Research article

Strategy for reducing rubber wear emissions: The prospect of using calcium lignosulfonate

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Abstract. This study explores the transformative potential of calcium lignosulfonate (CaL) as a sustainable additive in rubber composites based on nitrile rubber (NBR) and styrene-butadiene rubber (SBR). Through comprehensive mechanical testing, fatigue crack growth (*FCG*) analysis, and scanning electron microscopy (SEM), we evaluated the tensile strength, elongation at break, surface morphology, and crack growth behavior of these innovative composites. By incorporating CaL into carbon black-reinforced rubber compounds (RUB/CB) based on nitrile rubber and styrene-butadiene rubber, we achieved good dispersion of both components as well as satisfactory morphology, resulting in tensile strengths of 16.3 and 12.7 MPa, respectively. While the CB/CaL hybrid did not significantly influence the intrinsic strength of the rubber samples, the ultimate strength of these compounds increased drastically – over five-fold compared to RUB/CB – indicating great potential for real-life applications. This study underscores the promise of lignin-based additives in the development of eco-friendly, high-performance rubber materials.

Keywords: fatigue crack growth, failure analysis, polymer composites, elastomer, sustainable materials, environmental impact

1. Introduction

The development of sustainable rubber compounds is becoming increasingly popular due to the environmental concerns arising from the widespread use of polymers and the need to transition towards a circular economy. Rubber's unique properties make it irreplaceable in various applications, including tires, seals, conveyor belts, shoe soles, and medical implants. These products are subject to deterioration of rubber properties over time due to different effects and environmental conditions, which are causing molecular changes and can significantly impair rubber properties and, thus, the service life of rubber products. Therefore, to protect rubber products from diverse effects of environmental factors, rubber compounds are composed of various components that serve to both protect the rubber against specific influences and reinforce it. If the rubber is sufficiently protected by having an optimally reinforced structure with suitable reinforcing fillers, it will also be protected against degradation processes such as network failures, crack initiation, propagation, and the subsequent release of rubber particles of various sizes and their emission [1, 2].

Nowadays, the question of the impact of different chemical components of rubber on various aspects

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of the environment is being addressed globally, not only in the context of particle pollution from tire wear. However, tire wear remains the most critical issue, leading to the future degradation of worn rubber particles and release of various chemical constituents, including fillers and additives, into the environment [3–5]. The chemical analysis of ground tire revealed that in addition to carbon, a significant amount of silane (up to 8%), sulfur, zinc and iron (up to 1% each) can be found. When tire and road wear particles were analyzed, these amounts proved to be even higher [6]. Various ecotoxicological investigations have confirmed that some of these released chemicals or their transformation products can induce various biological responses in diverse organisms, e.g. [7–9]. For example, the widely-used antiozonant N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), which reacts with ozone to produce toxic 6PPD quinone, can cause acute and chronic toxicity to aquatic wildlife [7, 8, 10, 11]. Therefore, the presence of rubber chemicals in the environment and biota, their degradation, and their potential toxicity are major concerns. The optimal global solution to this problem is to replace environmentally and organism-harming chemical components with naturalbased, completely environmentally friendly materials [12, 13]. One such raw material of natural origin could be lignin. The term 'lignin' encompasses a diverse class of lignins, summarizing their chemical characterization and structural elements. The lignin macromolecule is composed of cross-linked phenylpropane structural units, namely *p*-hydroxyphenyl, guaiacyl, and syringyl, derived from lignin precursors para-coumaryl, coniferyl, and sinapyl alcohols. Lignin is a thermoplastic amorphous polymer with a glass transition temperature (T_g) that ranges from 90 to 170 °C [14]. Its $T_{\rm g}$ depends on various factors such as the method of isolation, absorbed water, molar mass (M_h) , and thermal history. The primary source of lignin is the pulp and paper industry, where it is extracted from black liquor or from lignocellulosic biorefineries. The use of technical lignin in value-added applications is limited due to several factors: a non-uniform chemical structure and unique chemical reactivity of each batch, the presence of various organic and inorganic impurities and the differences in chemical and physical characteristics arise from different origins and the use of different separation and purification processes. However, these limitations can be addressed through the

individual evaluation of various lignin types. Lignosulfonates, a subgroup of lignins produced through acid-catalyzed sulfite processes, are of particular interest in this study. This process involves delignificatin of wood using a solution of sulfuric acid and its salts (usually Ca²⁺, Na⁺, Mg²⁺, NH⁴⁺) at high temperatures ranging from 140-170 °C. Sulfite delignification is standardly characterized by a pH value which is usually in the range of pH 1-5. During sulfite pulping, hydrolysis and subsequent sulfonation of ether bonds occur to form a water-soluble product with relatively high molecular weight compared to other types of lignin and with a lower concentration of phenolic functional groups [15-21]. However, due to its large particle size and lack of interfacial adhesion with the rubber matrix, lignin, in general, has not been found to significantly reinforce rubber composites [22, 23]. The investigation of composites featuring diverse lignin types and varying lignin concentrations was documented in reference [24]. It was observed that the high molecular weight of lignin leads to agglomeration, with the propensity for agglomeration escalating with higher lignin content. Lignin's incompatibility with several non-polar polymers arises from the presence of polar sites, thereby exhibiting higher compatibility with polymers containing similar polar sites [25]. Therefore, research has been conducted to optimize the processing method to improve the compatibility of lignin with rubber and enable it to exhibit good dispersion [18, 24, 26–30].

In general, to enhance the resistance of rubber to mechanical loads, it is reinforced with fillers, primarily carbon black (CB) [2]. The addition of fillers to rubber generally enhances its properties, including modulus, tensile strength as well as fatigue crack growth (FCG) resistance, which, however, are mainly associated with 'CB reinforcement'. Furthermore, the most significant effect on rubber abrasion in terms of material composition can be attributed to CB in general [31–33]. CB and lignin exhibit different surface activities, but both agglomerate in rubber compounds due to various factors. CB filler-filler interactions are primarily van der Waals interactions. Lignin's molecular complexity enables diverse noncovalent interactions, including H-bonding, $\pi - \pi$, π -cation, electrostatic, hydrophobic, and van der Waals interactions. These interactions facilitate seamless hybridization of lignin with inorganic particles, dictating interphase development in resulting hybrid fillers [15, 23, 34]. Optimizing functional group exposure and configuration is crucial for supramolecular complexation, achievable through lignin type selection, modification, or synthesis approach. Hybridization of lignin with CB offers benefits, utilizing π - π interactions to produce hybrid filler for rubber compounds (RUB) [15]. This overcomes concerns about lignin's large particle size impacting mechanical properties, as lignin coats CB particles, suppressing CB networking and improving dispersion. Although hybrid fillers are common, enhancing interfacial interaction remains an area for improvement [25, 35].

As mentioned above, the degradation of rubber leads to its fracture, an undesirable process that significantly reduces its service life and promotes the emission of rubber components into the environment. Mechanical or chemical degradation typically begins with the occurrence of micro-cracks in the rubber matrix. But how does this mechanism work and how is it possible to achieve increased material resistance to the emission of rubber particles and individual chemical components?

Fatigue refers to the gradual deterioration of the material properties during service life, which in rubber technology indicates the failure resulting from crack initiation and growth [2]. When rubber is exposed to real conditions, surface embrittlement and the formation of surface micro-cracks occur, with the surface of such a crack immediately attacked again by the chemical reactant, thus accelerating the formation and propagation of new cracks. This results in increasing distortion of the rubber matrix both on the surface and deep into the material volume, allowing chemical components to diffuse through the cracks and generating the first rubber particles of very small dimensions. Generally, fatigue failure involves three phases. The first phase is crack nucleation associated with endurance limit or also called intrinsic strength (T_0) , where if the energy input is lower than this value, no cracks can be created. If energy input is above this value, it causes nucleation and propagation of cracks [36, 37]. The so-called Thomas plot shows these effects in Figure 1. With increased mechanical loading, the fatigue crack growth of all previously initiated cracks proceeds over a broad range of tearing energies between the T_0 , and the critical tearing energy or ultimate strength $(T_{\rm C})$ (Figure 1). In this region, the dependence of the fatigue crack growth rate on the tearing energy is linear [38-41].



Figure 1. Schematic representation of crack growth rate in rubber [42].

Fatigue crack growth behavior in this area is mainly influenced by the rubber composition, where in order to increase the resistance to crack propagation, the curve should have the lowest possible slope in low absolute values as it reaches high $T_{\rm C}$ values. Ensuring these properties and increasing resistance to fatigue crack growth will again reduce the emission of chemical components as well as particles into the environment. Additionally, it is necessary to consider the crosslink density of rubber, which is formed during the curing process. Based on previously published studies, it is generally known that the stiffness of rubber increases monotonically with increasing crosslinking density, which results in the fact that although the strength of the material increases, it becomes more brittle and prone to crack initiation and its rapid propagation still at lower deformations [43, 44]. Robertson et al. [42] described the influence of reinforcing fillers, such as carbon black, on the mechanics of fatigue crack growth. The physical adsorption and chemical bonding of parts of the polymer chain to the surface of carbon black particles will affect the mechanics of intrinsic strength T_0 . However, since even the smallest carbon black grades are significantly larger than a polymer network chain between crosslinks, cracks are either forced to bypass these particles or fracture them. In this work, we explore the impact of lignin, specifically in the form of calcium lignosulfonate (CaL), on the initiation and propagation of cracks under mechanical loading. While the influence of particulate fillers on the fracture mechanics of rubber has been studied extensively, to the best of the authors' knowledge, the effect of lignin on fracture mechanics has yet to be thoroughly examined. Given the numerous articles on lignin's use in the rubber industry, this aspect warrants in-depth investigation. Our goal is to demonstrate that lignin is a promising additive that can enhance rubber's resistance to fracture, thereby reducing the emission of chemical components and rubber particles into the environment.

2. Experiment and materials

Nitrile rubber (NBR) (SKN 3345, Sibur International, Moscow, Russia) with a content of acrylonitrile ranging from 31 to 35% was used as a rubber matrix for the first set of prepared compounds and styrenebutadiene rubber (SBR) (Kralex 1502, Synthos Kralupy, Kralupy nad Vltavou, Czech Republic) with a content of styrene of 23.5% was used as a rubber matrix for the second set of prepared compounds. Carbon black (CB) (CONTINEX N330, Continental Carbon Company, Belgium) was used as a reinforcing filler on its own or combined with calcium lignosulfonate (CaL) (Borrement CA120, Borregaard Deutschland GmbH, Germany) as a sustainable component of rubber compounds. The pH of CaL is 4.5 (10% solution) with an average molecular weight of 24000 g·mol⁻¹, 1.57 mmol·g⁻¹ of phenolic hydroxyl groups, and approximately 5% content of calcium [45]. Glycerol (Gly) (≥99%, Sigma-Aldrich, St. Louis, MO, USA) was used to plasticize CaL. The specific selection and content of plasticizer was based on previous research, as well as the content of CB and CaL. For the cross-linking of the rubber compounds, a sulfur vulcanization system containing zinc oxide (Slovzink a.s., Košeca, Slovakia), stearic acid (Setuza, Ústí nad Labem, Czech Republic), *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS) (Duslo a.s., Šal'a, Slovakia) and sulfur (Siarkopol Tarnobrzeg, Poland) was used. The complete formulations of each investigated compound filled with CB, CaL or hybrid CB/CaL with NBR or SBR as a rubber matrix are listed in Table 1. The quantity of additives remained constant throughout the experiment, with CB at 25 phr, CaL at 30 phr, and Gly at 15 phr. The quantity of additives in rubber formulations was meticulously determined based on prior experimental works related to the production of rubber compounds with incorporated CB, CaL, and glycerol in laboratory conditions and are published in [26, 46–48].

Rubber compounds were prepared using a semi-industrial kneading machine Buzuluk (Buzuluk Inc., Komárov, Czech Republic) in two mixing steps at 90 °C and 55 rpm. Rubber was first put into a chamber and plasticated for 1 min, then zinc oxide and stearic acid were added, and after 1 min, CB or CaL were introduced. The mixing process continued for next 3 min. The rubber compounds were taken out from the chamber and additionally homogenized using the two-roll mill. In the second step, sulfur and accelerator were applied, and the mixing process continued for 3 min at 90 °C and 55 rpm. Finally, the rubber compounds were sheeted and cooled down using the two-roll mill (rubber compounds RUB/CB, RUB/CaL). The rubber compounds with applied both CB and CaL were fabricated in the same way, but CB was introduced first, and after 1 min, CaL was applied (rubber compounds RUB/CB/CaL). The mixing process in the first step continued for 2 min. Glycerol was pre-mixed with CaL and added to the kneader chamber, following the same procedure as before. The second step of the mixing process for all rubber compounds was the same, meaning that after adding sulfur and accelerator, subsequent mixing was performed for 3 min at 90 °C and 55 rpm.

The curing characteristics were investigated using an oscillatory rheometer (MDR 2000, Alpha Technologies, Akron, OH, USA) according to the STN 62 1416 at a temperature of 170 °C. A standard sheet of the dimensions 150×150 mm and 2 mm thick were

Ingredients	Amount [phr]						
	RUB	RUB/CB	RUB/CaL	RUB/CaL/Gly	RUB/CB/CaL	RUB/CB/CaL/Gly	
Rubber	100	100	100	100	100	100	
ZnO	3	3	3	3	3	3	
Stearic acid	2	2	2	2	2	2	
CBS	1.5	1.5	1.5	1.5	1.5	1.5	
Sulfur	3	3	3	3	3	3	
Carbon black	-	25	-	-	25	25	
Calcium lignosulfonate	-	-	30	30	30	30	
Glycerol	-	-	_	15	-	15	

Table 1. Rubber compounds composition.

cured for the determination of tensile properties, and then sheets of the dimensions $100 \times 10 \times 1.5$ mm were prepared for the determination of intrinsic strength, T_0 , and ultimate strength, T_C . The curing process was carried out using a hydraulic press at a temperature of 170 °C and pressure of 15 MPa according to their optimum curing times. The crosslink density, v was determined by measuring the equilibrium swelling of the vulcanizates in xylene after 30 h at laboratory temperature. The cross-link density was calculated using the Flory-Rehner equation modified by Krause [49], based on the equilibrium swelling state. For the calculations, the Flory-Huggins interaction parameters were used, which for NBR in xylene is 0.5316, while for SBR in xylene, it is 0.3908. Physical-mechanical properties were measured using a Zwick Roell/Z 2.5 appliance (Zwick GmbH & Co.KG, Ulm, Germany) in accordance with the technical norm ISO STN 37 (62 1436). The tensile test was performed at an extension rate of 500 mm/min with an initial distance between clamps of 50 mm. The hardness was measured using a durometer (Zwick GmbH & Co.KG, Ulm, Germany) in accordance with the technical norm ISO STN 7619 and expressed in Shore A. The results of all mechanical properties are an average of five parallel measurements. The surface morphology and microstructure of composites were observed using a scanning electron microscope JEOL JSM-7500F (Jeol Ltd., Tokyo, Japan). The samples were initially frozen in liquid nitrogen, fractured, and then coated with a layer of gold on the fracture surface. The electron source used was a cold cathode ultra-high vacuum (UHV) field emission gun. The acceleration voltage ranged from 0.1 to 30 kV, resulting in a resolution of 1.0 nm at 15 kV and 1.4 nm at 1 kV. Scanning electron microscopy (SEM) images were captured by CCD-Camera EDS (INCA X-ACT, Oxford Instruments, Abingdon, UK). Finally, the fatigue crack growth behavior has been determined using a simple approximation of the intrinsic strength, T_0 , and ultimate tear strength, T_C values. To determine both intrinsic strengths, T_0 and ultimate strength, T_C values of the rubber compounds studied, an Intrinsic Strength Analyser (ISA, Coesfeld GmbH & Co. KG, Germany) was used. The application of the power law approximation between these two probabilities is based on the fact that the intrinsic strength, T_0 , occurs approximately at a crack growth rate of 10^{-8} mm/cycle, and the ultimate strength, T_C , occurs at a crack growth rate of 10^{-2} mm/cycle. This strategy was first introduced in the following study [50]. Details of this test methodology and test equipment can be found in previous publications, *e.g.*, [42, 51–54].

3. Results and discussion

Fatigue crack growth (FCG) is a crucial factor in determining the durability of rubber products. Quantifying crack growth properties in elastomers is of immense industrial interest as it provides invaluable insights to develop the most durable products possible.

Figure 2 and Figure 3 represent the double logarithmic plot of tearing energy and T vs. crack growth rate (da/dn) of compounds based on NBR and SBR, respectively. The intrinsic strength of unfilled crosslinked rubber relies on chain stiffness, the molecular weight $M_{\rm C}$ of the main chain bond, dissociation energy, and crosslink density. Typically, higher cross link density entails greater energy needed for all bonds to stretch and reach the bond dissociation energy [42]. Conversely, the length of individual crosslinks also holds significance. All bonds in the network chain must stretch to the bond dissociation energy before one bond can break. Hence, a higher $M_{\rm C}$ implies a higher total energy required. Lower cross-link density also signifies fewer chains intersecting the crack path. Polymer type is also crucial;



Figure 2. *FCG* rate, d*a*/d*n*, as a function of tearing energy, *T*, for composites based on nitrile rubber (NBR).



Figure 3. FCG rate, da/dn, as a function of tearing energy, T, for composites based on styrene-butadiene rubber (SBR).

chain diameter correlates with molecular weight per backbone bond M_0 (molecular weight between two cross-links). Therefore, polymer chains with lower M_0 are thinner, requiring more chains to break per area of the crack [42]. When comparing the intrinsic strength of unfilled NBR and unfilled SBR (Figure 4a), one can see that T_0 of SBR is higher. This observation can be attributed to the higher chain stiffness, stemming from its large styrene side groups and possibly a lower cross-link density (as seen in Figure 5). This is consistent with findings from prior studies [42, 55]. The actual energy needed to grow a crack in rubber can be significantly larger than the energy for crack initiation (intrinsic strength) due to the viscoelastic dissipation.

The *ISA* can quantify the positions of the two ends of the *FCG* curve – the intrinsic and ultimate strength, where the slope of each curve represents the ability of a crack to propagate. Here a power law dependency is observed, which mathematically can be represented as Equation (1):



Figure 5. Apparent cross-link density of studied composites.

$$\frac{\mathrm{d}a}{\mathrm{d}n} = bT^{\mathrm{m}} \tag{1}$$

where the exponent m defines the slope of the ability of a crack to propagate and b is the material constant

Table 2. The list of evaluated parameters of material constant b and m, which define the stable crack growth rate given byEquation (1), for composites based on nitrile rubber (NBR).

	RUB	RUB/CB	RUB/CaL	RUB/CaL/Gly	RUB/CB/CaL	RUB/CB/CaL/Gly
b	$2 \cdot 10^{-14}$	$1 \cdot 10^{-13}$	$2 \cdot 10^{-13}$	3.10-13	$8 \cdot 10^{-13}$	$2 \cdot 10^{-12}$
т	3.39	2.80	2.64	2.52	2.35	2.07

Table 3. The list of evaluated parameters of material constant b and m, which define the stable crack growth rate given by Equation (1), for composites based on styrene-butadiene rubber (SBR).

	RUB	RUB/CB	RUB/CaL	RUB/CaL/Gly	RUB/CB/CaL	RUB/CB/CaL/Gly
b	$6 \cdot 10^{-15}$	$4 \cdot 10^{-13}$	$7 \cdot 10^{-14}$	$2 \cdot 10^{-12}$	$4 \cdot 10^{-12}$	$6 \cdot 10^{-12}$
т	3.55	2.48	2.93	2.17	2.02	1.89



Figure 4. a) Intrinsic strength and b) ultimate strength of composites with NBR and SBR as a rubber matrix.



Figure 6. *FCG* exponent m given by Equation (1) of composites with NBR and SBR as rubber matrix.

[56]. The constants calculated for studied compounds based on NBR and SBR are listed in Table 2 and Table 3 respectively. As previously described, in order to increase the resistance to crack growth, the curve should have the lowest slope possible and, therefore, the lowest exponent m. As seen in Figure 6, the values of exponent m clearly point out the lowest resistance to crack growth for unfilled rubber compounds, thus showing the ability of lignosulfonate to increase resistance to FCG.

The incorporation of reinforcing fillers such as CB is known to reduce FCG rates. The addition of filler introduces additional mechanisms by which strain energy can be dissipated [1]. In general, strong interfacial adhesion is formed between rubber chain segments and CB. The rubber chains in the proximity to the filler are so strongly physically adsorbed or chemisorbed on the surface of CB particles that they behave as a polymer in glassy state and contribute to the increase in apparent cross-linking density, so in addition to providing greater energy dissipation, dispersed particles serve to deflect or arrest growing cracks [1, 57]. When reinforcing fillers such as CB are added, $T_{\rm C}$ increases in both NBR and SBR-based compounds (Figure 4b), as could be expected. However, the increase in T_0 cannot be solely explained by considering filler-rubber interactions and associated mobility effects.

CaL has a high molecular weight and does not behave as a typical particle-like filler. From morphology analysis in Figure 7 and Figure 8 it can be seen that thermomechanical plasticization of CaL occurs, followed by the formation of smooth but rigid CaL domains. The incorporation of CaL to NBR caused

increased from T_0 and T_C even higher than for NBR/CB blends, which could not only be attributed to the size and toughness of the respective fillers – where CaL created much larger domains as observed in morphology analysis (Figures 7b and 7c) - but also with the fact that CaL is a polymer with highly branched 3D structure, with a high content of phenolic hydroxyl groups. For a crack to propagate in NBR/CaL, physical interactions formed between phenolic hydroxyl groups and polar nitrile groups in NBR [58] need to be disrupted. In NBR/CB, the interactions between CB and NBR are mainly a combination of physical adsorption and filler network formation, which in this particular case seems to be more easily disrupted than those in NBR/CaL. This hypothesis can be supported by the fact that $T_{\rm C}$ of SBR/CaL is much lower than $T_{\rm C}$ of SBR/CB. In this case, the interactions between SBR and CaL are not as strong as between NBR and CaL because SBR is non-polar rubber, so the interface is much more easily disrupted. This can be further supported by the comparison of morphology in Figures 7c and 8c. In Figure 7c, it is shown that CaL creates smooth parts with a clear NBR-CaL interface, but in Figure 8c, the inhomogeneous structure with surface voids and cavities confirms that mutual compatibility and adhesion between CaL and SBR are weak.

Morphological characteristics also support the results of mechanical characteristics (Table 4), where the incorporation of CaL into NBR led to improved properties when compared to pure NBR, with an increase of 1 MPa in tensile strength. When considering the stress-strain curves (Figure 9), the initial slope or initial high modulus at a low strain can be attributed to a hydrogen-bonded network [58] formed between hydroxyl groups of lignin and nitrile groups in NBR. On the other hand, the mechanical properties of CaL/SBR blend deteriorated by 0.5 MPa (Table 5) when compared to pure SBR. When comparing the stress-strain curves of NBR and NBR/CaL with the curves of SBR and SBR/CaL, one can see that while the increment in initial slope in NBR-based samples after adding CaL is significant, there is no difference between the initial part of stress-strain curves of SBR and SBR/CaL. This supports the consideration for the formation of physical interactions between NBR and CaL, as in the SBR matrix, there are no possible sites for hydrogen bonding.

Comparison of T_0 values for compounds based on NBR and SBR (Figure 4a) reveals a consistent trend,



Figure 7. SEM microscopy of fracture surfaces (magnification 250×) of vulcanizates based on nitrile rubber (NBR), a) RUB, b) RUB/CB, c) RUB/CaL, d) RUB/CaL/Gly, e) RUB/CB/CaL, f) RUB/CB/CaL/Gly.

although larger deviations were observed in SBRbased compounds. This could be attributed to inferior morphological characteristics of SBR-based compounds, as previously discussed, underlining the sensitivity of *ISA* measurement. The enhancement of mechanical properties can be achieved by utilizing CB/CaL hybrid filler discussed earlier. As seen in Table 4 and Table 5, the tensile strength of 16.30 and 12.73 MPa for NBR and SBR, respectively, was achieved by utilizing CB/CaL



Figure 8. SEM microscopy of fracture surfaces (magnification 250×) of vulcanizates based on styrene-butadiene rubber (SBR), a) RUB, b) RUB/CB, c) RUB/CaL, d) RUB/CaL/Gly, e) RUB/CB/CaL, f) RUB/CB/CaL/Gly.

hybrid filler. The effectiveness of this CB/CaL hybrid based on mechanical properties is comparable to nitrile rubber filled with 50 phr of carbon black, which was observed in previous studies [59]. On the other hand, applying 50 phr of calcium lignosulfonate into NBR was not as successful, where tensile

strength reached only about 4 MPa [24]. As expected, a combination of CB and CaL also resulted in improved distribution and dispersion of both components in the rubber matrix and, thus, the formation of a homogeneous structure (Figures 7e and 8e). A similar synergic effect could be expected for T_0 and

	Tensile strength	Elongation at break	Modulus 100	Hardness
	[MPa]	[%]	[MPa]	[ShoreA]
NBR	2.95±0.18	252±17	1.37±0.04	42.0±0.7
NBR/CB	12.94±0.55	315±11	2.58±0.11	55.6±0.2
NBR/CaL	4.03±0.16	485±12	1.51±0.01	46.0±0.8
NBR/CaL/Gly	5.41±0.17	597±13	1.01±0.01	38.8±0.6
NBR/CB/CaL	16.30±0.65	594±11	2.28±0.07	50.8±0.7
NBR/CB/CaL/Gly	14.51±0.40	695±6	1.44±0.04	46.4±0.5

Table 4. Mechanical properties of vulcanizates based on nitrile rubber (NBR).

Table 5. Mechanical properties of vulcanizates based on styrene-butadiene rubber (SBR).

	Tensile strength	Elongation at break	Modulus 100	Hardness
	[MPa]	[%]	[MPa]	[ShoreA]
SBR	2.14±0.10	228±9	1.20±0.02	41.8±0.4
SBR/CB	9.17±0.58	284±12	2.30±0.05	54.2±0.2
SBR/CaL	1.45±0.06	259±11	0.95±0.03	33.0±0.5
SBR/CaL/Gly	6.81±0.81	823±45	0.76±0.02	38.8±0.6
SBR/CB/CaL	12.73±0.58	642±17	2.42±0.18	52.2±0.4
SBR/CB/CaL/Gly	13.17±0.93	746±34	1.45 ± 0.02	49.0±0.5

 $T_{\rm C}$, but here, it has to be taken into account that generally, the greater the amount of filler in the compound, the reduced. Based on previous research [60] even 80 phr of CB/lignin hybrid (with 3/1 ratio) provides good mechanical properties– thus, ongoing research should be focused on the overall amount of filler and its effect on *FCG*. Another point in the crack growth rate is that as cracks propagate, the rubber undergoes significant energy dissipation and viscoelastic deformation. Lignin-filled rubber composites, in general, should have different crack growth behavior due to less effective stress transfer and energy dissipation mechanisms compared to carbon



Figure 9. Stress-strain curves of vulcanizates based on nitrile rubber (NBR), with enlarged initial part of the stress-strain curves of NBR and NBR/CaL vulcanizates.

black. These mechanisms should slow down the crack growth progression by absorbing some of the applied energy, but as seen in a previous study [61], the stress transfer from the rubber matrix to CaL may not be sufficient. This can surely be improved by the incorporation of plasticizers. The main purpose for the application of glycerol was to plasticize lignosulfonate, make it softer, and enable its better distribution within the rubber matrix. This proved to be correct, and improved RUB/CaL/Gly interface can be seen in morphology analysis in Figures 7d and as well as in RUB/CB/CaL/Gly in Figures 7f and 8f. However, small molecules of glycerol also enter in-



Figure 10. Stress-strain curves of vulcanizates based on styrene-butadiene rubber (SBR), with enlarged initial part of the stress-strain curves of SBR and SBR/CaL vulcanizates.

termolecular space between elastomer chains and disrupt intra- and intermolecular forces between rubber chain segments and their physical entanglements. This leads to the reduction of internal friction and an increase in rubber chains' elasticity and mobility. While the presence of glycerol causes a decrease in cross-link density (Figure 5), the mechanical properties (Table 4 and Table 5) of RUB/CaL/Gly are much improved. This statement also applies when different amounts of CaL are incorporated, and the amount of 30-35 wt% of glycerol (related to CaL content) is used [48]. When focusing on crack growth, the addition of plasticizer or processing oil to rubber compounds requires caution, as these additives can reduce T_0 . Minimizing plasticizer content while ensuring proper filler dispersion and processing is therefore desirable. As depicted in Figure 4, this balance has been achieved. When glycerol was applied to RUB/CB/CaL/Gly, the mechanical properties slightly deteriorated, but $T_{\rm C}$ drastically increased, which is indicative of the formation of a filler network with the ability of great energy dissipation. The exponent m (Figure 6) for RUB/CB/CaL/Gly is also the lowest among the tested compounds. It can be concluded that this compound has enhanced resistance against crack initiation but also a more stable crack growth propagation process.

These compounds are thus engineered to sustain high mechanical loads while significantly reducing the emission of chemical or rubber components into the environment. Achieving the optimal balance of mechanical properties and reduced wear in rubber composites depends on the specific application, requiring precise formulation and integration of individual components to meet desired performance criteria.

4. Conclusions

Calcium lignosulfonate is a suitable and sustainable component for rubber compounds, provided that good dispersion and interfacial adhesion are achieved. For this reason, nitrile rubber was chosen as the primary rubber matrix, where hydrogen bonding can be expected, ensuring a satisfactory interface. By incorporating CaL into carbon black-reinforced rubber compounds based on nitrile rubber and styrene-butadiene rubber, we achieved good dispersion of both components as well as satisfactory morphology, resulting in tensile strengths of 16.30 and 12.73 MPa, respectively. While this synergistic effect was expected in FCG, the stress transfer and energy dissipation mechanisms proved to be even better with the addition of glycerol as a plasticizer. Although the CB/CaL hybrid did not significantly influence the intrinsic strength of the rubber samples, the ultimate strength of these compounds increased drastically – over five-fold compared to RUB/CB – indicating great potential for real-life applications.

Our research suggests that utilizing CaL can significantly extend the life of rubber products, directly reducing rubber particle emissions into the environment. These findings also indicate that the material is likely to exhibit similar advantageous properties during abrasion and real-world usage. All assumptions will be experimentally verified through extensive rubber wear analysis, ensuring the results' reliability for practical applications.

Future work should focus on optimizing the combination of these components to tailor rubber composites for specific industrial applications, thereby achieving the desired balance of mechanical strength and environmental sustainability through wear reduction. These findings pave the way for the development of next-generation rubber materials that are not only high-performing but also eco-friendly.

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