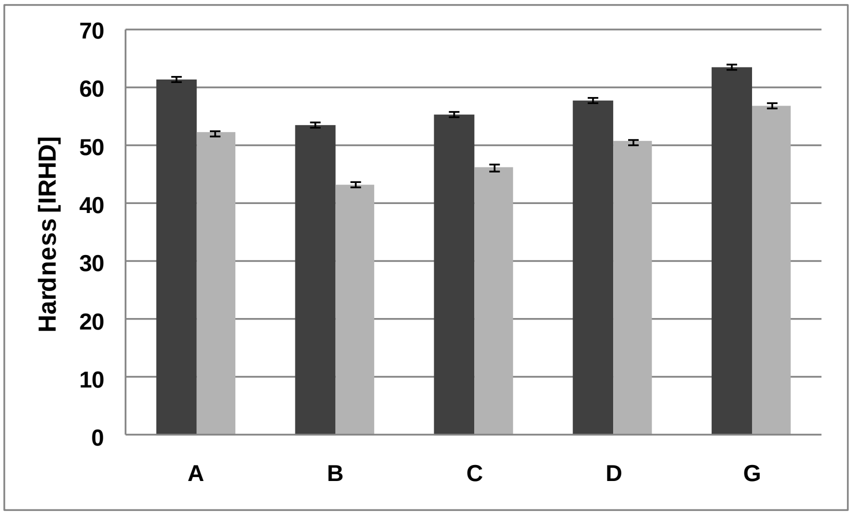

Fig. 4. Dependence of hardness on the rubber composites. ■ hardness at 23 °C, ■ hardness at 100 °C. Column A: 65 phr of carbon black; Column B: 50 phr of carbon black + 15 phr of biomass; Column C: 50 phr of carbon black + 15 phr of purified lignin; Column D: 50 phr of carbon black + 15 phr of modified commercial lignin; and Column G: 50 phr of carbon black + 15 phr of HMT pre-reacted lignin. Level of confidence 95%.

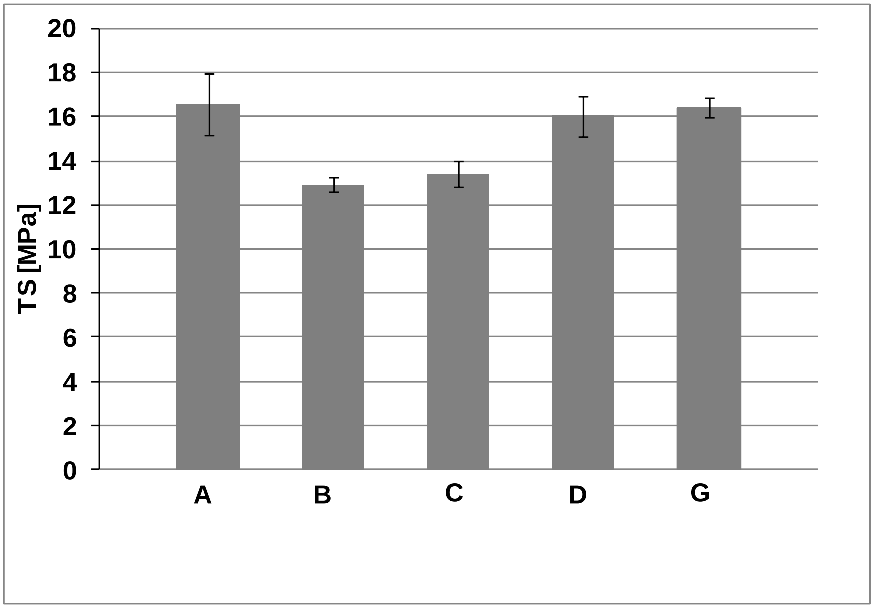

Fig. 5. Comparison of tensile strength of the rubber composites. Column A: 65 phr of carbon black; Column B: 50 phr of carbon black + 15 phr of biomass; Column C: 50 phr of carbon black + 15 phr of purified lignin; Column D: 50 phr of carbon black + 15 phr of modified commercial lignin; Column G: 50 phr of carbon black + 15 phr of HMT pre-reacted lignin. Level of confidence 95%.

The tensile strength for rubber composites with biomass (B) and purified lignin (C) were strongly reduced in comparison to the carbon black reference (A) (Fig. 5). The presence of HMT increased the tensile strength in the commercial lignin (D) as well as in the pre-reacted lignin (G), resulting in values similar to those of the reference carbon black.

The dispergrader data reported in Table 3 highlighted a non-homogeneous dispersion of filler in the polymeric matrix in all analysed rubber composites. The X value, a measure of the dispersion of filler in the polymeric matrix, was even lower than the threshold limit value. This result was attributed to the filler particle size that, together with the filler loading, determines the effective contact area between the filler and polymeric matrix. Furthermore, the structure or the degree of irregularity of the filler unit plays an essential role in the restrictive motion of elastomer chains under strain. Fillers with particle sizes larger than 10 µm do not have reinforcement capabilities and may have detrimental action. Fillers with particle sizes between 1 and 10 µm are used as diluents and usually have no significant effect on rubber properties. Semi-reinforcing fillers range from 100 to 1000 nm. Fillers in the range from 10 nm to 100 nm can significantly improve rubber properties. The average particle size of carbon black is in the range from 10 nm to 500 nm, while the initial lignin particle size in the current study was in the range of tenths of microns (Fig. 1). Lignin particles are linked through hydrogen bonds, which leads to the growth of the lignin structure and prevents the dispersion of the particles during the rolling operation of the filled rubber. The average particle size is one of the main parameters affecting the mechanical properties of rubber composites. Particle size affects the available surface area for interaction with the polymer matrix. To improve the reinforcement of the polymeric matrix with lignin, a method to reduce the particle size should be investigated. Furthermore, the chemical natures of filler influence the dispersion of filler in the elastomers. Carbon black, which has a relatively non-polar surface, has more interactions with the non-polar hydrocarbon rubber. Because of the presence of strong polar groups in lignin (mainly hydroxyl groups), a poor interfacial adhesion with the nonpolar hydrophobic matrix is expected. The hydrophilic character of lignin is incompatible with the hydrophobic polymer matrix. Chemical modifications of lignin, such as hydrophobisation or the addition of compounds for making them compatible with polymeric systems, could be a possible solution to improve lignin-polymer interactions.

CONCLUSIONS

1. Lignin has some disadvantages as a rubber-reinforcing filler, such as its large particle size, strong polar surface, and the high tendency of lignin particles to adhere together by intermolecular hydrogen bonding, forming agglomerates.
2. The addition of modified sulphur-free lignin into the elastomer matrix shows that this natural polymer, which can be derived as a by-product of the papermaking or bioethanol production processes, could have a potential application in the rubber industry. Modified commercial lignin and HMT-prereacted lignin are better reinforcement in rubber composites in comparison to purified lignin alone, but they did not achieve the performance of carbon black.

3. Primary factors that affect the reinforcement ability of rubber fillers are the size and shape of particles, chemical nature, dispersibility, and tendency to agglomerate. The dispersion quality has a direct impact on the final product properties. Mechanical properties can be in part associated with defects caused by insufficient filler dispersion in the rubber matrix.

REFERENCES CITED

Adler, E. (1977). "Lignin chemistry-Past, present and future," *Wood Sci. Technol*. 11(3), 169-218.

Benko, D. A., Hahn, B. R., Cohen, M. P., Dirk, S. M., and Cicotte, K. N. (2010). "Functionalized lignin, rubber containing functionalized lignin and products containing such rubber composition," U.S. Patent 2010/0204368 A1.

Bertini, F., Canetti, M., Cacciamani, A., Elegir, G., Orlandi, M., and Zoia, L. (2012). "Effect of ligno-derivatives on thermal properties and degradation behaviour of poly(3-hydroxybutyrate)-based biocomposites," *Polymer Degradation and Stability* 97(10), 1979-1987.

Billa, E., Koukios, E. G., and Monties, B. (1998). "Investigation of lignins structure in cereal crops by chemical degradation methods," *Polym. Degrad. Stab*. 59(1-3), 71-75.

Bono, P. J., Barakat, A., Lepifre, S., and Loira, J. H. (2008). "Methods for producing modified aromatic renewable materials and compositions thereof," U.S. Patent 2008/0021155 A1.

Boutsicaris, S. P. (1984). "Lignin reinforced synthetic rubber," U.S. Patent 4477612.

BS ISO 37 (2005). "Determination of tensile stress-strain properties."

Ciobanu, C., Ungureanu, M., Ignat, L., Ungureanu, D., and Popa, V. I. (2004). "Properties of lignin-polyurethane films prepared by casting method," *Ind. Crops Prod*. 20(2), 231-241.

Dargaville, T. R., De Bruyn, P. J., Lim, A. S. C., Looney, M. G., Potter, A. C., Solomon, D. H., and Zhang, X. Q. (1996). "Chemistry of novolac resins. II. Reaction of model phenols with hexamethylenetetramine," *Journal of Polymer Science Part A-Polymer Chemistry* 35(8), 1389-1398.

Davidson, M. J. G., and Wunder, R. H. (1977). "Latex coagulation process using lignin compound," U.S. Patent 4025711.

Doughty, J. B. (1967). "Method of dry-milling carboxylic elastomers and alkali lignins," U.S. Patent 3325427.

Doughty, J. B., and Charleston, S. C. (1966). "Lignin reinforced rubber and method of preparation thereof," U.S. Patent 3247135.

Falkehag, S. I. (1972). "Hexamethylene tetramine derivates of alkali lignins," U.S. Patent 3697497.

Furlan, L. T., Rodrigues, M. A., and De Paoli, M. A. (1985). "Sugar cane bagasse lignin as stabilizer for rubbers: Part III--Styrene/butadiene rubber and natural rubber," *Polymer Degradation and Stability* 13(4), 337-350.

Gregorová, A., Košíková, B., and Moravčík, R. (2006). "Stabilization effect of lignin in natural rubber," *Polymer Degradation and Stability* 91(2), 229-233.

Griffith, T. R., and MacGregor, D. W. (1953). "Aids in vulcanization of lignin–natural rubber coprecipitates," *Industrial and Engineering Chemistry* 45(2), 380-386

ISO 11345 (2006). "Assessment of carbon black and carbon black/silica dispersion."

ISO 48, 1994 AMD 1 (1999). "Determination of hardness (hardness between 10 and 100 IRHD)."

Jung, C. O. (2008). "Rubber composition for tire treads," Patent KR 2003042888

Kosikova, B., Alexy, P., and Gregorova, A. (2003). "Use of lignin products derived from wood pulping as environmentally desirable component of composite rubber materials," *Wood Res*. 48(1/2), 62-67.

Košíková, B., and Gregorová, A. (2005). "Sulfur-free lignin as reinforcing component of styrene–butadiene rubber," *Journal of Applied Polymer Science* 97(3), 924-929.

Kramarova, Z., Alexy, P., Chodak, I., Spirk, E., Hudec, I., Kosikova, B., Gregorova, A., Suri, P., Feranc, J., Bugaj, P., and Duracka, M. (2007). "Biopolymers as fillers for rubber blends," *Polym. Adv. Technol.* 18(2), 135-140.

Kumaran, M. G., and De, S. K. (1978). "Utilization of lignins in rubber compounding," *Journal of Applied Polymer Science* 22(7), 1885-1893.

Lapierre, C., Pollet, B., and Rolando, C. (1995). "New insights into the molecular architecture of hardwood lignins by chemical degradative methods," *Res. Chem. Intermed*. 21(3-5), 397-412.

Lewis, N. G., and Yamamoto, E. (1990). "Lignin: Occurrence, biogenesis and biodegradation," *Annu. Rev. Plant Mol. Biol*. 41(1), 455-496.

Lin, S. Y., and Lebo Jr., S. E. (1995). "Lignin," in: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 15, 4th Ed., pp. 268-289.

Lora, J. H., and Glasser, W. G. (2002). "Recent industrial applications of lignin. A sustainable alternative to nonrenewable materials," *J. Polym. Environm*. 10(1-2), 39-48.

Lora, J., Naceur, B. M., and Gandini, A. (2008) "Industrial commercial lignins: Sources, properties and applications," in: *Monomers, Polymers and Composites from Renewable Resources*, B. M. Naceur and A. Gandini (eds.), Elsevier, Amsterdam, pp. 225-241.

Nando, G. B., and De, S. K. (1980). "Effect of lignin on the network structure and properties of natural rubber mixes vulcanized by conventional, semiefficient and efficient vulcanization systems," *Journal of Applied Polymer Science* 25(6), 1249-1252.

Northey, R. A. (1992). "Low-cost uses of lignin," *ACS Symposium Series* 476, 146-175.

Otto, S. (2005). "New reference value for the description of filler dispersion with the Dispergrader 1000 NT*," KGK Kautschuk Gummi Kunststoffe* 58(7-8), 390-393.

Salanti, A., Zoia, L., Tolppa, E. L., and Orlandi, M. (2012). "Chromatographic detection of lignin-carbohydrate complexes in annual plants by derivatization in ionic liquid," *Biomacromolecules* 13(2), 445-454.

Salanti, A., Zoia, L., Tolppa, E. L., Giachi, G., and Orlandi, M. (2010). "Characterization of waterlogged wood by NMR and GPC techniques," *Microchemical Journal* 95(2), 345-352.

Sarkanen, K. V., and Ludwig, C. H. (1971). *Lignins: Occurrence, Formation, Structure and Reactions*, Wiley-Interscience, New York.

Savel'eva, M. B., Onishchenko, Z. V., Bogomolov, B. D., Tiranov, P. P., Lebed, I. G., and Kadantseva, Y. A. (1983). "Technical lignins as promising ingredients for sole rubbers," *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Legk. Prom-sti*. 26(6), 53-56.

Setua, D. K., Shukla, M. K., Nigam, V., Singh, H., and Mathur, G. N. (2000). "Lignin reinforced rubber composites," *Polymer Composites* 21(6), 988-995.

Shusheng, L., and Xiansu, C. (2010) "Application of lignin as antioxidant in styrene butadiene rubber composite," *AIP Conf. Proc*. 1251, 344-347.

Sluiter, A. H., Ruiz, B., Scarlata, R., Sluiter, C., Templeton, J., and Crocker, D. D. (2008). "Determination of structural carbohydrates and lignin in biomass laboratory analytical procedure," NREL Report No. TP 510-42618.

Yeh, T. F., Yamada, T., Capanema, E., Chang, H. M., Chiang, V., and Kadla, J. F. (2005). "Rapid screening of wood chemical component variations using transmittance near infrared spectroscopy," *J. Agric. Food Chem.* 53(9), 3328-3332.

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