Surface Modification of Lignosulfonates for Reinforcement of Styrene–Butadiene Rubber Compounds

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ABSTRACT: In this study, surface modification of lignosulfonates (LSs) was investigated for potential reinforcement of styrene–butadiene rubber compounds. Lignins are naturally occurring amorphous, highly branched polymers consisting of aromatic and aliphatic segments with polar functional groups such as hydroxyl, methoxy, carbonyl, and carboxyl. The polarity and hydrophilic nature render lignin incompatible with nonpolar rubber materials. In this study, cyclohexylamine (CA) modification of LS was evaluated for enhancement of compatibility with rubber via proton transfer and hydrogen bonding interactions. X-ray photoelectron spectroscopy data confirm attachment of CA onto the surface of LS. The cure and scorch times of rubber compounds were shortened, and the crosslink density enhanced with an increase of the amount of CA in modified LS. The tensile strength at break increased by almost 45%; the 100% modulus and elongation at break also showed significant improvements. The values of storage modulus and loss tangent increased by 13% and 18%, respectively. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40123.

INTRODUCTION

Lignin is a naturally occurring three-dimensional polymer consisting of phenyl propane units interconnected by a variety of carbon–carbon or ether-like carbon–oxygen–carbon bonds.[1] Lignin is present in the wood cell walls along with cellulose and hemicellulose and is considered the second most abundant organic material available on earth behind cellulose.[2,3] It imparts rigidity to the cell walls in plants and is also responsible for their impact, bending, and compressive deformation.[4] Lignins are polar hydrophilic molecules with surface energies ranging from 53 to 56 mJ/m^2.[5] The polar component of the surface energy varies only slightly with the source of lignocellulosic materials or with the delignification process adopted for separation of lignin.[5] For example, the sulfite pulping delignification process introduces more polar sulfonate groups into the lignin molecules.[6] A representative structure of calcium salt of lignosulfonate (LS) is shown in Figure 1 (redrawn from Ref. 7). The abundance of polar functional groups on lignin surfaces and the prospect of their chemical modification by various means make lignins attractive as reinforcing fillers for consideration in plastics and rubber industry. Other positive factors favoring extensive research work on lignin as reinforcing fillers in plastic and rubber composites are its abundance, cost competitiveness, and biodegradability.[8,9]

A number of studies exist on lignin-based rubber compounds in which the focus has been on reinforcement, dynamic mechanical properties, and rolling resistance.[10–16] The first study on reinforcement of rubber by introduction of lignin dates back to Dawson in 1949.[10] Nevertheless, a significant portion of the work on lignin in conjunction with rubber reinforcement reports very little to no reinforcement of mechanical properties. Kumaran et al.[17] showed that lignin masks certain crosslinking sites in natural rubber (NR) and causes reduction of crosslink density. This leads to lowering of strain-induced crystallization, tensile strength, and hardness. Alexy et al.[12] also reported longer curing times and lower crosslink density with very little increase in tensile strength on addition of LSs to styrene–butadiene rubber (SBR). Poor reinforcement originates from low value of elasticity owing to inefficient vulcanization. Because of its acidity and polar nature, lignin is known to block the vulcanization sites of the polymer chains and to interact with the molecules of curing agents such as zinc oxide, stearic acid, and amide-based curing agents.[11,14,18] The incompatibility of polar lignin with nonpolar rubber matrix also leads to inefficient load transfer at the polymer–particle interfaces. These factors have so far deterred widespread usage of lignin in compounds of commercial thermoplastics and elastomers. An additional factor, not considered in literature but utterly important, is the size of lignin particles.

This study addresses the issues associated with polarity of lignin and demonstrates how surface modification of lignin can produce compatibility with nonpolar rubber and yields reinforcement. Setua et al.[19] modified lignin with benzoyl peroxide and
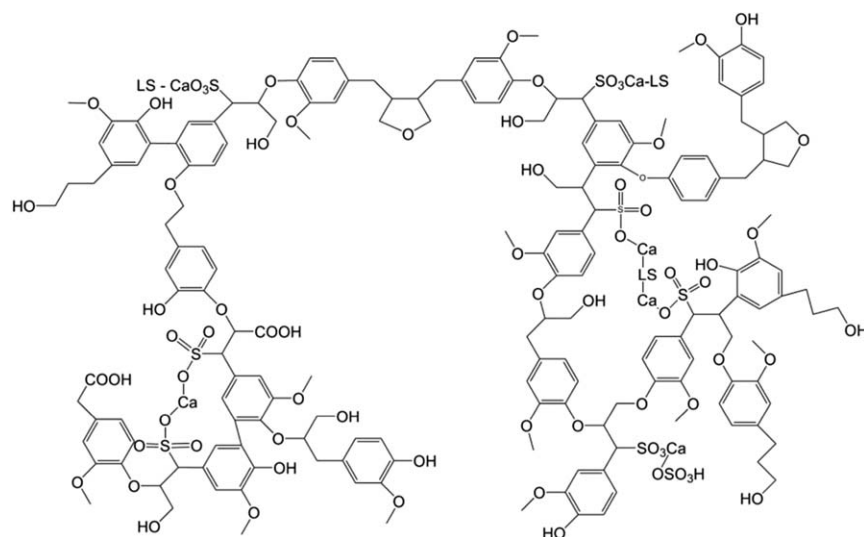
Figure 1. Representative structure of calcium lignosulfonate.

showed that an increase in polarity of lignin produced superior oil and fuel resistance in comparison with nitrile rubber compounds filled with carbon black. In this case, the new functional groups on lignin improved interactions with polar nitrile rubber.

It is apparent that benzoyl peroxide modification is not appropriate for development of compounds of nonpolar rubbers such as NR, synthetic isoprene rubber, and SBR. In this context, Benko et al.[20] functionalized lignin by esterification or silylation and obtained higher mechanical properties and improved rolling resistance in compounds of modified lignin, nonpolar rubber, and carbon black. It appears that the functionalization reactions were tedious and involved organic solvents and catalysts. The study, however, did not present insight on how esterification or silylation of lignin improved its interactions with rubber.

In this work, an easy and environmentally benign process was adopted for lignin modification. LS was modified in water by using cyclohexylamine (CA), a weak base. LS contains the same fundamental lignin structures with the sulfonate groups attached to the backbone. These sulfonate groups assist in water solubility. As lignin surface in LS is acidic,[7,19] the polarity of lignin surface can be suppressed via acid–base reactions with CA. In addition, lignin–CA interactions can also occur via hydrogen bonding; materials with acidic surfaces are known to form strong hydrogen bonds with basic materials as has been reported for silica.[21] These interactions increase the C—C bond concentration on the surfaces of LS particles and can produce compatibility with nonpolar rubber molecules. Liu et al.[22] used CA to modify the surfaces of silica particles. They showed that CA-modified silica improves dispersion and increases compatibility with rubber matrix.

EXPERIMENTAL

Materials
Lignin used in this study was a calcium lignosulfonate D618 obtained from Borregaard Lignotech. This grade of LS is a light yellowish brown powder and is soluble in water. N330 grade of carbon black manufactured by Sid Richardson (Fort Worth,

TX) was used. SBR used in this study was obtained from Goodyear Tire and Rubber Company in the form of grade SLF18B10. The rubber had a bound styrene content of 18.5% by weight. The CA used for modification of LS was obtained from Sigma-Aldrich, grade Reagentplus®. Several other ingredients were used: zinc oxide in powder form and stearic acid in bead form, sulfur curing agent (Rubber Maker), and N-cyclohexylbenzo-thiazole-2-sulfenamide (CBS) accelerator, all obtained from Akrochem Corporation (Akron, OH).

Modification of Calcium Lignosulfonate
LS (20 g) was stirred in 100 mL deionized water. The solubility of LS in water at room temperature was found to be ~ 240 mg/mL. A solution of CA in water was added to the solution of LS and stirred for 1 h. Aqueous solutions of CA at three concentrations were used to modify the LS particles: 0.05, 0.1, and 0.25 g of CA per gram of LS. Water from the solution was then evaporated by heating on a hot plate with continuous stirring. The product was dried in vacuum oven overnight at 80°C to remove residual water. Excess CA was removed from modified LS particles by stirring in toluene for 2 days. The suspension in toluene was filtered, and the particles were dried in vacuum oven overnight at 80°C.

Compounding
The compounds of modified LS particles and rubber were prepared in two steps. In the first step, rubber was mixed with zinc oxide, stearic acid, and the fillers in a Brabender Plasticorder internal mixer (80 cm³ internal volume) at a rotor speed of 65 rpm and a fill factor of 0.7 at 80°C. The rubber was masticated for 60 s and then mixed with the rest of the ingredients for 5 min. In the second step, the compounds obtained from Step 1 were mixed with sulfur and CBS accelerator using a two-roll mill for 5–7 min at a speed of 15 rpm at a roll temperature of 40°C. The following recipe was used based on 100 parts by weight of SBR: stearic acid (1 phr), zinc oxide (3 phr), sulfur (1.75 phr), CBS (1 phr), and modified LS particles (30 phr). SBR compound without LS particles was also prepared as a control material.

The rubber compounds were cured in a compression molding press at 160°C. The time needed to reach 95% of the maximum torque (t_{95}) was taken as the optimum curing time. A sheet mold with dimensions 150 mm × 150 mm and a thickness of 1.5 mm was used for curing. The cured materials were used for evaluation of reinforcement behavior and for characterization of filler dispersion.

Characterization

X-ray Photoelectron Spectroscopy. The changes in functional group types and contents on LS particle surfaces due to modification by CA were examined by X-ray photoelectron spectroscopy (XPS) method. Four different powder samples were used for XPS analysis: unmodified LS, LS-0.05CA, LS-0.1CA, and LS-0.25CA. The powder sample LS-0.25CA represents modified LS particles with 0.25 g CA per gram of LS particles used in modification. The XPS spectra were taken using a PHI 5000 VersaProbe II Scanning XPS microprobe™ under high vacuum conditions with a pressure of 10^{-7} Pa and an Al Kα radiation source. The survey scans were used to evaluate the percentage of different atoms present on the surface of LS particles. The high-resolution scans of C1s were used to determine the levels of C—C bonds present on the surfaces before and after modification with CA.

Thermogravimetric Analysis. TA Instrument's Q500 thermogravimetric analyzer was used to determine the amount of bound CA on the LS particles. The modified lignin powder after preparation as described was dried in vacuum oven for 48 h before subjecting to thermogravimetric analysis (TGA). The powders were heated from room temperature to 400°C using a temperature ramp rate of 20°C/min. The TGA analysis was carried out in nitrogen environment.

Cure Analysis. The cure characteristics of the compounds were evaluated using ∼ 5 g rubber compounds in a Moving Die Rheometer (MDR 2000) at a temperature of 160°C, a frequency of 1.67 Hz, and a strain of 7%. The plots of torque versus time were recorded, and the curing parameters such as scorch time and cure time (t_{95}) were calculated.

Mechanical Property Measurements. Dumbbell-shaped specimens (ASTM D-412, Type C) for tensile tests were punched out of cured sheets. These tests were carried out at room temperature on an Instron® 5567 tensile tester at a crosshead speed of 500 mm/min. A minimum of five specimens were tested per sample.

Crosslink Density. The crosslink density of cured rubber compounds was determined from swelling test. About 0.5 g vulcanizate was submerged in toluene for 72 h, and the weight of the swollen sample was measured. Afterward, the sample was dried in a vacuum oven for 24 h at 60°C, and its weight was measured again. The crosslink density (ν_e) of the vulcanizates was calculated in kmol/m^3 from the Flory–Rehner equation[23] given below:

$$\nu_e = -\frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_1\left(V_r^{\frac{1}{3}} - \frac{1}{2}V_r\right)}. \tag{1}$$

In eq. (1), V_1 is the molar volume of toluene (106.28 cm^3/mol), χ is the rubber–solvent interaction parameter, for SBR–toluene system, $\chi = 0.446$,[24] and V_r is the rubber volume fraction in swollen gel given in eq. (2).

$$V_r = \frac{\frac{W_{\mathrm{dry}}}{\rho}}{\frac{W_{\mathrm{dry}}}{\rho} + \frac{W_{\mathrm{solvent}}}{\rho_{\mathrm{solvent}}}}. \tag{2}$$

In eq. (2), W_{dry} is the dry weight of rubber, ρ is the density of rubber, W_{solvent} is the weight of solvent in the swollen gel, and ρ_{solvent} is the density of the solvent. The Kraus correction factor[25] for calcium lignosulfonate is unknown and was not applied in this work. Consequently, the data reported here are termed apparent crosslink density.

Dynamic Mechanical Analysis. The dynamic mechanical properties of cured rubber compounds were determined using a TA Q200 instrument and sample of dimension 10 mm × 4.02 mm × 1.5 mm cut from cured sheets. Strain sweep tests were performed at 60°C and 1 Hz frequency. The values of storage modulus (E') and loss tangent (tan δ) were recorded at 0.1% strain and 10% strain, respectively. The values of tan δ were measured specifically at 60°C. The damping factor at 60°C gives a direct indication of the viscous dissipation and rolling resistance in rubber compounds.[22,26]

Scanning Electron Microscopy. A high-resolution scanning electron microscope (SEM; JEOL JSM5310) was used to examine the fracture surface of rubber vulcanizates filled with unmodified and modified LS molecules. SEM images were also used to obtain particle sizes. The diameter of 40 particles was measured using Image J software for a given specimen. The vulcanizates were cold fractured in liquid nitrogen followed by sputter coating for 1.5 min by a layer of silver under argon gas atmosphere before taking images by SEM. The operating voltage of SEM was 5 kV.

RESULTS AND DISCUSSIONS

Modifications in Lignosulfonates

Surface Functional Groups Using XPS Spectra. The binding of CA onto the surface of LS was examined using XPS. The survey spectrum was used to identify the relative amounts of carbon and oxygen atoms present on the surface of LS particles. The relative amounts of carbon-based functional groups on the surface were identified from deconvolution of C1s peaks observed in the high-resolution spectra. Figure 2 shows the survey spectra and the high-resolution C1s spectra for unmodified and modified LS. The relative ratio of carbon and oxygen atoms present and the relative area percentage of C—C bonds present on the LS surface before and after modification with CA are listed in Table I.

Figure 2(a) shows the peaks due to carbon, oxygen, sulfur, and calcium, indicating that these detectable atoms were present on the surface of LS particles as is expected from its structure presented in Figure 1. Carbon and oxygen atoms constitute the bulk of surface composition with 60% and 35%, respectively, of the total atoms present on the particle surface (see Table I). In Figure 2(b), the C1s high-resolution spectrum for LS is deconvoluted into two main peaks corresponding to C—C bonds (284. 7 eV) and C—O bonds and C—S bonds (286.3 and 286.2 eV). The peaks corresponding to C—O bonds and C—S bonds
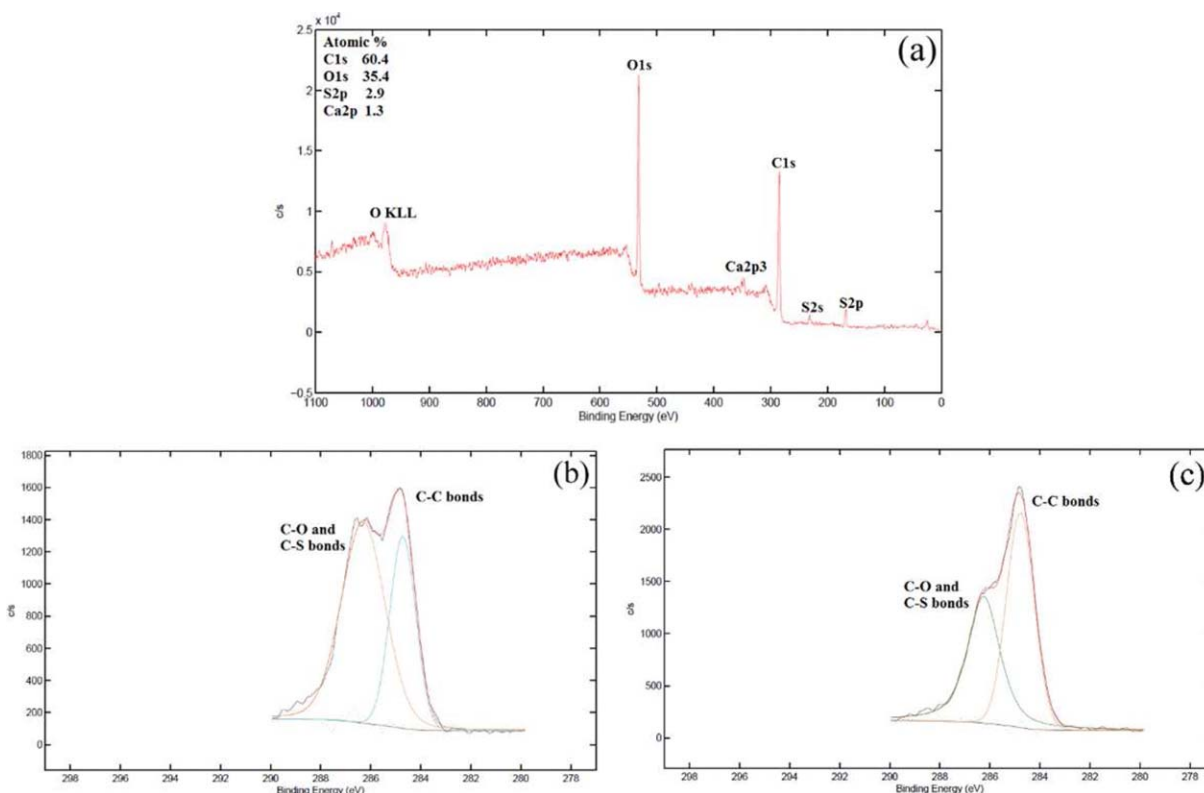
Figure 2. Representative XPS curves: (a) survey spectra and C1s high-resolution spectra for (b) unmodified LS and (c) LS modified with 0.1 g of CA per gram of LS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

overlap with each other, thus the peak in Figure 2(b) shows the total contribution of these two functional groups.[27] Figure 2(c) presents the C1s high-resolution spectrum of LS particles modified with 0.1 g of CA per gram of LS. The increase in peak area corresponding to the C—C bonds is clearly evident. The area under the curve of C—C bonds is listed in Table I. The presence of CA in modified LS should change the relative amounts of carbon and oxygen atoms due to high carbon content in CA molecules.

The C:O ratio and the % area of C—C bonds on the surfaces of LS particles increase with an increase of CA concentration in the modification step (Table I). This is not surprising as CA binds onto the LS particle surfaces. Consequently, the number of carbon atoms on the surface increases relative to the number of oxygen atoms. Similar trend is observed for % area of C—C bonds calculated from the area under the curve of the C—C bonds peak and the total area under the curve of the C1s spectra. The quantity of C—N bonds could not be evaluated using XPS because of the limited sensitivity of XPS toward nitrogen and smaller amounts of C—N bonds in comparison with C—C bonds on the surfaces of modified LS particles. The data presented in Table I give a clear indication of the presence of CA on the surfaces of modified LS particles. An immediate consequence of the presence of CA on modified LS particle surface is reduction of polarity.

Thermogravimetric Analysis. The amount of CA bound to LS particle surfaces was determined from TGA data. The difference

in weight loss between modified LS particles and unmodified LS particles followed up to 250°C yielded information on the amount of bound CA. It was perceived that a thermal scan up to 250°C would allow removal of all bound CA. Note in this context that bound CA would need more thermal energy than needed for boiling of CA at ∼ 130°C. The weight loss at or below 250°C would also include bound or physically adsorbed water from the LS particle surfaces. We assumed that the amount of water adsorbed was the same in modified and unmodified specimens. Figure 3(a) shows the weight percent of LS and modified LS as function of temperature obtained from TGA. The amount of CA bound to the LS particle surfaces as function of concentration of CA in aqueous solution used in the modification step is presented in Figure 3(b).

It is seen in Figure 3(b) that the amount of CA bound onto the LS particle surfaces increases with an increase of the

Table I. Ratio of Carbon and Oxygen Atoms and the % of Area Under C—C Bond Peak in XPS Spectra Obtained for Unmodified and Modified LS

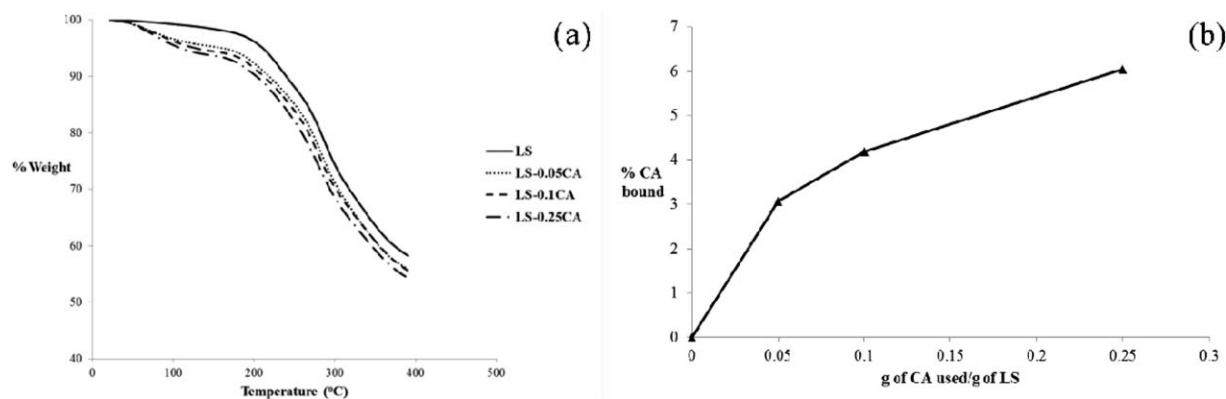| Compounds	C:O ratio	% Area of C—C bonds
Unmodified LS	1.7	34.4
LS-0.05CA	1.9	43.2
LS-0.1CA	2.2	53.5
LS-0.25 CA	3	67

Figure 3. (a) TGA curves for unmodified LS and LS modified with CA, and (b) weight percent of CA bound onto the surfaces of LS particles.

concentration of CA used in the modification process. If all CA molecules taken in the solution, for example, 0.05 g CA per g of LS had adsorbed onto the LS particle surfaces, TGA analysis should yield $\sim$ 4.75 wt % CA in modified LS particles. Instead, only 3 wt % CA remained on LS particle surfaces. The amount of CA adsorbed onto LS particles increases to around 6 wt % when compared with a possible maximum of $\sim$ 20 wt % CA for CA concentration of 0.25 g per g of LS. It is apparent from Figure 3 that the amount of bound CA would reach a plateau at even higher concentration. However, concentration higher than 0.25 g CA per g of LS was not tried.

Particle Surface Morphology. The morphology of particles before and after modification with CA was examined by SEM. Representative SEM images are presented in Figure 4. Figure 4(a) reveals that unmodified LS powder consists of random shaped particles with some particles showing size in excess of 100 μm. A significant reduction in LS particle size occurred due to modification as seen in Figure 4(b). The sizes of 40 representative particles gleaned from SEM images using ImageJ software were analyzed for particle size distribution. These data are presented in Figure 5.

The reduction in particle size on modification can be attributed to reduction in polarity of the particles. The particles underwent much less agglomeration during particle isolation when compared with unmodified LS particles. The lignin molecules after modification with CA could not form large sized agglomerates because of their lowered polarity.

As seen in Figure 5, the size distribution shifts to smaller particle sizes with an increase in CA concentration from 0.05 to 0.1 g/g of LS. This is intuitive as higher concentration of CA leads to lower polarity, which in turn reduces the agglomeration tendencies of LS particles. However, further increase of the concentration of CA shifts the size distribution to slightly higher particle sizes. Although this was not investigated further, one can hypothesize that excess amine groups on the surfaces of LS particles at 0.25 g of CA per g of LS promote agglomeration via hydrogen bonding.

Cure Characteristics

The rubber compounds were cured at 160°C using MDR. Cure parameters such as scorch time, cure time, and crosslink density of unmodified and modified LS filled SBR are summarized in Table II. It is apparent from the data presented in Table II that the scorch time and the cure time of rubber compounds with unmodified LS are much higher when compared with those of unfilled rubber. Such an increase in scorch time and cure time indicates inefficient vulcanization of rubber compounds in the presence of unmodified LS. The polar fillers, such as LS and silica, are known to interact strongly with the curing agents and to adsorb the molecules of accelerator and other curing agents onto their surfaces. In addition, lignin can absorb moisture because of its hydrophilic nature, which in turn can adversely affect the curing behavior of rubber compounds. These effects hindered the curing process as was reported earlier in the
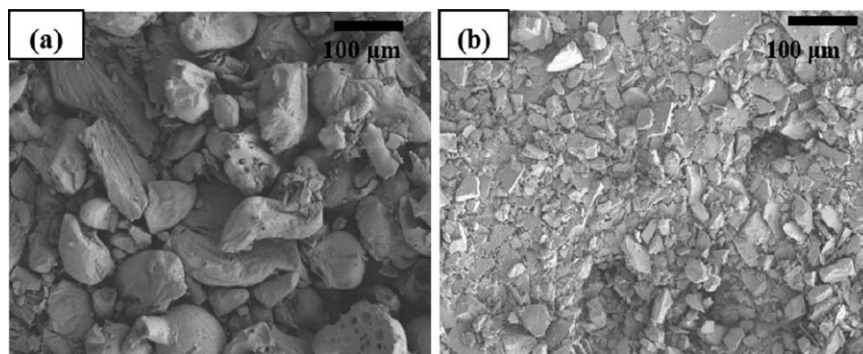

Figure 4. SEM morphology of (a) unmodified LS and (b) modified LS with 0.1 g of CA per gram of LS in modification step.
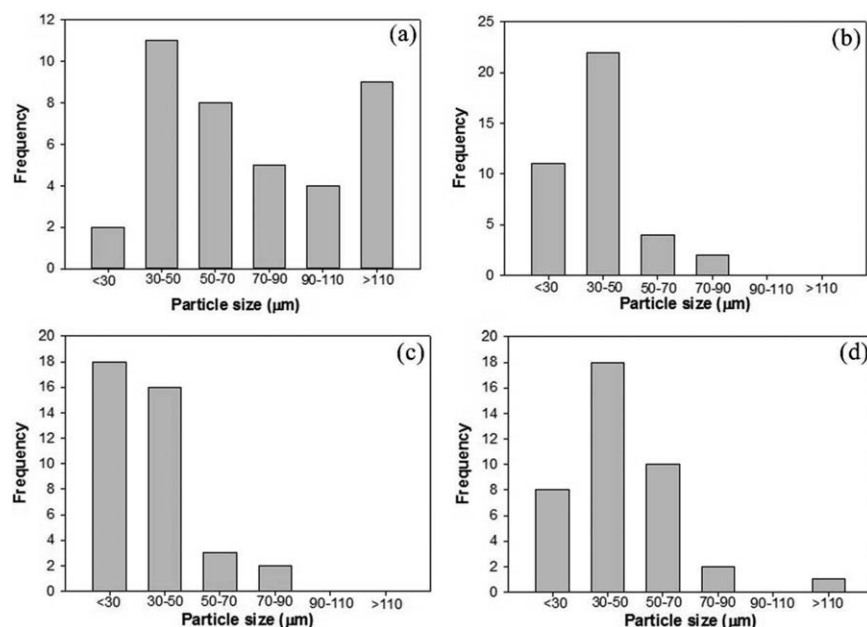
Figure 5. Particle size distribution: (a) unmodified LS and (b–d) modified LS particles: (b) LS-0.05 CA, (c) LS-0.1 CA, and (d) LS-0.25 CA.

context of curing of rubber in the presence of lignin and silica.[11,14,18,21]

It is also evident from the data presented in Table II that the modification of LS with CA significantly reduced the scorch time and the cure time in comparison with unmodified LS. In one case—with 0.25 g CA per gram LS—the cure time is seen to be lower than the unfilled rubber. The crosslink density also increased with an increase of concentration of CA in the modified LS. However, the rate of increase of crosslink density slows down considerably for CA concentration above 0.1 g of CA per gram of LS. In addition, the values of crosslink density obtained with modified LS are lower than that of unfilled SBR (Table II). Kumaran and De[14] attributed lower and slower crosslinking to masking of cure sites of rubber by lignin particles. In this work, the modified LS particles quite possibly lost some of its masking abilities due to coverage by CA molecules. One can attain additional crosslinking, higher crosslink density, and higher mechanical properties by aging the samples for extended periods of time at above the room temperature. However, this was not investigated in this work.

In addition, the presence of CA in modified LS contributes two effects. First, the CA molecules cover the surfaces of LS particles and reduce their polarity. As a consequence, the modified LS particles can no longer adsorb as many curing agent molecules. Second, amine compounds are known to accelerate the curing process and to produce higher degree of crosslinking.[28,29]

Tensile Properties of Cured Rubber Compounds
The effect of CA modification of LS on tensile strength at break, strain at break, and 100% modulus are presented in Figure 6. The tensile strength at break increases significantly on modification of LS with CA, reaching a 45% increase in strength for compound containing LS particles treated with 0.1 g of CA per

gram of LS. In comparison, the tensile strength dropped slightly for compound containing LS particles treated with 0.25 g of CA per gram of LS. Note that tensile strength is a failure property and is strongly affected by the particle size.[30] The trend in tensile strength values correlates well with the particle size distribution data presented in Figure 5. Recall that particle size distribution moved slightly to higher sizes for LS particles treated with CA of concentration 0.25 g/g of LS. This increase in particle size is quite possibly responsible for lower values of tensile strength and elongation at the break for compounds containing LS particles treated with 0.25 g CA per g of LS.

The strain at break data follow a trend similar to the tensile stress. The values of strain at break increases gradually to greater than 400% with an increase of CA concentration to 0.1 g of CA per gram of LS and then drops to about 300% at CA concentration of 0.25 g of CA per gram of LS, which is slightly lower than that of the compound with unmodified LS [Figure 6(b)]. It is learned from the data in Table II that crosslink density increased with an increase of CA concentration in LS modification step. Therefore, one would expect a reduction in elongation at break[21] at higher concentration of CA, as the

Table II. Cure Parameters for SBR Compounds Filled with Unmodified LS and Modified LS Particles

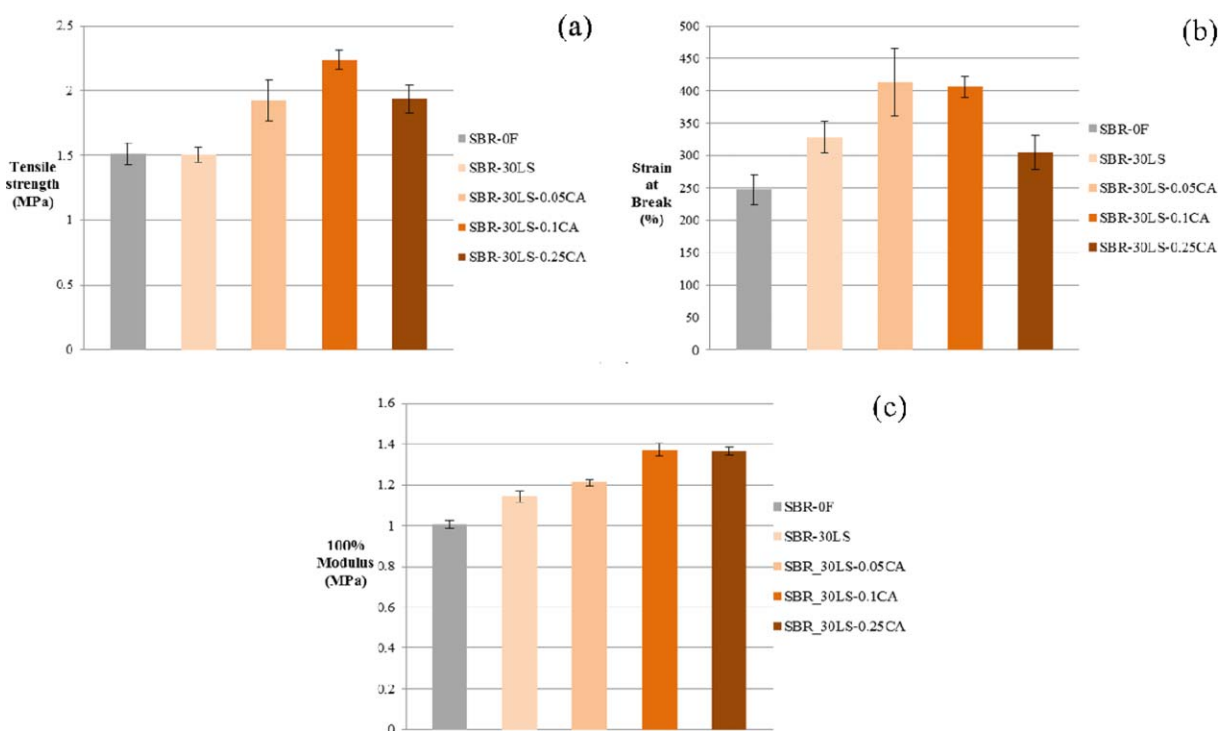| Compound	Scorch time (min)	Cure time (min)	$(XLD)_{app}$ (kmol/m^3)
SBR-0F	5	12	0.08
SBR-30LS	10	23	0.04
SBR-30LS-0.05 CA	9	20	0.046
SBR-30LS-0.1 CA	7	14	0.06
SBR-30LS-0.25 CA	5	10	0.07

Figure 6. Effect of increasing CA concentration on (a) tensile strength at break, (b) strain at break, and (c) 100% modulus of LS-filled SBR vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

material cannot elongate much due to increased stiffness in systems with higher crosslink density. The anomalous trend in Figure 6(b) can be rationalized based on improved compatibility between rubber and modified LS particles, which leads to improved stress transfer between the filler particles and the rubber domains, yielding higher strain at break. At higher CA concentrations, for example, at 0.25 g of CA per gram of LS, the higher crosslink density and stiffer chains outweigh the effect of stress transfer and produce lower strain at break. The increase

of chain stiffness due to higher values of crosslink density results in an increase of 100% modulus [Figure 6(c)]. The 100% modulus also shows an increase with an increase of CA concentration in modification of LS particles.

Morphology of Rubber Compounds

The effect of CA modification on morphology of cured compounds was studied using SEM images. The SEM images of representative fracture surfaces of cured compounds with unmodified LS and LS modified with 0.1 g of CA per gram of
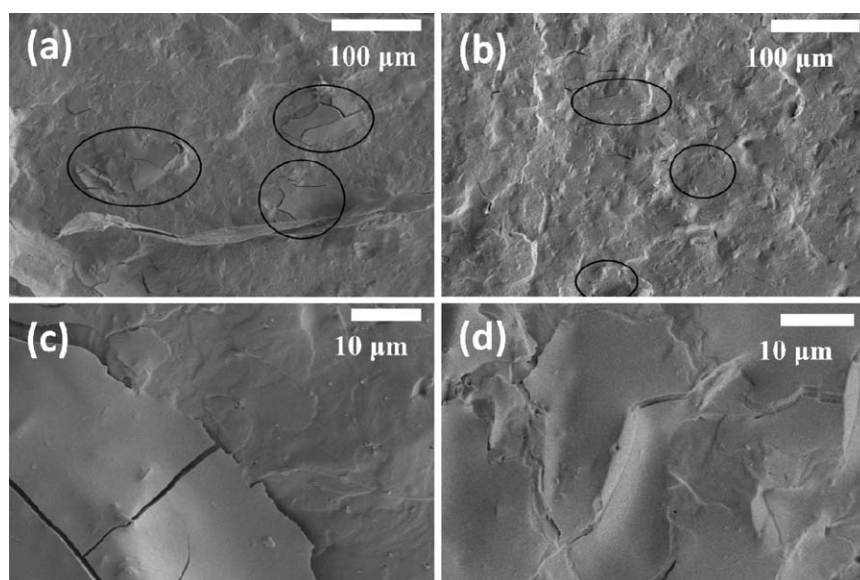

Figure 7. SEM images of fractured surfaces of (a–c) SBR-30LS and (b–d) SBR-30LS-0.1CA compounds.

Table III. Effect of CA Modification on the Dynamic Properties of SBR Vulcanizates

S.No.	Compound	E' at 0.1% strain (MPa)	Tan δ at 10% strain
1	Unfilled SBR	2.9	0.05
2	SBR-30LS	3.7	0.08
3	SBR-30LS-0.05 CA	3.9	0.08
4	SBR-30LS-0.1 CA	4.1	0.07
5	SBR-30LS-0.25 CA	4.2	0.065

LS are presented in Figure 7. It is apparent that unmodified LS particles show cracks in Figure 7(a,c), which appeared during fracture of samples in liquid nitrogen. On the other hand, the modified LS particles do not show cracks as they are much softer and of smaller size due to lower levels of agglomeration.

It is also apparent from SEM images in Figure 7(c,d) that the interfaces of LS particles with rubber appear much smoother for modified LS particles. The reduced polarity of modified LS particles in this case helped to improve the interactions with rubber phase by creating a smooth interface across which stress transfer can occur more efficiently.

Dynamic Mechanical Analysis

The dynamic mechanical analysis data obtained from strain sweep experiments at 60°C are listed in Table III. The storage modulus at 0.1% strain (E') and tan δ at higher strain level of 10% are reported. As seen from these data, the storage modulus increases with increasing concentration of CA in modified LS particles and correlates well with the crosslink density data presented in Table II. The reduction in polarity due to modification of LS particles also deterred the interactions between LS particles and the cure components. This in turn helps to achieve higher values of crosslink density and higher values of storage modulus for a given amount of curing agent.

The higher value of crosslink density in the case of modified LS also plays an important role in reduction of the value of tan δ. An increase in crosslink density value indicates higher elasticity of the vulcanizates and higher values of storage modulus as discussed earlier. This in turn lowers the value of loss tangent. However, tan δ is also dependent on the rubber–filler and filler–filler interactions. As modified LS particles interact better with rubber phase and do not form large size agglomerates due to lower polarity, the filler–filler networking in rubber compound was quite possibly reduced. This, in turn, caused a reduction of the value of tan δ.

CONCLUSIONS

A method was developed to modify the surface of lignin to lower its polarity and to increase the concentration of C—C bonds on its surface so that modified LS particles become more compatible with nonpolar rubber matrix such as SBR. The reduced polarity also helped to lower the particle size of modified LS particles during isolation from a solution in water. The modification of LS with CA alleviated the concerns of inefficient curing encountered with unmodified LS particles. As a

consequence, the cure characteristics improved, and higher crosslink density was achieved for compounds prepared with modified LS particles. The values of tensile strength and strain at break also improved as a result of better stress transfer across the interface of rubber and LS particles. The values of storage modulus increased, and tan δ decreased with the increase of CA content on modified LS particle surfaces. The method of modification presented in this work has strong promise in the reduction of rolling resistance of filled rubber compounds.

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