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Research article

Utilization of composite ZnO in SBR/BR compounds and its effect on the cure and physicomechanical properties

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Abstract. Zinc complexes have a considerable impact on human health and the environment, especially on aquatic wildlife. One of the primary sources of zinc release to the environment is worn rubber particles from tires. The environmental footprint of zinc oxide (ZnO) during production, use, and landfilling has prompted researchers to reduce its use in rubber formulations due to ecological and economic concerns. In this study, composite ZnO materials where ZnO particles are coated on precipitated calcium carbonate ($CaCO_3$) are used in styrene butadiene rubber/butadiene rubber (SBR/BR) compounds, and their performance is compared with white seal ZnO and active ZnO. Trial compounds are prepared on a laboratory scale using composite ZnO materials with ZnO:$CaCO_3$ ratios of 40:60, 60:40, and 90:10, and control compounds with white seal and active ZnO. All compounds are tested to evaluate their curing and physico-mechanical properties. It is observed that the surface area of ZnO plays an essential role in crosslink density and, hence, compound performance. Trial materials have no negative effect on the curing and mechanical properties of the compounds. Thus, it is concluded that composite ZnO materials can be used as alternatives to both white seal ZnO and active ZnO. They have environmental and economic advantages due to their lower ZnO content. The compound recipe has the potential to be used for tire tread compounds.

Keywords: *zinc oxide, rubber, curing behavior, mechanical properties*

1. Introduction

Zinc oxide, one of the most essential metal oxides, has been widely utilized in various fields, including plastics, ceramics, glass, cement, paints, fire retardants, etc., over the past 100 years [1, 2]. Its excellent UV-blocking activity provides its use as a UV stabilizer in sunscreens and in personal care products such as cosmetics [3]. It also has a high potential for optoelectronic applications due to its unique optical and electrical properties [4]. Furthermore, its antibacterial and antifungal properties provide its use in tissue engineering [5–7]. Another significant usage of ZnO is in the rubber industry as a chemical activator in sulfur vulcanization [8], and its consumption reaches an annual production of 105 tons [9]. Generally, to obtain an effective dispersion in rubber formulations, it is used as 3 to 5 parts per hundred rubber [phr] in recipes involving sulfur curing systems [8, 10, 11]. In rubber technology, ZnO is an activator with appropriate fatty acid combinations such as stearic acid, lauric acid, and their zinc salts [12, 13]. Thus, an intermediate salt complex, which is more effective in activating sulfur in rubber compounds, is generated, and higher vulcanization rates are achieved together with accelerators [14]. Higher crosslink density is attained by promoting short sulfide crosslinks, reducing vulcanization time [15]. This provides both energy saving and reduction of process costs [16]. Despite the positive effects of ZnO in many industries, zinc causes some environmental problems [17]. The European Council Directive 2004/73/EC emphasizes that keeping the zinc

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level released to the environment in various ways at a certain level is essential due to its toxic effects on aquatic life [18, 19]. Zinc is released into the atmosphere in many ways [20]. The first release is through wastewater and other releases after the production of zinc material [21]. In the next stage, the second use, rubber products are released into the environment by recycling rubber products [22]. Furthermore, landfill leaching introduces zinc into the atmosphere [23]. However, the biggest reason for mixing with groundwater is the dust particles that come out with the wear of the tires [24].

Thus, the release of zinc to nature should be controlled, and it is important to keep the amount of zinc in rubber compounds at low levels. Considering both environmental restrictions and economic effects, studies to reduce the amount of zinc in rubber products have gained a huge interest in recent years. In general, there are two routes to provide this: (i) to increase zinc activity in the rubber matrix during the vulcanization step and hence to increase the availability of zinc ions for the reaction, and (ii) to replace ZnO by other activators that are less detrimental to the environment. The reactivity, physical, and chemical properties of ZnO are affected by the manufacturing process [25–27], the surface area [1], particle size [10], and morphology that influence the size of the interphase between crosslinking agent and rubber chain [28, 29]. Akhlaghi *et al*. [30] have used zinc oxide nanoparticles to investigate its effects on isothermal cure kinetics, morphology, and mechanical properties of ethylene propylene diene monomer (EPDM) rubber. It has been observed that replacing the conventional ZnO used in the recipe with ZnO nanoparticles allows a lower usage in the recipe, provides a shorter curing time, and provides a higher crosslink density. At the same time, the kinetic analysis of curing has revealed that the activation energy of the curing reaction decreases significantly with a decrease in ZnO particle size. For this reason, it has been reported that EPDM systems activated with ZnO nanoparticles improve the curing and mechanical properties. Taghvaei-Ganjali *et al*. [31] have reported that the effective area of the material is increased by using surface-modified zinc oxide in the rubber formulations. Surface-modified conventional ZnO and ZnO nanoparticles by polyethylene glycol and polypropylene glycol have been used in natural rubber/styrene butadiene rubber (NR/SBR) blend to improve rubber properties by providing better hydrophobicity of particles, and thus better dispersion. It has been reported that both modified ZnO types provide better physico-mechanical properties and effectively reduce ZnO content in compound recipes [31]. Sahoo *et al*. [1] have synthesized ZnO nanoparticles with a 30–70 nm size range by homogeneous precipitation and calcination method and used them in natural rubber and nitrile butadiene rubber (NBR) based recipes to reduce the amount of ZnO. They have reported that due to the increase in crosslink density, a significant increase has been observed in torque values, resulting in better mechanical properties compared to conventional ZnO [1]. Przybyszewska *et al*. [32] have investigated the effect of the morphology of ZnO nanoparticles on the activity of crosslinking in carboxylated nitrile rubber-based compounds. They have observed that ZnO nanoparticles having snowflake morphology influence the curing system positively. In this way, reducing the amount of ZnO in the rubber matrix is possible up to 40% compared to compounds containing micro-sized commercial ZnO activators [32]. Bieliński *et al*. [33] have used ZnO nanoparticles in powder form with varying morphology in SBR-based compounds. The results have revealed that the morphology of nano ZnO activator particles influences activation energy for vulcanization, crosslink density, and mechanical properties of the rubber vulcanizates. The one with hybrid morphology (flat-ended rod-like particles on a 'cauliflower' base) provides improved interaction with zinc in the polymer matrix during vulcanization and results in an effective curing system when replaced with conventional ZnO [33]. Heideman *et al*. [34] have studied alternative metal oxides, various zinc complexes, and a novel activator for vulcanization systems of solution styrene butadiene rubber (s-SBR) based compounds to replace traditional ZnO. Calcium oxide (CaO) and magnesium oxide (MgO) in the vulcanization system have shown that they can be good alternatives to ZnO due to their positive effect on the curing rate. On the other hand, using zinc-m glycerolate as an alternative to ZnO is also possible since it does not negatively affect the curing properties. In addition to various metal oxides and zinc complexes, clay material loaded with Zn^{+2} ions on the surface is also investigated in the study, and based on the results, it has been concluded that this novel activator provides a new route to reduce zinc levels and helps to minimize its environmental impact [34]. Alam *et al*. [19]

have described the interactions between zinc and non-zinc-based crosslinking accelerators in the presence of magnesium oxide to identify a substitute cure activator for zinc oxide in the vulcanization of natural rubber to reduce its environmental hazard. The findings of the experiments have shown that complete zinc-oxide-free rubber vulcanization is possible without a substantial deterioration in mechanical properties. Furthermore, vulcanization in the presence of magnesium oxide is approximately five times faster than vulcanization in the presence of a zinc-oxide-based cure activator in rubber vulcanization [19]. Bunsanong *et al*. [35] have investigated an alternative way for curing NR with the accelerator-free and zinc-free systems by using pre-vulcanized modified NR latex (NR-*g*-PVBC) in the presence of adipic acid dihydrazide (ADH). The results have shown that the NR-*g*-PVBC films with ADH have a substantially higher tensile strength than those without ADH. Additionally, films containing ADH have shown higher storage modulus (E') in the rubbery plateau region than films without ADH. These findings support that adding ADH to the film causes a crosslinking reaction. As a result, the study demonstrates that the preparation of a novel kind of pre-vulcanized latex can be made by grafting poly(vinyl benzyl chloride) onto NR particles, and this new framework has been considered a more environmentally friendly system than the traditional one [35].

Another approach to reducing the use of ZnO in rubber compounds for environmental concerns is to use a support material for ZnO instead of using it as a monolithic material. Support materials used in literature for this purpose are $CaCO_3$ [17, 36], silica [37], and cellulose [38]. Thaptong *et al*. [17] used a composite ZnO material with ZnO coated on a $CaCO_3$ core in a based tire tread compound [36]. The cure and mechanical properties of the trial compounds have been investigated and compared with the control compound prepared using active ZnO. No significant change is observed in the curing characteristics of the compounds, although composite materials caused a slightly shorter optimum cure time (t_{90}) and a slightly higher cure rate index (CRI). $CaCO_3$ core material is also used by Vatansever *et al*. [36] in an SBR-based rubber compound. The aging properties of the trial compounds have been investigated and compared with the control compound prepared using active ZnO. It is concluded that lower ZnO consumption may obtain similar cure, mechanical, and aging properties. In a study by Kumbalaparambil *et al*. [37], the main focus was using ZnO-anchored silica in NR/SBR-based compounds. *In-situ* formation of ZnO-anchored silica particles was provided during mixing. Different types of ZnO are used, including active, nano, octylamine modified, and conventional ones, to offer covalent bonds such as Si–O–Zn. Except for the modified ZnO-containing compounds where cure properties are adversely affected, the other trial compounds have displayed similar cure characteristics to the control compound with conventional ZnO. Best mechanical properties are obtained for the trial compound having active ZnO. Boopasiri *et al*. [38] have used a new type of ZnO fabricated by depositing ZnO on a microcrystalline cellulose (MCC) surface using an ultrasonic-assisted hydrothermal process. Trial compounds have been prepared using an NR-based recipe; cure and mechanical properties are compared with the control compounds using white seal ZnO. The trial compounds displayed higher t_{90} compared to the control ones. Although no significant difference is observed in the mechanical properties (tensile strength, elongation at break, modulus, hardness), the trial material provided a lower compression set. Higher crosslink density has been attained using trial ZnO material. In this study, styrene butadiene rubber/ butadiene rubber (SBR/BR) blend, which has not been studied earlier with composite ZnO activators, is used and curing and mechanical properties of the trial compounds are investigated to be compared with the controls having commercial activators (white seal ZnO and active ZnO). Composite ZnO materials have different amounts of ZnO deposited on the surface of a $CaCO_3$ core material. The study's primary goal is to explore the possibility of reducing the amount of ZnO used in rubber matrices by replacing conventional materials with composite ZnO without sacrificing the compound's performance and providing environmental and economic gains.

2. Experimental

2.1. Materials

All mixing ingredients are used as received. SBR has 35% bound styrene, and 26.4% vinyl content is used, having 188 kg/mol molecular weight and 75 ML (1+4) Mooney viscosity at 100 °C. BR having 62 ML (1+4) Mooney viscosity at 100 °C is utilized. N234 grade carbon black is used as reinforcing filler with the statistical thickness surface area (STSA) of 112 m^2/g. Stearic acid has a 54 °C final melting point, and sulfur, which has 0.077% heat loss, is used in the curing system. *N*,*N*′-diphenylguanidine (DPG), and *N*-tert-butyl-2-benzothiazolimesulfonamide (TBBS) are accelerators with melting points of 146.1 and 109.5 °C, respectively. *N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine (6PPD) is used as an antioxidant having a melting point of 46.0 °C and microcrystalline wax is used as an antiozonant having congealing point of 66 °C and 6.84 mm^2/s viscosity at 100 °C. Aromatic oil is a processing agent with 12.9 MPa·s viscosity at 20 °C. Different types of ZnO are used: (i) white seal zinc oxide (WS–ZnO), (ii) active zinc oxide (Ac–ZnO), and (iii) composite ZnO materials. Composite ZnO materials are wet by coating ZnO particles (20–40 nm) on precipitated $CaCO_3$ particles (50–200 nm) as core. ZnO:$CaCO_3$ ratios of the materials are 40:60 (C–$ZnO_{40:60}$), 60:40 (C–$ZnO_{60:40}$), and 90:10 (C–$ZnO_{90:10}$). Properties like specific surface area and ZnO content affecting the activation ability of all types of ZnO used in this study are given in Table 1. The morphology and elemental analysis of the ZnO materials are investigated using a scanning electron microscope (SEM, TESCAN VEGA3, Czechia) and an energy dispersive X-ray spectrometer (EDS, EDAX ELEMENT, USA). The samples are spread on carbon tabs and coated by gold using a sputter coater (BIO-RAD E5150, UK) for morphology studies and coated by carbon using a carbon coater (EMITEC K950X, UK) for EDS analysis. In Figure 1, the morphologies of control ZnO agglomerates are characterized, and SEM images indicate that both ZnO materials have a typical wurtzite crystal structure and Ac–ZnO has a higher surface area compared to WS–ZnO due to its smaller particle size. Figure 2 shows the morphologies of composite ZnO materials, and a change in morphology is visible since ZnO is coated on $CaCO_3$. By considering the EDS mapping given in Figure 3, it is clear that the composite design of the supplier has been successfully achieved, and a dense ZnO phase fully covers the surface of the core material.

Table 1. Properties of types of ZnO used.

Type	Specific surface area, BET [m^2/g]	$CaCO_3$ [wt%]	ZnO [wt%]
WS–ZnO	5.1	0.0	99.7
Ac–ZnO	49.2	0.0	96.1
C–$ZnO_{40:60}$	15.0	58.8	41.2
C–$ZnO_{60:40}$	20.0	36.4	63.6
C–$ZnO_{90:10}$	40.0	8.5	91.5

The total surface area of coat and core material for composite ZnO types.

2.2. Compound preparation

An internal BR1600 Banbury mixer with a 1.2 L total volume manufactured by Farrell, USA, is used in the compounding procedure. The recipe is adapted from literature [39] and prepared in two steps, the master batch and the final batch, as given in Table 2

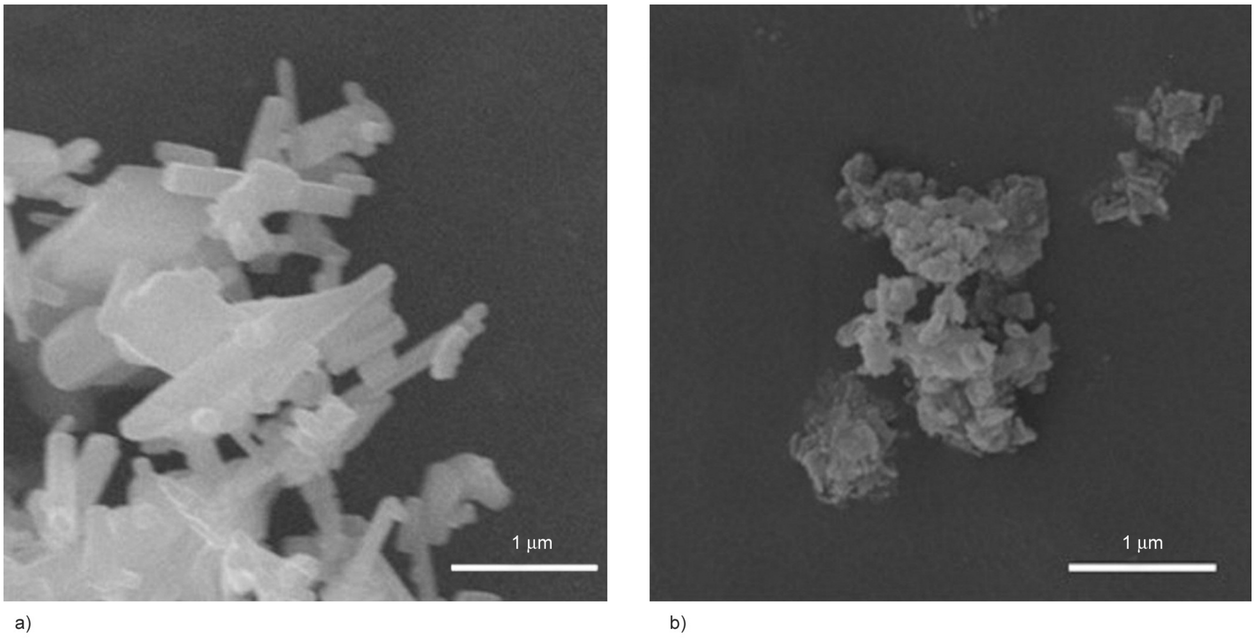

Figure 1. SEM images showing the morphologies of control ZnO materials; a) WS–ZnO and b) Ac–ZnO.

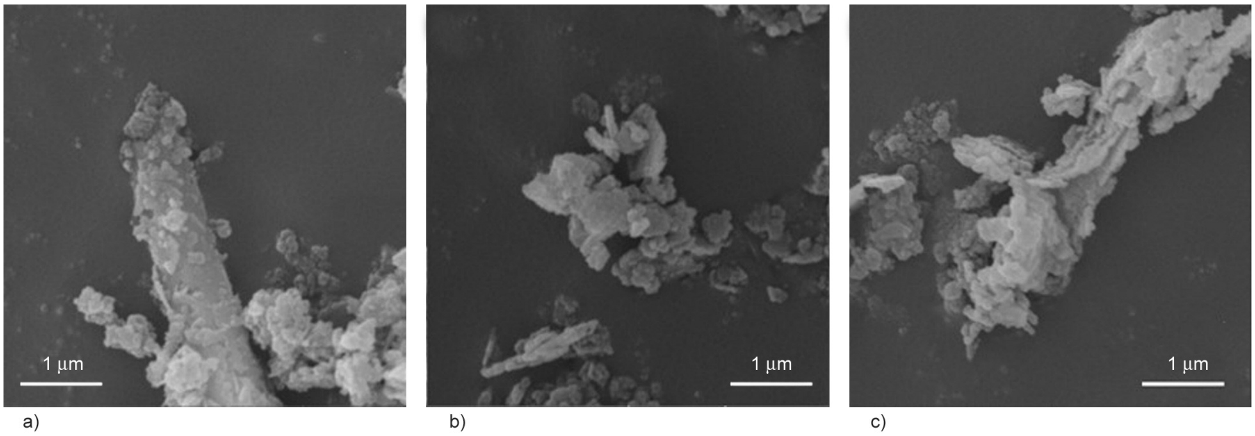

Figure 2. SEM images showing the morphologies of composite ZnO materials; a) C–$ZnO_{40:60}$, b) C–$ZnO_{60:40}$ and c) C–$ZnO_{90:10}$.

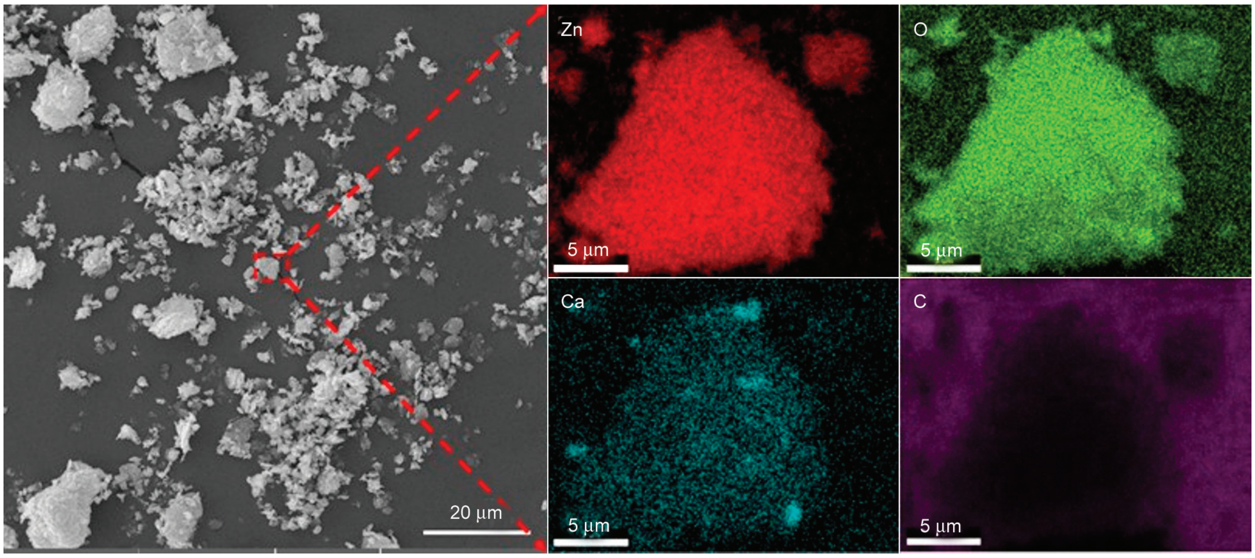

Figure 3. EDS mapping showing the elemental distribution for C–$ZnO_{90:10}$.

and Table 3. Masterbatch preparation is started with the SBR/BR mastication step for 30 s at 90 rpm. Then carbon black, stearic acid, some part of (2.5 phr) ZnO, and wax are added. The compound is mixed for 320 s more and dumped at 130 °C. The final batch is prepared by loading the master batch and mixing it for 20 s at 70 rpm. Then, the remaining part (0.5 phr) of ZnO, sulfur, and other chemicals are added, combined for 120 s, and dumped at 105 °C. The prepared compound is milled several times at 70 °C using a laboratory mill to attain 2.2 mm thickness. The milled compound is left to cool at room temperature. Three lots, 1200 g each, are prepared for each compound recipe, and all data are given as the average of these three lots. Tensile test specimens are cured in a laboratory platen press LPC029 hot press (Fontijne, USA) at 160 °C for 15 min under 345 kN force (corresponds to 12.32 MPa pressure).

Table 2. SBR/BR master batch recipe[*].

Material	**Compound code**				
	TC1	**TC2**	**TT4**	**TT6**	**TT9**
SBR	70.0	70.0	70.0	70.0	70.0
BR	30.0	30.0	30.0	30.0	30.0
N-234 black	55.0	55.0	55.0	55.0	55.0
Aromatic Oil	20.0	20.0	20.0	20.0	20.0
WS–ZnO	3.0	–	–	–	–
Ac–ZnO	–	3.0	–	–	–
C–$ZnO_{40:60}$	–	–	3.0	–	–
C–$ZnO_{60:40}$	–	–	–	3.0	–
C–$ZnO_{90:10}$	–	–	–	–	3.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5
Microcrystalline wax	0.5	0.5	0.5	0.5	0.5
Total	**180.0**	**180.0**	**180.0**	**180.0**	**180.0**

[*] The values are given in phr unit, used in compound formulations, and stand for parts per hundred parts of rubber.

Table 3. SBR/BR final batch recipe*.

Material	Compound code				
	TC1	**TC2**	**TT4**	**TT6**	**TT9**
Masterbatch	180.0	180.0	180.0	180.0	180.0
6PPD	1.0	1.0	1.0	1.0	1.0
TBBS	1.0	1.0	1.0	1.0	1.0
DPG	0.4	0.4	0.4	0.4	0.4
Sulfur	1.8	1.8	1.8	1.8	1.8
Total	**184.2**	**184.2**	**184.2**	**184.2**	**184.2**

*The values are given in phr unit, used in compound formulations, and stand for parts per hundred parts of rubber.

2.3. Compound characterization

2.3.1. Mooney viscosity

Mooney viscosity and Mooney scorch measurements are carried out by Mooney MV 2000E (Monsanto, United Kingdom), having an operating temperature of 25–200 °C and rotor speed of 0.1–20 rpm to obtain information about the viscosity, scorch properties, and processability of elastomers. Tests are performed at 130 °C by ASTM D1646.

2.3.2. Moving die rheometer (MDR)

Cure properties are tested using moving die rheometer MDR 2000 (Alpha Technologies, USA) operating at 25–200 °C and 1.667 Hz under isothermal test conditions with constant strain and frequency according to ASTM D5289. MDR results were taken at 160 °C for 15 min. The cure rate index (CRI) is the rate of curing reaction based on the differences between optimum cure time (t_{90}) and scorch time (t_{s2}). The cure rate index equation is given in Equation (1):

$$CapCRI = \frac{100}{t_{90} - t_{s2}} \quad [\%] \tag{1}$$

2.3.3. Tensile and hardness properties

Mechanical properties are obtained after curing all compounds at LPC029 hot press (Fontijne, USA). Each test is repeated at least five times, and average values are reported. Tensile testing is performed on a T2000 Tensile Tester (Alpha Technologies, USA) at a crosshead speed of 300 mm/min at room temperature (23±2 °C) according to ASTM D412. Tensile strength, elongation at break, and modulus values at various elongations are reported. Test samples prepared according to ASTM D412 standard are aged in Heraeus ovens (Heraeus, Germany) for 24, 48, 72 and 96 h at 100 °C and tested at room temperature. Hardness, tensile strength (*TS*), elongation at break (*EB*), and modulus values at 100% strain (M100) and 300% strain (M300) of cured compounds are evaluated. Comparison of retention of *TS*, *EB*, and modulus values are calculated with the formula given in Equation (2):

$$Retention = \frac{aged\ value}{original\ value} \cdot 100 \quad [\%] \tag{2}$$

Hardness measurements are carried out in Zwick/Roell 5109 (Zwick/Roell, Germany) hardness measuring device according to ASTM D2240 (Shore A) standard.

2.3.4. Tear resistance

A tear resistance test is applied to measure the tear strength value of vulcanized rubbers. It is performed in the tensile device according to ASTM D624-00; the tear strength of the compounds is investigated. The tear resistance of rubber is a mechanical tear process that begins and spreads in a region exposed to high stress caused by a cut, defect, or deformation. Tear strength tests are applied using two different methods. A dumbbell-type sample, which is notched in the middle with crescent-shaped strip ends, is used in the Tear B test. The force, therefore, moves mainly along the major axis and perpendicular to the notch, indicating the propagation/progression behavior of the tear. In the Tear C test, the sample is prepared using the dumbbell type with 90° angled, not notched strip ends. The force acts on the test piece in the direction of grip separation, parallel to the strip ends of the sample, and the force that will initiate tearing or tearing is measured at the stress concentration located at the peak of 90°.

2.3.5. Flexometer

The life of rubber compounds is limited by the generation of heat, which is usually caused by the tire flexing during use. The heat generation of the material is measured with a flexometer. The flexometer test is performed with cylindrical samples prepared according to the ASTM D3182 standard and ASTM D623-07 standard by using BF Goodrich Model II (Tech Pro, USA). Heat production of compounds by stretching under constant load/constant compression value of the compounds is investigated. In the standard experimental mode performed under constant load, the change in sample length and the temperature increase at the base of the sample are recorded using a certain cyclic compression set. The permanent deformation value (C) from the sample size measurement is calculated by Equation (3) where t_0 is the original specimen thickness and tf is the specimen thickness after testing:

$$C = \frac{t_0 - t_f}{t_f} \cdot 100 \quad [\%] \tag{3}$$

2.3.6. Crosslink density

The swelling test is performed according to ISO 1817. The specimens with dimensions 30×5×2 mm are prepared and weighed (m_0) before immersing in toluene for 72 h at room temperature. After swelling, samples are weighed (m_1), and the excess solvent on the specimen's surface is removed by filter paper. The specimens are dried at 70 °C in an oven until a constant weight (m_2) is obtained. The swelling ratio (Q) is calculated according to Equation (4):

$$Q = \frac{m_1 - m_0}{m_0} \cdot 100 \quad [\%] \tag{4}$$

The crosslink density (V_c) is calculated by using Flory-Rehner equation [40] as given in Equations (5)–(7) shown:

$$M_c = \frac{-p_p V_s V_r^{\frac{1}{3}}}{\ln(1 - V_r) + V_r + \chi V_r^2} \tag{5}$$

$$V_r = \frac{\frac{m_2 - m_f}{p_p}}{\frac{m_2 - m_f}{p_p} + \frac{m_1 - m2}{p_s}} \tag{6}$$

$$V_c = \frac{1}{2M_c} \tag{7}$$

where M_c – average molecular weight between crosslinks, V_r – molar fraction of the swollen rubber, V_s – molar volume of the toluene (106.4 cm^3/mol), p_p – density of solvent, p_s – density of rubber blend, χ – Flory-Huggins polymer-solvent interaction parameter, m_f – weight of the filler (carbon black).

Flory-Huggins polymer-solvent interaction parameter in Equation (5) can be calculated by Equation (8):

$$\chi = \chi_\beta + \frac{V_s(\delta_s - \delta_r)^2}{RT} \tag{8}$$

where χ_β – entropy contribution and can be taken as 0.34, δ_s – solubility parameter of solvent (18.35 (J/cm^3)$^{1/2}$), δ_r – solubility parameter of rubber blend, R – universal gas constant (8.314 J/(mol·K)), T – absolute temperature (293.15 K).

Solubility parameter of rubber blend is calculated by Equation (9):

$$\delta_r = \delta_1 \phi_1 + \delta_2 \phi_2 \tag{9}$$

where δ_1 – solubility parameter of SBR (17.04 (J/cm^3)$^{1/2}$), δ_2 – solubility parameter of BR (17.15 (J/cm^3)$^{1/2}$), ϕ_1 – volume fraction of SBR, ϕ_2 – volume fraction of BR.

3. Results and discussion

Trial compounds using composite ZnO materials with ZnO:CaCO$_3$ ratios of 40:60, 60:40, and 90:10 together with control compounds having white seal ZnO and active ZnO are characterized to determine their curing and physico-mechanical properties.

3.1. Mooney viscosity

Results of the Mooney viscosity tests are given in Figure 4 for one of the prepared lots and average values of three lots are tabulated in Table 4. Initial maximum viscosity (IV), minimum viscosity after initial value (MV) and viscosity at 4 min test time after 1 min pre-heating time (ML (1+4)) are given in the table in Mooney units (MU), where 1 MU equals to

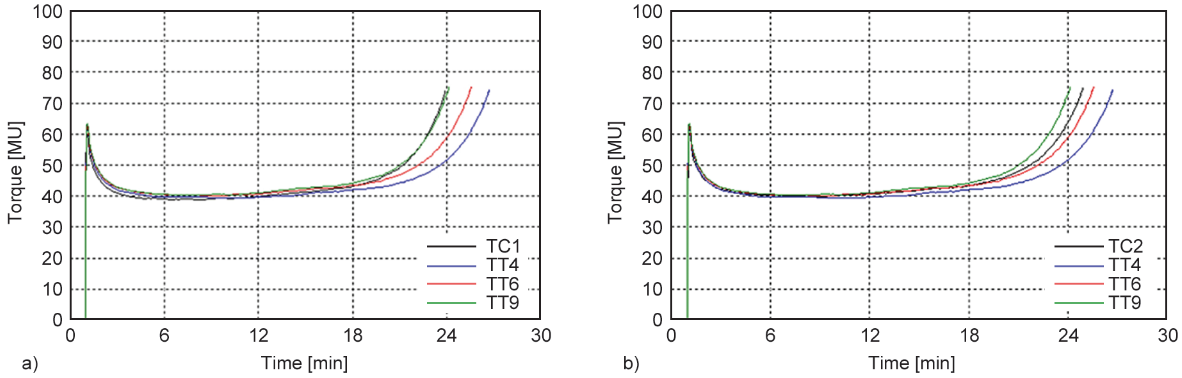

Figure 4. Mooney graphs of the trial compounds compared to a) TC1 and b) TC2.

Table 4. Mooney results.

Mooney (130 °C)	Unit	Compounds code				
		TC1	TC2	TT4	TT6	TT9
IV	MU	60.50±1.21	60.40±0.46	61.50±0.42	61.65±0.92	63.15±0.21
MV	MU	39.20±0.61	39.63±0.46	39.75±0.49	40.15±0.07	40.30±0.01
ML (1+4)	MU	39.60±0.61	40.17±0.49	40.40±0.42	40.80±0.14	40.95±0.07
t_5	min	18.24±0.58	19.44±0.24	19.95±1.58	19.35±0.75	18.98±0.08
t_{35}	min	23.65±0.59	24.90±0.22	25.38±1.85	24.75±1.12	24.16±0.04

0.083 N·m. Scorch time (t_5) and cure time (t_{35}) correspond to the times at viscosity increase of 5 MU and 35 MU over MV, respectively. As can be seen in Table 4, viscosity values are similar for all compounds. Scorch time indicates the period that the rubber compound can be processed at the given temperature before curing, which is similar to TT4 and TT6 compounds and comparable to TC2. Thus, trial materials C–$ZnO_{40:60}$ and C–$ZnO_{60:40}$ show similar effects as Ac–ZnO regarding scorch time and provide safer and controlled curing. On the other hand, TT9 has a similar t_5 value as TC1 due to the high ZnO content of the trial material C–$ZnO_{90:10}$. The cure time t_{35} is similar for all compounds, indicating that cure properties are not affected by the trial materials. It can be concluded from the Mooney viscosity data that composite ZnO materials do not affect viscosity and have similar processability as the control material; besides, they can even reduce the risk of scorch. These results agree with the work of Vatansever *et al*. [36].

3.2. MDR

Results of the MDR tests are given in Figure 5 for one of the prepared lots and average values of three lots are tabulated in Table 5. During the test, as the compound heats under pressure, the torque decreases due to the decrease in viscosity, and the lowest registered torque value is recorded as minimum torque (M_L). It is a measure of the rigidity and viscosity of the non-vulcanized compound. As curing begins, the torque increases proportionally. The maximum torque value is recorded as maximum torque (M_H), and it is related to the mechanical properties of the compound. Torque difference ($M_H – M_L$) represents the extent of crosslink density. The cure rate index (*CRI*) has been defined in Equation (1). The induction time (t_{s2}) is the scorch time for viscosity to rise two units above M_L. The curing times t_{10}, t_{50}, and t_{90} correspond to the times at which 10, 50 and 90% of curing have already taken place, respectively. Torques values at t_{s2} (S' at t_{s2}), t_{10} (S' at t_{10}), t_{50} (S' at t_{50}), and t_{90} (S' at t_{90}) are also reported in the table. M_L values in Table 5 agree with MV data given in Table 4, indicating that all compounds have similar processability. Since the surface area of Ac–ZnO and trial composite ZnO materials are similar (Table 1), compounds prepared with these materials have higher M_H values compared to the TC1 compound due to their expected higher mechanical properties. A similar trend has been observed by Thaptong *et al*. [17]. The t_{s2} values related to the scorch time are in agreement with the t_5 values in Mooney data (Table 4). *CRI* values of the control and trial compounds are

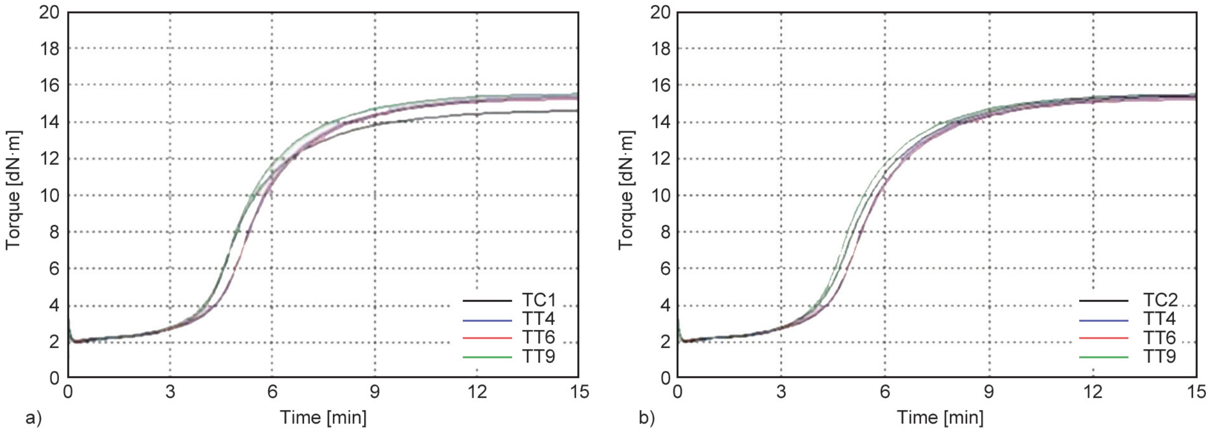

Figure 5. MDR graphs of the trial compounds compared to a) TC1 and b) TC2.

Table 5. MDR results.

MDR (160 °C)	Unit	Compound code				
		TC1	TC2	TT4	TT6	TT9
M_L	dN·m	2.01±0.05	1.99±0.02	2.03±0.01	2.05±0.05	2.03±0.04
M_H	dN·m	14.74±0.29	15.33±0.22	15.31±0.05	15.30±0.08	15.23±0.26
$M_H - M_L$	d·Nm	12.73±0.24	13.33±0.25	13.28±0.05	13.25±0.16	13.20±0.23
CRI	%/min	24.53±1.58	24.55±0.78	25.09±1.58	25.23±1.33	25.28±0.49
t_{s2}	min	3.97±0.12	4.14±0.08	4.28±0.17	4.22±0.16	4.02±0.02
t_{10}	min	3.54±0.09	3.70±0.07	3.85±0.15	3.80±0.14	3.61±0.02
t_{50}	min	4.94±0.11	5.34±0.09	5.38±0.24	5.35±0.22	5.06±0.02
t_{90}	min	8.15±0.24	8.22±0.12	8.27±0.42	8.19±0.36	7.97±0.17
S' at t_{s2}	dN·m	4.02±0.06	4.00±0.03	4.04±0.01	4.05±0.05	4.04±0.05
S' at t_{10}	dN·m	3.28±0.08	3.33±0.01	3.35±0.02	3.37±0.05	3.35±0.07
S' at t_{50}	dN·m	8.37±0.17	8.67±0.10	8.67±0.02	8.67±0.02	8.64±0.15
S' at t_{90}	dN·m	13.47±0.26	14.00±0.20	13.98±0.05	13.97±0.07	13.90±0.23

very similar (Table 5), as seen from the MDR curves' slopes (Figure 5). The average values of cure times and torque values of all the compounds in Table 5 are close to each other within the given standard deviations. Thus, it can be concluded that the composite ZnO materials provide similar cure properties as compared to control materials, WS–ZnO and Ac–ZnO.

3.3. Tensile and hardness properties

Tensile properties of the control and trial compounds are determined, and average values for the three lots are reported. Tensile strength and elongation at break data for unaged and aged samples are shown in Figure 6 and Figure 7. As can be seen from the data, the unaged values for tensile strength are comparable for all the compounds when standard deviations (±2.80) are considered, indicating that composite ZnO materials do not affect this property. Similar results have been emphasized by Thaptong *et al*. [17]. All compounds show similar thermal aging behavior as well. Similar behavior is observed for elongation at break data; samples having higher tensile strength have lower elongation as expected.

Modulus data, namely stress values at 100% (M100) and 300% (M300) elongation, are shown in Figure 8. Upon aging, all compounds exhibit increased modulus data, which can be explained by continuing the cross-linking. Thus, increased crosslink density restricts polymer chain mobility and increases the modulus values. Data shown in Figure 9 indicate that all compounds have similar hardness levels initially, and by aging, hardness increases as expected. Up to 48 h aging, due to the increased crosslink density,

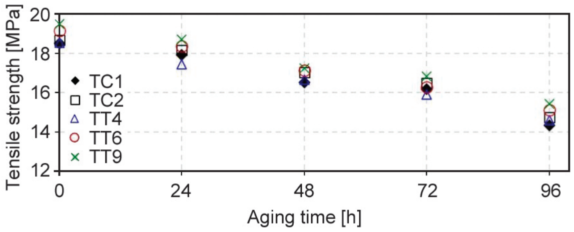

Figure 6. Change of tensile strength upon aging at room temperature.

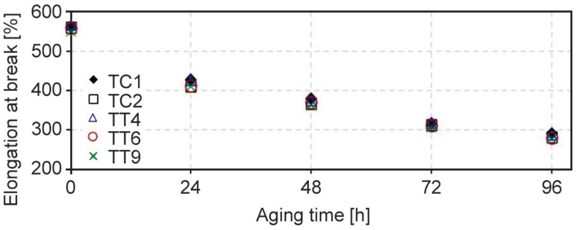

Figure 7. Change of elongation at break upon aging at room temperature.

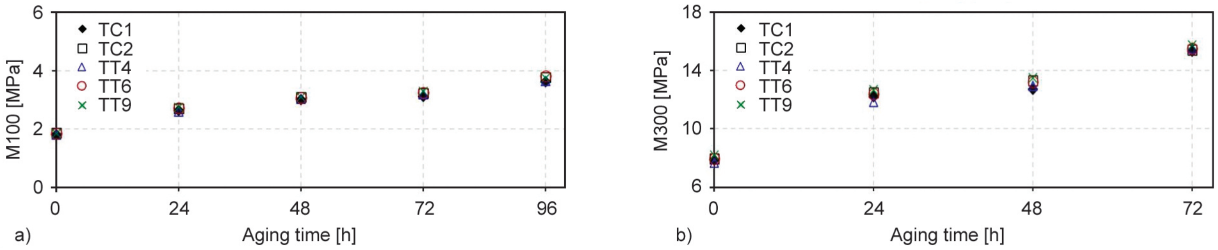

Figure 8. Change of a) M100 and b) M300 modulus upon aging at room temperature.

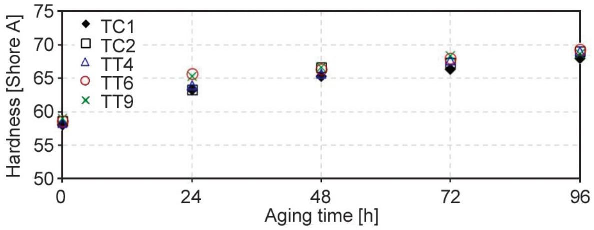

Figure 9. Change of hardness upon aging at room temperature.

hardness increase is more prominent, which slows down at more extended aging periods.

The retention data calculated using Equation (2) are given in Table 6 and show the loss/gain in the properties by thermal aging. As seen from the table, at the longest aging time (96 h), loss in tensile strength is 23 and 21% for control compounds TC1 and TC2, while it is 22, 19, and 17% for trial compounds TT4, TT6, and TT9, respectively. Similarly, loss in elongation is 48 and 50% for control compounds TC1 and TC2, while 49, 50, and 50% for trial compounds TT4, TT6, and TT9, respectively. These results clearly show that the aging behavior of trial compounds is very similar to the control compounds. The gain in moduli supports the trend in tensile strength and elongation data. M100 values at the longest aging time reveal 99 and 101% gain in control compounds TC1 and TC2, while the gain is 100, 106, and 102% for the trial compounds TT4, TT6, and TT9, respectively. Similarly, M300 values indicate a gain of 94 and 94% in control compounds TC1 and TC2, while the gain is 102, 95, and 92% for the trial compounds TT4, TT6, and TT9, respectively, for this aging time. Since 300% elongation could not be achieved for the 96 h aged compounds, gain values could not be calculated due to the lack of M300 data, but 72 h data support the above findings.

Table 6. Retention of tensile, elongation, and modulus values upon aging.

Retention	Aging time [h]	Compound code				
		TC1	TC2	TT4	TT6	TT9
Tensile strength	0	100	100	100	100	100
	24	97	97	93	98	100
	48	89	91	89	92	92
	72	87	88	85	87	90
	96	77	79	78	81	83
Elongation at break	0	100	100	100	100	100
	24	76	73	75	74	74
	48	68	66	66	66	66
	72	57	56	56	56	56
	96	52	50	51	50	50
M100	0	100	100	100	100	100
	24	144	145	142	147	147
	48	165	165	167	166	167
	72	172	173	175	175	177
	96	199	201	200	206	202
M300	0	100	100	100	100	100
	24	155	157	154	156	155
	48	162	167	168	167	165
	72	194	194	202	195	192

3.4. Tear properties

Results of the tear B and C tests are given in Table 7. Four tests are carried out for each lot, and lot averages are tabulated. The data for tear test B, related to the resistance of the compound to crack propagation, show that compounds with composite ZnO materials having high ZnO content (TT6 and TT9) have similar behavior as the control compound having Ac-ZnO. This can be explained by the large surface area, namely the small particle size of the ZnO powders. These results agree with the tensile strength and MDR data (M_H). The trial compound TT4 prepared with C–$ZnO_{40:60}$, having the lowest ZnO and comparatively lower surface area among the trial materials, behaves similarly to the control compound TC1 rather than TC2. The variation in tear B test data can also be attributed to the notch in the test samples. Tear test C results, on the other hand, are similar for all control and trial compounds as expected, and they all have similar resistance to crack initiation.

3.5. Flexometer

The heat generation of the compounds operated under constant pressure is measured with the flexometer device, and the results are given in Table 8. The table also includes compression set data determined by the same instrument. Both heat build-up and compression set results show that trial compounds (TT6 and TT9)

Table 7. Tear strength [N/mm] data of the compounds.

Tear test	Compound code				
	TC1	TC2	TT4	TT6	TT9
B	82.33±2.52	90.63±1.94	82.78±1.50	89.67±1.15	92.50±2.12
C	112.00±1.00	112.50±0.35	111.67±1.04	113.67±0.58	113.50±0.71

Table 8. Flexometer test results.

Property	Unit	Compound code				
		TC1	TC2	TT4	TT6	TT9
Heat build-up	°C	149.28±2.27	146.68±1.75	149.30±2.82	146.09±2.28	145.68±1.61
Compression set	%	7.37±1.42	7.04±0.14	8.00±0.85	6.82±0.59	6.56±0.05

perform similarly to the control compound TC2, indicating that their resistance to heat generation and permanent deformation are similar. The performance of trial compound TT4 is similar to control compound TC1 rather than TC2 due to composite ZnO material C–ZnO$_{40:60}$'s properties. This data confirms the tensile strength, MDR, and tear strength results.

3.6. Crosslink density

Crosslink reactions are essential since they affect the properties and performance of rubber compounds. To find the crosslink densities of the compounds, swelling experiments are carried out, and results are tabulated in Table 9. Swelling ratios (Q) are determined by the swelling test in toluene, and using the Flory Rehner equation (Equations (5)–(7)), crosslink densities (V_c) and average molecular weights between crosslinks (M_c) are calculated. All control and trial compounds exhibit similar performance in the swelling test ; hence, they have the same barrier ability to toluene uptake,a resulting in similar crosslink densities An inverse relationship exists between crosslink density and average molecular weight between crosslinks. Higher V_c value denotes less flexible rubber chain in the network and allows lower toluene uptake.

4. Conclusions

Within the scope of this study, composite ZnO materials are used as activators in SBR/BR based rubber compounds. Their performance is compared with control compounds with conventional white seal ZnO and active ZnO. The goal is to reduce ZnO content in rubber formulations due to ecological and economic concerns. The trial composite ZnO materials that are commercially available are produced by coating ZnO particles on precipitated $CaCO_3$, and three types are used with ZnO:$CaCO_3$ ratios of 40:60, 60:40, and 90:10. Laboratory scale compounds are prepared with control and trial ZnO materials, and all compounds are evaluated to determine their curing and physico-mechanical properties. Mooney viscosity data show that trial compounds prepared with composite ZnO materials have similar processability to the control compounds prepared with conventional ZnO materials; they can even reduce the risk of scorching. MDR results reveal that the cure properties of both control and trial compounds are similar. Mechanical properties are determined by tensile tests, hardness measurements, and tear tests, and a flexometer is used to determine heat build-up and compression set. Tensile strength and elongation at break values are comparable for all the compounds when standard deviations are considered, indicating that composite ZnO materials do not affect these properties. Thermal aging studies at 100 °C reveal that the aging behavior of the compounds is also similar. Regarding mechanical properties, modulus values need to be considered rather than tensile strength values in rubber technology. Thus, the moduli, namely the stress values at 100% (M100) and 300% (M300) elongation, are also compared for the trial and control compounds. Shore A hardness data indicate that all compounds have similar hardness values. Tear tests are carried out to determine the resistance of the compounds to crack propagation (tear B) and crack initiation (tear C). In the tear B test, trial compounds with composite materials with 60 and 90% ZnO perform similarly to the control compound with active ZnO. On the other hand, the trial compound with composite material with 40% ZnO performs similarly to the control compound with white seal ZnO, which can be explained by its lowest surface area among the trial

Table 9. Crosslink density test results.

Property	Unit	Compound code				
		TC1	TC2	TT4	TT6	TT9
Q	%	2.10±0.04	2.05±0.01	2.11±0.02	2.04±0.01	1.96±0.06
V_c ($\cdot 10^{-5}$)	mol/g	7.16±0.03	7.23±0.02	7.13±0.02	7.23±0.01	7.38±0.01
M_c ($\cdot 10^{3}$)	g/mol	6.98±0.03	6.92±0.02	7.01±0.03	6.92±0.02	6.77±0.02

materials. Tear test C results are similar for all control and trial compounds, as expected from tensile strength data, and they all have similar resistance to crack initiation. Flexometer data giving the compounds' heat build-up and compression set performance reveal a similar trend as observed in the tear B test. Crosslink densities of the compounds are determined by swelling tests and calculations according to Flory-Rehner's theory. The results indicate that all compounds have the same barrier ability to toluene uptake and reveal similar crosslink densities. Considering all data for curing and physico-mechanical properties of the control and trial compounds, it can be concluded that composite ZnO materials are possible alternatives to conventional ZnO materials, and they can be preferred due to both environmental and economic concerns since they provide less ZnO usage in rubber compounds.

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