

Synergistic Effect of Zinc Oxide and Magnesium Oxide Co-Cure Activators on Polybutadiene Rubber Vulcanization: Mechanical Properties and Thermal Characteristics

Gnanu G. Bhatt*, Raj Vasani, Siddhant Patil, Pratik Bagul and Ujjwal Vig

Department of Rubber Technology, Lalbhai Dalpatbhai College of Engineering, 380015, Ahmedabad, Gujarat, India

Abstract: Zinc oxide (ZnO) is widely recognized as an effective cure activator in the sulphur vulcanization of polybutadiene rubber (PBR). However, its high toxicity to aquatic organisms has raised environmental concerns, prompting the search for non-toxic alternatives. Despite this, no industrially viable substitute has been identified. This study explores the potential of using a combination of ZnO and magnesium oxide (MgO) to reduce ZnO levels while enhancing vulcanization performance. The crosslinking density and thermal stability of the vulcanized PBR were assessed to evaluate the efficacy of MgO. The results demonstrate that the inclusion of MgO as a co-activator significantly accelerates the vulcanization rate. Specifically, formulations with 60% MgO exhibited a tensile strength of 1.1 MPa, elongation at break of 111%, and hardness of 46 Shore A. When using MgO exclusively, the material achieved a tensile strength of 1.4 MPa, elongation at break of 212%, and hardness of 43 Shore A, with an abrasion loss of 64.82 mm³. Swelling studies revealed that crosslink density was highest in the PBR formulation with 3 phr MgO and 2 phr ZnO, exhibiting the lowest swelling index (3.10). As MgO content increased, the swelling index also rose, indicating reduced crosslink density. The highest swelling index (4.24) was observed in the formulation with 5 phr MgO, confirming weaker crosslink formation. These results highlight that MgO alone lacks the ability to form an effective sulfurating complex, but when combined with ZnO, it enhances crosslinking efficiency and vulcanization performance. The use of MgO, either alone or in combination with ZnO, presents a viable approach for developing environmentally friendly PBR compounds with potential applications in high-performance elastomers such as tires.

Keywords: Co-activator, Crosslink density, Thermal stability, Tensile strength, elongation at break.

1. INTRODUCTION

The sulphur vulcanization was developed by Charles Goodyear in 1839. He found that rubber chains could be linked together i.e. vulcanized by heating with sulphur and white lead. In the process, sulphur bridges between the rubber chains. (chapter 1 the Vanderbilt rubber handbook 13th edition) It was reported in 1905 that ZnO acts as reinforcing filler for rubber compounds. But in 1912, they started using a lot of carbon black in tire treads instead of ZnO to get better physical properties. Then, to cut down on vulcanization time, they added inorganic activators/accelerators like lead oxide, magnesium oxide, and calcium oxide. In the early 1920s, they figured out how activators work. They found out that combining ZnO with stearic acid (SA) speeds up vulcanization and boosts rubber properties, even without accelerators. Fatty acids like stearic acid help dissolve zinc in the system and release zinc ions to form complexes with accelerators.

The combination of Zinc oxide (ZnO) and fatty acid (stearic acid) has proven to be the most successful

cure activator system in the rubber industry, typically used at concentrations of 2-5 phr for ZnO [2,8] and 0.5-3 phr for stearic acid. Specifically, a formulation with 5 phr ZnO and 2 phr stearic acid is standard in tire manufacturing, offering enhanced modulus, low heat build-up, and good abrasion resistance. ZnO also facilitates adhesion between brass-coated steel cords and rubber in tires [21]. Approximately 105,000 tons of ZnO are produced annually, with 50-60% being utilized in the rubber industry.

There is substantial evidence that zinc plays a crucial role in cross-linking [1], particularly in enhancing cross-linking efficiency. Although zinc is generally considered one of the least harmful heavy metals, in 1985, the Dutch Ministry of the Environment classified zinc on a priority list of substances suspected to have negative environmental effects. While zinc is a heavy metal, it is also a natural, recyclable element integral to our environment. It is the 17th most common element in the earth's crust and is essential for human, animal, and plant health. However, zinc compounds, especially soluble ones, are classified as ecotoxic to aquatic organisms, leading to potential restrictions on ZnO production and application [4].

ZnO is widely used in rubber production, disposal, and recycling, with environmental releases occurring

*Address correspondence to this author at the Department of Rubber Technology, Lalbhai Dalpatbhai College of Engineering, 380015, Ahmedabad, Gujarat, India; E-mail: ggbbhatt@ldce.ac.in

through manufacturing emissions and wear of products such as tires. Considering upcoming environmental regulations and eco-labelling requirements for vehicle tires, it is required to minimize Zinc Oxide content in rubber compounds for both environmental and economic reasons [3]. The increasing emphasis on environmental protection has driven the demand for products with minimal environmental impact.

Other metal oxides, such as MgO, CaO, PbO, CuO, and NiO, can also serve as curing activators. In this study, MgO was selected as a cure activator due to its superior performance compared to other metal oxides [10]. While nano-particles of MgO are not preferred as co-cure activators due to their higher cost, complex synthesis [11], and greater toxicity, micro-MgO has proven to be more eco-friendly and produces lower toxicity than ZnO [6,9].

Magnesium oxide (MgO) is not widely used in the tire industry as its properties do not fully match those of ZnO, which remains the dominant activator. However, research suggests that significant improvements can be achieved using a combination of two accelerators, where one acts as the primary and the other as a secondary accelerator. MgO alone does not provide optimal properties due to its lack of sulfurating complexes formed during vulcanization. However, metal oxide such as MgO can undergo reactions similar to Zinc Oxide with vulcanization accelerators, despite some limitations. While it seems unlikely to completely replace ZnO with MgO in tire applications, a partial replacement using a combination of both MgO and ZnO can achieve balanced properties with reduced environmental impact.

The synergistic effect of MgO and ZnO in vulcanization is evident [7], particularly in the presence of zinc ions in the accelerator, leading to higher cross-link network compared to using only primary accelerator. Research and practical studies demonstrate that using MgO and ZnO together promotes mutual interaction between accelerators, enhancing cross-link density and improving curing properties. MgO, which also acts as an acid acceptor during vulcanization, shows an improved cure rate. Thus, combining MgO with ZnO can yield optimal curing results while being more cost-effective, less toxic, and abundant, ultimately reducing environmental toxicity without compromising the properties of the rubber compound.

This study presents practical tests and chemical analyses of activators, highlighting how MgO can be

effectively used as a cure activator alongside ZnO in the vulcanization of polybutadiene rubber. The article also discusses the type of vulcanization system employed and compares the properties of the vulcanized product with varying levels of MgO and ZnO in polybutadiene rubber.

Studies have shown that using Magnesium Oxide as a activator can effectively reduce Zinc Oxide levels in rubber vulcanization, particularly when combined with ZnO in binary accelerator systems. These systems, which involve mutual interactions between thiuram and thiazole functional groups, enhance curing properties such as cross-link density and mechanical modulus more effectively than only primary accelerator systems.

In this study, we explore the use of magnesium oxide as a co-cure activator alongside zinc oxide in the vulcanization of polybutadiene rubber. We focus on a low-sulphur, binary accelerator system to examine the interactions between accelerators and activators. An efficient vulcanization (EV) system, characterized by a high accelerator-to-sulphur ratio, is selected for its ability to produce a higher proportion of mono- and disulfide cross-links, offering superior thermal stability compared to conventional (CV) and semi-efficient vulcanization (SEV) systems. The investigation encompasses the curing behaviour, mechanical properties, and thermal stability of the vulcanized rubber, with particular emphasis on fracture toughness, a critical parameter for applications in stretchable mechanical and electronic devices. Additionally, we propose and discuss potential mechanisms of chemical interactions between the cure activators in detail.

MgO lowers activation energies in vulcanization by enhancing ZnO's efficiency, stabilizing curing reactions, and improving crosslink formation. In EV systems, it significantly reduces activation energy, while in SEV systems, its effect is moderate, mainly improving curing uniformity and thermal stability. Arrhenius plots reveal these kinetic changes [19-20].

2. MATERIALS AND METHODS

2.1. Materials

ZnO, Stearic acid, sulphur and polybutadiene rubber [12]. Cisamer 01 is solution polymerised High Cis -1,4 Polybutadiene rubber produced using complex organometallic catalyst based on JSR Technology

Table 1: Mixing Composition of Different Ingredients in phr (Per Hundred Grams of Rubber)

Formulation	Mixing Composition				
	1-MgO/4-ZnO	2-MgO/3-ZnO	3-MgO/2-ZnO	4-MgO/1-ZnO	5-MgO
PBR	100	100	100	100	100
MgO	1	2	3	4	5
ZnO	4	3	2	1	-
Steric acid	1.5	1.5	1.5	1.5	1.5
TMTD	0.72	0.72	0.72	0.72	0.72
MBTS	2	2	2	2	2
SULPHUR	0.5	0.5	0.5	0.5	0.5

(PBR density = 0.92 g/cm³, Mw 40000 g/mol) were supplied by the. Cure accelerator tetra methyl thiuram disulfide (TMTD), 2-mercaptobenzothiazole disulfide (MBTS) and Light magnesium oxide fine powder were purchased from OPULIN Chemical Industry Co. Ltd.

2.2. Rubber Compounding

The polybutadiene rubber [12] was first masticated by using a mixing mill sized at 14"x30". Mastication took approximately 9 minutes, followed by a 3-minute mixing of activator and stearic acid. Afterward, accelerators and sulphur were added and mixed for an additional 3 minutes. Once mixing was complete, the compounded rubbers were cut into sheets.

The friction ratio determines the difference in surface speeds of the front and rear rollers, generating shear forces that help break down the rubber structure and disperse fillers, activators, and accelerators uniformly. During mastication, a higher friction ratio promotes mechanical shear, leading to molecular scission in the rubber chains, which reduces viscosity and improves process ability. A properly selected friction ratio ensures efficient incorporation of curatives and prevents agglomeration of particles, leading to better cross linking efficiency and improved mechanical properties. The selected speeds help regulate the heat generation during processing. Excessive heat can cause premature cross linking or degradation of sensitive additives. Higher roller speeds generally lead to faster mixing and dispersion, but they must be optimized to avoid excessive energy input that can alter the rubber's properties. Proper mixing prevents filler aggregation, leading to uniform stress distribution, enhancing toughness and elasticity. Well-dispersed curatives ensure the formation of a stable vulcanization network, enhancing resistance to thermal degradation. To maintain consistency, the friction ratio between the front and rear rollers was kept at 1.2:25, with roller

speeds set at 26 and 20 rpm, respectively. During mastication, the nip gap between the rollers was maintained at 2 mm, while for the remainder of the process, it was adjusted to 0.7 mm. We have done mixing of our compound at Raghuvanshi Rubber Industries. TMTD is a fast-acting, primary accelerator that provides a high cross-linking efficiency, especially in low-sulfur and efficient vulcanization (EV) systems. It also acts as a sulfur donor, helping to form mono- and disulfide cross-links that enhance thermal stability. MBTS is a moderate-speed accelerator that helps regulate the curing process and prevents premature vulcanization (scorching). It synergizes with TMTD, ensuring better control over the reaction kinetics and improving mechanical properties such as tensile strength and elasticity [22].

2.3. Measurements of Cure Characteristics

Approximately 5 grams of compounded rubber were placed into the cavity of a Rheometer (MDR) to assess curing characteristics at 150°C. The Moving Die Rheometer generated rheographs depicting torque versus time curves, from which various curing parameters were derived.

These parameters include:

Lowest torque (ML)

Highest torque (MH)

Torque difference (Δ torque = MH – ML)

Scorch safety time (ts2)

Optimum curing time (tc90)

Cure rate index (CRI = 100 / (tc90 - ts2))

Rate of vulcanization (Rv = (Mt90 - Mt2) / (tc90 - ts2))

These parameters provide insights into the rubber's curing behaviour under specified conditions.

2.4. Mechanical Properties of Rubber Vulcanizates

Mechanical properties of rubber vulcanizates, we cured rubber compound according to their respective t_{c90} values using a press moulding machine, applying a pressure of 100 psi. The resulting sheets had a thickness of 2 mm. To mitigate the effects of aging due to environmental temperature variations, the cured sheets were stored in a cool environment. Prior to testing, the sheets were conditioned at room temperature for 24 hours. Dumbbell-shaped specimens, conforming to the ASTM D-412, were then extracted from these sheets. Tensile tests were performed on a universal testing machine. From the stress-strain data, key tensile properties such as the modulus at 100% elongation (M100), modulus at 300% elongation (M300), tensile strength (T.S.), and elongation at break (E.B.) were determined.

3. RESULTS AND DISCUSSION

3.1. Curing Characteristics

The curing curves for various rubber vulcanizate samples are presented in Figure 1a. The rheographs reveal that all cure curves exhibit a similar pattern, characterized by a marching trend. When using MgO as the sole activator, the t_{s2} value (scorch time) Figure 1b is significantly lower compared to the ZnO-only activation system. This indicates that the scorch safety in the MgO-based activator system is poor, as MgO rapidly breaks polysulfide linkages but is not able to regenerate them into stable cross-links.

Conversely, the ZnO-only activation system shows a much higher t_{s2} time, reflecting greater scorch safety; however, the time required to achieve optimum curing is considerably longer. When MgO and ZnO are used in combination, both scorch safety and activation time are improved, as shown in Figure 1b. Zinc Oxide, in the presence of curing accelerators and sulphur, produces an active sulfurating agent complex, whereas Magnesium Oxide does not generate such an active complex but instead decomposes accelerators more quickly, initiating vulcanization earlier. It can be inferred that MgO, when used as a co-cure activator, may enhance the formation of a zinc-accelerator complex more effectively than ZnO alone.

Given that MgO can degrade higher-ranked sulfur bridges, employing a high accelerator-to-sulfur ratio,

characteristic of an efficient vulcanization (EV) system, is likely the most suitable choice. This approach leverages the benefits of Magnesium Oxide as a co-activator more effectively than semi-efficient (SEV) or conventional (CV) systems [15].

The higher torque value (ML) observed in MgO-based vulcanizates (MgO-5) can be attributed to the faster rate of vulcanization. Although there is a slight increase in ML, it does not negatively impact the flow properties of the compounded rubber during molding. The MH value increases as the phr of MgO rises from 1 to 5, with the highest MH value observed in the MgO-2 and ZnO-3 combination.

At higher doses of MgO, scorch safety is significantly lower compared to its combination with ZnO. As illustrated in the Figure 1b, the highest scorch safety is achieved in the MgO-1 and ZnO-4 combination, owing to the slower reactivity of ZnO. It is evident from the data that MgO-based compounds exhibit lower scorch safety compared to ZnO-based compounds. This is because, in the presence of MgO, accelerators decompose more rapidly, initiating the crosslinking reaction much earlier. Conversely, Zinc Oxide reacts more slowly with accelerators to form the active sulfurating complex, leading to a slower onset of the crosslinking reaction. Consequently, the ZnO-only activator system demonstrates higher scorch safety than other compounds. Although MgO as a co-activator provides lower scorch safety values, these can be improved by controlling the vulcanization rate through reduced vulcanization temperatures.

Optimum cure time is a crucial parameter, as both excessively high and low values can result in inferior vulcanizate properties. The different optimum cure times are presented in the Figure 1c. As the MgO dosage increases, the optimum cure time decreases. This is likely due to the inherent properties of polybutadiene rubber (PBR), particularly its spontaneous cross linking tendency during vulcanization. PBR requires less sulfur than other diene rubbers to achieve optimal cross linking. The combination of MgO-4 and ZnO-1 results in a very low optimum cure time, indicating that Magnesium Oxide as a co-activator may be more cost-effective for rubber vulcanization compared to using Zinc Oxide alone as a single-site cure activator.

A critical step in vulcanization is the formation of a metal complex between the activator and the accelerator (Ac-S-Zn-S-Ac). Tetra Methyl Thiuram

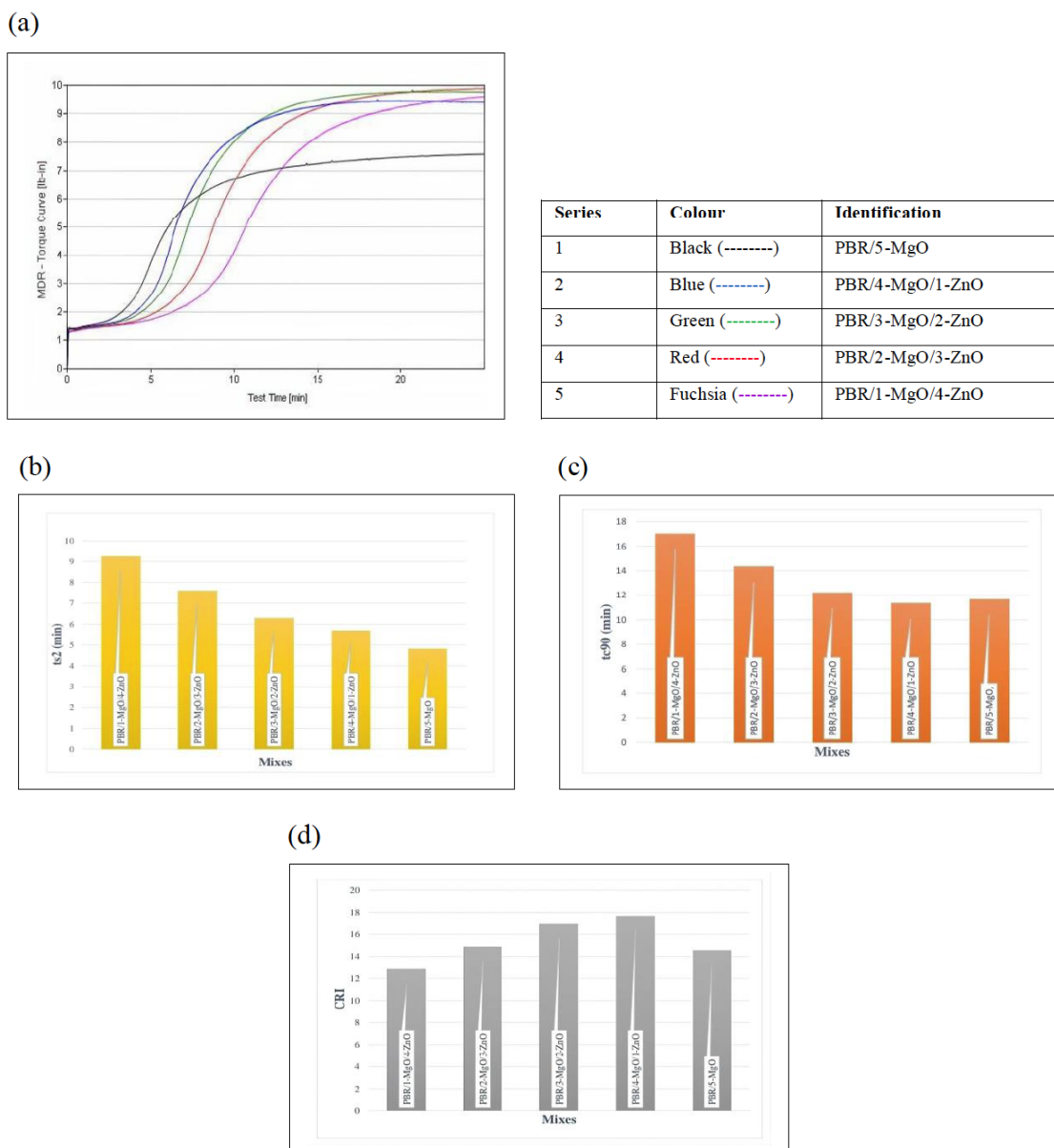


Figure 1: curing characteristic of rubber vulcanizates (a) Rheographs of PBR samples (b) Ts2 (Induction time) (c) TC90 (Optimum Cure Time) (d) CRI (Cure Rate Index).

Disulfide (TMTD), an ultra-fast accelerator, forms a zinc-dithiocarbamate complex in the presence of ZnO as an activator. This zinc-dithiocarbamate is then processed into an active sulfurating complex in the presence of sulfur, which ultimately undergoes cross-linking. When ZnO and cure accelerators are present, thiocarbamic acid is formed, which undergoes an acid-base type reaction. The combination of thiuram disulfide and ZnO produces a catalytic complex that promotes increased cross linking between rubber chains. It is believed that after cross linking, the complex reverts to dithiocarbamate, which has low cross linking efficiency on its own. However, in the presence of a secondary accelerator (an oxidizing

agent), dithiocarbamate can be converted back to thiuram disulfide.

In single accelerator systems where dithiocarbamate is used, higher crosslink density is not achieved. However, in binary systems (TMTD and MBTS), thiuram sulfide is formed, which results in a higher crosslink density [13,14]. Adding thiuram sulfide externally does not yield the same level of crosslinking.

The Cure Rate Index (CRI) is illustrated in Figure 1d. As the proportion of MgO increases from 1 to 4 phr, the CRI values of the compound rise accordingly. However, when MgO is used as the sole activator, the CRI value slightly decreases. From the equation, it is

evident that CRI is influenced by both scorch safety and optimum cure time. In systems where ZnO is used as the sole activator, the optimum cure time is higher, leading to a slower vulcanization rate.

In contrast, the vulcanization rate increases when MgO is used in combination with ZnO as a co-activator. When MgO is used alone as an activator, the vulcanization rate decreases. This suggests that MgO, when employed as a co-activator, enhances the vulcanization rate more effectively than a ZnO-based activator system. This is because MgO reacts with dimethyl dithiocarbamic acid to form magnesium dimethyl dithiocarbamate, which accelerates the vulcanization process. In the presence of MgO, the accelerator decomposes more rapidly, producing an excessive amount of zinc-accelerator complex, which efficiently vulcanizes the rubber.

3.2. Crosslink Density

In our study, the use of MgO as a single activator resulted in a significantly low crosslink density. This outcome is attributed to the formation of magnesium-dithiocarbamate in the presence of Magnesium Oxide as a co-activator. However, the magnesium-dithiocarbamate produced does not exhibit catalytic reactivity necessary for final crosslink formation. Interestingly, when ZnO is introduced, the magnesium-dithiocarbamate is converted into zinc dithiocarbamate, with the conversion efficiency depending on the amount of ZnO present. Notably, this reaction leads to the formation of the zinc accelerator complex at a higher rate compared to a system using ZnO as the sole activator. Cross link density of MgO 5 - 1.04×10^{-4} mol/cm³, MgO 4 - 1.59×10^{-4} mol/cm³, MgO 3 - 2.15×10^{-4} mol/cm³, MgO 2 - 1.92×10^{-4} mol/cm³, MgO 1 - 2.06×10^{-4} mol/cm³. The study reveals that the MgO-ZnO ratio significantly influences crosslink density and mechanical properties. Using MgO alone results in low crosslink density due to the formation of inactive magnesium-dithiocarbamate, whereas adding ZnO facilitates its conversion into zinc-dithiocarbamate, enhancing crosslinking efficiency. As MgO increases, tensile strength improves, but elongation at break decreases, indicating reduced flexibility. As MgO increases and ZnO decreases, crosslink density increases up to a peak (MgO 3:2 ZnO ratio) and then declines. This suggests that an optimal MgO-ZnO balance is needed for maximum crosslink formation.

3.3. Swelling Index

The swelling index trends in Figure 2 indicate variations in crosslink density among different PBR-

MgO compositions. PBR-MgO 1 and PBR-MgO 2 exhibit similar swelling indices, while PBR-MgO 3 shows the lowest swelling index (3.10), suggesting the highest crosslink density among all samples. As the MgO dosage increases, the swelling index also increases, with PBR-MgO 4 and PBR-MgO 5 displaying higher swelling values (3.39 and 4.24, respectively) compared to PBR-MgO 1, 2, and 3. Beyond PBR-MgO 4, the swelling index rises sharply due to reduced crosslink density. Notably, PBR-MgO 5 has the highest swelling index and the lowest crosslink density, confirming that when MgO is used alone, it lacks the sulfurating complex and catalytic activity required for effective crosslink formation [16,17].

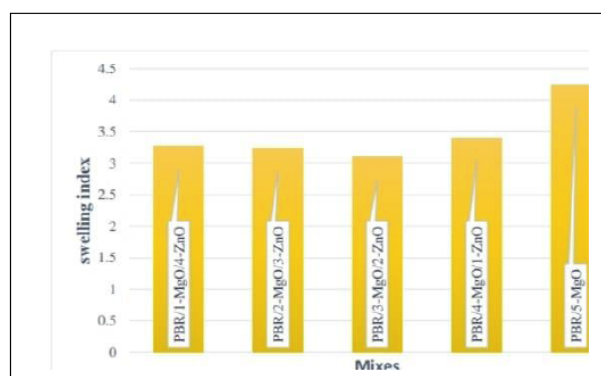


Figure 2: Swelling Index of PBR Samples.

3.4. Reaction Mechanism

The Tetra methyl thiuram disulfide(TMTD) at high temperature decompose to form Thiuram sulphenyl radical which on recombination form tetramethyl thiuram polysulphide(TMTP).

The tetramethyl thiuram polysulfide(TMTP) reacts with butadiene chain the thiuram polysulphenyl forms link with rubber and other part of TMTP reacts with other MBTS to form TMTD.

The formation of crosslink precursor from which the polysulfide ring remains with rubber chain and remaining structure gets separated, this complex then abstract the allylic hydrogen from rubber chain to form dimethyl dithiocarbamic acid [5].

The butadiene polysulfide linkage complex then react with another butadiene polysulfide linkage to form final crosslink is illustrated in Figure 3.

3.5. Reaction Mechanism

The formation of dimethyl dithiocarbamic acid due to the reaction between butadiene chain and

TMTP(tetramethyl thiuram polysulphide) after formation of crosslink precursor complex.

This dithiocarbamic acid reacts with MgO, due acid acceptor property of MgO it reduce acidity and form magnesium dimethyl dithiocarbamic [7]. Due to low catalytic reactivity of MgO it unable to form active sulphurating complex, the ZnO then replace the MgO.

After replacing MgO it forms active sulphurating agent complex which is more efficient than the normal active sulphurating agent complex formed using ZnO as a single activator.

This active sulfurating agent complex then reacts with rubber hydrocarbon(butadiene) to form dimethyl dithiocarbamic acid rubber complex, ZnO and dithiocarbamic acid.

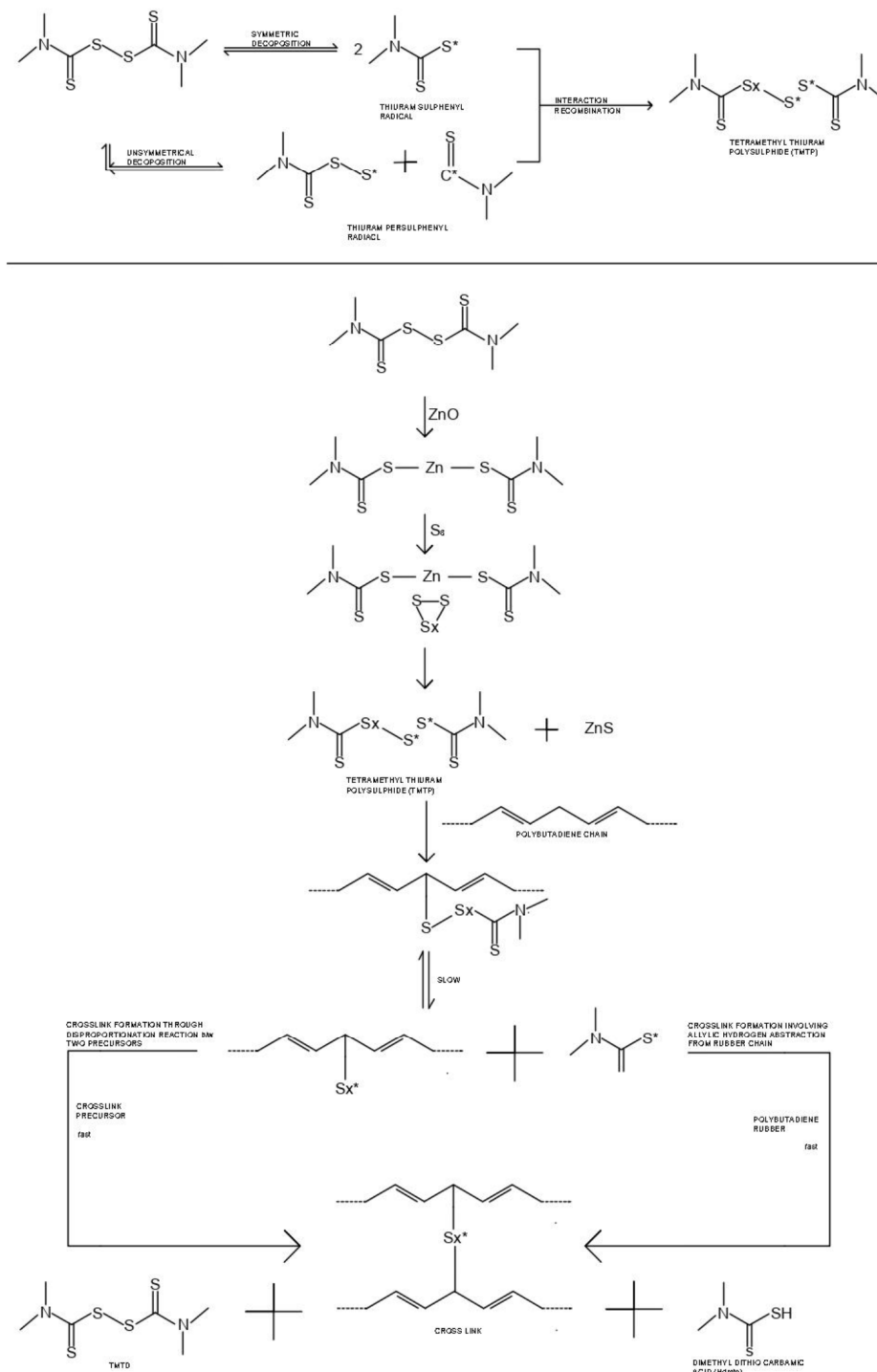


Figure 3: Possible reaction mechanism between accelerator and rubber molecule.

The dimethyl dithiocarbamic acid rubber complex reacts with other rubber hydrogen complex to form crosslinking between two rubber chains is illustrated in Figure 4 [18].

3.6. Tensile Mechanical Properties

The tensile and mechanical properties are plotted in Figure 5a. We can say that the tensile strength of only MgO based compound is higher as compared to ZnO based activator system, as the MgO proportion has increased the tensile strength simultaneously increased. The elongation at break value has decreased as the proportion of MgO has increased which is shown in Figure 5b. It can be observed that Magnesium Oxide/Zinc Oxide binary activator at 3:2

ratio provides the best values (1.1 MPa in M100) among the compounds.

3.7. Abrasion loss(gm)

ASTM D9563 measures the abrasion resistance of rubber, not hardness. To perform the test, prepare a rubber specimen button as per ASTM 2240 and the thickness of around 6 mm. The specimen is mounted in an abrasion testing machine, where it is rubbed against an abrasive surface under a fixed load. After a specified number of cycles, the wear is measured in terms of volume loss (mm³) or weight loss (mg), which indicates the material's abrasion resistance. This test helps assess how well rubber withstands wear and tear in various applications.

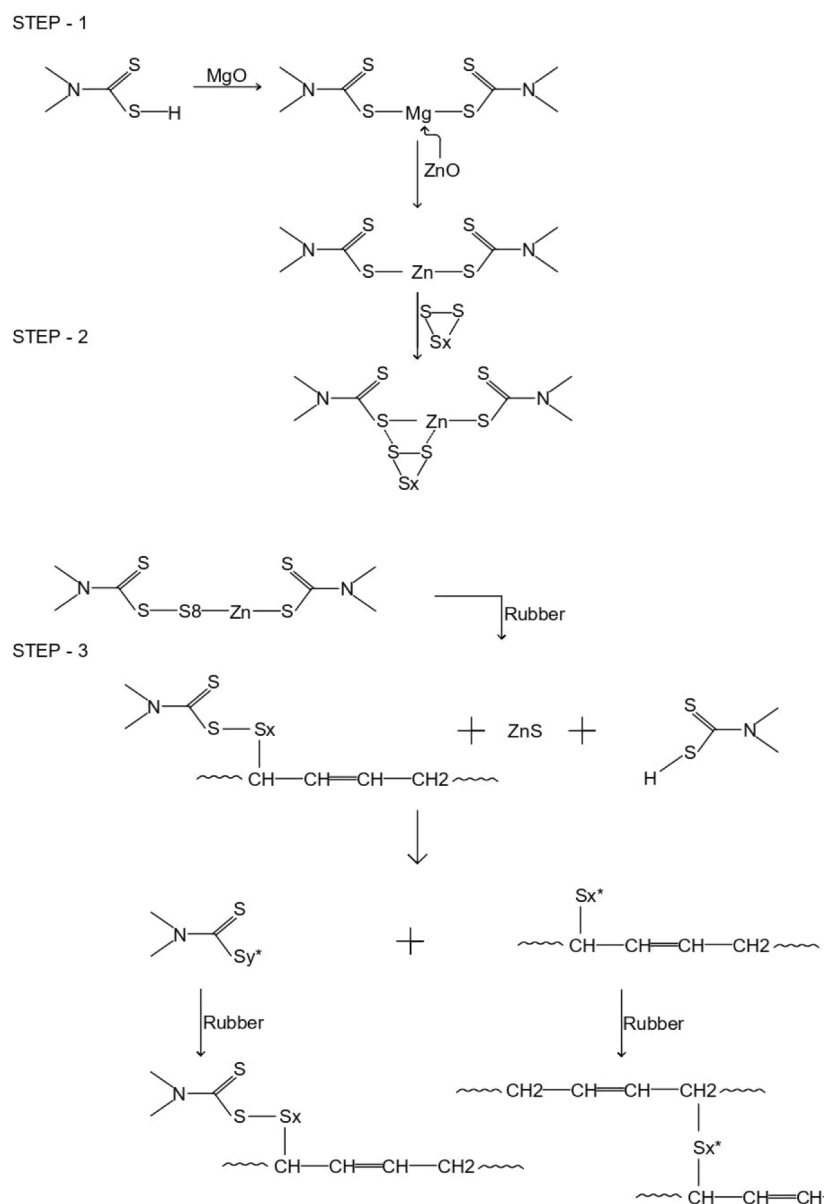


Figure 4: Possible reaction mechanism between dithiocarbamic acid and MgO.

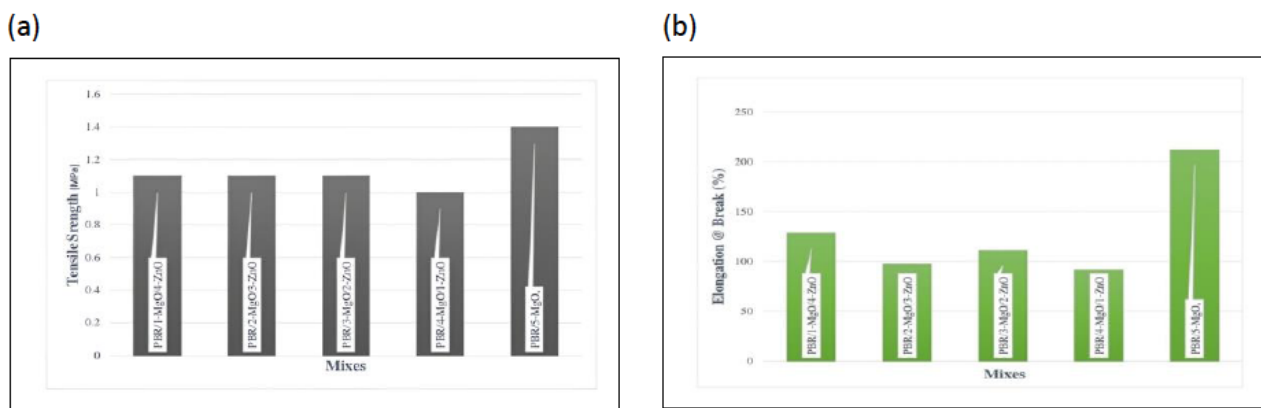


Figure 5: (a) Tensile mechanical properties of vulcanized rubber (MPa) (b) Elongation @ Break (%).

The abrasion loss in gm have plotted in Figure 6. As the percentage of MgO increases from 1 to 4 phr, the abrasion loss increases rapidly. The lowest abrasion loss has been observed in MgO-5, at the time of testing material test specimen was coming out of the fitting arrangement. Because the material was not cured due to absence of formation of zinc sulphurating agent complex, the main reason for crossing linking is the formation of zinc sulphurating agent which will form crosslink between two chains by attaching Sulphur to it and separate out at the time of cross linking.

The highest abrasion resistance we have obtained in 1-MgO/4-ZnO so we can conclude that as the MgO proportion increases the abrasion loss increase with it.

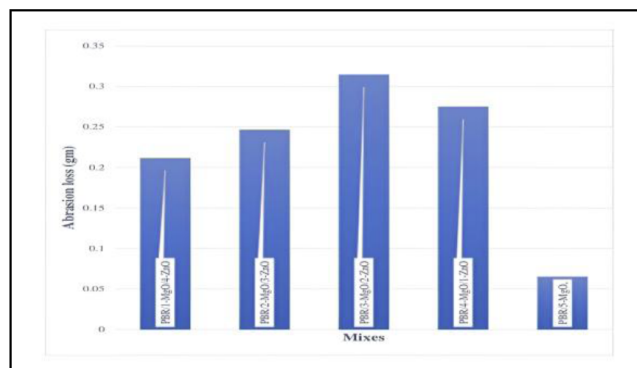


Figure 6: Abrasion loss values of vulcanized rubber samples (gm).

3.8. Hardness

The Method of Measuring the hardness of rubber is done using ASTM D2240, the specimen (or "button") should typically have a thickness of at least 6.35 mm (0.24 inch). Use a Type A durometer, ensuring the indenter is perpendicular to the surface. Press the durometer onto the specimen with a steady force and record the hardness value after 15 seconds.

As the MgO proportion has increased hardness gradually increased till 3 phr above it the hardness has decreased and at 5-MgO the lowest hardness we observed in Figure 7. Because crosslinking density in 5-MgO is very low, At 2 and 3 phr of MgO the highest hardness value we have observed due to the the formation of higher zinc sulphurating complex, the tendency of formation of dithiocarbamate in MgO has higher compared to ZnO, if we combine the MgO and ZnO the highest crosslinking density we observe due to the Synergism effect.

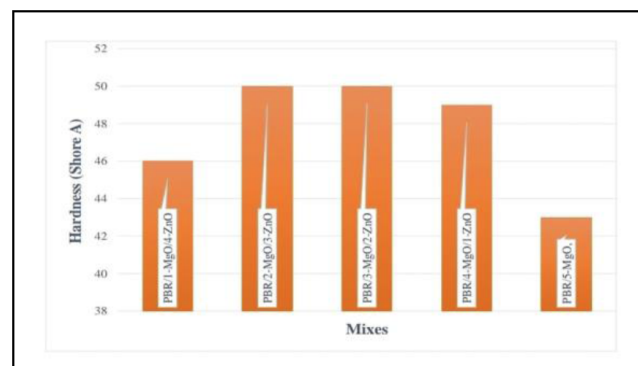


Figure 7: Hardness (Shore A).

CONCLUSION

This study highlights the critical interplay between Magnesium Oxide (MgO) and Zinc Oxide (ZnO) in optimizing rubber vulcanization, showcasing how their combined use enhances both curing characteristics and material performance. While MgO accelerates the vulcanization process, it compromises scorch safety due to its rapid breakdown of polysulfide linkages. In contrast, ZnO offers superior scorch safety but leads to slower vulcanization. However, the synergistic effect of MgO and ZnO provides a balanced solution, improving both scorch safety and curing efficiency, with the highest crosslink density achieved through their

combination, especially at elevated accelerator-to-sulfur ratios. The tensile strength of MgO-based compounds increases with its proportion, though elongation at break decreases, with optimal mechanical properties observed in a 3:2 MgO/ZnO blend. Additionally, the swelling index and abrasion resistance correlate closely with crosslink density, showing that higher MgO content reduces crosslinking and increases swelling, while excessive MgO worsens abrasion resistance. Hardness peaks at 2-3 phr of MgO, where the formation of a zinc-sulfurating complex is most effective. Ultimately, the MgO-ZnO combination emerges as a highly efficient vulcanization system, offering a balance of enhanced strength, durability, and processability suitable for a wide range of applications.

KEY *OUTCOMES*

- Optimized curing results.
- Enhanced mechanical properties (tensile strength, elongation, and hardness)
- Balanced material properties suitable for demanding applications

INDUSTRIAL IMPLICATIONS

The ZnO-MgO activator combination has significant potential for advancing PBR-based material performance, particularly in industries requiring strength and thermal resilience, such as automotive and tire manufacturing.

FUTURE RESEARCH DIRECTIONS

This study establishes a basis for optimizing activator ratios and enhancing co-curing systems in rubber vulcanization. Future research should explore the impact of varying accelerator types and dosages to further refine crosslink formation. Investigating alternative metal oxides as co-activators could provide insights into their catalytic efficiency compared to MgO-ZnO systems. Additionally, studying the long-term thermal and oxidative stability of these formulations would be crucial for high-performance applications.

RECOMMENDATIONS

- Investigate optimal MgO-ZnO ratios for specific applications
- Explore co-curing systems in other rubber technologies

- Develop scalable manufacturing processes for ZnO-MgO-based PBR compounds

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of Raghuvanshi Rubber Industries for conducting the mixing of the rubber compound, and Reliance Industries Limited for performing various tests on the rubber compound at their esteemed Industry.

REFERENCES

- [1] Butuc G, Janssen A, van, Kees *et al.* Role of zinc oxide in sulfur crosslinking. In: Rubber & plastics news. 2020; 2020(10): 16-19.
- [2] Chukwu M, Ekhatior I, Ekebafé L. Effect of zinc oxide level as activator on the mechanical properties of natural rubber composite. Nigerian Journal of Technology 2019; 38(3): 675. <https://doi.org/10.4314/njt.v38i3.19>
- [3] Heideman G. Reduced zinc oxide levels in sulphur vulcanisation of rubber compounds: mechanistic aspects of the role of activators and multifunctional additives. Enschede University of Twente 2004; p. 197.
- [4] Fosmire G. Zinc toxicity. American Journal of Clinical Nutrition 1990; 51(2): 225-227. <https://doi.org/10.1093/ajcn/51.2.225>
- [5] Anu J, Benny G, Madhusoodanan KN. Current status of sulphur vulcanization and devulcanization chemistry: process of vulcanization 102-105
- [6] da Silva AA, da Rocha EB, Linhares FN, de Sousa AMF, Carvalho NM, Furtado CR. Replacement of ZnO by eco-friendly synthesized MgO in the NBR vulcanization. Polym Bull 2022; 79: 8535-8549. <https://doi.org/10.1007/s00289-021-03921-5>
- [7] Md Najib Alam, Vineet Kumar And Sangshin Park Article Advances in rubber compound using zno & mgo as co-cure activator 1-17.
- [8] Heideman G, Datta RN, Noordermeer JWM, van Baarle B. Effect of zinc complexes as activator for sulfur vulcanization in various rubbers. Rubber Chem Technol 2005; 78: 245-257. <https://doi.org/10.5254/1.3547881>
- [9] Siti NQM, Kawahara S. Evaluating performance of magnesium oxide at different sizes as activator for natural rubber vulcanization. Int J Adv Chem Eng Biol Sci 2016; 3: 97-101. <https://doi.org/10.15242/IJACEBS.IAE0516404>
- [10] Akvochem corporation MgO used in rubber compound.
- [11] Roy K, Alam MN, Mandal SK, Debnath SC. Preparation of zinc-oxide-free natural rubber nanocomposites using nanostructured magnesium oxide as cure activator. J Appl Polym Sci 2015; 132: 42705. <https://doi.org/10.1002/app.42705>
- [12] Kuzma LJ, Poly butadiene rubber, Maurice Morton, 235
- [13] Alam MN, Kumar V, Potiyaraj P, Lee DJ, Choi J. Synergistic activities of binary accelerators in presence of magnesium oxide as a cure activator in the vulcanization of natural rubber. J Elastomers Plast 2022; 54: 123-144. <https://doi.org/10.1177/00952443211020794>
- [14] Alam MN, Mandal SK, Roy K, Debnath SC. Synergism of novel thiuram disulfide and dibenzothiazyl disulfide in the vulcanization of natural rubber: Curing, mechanical and aging resistance properties. Int J Ind Chem 2014; 5: 8. <https://doi.org/10.1007/s40090-014-0008-6>

- [15] Boonkerd K, Deeprasertkul C, Boonsomwong K. Effect of sulfur to accelerator ratio on crosslink structure, reversion, and strength in natural rubber. *Rubber Chem Technol* 2016; 89: 450-464.
<https://doi.org/10.5254/rct.16.85963>
- [16] Hild G. Interpretation of equilibrium swelling data on model networks using affine and 'phantom' network models. *Polymer* 1997; 38(13): 3279-3293.
[https://doi.org/10.1016/S0032-3861\(96\)00878-6](https://doi.org/10.1016/S0032-3861(96)00878-6)
- [17] S Mohammad Poor - 2015 Study of the mechanical behaviour of high cis-polybutadiene rubber: structure to property correlation.
- [18] Alam MN, Mandal SK, Debnath SC. Effect Of Zinc Dithiocarbamates And Thiazole-Based Accelerators On The Vulcanization Of Natural Rubber. *Rubber Chemistry And Technology* 2012; 85(1): 120-131.
<https://doi.org/10.5254/1.3672434>
- [19] Khang TH, Ariff ZM. Vulcanization kinetics study of natural rubber compounds having different formulation variables. *Journal of Thermal Analysis and Calorimetry* 2011; 109(3): 1545-1553.
<https://doi.org/10.1007/s10973-011-1937-3>
- [20] Alam MN, Kumar V, Jeong SU, Park S. Enhancing rubber vulcanization cure kinetics: Lowering vulcanization temperature by addition of MGO as Co-Cure activator in ZNO-Based cure activator systems. *Polymers* 2024; 16(7): 876.
<https://doi.org/10.3390/polym16070876>
- [21] Chowdhury SG, Chanda J, Ghosh S, Banerjee K, Banerjee SS, Das A, Ghosh P, Bhattacharyya SK, Mukhopadhyay R. Impact of adhesive ingredients on adhesion between rubber and brass-plated steel wire in tire. *Polymer Engineering and Science* 2020; 60(8): 1973-1983.
<https://doi.org/10.1002/pen.25444>
- [22] Nabil H, Ismail H, Azura A. Optimisation of accelerators and vulcanising systems on thermal stability of natural rubber/recycled ethylene-propylene-diene-monomer blends. *Materials & Design (1980-2015)* 2013; 53: 651-661.
<https://doi.org/10.1016/j.matdes.2013.06.078>

Received on 12-01-2025

Accepted on 20-02-2025

Published on 25-03-2025

<https://doi.org/10.6000/1929-5995.2025.14.02>© 2025 Bhatt *et al.*

This is an open-access article licensed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the work is properly cited.