

Mechanochemical Methacrylation of Lignin for Biobased Reinforcing Filler in Rubber Compounds

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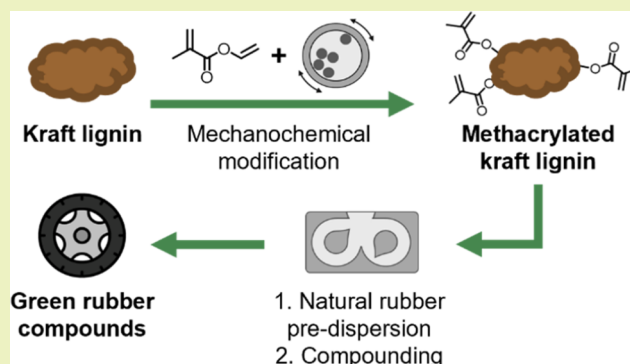
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ABSTRACT: The inclusion of biobased materials as fillers for rubber compounds is an emerging topic in the tire industry. This study investigates the use of kraft lignin, a byproduct of the paper industry, as an alternative reinforcing filler for rubber compounds. Methacrylation of lignin was achieved through mechanochemistry, resulting in an estimated functionalization degree of 22% for aliphatic and 17% for phenolic hydroxyl groups. The modified lignin was pre-dispersed in natural rubber via coprecipitation with a natural rubber latex. The reinforcing effect of lignin was tested in model tread and sidewall compounds by using either a sulfur or peroxide vulcanization system. Dynamic mechanical tests revealed that methacrylated lignin enhances compatibilization, dispersion, and stiffness within the elastomeric matrix more effectively than unmodified lignin due to covalent bond formation during vulcanization. In peroxide-cured composites, functionalized lignin combined with silica exhibited a higher storage modulus and lower hysteresis compared to unmodified lignin, suggesting potential for designing fuel-efficient tires.

KEYWORDS: lignin modification, mechanochemistry, natural rubber, elastomers, biobased filler



1. INTRODUCTION

Nowadays, sustainability has become one of the main focuses in industry. Research is oriented toward the development of products made from biobased materials, derived from sustainable resources, and with a lower carbon footprint.^{1,2} In the tire industry, carbon black is one of the most commonly used fillers for imparting the desired mechanical properties to rubber compounds. However, its production and release into the environment are considered rather nonsustainable and hazardous.³ Along with reinforcement, carbon black imparts high hysteresis to rubber composites, with a negative impact on rolling resistance, hence fuel consumption, of tires, which are associated with higher polluting emissions and costs of locomotion. In order to address both sustainability and performance issues, “white” fillers, especially silica, have been developed and resulted in an improved hysteresis while maintaining sufficient reinforcement.⁴ Silica is conventionally derived from sand by precipitation with strong acids and pyrogenic treatment of silicon tetrachloride and more rarely from biomass.

The development of some different biobased fillers as substitutes for commonly used fillers in various industries has then been of particular interest over the years. Most of the studies include materials obtained from biomass, e.g., cellulose, silica obtained from rice husks, and lignin. Among them, lignin

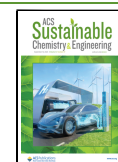
is of particular interest since it is one of the most available biopolymers on earth, second only to cellulose, and it is widely available as a byproduct of different pulping processes. Kraft lignin, obtained during the kraft process, is typically used as fuel to produce the energy needed by the process.^{5–7} Its use as a biofiller in rubber compounds has gained attention as a valid alternative and adjuvant to conventional reinforcing fillers thanks to its good physical–chemical properties, including antioxidant activity and thermal stability. Moreover, lignin is also a rather cheap material, and its inclusion in rubber can lead to weight reduction, hence fuel savings in working conditions.^{8,9} However, incorporating lignin in a rubber matrix requires overcoming the limited compatibility between the two materials.¹⁰ This is due to the polarity of the lignin molecules, which results in strong self-interactions. As a consequence, lignin is often chemically modified to enhance its dispersion in the elastomeric matrix and improve its interfacial adhesion to the rubber macromolecules.⁸ The abundance of functional

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groups in lignin suggests the possibility of a chemical modification in order to enhance its appropriate compatibility with the rubber matrix.¹¹ The reinforcing capacity of lignin strongly depends on strong interfacial adhesion to the rubber matrix. As a result, to improve the reinforcing effects of lignin, it is possible to functionalize lignin so that covalent bonds can be formed with rubber macromolecules during vulcanization.^{12,13}

In the literature, many wet chemistry synthetic strategies have been reported for the chemical modification of lignin.¹⁴ The most targeted groups include aliphatic alcohols, phenols, and carboxylic acids. The most popular approaches comprise the use of organic solvents as reaction media, as such being affected by a high environmental impact and use of hazardous chemicals.^{15,16}

However, mechanochemistry can be regarded as an alternative to run reactions in the solid state, taking advantage of the mechanical energy to trigger chemical transformations. As such, this process is associated with the avoidance or saving of organic solvents, waste reduction, and yields quantitatively increased thanks to a reduction of extensive workup procedures.^{17–19} Mechanochemical modifications of lignin reported in the literature mainly include the reduction in particle size associated with milling and its depolymerization. Few studies have been devoted to the chemical functionalization of lignin.^{20,21} Some attention has been attracted by the esterification of polar hydroxyl groups of lignin; their conversion was achieved for lignin model compounds by using noncyclic or cyclic anhydrides as acylating agents with enzymes to catalyze the reaction.²² However, this strategy afar from green chemistry best practices due to drawbacks associated with poor atomic efficiency, enzyme loss, and the use of hazardous chemicals.²³ A more interesting approach by Guo et al. described the possibility to functionalize organosolv lignin by mechanochemical transesterification using methyl oleate as an acyl donor and potassium hydroxide as a catalyst instead of enzymes, reporting a 25% functionalization of hydroxyl groups.²⁴

Based on these conditions, in the present work, we further developed and explored the concept of transesterification of lignin with the use of enol esters as acyl donors. The release of an enol, which tautomerizes into the corresponding ketone, during their reaction leaves no free nucleophile and makes the reaction irreversible, allowing for the reaction to be carried out under milder conditions.^{16,25} Among the acyl donors tested, methacrylates were included in order to compatibilize lignin with the rubber matrix. The presence of active double bonds was expected to ensure the formation of covalent bonds between lignin and rubber molecules during vulcanization, potentially leading to better mechanical reinforcement of the final material compared with unmodified lignin. The effectiveness of functionalization of lignin was assessed by NMR spectroscopies (¹H and ³¹P), attenuated total reflectance-Fourier transform infrared (FT-IR/ATR), and gel permeation chromatography (GPC) analysis, as previously reported in other works.^{26–28}

Previous works have evidenced that the direct mixing of dry lignin into rubber compounds results in poor dispersion of the filler in the matrix and hence a degradation of the mechanical performances. To overcome this, lignin/natural rubber pre-dispersions were prepared using a known coprecipitation technique.^{10,29,30} Then, various synthetic/natural rubber compounds filled with methacrylated lignin and silica were

prepared by mechanical mixing. Silica has been selected as the technological reference for conventional fillers, since it already embodies an improvement in terms of sustainability and performance when compared to the dominant technology of carbon black. The present study reports an advancement in the field of “white” fillers by increasing the renewable content and hence the sustainability of rubber compounds. The study involved the analysis of vulcanization characteristics in both a peroxide- and a sulfur-based system, along with the mechanical properties (static and dynamic) of the final tire compounds. Performances were evaluated by comparing rubber composites including methacrylated lignin with suitable references filled with silica and unmodified softwood kraft lignin.

2. EXPERIMENTAL SECTION

2.1. Reagents and Materials. Lignins investigated included herbaceous alkaline lignin Protobind P1000 (Green Value, Switzerland) and BIOPIVA 100 (KL, UPM, Finland) softwood kraft lignin (solid content: 55% wt.). Their properties in terms of hydroxyl group content and molecular weight are summarized in Tables S6 and 3, respectively. The following materials were used for rubber compounding: commercial grade stabilized natural rubber latex high ammonia 60% wt. (Von Budit Co., Thailand), styrene butadiene rubber SLR 4630 (SBR, Synthos, Poland), natural rubber SIR20 (NR, Aneka Bumi Pratama, Indonesia), butadiene rubber CB25 (BR, Lanxess, Germany), silica ZEOSIL 1165MP (SiO₂, Solvay, Belgium), 3-(Triethoxysilyl)propylmethacrylate (TEMS, JH silanes, China), bis(triethoxysilylpropyl)disulfide 50 wt % CB supported (TESPD, JH silanes, China), soluble sulfur (S, Zolfoindustria, Italy), oil-extended sulfur oleate 66% Crystex OT 33 (S₆₀, Eastman), zinc oxide (ZnO, Zincol ossidi, Italy), stearic acid (SA, Sogis, Italy), *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS, GENERAL QUIMICA, Spain), *N*-1,3-dimethylbutyl-*N'*-phenyl-*p*-phenylenediamine (6PPD, Flexsys), and peroxide-based vulcanizing agent LUPEROX 101XL45 (LUPEROX, Arkema, France). All other reagents and solvents (ACS grade) were purchased from Sigma-Aldrich and used as received without further purification.

2.2. Mechanochemical Modification of Lignin. The optimized procedure for the preparation of the biobased filler for tire compounds proceeds as follows: softwood kraft lignin (dry content of 5 g) and sodium hydroxide (0.7 mol/mol_{TOT(OH)}) were introduced in a 250 mL planetary ball mill jar made of steel equipped with balls of the same material (17 spheres Ø 7 mm, 2 spheres Ø 10 mm). The mixture was ground at 500 rpm for 30 min in a PM 100 planetary ball mill (Retsch, Germany). Vinyl methacrylate (0.3 mol/mol_{ROH+PHOH}) was introduced, and the mixture was milled for an additional 4 h. The content of the jar was transferred into a centrifuge tube with the help of deionized water. HCl solution (0.1 M) was added to induce the neutralization of lignin salt and the precipitation of the product, which was recovered after centrifugation and two additional washes with water. The product (modKL) was then freeze-dried and isolated as a brownish powder.

The design and optimization of the reaction, previously carried out on a smaller scale (200 mg dry content), was conducted using a 50 mL planetary steel ball mill jar equipped with 10 steel balls (Ø 7 mm) and by varying lignin, reaction time, base, and acyl donor (SI).

2.3. Characterization of Lignin and Its Derivatives.
2.3.1. Fourier Transform Infrared Spectroscopy (FT-IR/ATR). Attenuated total reflectance (ATR) infrared spectroscopy was used for qualitative characterization of lignin samples. Spectra were recorded with a Nicolet iS10 spectrometer (Thermo Scientific) equipped with an iTR Smart device (total scans 32, range 4000–650 cm⁻¹, resolution 1 cm⁻¹).

2.3.2. ¹H and ³¹P Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H NMR data was acquired by dissolving a lignin sample (25–30 mg) in *d*₆-DMSO (750 μL) and spectra were registered with an Avance 500 MHz NMR spectrometer (Bruker, Germany).

Table 1. Formulation Used for the Preparation of the SBR/NR Compounds Filled with Lignin and Their References^a

sample	peroxides vulcanization				sulfur vulcanization				
	50Si-P	35Si-P	35Si + 25KL-P	35Si + 25modKL-P	50Si-S	50Si TEMS-S	35Si-S	35Si + 25KL-S	35Si + 25modKL-S
SBR	102.75				102.75				
NR	25	25			25	25	25		
MB NR/KL			50					50	
MB NR/modKL				50					50
SiO ₂	50	35	35	35	50	50	35	35	35
6PPD	2				2				
TEMS	4	2.8	2.8	2.8		4			
LUPEROX	2.3	2.3	2.3	2.3					
TESPD		8		5.6	5.6	5.6			
SA + ZnO + CBS + S					1 + 1 + 3 + 1				

^aQuantities expressed in phr: parts per hundred rubber.

Table 2. Formulation Used for the Preparation of the BR/NR Compounds Filled with Lignin and Their References^a

Sample	peroxides vulcanization			sulfur vulcanization		
	40Si-P	10Si + 50KL-P	10Si + 50modKL-P	40Si-S	10Si + 50KL-S	10Si + 50modKL-S
BR	50			50		
NR	50			50		
MB NR/KL		100			100	
MB NR/modKL			100			100
SiO ₂	40	10	10	40	10	10
6PPD	2			2		
TEMS	3.2	0.8	0.8			
LUPEROX	2.3	2.3	2.3			
TESPD				6.4	1.6	1.6
SA + ZnO + CBS + S _{eo}				2 + 3 + 1 + 2		

^aQuantities expressed in phr: parts per hundred rubber.

Prior to the ³¹P NMR analyses, phosphorylation was performed. Samples were prepared by dissolving accurately weighed lignin samples (20 mg) in a pyridine-deuterated chloroform solution (1.6:1 v/v, 700 μ L) containing 1 mg·mL⁻¹ chromium-(III) acetylacetonate (Cr(acac)₃). Then, 100 μ L of endo-*N*-hydroxy-5-norbornene-2,3-carboximide solution (e-HNDI, 121.5 mM, CDCl₃/pyridine 4.5:0.5 v/v) was added, along with 100 μ L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as the derivatizing agent.³¹ ³¹P NMR spectra of phosphorylated samples (800 μ L) were acquired with an Avance 500 MHz NMR spectrometer (Bruker, Germany) and quantitative data elaborated as reported in the protocol by Meng et al. The quantitative data reported in this paper have a maximum standard deviation of 2×10^{-2} mmol·g⁻¹, while the maximum standard error is 1×10^{-2} mmol·g⁻¹.

2.3.3. Gel Permeation Chromatography (GPC) Analyses. Prior to gel permeation chromatography analyses, acetylation of the samples was performed.³² Briefly, 20 mg of each lignin sample were acetylated in a pyridine-acetic anhydride solution (1:1 v/v, 2 mL) and kept overnight at 40 °C. After stripping with ethanol, toluene, and chloroform (25 mL \times 3 each solvent), the sample was dried in vacuum. The acetylated lignin was solubilized in tetrahydrofuran for GPC analysis and filtered through a 0.2 μ m syringe Whatman Puradisc filter (U.K.).

GPC analyses were conducted on an Agilent 1100 Series (Agilent Technologies, Germany) liquid chromatograph connected to a UV-vis detector set at 280 nm. The injection port was a Rheodyne loop valve equipped with a 20 μ L loop. The mobile phase was inhibitor-free tetrahydrofuran (THF). The operational conditions were: sample concentration 2 mg·mL⁻¹; flow rate 1 mL·min⁻¹; injection volume 20 μ L; column system composed by Agilent PLgel 5 μ m (500 Å), Agilent PLgel 5 μ m (1000 Å), and Agilent PLgel 5 μ m (10,000 Å) connected in series; temperature 25 °C. Polystyrene standards (3×10^6 –162 g·mol⁻¹) from Polymer Laboratories were used for calibration. The evaluation of the number-average molecular weight (M_n) and the

weight-average molecular weight (M_w) of the extracted lignin samples was performed according to the methodology developed by Himmel.³³ Moreover, the ratio $D = M_w/M_n$, defined as the dispersity index, was also calculated. The M_n and M_w values reported are the average of three analyses ($M_w \pm 1000$ g·mol⁻¹; $M_n \pm 100$ g·mol⁻¹, $P = 0.05$, $n = 3$).

2.4. Preparation of NR/Lignin Masterbatches (MB). NR/lignin masterbatches were prepared via a coprecipitation method.¹⁰ A proper amount of lignin or modified lignin was dissolved in water (12 mL per gram of lignin) by adjusting the pH to 10.5–11 by the dropwise addition of NaOH aqueous solution (1 M). The solution was then gently poured into a beaker containing a proper amount of 60% w/w natural rubber latex. The resulting emulsion was stirred for 30 min, and finally, sulfuric acid (10% w/w) was added gradually to induce coagulation, which was evaluated by visual inspection. The paste was filtered off on a Büchner funnel and repeatedly washed with excess water until a pH of 6 was obtained. The thick paste was dried at 45 °C for about 60 h. The amounts of lignin and natural rubber latex were calculated to obtain masterbatches with a final lignin concentration of 50% w/w or 100 phr (which stands for *parts per hundred rubber*, referring to the percentual mass ratio between the specific ingredient and the total rubber quantity in the formulation). The obtained masterbatches were called MB NR/KL and MB NR/modKL when prepared with KL and modKL, respectively.

2.5. Preparation of Rubber Model Compounds. To assess the novel biobased filler efficacy as a reinforcing filler in tires, industrial-type compounds for tread and sidewall were produced. The procedure consisted of mixing additives into neat rubber or rubber/lignin mixtures. Details of the two-step procedure followed for compounding are reported in Table S1. The mixing was carried out in a Brabender mixer with an internal chamber of 50 mL. The fill factor, defined as the volume of the ingredients divided by the volume of the chamber, was 0.9.

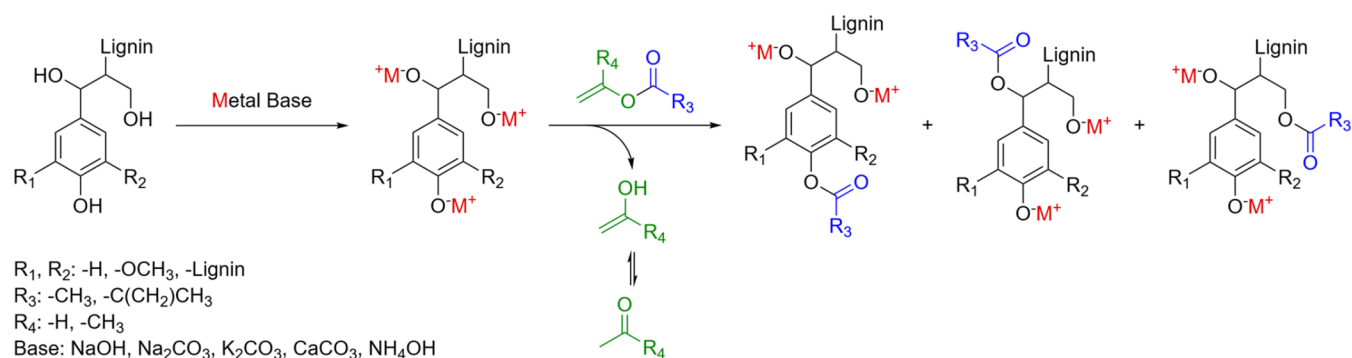


Figure 1. Reaction diagram for the mechanochemical functionalization of lignin with enol esters as acyl donors.

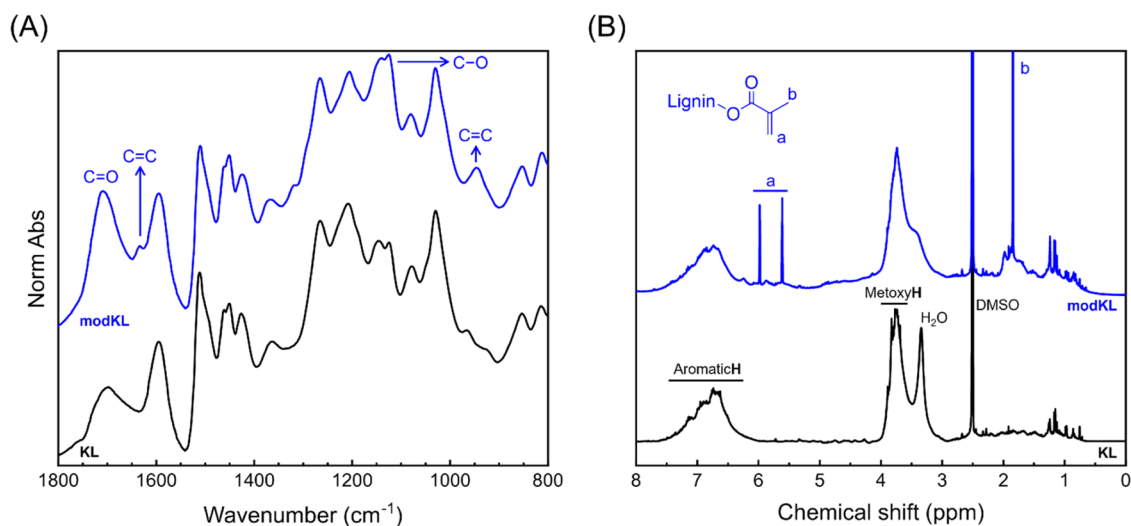


Figure 2. Characterizations of softwood kraft lignin (KL, black) and its corresponding methacrylated derivative (modKL, blue). (A) FT-IR/ATR spectra, absorbances normalized with the 1510 cm⁻¹ peak; (B) ¹H NMR spectrum, intensities normalized with the aromatics peak.

The obtained rubber compounds differed by: type and quantity of filler used, i.e., silica, KL, and modified KL; by vulcanization system, i.e., peroxides (-P), in order to assess the reactivity of the methacrylic groups present in modKL, and sulfur (-S) which is the main system used in the tire industry; type of rubbers used in the blend, i.e., SBR/NR and BR/NR. Formulation of the rubber compounds produced is summarized in Tables 1 and 2 for SBR/NR and BR/NR compounds, respectively.

2.6. Characterization of Rubber Model Compounds.

2.6.1. Vulcanization Kinetics and Dynamomechanical Analyses (DMA). Measurements were performed with a Rubber Process Analyzer RPA 2000 (Alpha Technologies, Germany). Rubber compound samples (5.5 g) were cut and placed between two thin Mylar films measuring 4 × 4 cm². First, vulcanization kinetics were analyzed for 15 min in the range of 25–170 °C (1.6 Hz, 0.5°), obtaining information regarding the viscosity of the compound during the process. Then, DMA on the cured sample was conducted with a strain sweep in the range of 0.1–10 °C (70 °C, 1.6 Hz), obtaining modulus and loss coefficient data.

2.6.2. Tensile Properties. Tensile stress–strain curves were obtained using a Zwick/Roell (Germany) tensile testing machine. The testing parameters complied with the ISO 37 and UNI 6065 standards. Specimens for tensile tests were prepared as follows: rubber compounds rest at room temperature for 24 h after being mixed. Afterward, they were flattened into 8 mm thick sheets by a two-roll mill and cured in a hydraulic press at 170 °C, pressure 4.3 bar, for 10 min. For each sheet, three dumbbell-shaped test specimens were die-cut and their thickness was measured. Data were reported as the means of three analyses, and the median sample was plotted.

3. RESULTS AND DISCUSSION

3.1. Mechanochemical Esterification of Lignin. The design of the mechanochemical modification of lignin was conducted first on an herbaceous alkaline lignin. Starting from previous work²⁴ direct mixing of lignin, vinyl acetate, and sodium hydroxide did not result in any modification of the substrate, as investigated by FT-IR/ATR. A pretreatment with the base before the addition of the acyl donor was therefore introduced in order to convert the hydroxyl groups of lignin into alkoxides, which could act as better nucleophiles. An overview of the optimized process is depicted in Figure 1. A screening of different reaction times (Table S2), bases (NaOH, Na₂CO₃, K₂CO₃, CaCO₃ and NH₄OH; Table S4), and acyl donors (vinyl acetate (VA), vinyl methacrylate (VM) and isopropenyl acetate (IA); Table S3) was conducted, and stoichiometric amounts were optimized for the esterification of softwood kraft lignin (Table S5).

Modified softwood kraft lignin was chosen as the substrate for the development of the biobased filler for rubber compounds, as it is widely available on an industrial level as a wet powder containing 40–70% solid content. It was revealed that an initial drying of the lignin led to greater esterification levels, probably due to the prevention of hydrolysis competing with esterification. However, drying the lignin on a large scale would not be feasible, as it requires a considerable amount of energy. Moreover, a high degree of esterification would be detrimental to the production of NR/

lignin masterbatches by coprecipitation, as this process relies on lignin's solubility properties resulting from the presence of phenolic groups and carboxylic acids. Additionally, an extensive esterification of phenolic groups would decrease the antioxidant properties of lignin, which proved to improve the thermal stability of natural rubber compounds.^{10,34} Among the various acyl donors evaluated during testing, the VM was selected in order to make lignin active during the vulcanization process. Transesterification with vinyl esters is driven by the release of acetaldehyde, which is classified as a phase-out substance by the European Chemical Agency. The release of rather safer byproducts would be preferable, IA was tested as a proof of concept, proving the feasibility of achieving transesterification by generating acetone as a byproduct. Sodium hydroxide was preferred over carbonate salts due to the weaker alkalinity of the latter, which required a higher stoichiometric quantity of base to achieve comparable results. Furthermore, the use of HCl to neutralize the lignin salt during the purification process resulted in significant effervescence, making scale-up difficult.

A qualitative proof of functionalization was provided by FT-IR/ATR and ¹H NMR, which both showed the appearance of peaks related to the presence of the methacrylic group.³⁵ By comparing the FT-IR/ATR spectra of the modified lignin with the starting material shown in Figure 2A, it was possible to observe the presence of the methacrylic carbonyl group with an increase of the intensity for the broad peak typical of the carbonyl group (C=O stretch, 1695–1740 cm⁻¹) associated with both the functionalities originally present on lignin (1695–1720 cm⁻¹) and the introduced methacrylic functionalities (1740 cm⁻¹); as well as an increase in the peak associated with ester bonds (C–O esters stretch, 1100–1150 cm⁻¹). Another increase in intensity was observed for the peaks at 1640, 1600, and 950 cm⁻¹ which are associated with the methacrylic double bond. Finally, a decrease in the intensity of signals associated with aliphatic alcohols (C–OH, 1030 cm⁻¹) was also observed, indicating their consumption in ester formation. The presence of acid residues, which could have possibly originated by the hydrolysis of the ester without its incorporation in lignin structure, was carefully addressed by the multistep washing procedure. For this reason, no increase in the content of carboxylic acids was detected by FT-IR/ATR.

The ¹H NMR spectrum (Figure 2B) of unmodified kraft lignin is characterized by the presence of two main broad peaks related to aromatic and methoxy protons at 6–7.5 and 3–4 ppm, respectively. The modified derivative showed additional peaks associated with the presence of methacrylate functionalities. Peaks a corresponds to the two different protons on the methacrylic double bond, while peak b is related to the methyl group, multiplicities of the peaks a were not observable. Two more signals are present due to traces of solvents (water and dimethyl sulfoxide (DMSO)).

³¹P NMR analysis of phosphitylated samples allowed for the quantitative estimation of the hydroxyl content before and after functionalization, leading to the assessment of the esterification degree. Table 3 reports the hydroxyl content detailed by type of hydroxyl group. ³¹P NMR data evidenced a decrease in the content of aliphatic and phenolic alcohols after mechanochemical modification, indicating them as the main reactive groups with vinyl methacrylate. The corresponding degrees of esterification were calculated to be 22 and 17% for aliphatic and phenolic hydroxyl groups, respectively. As previously mentioned, a low degree of esterification was

desired for the processability of the material during the preparation of natural rubber masterbatches. The multistep washing procedure addressed the possible presence of residues of acrylic acid as a product of the side reaction of hydrolysis of vinyl methacrylate. For this reason, the content of carboxylic acids increased only negligibly upon mechanochemical treatment.

In the literature, milling lignin in the presence of a large excess of NaOH (i.e., 1–10 equiv) was reported to provoke lignin degradation into fragments with a lower molecular weight.²⁴ Gel permeation chromatography analyses allowed verification that the optimal procedure presented here did not result in any depolymerization of the starting material (Table 3

Table 3. Calculated Hydroxyl Group Content Measured by ³¹P NMR Spectroscopy and Molecular Weight Distributions (M_n and M_w) and Dispersity (\mathcal{D}) Measured by GPC Analysis

sample	KL	modKL
Hydroxyl Group Content (mmol·g ⁻¹)		
aliphatic – OH (ROH)	1.60	1.25 (–22%)
syringyl and condensed – OH	1.37	1.17
guaiacyl – OH	1.58	1.26
hydroxyphenyl – OH	0.15	0.14
total phenolic – OH (PhOH)	3.10	2.57 (–17%)
carboxylic acids (COOH)	0.50	0.55 (+5%)
total – OH (TotOH)	5.20	4.37 (–16%)
Molecular Weight		
M_n (g·mol ⁻¹)	2800	2300
M_w (g·mol ⁻¹)	6300	5200
\mathcal{D}	2.2	2.3

and Figure S2). GPC studied the possible evolution of molecular weight of lignin upon mechanochemical treatment, associated with possible degradation and repolymerization phenomena. The analyses confirmed that the reaction conditions used for the modification of lignin did not significantly affect its molecular weight distribution, indicating that no significant degradation has occurred. Sharp peaks visible at low molecular weights (100 g·mol⁻¹ ca.) were associated with residual unreacted solvents from the acetylation process necessitated for the preparation of the sample for the analysis. The peaks related to low molecular weight components could not be attributed to residual methacrylic acid or unreacted vinyl methacrylate since at the experimental wavelength (280 nm) such molecules could not be detected.

The process developed for the methacrylation of kraft lignin, when compared to other esterification procedures present in the literature, allowed us to obtain modified lignin derivatives with a lower consumption both in terms of reactant, solvents, and extensive workup procedures. Reported procedures rely on the usage of catalysts leading to recovery challenges;^{35,36} highly reactive molecules like acyl chlorides or with a bad atom economy (anhydrides).^{37–39}

3.2. Technical Elastomeric Compounds Containing Mechanochemically Modified Lignin. **3.2.1. SBR/NR Composites Containing Lignin and Silica as Fillers for Tire Tread.** Compounds based on styrene butadiene rubber (SBR) and natural rubber (NR) blends were studied in order to develop tire treads, including a mixture of silica and lignin as reinforcing fillers. The presence of SBR in the elastomer, which has a relatively high glass transition temperature when

Table 4. Vulcanization Kinetics Data Minimum (M_L) and Maximum (M_H) Torque, Optimum Cure Time (t_{90}), and Dynamomechanical Analysis ($G'_{9\%}$, $\tan \delta_{9\%}$, $\Delta G'_{0.4-10\%}$) of SBR/NR Composites Filled with Silica (Si) and Softwood Kraft Lignin (KL) or Its Corresponding Methacrylated Derivative (modKL), Vulcanized by Peroxides (-P) or by Sulfur (-S)

SBR/NR compound	M_L dNm	M_H dNm	t_{90} min	$G'_{9\%}$ MPa	$\tan \delta_{9\%}$	$\Delta G'_{0.4-10\%}$ MPa
50Si-P	3.96	12.4	7.88	1.35	0.16	0.70
35Si-P	2.79	8.15	7.83	0.81	0.15	0.22
35Si + 25KL-P	3.24	7.62	7.66	1.01	0.19	0.60
35Si + 25modKL-P	2.61	5.62	8.17	0.76	0.16	0.22
50Si-S	3.76	14.1	4.56	1.21	0.14	0.82
50Si TEMS-S	3.04	12.1	5.89	0.91	0.15	0.72
35Si-S	2.96	10.9	3.98	0.84	0.10	0.20
35Si + 25KL-S	3.59	10.5	6.11	1.03	0.13	0.45
35Si + 25modKL-S	4.05	11.6	6.06	1.21	0.14	0.73

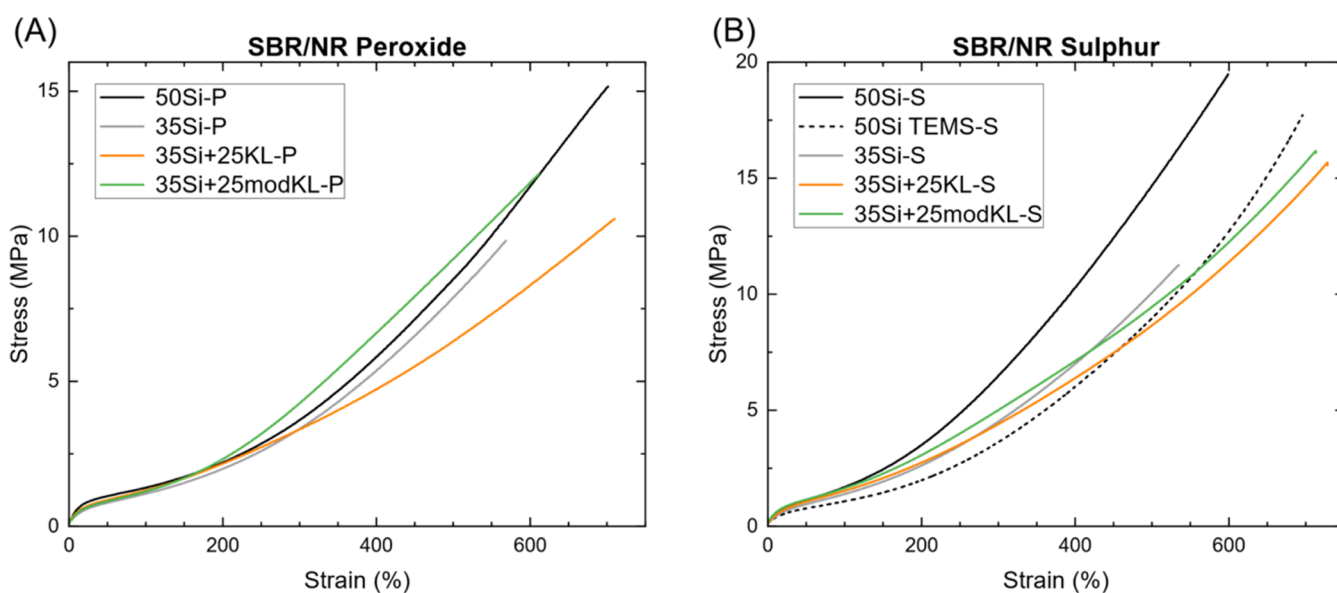


Figure 3. Stress/strain curves of composites of SBR/NR cured with peroxide (A) or sulfur (B) systems; filled with silica (Si) and softwood kraft lignin (KL) or its corresponding methacrylated derivative (modKL).

compared to other common rubbers used in tire technology (e.g., isoprene and butadiene rubbers), is crucial for application in tire treads where traction is a required performance parameter.

As a first screening, compounds vulcanized by peroxides (-P) were prepared to evaluate and exalt the reinforcing effect of methacrylated lignin in comparison with unmodified lignin, taking into account the particularly high reactivity of peroxides toward activated C=C double bonds.^{34,40} Reference compounds were reinforced by silica (Si) compatibilized with a methacryloyl silane, which mimicked the methacrylic functionalization of modified lignin, sharing the same reactivity during curing. Reference compounds filled with 50 and 35 phr of silica (50Si-P and 35Si-P, respectively) represent the upper and lower limits, respectively, in terms of storage modulus ($G'_{9\%}$). While the first compound had a filler content above the percolation limit, the latter fell below that value and was characterized by a lower storage modulus and hysteresis ($\tan \delta_{9\%}$) (Table 4). Rubber compounds filled with lignin included 25 phr of either unmodified or methacrylated kraft lignin (KL and modKL, respectively) in partial substitution of 15 phr of silica (35Si + 25KL-P and 35Si + 25modKL-P), this decision being driven by the well-known weaker reinforcing performances of lignin compared to silica.⁸ The addition of lignin on top of silica was associated with an increment in both

the storage modulus and hysteresis. Noticeably, the use of functionalized lignin was related to higher storage modulus and lower $\tan \delta$ values than milled lignin, with the latter property reaching the same value as the 50Si-P reference compound. Since hysteresis is linked to rolling resistance for tread compounds, reducing its value could result in an increment in the fuel efficiency of the vehicle. Tensile tests (Figure 3) showed that the presence of lignin was linked to an overall decrease in stress at break; however, this parameter improved in the case of functionalization, when compared to lignin. The improvement in the maximum stress and increase in the ratio between stress values at 300 and 100% strains ($\sigma_{300\%}$ and $\sigma_{100\%}$) can be interpreted as a result of an enhanced dispersion of the filler inside the rubber matrix in the case of functionalized lignin with respect to milled lignin (data are also reported in Table S7). The presence of lignin during the curing process proved not to affect the vulcanization kinetics since the optimum curing time (t_{90}) did not noticeably change, and the highest torque during the process was considerably reduced.

Peculiar characteristics in rubber compounds, i.e., aging resistance and low compression set, can be achieved by peroxide curing which, however, cannot lead to the tensile strengths and dynamic properties guaranteed by sulfur vulcanization.⁴¹ SBR/NR compounds for tire tread manufac-

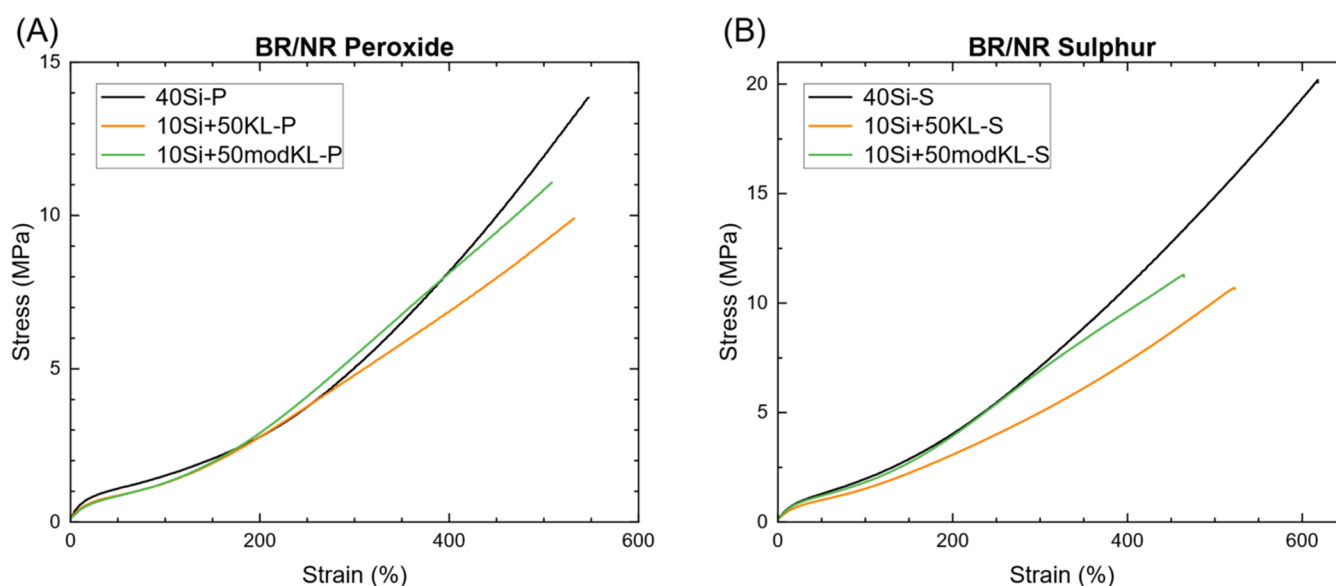


Figure 4. Stress/strain curves of composites of BR/NR cured with peroxide (A) or sulfur (B) systems, filled with silica (Si) and softwood kraft lignin (KL) or its corresponding methacrylated derivative (modKL).

Table 5. Vulcanization Kinetics Data Minimum (M_L) and Maximum (M_H) Torque, Optimum Cure Time (t_{90}) and Dynamomechanical Analysis ($G'_{9\%}$, $\tan \delta_{9\%}$, $\Delta G'_{0.4-10\%}$) of BR/NR Composites Filled with Silica (Si) and Softwood Kraft Lignin (KL) or Its Corresponding Methacrylated Derivative (modKL), Vulcanized by Peroxides (-P) or by Sulfur (-S)

BR/NR compound	M_L dNm	M_H dNm	t_{90} min	$G'_{9\%}$ MPa	$\tan \delta_{9\%}$	$\Delta G'_{0.4-10\%}$ MPa
40Si-P	4.35	13.0	7.85	1.39	0.21	0.56
10Si + 50KL-P	4.25	7.57	7.37	1.08	0.23	0.24
10Si + 50modKL-P	2.61	5.62	8.17	0.76	0.16	0.22
40Si-S	5.16	18.3	7.09	1.69	0.16	0.82
10Si + 50KL-S	4.09	11.9	7.63	1.12	0.14	0.18
10Si + 50modKL-S	3.68	21.5	4.25	1.51	0.07	0.28

turing were vulcanized by sulfur (-S), using an efficient vulcanization system comprising small amounts of sulfur and high amounts of accelerator (CBS), capable of producing short sulfur bridges which also made the compound thermally stable. Reference compounds 50Si-S and 50Si TEMS-S shared the same filler content but differed in the chemical used to compatibilize silica. TESPd containing disulfide group was used in the former compound while TEMS (including methacrylic moieties) was added in the latter. 50Si-S was characterized by a higher cross-link density that was estimated by the difference between the moment of highest and lowest torque, M_H and M_L , during the vulcanization process. The superior cross-linking degree was reflected in higher rigidity (lower maximum strain), improved stress at 300% strain, and superior storage modulus when compared to the latter, 50Si TEMS-S, containing methacryloyl silane. This difference in cross-link density and overall properties was connected to the higher activity of disulfides in vulcanization with respect to methacrylic functions. Despite these differences, the two reference compounds showed similar ultimate properties and hysteresis values, suggesting promising results for fillers, in particular, lignin, compatibilized with a methacrylic function. When comparing compounds with the same silica content, the addition of lignin was associated with better values of storage modulus and maximum stress than reference (35Si-S), while $\tan \delta$ moderately increased. With respect to model compound 50Si-S, the partial substitution of silica with lignin (35Si + 25KL-S) or methacrylated lignin (35Si + 25modKL-S) resulted

in lower rigidity (namely, decrease in maximum strain) and lower maximum stress. Methacrylated lignin was associated with both a higher rigidity and storage modulus (G') than milled lignin, confirming the efficiency of functionalization in grafting the macromolecules of the elastomeric matrix and immobilizing them. Vulcanization kinetics, evaluated with the optimum curing time (t_{90}) were slowed down in the presence of both lignin and modified lignin, meaning that lignin interacts and affects the sulfur vulcanization process.

By comparison of tensile tests of compounds containing unmodified lignin and its methacrylated derivative vulcanized with the two different curing systems, different behaviors could be noticed. The mechanical performances of composites reinforced with the two lignins showed little differences when cured with sulfur, meaning that functionalization of the filler had a limited impact on the final properties of the material. Conversely, in the case of peroxide curing, methacrylation of lignin tremendously affected the mechanical performance of the composite. The more or less pronounced effect of methacrylation in the two curing systems could be ascribed to the differences in their vulcanization mechanisms and kinetics. When a zinc activator is used in accelerated sulfur vulcanization, the sole mechanism of cross-link is the abstraction of allylic hydrogen atoms, rather than the addition to C=C double bonds which takes place when zinc is missing. Conversely, peroxide curing can proceed by both abstraction of hydrogen and addition to the double bond of the methacrylic function. The higher reactivity of peroxides to olefinic moieties

accounts for the more marked differences of the final characteristics of compounds filled with unmodified and methacrylated lignin with respect to sulfur-cured composites.⁴⁰

3.2.2. BR/NR Composites Containing Lignin and Silica as Fillers for Tire Sidewall. Tire sidewalls, being the outer surface of the tire, have to protect it from aging, abrasion, and tear. Typically, butadiene rubber (BR) and natural rubber (NR) blends with high concentrations of antidegradants are used.⁴² Model BR/NR compounds were studied in order to develop tire sidewalls, including a mixture of silica and lignin as reinforcing fillers (Figure 4 and Table 5). Lignin-containing compounds were prepared by substituting 75% of the silica included in reference compounds.

As previously done, composites were first produced and characterized with a peroxide curing system given the higher reactivity of methacrylates toward this system. The partial substitution of 30 phr of silica with 40 phr of lignin (10Si + 50KL-P and 10Si + 50modKL-P) resulted in higher rigidity which reflected in weakly lower maximum elongation and moderately inferior stress at break when compared to the reference compound with 40 phr of silica (40Si-P). The introduction of lignin was also associated with a slight increment in hysteresis and a decrement in modulus. The use of methacrylated lignin allowed for the decrease in hysteresis, reaching even lower values than reference compound 40Si-P. Moreover, functionalization was accompanied with high compatibilization of the filler with the matrix, as shown by the low value of M_L . 10Si + 50modKL-P also presented a $\sigma_{300\%}/\sigma_{100\%}$ ratio higher than the other two compounds, proving a better dispersion of the filler inside the polymeric matrix and the covalent binding of lignin with rubber during vulcanization.

Sulfur-vulcanized BR/NR composites were then studied to better mimic technologically relevant formulations. These compounds were vulcanized with a system poor in accelerator and rich in sulfur, resulting in long polysulfide bridges. These bridges are essential for withstanding the intense deformation experienced by tire sidewalls during operation, including abrasions and tears.⁴³ Sulfur (S8) is known to be poorly soluble in dienic polymers and migrate toward the surface of the composite. To address these solubility challenges, the vulcanizing agent used here was oil-extended sulfur capable of releasing S8 during vulcanization. The partial substitution of silica with lignin (10Si + 50KL-S and 10Si + 50modKL-S) resulted in stiffer compounds, implying a lower maximum elongation for the lignin-containing compounds. Maximum stress was also reduced when substituting silica, but the usage of methacrylated lignin showed an increase in the $\sigma_{300\%}/\sigma_{100\%}$ ratio meaning a good filler dispersion inside the matrix and an improvement both in terms of storage modulus and hysteresis when compared to lignin. Vulcanization of 10Si + 50modKL-S was faster compared to the other compounds and was attributed to the presence of methacrylic acid residues from the modification process as detected by ³¹P NMR, which presumably acted as a coaccelerator.

4. CONCLUSIONS

An innovative mechanochemical procedure was set up for the chemical modification of lignin, which could be easily implemented in current industrial processes for the preparation of highly loaded natural rubber predispersions for the preparation of rubber compounds. Mechanochemistry allowed running reactions in the solid state, avoiding organic solvents,

limiting workup procedures, and reducing wastes with respect to wet chemistry syntheses. Aliphatic alcohols and phenols in lignin were esterified in the presence of a base as the activator and enol ester as the acyl donor. The study of the role of the activator evidenced the need for an alkaline compound to trigger the desired functionalization. In the tested experimental conditions, a hydroxide or carbonate of alkali metals was required to deprotonate acidic hydroxyl groups in lignin. The employment of enol esters instead of more conventional acyl donors, i.e., anhydrides and acyl chlorides, was associated to a higher atom efficiency and the avoidance of halogenated reagents. The release of an enol, which easily tautomerized to the corresponding ketoform, constituted the driving force for the formation of the desired ester and rendered the reaction irreversible, allowing for the functionalization of targeted groups, reaching 35% conversion. The mechanochemical treatment related to this procedure was not associated with any significant degradation of the starting material into lower molecular weight fragments. These evidence demonstrated the applicability of this innovative synthetic procedure to lignins with different botanical sources and isolation processes, without significantly compromising their integrity. The material was produced on a relatively large scale (ca. 5 g) allowing the production of elastomeric compounds comprising lignin as a filler in association with silica.

The mechanical performances of industrial SBR/NR and BR/NR tire compounds were investigated. In all compounds, dynamic mechanical tests evidenced that methacrylation ensured an enhanced compatibilization and hence dispersion of lignin inside the elastomeric matrix with respect to unmodified lignin. Methacrylation of lignin was also associated with increased stiffness with respect to composites with unmodified lignin. These phenomena were connected to a restriction in the polymer chain dynamics of the rubber layers in direct contact with the filler. These observations confirmed that methacrylated lignin was covalently bound to rubber molecules during vulcanization. In the case of peroxide-cured composites, functionalized lignin, when associated with silica, was accompanied by higher storage modulus and lower hysteresis values than lignin, with the latter property reaching similar values as reference compounds. Sulfur-vulcanized compounds with methacrylated lignin were characterized with a higher storage modulus than unmodified lignin, however not reaching the same tensile properties as composites solely reinforced by silica. Intriguingly, the use of methacrylated lignin was accompanied by a lower hysteresis if compared to reference compound filled with silica, paving the way for the design of fuel-efficient tires.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c05036>.

Detailed description and data on the following topics: additional characterization methods, procedure for the preparation of model rubber compounds, development of the mechanochemical procedure, and additional characterization data of lignins and rubber compounds (PDF)

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Notes

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