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Characterization of Natural Rubber, Styrene Butadiene Rubber, and Nitrile Butadiene Rubber Monomer Blend Composites Loaded with Zinc Stearate to Be Used in the Solid Tire Industry

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Abstract: Vulcanization is an important step in the manufacture of solid tires in which the crosslinking process occurs. In vulcanization, the materials commonly used as activators and coactivators are ZnO and stearic acid, respectively. In this research, ZnO and stearic acid were replaced with zinc stearate to improve the characteristics of vulcanized rubber. Zinc stearate was applied in four formulas with a composition of 5 to 9 phr. A formula that is often used in the rubber industry was used as a comparison, and ZnO and stearic acid of 5 phr and 2.5 phr, respectively, were applied. The rubber compound for solid tire production was developed using an open mill at a compounding temperature of 45 °C ± 5 °C. The vulcanization process of developing the rubber compound into vulcanized rubber was carried out at 150 °C for 20 min. Rubber compound test results showed that the use of zinc stearate at a ratio of 8 phr accelerated the curing time (t_{90}) between 58.3% and 69%, the scorch time (ts2) between 22.4% and 95.5%, and the torque delta (Δ_s) between 17.67 and 24.21 kg-cm. In addition, the vulcanized rubber mechanical properties test results for the compression set parameter increased between 28.6% and 57.1%. Scan results with SEM–EDS showed that using ZS could improve the homogeneous distribution of the material in the vulcanized matrix of solid tire rubber.

Keywords: curing time; rubber compound; rubber vulcanizate; solid tire; zinc stearate

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1. Introduction

Natural rubber (NR) with a cis-1,4-polyisoprene structure has high tensile strength, elasticity, and dynamics, and it is widely used for various purposes, including the manufacture of solid tires [1,2]. Solid tires in the manufacturing process are inseparable from natural rubber, synthetic rubber, activators, coactivators, fillers, softeners, antioxidants, accelerators, vulcanization agents, and other additives. Zinc oxide (ZnO) and stearic acid (SA) are reactive substances that easily diffuse into the rubber matrix. These two materials are widely used in the rubber industry and have an important role in the rubber vulcanization process [3]. The annual global production of ZnO is more than 25 million tons, and more than 50% of it is used for activators in the rubber industry [4].

In addition, accelerators in rubber vulcanization are widely used from elements of thiazole, sulfenamide, thiuram, dithiocarbamate, and guanidine [4]. This material plays an important role in the vulcanization process as it forms cross-links in the rubber matrix. Cross-links are formed in the rubber matrix due to the presence of elemental sulfur as a vulcanizing agent [5,6]. Vulcanization is a chemical reaction process that forms rubber products [7]. The vulcanizing agent serves to link polymer chains through cross-linking reactions.

ZnO and SA in rubber compounds are used in various ratios, according to the rubber product produced [8]. According to Habeeb et al. [9], using ZnO with a ratio of 2 phr can increase the tensile strength and hardness of vulcanized rubber before and after aging. Torani et al. [10] reported that using ZnO 3 phr can improve the mechanical properties of a rubber vulcanizate. Ján Kruželák et al. [11] used ZnO 3 phr and stearin 2 phr to study NR rubber-based magnetic composites. Poh and Jaffri. [12] used ZnO 5 and stearic acid 2 in an abrasion resistance study of two levels of epoxidized NR (ENR 25 and ENR 50). Ismail and Chung [13] used ZnO 5 phr and SA 3 phr in their study on making rubber compounds using filler from rice husk ash. Both ZnO and SA at various ratios have been widely used to manufacture solid tires. Nasruddin and Bondan [14] used ZnO 4.85 phr and stearic acid 2.15 phr to manufacture solid tires for forklifts. Wilaiwong and Smitthipong [15] have studied the effect of ZnO on tire rubber compounds' physical and mechanical properties.

The use of zinc stearate (ZS) as an activator and coactivator in various rubber industries and by researchers has not been widely studied. This study used zinc stearate [$Zn(C_{18}H_{35}O_2)_2$] for the development of rubber composites into solid tires. ZnO as an activator and SA as a coactivator in the vulcanization process the accelerator's performance to form cross-links [16,17]. The advantages of ZS in the manufacture of rubber compounds are accelerating curing time and scorch time, increasing the density of vulcanizate cross-links, and improving the mechanical properties of the vulcanizate. In addition, the use of ZS for the manufacture of rubber compounds can minimize the excess ratio of ZnO and stearic acid [18]. Cross-links density was defined and proposed by Flory in the 1950s based on measurements of swelling equilibrium [19]. The use of ZS in this study aims to accelerate the curing time (t_{90}), score time (ts_2), and delta torque (Δs) in the manufacture of a rubber vulcanizate. In addition, using ZS improves the additives' distribution into the rubber vulcanization matrix.

2. Materials and Methods

2.1. Materials

The materials used included natural rubber (NR) (SIR-20, place of origin: PT Mardec Musi Lestari, Indonesia). They also included styrene butadiene rubber (SBR-1502) specific gravity of 1.6–1.7 g/cm^3, hardness: 70–80 Shore A, tensile strength: 2–2.5 Mpa, and elongation at break: 300–400% (place of origin: China); nitrile butadiene rubber (NBR-2665, place of origin: Russian Federation); zinc oxide (ZnO) with a purity of 99.7% (place of origin: Hebei, China); and stearic acid (SA) Mf: $C_{18}H_{36}O_2$ with a purity of 99% (place of origin: China). Zinc stearate (ZS) with a moisture content of 0.2–1%, 118, a specific gravity of 1.1 g/cm^3, the fatty acid content of 0.0–0.3%, and a melting point of 125 °C was also used [20] (ZS place of origin: Agency for the Assessment and Application of Technology, Indonesia (BPPT)). Kaolin 400 mesh (place of origin: Tanjung Pandan Belitung, Indonesia); glycol (PEG-4000) with a purity of 99% (place of origin: China); carbon black N330 with a purity of 99.9% (place of origin: Henan, China); $CaCO_3$ 400 mesh (place of origin: Indonesia); silica oxide (SiO_2) with a purity of 96.0% (place of origin: Indonesia); resin coumarone indene Mf: C_{90}, Cas no.: 63393-89-5 with a softening point of 80–110 °C (place of origin: China); white solid paraffin wax (CnH_2n + 2.IOCL) with a melting point of 63 (±2) degree Celsius (area of origin: China); dioctyl Phthalate (DOP) oil liquid plasticizer, Mf: $C_{19}H_{33}C_{l5}O_2$, Einecs no.: 247-864-7 (place of origin: Zhejiang, China); antioksidan BHT (2,6-di-tert-butyl-4-methyl fenol), $C_{15}H_{24O}$, berat molekul 220.36, Mf: $C_{15}H_{24O}$ (place of origin: China); N-Isopropyl-N′-phenyl-1,4-phenylenediamine (IPPD) chemical auxiliary agent rubber antioxidant, Einecs no.: 202-969-7, Mf: $C_{15}H_{18}N_2$ (area of origin: Jiangsu, China); rubber accelerator tetramethyl thiuram disulfide (TMTD), Einecs no.: 205-286-2 with a purity of 96%; Mf: $C_6H_{12}N_2S_4$ purity of 98% min (place of origin: Jiangsu, China); diphenyl guanidine (DPG) MF: $C_{13}H_{13}N_3$, Einecs no.: 203-002-1 with a density of 1.08–1.19 and a purity of 99% (place of origin: China); rubber accelerator CBS/CZ N-Cyclohexyl-2-benzothiazole sulfenamide, Mf: $C_{13}H_{16}N_2S_2$, Einecs no.: 202-411-2 (place of origin:

Shandong, China); and rubber vulcanizer sulfur/OT20 used in tire sulfur with a purity of 99% (place of origin: Indonesia) were all used in this study.

2.2. Experimental Procedure

This research was conducted using five formulas to compare with the VBP-01 formula using ZnO 5 phr (activator) and stearic acid 2.5 phr (coactivator). ZS as the research object consisted of four formulas with the respective comparisons of VBP-02 ZS 6 phr, VBP-03 ZS 7 phr, VBP-04 ZS 8 phr, and VBP-05 ZS 9 phr. The experiment was carried out three times with the ratio of each material, as shown in Table 1.

Table 1. Rubber compound formulations.

Material	Ratio Formula *				
	VBP-01	**VBP-02**	**VBP-03**	**VBP-04**	**VBP-05**
NR	60.00	60.00	60.00	60.00	60.00
SBR	15.00	15.00	15.00	15.00	15.00
NBR	15.00	15.00	15.00	15.00	15.00
ZnO	5.00	-	-	-	-
SA	2.50	-	-	-	-
ZS	0.00	6.00	7.00	8.00	9.00
PEG-4000	4.00	4.00	4.00	4.00	4.00
Black carbon	60.00	60.00	60.00	60.00	60.00
$CaCO_3$	10.00	10.00	10.00	10.00	10.00
Kaolin	10.00	10.00	10.00	10.00	10.00
Silica	10.00	10.00	10.00	10.00	10.00
Coumarone resin	1.25	1.25	1.25	1.25	1.25
Paraffin wax	1.25	1.25	1.25	1.25	1.25
DOP	8.00	8.00	8.00	8.00	8.00
BHT	1.75	1.75	1.75	1.75	1.75
IPPD	1.75	1.75	1.75	1.75	1.75
TMTD	1.00	1.00	1.00	1.00	1.00
DPG	1.00	1.00	1.00	1.00	1.00
CBS	1.00	1.00	1.00	1.00	1.00
Sulfur	2.50	2.50	2.50	2.50	2.50

Annotation: VBP: vulcanized solid rubber tire; * sample ratio in parts per hundred of rubber (phr).

2.3. Mastication and Compounding

This study used five formulas consisting of VBP-01 (comparison formula), VBP-02, VBP-03, VBP-04, and VBP-05. The ratio of ingredients for each formula is shown in Table 1. The NR of all formulas (VBP-01 to VBP-05) was chewed using an open mill machine (tow-roller open rubber mixing mill model XK) until it was soft (3 min). Furthermore, synthetic rubber (SBR and NBR) was added while continuing to grind until it was homogeneous (3 min). VBP-01 as a control formula was used while continuing to grind and adding ZnO and SA until it was homogeneous (2 min). For formulas VBP-02 to VBP-05, while continuing to grind, ZS was added with the ratio of each ingredient, as shown in Table 1 (2 min). Furthermore, for all formulas ranging from VBP-01 to VBP-05, carbon black, $CaCO_3$, kaolin, silica, fly ash, DOP, PEG-4000, indene coumarone resin, paraffin wax, BHT, and IPPD were added until it was homogeneous in the rubber matrix (4 min). After all the ingredients were homogeneous in the rubber matrix, and while continuing to grind, we added TMTD, DPG, CBS, and sulfur until it was homogeneous (3 min). The result of rubber mastication and compounding is referred to as rubber compound. Vulcanization of rubber compound into vulcanized rubber tires was carried out at 150 °C for 18 min.

2.4. Testing Method

The ripening of the rubber compound was tested at a temperature of 150 ºC using Monsanto's Moving Die Rheometer (MDR 2000 Alpha Technologies) [21], according to ISO 3417: 2008. The test parameters were maximum torque (S' max), minimum torque (S' min), opt cure time (t_{90}), and scorch time (ts_2). The mechanical properties of rubber vulcanizates were tested before and after aging, including specific gravity (according to ASTM D.297-15), hardness (according to ASTM-D.2240-15), and abrasion resistance (according to D.5963-04 (ra2015)), with compression set at 25% at 70 °C for 72 h D.395-16e1, tensile strength (isotropic) D.412.16, tear strength D.624-00 (ra2012), and elongation at break D.412.16. Pores and elements were characterized in vulcanized rubber EDS using X-ray media emitted from the test object when bombarded by the SEM electron beam to identify the elemental composition of the test object on the surface being tested. It was captured by the detector so that its elements were known. Testing refers to the ASTM E 1508-98 method (E1508, 2003), ASTM E 1829-02 (ASTM, 2014), and ASTM E 986-97 (Ireland, 1997).

3. Results

3.1. Characteristics of Maturation of Rubber Compound

The results of the delta torque (Δ_S), curing time (t_{90}), and scorching time (ts_2) tests of the VBP-01 rubber compound using ZnO and SA as control formulas were higher than VBP-02 to VBP-05. The difference in the results of the delta torsion test was caused by the difference in the activity of ZnO and stearic acid (VBP-01) with ZS (VBP-02 to VBP-05) in the vulcanization process to accelerate the formation of cross-linking reactions. Increasing the ZS ratio sped up the reaction time of forming cross-links with polysulfide accelerators. ZnS, sulfur and a vulcanization accelerator accelerated the rubber molecule's cross-linking reaction. ZS in the vulcanization process on the rubber matrix was the first element directly involved in increasing the accelerator's performance, which formed cross-link reactions. According to Ikeda et al. [22], the reaction between ZnO and stearic acid speeds up the cross-linking reaction, which contains elemental sulfur in the rubber matrix. ZnO in the vulcanization process [23] stabilizes curing by activating sulfur vulcanization, increasing torque, and reducing drying time and scorching time [15].

Torsion delta describes the formation of cross-links during vulcanization. If the torque delta increases, the cross-links formed also increase. According to Smejda-Krzewicka et al. [24], the greater the torque increase, the more the cross-links density increases. Torsion delta is often used as a reference to determine crosslink density [25]. The density of the formed cross-links affected the molecular structure and mechanical properties of vulcanized rubber. Cross-link density affected hardness, abrasion resistance, permanent compression, and other mechanical properties. In addition, cross-link density affected torque delta, curing time, and scorching time. According to Zhao and Zhao [26], the density of cross-links affects the differences in the mechanical properties of vulcanized rubber.

Curing time shows the maturation time of rubber compounds up to 90% [27]. Short curing time in the vulcanization process is an option to determine production time. Using ZS in the vulcanization process of rubber compound into rubber vulcanizate from the test data accelerated the drying time (t_{90}) between 58.3% and 69%.

The scorch time test (ts_2) results for the VBP-01 formula were longer than the rubber compound using ZS. In addition, the use of ZS 7.00 phr (VBP-04) to 9.00 phr (VBP-05) in the vulcanization process accelerated the scorch time between 22.4% and 95.5% (Table 2). This happened because ZS can accelerate and complement each other during the vulcanization process [28,29]. According to Smejda-Krzewicka et al. [24], the vulcanization rate is affected by the ratio of ZnS added. The use of ZS from the results of this study increased the rate of vulcanization. This can be seen from the results of testing the characteristics of rubber compound ripening (Table 1).

Table 2. The characteristics of rubber compound ripening.

Curing Characteristic Rheometer, 150 °C	VBP-01	VBP-02	VBP-03	VBP-04	VBP-05
S* maximum, kg-cm	30.21	22.03	23.19	18.85	26.16
S* minimum, kg-cm	3.79	1.69	1.69	1.18	1.95
Delta torsion (Δs), kg-cm	26.45	20.34	21.50	17.67	24.21
Opt cure time (t_{90}), min;sec	9;12	2;53	2;56	2;51	3;50
Scorch time (ts_2), min;sec	1;07	0;05	0;07	0;52	0;46

3.2. Mechanical Properties of a Rubber Vulcanizate

3.2.1. Specific Gravity

The specific gravity of vulcanized rubber describes the density of space per cubic centimeter that is occupied by additives and fillers. Results from the VBP-01 specific gravity test were 1.234 g/cm^3 before aging and 1.232 g/cm^3 after aging. The specific gravity value of VBP-01 was higher than the specific gravity of VBP-02, but it was lower from VBP-03 to VBP-05. The specific gravity values of VBP-03 to VBP-05 before and after aging increased (Figure 1a) in direct proportion to the increase in the ZS ratio (Table 1). The increase in specific gravity was affected by an increase in the ZS ratio added to the rubber compound during compounding. ZS and DOP in the compounding process accelerated the stretching of the molecular structure of the NR mixture with synthetic rubber. The addition of plasticizers into the rubber matrix can increase the strain and mobility of polymer chains [30]. Stretching the molecular structure of the rubber mixture using DOP accelerated the distribution of additives and fillers into the rubber mixture matrix.

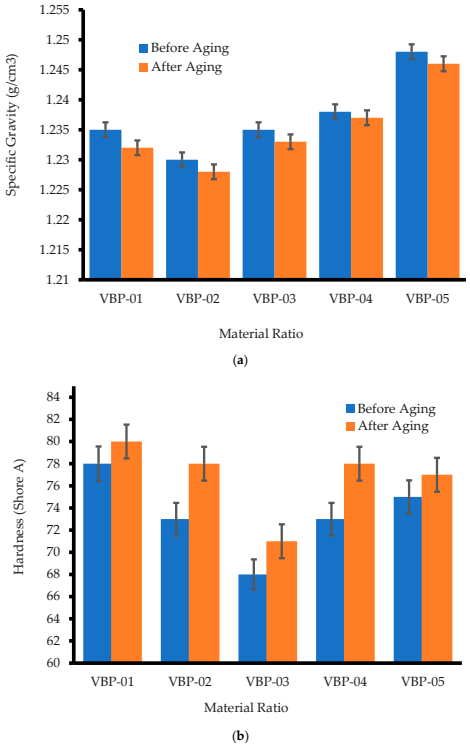
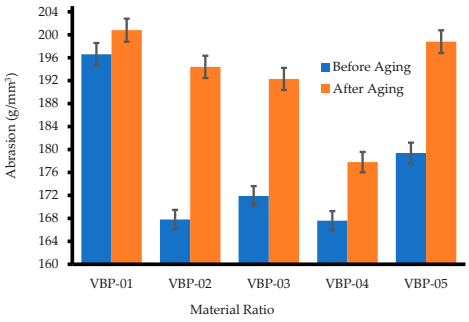
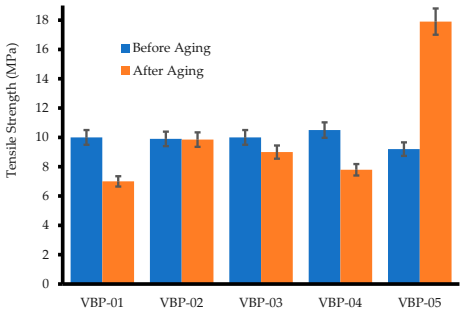


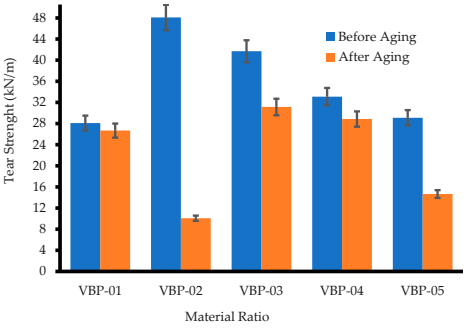
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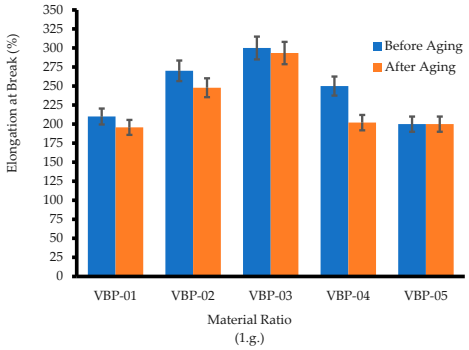
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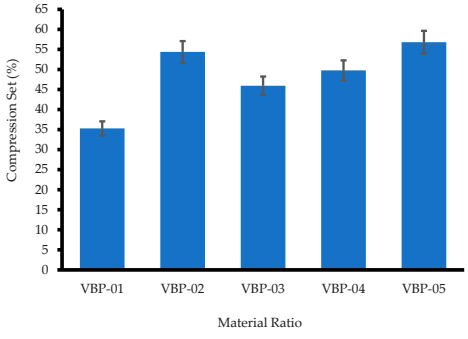


(**e**)



(**f**)

Figure 1. *Cont.*



(**g**)

Figure 1. (**a**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) before and after aging on specific gravity. (**b**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) before and after aging on hardness. (**c**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) before and after aging on abrasion. (**d**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) before and after aging on tensile strength. (**e**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) before and after aging on tear strength. (**f**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) before and after aging on elongation at break. (**g**) The effect of comparisons of ZnO with SA (VBP-01) and ZS (VBP-02-VBP-05) on compression set before aging.

The increase in the ZS ratio from 6.00 to 7.00 phr (Table 1) based on the calculated results reduced the weight of other materials. As with the VBP-03 formula, an increase in the ratio of ZS 7.00 phr to weight occurred as NR decreased to 0.428% and SBR and NBR decreased to 0.434% from the weight of the previous material (VBP-02). According to Setianto et al. [20], the specific gravity of ZS from BPPT used in this study was 1.1 g/cm^3. Increases in the ZS ratio in the same volume and space, taking into account the specific gravity, led to increases in the specific gravity of rubber vulcanizate. This is because there was a reduction in materials with low boiling points in the aging process.

3.2.2. Hardness

ZS in the vulcanization process of rubber compounds improved the accelerator's performance and increased the vulcanization speed, forming cross-link reactions. The cross-links formed affect the hardness value. The cross-linking reaction is formed by the presence of sulfur compounds [31]. In the vulcanization of rubber compounds, the molecular chains were linked by cross-links formed by sulfur with the rubber molecules. Cross-links formation in the rubber matrix can increase hardness [32]. Hardness correlated with cross-link density. The vulcanized rubber became stiffer and harder where cross-links were formed. The ratio of sulfur as a vulcanizing agent in this study was conditioned (Table 1). Changes influenced the cross-link reaction that was formed in the ZS ratio.

VBP-01 rubber vulcanizate hardness test results before aging are available in 78 Share A and 80 Share A after aging. The results of the VBP-01 hardness test before and after aging were higher than the hardness values of VBP-02 to VBP-05 (Figure 1b). Changes influenced the difference in hardness values that occurred in the ZS ratio and the possibility of agglomeration between particles in the rubber matrix. When the ZS ratio increased from VBP-03 to VBP-04 (Table 1), the hardness value before aging decreased to 6.85%, and the value after aging increased to 8.97%. Furthermore, when comparing ZS 7 phr (VBP-03) with 8 phr (VBP-04), there was an increase in hardness of 6.85% before aging and 9.97% after aging. In ratio ZS 9 (VBP-05), hardness before aging increased by 2.67%, but after aging, it decreased by 1.28%. According to Saeed [33], the hardness increases as a function of the cross-links. Besides being influenced by ZS, the hardness value is also influenced by plasticizer, filler homogeneity, material surface area, cross-link density, and the vulcanization process [34]. In addition, the increase in hardness after aging occurred

due to the evaporation of volatile molecules during the aging process. Evaporation that occurs causes the material to become denser and reduces its elasticity [35].

3.2.3. Abrasion

Abrasion resistance is defined as the ability of the cross-links that make up vulcanized rubber to resist friction with other objects. The cross-links formed can improve dynamic properties and abrasion resistance [36]. The test results for the VBP-01 sample before aging experienced 196.6 mm^3 or 11.6% abrasion before aging and 200.8 mm^3 or 20.83% abrasion after aging. VBP-01, as a control formula using ZnO and SA, experienced more abrasion than rubber vulcanizate that used ZS. The VBP-04 vulcanized rubber abrasion test results before aging were 167.6 mm^3 and experienced 18.97% abrasion, and after aging, they were 177.8 mm^3 (18.44%). The overall use of ZS from VBP-02 to VBP-05 test data had better abrasion resistance than VBP-01 (Figure 1c). ZS in the rubber compound, together with the accelerator, formed a complex compound from the reaction with sulfur.

The increase in abrasion after aging occurred due to the evaporation of materials with low boiling points. The aging process was carried out at 70 °C for 72 h. Evaporation of the low-boiling material during aging formed pores between the vulcanized rubber molecules and weakened the intermolecular bonds. This caused vulcanized rubber to become easily abrasive.

ZS rubber vulcanizate test results had better activity in forming intermolecular bonds in the rubber matrix than ZnO and as (VBP-01). ZnO in rubber compounds can reduce heat and increase abrasion resistance [37]. This shows that ZS can improve accelerator performance during vulcanization by forming stronger intermolecular bonds. Abrasion resistance describes the density of intermolecular cross-links. As the cross-link density increased, the abrasion resistance increased, the hardness increased, and the intermolecular bonds became stronger.

3.2.4. Tensile Strength

Tensile strength is the force required to pull a material to break [38–42]. The result of tensile strength before an aging test for formula VBP-01 was the same as VBP-03 (10 MPa) but slightly lower than formula VBP-04 (10.5 MPa). The tensile strength test results of VBP-01 after aging were lower than those of VBP-02 to VBP-05 (Figure 1d). The tensile strength results after the aging test experienced a significant increase. The increase in tensile strength after aging was probably caused by the cross-linking reaction that continued during aging, which was carried out at 70 °C for 72 h.

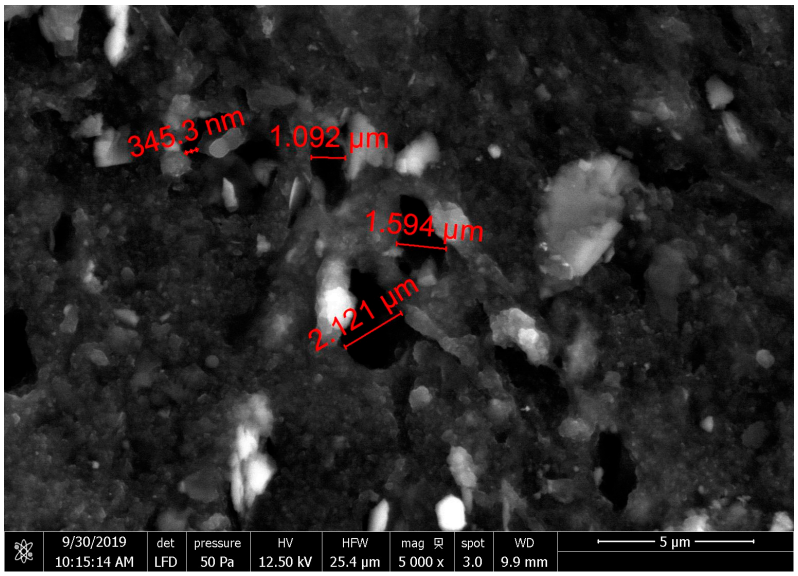
The ability of vulcanized rubber to withstand tensile strength was affected by cross-linking strength ZS with an accelerator and sulfur to increase cross-linking in the rubber matrix. The interaction of sulfur with NR via unsaturated active sites formed the cross-links. Polymer composites produce cross-linked precursors that bind polymer chains together [4]. During vulcanization, the rubber matrix had reactive edges that formed cross-links to increase tensile strength. Activators and accelerators function to increase the rate of vulcanization by forming cross-links [43].

Adding a coupling agent increased the distribution and homogeneity of the filler into the rubber matrix so that the bond strength formed between the filler molecules and the rubber matrix molecules. The differences influenced the distribution of fillers in the polarity of natural rubber and synthetic rubber and the interaction of the cyano groups with the hydroxyl groups of silica. The coupling agent improves adhesion and reduces the surface energy of the filler [44]. ZnO, together with the accelerator and sulfur through the rubber vulcanization process, can increase the tensile strength and elasticity of vulcanized rubber [45,46].

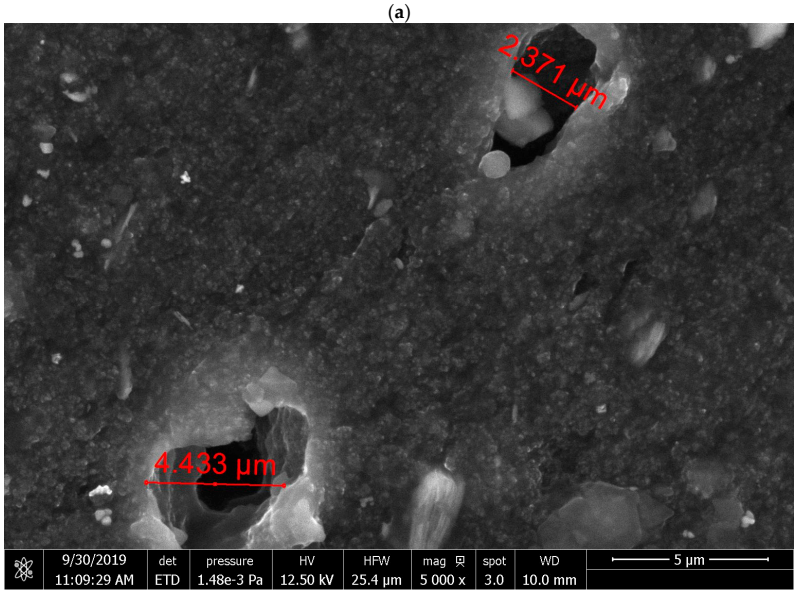
3.2.5. Tear Strength

The effect of ZS on tear strength parameters before and after aging for VBP-01 was significantly different from the tear strength test results for VBP-02 to VBP-05 vulcanized

rubber (Figure 1e). Using ZS at a ratio of 6 phr (VBP-02) before aging, the tear strength value increased to 41.58% from VBP-01, and the tear strength of VBP-02 decreased to 62.22% from VBP-01 after aging. The tear strength of VBP-03 before aging increased by 32.61% from VBP-01 before aging and 12.07% after aging. During the aging process, the heat was transferred to the inside of the vulcanized rubber. At the same time, the molecules of the rubber composite moved together with the release of volatile substances. During the aging process, intermolecular bonds can be moved, which causes a change in the material's mechanical properties [47]. This phenomenon can cause intermolecular bonds to become weak. In addition, there is a cutting of atomic chains and changes in physical properties during aging [48]. The reduction in tear strength was also caused by the formation of pores between the vulcanized rubber molecules during the aging process. The pores formed in each sample can be seen from the SEM test results in Figure 2a–e.

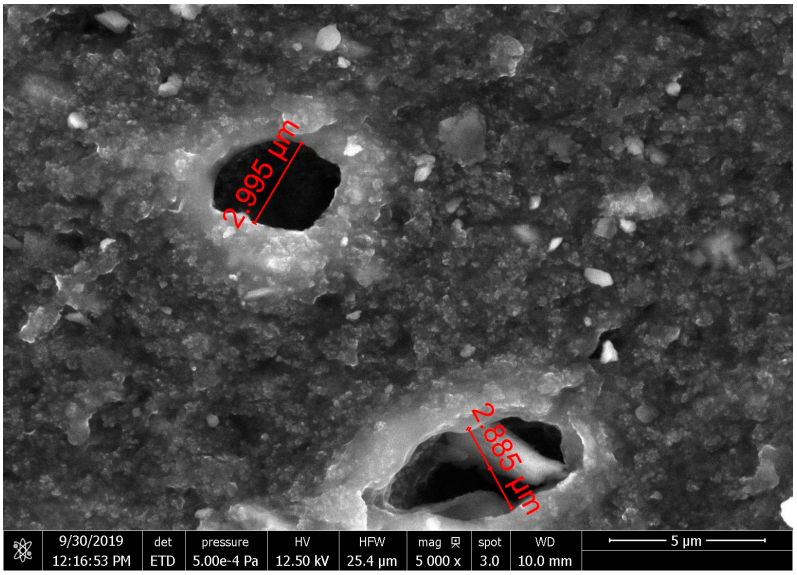


(**a**)

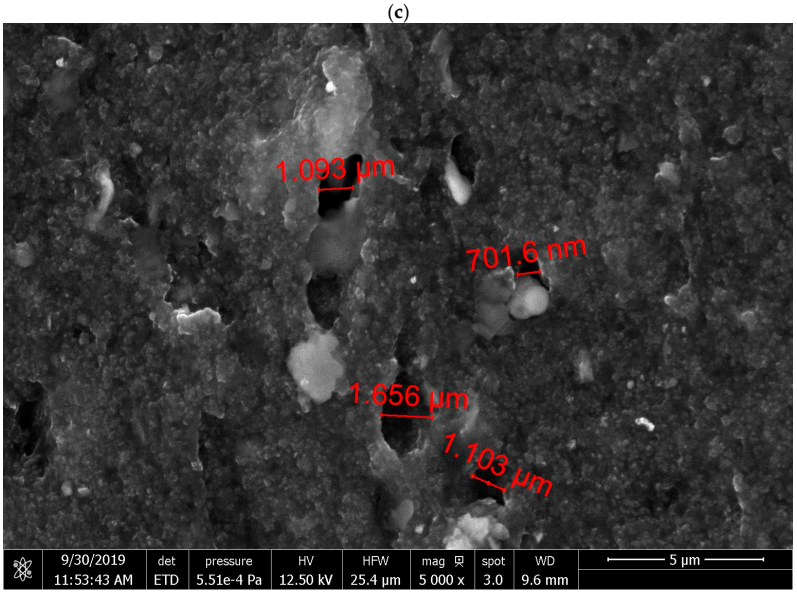


(**b**)

Figure 2. *Cont.*

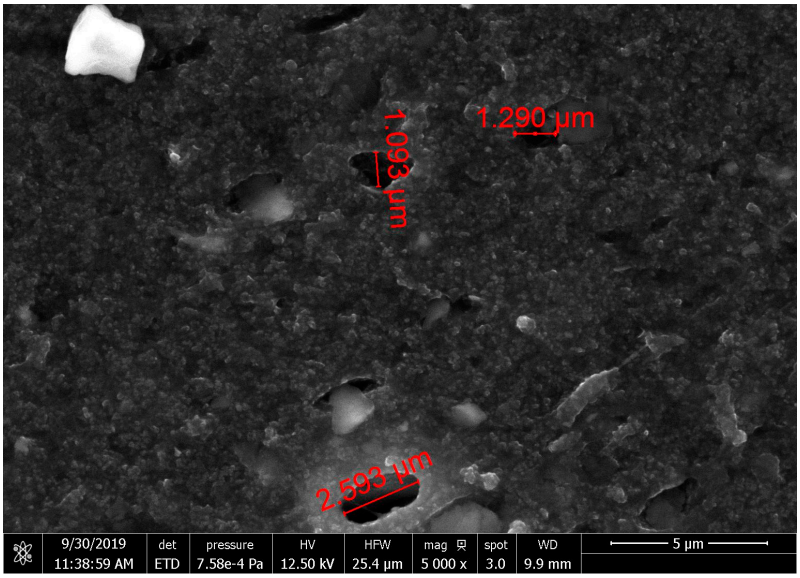


(**c**)



(**d**)

Figure 2. *Cont.*



(**e**)

Figure 2. (**a**) The effect of ZnO 5.0 phr and 2.5 phr stearic acid (VBP-01). The effect of ZS on the rubber vulcanizates for solid tires with compositions: (**b**) ZS 6 phr (VBP-02), (**c**) ZS 7 phr (VBP-03), (**d**) ZS 8 phr (VBP-04), and (**e**) ZS 9 phr (VBP-05) to the pore diameter formed and the distribution of the material using SEM photo at 5000x magnification.

3.2.6. Elongation at Break

Elongation at break rubber vulcanizate means adding length until it breaks when the sample is withdrawn. The higher the value of Elongation at break, the higher the energy used to tear the vulcanized rubber. The test results for the VBT-01 vulcanized rubber samples for Elongation at the break before aging experienced a break of up to 28.1 kN/m lower than samples VBP-01 to VBP-05. According to Poikelispää et al. [49], the decrease in elongation at break is related to the mobility of the available polymer chains. The Elongation results at the break after aging VBP-01 were higher than VBP-02 and VBP-05 but lower than VBP-03 and VBP-04. According to Smejda-Krzewicka et al. [25], the presence of ZnS affects the properties of vulcanized rubber.

Based on Figure 1f, the Elongation at break of VBP-02 before aging significantly increased to 41.58% of VBP-01. High Elongation at break describes higher material elasticity [50]. According to Rahmah [51], the increase in Elongation at break occurs due to the formation of strain crystals which cause more stiffness in the polymer chain. Furthermore, according to Ahmed et al. [52], an increase in Elongation at break occurs alongside an increase in intermolecular bonds caused by the formation of cross-links.

The activity of ZS and accelerators in the vulcanization process increased the cross-linking reaction. The presence of silica as a reinforcing filler reacted with the polymer to form C-SiO bonds and increase cross-linking. In contrast, an increase in cross-link density follows an increase in the ZS ratio [46]. The use of ZS as a substitute for conventional ZnO and stearic acid in the vulcanization process of rubber compounds can improve the physicomechanical properties of a rubber vulcanizate, such as elongation at break [17]. This is because the number of molecules carrying out the reaction increased with an increase in the ZS ratio. According to Antony [53], increasing the ZS ratio can increase the elongation at break. This is because the number of molecules carrying out the reaction increases with an increase in the ZS ratio.

3.2.7. Compression Set

Compression set rubber vulcanizate is the ability to withstand loads and return to its original state after receiving loads. Natural rubber is a polymer that can withstand loads and return to its original state after receiving loads [54,55]. The molecular structure and

bonds between the materials formed influenced compression set rubber vulcanizate. ZS in the vulcanization process from the test results data increased the permanent compression of rubber vulcanization (Figure 1g). A significant increase in compression sets up to 22.45% occurred at a ratio of ZS 5.00 phr (VBP-02) and 23.45% at a ratio of ZS 9.00 phr (VBP-05). This increase was higher than the increase when using ZnO and SA VBP-01 (14.57%). The compression set was inseparable from the formation of cross-links in the rubber matrix. According to Hamzah and Alibadi [56], the number of cross-links formed strengthens the intermolecular bonds and influences the vulcanized rubber surface to withstand loads. The cross-links in the rubber vulcanization matrix expanded the intermolecular space. This is because the cross-linking reaction caused the space in the rubber vulcanizate matrix to enlarge. Cross-links provide better dynamic properties [36]. The formed cross-linking response was mainly on the carbon–carbon double bond (C=C), which originated from elemental sulfur.

3.3. Morphological Properties of Vulcanized Rubber

The homogeneity of the material and the pores formed in the VBP-01 to VBP-05 rubber vulcanizate matrix determine the mechanical properties and product quality, so scanning is required. SEM–EDS [57] is a widely used tool for scanning many products.

SEM–EDS scan results with a magnification of 5000 times on samples VBP-01 to VBP-05 (Figure 2a–e) showed differences in particle distribution, pore diameter, and several types of elements in the matrix vulcanized rubber. The difference was caused by the difference in the ZS ratio used. In addition, during compounding using an open mill and vulcanization using a hot press, there was a possibility of agglomeration of polysulfide materials accompanied by cross-linking reactions. According to Tamási and Kollár [58], polysulfide cross-links originate from the reaction of four to six sulfur atoms which produce sulfur bridges.

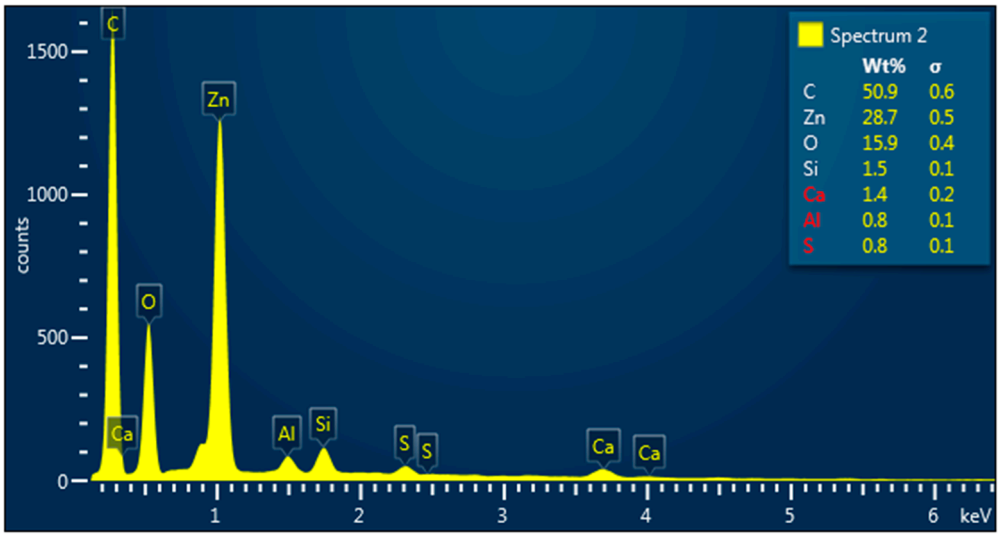
Polysulfide cross-links and sulfur bridges can affect the homogeneity of the material and the pore diameter. This event occurs due to the formation of heat by sulfur by forming mono-, bi-, and poly-sulfide bridges between polymer chains [4]. Scan results with SEM for the VBP-01 sample are shown in Figure 2a. There were pores between the rubber vulcanizate molecules. The existing pores formed by the gas during vulcanization were then trapped in the vulcanized rubber. The pore diameters that were formed were not uniform as each measured 345.50 µm, 1.092 µm, 1.594 µm, and 2.121 µm. According to Kim et al. [59], the formed pores are caused by heat propagation on the rubber vulcanization matrix, which forms gas bubbles. Heat propagation in vulcanized rubber contained elements C and O, which decomposed into CO_2, and was then trapped between the rubber molecules.

Regarding the results of the SEM-EDS scan of the VBP-02 sample (Figure 2b), the particle distribution was relatively homogeneous compared with the VBP-01 sample. The VBP-02 sample, as a result of the SEM-EDS scan, had pores with diameters from 2.371 µm to 4.433 µm. The VBP-03 sample had pores with diameters from 2.885 µm to 2.995 µm (Figure 2c). In addition, the material ratio also affects the dispersion and the bonding power between the rubber matrix molecules [60]. The difference in the ZS ratio for all treatments affected the pore diameter and intermolecular bonds of the vulcanized rubber-forming material.

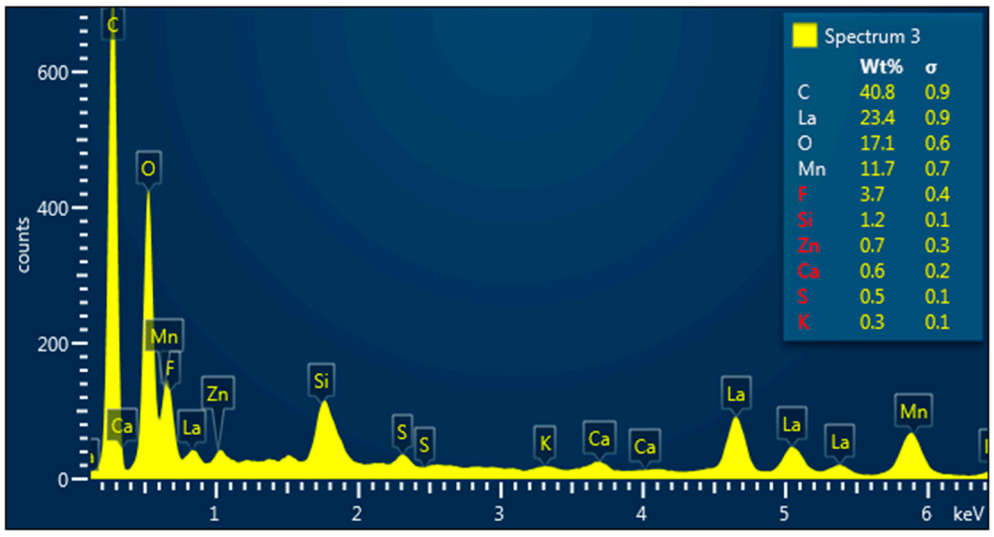
The results of the SEM scan for the VP-04 sample using the ZS8 phr showed that the distribution of the material into the rubber matrix was relatively homogeneous. SEM results detected pore diameters of 701.6 µm, 1.093 µm, 1.103 µm, and 1.656 µm (Figure 2d). ZnO has long, medium, and short hexagonal crystal structures [61]. According to Saeed et al. [33], ZnO can strengthen the filler and improve the mechanical properties of vulcanization.

The increase in the ratio of ZS 9 phr (VBP-05) from the SEM scan results showed that the material distributed in the vulcanized rubber matrix was almost homogeneous, and there were pores between the vulcanized rubber. The pores between the vulcanized rubber matrices were 1.093 µm, 1.290 µm, and 2.593 µm in diameter (Figure 2e). According to Arayapranee and Rempel [62], pores are formed due to agglomeration between materials.

The SEM-EDS photos showed that the elements present were different and pores with different diameters formed on all sample surfaces. SEM-EDS can perform elemental analysis on microscopic sections of materials or contaminants that may be present [63]. SEM-EDS results for sample VBP-01 (Figure 3a) in spectrum 2 contained several elements, including C with a peak area of 50.95% Wt, Zn with a peak area of 28.7% Wt, O with a peak area of 15.9% Wt, Si with a peak area of 1.5% Wt, Ca with a peak area of 1.45% Wt, and Al and S with peak areas of 0.8% Wt.

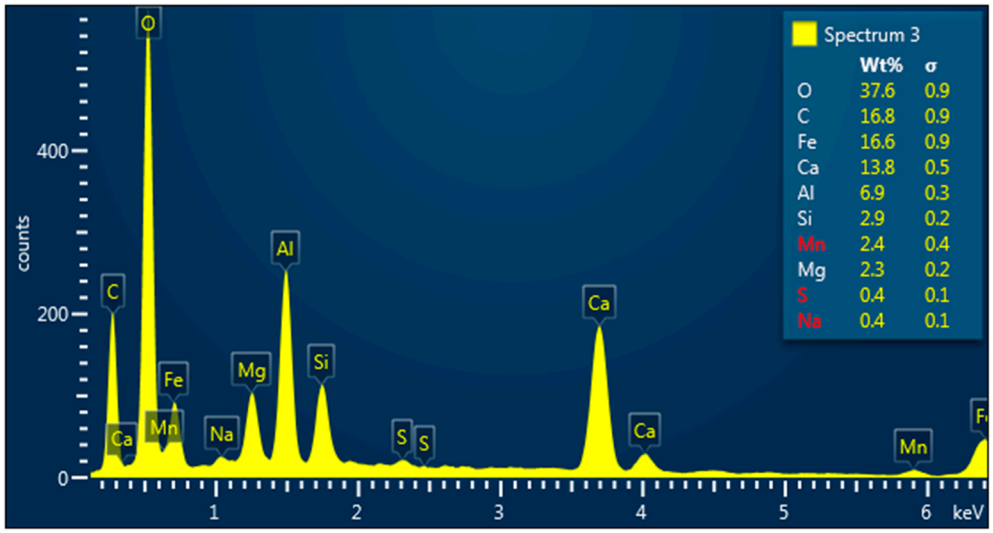


(**a**)

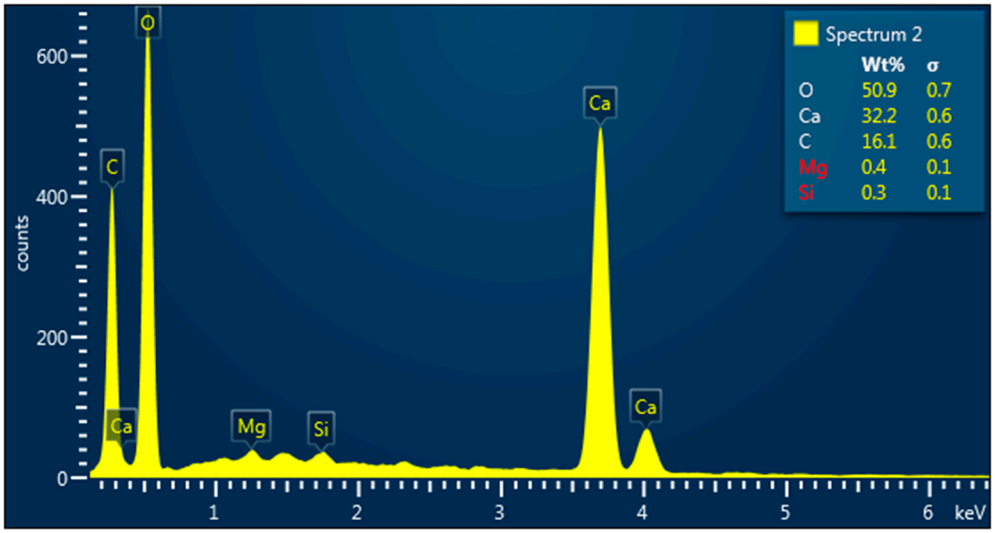


(**b**)

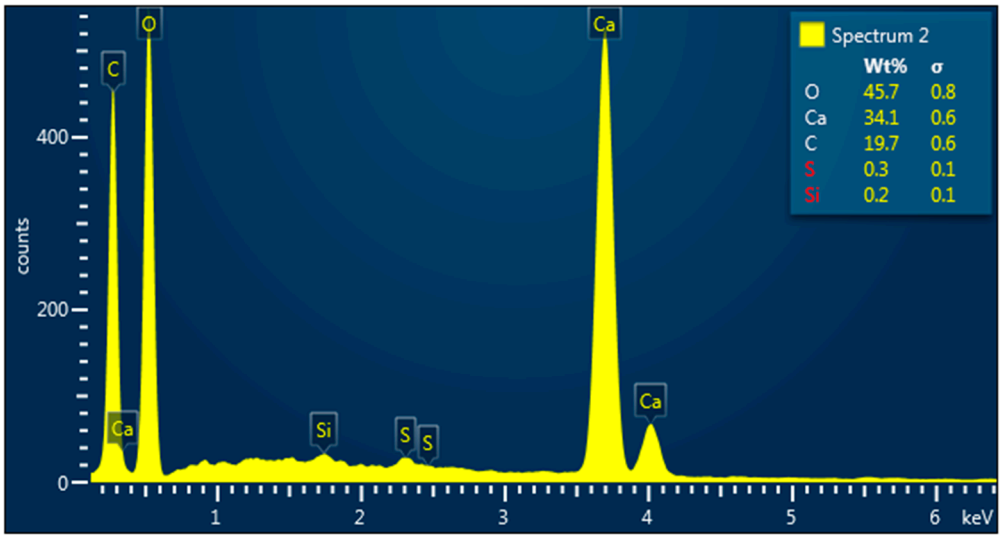
Figure 3. *Cont.*



(**c**)



(**d**)



(**e**)

Figure 3. The spectrum of EDS retreaded solid tire using: (**a**) ZnO 5.0 phr and SA 2.5 phr (VBP-01); (**b**) ZS 6.0 phr (VBP-02); (**c**) ZS 7.0 phr (VBP-03); (**d**) ZS 8.0 phr (VBP-04); and (**e**) ZS 9.0 phr (VBP-05).

Each element, as in Figure 3a–e, had a different peak height and area. Elements C, Zn, and O dominated the elements in sample VBP-01 (Figure 3a). According to Modi. [64], Zn and O elements have a hexagonal morphology. This element comes from ZnO, stearic acid, accelerator, and fillers.

The results of the SEM-EDS reading of sample VBP-02 (Figure 3b) contained elements C 40.8% Wt, La 23.4% Wt, O 17.1% Wt, Mn 11.7% Wt, F 3.7% Wt, Si 0.7% Wt, Ca 0.6% Wt, S 0.5% Wt, and K 0.3% Wt. The VBP-02 sample was dominated by C, La, and Mn elements. The peak height and area of each EDS reading were affected by the vulcanization rate, cross-linking reactions, and intermolecular interactions of the materials used.

SEM-EDS results for sample VBP-03 (Figure 3c), which contained oxygen (O) 37.6% Wt, were higher than the element present. SEM results of EDS detection were C 18.8% Wt and Fe 16.6% Wt. These two elements were 50% Wt lower than oxygen. In addition, there were elements of Ca 13.8% Wt, Al 6.9% Wt, Si 2.9% Wt, Mn 2.4% Wt, and Mg 2.3% Wt.

The content of Si and Na were both 0.4% Wt. VBP-04 (Figure 3d) and VBP-05 (Figure 3e) contained elements of O, Ca, and C, with the highest peaks over a large area dominating the constituent elements of solid tire rubber vulcanization.

The number of elements was affected by intermolecular bonds, the material formed during vulcanization, and cross-linking reactions. This allows interfacial chemical exchange by forming cross-links from the occurring reactions [65]. Based on the existing data, ZS increased the speed of cross-linking reactions. As an indicator, the number of free elements in the form of cations was less than the elements in the VBP-01 sample (Figure 3a) as a control sample.

4. Conclusions

The application of zinc stearate as a substitute for ZnO and stearic acid in the vulcanization of rubber compounds showed an increase in setting time (t_{90}), time score (ts_2), and delta torque (Δ_S). In addition, using ZS improved the mechanical properties of vulcanized rubber. The results of the SEM-EDS photos show that pores with different diameters formed on all sample surfaces. The peak height and area of the EDS readings reflected the element concentrations that were present. The constituents that were present were affected by the ZS ratio, the vulcanization rate, the cross-linking reactions, and the interactions between the forming molecules.

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