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Article

Role of Zinc Oxide in the Compounding Formulation on the Growth of Nonstoichiometric Copper Sulfide Nanostructures at the Brass– Rubber Interface

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ABSTRACT: Tire technology has evolved substantially by the introduction of brass-coated steel cords (BCSCs) in radial tires. The durability of radial tires is dependent on the integrity of the brass-rubber interface composed predominantly of nonstoichiometric copper sulfide ($Cu_{2-x}S$, where x = 1 to 2) nanostructures whose morphology and characteristics are dependent upon the crucial rubber additive, ZnO. Its higher concentration impacts environmental sustainability, while at lower levels, there is insufficient bonding between steel and the rubber thus affecting tire's safety. This brings in the need for an optimum ZnO concentration to be used in radial tires and is thus the theme of the present work. The changes in the properties of interfacial nanostructures such as morphology, thickness, crystallinity, and chemical composition were studied at various ZnO concentrations. We adopted our previously reported methodology, the "brass mesh experiment", to investigate the thickness of nanostructures at varied ZnO concentrations using transmission



electron microscopy (TEM). Significant results were obtained from field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Raman imaging and X-ray photoelectron spectroscopy (XPS). In conjunction with a more practical experimental technique, namely the measurement of pull-out force (POF), it has been concluded that 9 parts per hundred rubber (PHR) ZnO is essential for the optimum growth of nanostructures and is considered to be the optimum for the composition studied. We believe that the scientific approach outlined in the manuscript would help the tire- and the material science communities to widen the knowledge of understanding sustainability in tire industries. It is estimated that the optimization presented here can save \$400–450 million for the tire industry and 2.4 million tons of ZnO per year.

INTRODUCTION

Brass-coated steel cords (BCSCs) are widely used to construct the complex structure of radial tires (RTs) to enhance product durability and performance.¹ Conventionally, a ~200 nm thick brass coating on steel cords is, in fact, the adhesion promoter that remarkably improves the bonding between rubber and steel cords by building up a robust bonding interface resistant to high temperature and dynamic loading.² Of the many materials that are involved in the complex tire manufacturing processes,³ zinc oxide (ZnO), the vulcanization activator, plays a vital role in adhesion between brass and rubber.⁴ Because of the supreme physical and chemical properties of ZnO, the tire industry remains its largest market (~60%), estimated to be 120 million metric tons per year, accounting for 3.0 billion tires manufactured annually.⁵ A typical tire contains 1–3% of ZnO by weight.^{6,7} Zinc leaching from tires is known, and it is classified to be toxic for the aquatic environment above 2 ppm, according to a directive of the European Union.⁸⁻¹⁰ The International Programme on Chemical Safety (IPCS) has recommended regulatory criteria for Zn, assessing an optimum ZnO level in rubber products vital for reducing harmful

environmental impact.¹¹ Also, higher ZnO concentrations (more than the optimum level) in the rubber compound increases the overall mass of the tire because of its higher specific gravity compared with other ingredients, which cause undesirable attributes such as high rolling resistance (RR) and consequently higher fuel consumption and associated negative contribution to the carbon footprint.¹²

Apart from ecological issues, an optimum concentration of ZnO is of significance in the tire industry for increased strength at operating conditions.¹³ However, studies to arrive at an optimum concentration of ZnO require a thorough understanding of the morphology, interface thickness, and chemical composition for desired adhesion. There is a positive

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Figure 1. Morphology and thickness of the interface. FE-SEM images of vulcanized steel cords with (A) 6, (B) 9, and (C) 12 PHR ZnO loadings. AFM images portraying the interface roughness for (D) 6, (E) 9, and (F) 12 PHR ZnO.



Figure 2. Bright-field TEM images of the nanostructures grown over brass mesh at (A) 6, (B) 9, and (C) 12 PHR ZnO. Corresponding high-resolution TEM images are in (D-F). Scale: 5 nm.

correlation between ZnO concentration and the cost incurred for tire production, that is, per unit increase in PHR (parts per hundred rubber, PHR - a measurement used by rubber chemists to denote weight), increases \sim \$400–450 million annually for tire industries globally. This is significant as many tire chemists are unaware of the impact of ZnO on the interfacial properties, contributing to increased tire manufacturing costs and reduced environmental sustainability.¹⁴

In recent years, there has been a growing interest in knowing how the two sources of ZnO (one from the rubber compound—a term referring to a mixture of rubbers, fillers, vulcanization activators, accelerators, promoters, etc.--and the other already present in the BCSCs) affect the formation of the bonding interface. Recent literature has highlighted how these different sources of ZnO affect the steel cord-rubber adhesion through the inclusion of isotopically labeled Zn (⁶⁴Zn) in the rubber compound, using secondary ion mass spectrometry (SIMS).⁴ The study was further advanced by interpreting the origin of ZnS from ZnO added to the rubber compound. It has been proved that the formation of ZnS at the interface is known to be disadvantageous as it weakens the interfacial bonding with rubber.^{2,15} Interesting correlations between the microstructure changes (interfacial thickness) and the associated mechanical properties such as pull-out force

(POF), tensile strength, modulus, and elongation at break have been studied. It was found that with the increase in interfacial thickness, the POF decreases, corresponding to lower interfacial strength. However, only very little is known on how variations in the concentration of ZnO as a compounding ingredient affect the morphology, interface thickness, crystallinity, and chemical composition of nanostructures at the brass-rubber interface.

Most studies have focused on explaining the optimum concentration of ZnO in the adhesion interface based on pullout force (POF) and physical properties of the rubber compound such as modulus, tensile strength, and Mooney viscosity.¹⁶ Additionally, not many reports have highlighted the environmental concerns caused because of tire-related issues such as the tire weight and the associated fuel consumption based on desired ZnO concentration for better interfacial bonding.¹⁷ To fill this knowledge gap, in this paper, we present a detailed study of improving the sustainability of the tire industry through understanding the changes in critical interfacial parameters such as morphology, interfacial thickness, and chemical composition of the adhesive interface to arrive at the optimum ZnO concentration in the rubber compound. We found that varying ZnO concentrations in rubber compounds can be used to control these parameters.

We observed that the average surface roughness of the interfacial nanostructures increased from ~29 to ~90 nm by varying the ZnO concentration. Therefore, we followed an alternative approach to enhance sustainability that is advantageous to the established methods by quantifying the nanoscale features of the interface at various ZnO concentrations and correlating them with the bulk properties of the tires. Additionally, the brass mesh experiment,² a new methodology reported by us recently, which is also a viable approach, was adopted in this study to measure the interfacial thickness. The correlation between the interfacial thickness and its bonding strength with rubber was established by a more practical methodology, namely the pull-out force (POF) measurements. We believe that the present findings would help the rubber compounders to choose the optimum ZnO concentration suited for the formulation, thus reduce manufacturing costs, and improve sustainability.

RESULTS AND DISCUSSION

Morphology and Measurement of the Thickness of the Brass-Rubber Interface. Morphology and roughness of the nanostructures at the interface imaged at three different ZnO concentrations (6, 9, and 12 PHR) are shown in Figure 1. An increase in the density of nanostructures accompanied by a morphology change was noted with an increase in ZnO concentration (Figure 2A-C). As shown in Figure 1A, the nanostructures have started to grow at 6 PHR of ZnO loading. Interface formed at 6 PHR had a combination of flaky and circular structures, indicating that this kind of an interface was still in the process of growing. The interface transitioned to completely flaky/leafy structures at 9 PHR ZnO, as evident from Figure 1B. At 12 PHR ZnO loading, the flaky nanostructures were transformed into dense flower-shaped structures (Figure 1C). Figure S2 depicts large area SEM and EDS data corresponding to Figure 1A-C. One of the significant findings from the SEM-EDS data is the increase in the atomic% of Cu, S, O, and Zn of the nanostructures with an increase in the ZnO concentration. It was noted that the interface formed in Figure 1C had more Cu and S than in Figure 1A. Thus, an increase of ZnO in the rubber compound promotes an increased percentage of active sulfurating species to react with Cu and Zn to form copper- and zinc sulfides. Also, EDS analysis revealed significantly higher O and Zn atomic% changes as a function of the ZnO concentration.

The surface roughness of the nanostructures at different ZnO loadings was measured using Atomic Force Microscopy (AFM) (Figure 1D–F). As can be seen from Figure S3, the average surface roughness was high for the vulcanized interface compared to the unreacted state. Significantly, interface roughness with 6, 9, and 12 PHR of ZnO was 29, 73, and 90 nm, respectively. The present findings confirm a direct correlation between the surface roughness and morphology of the interfacial nanostructure with ZnO concentration.

The concentration of ZnO in the rubber compound, to a large extent, affects its interaction with the vulcanization accelerator.¹⁸ For instance, a higher ZnO PHR increases the cross-linking of the rubber.^{16,19} ZnO, along with stearic acid, increases the rubber cross-linking by forming S bridges. This leads to higher active sulphurating species available to the interface leading to a larger interface growth. A higher ZnO concentration in rubber compound leads to the formation of higher concentrations of $Cu_{2-x}S$ and ZnS at the interface, leading to increased nanostructure size and roughness.

However, at lower concentrations, the accelerator devoid of sufficient ZnO for vulcanization extracts zinc from the brass. This leads to higher $CuS/Cu_{2-x}S$ thickness as the brass becomes rich in Cu. Thus, both higher and lower ZnO concentration in rubber compounds lead to difficulties in forming the right interface, thereby drastically affecting the adhesion properties.

To understand the role of ZnO in controlling the interfacial thickness, we adopted a simple technique, the "brass-mesh" experiment.² Figure 2A-C portrays the nanostructures grown on the brass mesh with different concentrations of ZnO in the rubber compound. Multiple TEM images were taken from different regions of the brass-mesh. Figure 2A shows the nanostructures grown on the brass grid at 6 PHR ZnO. The nanostructures formed do not have a proper dendritic structure because of the insufficient amount of the active sulfurating species at the interface. The nanostructures grow denser, accompanied by a change in dendritic morphology from flaky/ leafy to flower-shaped, from 9 PHR to 12 PHR ZnO (Figure 2B,C). In panels D-F, respectively, of Figure 2, we show highresolution TEM images of the nanostructures formed on the brass mesh at 6, 9, and 12 PHR ZnO that were then correlated with XRD, Raman images, and XPS (Figures 3, 4, and 5),



Figure 3. Crystallinity of the adhesion interface. XRD patterns of the vulcanized BCSCs at different ZnO concentrations, showing the various phases of nanoscale materials existing at the interface.

respectively, to confirm the chemical substances. The lattice spacings of 2.6, 3.2 and 3.4 Å at 6 PHR ZnO correspond to the presence of planes of CuS [(103)], Cu_{1.8}S [(101)], and ZnS [(111)] at the adhesion interface, which are consistent with the XRD results.^{20–22} Thus, the interfacial nanostructures formed due to vulcanization with 6 PHR ZnO had the composition of a mixture of CuS, Cu_{1.8}S, and ZnS. At 9 and 12 PHR ZnO, analysis shows the presence of CuS [(103)], Cu_{1.8}S [(101)], Cu₂S [(101)], and ZnO [(100)] confirmed by the presence of 2.8, 3.1, 3.3, and 3.4 Å lattice spacings.²³

As shown in Figure 2A-C, it is apparent that the nanostructures grew in size with the increase in ZnO concentration. Additionally, the crystallinity of the nanostructures changed from 6 PHR to 9 PHR ZnO. A higher ZnO concentration in rubber compound facilitates a higher



Figure 4. Raman spectra of BCSC at ZnO concentrations of (A1) 6, (B1) 9, and (C1) 12 PHR. Images A2, B2, and C2 correspond to confocal Raman maps at 267 cm⁻¹ (scale: 20 μ m). A3, B3 and C3 are maps at 475 cm⁻¹ and A4, B4, and C4 are maps at 580 cm⁻¹. Images A2–A4 correspond to 6 PHR, images B2–B4 correspond to 9 PHR, and images C2–C4 correspond 12 PHR ZnO concentrations, respectively. The color bar on the right represents the CCD counts.

concentration of active sulphurating species and hence a higher concentration of $Cu_{2-x}S/ZnS/ZnO$, resulting in higher interfacial thickness.

From Figure S4A, it is also seen that the average interfacial thickness increased from ~65 nm to ~114 nm when the ZnO concentration was varied from 6 to 12 PHR. Upon comparing aged and unaged POF (Figure S4B-D), there was a steep increase in POF for the unaged. When the interface is aged, there was an initial rise in the POF for 6 PHR and 9 PHR followed by a drop at 12 PHR, which is predominantly attributed to two main reasons: the first being the catalytic activity of ZnO at higher concentrations, causing oxidative degradation of the interface; and the second being a change in the composition of the interface.²⁴ In addition, crystalline interfacial nanostructures in the aged interface also correspond to the reduction of POF.²⁵ Hence, it can be inferred that the addition of 9 PHR ZnO in the rubber compound formulation of the ply region of a tire is sufficient for a suitable interface thickness and excess ZnO can be avoided. We wish to point out that the POF values reported in the present manuscript are higher than those in the above-mentioned literature as the present experiments were conducted under realistic tire vulcanization conditions, and the formulation had a higher concentration of adhesion promoters than those reported in literature.^{26,27}

Mooney viscosity (MV) of the compounds was measured to understand the processability of the rubber compounds and Figure S5A,C shows the MV and moment highest (MH) of the rubber compound at different ZnO concentrations. At a higher MV and MH, the rubber compound was difficult to be processed for vulcanization, while a lower MV would lead to air blisters in the vulcanized material. An increase in MV was noted with an increase in ZnO, inferring that the rubber compound would be hard to process for vulcanization. It was also noted that no air blisters were formed at 6 PHR. It is interesting to note from Table S2 that the cross-link density of rubber compounds increased with an increase in ZnO concentration. This result further corroborates with the fact that higher ZnO promotes higher active sulfurating agents for vulcanization. Figure S5B shows the tensile strength of the rubber compound as a function of ZnO concentration. Tensile strength signifies the stress that the rubber compound can tolerate before failure and is generally expressed in MPa.^{28,29} The tensile strength decreased significantly with an increase in ZnO concentration, inferring an easy failure of the rubber compound at 12 PHR. Figure S5D shows that the modulus of rubber is lower at 9 PHR of ZnO addition, and this significant observation can be related to the flexibility of the rubber compound. In summary, physical properties such as tensile strength, modulus, and cross-linking density of rubber compound, along with corroboration of results obtained from POF and interfacial thickness measurements, suggested the optimum ZnO concentration as 9 PHR.

Fully crystalline nanostructures make the interface brittle, leading to interface failures.^{2,25} Hence it is essential to understand the crystallinity of the different species formed under different ZnO loadings. For this, we carried out XRD measurements on vulcanized BCSCs with rubber compounds having different ZnO loadings to find the chemical identity and crystallinity of nanostructures. Figure S6 shows the XRD pattern of unvulcanized BCSC, and Figure 3 shows the XRD patterns of the interface after vulcanization with different loadings of ZnO in the rubber compound. We confirmed that the interface consists of a mixture of copper sulfides, ZnO and ZnS. Low ZnO concentration (6 PHR) in the rubber compound leads to the formation of CuS (ICSD code: 24586, confirmed by the presence of peaks at 2θ values of 10.7, 21.6, 31.6, 32.6, and 42.9 2 degrees), Cu_{1.8}S (ICSD code: 69756, confirmed by the presence of peaks at 2θ values of 19.5, 22.6, 32.2, and 37.9) and ZnS (ICSD code: 107133, confirmed by the presence of peaks at 2θ values of 26.9, 27.1, 27.8, 28.5, 29.0, 30.5, and 32.4). At higher ZnO loadings (9 and 12 PHR), the interface consists of a mixture of CuS, $Cu_{1.8}S$, Cu_2S (ICSD code: 200986, confirmed by the presence of peaks at 2θ values



Table 1. Brass-Rubber Interface Thickness and Composition Found at Various ZnO Concentrations

Figure 5. High-resolution XPS spectra of the chemical species formed at the brass rubber interface at 6, 9, and 12 PHR ZnO. Dark lines represent the background, and the colored peaks portray peak fitting.

of 26.2, 29.1, and 37.2), and ZnO (ICSD code: 29272, confirmed by the presence of peaks corresponding to 2θ values of 31.8, 34.5, and 36.3). Table 1 summarizes the thickness, surface roughness, and chemical composition of the interface at various ZnO loadings. Since the chemical species formed at 9 and 12 PHR are the same, the results are corroborated with POF measurements, wherein beyond 9 PHR, a decrease in POF was noted. A detailed look at Raman mapping was expected to give conclusive information on the optimum ZnO concentration. Note that the Cu–S system forms several phases, and many are detected at the interface.²⁵

Raman imaging and XPS provide qualitative information on the chemical state of the nanostructures formed on the surface of vulcanized BCSCs. Spectra, A1, B1, and C1, respectively, of Figure 4 represent the Raman spectra at 6 PHR, 9 PHR, and 12 PHR ZnO. At 6 PHR (Figure 4A1), vibrational modes at 475 (A_{1g} LO mode) and 267 cm⁻¹ (A_{1g} mode) are seen and are attributed to the presence of CuS. The most dominant modes seen at 9 PHR and 12 PHR (Figure 4B1,C1) of ZnO are 580, 437, and 475 cm⁻¹, corresponding to the E_2 and E_1 LO modes of ZnO and A_{1g} LO mode of CuS. 30,31 The chalcocite (Cu_2S) phases identified in TEM and XRD for 9 PHR and 12 PHR are unseen in Raman as Cu₂S is Raman inactive.³⁰ Confocal Raman image (Figure S7) shows the appearance of the BCSC with varying ZnO concentrations. It is interesting to note that there is a visible difference between reacted and unreacted BCSCs.^{24,25} Raman imaging (Figure 4A2 to C4) of specific regions (i.e., using 267, 475 (specific to CuS) and 580 cm⁻¹ (specific to ZnO)) selected from confocal Raman image was performed to understand the distribution of chemical species at the interface. The bright regions in the

Raman heat maps in (Figure 4A2–C4) correspond to the presence of CuS and ZnO, and the color bar represents the CCD counts. Raman images corresponding to 267 cm^{-1} are shown in Figure 4A2, B2, and C2, and those due to 475 cm^{-1} are shown in Figure 4A3, B3, and C3. The concentration of CuS (as represented by the CCD values) along the vulcanized BCSCs decreased with an increase in ZnO concentration, and it is apparent that the concentration of CuS is higher at 9 PHR ZnO. Figure 4A4, B4, and C4, respectively, present Raman mapping of the 580 cm⁻¹ feature, where the concentration of ZnO along the vulcanized BCSC increased with an increase in the ZnO concentration. From the Raman imaging, the concentration of CuS and ZnO at the interface can be understood.

We have taken three different samples of brass cords with different ZnO concentrations with different areas for confocal Raman mapping. Thus, CCD count scales are different for the three samples. Moreover, it is evident from Raman spectra and confocal Raman images (Figure 4B2,B3) that the CuS concentration is higher at 9 PHR ZnO. Raman spectra from multiple locations were collected, and a similar trend in intensities of peaks at 280, 475, and 580 cm⁻¹ was observed. Based on the CCD counts (in Raman images), we can state that the concentration of CuS is higher in 9 PHR than 6 PHR. Additionally, in spectrum B1, it was seen that peaks at 280 and 475 cm⁻¹ were 20-fold intense than that at 580 cm⁻¹, and it appeared submerged.

Our experiments corroborate with the aged-POF (Figure S4C,D) that higher ZnO concentration (12 PHR) in rubber compound results in the buildup of ZnO at the brass-rubber interface. These values correlate reasonably well with the

concept that the formation of ZnO at the interface reduces adhesion. At 9 PHR ZnO, aged- and unaged-POF showed maximum interfacial strength, and the results are in good agreement with the Raman heat maps in Figure 4B2,B3. This highlights the higher concentration of CuS at 9 PHR ZnO and demonstrates the advantage of using Raman heat maps in evaluating brass-rubber interface in RTs.

XPS analysis was carried out to determine the oxidation state of the species at the interface formed under different ZnO loadings. Figure 6 shows the XPS spectrum in the $2p_{3/2}$ and $2p_{1/2}$ region of S, Cu, and Zn. The binding energy (BE) values change at different ZnO concentrations, indicating varied chemical species at the interface. Figure 5 represents the formation of two types of S (copper sulfide and sulfate/ sulfonate) at all ZnO concentrations at 161.2 and 169 eV, respectively. Sulfate/sulfonate species appear due to X-ray irradiation of sulfides on surfaces and need not be due to their presence on the native surface.³² High-resolution XPS revealed the formation of CuS and ZnS (BE at 932.2 and 1021.8 eV, respectively) at 6 PHR ZnO.^{33,34} As the concentration of ZnO increases (i.e., at 9 and 12 PHR), a change in the chemical state of the interface was noted. Composition of the interface at 9 and 12 PHR ZnO loading in the rubber compound showed the presence of Cu_2S (BE = 932.8 eV) and ZnO (BE = 1022.5 eV).² Due to minor difference in the binding energies between them, it has become difficult to distinguish between the species. Thus, a Wagner plot (Figure S8) was used to differentiate between CuS, Cu₂S, ZnO, and ZnS.^{35,36}

The relative atomic percentages of Cu, Zn, S, and O present at the interface due to vulcanization at different ZnO loadings are presented in Table S1. Interestingly, the increase in atomic % of Zn and O accounts for the increase in ZnO accumulation at the interface and corroborates with the Raman heat maps. It was found that the atomic% of Cu and S on the surface increased from 6 to 12 PHR ZnO, which relates to the increasing POF in the unaged state (Figure S4 B). Accumulation of ZnO at the brass-rubber interface at 12 PHR (found through XPS) provides additional evidence for the decline in POF during aging. Furthermore, Figure S9 shows the ply region of a RT. An enlarged image of the ply region showing the nanostructure interlocking with the rubber compound resulting in better durability with optimum ZnO concentration is also shown. Thus, the XPS and Raman heat maps also conclude that the optimum dosage is 9 PHR in the studied formulation.

CONCLUSIONS

This study highlights the importance of enhancing sustainability of the tire industries by optimizing the ZnO concentration and consequently reducing the manufacturing costs. Our work has led to a detailed study of the change in critical interfacial parameters such as morphology, interfacial thickness, and chemical composition of the adhesive interface to arrive at the optimum ZnO concentration needed in the rubber compound formulations. Various performance-enhancing properties of RTs, such as the morphology, interfacial thickness, and the chemical state of the interface have been studied at different PHR of ZnO (6, 9, and 12 PHR) using various analytical techniques. The morphology of the interface changed as a function of ZnO loading in the rubber compound formulation. A simple methodology, "the brass mesh experiment," was adopted to measure the thickness of the nanostructures at the brass-rubber interface. The nanostruc-

concentration of ZnO increased. The tires have to be run on the road or lab conditions (say an endurance test) at different operation times (12, 48, or 96 h) to simulate operating conditions in roads. However, using the filter paper method (which is a model study adopted for compound evaluation), the evolution of interfacial nanostructure with the above operating conditions cannot be studied as a real tire cannot be made with filter paper inside. Thus, understanding the evolution of nanostructures under aging conditions such as salt, heat, or humidity aging to understand them better was taken up for the present work. X-ray diffraction studies, Raman, and XPS confirmed varying chemical composition of the interface with the increase in ZnO concentration. From XRD, it was noted that the optimum ratios of CuS, Cu_{1.8}S, Cu₂S, and ZnO were formed at 9 PHR ZnO concentration, which might be the reason for the retention of adhesion during aging. In addition, Raman imaging revealed a higher concentration of CuS at 9 PHR. A decrease in interfacial strength at 12 PHR was predicted due to a high concentration of ZnO at the interface. XPS results further confirmed the presence of ZnO at 12 PHR in the brass-rubber interface. Comparison of results from analytical studies with a more practical measurement, aged-POF (heat-aged POF: 124.8 kgF and salt-aged POF: 64.8 kgF) inferred that 9 PHR was the optimum. The cost-saving for tire industries globally in using an optimum ZnO concentration is estimated to be \sim \$400-450 million per year. In addition, the tire manufacturers use ~12–15 PHR of ZnO in the belt and ply region of an RT. With the incorporation of 9 PHR ZnO in the belt and ply region, the usage can be reduced by 30%. This will bring relief for the growing environmental concerns of Zn release from end-of-life tires. Also, the present work will help the tire scientific community optimize ZnO content in their formulations, reduce the weight of RT, and bring down the manufacturing cost. We note that tests such as endurance, high-speed durability and strength at varying load, speed, and inflation pressure with 9 PHR ZnO will simulate tire performance closer to reality. From a futuristic perspective, the ZnO build-up mechanism at the interface at higher ZnO concentration could be studied using atom probe tomography (APT) and atomistic simulations.

tures grew in thickness from ~65 nm to ~114 nm as the

MATERIALS AND METHODS

Materials required for the preparation of the rubber mix were obtained from different manufacturers. The ZnO powder (99.9%) was obtained from J.G. Chemicals, Gujarat, and stearic acid (S.A) was purchased from Jocil, India. Silica (99.9%) and carbon black were purchased from Madhu Silica and Birla Carbon, India, respectively. Whatman No.42 filter paper was procured from GE Healthcare, Bangalore. BCSCs were obtained from Bekaert, Pune, and stored in optimum humidity conditions, and brass foil was procured from Krishna copper private limited, Gujarat. All the materials and chemicals were used as obtained from the suppliers.

a. Preparation of Rubber Compound with Different Concentrations of ZnO. A standard ASTM procedure was followed for preparing the rubber compound. First, rubber and other chemicals such as carbon black and ZnO were weighed using a Mettler Toledo weighing machine. The rubber compound preparation follows a two-step procedure to disperse the rubber additives with the polymer better, using an internal mixer. Stage 1 involves mixing natural rubber, S.A,



Figure 6. Schematic showing the preparation of the vulcanization setup for POF measurement of BCSC. (A) Unvulcanized rubber compound and BCSC before vulcanization. (B) Mold setup showing cavity and bottom lid. (C) Unvulcanized rubber compound and BCSC placed inside the mold cavity. (D) Rubber block with BCSC removed and trimmed after vulcanization. (E) Vulcanized rubber block placed in Instron 3300 instrument for POF measurement. (F) BCSC pulled out from vulcanized rubber block and POF is measured. Steps are in the sequence of A to F.

and carbon black along with different concentrations of ZnO. Then, each batch of the rubber mix was discharged from the internal mixer at 150 $^{\circ}$ C. In stage 2, the rubber batch from step 1 was cut into strips followed by the gradual addition of S and accelerator. Finally, the rubber mix was passed through a two-roll mill six times as per ASTM D2229.

b. Vulcanization of the Rubber Mixture with BCSCs for POF Measurement. This section deals with the preparation and determination of force needed to pull a BCSC from a block of vulcanized rubber. The BCSC and the rubber compound, cut to the desired dimensions, were kept ready for the molding process, as illustrated in Figure 6A. A mold (capable of producing four test blocks with 200 mm length and 12.5 mm thick samples) was chosen to vulcanize the BCSCs with the rubber mix (Figure 6B). The rubber compound was cut to the size of the mold cavity and placed on either side of BCSCs (Figure 6C). Later, the steel cords were placed over the rubber inside the mold. Another layer of rubber was carefully placed over the prepared base. This construction was gently pressed using a wooden dowel. The rubber blocks with BCSCs embedded between them were carefully removed from the block and stored at 23 ± 2 °C until vulcanization.

Preheating of the mold was done in a press at 140 °C for 40 min, and the press chosen for vulcanization had a capacity of exerting pressure greater than 3.5 MPa on the mold during vulcanization. Later, the rubber-BCSC assembly was placed on the mold and closed using the top plate of the mold. Postvulcanization, the vulcanized rubber block with BCSC was taken out of the mold (Figure 6D). The POF of this rubber block was measured by an Instron 3300 series universal testing system. In the next step, the vulcanized rubber block was pushed into the lower fixture of the instrument, and the steel cords were clamped to the upper grip (Figure 6E). Finally, the equipment measured the maximum force required to extract the cord from the vulcanized rubber block (Figure 6F).

Brass Mesh Experiment to Measure the Interfacial Thickness. Brass foil (brass composition equivalent to that of industrial BCSCs) having a thickness of 0.3 mm was procured from Krishna Copper Private Limited, Gujarat. Later, the brass foil was cut to the dimension of a TEM grid with a YAG laser, Nd:YAG Laser Tech., India, operating at a power of 800 W (Figure S1). The laser-cut brass mesh was used for vulcanization and subsequent measurement of the interfacial thickness.

Sample Preparation Technique Using Filter Paper Methodology. A filter paper (Whatman grade 42 filter papers obtained from GE Healthcare Life Science, Bangalore) was placed between rubber and BCSCs to separate them after vulcanization. Filter paper allows sulfur, accelerator, and metal ions from the rubber compound to pass through it to react with the surface of BCSCs without the direct interaction of NR and carbon black with BCSCs. Samples vulcanized with the filter paper methodology gave a clean reacted surface that was used for spectroscopic and microscopic investigations.

Aging of the Brass—Rubber Interface after Vulcanization for POF Measurements. One way to quantify the durability of radial tires is to know the distance the tire has run in its lifetime without any failure issues such as ply separation, sidewall damage, and cracks. In order to study such failures, one has to wait for months to complete the field-level evaluations. However, in compound level, as in the present case, accelerated aging experiments were conducted in the laboratory to simulate field-level evaluations and verified by POF experiments to substantiate the durability of the ply region. Thus, aging experiments that resulted in faster adhesion interface degradation were conducted. Two types of aging experiments were carried on the vulcanized rubber blocks with BCSCs i.e., heat (or thermal) and salt aging. Heat aging was conducted at 100 °C for 1 week in an industrial lab oven, and salt aging was carried out by immersing the vulcanized blocks in a solution containing 20% sodium chloride (NaCl) for 1

week at room temperature. All the test blocks were used unaltered for POF measurements after aging.

Characterization. Scanning electron microscopy (SEM) was done with a Thermo Scientific Verios G4 UC FE-SEM at an acceleration voltage of 5 kV. Atomic force microscopy (AFM) of the interface was performed using Witec Alpha 300S operated in noncontact mode. High-resolution transmission electron microscopy (HR-TEM) was done with a JEOL 3010 instrument at an operating voltage of 200 kV. X-ray diffraction (XRD) patterns of vulcanized BCSCs were collected by Bruker D8 discovery diffractometer using Cu K α radiation (wavelength = 1.54 Å), and the results were analyzed using X'Pert HighScore software. XPS spectra of the vulcanized interface were collected using an Omicron ESCA probe spectrometer with a polychromatic Al K α X-ray source (hv = 1486.6 eV).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06207.

Schematic of laser cut mesh from brass foil; large area SEM images and EDS data of vulcanized cords; AFM of BCSC showing surface roughness; graphical representation showing the brass-rubber interface thickness, unaged and aged pull out force; physical properties of rubber compound with different ZnO concentration; XRD pattern of unvulcanized brass-coated steel cord; LED white light image of unreacted and reacted BCSC; Wagner plots of Cu 2p_{3/2} and Zn 2p_{3/2} regions for compound identification at brass-rubber interface; schematic showing ply region of a radial tire and an enlarged image of the ply region showing the nanostructures interlocking with the rubber compound; relative atomic% obtained from XPS; total cross-link density of rubber compound at different ZnO concentrations (PDF)

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REFERENCES

(1) Nah, C.; Sohn, B. Y.; Park, S.-J. Adhesion of brass/cobalt/ copper-plated steel cord to a typical rubber compound. *J. Adhes. Sci. Technol.* **2002**, *16*, 653–667.

(2) Kannan, M. P.; Som, A.; Ahuja, T.; Subramanian, V.; Nair, A. S.; Pradeep, T. Nonstoichiometric Copper Sulfide Nanostructures at the Brass-Rubber Interface: Implications for Rubber Vulcanization Temperature in the Tire Industry. *ACS Appl. Nano Mater.* **2020**, *3*, 7685–7694.

(3) Vanooij, W. J.; Harakuni, P. B.; Buytaert, G. Adhesion of Steel Tire Cord to Rubber. *Rubber Chem. Technol.* **2009**, *82*, 315–339.

(4) Fulton, W. S.; Sykes, D. E.; Smith, G. C. SIMS depth profiling of rubber-tyre cord bonding layers prepared using 64Zn depleted ZnO. *Appl. Surf. Sci.* **2006**, *252*, 7074–7077.

(5) Mishra, Y. K.; Adelung, R. ZnO tetrapod materials for functional applications. *Mater. Today* **2018**, *21*, 631–651.

(6) Milani, M.; Pucillo, F. P.; Ballerini, M.; Camatini, M.; Gualtieri, M.; Martino, S. First evidence of tyre debris characterization at the nanoscale by focused ion beam. *Mater. Charact.* **2004**, *52*, 283–288. (7) Dimkpa, C. O.; Latta, D. E.; McLean, J. E.; Britt, D. W.; Boyanov, M. I.; Anderson, A. J. Fate of CuO and ZnO Nano- and Microparticles in the Plant Environment. *Environ. Sci. Technol.* **2013**, *47*, 4734–4742.

(8) Li, M.; Pokhrel, S.; Jin, X.; Mädler, L.; Damoiseaux, R.; Hoek, E. M. V. Stability, Bioavailability, and Bacterial Toxicity of ZnO and Iron-Doped ZnO Nanoparticles in Aquatic Media. *Environ. Sci. Technol.* **2011**, *45*, 755–761.

(9) Tang, Y.; Xin, H.; Yang, S.; Guo, M.; Malkoske, T.; Yin, D.; Xia, S. Environmental risks of ZnO nanoparticle exposure on Microcystis aeruginosa: Toxic effects and environmental feedback. *Aquat. Toxicol.* **2018**, *204*, 19–26.

(10) Skidmore, J. F. Toxicity of Zinc Compounds to Aquatic Animals, with Special Reference to Fish. *Q. Rev. Biol.* **1964**, *39*, 227–248.

(11) Youssef, M. S.; Elamawi, R. M. Evaluation of phytotoxicity, cytotoxicity, and genotoxicity of ZnO nanoparticles in Vicia faba. *Environ. Sci. Pollut. R.* **2020**, *27*, 18972–18984.

(12) Amari, T.; Themelis, N. J.; Wernick, I. K. Resource recovery from used rubber tires. *Resour. Policy* **1999**, *25*, 179–188.

(13) van Ooij, W. J.; Kleinhesselink, A. Application of XPS to the study of polymer-metal interface phenomena. *Appl. Surf. Sci.* **1980**, *4*, 324–339.

(14) Fulton, W. S. Tire-Cord Adhesion: How the Source of Zinc Can Influence the Structure of the Bonding Interface. *Rubber Chem. Technol.* **2006**, *79*, 790–805.

(15) Ozawa, K.; Kakubo, T.; Amino, N.; Mase, K.; Ikenaga, E.; Nakamura, T. Angle-Resolved HAXPES Investigation on the Chemical Origin of Adhesion between Natural Rubber and Brass. *Langmuir* 2017, 33, 9582–9589.

(16) van Ooij, W. J.; Weening, W. E.; Murray, P. F. Rubber Adhesion of Brass-Plated Steel Tire Cords: Fundamental Study of the Effects of Compound Formulation Variations on Adhesive Properties. *Rubber Chem. Technol.* **1981**, *54*, 227–254.

(17) Jeon, G. S.; Han, M. H.; Seo, G. Effect of ZnO contents at the surface of brass-plated steel cord on the adhesion property to rubber compound. *Korean J. Chem. Eng.* **1999**, *16*, 248–252.

(18) van Ooij, W. J. Mechanism and Theories of Rubber Adhesion to Steel Tire Cords—An Overview. *Rubber Chem. Technol.* **1984**, *57*, 421–456.

(19) van Ooij, W. J. Mechanism of Rubber-To-Brass Adhesion: Effect of Rubber Composition on the Adhesion. *Rubber Chem. Technol.* **1978**, *51*, 52–71.

(20) Liu, Y.; Zhu, G.; Yang, J.; Bao, C.; Wang, J.; Yuan, A. Phase purification of Cu-S system towards Cu1.8S and its catalytic properties for a clock reaction. *RSC Adv.* **2015**, *5*, 103458–103464.

(21) Park, H.; Kwon, J.; Kim, J.; Park, K.; Song, T.; Paik, U. Facile Growth of Metal-Rich $Cu_{1.75}S$ and $Cu_{1.8}S$ Microspheres Assembled with Mesoporous Nanosheets and Their Application in Na-Ion Batteries. *Cryst. Growth Des.* **2020**, *20*, 3325–3333.

(22) Pattrick, R. A. D.; Mosselmans, J. F. W.; Charnock, J. M.; England, K. E. R.; Helz, G. R.; Garner, C. D.; Vaughan, D. J. The structure of amorphous copper sulfide precipitates: An X-ray absorption study. *Geochim.* **1997**, *61*, 2023–20366.

(23) Peng, M.; Ma, L.-L.; Zhang, Y.-G.; Tan, M.; Wang, J.-B.; Yu, Y. Controllable synthesis of self-assembled Cu2S nanostructures through a template-free polyol process for the degradation of organic pollutant under visible light. *Mater. Res. Bull.* **2009**, *44*, 1834–1841.

(24) Baldwin, J. M.; Bauer, D. R.; Ellwood, K. R. Rubber aging in tires. Part 1: Field results. *Polym. Degrad. Stab.* **2007**, *92*, 103–109.

(25) Patil, P. Y.; van Ooij, W. J. Mechanistic Study of the Effect of Adhesion-Promoter Resins on the Crystal Structure of the Copper Sulfide Adhesion Layer at the Rubber-Brass Interface. *Rubber Chem. Technol.* **2006**, *79*, 82–93.

(26) Jeon, G. S.; Seo, G. Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-plated Steel Cord. Part II. Cure Time. J. Adhes. 2001, 76, 223–244.

(27) Jeon, G. S. Adhesion Between Rubber Compounds Containing Various Adhesion Promoters and Brass-Plated Steel Cords. Part I. Effect of Sulfur Loading in Rubber Compounds. *J. Adhes. Sci. Technol.* **2008**, *22*, 1223–1253.

(28) Khan, I.; Poh, B. T. Natural Rubber-Based Pressure-Sensitive Adhesives: A Review. J. Polym. Environ. 2011, 19, 793-811.

(29) Larsen, I. L.; Thorstensen, R. T. The influence of steel fibres on compressive and tensile strength of ultra high performance concrete: A review. *Constr. Build. Mater.* **2020**, *256*, 119459.

(30) Baert, K.; Breugelmans, T.; Buytaert, G.; Brabant, J. V.; Hubin, A. The combination of surface enhanced Raman spectroscopy and an ionic liquid as a model system to study the adhesion interface between sulfur and brass. *J. Raman Spectrosc.* **2013**, *44*, 377–381.

(31) Shawky, A.; El-Sheikh, S. M.; Gaber, A.; El-Hout, S. I.; El-Sherbiny, I. M.; Ahmed, A. I. Urchin-like CuS nanostructures: simple synthesis and structural optimization with enhanced photocatalytic activity under direct sunlight. *Appl. Nanosci.* **2020**, *10*, 2153–2164.

(32) Uhlig, S.; Möckel, R.; Pleßow, A. Quantitative analysis of sulphides and sulphates by WD-XRF: Capability and constraints. *Xray Spectrom.* **2016**, *45*, 133–137.

(33) Biesinger, M. C. Advanced analysis of copper X-ray photoelectron spectra. *Surf. Interface Anal.* **2017**, *49*, 1325–1334.

(34) Vdovenkova, T.; Vdovenkov, A.; Tornqvist, R. ZnS wide band gap semiconductor thin film electronic structure sensitivity to Mn impurity. *Thin Solid Films* **1999**, *343-344*, 332–334.

(35) NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20; National Institute of Standards and Technology: Gaithersburg, MD, 2000.

(36) Wagner, C. D. Auger lines in x-ray photoelectron spectrometry. *Anal. Chem.* **1972**, *44*, 967–973.