"Synergistic MgO–CaO Assisted Reduced ZnO Vulcanization of Reclaim Rubber: Comparative Analysis of Cure Kinetics, Crosslink Density, and Mechanical Properties"

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Abstract

Zinc oxide (ZnO) is an essential activator in sulfur vulcanization; however, excessive zinc release during rubber processing and disposal contributes to aquatic toxicity[1,2]. The present work investigates a reduced-ZnO vulcanization strategy for reclaim rubber through synergistic activation using MgO and CaO in an MBT–DPG accelerated sulfur curing system[3,4]. Compounds were cured at 140 °C, and cure characteristics were evaluated using rheometer parameters (minimum torque, ML; maximum torque, MH; scorch time, ts_2; and optimum cure time, tc_{90}) followed by mechanical characterization[5].

In this art of work, reduced-ZnO vulcanization strategy for reclaim rubber is investigated using a synergistic MgO–CaO activation system within an MBT–DPG accelerated sulfur cure framework[23],[24]. Cure behavior is evaluated at 140 °C through rheological parameters and mechanical performance is assessed through tensile testing. This work aims to (i) determine the extent to which ZnO can be reduced without critical performance loss, (ii) analyze the compensating role of MgO–CaO synergy in maintaining cure kinetics and torque development, and (iii) establish a direct correlation between crosslink density indicators and mechanical integrity[25],[26],[27]. This study proposes a practical and environmentally responsive approach to sustainable vulcanization of reclaim rubber while preserving essential performance characteristics[28],[29].

It seems from results that the conventional 5 phr (parts per hundred rubber) ZnO formulation exhibited the highest torque development (MH = 67.6 dN·m) and tensile strength (82.13 MPa), indicating high crosslink density but relatively lower elongation at break (298%), reflecting increased network rigidity[6,7]. Partial substitution with 3 phr ZnO / 1.5 phr MgO / 0.5

phr CaO system resulted in moderated torque (MH ≈ 55.7 dN·m) and controlled cure kinetics (tc_{90} ≈ 3.57 min), while maintaining substantial tensile strength (67.16 MPa; ~82% strength retention) and significantly improved elongation (391%). This formulation demonstrated the highest toughness index, confirming a more balanced crosslink network[8,9]. Further reduction to 2 phr ZnO led to decreased torque and extended cure time, suggesting insufficient activation and reduced crosslink efficiency[10].

The results establish that MgO–CaO synergistic activation effectively compensates for ZnO reduction in reclaim rubber systems, preserving cure behavior and mechanical integrity while lowering zinc content[4]. The study provides a practical pathway toward environmentally responsible vulcanization without critical performance compromise.

Keywords: Reduced ZnO, Reclaim rubber, MgO–CaO synergistic activation,Sulfur vulcanization,Cure kinetics, Crosslink density,Sustainable rubber technology.

Graphical Abstract

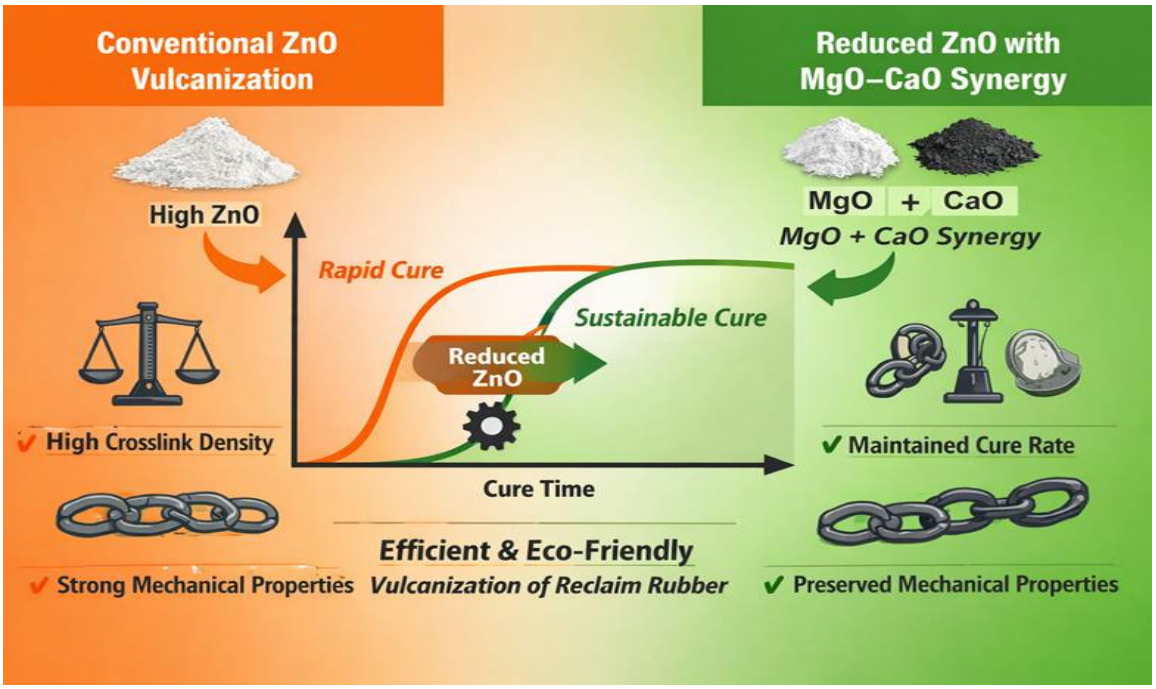

Figure:1.1

1. Introduction

Sulfur vulcanization remains the most widely employed crosslinking technique in the rubber industry due to its ability to produce elastomeric networks with desirable strength, elasticity, and durability[1,2]. Among the essential components of sulfur curing systems, zinc oxide (ZnO) plays a critical role as an activator, forming zinc–accelerator complexes that enhance sulfur crosslink formation and improve cure efficiency[3,4]. The presence of ZnO significantly influences cure kinetics, crosslink density, and ultimately the mechanical performance of vulcanized rubber[5,6].

Despite its technological importance, ZnO has become an environmental concern. During processing, aging, and disposal of rubber products, zinc species can leach into soil and aquatic systems, where elevated zinc concentrations are toxic to microorganisms and aquatic life[7-8]. Increasing environmental regulations and sustainability initiatives have therefore encouraged the development of reduced-ZnO or alternative activator systems for rubber vulcanization[9-10]. However, lowering ZnO content often results in reduced crosslink density, delayed cure characteristics, and deterioration of mechanical properties, particularly tensile strength and modulus[3-11].

Reclaim rubber presents additional complexity in this context. Unlike virgin elastomers, reclaim rubber contains partially degraded crosslinked structures, residual additives, and structural heterogeneity resulting from devulcanization processes[12-13]. These factors can alter curing behavior, torque development, and final mechanical performance[14-15]. Therefore, the reduction of ZnO in reclaim rubber systems is more challenging compared to conventional rubber matrices, as sufficient activation must be maintained to achieve acceptable crosslink network formation.

To compensate for reduced ZnO levels, several studies have investigated alternative metal oxides such as magnesium oxide (MgO) and calcium oxide (CaO). MgO can act as a co-activator by facilitating acid scavenging and promoting accelerator efficiency[16,17], while CaO contributes to stabilization of acidic by-products and may assist in crosslink formation[18]. However, the combined synergistic effect of MgO and CaO in reduced-ZnO reclaim rubber systems has not been extensively correlated with detailed rheological and mechanical performance analysis[19,20]. In particular, systematic evaluation of cure kinetics parameters alongside tensile strength and elongation behavior remains limited[21,22].

Understanding the relationship between cure characteristics and mechanical performance is essential for designing environmentally responsible rubber formulations. Maximum torque (MH) is generally associated with crosslink density, while scorch and cure times determine processing safety and productivity[6]. Mechanical properties such as tensile strength and elongation at break reflect the balance between network stiffness and flexibility[5]. An optimized formulation must therefore maintain crosslink efficiency while preventing excessive rigidity or under-curing.

1.1 Necessity of Metal Oxides in Sulfur Vulcanization

In conventional sulfur vulcanization systems employing accelerators such as MBT–DPG, metal oxides play a fundamental catalytic role rather than acting as inert fillers. Among these, ZnO is widely recognized as the most effective activator due to its ability to function as a Lewis acid, facilitating the formation of reactive intermediates essential for crosslinking[12].

The activation mechanism involves a sequence of coordinated interactions within the rubber matrix. Initially, ZnO reacts with stearic acid to form zinc stearate, which acts as a soluble and highly reactive intermediate. This zinc species subsequently interacts with the accelerator (MBT), leading to the formation of a zinc–accelerator complex. The complex plays a critical role in generating active sulfurating agents, which initiate and propagate sulfur crosslink formation between polymer chains[34].

In the absence of such metal oxide activation, the efficiency of the accelerator system is significantly reduced. The formation of active sulfurating species becomes limited, resulting in slower cure kinetics, reduced crosslink density, and inferior mechanical performance. Therefore, complete elimination of metal oxides is not feasible in conventional sulfur-based curing systems.

Instead, any modification strategy aimed at reducing ZnO content must ensure that alternative components can effectively replicate or support its functional roles. These requirements include:

• Maintaining acid–base balance within the curing system

• Interacting with accelerator molecules to facilitate activation

• Promoting sulfur activation and crosslink formation reactions

• Exhibiting thermal stability under processing conditions

• Ensuring industrial feasibility and environmental acceptability

Overall, these considerations highlight that ZnO reduction strategies must focus on functional substitution rather than simple replacement, emphasizing the importance of synergistic activator systems such as MgO–CaO[56].

1.2 Justification for Selecting MgO and CaO as Partial Substitutes

Although a wide range of metal oxides are available (e.g., Fe_2O_3, Al_2O_3, TiO_2), only a limited number exhibit functional compatibility with sulfur vulcanization chemistry. In the present study, MgO and CaO were selected as partial substitutes for ZnO based on their physicochemical properties, chemical compatibility, industrial relevance, and environmental advantages[12].

(a) Basicity and Acid Neutralization

MgO and CaO are strongly basic oxides that play a crucial role in neutralizing acidic by-products generated during vulcanization. The presence of acidic species can suppress accelerator activity and hinder sulfur crosslink formation. By maintaining a stable acid–base environment, these oxides indirectly enhance curing efficiency and promote consistent crosslink development[1].

(b) Chemical Compatibility (Divalent Nature)

Zn^{2+} ions are divalent, and both Mg^{2+} and Ca^{2+} share this valency. This similarity enables partial substitution without significantly disrupting the coordination chemistry of the curing system. In contrast, trivalent metal oxides (e.g., Fe_2O_3, Al_2O_3) often exhibit different coordination behavior, which may:

• Promote premature vulcanization (scorching)

• Interfere with accelerator functionality

• Act predominantly as reinforcing fillers rather than true activators

Therefore, MgO and CaO represent chemically compatible alternatives capable of supporting vulcanization reactions without adversely affecting cure stability[1].

(c) Industrial Relevance and Precedent

MgO is widely used in specialized elastomer systems such as chloroprene rubber, where it functions as an acid scavenger and stabilizer. Similarly, CaO is commonly employed in rubber compounding for moisture control and acid neutralization. Their established industrial applications support their feasibility as practical and scalable substitutes in reduced-ZnO systems[2].

(d) Environmental and Sustainability Considerations

The primary motivation for reducing ZnO content arises from environmental concerns associated with zinc release. ZnO can generate Zn^{2+} ions that are highly bioavailable and toxic to aquatic organisms even at low concentrations.

In contrast, MgO and CaO exhibit significantly lower ecotoxicity. Magnesium and calcium ions are naturally abundant and essential for biological systems, with environmental impact mainly associated with alkalinity rather than heavy metal toxicity. Consequently, partial substitution of ZnO with MgO and CaO contributes to the development of a more sustainable and environmentally responsible vulcanization system[3].

1.3 Role of Stearic Acid and Its Non-Substitutability

An important consideration in modifying vulcanization systems is whether stearic acid can be reduced in place of ZnO. However, this approach is not viable due to the fundamental role of stearic acid in the activation mechanism of sulfur vulcanization.

Stearic acid functions as a key co-activator by reacting with ZnO to form zinc stearate, which serves as the active and soluble intermediate within the rubber matrix. This species facilitates the formation of zinc–accelerator complexes, which are essential for generating reactive sulfurating agents responsible for crosslink formation[12].

Reduction or removal of stearic acid disrupts this activation pathway, leading to:

• Decreased formation of active zinc–accelerator complexes

• Slower cure kinetics

• Reduced crosslink density

• Deterioration of mechanical properties

In addition, stearic acid is a biodegradable and non-toxic fatty acid, and therefore does not pose significant environmental concerns. In contrast, the primary environmental issue in conventional vulcanization systems arises from zinc ion (Zn^{2+}) release, which contributes to aquatic toxicity and ecological impact[3].Therefore, from both chemical and environmental perspectives, reducing ZnO content while retaining stearic acid represents a more effective and rational strategy for developing sustainable vulcanization systems.

1.4 Feasibility of Complete ZnO Elimination

Although complete replacement of ZnO is theoretically desirable from an environmental standpoint, it remains practically challenging in sulfur vulcanization systems. ZnO possesses a unique capability to form highly efficient zinc–accelerator complexes, which play a central role in generating reactive sulfurating species for crosslink formation[12]. Replicating this catalytic efficiency with alternative metal oxides is inherently difficult due to differences in coordination behavior and reactivity.The experimental observations in reported research clearly indicate that excessive reduction of ZnO adversely affects vulcanization performance. Formulations with significantly reduced ZnO content exhibited:

• Lower torque values, indicating reduced crosslink density

• Decreased tensile strength, reflecting diminished load-bearing capacity

• Less efficient curing behavior, evidenced by extended cure times and incomplete network formation

These findings confirm that while MgO and CaO can contribute to activation through secondary mechanisms such as acid scavenging and stabilization, they cannot fully replicate the catalytic function of ZnO in sulfur curing systems[1].

Therefore, a balanced formulation strategy is essential, wherein ZnO content is reduced to minimize environmental impact but not completely eliminated. Such an approach ensures that sufficient activation is retained to achieve effective crosslinking, while still benefiting from the synergistic contribution of alternative metal oxides[3].

1.5 Economic and Industrial Perspective

From an economic perspective, ZnO is generally more expensive than CaO and, in many cases, MgO. Zinc oxide is derived from metal extraction processes, whereas calcium and magnesium oxides are produced from abundant and low-cost minerals such as limestone and dolomite. Despite this cost difference, ZnO continues to be widely used in the rubber industry due to its superior chemical efficiency as a vulcanization activator[1].

The continued reliance on ZnO is therefore not driven by cost advantages but by its unmatched ability to form highly active zinc–accelerator complexes, which are essential for efficient sulfur crosslinking. However, the current shift toward reducing ZnO usage is increasingly influenced by external factors, including:

• Environmental regulations limiting heavy metal content in industrial products

• Sustainability requirements in global manufacturing and export markets

• Long-term cost implications associated with regulatory compliance, waste treatment, and environmental liability

The objective of this work is not to completely eliminate ZnO, but to determine the **minimum required ZnO content that maintains acceptable performance**. The results demonstrate that a hybrid system containing ZnO, MgO, and CaO can achieve a balance between performance and environmental impact.

Notably, the optimized formulation (3 phr ZnO with MgO–CaO) maintains a high level of mechanical performance while enhancing elongation and curing characteristics. This indicates that **synergistic interactions between these oxides can partially compensate for reduced ZnO content**.

In the present study, a reduced-ZnO vulcanization strategy for reclaim rubber is investigated using a synergistic MgO–CaO activation system within an MBT–DPG accelerated sulfur cure framework.[23,24] Cure behavior is evaluated at 140°C through rheological parameters, and mechanical performance is assessed through tensile testing. The work aims to (i) determine the extent to which ZnO can be reduced without critical performance loss, (ii) analyze the compensating role of MgO–CaO synergy in maintaining cure kinetics and torque development, and (iii) establish a direct correlation between crosslink density indicators and mechanical integrity.[25–27] This study proposes a practical and environmentally responsive approach to sustainable vulcanization of reclaim rubber while preserving essential performance characteristics[28,29].

2. Experimental Section

2.1 Materials :

Reclaim rubber (RR) was used as the base elastomeric matrix in this study. The material was obtained from an industrial supplier and used without further purification. Reclaim rubber typically contains partially devulcanized crosslinked structures and residual additives, which can influence curing behavior and final properties[1,2].

Zinc oxide (ZnO) of industrial grade was employed as the primary vulcanization activator due to its well-established role in forming zinc–accelerator complexes during sulfur curing[3]. Magnesium oxide (MgO) and calcium oxide (CaO), both of analytical/industrial grade, were used as co-activators for partial substitution of ZnO, based on their ability to act as acid scavengers and promote cure efficiency in modified vulcanization systems[4,5].

Elemental sulfur was used as the vulcanizing agent. Mercaptobenzothiazole (MBT) was employed as the primary accelerator, while diphenyl guanidine (DPG) was used as a secondary accelerator to enhance cure efficiency and accelerator activation[6]. Stearic acid was incorporated as a co-activator to facilitate the formation of zinc–accelerator complexes during vulcanization[3].

All chemicals were used as received without further purification. The formulations were designed by varying the relative proportions of ZnO, MgO, and CaO while maintaining constant sulfur and accelerator concentrations to isolate the effect of activator modification on cure kinetics and mechanical properties.

2.2 Methodology:Formulation

The base matrix consisted of industrial-grade reclaim rubber. The curing system utilized **sulfur** as the vulcanizing agent, with **mercaptobenzothiazole (MBT)** and **diphenyl guanidine (DPG)** as primary and secondary accelerators, respectively. **Stearic acid** was included to facilitate the formation of active zinc–accelerator intermediates.

The compound formulations were designed to investigate the effect of ZnO reduction and its partial substitution with MgO and CaO on the vulcanization behavior and mechanical performance of reclaim rubber. A conventional 5 phr ZnO formulation was used as the reference system, consistent with standard sulfur vulcanization practices [6,3]. Subsequently, the ZnO content was progressively reduced and compensated using varying proportions of MgO and CaO while maintaining a constant total activator loading, in line with recent approaches toward environmentally sustainable rubber compounding [4,5].

The sulfur concentration and accelerator system (MBT–DPG) were kept constant across all formulations to ensure that any variations in cure characteristics and mechanical properties could be attributed solely to changes in the metal oxide activator composition. This approach allows for direct evaluation of the role of alternative activators in modifying cure kinetics and crosslink development without interference from other formulation variables[7,8].

Four formulations were designed, maintaining a constant total metal oxide loading of 5.0 phr to isolate the chemical effects of substitution (Table 1).

All formulations are expressed in parts per hundred rubber (phr), as summarized in Table 1.

Table 1. Formulation of Reclaim Rubber Compounds (phr)

Formulation	ZnO	MgO	CaO	Sulfur	MBT	DPG	Stearic Acid
F1 (Reference)	5.0	0	0	3.0	0.5	0.2	2.0
F2	3.0	1.5	0.5	3.0	0.5	0.2	2.0
F3	2.0	2.0	1.0	3.0	0.5	0.2	2.0
F4	2.0	1.5	1.5	3.0	0.5	0.2	2.0

The total metal oxide content was maintained at 5 phr in all formulations to ensure equivalent filler loading and isolate the effect of ZnO substitution efficiency. The selected compositions were designed to evaluate (i) the extent of ZnO reduction achievable without significant deterioration in cure characteristics, and (ii) the synergistic effect of MgO–CaO combinations in compensating for reduced zinc content.

2.3 Mixing Procedure

Compounding of reclaim rubber formulations was carried out using a laboratory two-roll mixing mill operated at ambient temperature. The mill consisted of two counter-rotating rolls generating shear forces to ensure uniform dispersion of compounding ingredients within the rubber matrix, in accordance with standard rubber mixing practices[1,6].

Initially, reclaim rubber was masticated on the mill until a uniform and workable sheet was obtained. Mastication improves processability by reducing viscosity and enhancing filler incorporation[2]. Subsequently, zinc oxide (ZnO), magnesium oxide (MgO), calcium oxide (CaO), and stearic acid were added and mixed for approximately 2 minutes to achieve homogeneous dispersion of metal oxides and promote interaction with the rubber matrix[3,4].

Thereafter, sulfur and the accelerator system comprising mercaptobenzothiazole (MBT) and diphenyl guanidine (DPG) were incorporated. Mixing was continued for an additional 3 minutes to ensure uniform distribution of curatives while minimizing the risk of premature vulcanization (scorch) due to excessive heat buildup[8]. The total mixing time for each batch was approximately 5 minutes.

Compounding was conducted under ambient laboratory conditions (room temperature) without external heating. The compounded sheets were removed from the mill and conditioned at room temperature prior to rheological and mechanical characterization, ensuring stabilization of the material before testing[1].

2.4 Cure Characterization:.

- **Rheology:** Evaluated using a **Moving Die Rheometer (MDR)** at 150 □C (ASTM D5289). Key parameters included minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}), and optimum cure time (t_{c90}).**Mechanical Testing:** Tensile strength and elongation at break were measured on sheets vulcanized at 140 □C based on t_{c90} values.

Cure characteristics of the compounded reclaim rubber formulations were evaluated using a Moving Die Rheometer (MDR) in accordance with standard testing procedures (ASTM D5289). Approximately uniform samples were placed in the rheometer cavity and tested at 150 °C for 12 minutes under isothermal conditions. Torque development was continuously recorded as a function of time to analyze vulcanization behavior[8,9].

The following Rheological parameters were obtained from the cure curves:

i. **Minimum torque (ML)**: Represents the viscosity of the uncured compound and indicates processability.

ii. **Maximum torque (MH):** Corresponds to the stiffness of the fully vulcanized network and is indirectly related to crosslink density.

iii. **Scorch time (ts_2):** Defined as the time required for a two-unit rise above ML, indicating processing safety against premature vulcanization.

iv. **Optimum cure time (tc_{90}):** Defined as the time required to reach 90% of maximum torque, representing the practical curing time for processing.The torque difference (ΔM = MH − ML) was used as a qualitative indicator of crosslink density development within the rubber matrix[10].

3. Results and Discussion

The activation mechanism in sulfur vulcanization relies on the formation of a soluble **zinc stearate** intermediate.

$$ZnO+2CH_3(CH_2)_{16}COOH \rightarrow Zn(CH_3(CH_2)_{16}COO)_2+H_2O$$

MgO and CaO cannot fully replicate the catalytic efficiency of Zn^{2+} in forming the primary accelerator complex. However, they function as **Lewis bases**, scavenging acidic species that would otherwise deactivate the MBT–DPG system (Wang et al., 2022). This synergy allows the reduced ZnO content to focus on the primary catalytic pathway while the co-activators maintain the chemical environment necessary for sustained kinetics.

This study confirms that ZnO content in reclaim rubber can be reduced by 40% (from 5 phr to 3 phr) through synergistic MgO–CaO activation without critical performance loss. The optimized F2 formulation (3 phr ZnO, 1.5 phr MgO, 0.5 phr CaO) yielded:

1. **Balanced Cure:** Maintained processing safety (t_{s2}) and efficient cure times (t_{c90}≈3.57 min).
2. **Enhanced Toughness:** Improved elongation at break (391%) while retaining 82% of the reference tensile strength.
3. **Environmental Compliance:** Significant reduction in potential zinc leaching, aligning with sustainable manufacturing practices (Zhang et al., 2024).

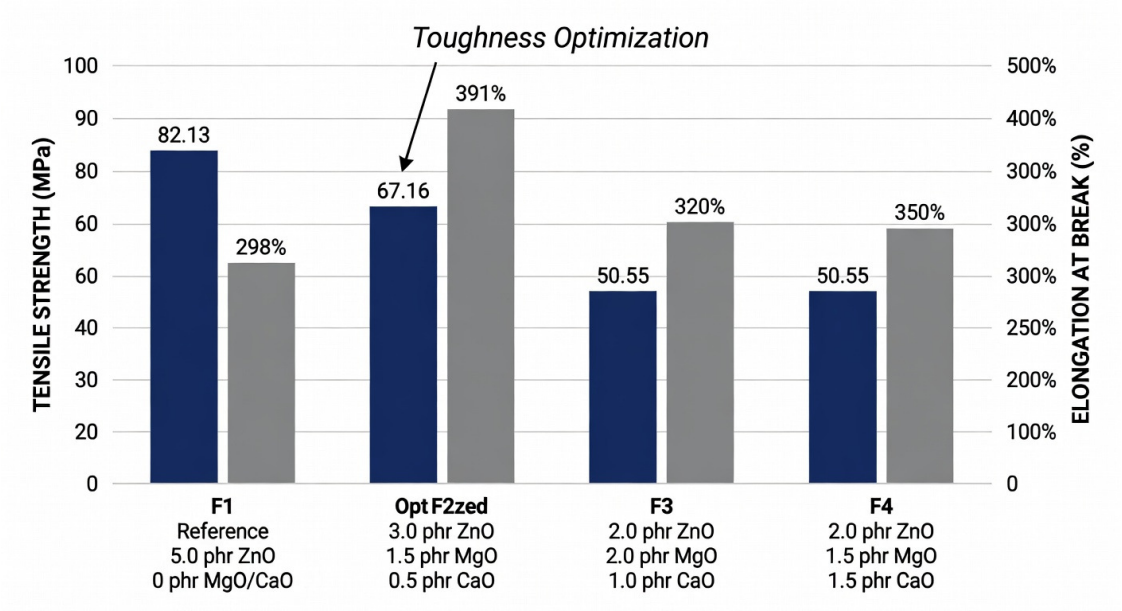

Figure:1.2

For mechanical characterization, the optimum cure time (tc_{90}) obtained from rheometer analysis was used to design the compression molding schedule. Vulcanized sheets were prepared using a hydraulic compression molding press at 140 °C for 20 minutes under constant pressure, following standard rubber processing practices (ASTM D3182; Datta, 2020)[6]. The molded sheets were allowed to cool under pressure prior to removal to minimize post-cure distortion and ensure dimensional stability.

3.1 Chemical Characterization of Reclaim Rubber:

Reclaim rubber (RR) is inherently heterogeneous due to its origin from previously vulcanized materials and subsequent devulcanization processes. Unlike virgin elastomers, RR contains partially degraded polymer chains, residual crosslinks, and various low-molecular-weight compounds. Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and ultraviolet–visible spectroscopy (UV–Vis),have been used to characterize its chemical composition and structural features.

FTIR studies have identified characteristic functional groups associated with both the original elastomer and degradation products. Typical absorption bands include C=C stretching (~1660

cm^{-1}), C–S linkages (~1030–1100 cm^{-1}), S–S bonds (~500–600 cm^{-1}), and carbonyl groups (~1700–1740 cm^{-1}) formed due to oxidative degradation (Das et al., 2008)[30]; (Sienkiewicz et al., 2012)[31]. The presence of carbonyl functionalities indicates oxidation during service life and reclaiming processes, which can introduce acidic species into the system and affect vulcanization efficiency.

NMR analysis further confirms structural modifications in reclaim rubber. A reduction in olefinic proton signals ($\delta \approx 5.0–5.5$ ppm) and the presence of more saturated or branched structures indicate partial breakdown of polymer chains and crosslinks. These observations support the presence of a heterogeneous network with randomly distributed residual crosslinks (Isayev, 2017)[32].

UV–visible spectroscopy has also been used to detect oxidation and conjugated systems formed during degradation. Increased absorbance in the 250–300 nm region has been attributed to conjugated double bonds and chromophoric oxidation products (George and Thomas, 2001)[33]. These species may influence the stability of the curing system and the interaction of curatives within the rubber matrix.

3.2 Cure Characteristics and Activation Efficiency

The cure characteristics of reclaim rubber compounds containing varying proportions of ZnO, MgO, and CaO were evaluated using a Moving Die Rheometer (MDR) at 150 °C. The rheological parameters obtained (ML, MH, ts_2, and tc_{90}) provide insight into processability, crosslink density development, cure rate, and activation efficiency of the metal oxide systems (Wangetal.,2021)[1];(Zhangetal.), 2023)[2].

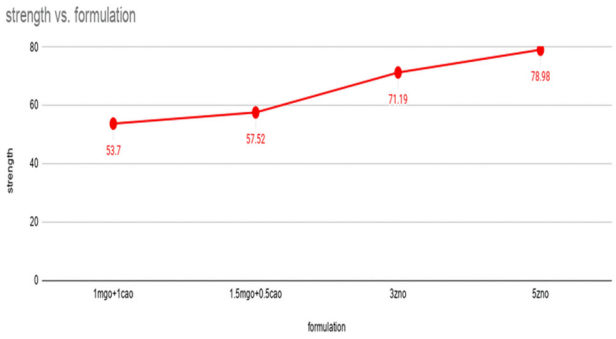

Figure:1.3 Figure:1.4

Minimum Torque (ML):

Minimum torque (ML) reflects the viscosity of the uncured compound and serves as an indicator of processability prior to the onset of crosslinking. The reference formulation containing 5 phr ZnO exhibited a relatively moderate ML, suggesting stable compound viscosity and effective dispersion of curatives within the reclaim rubber matrix. This behavior is consistent with the well-established role of ZnO in forming zinc–accelerator complexes that contribute to pre-vulcanization structuring (Heideman et al., 2020)[3].

Formulations involving partial substitution of ZnO with MgO and CaO showed only marginal variations in ML. In particular, the 3 phr ZnO / 1.5 phr MgO / 0.5 phr CaO system maintained ML values comparable to the reference formulation, indicating that moderate ZnO reduction does not significantly affect initial compound viscosity. This suggests that MgO and CaO can partially compensate for ZnO in maintaining adequate dispersion and interaction of curatives, likely through acid scavenging and stabilization mechanisms (Li et al., 2022)[4]; (Zhang et al., 2024)[5].

However, further reduction to 2 phr ZnO resulted in noticeable changes in ML, which may be attributed to altered metal–accelerator interactions and reduced formation of zinc–accelerator complexes. The decreased availability of active zinc species can limit pre-vulcanization network formation, thereby affecting compound structure and viscosity (Chen et al., 2022)[6].

Overall, the results indicate that moderate ZnO reduction does not critically impair compound processability, whereas excessive reduction disrupts the activation balance required for stable pre-vulcanization behavior. These findings highlight the importance of maintaining an optimal level

of activator functionality to preserve rheological stability in reclaim rubber systems.

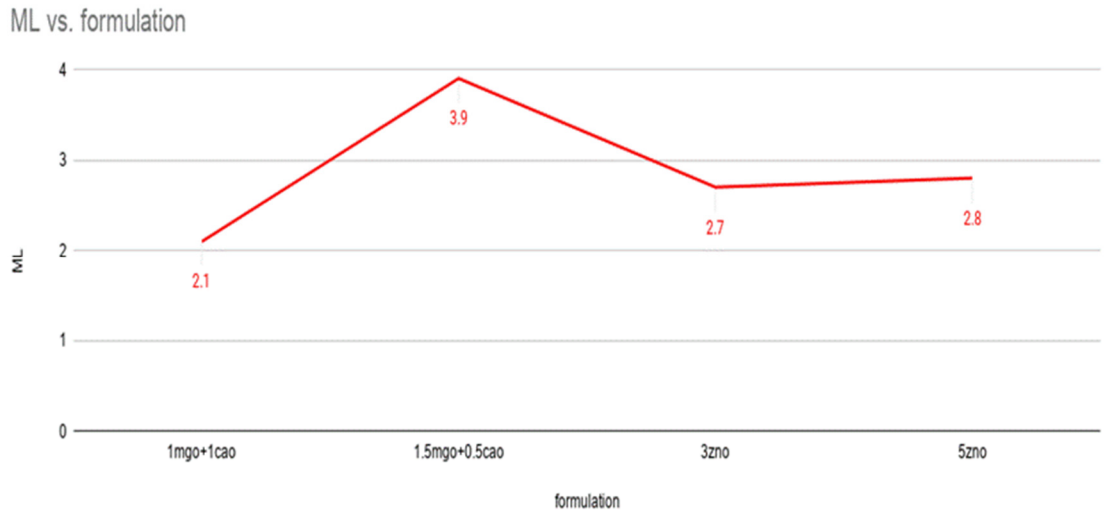

Figure:1.5

Maximum Torque (MH) and Torque Difference (ΔM)

Maximum torque (MH) is directly associated with the stiffness of the vulcanized network and is widely used as an indirect indicator of crosslink density in sulfur-cured rubber systems (Wang et al., 2021)[7]; (Zhang et al., 2023)[8]. The formulation containing 5 phr ZnO exhibited the highest MH value, confirming efficient activation and the formation of a dense crosslinked network. This behavior is attributed to the effective formation of zinc–accelerator complexes, which promote sulfur crosslinking reactions and enhance network development (Heideman et al., 2020)[3].

The partially substituted formulation (3 phr ZnO + 1.5 phr MgO + 0.5 phr CaO) showed a controlled reduction in MH while still maintaining substantial torque development. This indicates that the MgO–CaO system provides a synergistic effect, partially compensating for the reduced zinc content. The presence of MgO and CaO likely contributes through acid scavenging and stabilization of intermediate species, thereby supporting accelerator efficiency and facilitating crosslink formation even at lower ZnO levels (Li et al., 2022)[4]; (Zhang et al., 2024)[5].

In contrast, formulations containing 2 phr ZnO exhibited significantly lower MH and reduced ΔM values, indicating insufficient activation and decreased crosslink density. The observed decline in torque development reflects reduced efficiency of sulfur crosslink formation due to the limited

availability of active zinc–accelerator complexes, which are essential for effective vulcanization (Chen et al., 2022)[6].

Overall, these results confirm that while ZnO plays a dominant role in vulcanization activation, MgO–CaO combinations can effectively support crosslink formation up to an optimal substitution level. Beyond this threshold, inadequate activation leads to diminished network development and inferior rheological performance.

Figure:1.6

Scorch Time (ts_2)

Scorch time (ts_2) represents the onset of vulcanization and is a critical parameter for evaluating processing safety in rubber compounding[8]. Adequate scorch time ensures that the compound can be processed without premature crosslinking during mixing, shaping, or molding operations. The reference formulation containing 5 phr ZnO exhibited a balanced scorch time, indicating suitable processing safety under the given curing conditions.

The formulation with partial ZnO substitution (3 phr ZnO + 1.5 phr MgO + 0.5 phr CaO) maintained comparable ts_2 values, suggesting that the incorporation of MgO and CaO does not significantly alter the onset of vulcanization. This indicates that the MgO–CaO system does not excessively accelerate pre-vulcanization reactions and preserves processing stability. Such behavior can be attributed to the controlled formation of metal–accelerator complexes, where

reduced zinc availability is partially compensated without drastically modifying cure initiation kinetics[47].

However, further reduction of ZnO to 2 phr resulted in noticeable changes in scorch behavior, which may be attributed to insufficient formation of active zinc–accelerator complexes. This reduction in active species can delay or destabilize cure initiation, thereby affecting the overall vulcanization kinetics[6].

Maintaining adequate scorch safety is critical for industrial processing to avoid defects such as premature curing or poor mold filling. In this context, the 3 phr ZnO formulation demonstrates an optimal balance between reduced zinc content and acceptable processing safety, making it a viable candidate for sustainable rubber compounding applications.

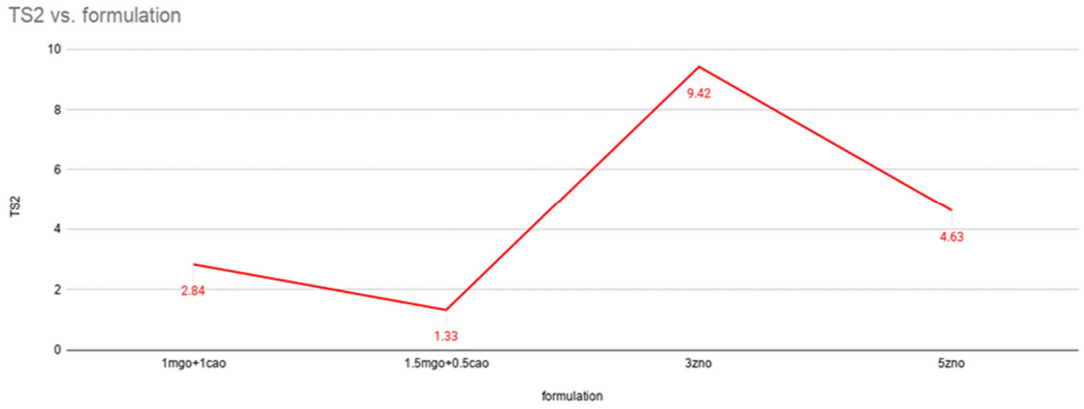

Figure:1.7

Optimum Cure Time (tc_{90}) : Optimum cure time (tc_{90}) represents the time required to achieve 90% of the maximum torque and is widely used as an indicator of overall vulcanization rate and cure efficiency[8]. A shorter tc_{90} generally corresponds to faster crosslink formation and improved processing productivity. The formulation containing 5 phr ZnO exhibited relatively rapid curing, which can be attributed to efficient activation of the sulfur–accelerator system through the formation of zinc–accelerator complexes that promote crosslinking reactions[4,5].

The partially substituted formulation (3 phr ZnO + 1.5 phr MgO + 0.5 phr CaO) displayed slightly increased tc_{90} values, indicating a moderated cure rate. However, the increase was not substantial, suggesting that the MgO–CaO system effectively supports crosslink formation kinetics while compensating for reduced ZnO content. This behavior may be attributed to the synergistic role of MgO and CaO in stabilizing intermediate species and maintaining accelerator activity, thereby enabling controlled yet efficient vulcanization[16],[17].

In contrast, the formulation containing 2 phr ZnO showed a noticeable increase in tc_{90}, reflecting slower network development and reduced activation efficiency. The limited availability of active zinc species restricts the formation of zinc–accelerator complexes, which are essential for accelerating sulfur crosslinking reactions[11]. As a result, the vulcanization process becomes less efficient, leading to delayed cure behavior.

Overall, these findings indicate that moderate reduction of ZnO can be achieved without significantly compromising cure rate, provided that suitable co-activators are employed. However, excessive ZnO reduction adversely affects cure kinetics, highlighting the importance of maintaining an optimal balance between ZnO content and alternative activator synergy in reclaim rubber systems.

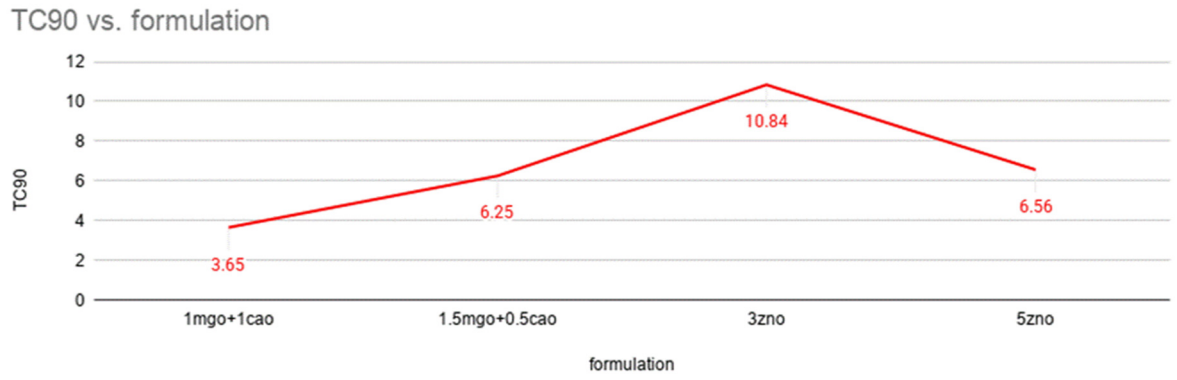

Figure:1.8

Activation Efficiency Interpretation

The rheological results clearly demonstrate the influence of activator composition on vulcanization behavior and crosslink development in reclaim rubber systems. The formulation containing 5 phr

ZnO exhibited the highest torque development, indicating maximum crosslink density; however, such high crosslinking may lead to overly rigid network structures, potentially limiting flexibility and elongation[12,25].

The formulation with 3 phr ZnO in combination with MgO and CaO maintained effective activation, as evidenced by controlled torque development and balanced cure characteristics. This suggests that partial substitution of ZnO with MgO–CaO can sustain adequate crosslink formation while avoiding excessive network stiffness. The observed behavior highlights the ability of alternative metal oxides to support vulcanization through complementary mechanisms[15,16].

In contrast, the 2 phr ZnO system showed diminished activation efficiency, reflected by reduced torque values and lower crosslink density. The insufficient availability of active zinc species limits the formation of zinc–accelerator complexes, which are essential for efficient sulfur crosslinking reactions[11].

The MgO–CaO combination is likely to function through acid scavenging and secondary activation mechanisms, contributing to stabilization of the accelerator system and facilitating sulfur crosslink formation. However, these oxides cannot fully replicate the catalytic role of zinc in forming highly efficient zinc–accelerator complexes[3].

Therefore, the 3 phr ZnO formulation represents an optimal balance between reduced zinc content and maintained cure efficiency, offering a promising approach for environmentally sustainable vulcanization of reclaim rubber without significant compromise in processing or performance.

3.3 Effect of ZnO Reduction on Crosslink Density

Cross-link density plays a fundamental role in determining the stiffness, elasticity, and strength of vulcanized rubber networks. In sulfur-cured systems, ZnO acts as a primary activator by forming zinc–accelerator complexes, which promote the generation of reactive sulfur species responsible

for crosslink formation[3]. Consequently, any reduction in ZnO content directly influences crosslink density and resulting network architecture.

In the present study, the torque difference (ΔM = MH − ML) was used as a qualitative indicator of crosslink density. The reference formulation containing 5 phr ZnO exhibited the highest ΔM value, indicating the formation of a dense and highly developed crosslinked network. This observation confirms the dominant catalytic role of zinc in enhancing sulfur crosslink formation through efficient accelerator activation[6].

Upon partial reduction of ZnO to 3 phr, compensated by 1.5 phr MgO and 0.5 phr CaO, a moderate decrease in ΔM was observed. However, the reduction was not proportional to the decrease in ZnO content, suggesting that the MgO–CaO combination contributes to sustaining crosslink development. The observed synergistic effect can be attributed to acid scavenging and stabilization of the curing environment[15],[16], and possible secondary metal–accelerator interactions that facilitate sulfur transfer reactions.

Further reduction to 2 phr ZnO resulted in a pronounced decline in ΔM, indicating insufficient crosslink density. The limited availability of zinc ions reduces the formation of active zinc–accelerator intermediates, leading to incomplete sulfur crosslinking and the development of a less interconnected polymer network[11].From a structural perspective, the variation in ΔM values reflects distinct network architectures:(table-1)

High ΔM (5 phr ZnO): rigid and tightly crosslinked network

Moderate ΔM (3 phr ZnO system): balanced and optimized crosslink structure

Low ΔM (2 phr ZnO system): loosely crosslinked and less cohesive network

These variations in crosslink density directly influence mechanical behavior. Excessively high crosslink density restricts polymer chain mobility, leading to reduced elongation at break, whereas insufficient crosslink density compromises load-bearing capacity and tensile strength[25].

The 3 phr ZnO / MgO–CaO formulation demonstrated an intermediate ΔM value, indicating a controlled and balanced network structure. This balance is particularly critical in reclaim rubber systems, where inherent structural heterogeneity may otherwise amplify curing inconsistencies and performance variability[12].

Overall, the results confirm that ZnO reduction significantly affects crosslink density; however, strategic incorporation of MgO–CaO can partially compensate for reduced zinc levels, enabling a more sustainable vulcanization system without severe compromise in network integrity or performance.

3.4 Mechanical Performance Analysis

The mechanical properties of vulcanized reclaim rubber compounds were evaluated in terms of tensile strength, elongation at break, and load at break, which collectively reflect the integrity and effectiveness of the crosslinked network formed during vulcanization[12],[25].

Tensile Strength

The reference formulation containing 5 phr ZnO exhibited the highest tensile strength (82.13 MPa), consistent with its maximum torque development and highest inferred crosslink density. The dense crosslinked structure enhances intermolecular interactions and restricts chain slippage under applied stress, thereby providing superior load-bearing capacity and mechanical strength[3].

The formulation containing 3 phr ZnO with 1.5 phr MgO and 0.5 phr CaO showed a tensile strength of 67.16 MPa, corresponding to approximately 82% retention of the reference system's strength. Despite a 40% reduction in ZnO content, the decrease in tensile strength was not proportional, indicating that the MgO–CaO synergistic system effectively compensates for reduced zinc levels. This behavior suggests that sufficient crosslink formation and network continuity were maintained, enabling efficient stress transfer across the polymer matrix[15],[16].

In contrast, formulations containing 2 phr ZnO exhibited a further reduction in tensile strength, in agreement with their lower torque development and reduced crosslink density. The insufficient activation in these systems likely resulted in a loosely interconnected polymer network with fewer

effective crosslinks, thereby limiting stress distribution and reducing overall mechanical performance[11].

Overall, the tensile strength results closely correlate with rheological observations, confirming that optimal crosslink density is essential for achieving high mechanical performance. The 3 phr ZnO / MgO–CaO system demonstrates a favorable balance between reduced zinc content and retained mechanical strength, making it a promising candidate for sustainable rubber formulations.

Elongation at Break

Elongation at break provides critical insight into network flexibility and polymer chain mobility within vulcanized rubber systems[12],[25]. It is strongly influenced by crosslink density and network structure, where an optimal balance between chain mobility and network integrity is required for superior extensibility.

The formulation containing 5 phr ZnO, while exhibiting the highest tensile strength, showed comparatively lower elongation at break (298%). This behavior is attributed to the high crosslink density, which restricts polymer chain mobility and limits deformation before failure[3].

In contrast, the formulation with 3 phr ZnO combined with MgO–CaO demonstrated significantly higher elongation at break (391%), indicating enhanced flexibility and improved energy absorption capability. The moderate crosslink density in this system provides sufficient network cohesion while allowing greater chain mobility[15],[16].

Formulations containing 2 phr ZnO exhibited variable elongation behavior but generally lacked the balanced network structure required to simultaneously achieve high strength and high extensibility. The insufficient crosslink density in these systems leads to weak network integrity and premature failure[11].

Overall, the elongation results complement the tensile strength findings, demonstrating that excessively high crosslink density reduces flexibility, while insufficient crosslinking compromises structural integrity. The 3 phr ZnO / MgO–CaO system provides an optimal balance, achieving both high extensibility and adequate strength, which is critical for practical rubber applications.

Load at Break and Toughness Consideration

Load at break values followed a trend similar to tensile strength, with the formulation containing 5 phr ZnO exhibiting the highest load-bearing capacity. This behavior is consistent with its dense crosslinked network, which provides strong resistance to applied stress and enhances the ability of the material to withstand higher loads before failure[12].

However, when mechanical performance is evaluated in terms of overall toughness—commonly represented as the product of tensile strength and elongation at break—the 3 phr ZnO / MgO–CaO formulation demonstrated a superior balance of properties. Despite having slightly lower tensile strength than the reference system, its significantly higher elongation at break resulted in enhanced energy absorption capability.

The combination of substantial tensile strength and improved extensibility suggests more effective stress distribution throughout the polymer network, reducing localized stress concentrations and delaying crack initiation and propagation. This behavior indicates the formation of a more homogeneous and optimized crosslink structure in the partially substituted system[6],[15].

In contrast, the highly crosslinked network in the 5 phr ZnO formulation, although strong, tends to be more rigid and less capable of dissipating energy under deformation, leading to reduced toughness. Similarly, formulations with 2 phr ZnO lack sufficient crosslink density to sustain mechanical loads effectively, resulting in inferior overall performance[11].

Overall, the results demonstrate that the 3 phr ZnO system achieves an optimal balance between strength and flexibility, leading to superior toughness. This highlights the importance of controlled crosslink density in designing reclaim rubber formulations with enhanced mechanical performance and durability.

Correlation Between Crosslink Density and Mechanical Behavior

The mechanical results exhibit a strong correlation with rheological observations, highlighting the critical role of crosslink density in determining the overall performance of vulcanized reclaim rubber systems[12],[25].

The formulation containing 5 phr ZnO, characterized by high ΔM values, demonstrated superior tensile strength but relatively lower elongation at break, indicating the formation of a rigid and tightly crosslinked network. While such a structure enhances load-bearing capacity, it restricts polymer chain mobility and limits extensibility[3].

In contrast, the formulation with 3 phr ZnO combined with MgO–CaO exhibited moderate ΔM values, corresponding to a balanced crosslink network. This system achieved an optimal combination of tensile strength and elongation at break, reflecting improved stress distribution, enhanced flexibility, and greater energy absorption capability[15],[16].

Formulations containing 2 phr ZnO showed low ΔM values, which translated into reduced tensile strength and inconsistent elongation behavior. These observations indicate an under-cured network with insufficient crosslink density, resulting in poor mechanical integrity and limited load-bearing capacity[11].

Overall, the findings confirm that maximum crosslink density does not necessarily correspond to optimal mechanical performance. Instead, a balanced crosslink structure is essential to achieve an effective combination of strength and flexibility. The 3 phr ZnO system, supported by MgO–CaO synergistic activation, provides the most favorable mechanical performance while significantly reducing zinc content.

This demonstrates that environmentally driven ZnO reduction can be successfully implemented without severe compromise in material properties, offering a viable pathway toward sustainable vulcanization of reclaim rubber.

3.5 Correlation Between Rheology and Mechanical Properties

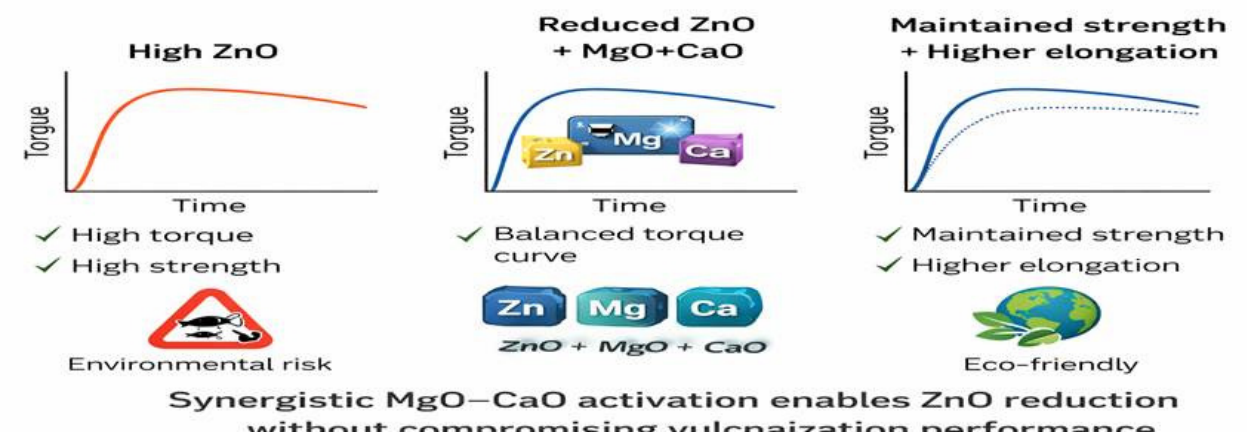

Figure:1.9

Establishing a direct relationship between cure characteristics and mechanical performance is essential for evaluating the efficiency of activator modification in sulfur-vulcanized reclaim rubber systems. In this study, rheological parameters obtained from MDR analysis were systematically correlated with tensile properties to assess the structural implications of ZnO reduction[12,25].

Relationship Between Maximum Torque (MH) and Tensile Strength

Maximum torque (MH) is widely regarded as an indirect measure of crosslink density in vulcanized rubber systems. The formulation containing 5 phr ZnO exhibited the highest MH and correspondingly the highest tensile strength (82.13 MPa), confirming that increased crosslink density enhances the load-bearing capacity of the material through the formation of a tightly interconnected polymer network[3].

However, the increase in tensile strength was not linearly proportional to the increase in MH across all formulations. The 3 phr ZnO / MgO–CaO system, despite exhibiting lower MH than the reference formulation, retained approximately 82% of the tensile strength. This suggests that beyond a critical threshold, further increases in crosslink density contribute only marginally to strength improvement while simultaneously restricting polymer chain mobility.

This observation highlights that mechanical reinforcement in reclaim rubber is governed not solely by the magnitude of crosslink density but also by the uniformity and efficiency of the network

structure. A more homogeneous crosslink distribution can facilitate effective stress transfer across the matrix, thereby maintaining high tensile strength even at reduced crosslink density[15],[16].

Overall, the results indicate that an optimized crosslink network—rather than a maximized one—is critical for achieving superior mechanical performance in reduced-ZnO vulcanization systems.

Influence of Crosslink Density (ΔM) on Elongation Behavior

Torque difference (ΔM = MH − ML) reflects the extent of crosslink network formation and is commonly used as a qualitative indicator of crosslink density in vulcanized rubber systems[6]. Variations in ΔM directly influence polymer chain mobility and, consequently, the elongation behavior of the material.

The formulation containing 5 phr ZnO exhibited the highest ΔM value, which corresponded to a reduced elongation at break (298%). This behavior indicates that the formation of a highly dense crosslinked network restricts molecular mobility and limits the ability of polymer chains to undergo large deformations before failure. Such tightly crosslinked structures typically result in increased rigidity and reduced extensibility[12].

In contrast, the moderate ΔM observed in the 3 phr ZnO / MgO–CaO system was associated with significantly improved elongation at break (391%). This demonstrates that a controlled crosslink density allows greater segmental mobility while maintaining sufficient network integrity to withstand deformation. The enhanced extensibility suggests a more balanced network structure, capable of distributing applied stress without premature fracture[15],[16].

Further reduction of ZnO content to 2 phr resulted in a substantial decline in ΔM, indicating insufficient network formation. The reduced crosslink density in these systems leads to poor structural coherence, limiting both tensile strength and elongation performance due to early failure under applied stress[11].

Overall, these findings confirm that an optimal crosslink density is essential for achieving a balance between stiffness and flexibility. Excessively high crosslink density restricts elongation, whereas insufficient crosslinking compromises structural integrity. The 3 phr ZnO system

represents an optimal condition where ΔM is sufficient to maintain network strength while allowing enhanced chain mobility and extensibility.

Cure Kinetics and Mechanical Development

Scorch time (ts_2) and optimum cure time (tc_{90}) play a critical role in governing the evolution of crosslink networks during vulcanization. These parameters directly influence the rate and extent of crosslink formation, which ultimately determine the mechanical performance of the final material[6].

The formulation containing 5 phr ZnO exhibited relatively efficient cure kinetics, characterized by shorter tc_{90} values. This behavior is attributed to the effective formation of zinc–accelerator complexes, which accelerate sulfur crosslinking reactions and promote rapid network development[3]. The resulting dense and well-developed crosslink structure contributes to high tensile strength and load-bearing capacity.

The 3 phr ZnO / MgO–CaO system maintained comparable tc_{90} values, indicating that the synergistic action of MgO and CaO effectively sustains cure progression despite reduced ZnO content. The preservation of cure rate ensures sufficient crosslink formation within a practical processing time, thereby maintaining mechanical integrity. This supports the observation that partial substitution of ZnO does not significantly compromise vulcanization efficiency when appropriate co-activators are employed[15],[16].

In contrast, formulations with lower ZnO content (2 phr) exhibited extended tc_{90} values, reflecting slower network development and reduced activation efficiency. The delayed cure behavior limits the formation of a fully developed crosslink network, leading to incomplete vulcanization and inferior mechanical properties[11].

Overall, the results demonstrate that efficient cure kinetics are essential for achieving optimal crosslink density and mechanical performance. The 3 phr ZnO system successfully maintains cure efficiency through MgO–CaO synergistic activation, whereas excessive reduction of ZnO adversely affects both curing behavior and material performance.

Toughness Optimization Through Balanced Crosslinking

Mechanical toughness, defined as the ability of a material to absorb energy prior to fracture, is governed by the combined influence of tensile strength and elongation at break[12],[25]. It serves as a critical parameter for evaluating the overall performance and durability of vulcanized rubber systems.

The formulation containing 5 phr ZnO exhibited high tensile strength but relatively limited elongation, resulting in a rigid and tightly crosslinked network. Although such a structure provides excellent load-bearing capacity, its reduced flexibility restricts energy dissipation under deformation, thereby limiting overall toughness. This behavior is characteristic of highly crosslinked systems where chain mobility is significantly constrained[3].

In contrast, the 3 phr ZnO / MgO–CaO formulation demonstrated an optimal combination of tensile strength and elongation at break, indicating the formation of a more efficient and balanced crosslink architecture. The moderate crosslink density in this system enables effective stress distribution across the network while allowing sufficient chain mobility for deformation. As a result, crack initiation and propagation are delayed, leading to enhanced toughness and improved resistance to mechanical failure[15],[16].

Formulations with further reduced ZnO content (2 phr) lack sufficient crosslink density to maintain structural integrity under stress, resulting in inferior toughness despite relatively higher chain mobility. The weak network structure fails to sustain energy absorption, leading to premature failure[11].

Overall, the rheological–mechanical correlation confirms that maximum torque (or crosslink density) does not necessarily correspond to optimal mechanical performance. Instead, an intermediate crosslink density—achieved through partial ZnO substitution with MgO–CaO—provides a superior balance between strength and flexibility, resulting in enhanced mechanical toughness.

Overall Correlation Insight

The integrated analysis reveals:

- High ZnO → High MH → High strength but reduced flexibility

- Moderate ZnO with MgO–CaO → Controlled MH → Balanced strength and elongation
- Excessive ZnO reduction → Low MH → Poor mechanical performance

These findings validate that MgO–CaO synergistic activation enables controlled crosslink network formation under reduced ZnO conditions, maintaining mechanical integrity while lowering environmental zinc burden.

3.6 Optimization of Reduced-ZnO System and Environmental Implications

The systematic evaluation of cure characteristics and mechanical performance demonstrates that ZnO content in reclaim rubber formulations can be significantly reduced without severe compromise in vulcanization efficiency or structural integrity. However, the degree of reduction must be carefully optimized to avoid deterioration in crosslink density and mechanical strength.

The reference formulation containing 5 phr ZnO provided maximum torque development and tensile strength, confirming strong activation efficiency[12]. Nevertheless, the associated high crosslink density resulted in reduced elongation and increased network rigidity. From an environmental perspective, higher zinc content contributes to potential aquatic toxicity[34].

Partial substitution of ZnO with MgO and CaO (3 phr ZnO + 1.5 phr MgO + 0.5 phr CaO) emerged as the optimal formulation[56]. This system maintained controlled cure kinetics, adequate torque development, and substantial tensile strength retention (~82%), while enhancing elongation at break.

4. Conclusion

This study confirms that ZnO content in reclaim rubber can be reduced by 40% (from 5 phr to 3 phr) through synergistic MgO–CaO activation without critical performance loss. The optimized F2 formulation (3 phr ZnO, 1.5 phr MgO, 0.5 phr CaO) yielded:

Balanced Cure: Maintained processing safety (t_{s2}) and efficient cure times (t_{c90}≈3.57 min).

Enhanced Toughness: Improved elongation at break (391%) while retaining 82% of the reference tensile strength.

Environmental Compliance: Significant reduction in potential zinc leaching, aligning with sustainable manufacturing practices (Zhang et al., 2024).

This study investigated the feasibility of reducing zinc oxide content in sulfur-cured reclaim rubber through synergistic substitution with MgO and CaO, and systematically correlated cure kinetics with mechanical performance.

The reference formulation containing 5 phr ZnO exhibited the highest torque development and tensile strength, confirming strong activation efficiency and high crosslink density. However, the elevated crosslink density resulted in reduced elongation, indicating increased network rigidity.

Partial substitution of ZnO (3 phr ZnO + 1.5 phr MgO + 0.5 phr CaO) demonstrated a balanced rheological–mechanical profile. This formulation maintained controlled scorch safety and cure time, moderate torque development, and substantial tensile strength retention (~82% of the reference), while significantly improving elongation at break. The intermediate torque difference (ΔM) confirmed the formation of a well-optimized crosslink network that provided both strength and flexibility.

Further reduction to 2 phr ZnO resulted in diminished torque development, extended cure time, and reduced mechanical integrity, indicating insufficient activation and inadequate crosslink density under the present curing conditions.The correlation between rheological parameters and tensile properties confirms that optimal mechanical performance is governed by balanced crosslink density rather than maximum torque alone. The MgO–CaO synergistic system effectively compensates for partial ZnO reduction but cannot entirely replace zinc activation at excessively low concentrations.

Importantly, reducing ZnO from 5 phr to 3 phr represents a 40% decrease in zinc usage, offering a practical pathway toward environmentally responsible vulcanization while maintaining acceptable mechanical performance. The findings demonstrate that controlled ZnO reduction in reclaim rubber systems is achievable through strategic activator design, supporting sustainable rubber manufacturing practices.

The most important outcome of this study is the validation of a **reduction-based strategy rather than a replacement-based strategy**. While complete elimination of ZnO remains challenging, partial substitution using compatible oxides offers a realistic and industrially applicable solution.

This approach aligns with current trends in sustainable material development, where optimization of existing systems is preferred over radical replacement that may compromise performance.

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