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# Removing hazardous additives from elastomer manufacturing

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ABSTRACT

Elastomers known as rubber are ubiquitous in industrial applications, but they often contain chronic additives, such as zinc oxide, tetramethylthiuram monosulfide (denoted TMTM), and copper dimethyldithiocarbamate (CDD) that has a higher melting point than the common vulcanization temperature. These additives are released into the environment either through the wear and tear of tires and the landfilling of waste rubber. It is imperative to identify and adopt safe, cost-effective alternatives to replace zinc oxide and TMTM, both of which have moderate chronicity rating. Styrene-butadiene rubber (SBR) in this study is cured by using sulphur, zinc stearate, and dipentamethylenethiuram hexasulfide (TRA). The curing characteristics and the morphology and mechanical properties of the cured SBR are investigated. Zinc stearate and TRA exhibit a commendable rating of zero in terms of both chronicity and toxicity, making them promising candidates for substituting chronic additives. Adding 0.25 phr of zinc stearate into SBR can significantly enhance the crosslinking density while exhibiting anti-reversion performance, in comparison with a recipe that includes 5 phr of zinc oxide and 8 phr of TMTM. Transmission electron microscopy reveals that the zinc oxide (nano) particles are not soluble in SBR, and thus only the particle surface contributes to vulcanization. TRA is "dissolvable" in SBR, making it an ideal replacement for CDD which is insoluble due to its high melting point. Therefore, we strongly advise against the utilization of curing additives with melting points that exceed the vulcanization temperature. This work contributes to the green manufacture of elastomers.

## 1. Introduction

Elastomers are essential in industry and household products. For instance, the tire industry alone accounts for 60% of global natural rubber consumption [1]. Malaysia, Indonesia, and Thailand are the three largest rubber manufacturers in the Southeast Asia [2], whilst China accounted for ~35% production of tyres worldwide in recent years [3]. Since Goodyear's discovery of rubber vulcanization in 1839, a range of curing activators and accelerators have been developed. However, these chemicals have various degrees of toxicity and chronicity, posing hazards to human beings and the environment. To provide a comprehensive overview of the potential health and environmental impacts of common curing activators and accelerators, we consulted the Chemwatch database. Tables 1-9 present those commonly used curing additives with a four-level rating system for both toxicity and chronicity: number 0 for minimum, 1 for low, 2 for moderate, 3 for high, and 4 for extreme.

Zinc oxide particles are commonly utilized as additives in the manufacture of elastomers. Approximately one million tons of zinc oxide are produced annually, with 50% used in the elastomer industry [4]. Unfortunately, the widespread use of zinc oxide in elastomer products, such as tires, has resulted in significant environmental concerns. As elastomer products wear down or are disposed of through incineration or landfill, toxic and chronic zinc oxide particles are released into the environment. It is estimated that up to 500,000 tons of zinc oxide particles are released annually [5].

According to Chemwatch, zinc oxide is rated 1 in toxicity and 2 in chronicity (Table 1), and its impact on the ecosystem and human health

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**Table 1**
Toxicity and chronicity of curing activators (as of June 2023).

| CAS Number | Name | Toxicity | Chronicity |
|---|---|---|---|
| 1314-13-2 | Zinc oxide | 1 | 2 |
| 57-11-4 | Stearic acid | 0 | 0 |
| 557-05-1 | Zinc stearate | 1 | 0 |

is concerning. For instance, research has found that urban areas exhibit concentrations of zinc up to ten times higher than rural areas mainly due to tyre wear [6]. Furthermore, a regulation (No. 1272/2008) from the European Parliament and the Council have identified zinc oxide as a substance that poses a significant risk to aquatic life, and its release into the environment must be prevented. Studies have also found that the presence of zinc oxide particles dwarfs thale cress, a flowering plant [7] and increases the risk of asthma in children [8]. In summary, the disposed zinc oxide particles present a risk to both the environment and public health.

The Supporting Information briefly introduces vulcanization mechanisms and presents the melting points and molecular structures of certain curing additives as well as rheometer graphs of our samples. The zinc-sulphur complex intermediate, which is formed via the reaction of zinc oxide, stearic acid, and sulphur, is a critical component in the vulcanization process [9,10]. Rather than direct participation in vulcanization, zinc oxide reacts with stearic acid to produce soluble zinc ions, which in turn form a zinc complex with the accelerator and the cleaved sulphur. However, the melting point of zinc oxide, ~1974 °C, is drastically higher than the vulcanization temperature. As a result, the zinc ions inside the zinc oxide particles would be unable to participate in vulcanization. From our perspectives, zinc oxide should be replaced with environmentally friendly additives due to chronicity.

Several studies have demonstrated that soluble zinc salts, when combined with accelerators and sulphur, can effectively promote the vulcanization of elastomers. For instance, Magdalena et al. found that zinc acetylacetonate, zinc gluconate, and zinc ricinoleate could be used as substitutes for zinc oxide. The resulting elastomer products showed higher damping properties in comparison with those produced using zinc oxide and stearic acid [11]. Similarly, Yang et al. reported that using a combination of zinc glycerolate and zinc laurate created low concentrations of zinc ions that were sufficient for satisfactory cross-linking and mechanical properties [12]. These findings suggest that zinc oxide is only indirectly involved in the vulcanization process; the soluble zinc salts contribute to the curing process by providing zinc ions.

Zinc oxide and stearic acid, as common additives, play a dominant role in the elastomer manufacturing industry. As illustrated in Fig. 1, these additives react with each other to form zinc stearate and release water molecules. Since the vulcanization of elastomers is undertaken in a closed mould under pressure at temperatures above 140 °C, water molecules transform into vapor, forming voids in the final product and compromising mechanical performance. Helaly et al. found that using zinc stearate as an activator improved the physico-mechanical properties of cured natural rubber [13]. Given the promising results of zinc stearate for vulcanization of natural rubber, further research is needed to investigate further the curing behaviour, reversion resistance, and mechanical properties of the resultant elastomers.

In addition to toxicity and chronicity, other limitations for many

**Table 3**
Toxicity and chronicity of curing accelerators - sulfenamides (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 95-33-0 | N-Cyclohexyl-2-benzothiazolesulfenamide | CBS (or CZ) | 2 | 3 |
| 95-31-8 | N-tert-Butyl-2-benzothiazolesulfenamide | TBBS (NS) | 3 | 3 |
| 102-77-2 | 2-(Morpholinothio) benzothiazole | NOBS (MBS) | 1 | 2 |
| 4979-32-2 | N,N-Dicyclohexyl-2-benzothiazolesulfenamide | DZ (DCBS) | 1 | 3 |
| 13752-51-7 | 4-Morpholinecarbodithioic acid | OTOS | 1 | 2 |

**Table 4**
Toxicity and chronicity of curing accelerators - thiuram (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 137-26-8 | Tetramethylthiuram disulfide | TMTD | 2 | 2 |
| 97-77-8 | Tetraethylthiuram disulfide | TETD | 2 | 2 |
| 1634-02-2 | Tetrabutylthiuram disulfide | TBTD | 1 | 2 |
| 97-74-5 | Tetramethylthiuram monosulfide | TMTM (or TS) | 2 | 2 |
| 10591-85-2 | Tetrabenzylthiuram disulfide | TBzTD | 1 | 0 |
| 971-15-3 | Dipentamethylenethiuram hexasulfide | DPTT (TRA) | 0 | 0 |

**Table 5**
Toxicity and chronicity of curing accelerators - dithiocarbamates (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 137-30-4 | Zinc dimethyldithiocarbamate | ZDMC (or PZ) | 4 | 2 |
| 14324-55-1 | Zinc diethyldithiocarbamate | ZDEC (EZ) | 2 | 2 |
| 136-23-2 | Zinc(II) dibutyldithiocarbamate | ZDBC (BZ) | 1 | 2 |
| 136-30-1 | Dibutyl carbamodithioic acid sodium salt | SDBC (TP) | 2 | 2 |
| 14634-93-6 | Zinc N-Ethyl-N-phenyldithiocarbamate | ZnEPDC (PX) | 1 | 0 |
| 14726-36-4 | Zinc dibenzyldithiocarbamate | ZBDC (ZTC) | 1 | 0 |
| 137-29-1 | Copper dimethyldithiocarbamate | CDD (TTCu) | 1 | 0 |
| 14484-64-1 | Ferbam | TTFe | 2 | 2 |
| 20941-65-5 | Tetrakis (diethyldithiocarbamato) -tellurium (IV) | TDEC | 1 | 1 |
| 55310-46-8 | Dibenzyldithiocarbamic acid sodium salt | SBEC | 2 | 2 |
| 21260-46-8 | Bismuth dimethyldithiocarbamate | TTBi | 1 | 0 |

**Table 2**
Toxicity and chronicity of curing accelerators - thiazoles (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 149-30-4 | 2-Mercaptobenzothiazole | MBT (or M) | 1 | 3 |
| 120-78-5 | 2,2′-Dithiobis(benzothiazole) | MBTS (or DM) | 1 | 2 |
| 155-04-4 | 2-Mercaptobenzothiazolezincsalt | ZMBT (or MZ) | 2 | 2 |
| 95-16-9 | Benzothiazole | BT | 2 | 0 |
| 1908-87-8 | 3-Methyl-1,3-thiazolidine-2-thione | MTT | 2 | 0 |

**Table 6**
Toxicity and chronicity of curing accelerators - thioureas (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 96-45-7 | 2-Imidazolidinethione | ETU | 2 | 3 |
| 105-55-5 | N,N′-Diethylthiourea | DETU | 2 | 2 |
| 102-08-9 | N,N′-Diphenylthiourea | DPTU | 3 | 2 |
| 109-46-6 | N,N′-Dibutylthiourea | DBTU | 2 | 0 |

**Table 7**
Toxicity and chronicity of curing accelerators – guanidines (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 102-06-7 | 1,3-Diphenylguanidine | DPG (D) | 2 | 2 |
| 97-39-2 | 1,3-Di-o-tolylguanidine | DOTG | 2 | 0 |

**Table 8**
Toxicity and chronicity of curing accelerators - dialkyldithiophosphates (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 68649-42-3 | zinc dialkyl dithiophosphate | ZDTP | 1 | 0 |

**Table 9**
Toxicity and chronicity of curing accelerators - organic ammonia (as of June 2023).

| CAS Number | Name | Abbreviation | Toxicity | Chronicity |
|---|---|---|---|---|
| 100-97-0 | Hexamethylenetetramine | HMTA | 1 | 2 |

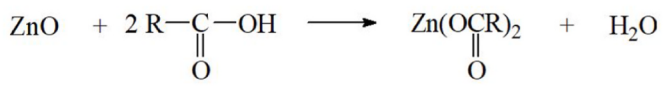



**Fig. 1.** Reaction between ZnO and $C_{17}H_{35}COOH$.

curing additives include (i) incompatibility with certain elastomers and (ii) melting points higher than the vulcanization temperature. As a result, the curing additives may not fully dissolve or disperse uniformly within the elastomer, hindering their participation in the vulcanization process. These undissolved additive particles may cause blooming, a phenomenon where the curing additives gradually diffuse onto the surface of the final product during service. Blooming leads to surface discoloration and in the long term contributes to environmental pollution as the additive particles become dislodged from the product.

The use of high-melting point curing additives should be avoided, as they do not melt during the vulcanization process. For example, copper dimethyldithiocarbamate (CDD), a commonly used curing accelerator, has a melting point of approximately 250 °C that is significantly higher than the typical vulcanization temperatures of 140 – 170 °C. As a result, these curing additive particles, including zinc oxide, are released into the environment during service and waste disposal. This is an increasingly serious environmental problem as many high-melting point accelerators have toxicity and chronicity ratings of 2 – 3. A hypothesis made herein was that a high-melting point curing accelerator would not melt and hence not well contribute to vulcanization — only the atoms or molecules on the surface of these particles can contribute to the vulcanization process, whilst the majority of the accelerator remains in the elastomer matrix after vulcanization.

This study aims to investigate the potential use of zinc stearate as a curing activator for sulphur vulcanization of styrene-butadiene rubber (SBR) and its suitability as a substitute for zinc oxide, which is limited by moderate chronicity. This work also aims to explore the possibility of substituting either high-melting point or toxic curing accelerators, such as tetramethylthiuram monosulfide (TMTM) and copper dimethyldithiocarbamate (CDD), with dipentamethylenethiuram hexasulfide (TRA) that has a lower melting point of 135 °C and is rated 0 in chronicity. The effects of zinc stearate fractions on the curing characteristics and mechanical properties of SBR will be examined. Furthermore, a comparison will be made between two batches of SBR, one cured with TMTM and zinc oxide and the other cured with TRA and zinc stearate, to determine the differences in their curing characteristics and mechanical properties. Transmission electron microscopy (TEM) will be employed to observe the dispersion and "dissolution" of the particles of curing activators and accelerators in SBR.

## 2. Experimental

### 2.1. Materials

Styrene-butadiene rubber (SBR, 1502) with 22.5 to 24.5% of bonded styrene was purchased from Jilin Petrochemical Co. Ltd. (Jilin, China). Curing accelerators dipentamethylenethiuram hexasulfide (TRA), copper dimethyldithiocarbamate (CDD), and tetramethylthiuram monosulfide (TMTM) were supplied by Jiaxing Beihua Polymer Additives Co. Ltd, China, whilst zinc stearate was obtained from CHNV Technology Co. Ltd, Guangdong, China. Other additives, such as zinc oxide, stearic acid, and sulphur, were purchased from various vendors. For the convenience of readers, the melting point of each curing additive is listed in the Supporting Information (SI) Table S1. Fig. S1 includes the molecular structures of TRA, TMTM, zinc stearate, and stearic acid.

### 2.2. Recipe design

Eight recipes were designed and presented in Table 10, to investigate the effect of the curing additives on the vulcanization time and mechanical properties of SBR. In each batch, SBR was processed with one recipe by a laboratory two-roll mill, and the weight of each additive was measured in parts per one hundred parts of the elastomer (phr). Recipes containing either zinc oxide & stearic acid or TMTM, i.e. SBR/ZnO-5 and SBR/TMTM-8, were used as the reference in Table 10. All recipes contain 2.5 phr of sulphur. Noteworthy is that 8 phr of TMTM was selected in Recipe SBR/TMTM-8 and 22 phr of CDD was taken in SBR/CDD-20. Although such high qualities are not used in the elastomer manufacturing industry, our aim is to reach a similar curing behavior to SBR/ZnO-5. Using a mixture of curing accelerators would make this research more complex.

### 2.3. Preparation of the SBR composites

By using a two-roll mill, SBR was mixed with additives according to the recipes outlined in Table 10. After all of the additives were added, the roll gap was minimized to form the mixture into a roll and then into a triangle shape. To ensure the additives were thoroughly processed and dispersed in the rubber, this sequential process of forming a roll and a triangle was repeated three times. An optimal curing time (T90) and curing curves were obtained at 140 °C using a rotorless rheometer (Jiangsu Xinzhenwei Test Machinery Co. Ltd.). Specifically, a rubber sample of 4.2 g in mass and ~5 mm in thickness was used for each test that lasted for 30–60 min or even longer, to obtain an optimal curing time (T90) for each recipe. All samples were vulcanized at 140 °C under a pressure of 15 MPa. The samples were then punched using a die to form dumbbell-shaped specimens for tensile testing.

### 2.4. Characterization

The tensile properties of the SBR samples were measured mainly in accordance with ASTM D412-16, by using an Instron 5567 at a strain

**Table 10**
Recipe of the SBR composites (phr is the measuring unit for all compositions).

| Recipe | SBR | Zinc oxide | Stearic acid | Zinc stearate ($ZnSt_2$) | Sulphur | Copper dimethyldithiocarbamate (CDD) | Tetramethylthiuram monosulfide (TMTM) | Dipentamethylenethiuram hexasulfide (TRA) |
|---|---|---|---|---|---|---|---|---|
| SBR/ZnO-5 | 100 | 5 | 2 | 0 | 2.5 | 0 | 0 | 1.0 |
| SBR/TMTM-8 | 100 | 5 | 2 | 0 | 2.5 | 0 | 8 | 0 |
| SBR/$ZnSt_2$-0 | 100 | 0 | 0 | 0 | 2.5 | 0 | 0 | 1.0 |
| SBR/$ZnSt_2$-0.25 | 100 | 0 | 0 | 0.25 | 2.5 | 0 | 0 | 1.0 |
| SBR/$ZnSt_2$-0.5 | 100 | 0 | 0 | 0.50 | 2.5 | 0 | 0 | 1.0 |
| SBR/$ZnSt_2$-1 | 100 | 0 | 0 | 1.00 | 2.5 | 0 | 0 | 1.0 |
| SBR/$ZnSt_2$-2 | 100 | 0 | 0 | 2.00 | 2.5 | 0 | 0 | 1.0 |
| SBR/TRA-1.5 | 100 | 0 | 0 | 0.25 | 2.5 | 0 | 0 | 1.5 |
| SBR/CDD-20 | 100 | 0 | 0 | 0.25 | 2.5 | 20 | 0 | 0 |

rate of 500 mm/min. The specimens, which had a width of 6 mm in the middle region, were clamped at an initial distance of ~20 mm, and marks were drawn to indicate the clamp positions. After the samples underwent fracture and separation in the tensile test, the determination of the tensile set or permanent set was carried out by measuring the distance between the two marks, precisely 10 min later. All measured properties were obtained as the median of at least three samples.

The hardness of the cured SBR was determined using a Type A durometer (Jiangsu Xinzhenwei Test Machinery Co. Ltd.) according to ASTM D2240-15. Each sample measured is ~6 mm in thickness, and a gap of ~6 mm was taken between two subsequent locations for measurement. Before any measurements were taken, the Shore A durometer was calibrated to ensure the pointer was at zero. The hardness was measured at five different points on each sample, and the arithmetic mean was taken. The reading was taken within 1 s after the indenter was pierced into a sample.

Transmission electron microscopy (TEM) was employed to investigate the particle size of additives in SBR and their dispersion or dissolution for four recipes: SBR/ZnO-5, SBR/$ZnSt_2$-0, SBR/$ZnSt_2$-0.25, and SBR/CDD-20. To prepare samples for TEM observation, the cured samples were cryo-microtomed at -80 °C to produce sections of ~60 nm in thickness.

## 3. Result and discussion

### 3.1. Zinc stearate versus zinc oxide for vulcanization

The initial focus of the work is to assess the viability of utilizing zinc stearate ($ZnSt_2$) as a substitute for zinc oxide (ZnO) and stearic acid in facilitating the processing and vulcanization of styrene-butadiene rubber (SBR). Two recipes, i.e. SBR/ZnO-5 and SBR/$ZnSt_2$-2, have been designed in Table 10, both of which contain the same fractions of sulphur and a curing accelerator dipentamethylenethiuram hexasulfide (TRA). The curing time was evaluated using a rotorless rheometer and the mechanical properties of the cured SBR were also investigated. Subsequently, the fraction of $ZnSt_2$ was modified to create mechanical properties that are similar to those of the benchmark recipe SBR/ZnO-5. As a result, four more recipes, i.e. SBR/$ZnSt_2$-0.25, SBR/$ZnSt_2$-0.5, SBR/$ZnSt_2$-1, and SBR/$ZnSt_2$-2, were developed in Table 10.

#### 3.1.1. Morphology of SBR containing zinc oxide and zinc stearate

Fig. 2 presents TEM micrographs of a cured sample of SBR/$ZnSt_2$-0 containing 1.0 phr of TRA as the curing accelerator. At both low and high magnifications, no curing additive particles can be observed except for some spherical impurities of 50–200 nm in diameter. This conclusion was verified by cryo-microtoming two more samples of SBR/$ZnSt_2$-0 and

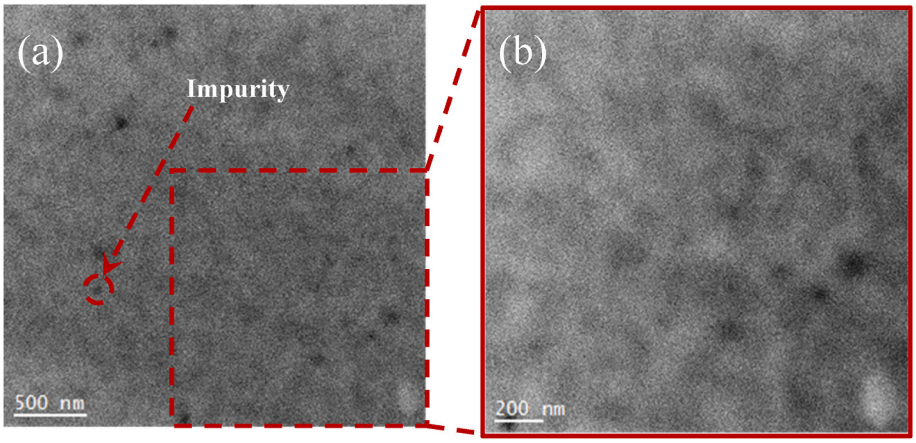



**Fig. 2.** Morphology of styrene-butadiene rubber (SBR) containing TRA as a curing accelerator.

examining the resulting sections via TEM. The observation suggests that all of the TRA particles seem to "dissolve" in the elastomer matrix and participated in the vulcanization process. Dissolution is a term used in chemistry, and it refers to the process of a solid substance (solute) becoming dispersed or dissolving into a liquid (solvent) to form a homogeneous mixture. For example, when table salt (solute) is mixed with water (solvent), it dissolves and forms a saltwater solution. In elastomer processing, it is desirable for all curing additive particles to fully dissolve and integrate with the elastomer macromolecules to promote vulcanization. However, accurately determining the extent of additive particle dissolution presents a challenge. This is because once the elastomer is cured, it becomes insoluble in solvents and does not melt upon heating, making it difficult to assess the complete dissolution of additive particles.

From our perspective, the dissolution of additive particles in elastomer during vulcanization is influenced by two primary factors: the melting point of the additive and its compatibility with the elastomer. The melting point of an additive plays a crucial role in its ability to dissolve in the elastomer matrix during the curing process. In the case of a curing additive with a melting point lower than the curing temperature, the additive during vulcanization has the potential to melt, flow, and penetrate into the elastomer macromolecules. This process allows the additive to react and crosslink with the elastomer, contributing to the curing reaction. Ideally, the penetration of the additive into the elastomer matrix should occur simultaneously with the curing reaction. This ensures that the additive is uniformly dispersed and reacts with the elastomer macromolecules, leading to a homogeneous mixture.

If an additive has a higher melting point than the curing temperature, it would not melt during vulcanization. Instead, only the surface of the additive particles would involve in the vulcanization process. In this scenario, the vulcanization reaction would primarily consume the atoms or molecules present on the surface of the additive particles. As the reaction progresses, these surface atoms or molecules would react with the elastomer macromolecules, forming crosslinks and contributing to the curing process. After vulcanization, the additive particles would generally remain in the elastomer matrix, although their size might slightly reduce due to the consumption of surface atoms or molecules. The extent of size reduction should depend on factors such as the reactivity of the additive, the curing conditions, and the duration of the vulcanization process.

Another critical factor is the compatibility between the additive particles and the elastomer. Compatibility refers to the chemical and physical affinity between the additive and the elastomer. When the additive is compatible with the elastomer, it has a higher tendency to disperse evenly and interact with the elastomer chains. This compatibility enhances the solubility and dissolution of the additive particles within the elastomer matrix during curing. When the particles of an additive are small in size and have good wetting properties, they have a higher tendency to disperse well within the elastomer matrix. This effective dispersion allows for better interaction between the additive particles and the elastomer macromolecules, effectively contributing to vulcanization. Small-sized particles offer a larger surface area per unit volume, facilitating intimate contact with the elastomer matrix. This increased contact area enhances the chances of successful wetting, where the elastomer macromolecules surround and adhere to the surface of the additive particles.

Fig. 3 depicts TEM micrographs of a vulcanized sample of SBR/ZnO-5. The captured images unequivocally reveal the presence of ZnO particles, displaying a notable classification into two distinct categories: rod-shaped and spherical. These particles exhibit lateral dimensions spanning a range of up to several hundred nanometres. The rod-shaped ZnO nanoparticles are ~400 nm in length and 100 nm in width. Notably, these particles are distinct from the impurities observed in Fig. 2 which have a diameter of ~100 nm. The presence of a large number of ZnO particles in SBR/ZnO-5 suggests that these particles are not consumed during the vulcanization process. Having a melting point of 1974 °C, ZnO particles never melt during vulcanization. Only the particle surface contributes $Zn^{2+}$ for the reaction with stearic acid ($C_{17}H_{35}COOH$) to form zinc stearate ($ZnSt_2$), as shown in Fig. 1. The unreacted ZnO particles could pose a significant environmental risk, because they in Table 1 are rated 2 in Chronicity by Chemwatch.

Fig. 4 contains TEM micrographs of a cured sample of SBR/$ZnSt_2$-0.25. Notably, no particles were observed, except for some impurities with a diameter of ~50 nm. This conclusion was verified by cryo-microtoming two more samples of SBR/$ZnSt_2$-0.25 and examining the resulting sections via TEM. The $ZnSt_2$ particles were likely "dissolved" in the elastomer matrix and participated in vulcanization. A preliminary conclusion can be drawn that $ZnSt_2$ is effective in substituting chronic ZnO for SBR vulcanization.

### 3.1.2. *Curing characteristics and essential mechanical properties of SBR containing either zinc oxide or zinc stearate*

Table 11 provides a comprehensive overview of the curing characteristics and essential mechanical properties associated with the curing recipes, including the maximum torque ($M_H$), the minimum torque ($M_L$), the difference between $M_H$ and $M_L$ ($\Delta M$), the optimum vulcanization time (T90), the theoretical curing time (T100), the difference between T90 and T100 ($\Delta T$), hardness, tensile strength, and permanent set.

The rheometer graphs for SBR/ZnO-5 and SBR/$ZnSt_2$-2 are presented in Fig. 5a, with their stress-strain graphs shown in Fig. 5b. Both recipes exhibit similar T90 values, indicating similar curing time. However, the maximum torque of the recipe containing zinc stearate ($ZnSt_2$) is higher than that of the recipe containing zinc oxide, indicating that $ZnSt_2$ might result in a higher degree of crosslinking. A high degree of crosslinking

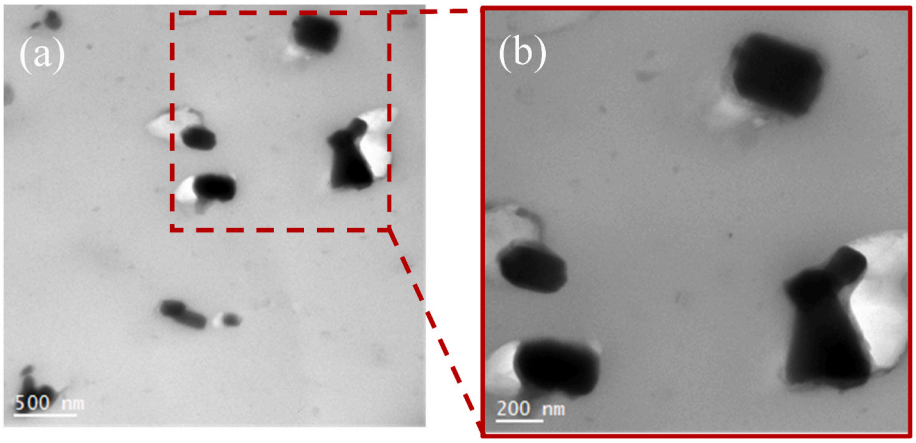



**Fig. 3.** ZnO particles in SBR after vulcanization.

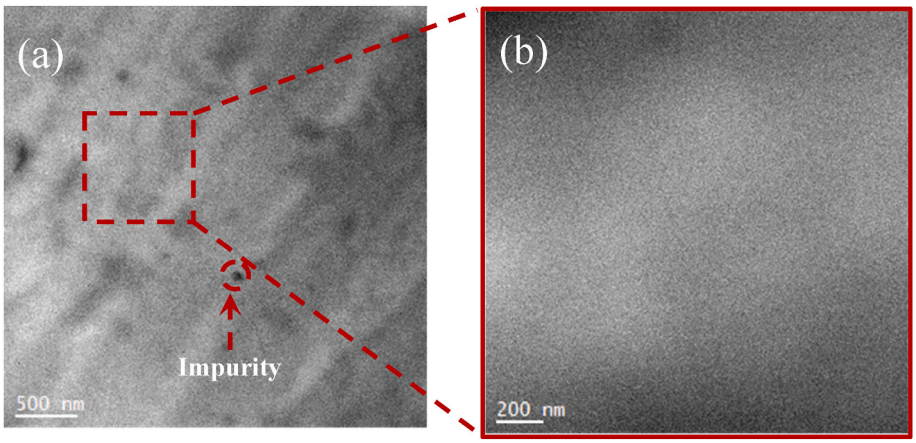



**Fig. 4.** Morphology of SBR containing zinc stearate ($ZnSt_2$).

**Table 11**
Curing characteristics and mechanical properties of SBR containing zinc oxide and zinc stearate.

| Sample | $M_H$, N·m | $M_L$, N·m | ΔM, N·m | T90, min | T100, min | ΔT, min | Hardness, Shore A | Tensile strength, MPa | Standard deviation of tensile strength | Permanent set, % |
|---|---|---|---|---|---|---|---|---|---|---|
| SBR/ZnO-5 | 3.83 | 3.01 | 0.82 | 9:28 | 13:40 | 4:12 | 49.0 | 1.65 | 0.08 | 5.4 |
| SBR/$ZnSt_2$-0 | 4.61 | 3.68 | 0.93 | 96:33 | 116:12 | 19:39 | 35.0 | 1.07 | 0.07 | 0.6 |
| SBR/$ZnSt_2$-0.25 | 4.09 | 2.43 | 1.66 | 28:16 | 55:21 | 27:05 | 41.0 | 1.39 | 0.03 | 0.6 |
| SBR/$ZnSt_2$-0.5 | 4.05 | 2.51 | 1.54 | 19:14 | 28:25 | 8:49 | 39.0 | 1.34 | 0.04 | 3.0 |
| SBR/$ZnSt_2$-1 | 3.97 | 2.47 | 1.50 | 16:31 | 19:58 | 3:27 | 37.0 | 1.20 | 0.04 | 4.3 |
| SBR/$ZnSt_2$-2 | 3.61 | 2.60 | 1.01 | 9:39 | 11:51 | 2:12 | 36.0 | 1.14 | 0.04 | 9.2 |

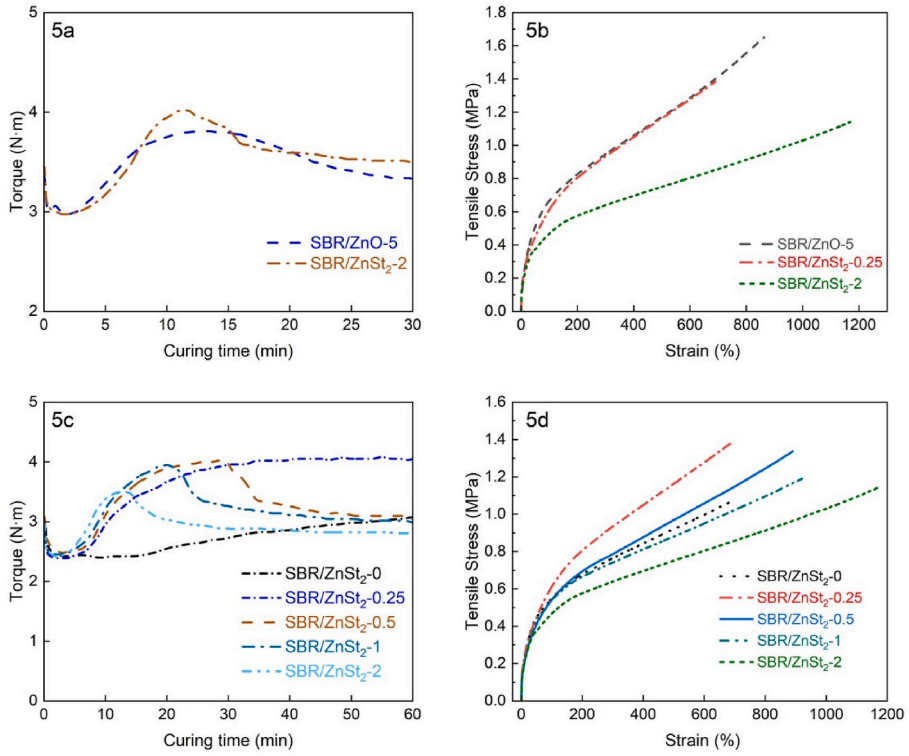



**Fig. 5.** Rheometer graphs and stress-strain graphs of SBR containing zinc oxide and zinc stearate ($ZnSt_2$).

often corresponds to high stiffness. These results mean that a comparable degree of crosslinking can be achieved using $ZnSt_2$.

The recipe SBR/$ZnSt_2$-2 containing 2 phr of $ZnSt_2$ in Table 11 exhibits a similar optimum vulcanization time to the recipe containing 5 phr of zinc oxide and 2 phr of stearic acid. Hence, $ZnSt_2$ could be applied as a new curing activator to replace the combination of chronic zinc

oxide and stearic acid. Noteworthy is that the results obtained from the rotorless rheometer do not guarantee sufficient mechanical performance. Therefore, we proceeded to investigate the mechanical properties of SBR cured with the two recipes.

While the crosslink density of SBR/$ZnSt_2$-2 is higher than that of SBR/ZnO-5, as indicated in Table 11, the mechanical properties of the two recipes show different trends. This implies that the crosslink density obtained from a rheometer testing needs to be verified by more testing. The hardness and tensile strength of SBR/$ZnSt_2$-2 are ~25% lower than those of SBR/ZnO-5. We endeavoured to find a specific fraction of $ZnSt_2$ that can result in similar mechanical properties to SBR/ZnO-5. Through careful recipe optimization and trials, we found that adding 0.25 phr of $ZnSt_2$ not only activated the vulcanization process but also resulted in a tensile strength of 1.39 MPa, which is close to the value of 1.65 MPa obtained for SBR/ZnO-5. The small difference in tensile strengths is likely due to the presence of ZnO nanoparticles in SBR, as explained below.

Fig. 3 illustrates the dispersion of ZnO nanoparticles in SBR. The surface of ZnO particles can react with stearic acid to release Zn ions to activate vulcanization, likely resulting in strong bonding between ZnO nanoparticles and the SBR matrix, which significantly enhances the mechanical properties of SBR. However, the use of ZnO nanoparticles poses negative environmental impacts. Moreover, the difference in tensile strength between SBR/$ZnSt_2$-2 and SBR/ZnO-5 is not significant, i.e. 1.14 MPa versus 1.65 MPa. This drawback can be overcome by incorporating safe and cost-effective nanomaterials, such as graphene nanoplatelets [14-18], which have zero toxicity and chronicity ratings. Therefore, a small amount of $ZnSt_2$ such as 0.25 phr can be utilized to activate vulcanization, replacing hazardous zinc oxide. The curing time T90 associated with SBR/$ZnSt_2$-0.25 is 28 min, and this can be further shortened in future research by using a mixture of curing accelerators.

To investigate the impact of different fractions of zinc stearate ($ZnSt_2$) on the curing characteristics and mechanical properties of SBR, we in Table 10 designed three recipes, SBR/$ZnSt_2$-0, SBR/$ZnSt_2$-0.5, and SBR/$ZnSt_2$-1, in addition to SBR/$ZnSt_2$-0.25 and SBR/$ZnSt_2$-2. The number at the end of each recipe indicates the fraction of $ZnSt_2$. As a benchmark, SBR/$ZnSt_2$-0 was formulated without $ZnSt_2$. Fig. 5c shows the rheometer graphs, whilst Fig. 5d depicts the corresponding stress-strain graphs of the vulcanized samples. Notably, the rheometer curve for SBR/$ZnSt_2$-0 was not fully captured in Fig. 5c due to its exceedingly long vulcanization time as revealed in Fig. S2.

In Fig. 5c, it is observed that all recipes exhibit significant difference between their maximum and minimum torque values, corresponding to the data in Table 11. SBR/$ZnSt_2$-0 does not appear to reach T90 due to the absence of $ZnSt_2$. Regardless of the fraction, $ZnSt_2$ acts as an activator, significantly increasing the vulcanization rate. Of all SBR/$ZnSt_2$ recipes, SBR/$ZnSt_2$-0.25 exhibits the highest maximum torque and the largest difference in torque. This suggests that the optimal crosslink density might be achieved at 0.25 phr of $ZnSt_2$. Therefore, only a small amount of $ZnSt_2$ is needed to activate the curing system, indicating its crucial role in vulcanization. Moreover, T90 reduces with the $ZnSt_2$ fraction, demonstrating the high efficiency of $ZnSt_2$ as a curing activator.

In Table 11, the time difference ΔT between T90 and the theoretical curing time (T100) increases from 19:39 min for SBR/$ZnSt_2$-0 to 27:05 min for SBR/$ZnSt_2$-0.25. Then ΔT decreases at higher fractions of $ZnSt_2$. It is worth to note that in Fig. 5c the torque values of SBR/$ZnSt_2$-0.5, SBR/$ZnSt_2$-1, and SBR/$ZnSt_2$-2 decrease obviously after T100, being less than SBR/$ZnSt_2$-0.25. This result indicates that an ideal curing performance is obtained at 0.25 phr of $ZnSt_2$ in the TRA and sulphur system, with anti-reversion capability.

Reversion is a phenomenon that occurs when the crosslinked network between macromolecules degrades due to prolonged vulcanization. To vulcanize thick elastomeric products, a wide plateau cure graph with anti-reversion performance is essential due to the following reason. Elastomers have low thermal conductivity, which means that thermal energy takes time to transport from the surface of a product to its core. As a result, the core temperature might be lower than the surface temperature. Consequently, the product core could be under-vulcanized, whilst the surface could be over-vulcanized. A wide plateau cure graph with good anti-reversion performance can address this challenge. SBR/$ZnSt_2$-0 has a longer plateau and good anti-reversion performance, but its curing time exceeds 90 min, which is unfeasibly long. On the other hand, those samples containing high fractions of $ZnSt_2$ exhibit poor anti-reversion performance. The reason for this phenomenon is not evident at this stage, and further research is needed in future.

As a result of activated vulcanization, adding 0.25 phr of $ZnSt_2$ significantly improves the mechanical properties of SBR, which is evidenced by higher hardness and tensile strength in comparison with SBR/$ZnSt_2$-0, although both demonstrate similar permanent set (Table 11). As the $ZnSt_2$ fraction increases, the hardness and tensile strength gradually deteriorate whilst permanent set increase. These trends align with the torque differences (ΔM) presented in Fig. 5c. To conclude, a low fraction of $ZnSt_2$, i.e. 0.25 phr, not only optimizes curing time but also significantly enhances the crosslink density and mechanical properties of SBR.

The crosslink density of SBR decreases with increasing the $ZnSt_2$ fraction, in agreement with the change in the mechanical properties. Excessive $ZnSt_2$ can induce a plasticizing effect in the cured elastomer; that is, the elastomer chains more readily slide past each other, reducing the reinforcement effect. With 2 phr of $ZnSt_2$, hardness and tensile strength are almost the same as SBR/$ZnSt_2$-0 which contains no $ZnSt_2$. Since a low fraction of $ZnSt_2$ such as 0.25 phr is sufficient for vulcanization, chronic zinc oxide in elastomer manufacturing can be replaced with a small amount of $ZnSt_2$ that is rated zero in chronicity. However, a challenge associated with SBR/$ZnSt_2$-0.25 is the curing time of ~30 min, which is not sufficiently cost-effective in industry. The curing time can be shortened in future research by adopting a mixture of curing accelerators.

### 3.2. TRA versus TMTM for vulcanization

To reduce the curing time of SBR/$ZnSt_2$-0.25 while maintaining its optimized mechanical properties, we designed a new recipe SBR/TRA-1.5 in Table 10, by keeping the fractions of $ZnSt_2$ and sulphur constant and adding 1.5 phr of TRA. In order to compare the curing efficiency of SBR/TRA-1.5 with common curing additives used in elastomer manufacturing, SBR/TMTM-8 was selected as a benchmark (TMTM is rated 2 in chronicity). Although a mixture of curing accelerators is often used in industry, such a practice makes research complex. Thus, only TMTM was selected in this study. By trials and errors, we found that 8 phr of TMTM led to a similar curing outcome to SBR/TRA-1.5. When SBR/TMTM-8 was randomly selected for replicability testing, we obtained a satisfactory outcome as detailed in the Supporting Information Fig. S3 and Table S2.

The rheometer graphs of SBR/TRA-1.5 and SBR/TMTM-8 are contained in Fig. 6a, whilst their corresponding stress-strain graphs are shown in Fig. 6b, with the data contained in Table 12. Both recipes exhibit similar T90 values. SBR/TRA-1.5 demonstrates a significantly reduced curing time of 18:01 min in Tables 12 and in comparison with SBR/$ZnSt_2$-0.25 which has a curing time of 28:16 min in Table 11. These results indicate that $ZnSt_2$ is an effective activator for vulcanization, as it leads to a markedly reduced curing time for SBR/TRA-1.5.

In Fig. 6a, the zero-chronic curing recipe SBR/TRA-1.5 displays a higher degree of crosslinking, curing plateau, and anti-reversion in comparison with the chronic recipe SBR/TMTM-8. The higher stiffness and strength of SBR/TMTM-8 in Fig. 6b might be attributed to the nano-reinforcement of ZnO. As discussed in Section 3.1.2, safe, cost-effective nanofillers such as graphene nanoplatelets and cellulose nanofibers can be employed to enhance the mechanical properties of SBR/TRA-1.5. In summary, TRA and $ZnSt_2$ can serve as the effective substitutes for

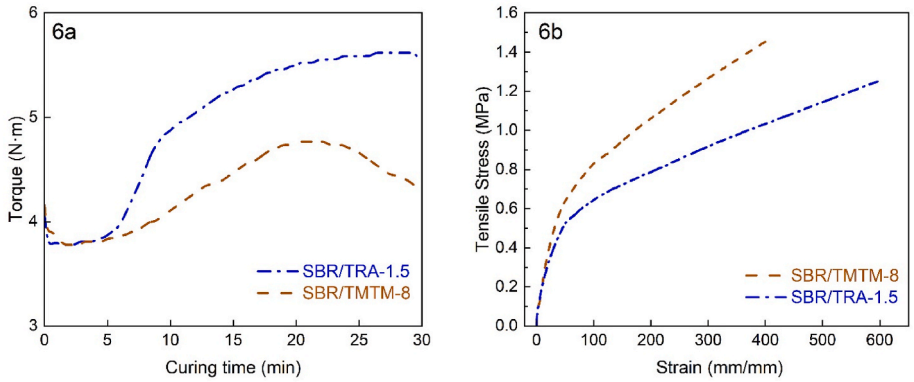



**Fig. 6.** Rheometer graphs and stress-strain graphs of SBR containing either TRA or TMTM.

**Table 12**
Curing characteristics and mechanical properties of SBR containing either TRA or TMTM.

| Sample | $M_H$, N·m | $M_L$, N·m | ΔM, N·m | T90, min | T100, min | ΔT, min | Hardness, Shore A | Tensile strength, MPa | Standard deviation of tensile strength | Permanent set, % |
|---|---|---|---|---|---|---|---|---|---|---|
| SBR/TRA-1.5 | 5.64 | 3.78 | 1.86 | 18:01 | 29:15 | 11:14 | 42.0 | 1.25 | 0.03 | 6.8 |
| SBR/TMTM-8 | 4.52 | 3.60 | 0.92 | 17:55 | 21:07 | 3:12 | 50.0 | 1.46 | 0.02 | 0.3 |

chronic curing additives, e.g. TMTM and zinc oxide.

### 3.3. Morphology of SBR containing a high-melting point curing accelerator

As described earlier, the use of high-melting point curing accelerators can lead to the presence of a substantial amount of unreacted accelerator particles in the elastomer matrix, which will finally release to the environment through both the wear and tear of elastomer products and the disposal of rubber waste. For instance, copper dimethyldithiocarbamate (CDD, CAS No. 137-29-1) has a melting point of 250 °C. Instead of using a mixture of curing accelerators, we selected CDD only for clarity of research. By trials and errors, we found that 20 phr of CDD could produce a desired curing effect, which resulted in a recipe SBR/CDD-20 in Table 10. The TEM micrograph in Fig. 7 shows spherical particles ranging 100 – 900 nm in diameter, which must be CDD because all other curing agents used in the recipe have lower melting points than the vulcanization temperature. This suggests that only the surface of the CDD particles participated in the vulcanization process, whilst a large portion of CDD particles remained unreacted. By contrast, no particles were detected in the elastomer matrix when TRA was used as a vulcanization accelerator. Hence, to minimize the accumulation of unreacted accelerators and their potential environmental impact, the elastomer manufacture sector is recommend using low-melting point, zero-chronic curing additives.

## 4. Conclusion

This study investigated zero-chronicity curing activators and accelerators for substitution of their chronic, unreacted counterparts for the vulcanization of styrene-butadiene rubber (SBR), to prevent chronic chemicals releasing into the environment. Zinc stearate ($ZnSt_2$, CAS No. 557-05-1) has been found to be an effective replacement for zinc oxide (CAS No. 1314-13-2) that has a chronicity rating of 2. The SBR sample cured with 0.25 phr $ZnSt_2$ has exhibited anti-reversion performance and a satisfactory degree of crosslinking in comparison with the sample cured with 5 phr of ZnO and 2 phr of stearic acid. However, the former revealed slightly lower tensile strength due to lack of reinforcement by ZnO nanoparticles. Increasing the $ZnSt_2$ fraction shortened the curing time and T90 but compromised both the anti-reversion performance and

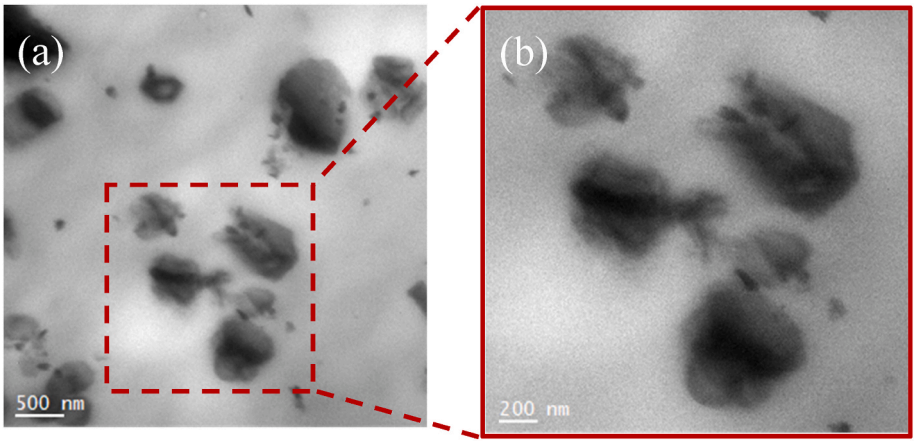



**Fig. 7.** CDD particles in SBR after vulcanization.

mechanical properties. A zero-chronicity curing accelerator dipentamethylenethiuram hexasulfide (denoted TRA; CAS No. 971-15-3) has been found to be a suitable substitute for the chronic curing accelerator tetramethylthiuram monosulfide (TMTM; CAS No. 97-74-5), as TRA particles can "dissolve" in the SBR matrix and fully involve in the vulcanization process. Since only the particle surface of a high-melting point curing accelerator CDD is involved in vulcanization, its application in elastomer manufacturing leads to the presence of large quantities of unreacted particles in the elastomer matrix, which are released to the environment in service.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.smmf.2023.100021.

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# Update

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Corrigendum

# Corrigendum for previously published articles

The potential conflict of interest of below papers published on previous issue of Smart Materials in Manufacturing were not disclosed. The appropriate "Declaration of Competing Interest" statements, provided by the Authors, are included below.

1. Biodegradable metallic suture anchors: A review [Smart Materials in Manufacturing Volume 1, 2023, 100005]

The authors declare the following personal relationships which may be considered as potential competing interests: Given Prof. Cuie Wen role as Editor-in-Chief of this journal, she was not involved in the editorial review or the decision to publish this article and had no access to information regarding its review.

2. Mechanical and corrosion properties of Mg–MgO and Mg–Al2O3 composites fabricated by equal channel angular extrusion method [Smart Materials in Manufacturing Volume 1, 2023, 100010]

The authors declare the following personal relationships which may be considered as potential competing interests: The author, Kaveh Rahmani, is currently employed by Basa Pars Sanat company. Other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

3. Removing hazardous additives from elastomer manufacturing [Smart Materials in Manufacturing Volume 1, 2023, 100021]

The authors declare the following personal relationships which may be considered as potential competing interests: The authors, Grant Schroeder and Andrew Henderson, are currently employed by Maric Flow Control Pty Ltd. Other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

4. A comprehensive study on the biodegradability, biocompatibility, and antibacterial properties of additively manufactured PLA-ZnO nanocomposites [Smart Materials in Manufacturing Volume 3, 2025, 100069]

The author(s) Antonella Sola is an Associate Editor, Cuie Wen is the Editor-in-Chief, and Yuncang Li is an Editorial Board Member for Smart Materials in Manufacturing and were not involved in the editorial review or the decision to publish this article. The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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