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To cite this article: C Börüban Bingöl *et al* 2024 *J. Phys.: Conf. Ser.* **2692** 012010

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Wear Behavior of SBR/BR Compounds Including Different ZnO Types

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Abstract. Zinc complexes have considerable impact on human health and environment especially on aquatic wildlife. One of the main sources of zinc release to the environment is worn rubber particles from tires. Environmental footprint of zinc oxide during production, ecological and economical concerns have prompted the researchers to reduce its use in rubber formulations. Rubber compounds used in the tread, which is the part of the tire in contact with road, must have high wear resistance. In order to determine the wear performance, laboratory wear tests need to be carried out prior to road tests. In the present study, a tread compound recipe based on SBR/BR blend is designed using conventional and composite ZnO materials having CaCO₃ as core. Wear behavior of the control and trial compounds prepared with these ZnO materials are tested at room temperature by using Lambourn test instrument. Wear rates and wear energies are calculated using the weight loss data at different slip rates. Based on the wear performance of the trial compounds as well as their cure and mechanical properties, it can be concluded that composite ZnO materials are good candidates to replace the conventional activators in rubber compounds to provide environmental and economic gains.

1. Introduction

A tire, a product that has complex structure and composition, is used to transfer motion from engine to the road. Tires have rubber, steel belts, textile overlays, reinforcing fillers, various additives (e.g., antiaging agents, stabilizers), and a vulcanizing system (e.g., sulfur, zinc oxide) [1, 2]. The rubber part of a tire is used to increase the fatigue and tear resistance and butadiene rubber and styrene butadiene rubber have impacts on rolling resistance, wear, and traction performance [3]. Reinforcing fillers are added to the rubber to improve its mechanical strength, hardness, and wear resistance [2]. Vulcanization reagents, including sulfur, fatty acids, activators (ZnO), and accelerators serve to achieve crosslinking process which primarily creates single, bisulfide, and polysulfide bonds for durability [4]. ZnO is believed to be an efficient activator that plays a prominent role in the first steps of vulcanization to improve the kinetics of the curing process and promote the short sulfide cross-link formation [5]. During use, 10-30 % of a tire tread is worn out and rubber particles that are also called as tire and road wear particles (TRWPs) are released into the environment [6, 7]. TRWPs are generated mechanically due to the shear forces between tire tread and road surface [8]. This phenomenon can be explained as thermomechanical process with local hot spots on tire surface reaching high temperature and causing some volatile content evaporation [9]. The wear factor, the total amount of material lost per kilometer,



depends on four parameters; (i) tire characteristics such as tread depth, construction, pressure, contact patch area, (ii) vehicle characteristics such as weight, load distribution, braking system, (iii) road surface with texture pattern, porosity, road material type, and (iv) vehicle operation such as speed, acceleration [10]. Following their generation, while some part of TRWPs is suspended in air as particulate matter, big part of them is deposited on roadside and find their way into surface water [11, 12]. Considering the usage amount of ZnO in a tread compound, it can be said that the wear-induced particles released into the environment also contain zinc complexes having high risk to enter aquatic environments through wastewater streams [13, 14]. Due to the zinc toxicity classification and its effects on aquatic wildlife, studies have increased to adjust the quantity of zinc entering the environment and investigate its ecological impact [15]. In the present study, it is aimed to decrease the ZnO content in a passenger tire tread compound by using composite ZnO materials in place of the conventional ones, without sacrificing from the wear performance and provide environmental and economic gains. The findings on SBR/BR compound support the data reported for the use of composite ZnO materials in SBR [16] and SSBR compounds [17].

2. Experimental

2.1. Materials

Raw materials are used as received in compound preparation. SBR with 35 % bonded styrene and 26.4 % vinyl content with 75 ML (1+4) Mooney viscosity at 100 °C and BR with a viscosity of 62 ML (1+4) Mooney at 100 °C are used as polymers. N234 grade carbon black is used as reinforcing filler with the STSA specific surface area of 112 m²/g. White seal zinc oxide (WS-ZnO), active zinc oxide (Ac-ZnO), and composite ZnO materials produced by via wet process by coating ZnO particles (20-40 nm) on precipitated CaCO₃ particles (50-200 nm) as core with ratios of 40:60 (C-ZnO_{40:60}), 60:40 (C-ZnO_{60:40}), and 90:10 (C-ZnO_{90:10}) are used as activators. Properties of the different types of ZnO used in this study are given in Table 1.

Table 1. Properties of different types of ZnO

Type	Specific surface area ^a , BET (m ² /g)	CaCO ₃ (wt. %)	ZnO (wt. %)
WS-ZnO	5.1	-	99.7
Ac-ZnO	49.2	-	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

^aTotal surface area of both coat and core material

2.2. Compound processing

SBR/BR based rubber compound is prepared in an internal mixer with 1.2 L capacity, according to the formulation adapted from literature [18] and the recipe is given in Table 2. The produced compound is milled several times at 70 °C to achieve a thickness of 2.2 mm using a laboratory mill and allowed to cool at room temperature.

Table 2. Formulation of SBR/BR compounds in parts per hundred of rubber (phr)

Raw 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
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

2.3. Characterization of SBR/BR vulcanizates

2.3.1. Cure characteristics

Mooney tests are performed by Mooney viscometer instrument having operating temperature 25-200 °C and rotor speed 0.1-20 rpm to gain information about the viscosity, scorch characteristics, and processability of the green compounds. The tests are carried out at 130 °C according to ASTM D1646. Cure properties are tested by Moving Die Rheometer (MDR, operating conditions: 25-200 °C and 1.667 Hz) under isothermal test conditions with constant strain and frequency according to ASTM D5289. Test conditions of 160 °C and 15 min are used. 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):

$$CRI = \frac{100}{(t_{90} - t_{s2})} \quad (1)$$

2.3.2. Mechanical properties

Tensile test specimens are cured for 15 min at 345 kN pressure in a laboratory press at 160 °C. Tensile Tester is used at a crosshead speed of 300 mm/min at room temperature (23±2 °C) to determine the tensile properties according to ASTM D412. Tensile strength, elongation at break, and modulus values (stress values at 100 %, 200 %, and 300 % strain) are reported. Hardness tests are also carried out by Shore A hardness instrument using the tensile sheets as stacked to proper thickness.

Resistance to abrasive wear of the compound influences the tread life and is determined by abrasion test given by ISO23337:2007 method using Lambourn Abrasion Tester. The Lambourn test is a simple

laboratory wear test that is performed on a wheel-shaped specimen against an abrasive wheel using a constant normal load (30 N) and constant slip rate (1-20 %). The test period is 5 min, and the sample temperature is monitored during the test. The weight loss of each compound is then simply compared to determine the wear performance grade at room temperature and linear wear rate, ν (thickness of rubber that is abraded away, in mm, per 1000 km of distance travelled) is calculated according to equation (2) for each wear test. Linear wear energy (ϵW) is the friction energy on the rubber surface caused by slippage between tread compound and road surface and is calculated according to equation (3) under different slip rate test conditions.

$$\nu = \frac{\Delta W \times (1000^4 \times 60)}{D_r \times D_d \times t \times D \times S_w \times \pi^2 \times S_d} \quad (2)$$

$$\epsilon W = \frac{(F_y - F_0) \times |Slip\ ratio\ (\%)|}{S_w \times S_d \times \pi} \quad (3)$$

where; ΔW (g): weight loss, t (s): testing time, D (g/cm³): density of compound, S_d (mm): sample diameter, S_w (mm): sample width, D_d (mm): abrasive wheel diameter, D_r (rpm): abrasive wheel speed, F_y (N): average force in the vertical direction exerted on the sample wheel during the test and F_0 (N): force in the horizontal direction which is equal to zero [19].

3. Result and discussion

3.1. Evaluation of cure properties

Mooney viscosity and MDR test results are given in Table 3. Mooney viscosity at 4 min test time after 1 min pre-heating, ML (1+4), are similar for all compounds. Scorch times determined by both Mooney (t_5) and MDR (t_{s2}) tests are in agreement with each other and similar for all compounds. Cure times (t_{90}) determined by MDR reveal that all compounds exhibit similar cure behavior. Torque difference ($M_H - M_L$) representing the extent of crosslink density are similar for all compounds. Cure rate index (CRI) given in equation (1) are very similar for control and trial compounds. Thus, it can be noted that composite ZnO materials have similar effects on cure properties of the compounds.

Table 3. Cure properties of the compounds

Properties	Unit	Compound Code				
		TC1	TC2	TT4	TT6	TT9
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
$M_H - M_L$	dNm	12.73±0.24	13.33±0.25	13.28±0.05	13.25±0.16	13.20±0.23
t_{s2}	min	3.97±0.12	4.14±0.08	4.28±0.17	4.22±0.16	4.02±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
CRI	-	24.53±1.58	24.55±0.78	25.09±1.58	25.23±1.33	25.28±0.49

3.2. Evaluation of mechanical properties

Mechanical properties of cured compounds are given in Table 4. Hardness, tensile strength, elongation at break, modulus values namely stress values at 100 % strain (M100), 200 % strain (M200), and 300 % strain (M300) are reported. Shore A hardness data indicate that all compounds have similar hardness values. When standard deviations are taken into account, tensile strength and elongation at break values are comparable for all compounds, demonstrating that composite ZnO materials have no adverse effect on these parameters. For the trial and control compounds, the moduli values M100, M200, and M300 are also comparable.

Table 4. Hardness and tensile test results

Properties	Unit	Compound Code				
		TC1	TC2	TT4	TT6	TT9
Hardness	Shore A	62.00±0.01	62.00±0.01	63.00±0.01	63.99±0.01	63.00±0.01
Tensile strength	MPa	18.14±2.82	19.05±0.93	18.42±3.34	18.81±4.28	19.04±5.22
Elongation at break	%	475.82±4.42	473.45±3.95	486.66±6.21	468.03±8.15	443.25±1.68
M100	MPa	2.13±0.36	2.25±0.07	2.19±0.74	2.31±0.19	2.34±0.34
M200	MPa	5.36±1.47	5.67±0.85	5.44±1.79	5.81±0.97	5.98±1.01
M300	MPa	9.93±2.48	10.49±0.96	10.05±2.75	10.72±2.36	10.93±0.04

One of the most important characteristics that determine the life of tire is wear resistance. Many test set-ups have been developed to test this property, and in this study, Lambourn abrasion tester is used. Tire wear is widely considered as a function of both abrasability and wear energy. The wear of rubber is not a material property, it is a system property, thus the wear conditions affect the results. Therefore, the wear tests are conducted at different slip rates to determine the wear properties of the studied compounds. A constant nominal load (30 N) is applied during the test and slip rates are chosen as 1 %, 3 %, 5 %, 7 %, 10 %, 12 %, 15 %, and 20 % to simulate driving and braking conditions from softer to harsher ones. The results for wear rates and wear energies are plotted against slip rate and given in Figure 1 and Figure 2, respectively. The data for 15 % slip rate is tabulated in Table 5. For all compounds, wear rate does not change at softer conditions (1-7 % slip rates) but increases at harsher conditions namely at higher slip rates as expected (Figure 1). Wear energy changes linearly with respect to the slip rate, and the rate of increase is similar for all compounds as seen from the slopes of the curves in Figure 2. The data in Table 5 indicate that all control and trial compounds have similar wear energies. Wear rates, on the other hand, are slightly higher for WS-ZnO and C-ZnO_{40:60} compared to the others which can be attributed to their lower surface areas.

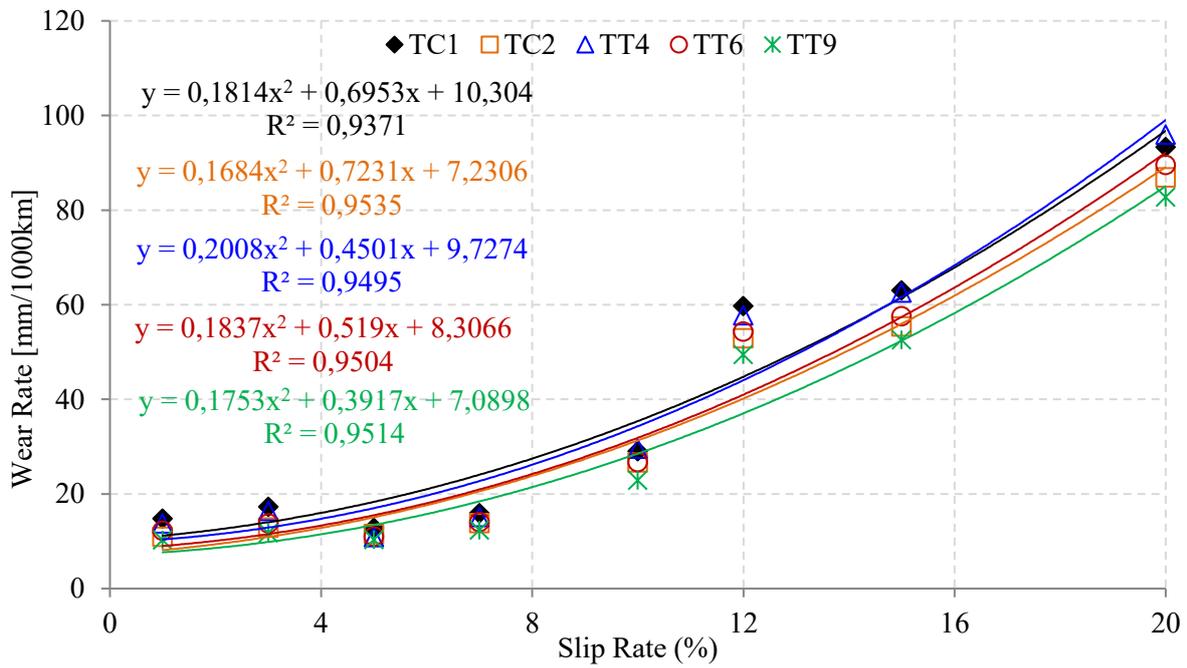


Figure 1. Variation of wear rate with respect to slip rate

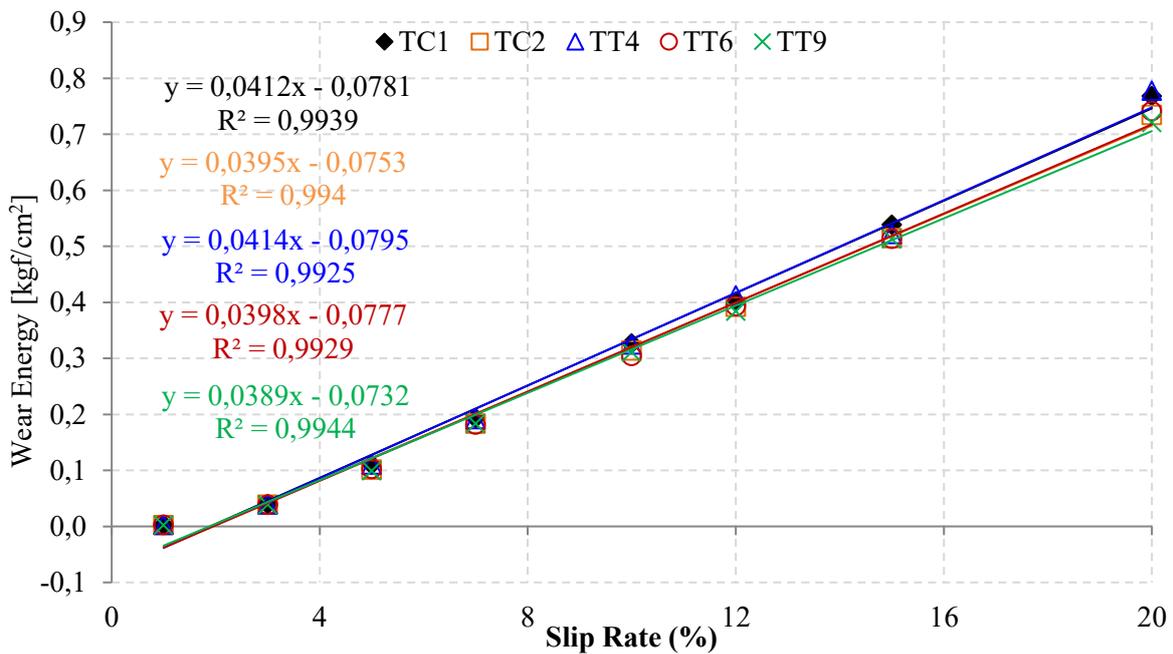


Figure 2. Variation of wear energy with respect to slip rate

Table 5. Wear results at 15 % slip rate

Compound code	Wheel diameter (mm)	Weight loss (g)	Sample temp. (°C)	Wear rate (mm/1000km)	Wear energy (kgf/cm ²)
TC1	69.28	0.11	26.83	63.06	0.54
TC2	69.25	0.09	27.38	55.43	0.51
TT4	69.24	0.10	27.15	62.57	0.52
TT6	69.25	0.08	27.27	57.59	0.51
TT9	69.25	0.08	26.97	52.54	0.51

4. Conclusion

In the present study, a tread compound recipe based on SBR/BR blend was designed by using composite ZnO materials having CaCO₃ as core, in order to decrease ZnO content in the compound. The cure behavior, mechanical properties, and wear performance of the trial compounds were compared with the control compounds having conventional ZnO types. It was observed that trial compounds had similar cure behavior as the control ones and the composite ZnO materials had no adverse effect on the mechanical properties. The wear performances of the compounds were determined by measuring the wear loss in a Lambourn test instrument and wear energies and wear rates were calculated. The results revealed that both control and trial compounds had similar wear performance. Thus, it can be concluded that composite ZnO materials are expected to be candidates to replace the conventional activators in rubber compounds to provide environmental and economic gains.

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