

# Effect of Modified Zinc Oxide-Silica Nanocomposites on Epoxidized Natural Rubber/Tire Waste Composites Properties

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**Abstract:** Epoxidized natural rubber (ENR) was blended with tire waste (TW) and modified zinc oxide-silica nanoparticles (ZnO-SiO<sub>2</sub>) using melt mixing, with NR acting as a compatibilizer to link the two incompatible phases—between the polar epoxy groups of ENR and the non-polar rubber in TW. Various ZnO-SiO<sub>2</sub> concentrations of 5, 10, 15, and 20 phr were investigated to determine their effects on cure characteristics, mechanical properties, and antibacterial efficiency of the received composites. It was found that adding ZnO-SiO<sub>2</sub> improved crosslink density, thereby enhancing the acceleration activity of the chemical crosslinking processes, which resulted in longer cure times and scorch times. Optimal loading of 20 phr enhanced the 100% and 300% moduli values to 1.29 and 3.73 MPa, respectively, along with a tensile strength of 10.52 MPa, highlighting the improved mechanical properties of the nanocomposite with ZnO-SiO<sub>2</sub> loadings. This optimal loading also provided superior antibacterial activity, achieving over a 99.0% reduction in bacterial presence within 24 h through releasing Zn<sup>2+</sup> ions and generating reactive oxygen species (ROS). At this concentration, the optimal values regarding ZnO-SiO<sub>2</sub> particles that can form further agglomerates are reached. These findings support the development of rubber composites with improved performance and durability, as well as enhanced antibacterial protection, for various rubber applications, including footwear, self-pads, and rubber floor mats, highlighting their significance in enhancing product safety and longevity.

**Keywords:** Natural rubber, Epoxidized natural rubber, Tire waste, Nanocomposites, Antibacterial efficiency

## 1. Introduction

In recent years, the development of sustainable materials has emerged as a critical response to environmental challenges while enhancing the performance of industrial products. The tire industry, in particular, generates a substantial global output of rubber goods, leading to significant tire waste. These tires are intricately cross-linked with chemical bonds and various additives [1], making their disposal time-consuming due to their non-degradability, often requiring incineration or landfilling [2]. However, these conventional disposal methods can contribute to environmental pollution through chemical blooming or combustion by-products. To mitigate these environmental impacts, recycling

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rubber into new materials or reclaiming it through devulcanization processes, which utilize chemicals and mechanical shear to break the crosslink bonds between polymer chains into smaller molecules, has gained traction [3]. Also, adding reclaimed rubber sourced from used tires significantly enhances environmental sustainability. This reclaimed rubber is integrated into the original rubber to add value. Natural rubber (NR), well-known for its exceptional flexibility, tensile strength, and resistance to abrasion and heat buildup during use [4], remains a cornerstone in the rubber industry. Nonetheless, its susceptibility to heat and oxidation restricts its application in specific environments.

To overcome these limitations, NR undergoes chemical modification through epoxidation to produce epoxidized NR (ENR). This process introduces epoxide groups into the molecular structure, thereby enhancing resistance to ozone, chemicals, oils, and non-polar solvents [5]. Despite these advancements, concerns persist regarding the antimicrobial properties of rubber products, especially in contexts where bacterial proliferation poses health risks. The integration of antibacterial agents, such as zinc oxide (ZnO), gold (Au), aluminium (Al), and titanium dioxide (TiO<sub>2</sub>) nanoparticles [6,7], presents a promising solution. While all these antibacterial agents exhibit antimicrobial properties, ZnO is particularly effective against a broad spectrum of bacteria, including both gram-positive and gram-negative strains [8]. ZnO also has high thermal conductivity, which enhances its performance in thermal applications and during the vulcanization process of rubber [8]. Additionally, ZnO is considered safe for human use compared to other nanoparticles, such as Au, Al, and TiO<sub>2</sub>, which can exhibit toxicity at high concentrations of uses, in particular, the Al nanoparticles that can be considered as a toxic metal element for human cells [9]. These factors collectively make ZnO a suitable choice for enhancing the performance and durability of rubber composites, especially in applications requiring antibacterial protection. It was found that the ZnO nanoparticles demonstrate a robust antimicrobial effect against bacteria, including *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) [10], disrupting bacterial cell walls and processes through reactive oxygen species (ROS) and Zn<sup>2+</sup> ion interference [11]. However, challenges arise from nanoparticle agglomeration within rubber matrices, as previous studies have shown that the formation of Zn–O–Zn bonds among particles results in strong agglomeration of ZnO [12]. This agglomeration reduces the properties of ZnO-filled rubber, indicating that modification of ZnO may be necessary to avoid this issue. One potential solution is to absorb ZnO nanoparticles onto silica nanoparticles (SiO<sub>2</sub>) surfaces, which enhances dispersion and interaction within the rubber matrix. The smaller particle size of SiO<sub>2</sub> improves the dispersion and distribution of ZnO inside the rubber matrix, thereby enhancing mechanical properties and antibacterial efficacy [13].

Therefore, this study aims to examine the use of modified ZnO by investigating the influence of ZnO-SiO<sub>2</sub> nanocomposites on the properties of ENR/tire waste (TW) composites, with NR acting as a compatibilizer to link the two incompatible phases—between the polar epoxy groups of ENR and the non-polar rubber in TW. This compatibilizer helps facilitate the distribution and interaction of these nanoparticles throughout the rubber matrix, leading to improved mechanical and antibacterial properties. With ENR with 25 mol% epoxide, another part of the molecular chains are the non-polar NR segments, which can be linked simply through the intermolecular force attraction with NR and TW chains. The present work focuses on characterizing cure characteristics, mechanical strength, and antibacterial properties to deliver sustainable, high-performance rubber materials by combining waste and ZnO compounds.

## 2. Methodology

### 2.1 Materials

Epoxidized natural rubber (ENR) with 25 mol% epoxide was obtained from Muang Mai Guthrie Co., Ltd. (Surat Thani, Thailand). Natural rubber (NR), grade STR5L, was purchased from Bossoftical Public Co., Ltd. (Songkhla, Thailand). Tire waste (TW) with a Mooney viscosity (ML[1+4] 100 °C) of 52.17, a specific gravity of 1.15, an ash content of 6.62 wt%, and a moisture content of 0.49 wt% was manufactured by Thai Rubb Tech Co., Ltd. (Bangkok, Thailand). Modified zinc oxide with silica nanoparticles (ZnO-SiO<sub>2</sub>), with a ZnO:SiO<sub>2</sub> ratio of 90:10 wt% and a particle size of 30 nm, was manufactured by Global Chemical Co., Ltd. (Samut Prakan, Thailand). Stearic acid was purchased from Imperial Chemical Co., Ltd. (Pathum Thani, Thailand). Dibenzothiazyl disulfide (MBTS) and sulfur were purchased from Flexsys Inc. (Termoli, Italy).

## 2.2 Preparation of the ENR/NR/TW composites

The rubber composites composed of ENR, NR, and TW in ratios of 40:10:50 phr were prepared through a melting mixing process using an internal mixer. The composites included varying loadings of ZnO-SiO<sub>2</sub>, specifically 0, 5, 10, 15, and 20 phr, to assess their effects on the properties of the ENR/NR/TW composites. The mixing was operated at a controlled temperature of 80 °C, a fill factor of 75%, and a rotor speed of 60 rpm. The composite was mixed according to the formulation and mixing steps detailed in Table 1. The ENR/NR/TW compound was then sheeted out through an opened two-roll mill to create the sheets. Finally, the crosslinked samples were produced based on the curing time determined from the cure test, using compression molding at a fixed temperature of 160 °C. It is noted that the ENR:NR:TW ratios were chosen related to the intrinsic properties of ENR on mechanical and durability performances from interaction with polar SiO<sub>2</sub> fillers, whereas the role of NR is to link ENR and TW for improving both phases' interactions.

**Table 1** Formulation of ENR/NR/TW filled with various ZnO-SiO<sub>2</sub> loadings

Ingredients	Content (phr*)	Mixing time (min)
ENR	40	3
NR	10	
Tire waste	50	
Stearic acid	1	1
ZnO-SiO <sub>2</sub>	0, 5, 10, 15 and 20	1
MBTS	1	1
Sulfur	2.5	2

\*phr = Parts per hundred of rubber

## 2.3 Characterizations

### Cure characteristics

Cure characteristics of the ZnO-SiO<sub>2</sub>-filled ENR/NR/TW compounds were obtained using a moving die rheometer (MDR). Samples of the respective compounds were tested at a temperature of 160 °C to determine the scorch time ( $T_{s2}$ ), cure time ( $T_{90}$ ), minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), and torque difference ( $M_H - M_L$ ) according to ASTM D5289.

### Mechanical properties

Tensile properties of ENR/NR/TW composites were performed using a universal testing machine (Zwick Z 1545, Zwick GmbH and Co. KG, Ulm, Germany) at room temperature. The crosshead speed was 200 mm/min, and the load cell capacity was 500 N. The samples were cut into dumbbell shapes according to ISO 37 (Type 2) from the molded sheets.

### Morphologies

The morphologies and elemental compositions of the fractured surfaces of the rubber composites were analyzed using scanning electron microscopy (SEM-EDX) (Phenom ProX, Thermo Fisher Scientific, Brno, Czech Republic). High-resolution images were captured at an accelerating voltage of 30 kV. The cross-sectional surfaces of the fractured composite samples were prepared by cryogenically cracking them in liquid nitrogen. Subsequently, the surfaces of the composites were coated with a thin layer of gold to prevent electrical charging before imaging.

### Antibacterial activity

The antibacterial activity of rubber composites against *Staphylococcus aureus* (*S. aureus*) was evaluated using the JIS Z2801 method. Bacteria were suspended in nutrient broth (NB medium) with an initial concentration of 10<sup>6</sup> colony-forming unit per milliliter (CFU/ml). The 0.4 ml of the bacterial suspension was dropped onto 5 cm x 5 cm sample test surface placed in a sterilized Petri dish. The droplet was covered with sterilized PE film to prevent the suspension from drying during the following process. The inoculated sample tests were then incubated at 35 °C for

24 h to facilitate bacterial growth. Subsequently, bacteria were recovered from the sample test and subjected to ten-fold serial dilution. The diluted bacterial suspensions were plated on a nutrient agar medium and incubated at 37 °C for 24 h. The antibacterial activity was expressed as the percentage reduction of bacteria, calculated using Equation 1.

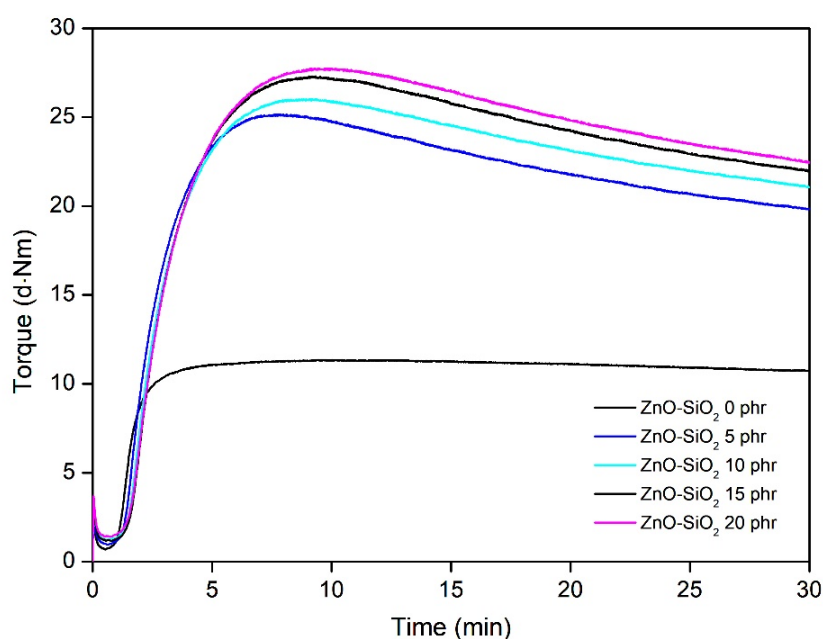
$$R = \frac{(A - B)}{A} \times 100 \quad (1)$$

Where  $R$  = Percentage reduction of bacteria (%)  
 $A$  = Log CFU per milliliter of viable bacteria after treatment (0 h)  
 $B$  = Log CFU per milliliter of viable bacteria before treatment (24 h)

### 3. Results and discussion

#### Cure characteristics

The effect of different loadings of modified ZnO-SiO<sub>2</sub> in ENR/NR/TW composites on curing characteristics is detailed in Figure 1 and summarized in Table 2. It can be seen that the torque difference ( $M_H - M_L$ ) increases with increasing ZnO-SiO<sub>2</sub> content. The  $M_H - M_L$  values serve as an indicator of the stiffness of the vulcanized rubber, which correlates with the crosslink density [14]. This increase is attributed to ZnO activating the vulcanization process, promoting the formation of sulfur crosslinks among the ENR and NR chains. Furthermore, the presence of SiO<sub>2</sub> aids in the better dispersion of ZnO particles, which enhances their effectiveness in the crosslinking process, as demonstrated in the increment of  $M_H - M_L$  values. The SiO<sub>2</sub>, with its smaller particle size and larger surface area, helps to physically separate the ZnO particles, preventing agglomeration. This improved dispersion increases the availability of ZnO nanoparticles throughout the rubber matrix, ensuring more uniform interaction with the rubber chains during vulcanization. On a chemical level, the surface of SiO<sub>2</sub> contains silanol groups (Si-OH), which are chemically active and can absorb accelerators used in the vulcanization process. They behave as acids, are chemically active, and can absorb accelerators [15]. This absorption reduces their effectiveness, resulting in longer scorch time ( $T_{s2}$ ) and cure time ( $T_{90}$ ) to form crosslinks than formulations without modified ZnO-SiO<sub>2</sub>.



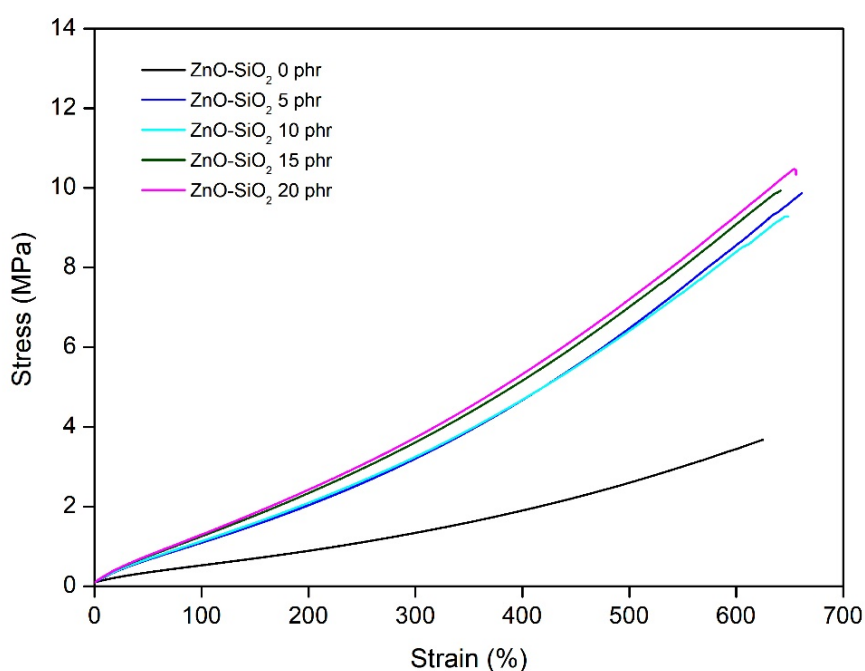
**Figure 1** Cure characteristic curves of ENR/NR/TW composites filled with different ZnO-SiO<sub>2</sub> loadings.

**Table 2** Cure characteristics of ENR/NR/TW composites filled with different ZnO-SiO<sub>2</sub> loadings

Formulations	Properties				
	T <sub>s2</sub> (min)	T <sub>90</sub> (min)	M <sub>L</sub> (d·Nm)	M <sub>H</sub> (d·Nm)	M <sub>H</sub> -M <sub>L</sub> (d·Nm)
ZnO-SiO <sub>2</sub> 0 phr	1:17	2:51	0.60	8.42	7.82
ZnO-SiO <sub>2</sub> 5 phr	1:29	4:41	0.84	18.57	17.73
ZnO-SiO <sub>2</sub> 10 phr	1:40	5:11	1.08	19.21	18.13
ZnO-SiO <sub>2</sub> 15 phr	1:44	5:29	1.03	20.15	19.12
ZnO-SiO <sub>2</sub> 20 phr	1:43	5:40	1.24	20.49	19.25

### Mechanical properties

The mechanical properties of ENR/NR/TW composites filled with different loadings of modified ZnO-SiO<sub>2</sub> are demonstrated in Figure 2 and summarized in Table 3. This indicates a notable enhancement of the composite properties relative to those without ZnO-SiO<sub>2</sub>. This improvement is attributed to the dual role of ZnO nanoparticles, which act as both an activator in the vulcanization process and a reinforcing filler regarding the existence of SiO<sub>2</sub>. The sulfur curing system uses ZnO as the activator; when rubber compounds are heated, ZnO interacts with the accelerator and sulfur, promoting the formation of polysulfide links between sulfur atoms. This reaction helps to create a network structure that significantly enhances the thermal and mechanical stabilities of the composite [16]. As a reinforcing filler, ZnO increases the tensile strength and load-bearing capacity of the material. The presence of SiO<sub>2</sub> further reinforces the composite and promotes better dispersion of ZnO nanoparticles within the rubber matrix, leading to improved load-bearing capacity. However, increasing ZnO-SiO<sub>2</sub> loading shows a slight decrease in tensile strength and no significant differences in elongation at break. This decline is primarily due to partial nanoparticle agglomeration, where the particles cluster together, reducing their effective surface area and interaction with the ENR/NR matrices. This agglomeration restricts the movement of rubber chains, reducing the overall flexibility of the matrix. As a result, there is an increase in the moduli values of 100% and 300%, indicating that the material becomes stiffer and less elastic.


**Figure 2** Stress-strain curves of ENR/NR/TW composites at different ZnO-SiO<sub>2</sub> loadings.

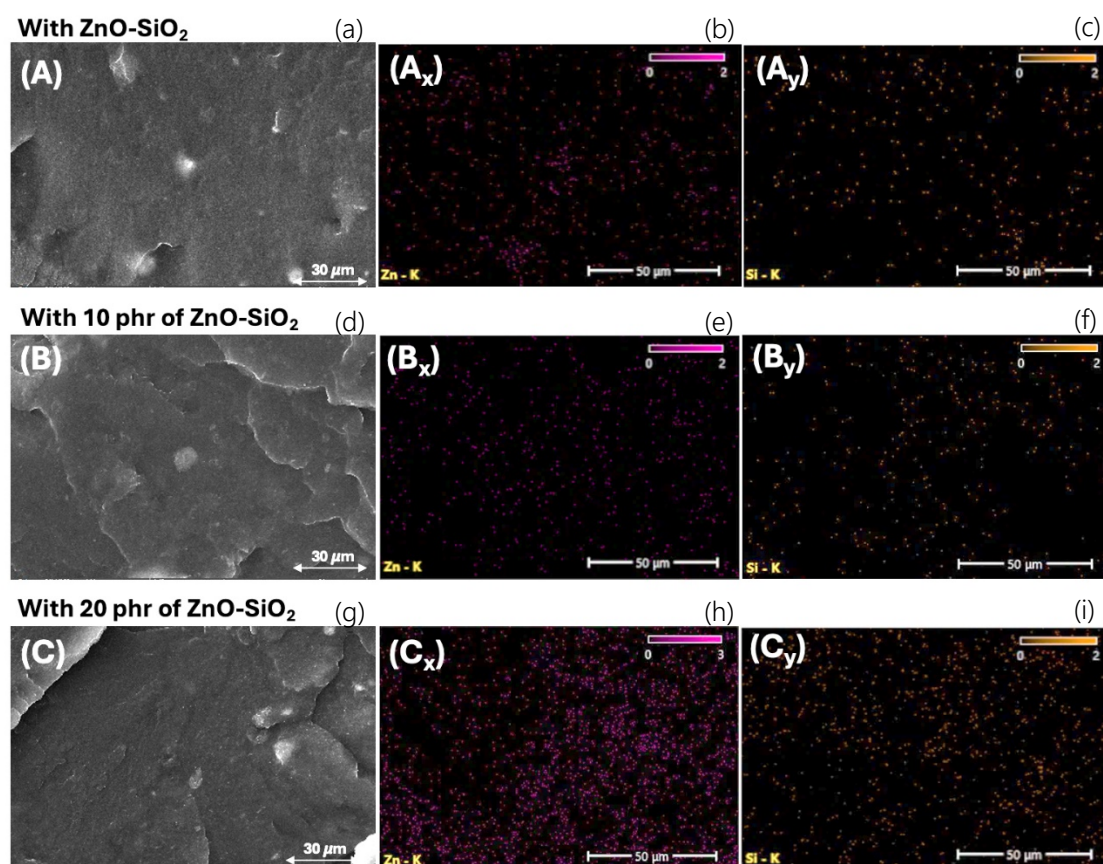


**Table 3** Mechanical properties of ENR/NR/TW composites at different ZnO-SiO<sub>2</sub> loadings

Formulations	Tensile strength (MPa)	Elongation at break (%)	100% Modulus (MPa)	300% Modulus (MPa)
ZnO-SiO <sub>2</sub> 0 phr	3.72±0.13	624.15±22.42	0.52±0.01	1.34±0.01
ZnO-SiO <sub>2</sub> 5 phr	10.15±0.47	665.89±16.40	1.09±0.02	3.22±0.03
ZnO-SiO <sub>2</sub> 10 phr	9.32±0.17	642.57±10.51	1.14±0.01	3.29±0.04
ZnO-SiO <sub>2</sub> 15 phr	9.94±0.23	629.31±12.12	1.27±0.03	3.69±0.07
ZnO-SiO <sub>2</sub> 20 phr	10.52±0.07	655.84±5.21	1.29±0.02	3.73±0.01

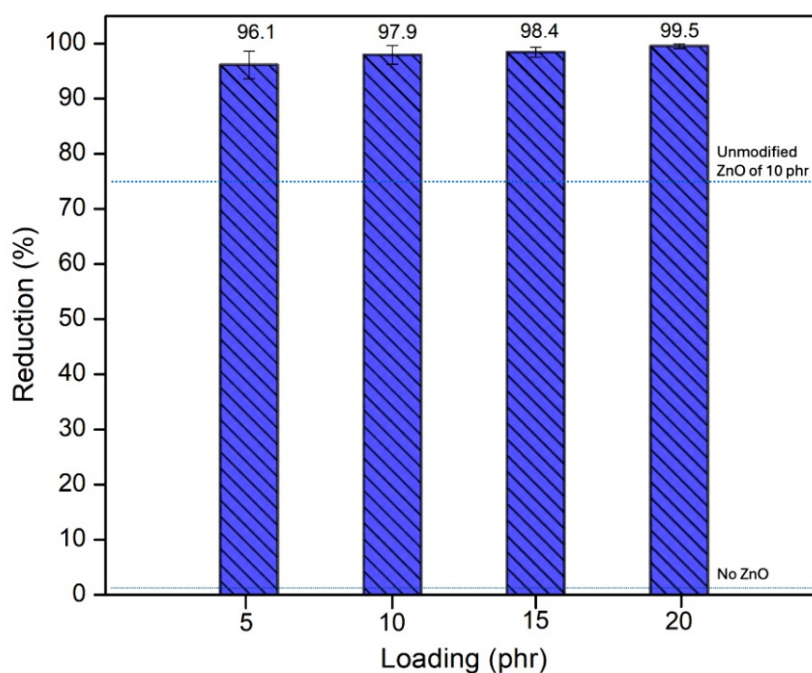
### Morphologies

The morphologies of ENR/NR/TW composites using SEM-EDX analyses are shown in Figure 3. It is observed that ZnO and SiO<sub>2</sub> particles are dispersed in rubber composites even without the addition of modified ZnO-SiO<sub>2</sub> (Figures 3(a)–(c)) due to the existing ZnO and SiO<sub>2</sub> in tire waste. In addition, it was found that adding modified ZnO-SiO<sub>2</sub> at 10 phr improves the overall dispersion of ZnO particles, as seen in Figures 3(d)–(f). This improved dispersion is attributed to the role of SiO<sub>2</sub> in promoting better distribution within the ENR/NR matrices. The presence of modified ZnO-SiO<sub>2</sub> helps facilitate a more uniform dispersion, enhancing some mechanical properties. At 20 phr loading, agglomeration of ZnO particles occurs, as observed in Figures 3(g)–(i). This agglomeration results in the clustering of particles, reducing their effective surface area and interaction with the rubber matrix. However, this clustering is not extensive, leading to no significant decrease in tensile strength and elongation at break.


**Figure 3** SEM micrographs and its EDX mapping of ENR/NR/TW composites without ZnO-SiO<sub>2</sub> (A)–(A<sub>y</sub>) and filled with ZnO-SiO<sub>2</sub> 10 phr (B)–(B<sub>y</sub>), and ZnO-SiO<sub>2</sub> 20 phr (C)–(C<sub>y</sub>).

### Antibacterial activity

The antibacterial activity of ENR/NR/TW composites was evaluated against *S. aureus*, as shown in Figure 4. The results indicate that ENR/NR/TW composites without adding modified ZnO-SiO<sub>2</sub> showed no antibacterial efficiency, whereas the blend with unmodified ZnO showed antibacterial at approximately 75.0%. However, adding modified ZnO-SiO<sub>2</sub> significantly enhanced antibacterial activity, achieving over a 90% reduction of *S. aureus*, a gram-positive bacteria, after 24 h at a loading of 5 phr for 90:10 %wt of ZnO:SiO<sub>2</sub>. With increasing ZnO-SiO<sub>2</sub>, the antibacterial activity has also increased as over 99.0% reduction was observed at a loading of 20 phr. This correlates with studies of Mou et al. [17], which have demonstrated a similar tendency for rubber composites to improve antibacterial properties after adding solely SiO<sub>2</sub> and ZnO hybrid nanofillers. These synergistic fillers effectively inhibit bacterial growth, particularly both *E. coli* and *S. aureus*, within 24 h. This significant antibacterial performance can be attributed to the photocatalytic process of modified ZnO-SiO<sub>2</sub> under visible light, which generates reactive oxygen species (ROS), including superoxide anions, hydroxyl radicals, and hydrogen peroxide. These ROS play a crucial role in disrupting the cell wall and DNA of the bacteria. It is seen that the release of Zn<sup>2+</sup> ions from the modified ZnO-SiO<sub>2</sub> further enhances the antibacterial effect by interfering with bacterial cell walls and cellular functions. The good dispersion of modified ZnO within the rubber matrix, facilitated by polar-polar intermolecular forces, ensures that ZnO ions are efficiently driven to the rubber surfaces. This effective dispersion increases the availability of Zn<sup>2+</sup> ions and ROS on the surface of the rubber composite, allowing them to interact more effectively with bacterial cell walls and cytoplasm, leading to enhanced antibacterial activity [18].



**Figure 4** Antibacterial activities of the ENR/NR/TW composites filled with different ZnO-SiO<sub>2</sub> loadings against *S. aureus* over a 24 h contact period. It is noted that the one with no ZnO-SiO<sub>2</sub> has no antibacterial performance.

### 4. Conclusion

This work investigates the effect of modified ZnO-SiO<sub>2</sub> on ENR/NR/TW composites, focusing on cure characteristics, mechanical properties, and antibacterial activity. The addition of ZnO-SiO<sub>2</sub> increases crosslink density in the composites by promoting the formation of crosslinks among the ENR/NR molecular chains. This was evidenced

by higher  $M_H$ - $M_L$  values with increased ZnO contents. The presence of silanol groups on the  $\text{SiO}_2$  surface in modified ZnO- $\text{SiO}_2$  absorbs accelerators, reducing their effectiveness and resulting in longer scorch and cure times compared to formulations without modified ZnO- $\text{SiO}_2$ . The addition of modified ZnO- $\text{SiO}_2$  also improves the mechanical properties of the composites. However, higher loadings can lead to a slight decrease in tensile strength and elongation at break. This is due to nanoparticle agglomeration, which reduces interactions and restricts chain movement, resulting in an increased modulus. In addition, modified ZnO- $\text{SiO}_2$  significantly improves bacterial interaction in the composites. High loading of ZnO- $\text{SiO}_2$  exhibits more than 99.0% for against *S. aureus* within 24 h. This is due to the enhanced  $\text{Zn}^{2+}$  ion release and ROS to the cell wall and DNA of the bacteria.

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