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EXPLORING THE CATALYTIC PROPERTIES OF ZINC COMPLEXES DERIVED FROM (E)-4-((2,6-DIHYDROXYPHENYL) DIAZENYL) BENZOIC ACID AND FURAN-2-YLMETHYLENE-(4-METHOXY-PHENYL)-AMINE IN RUBBER VULCANIZATION

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Abstract. Metal oxides, particularly zinc oxide (ZnO), play a vital role as activators in the sulfur-based vulcanization of unsaturated rubber. ZnO significantly enhances the efficiency of vulcanization, improves the mechanical properties of the vulcanizate and reduces curing time. However, its widespread use raises environmental and safety concerns due to its toxicity and persistence. In an effort to find a safer, eco-friendly alternative, we synthesized two novel zinc chelates incorporating an azo dye and a Schiff base. These complexes were designed to release Zn^{2+} ions in a controlled manner, enabling effective crosslinking during vulcanization. Rheometric analysis revealed that these chelates influenced cure characteristics similarly to ZnO. Additionally, mechanical testing conducted before and after thermal aging demonstrated their ability to maintain desirable strength and elasticity. With further structural refinement, these zinc chelates show strong potential as sustainable and non-toxic replacements for conventional ZnO, aligning with green chemistry principles and regulatory trends in rubber manufacturing.

Keywords: *Zinc chelates, rubber vulcanization, activators, physical properties.*

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1. Introduction

Vulcanization is a well-established large-scale process for cross-linking rubber chains, resulting in the formation of a three-dimensional network that enhances mechanical properties such as elasticity and tensile strength. Currently, sulfur-based rubber vulcanization is the most common method, generally performed at 140-150 °C, with the required curing time depending on the type of rubber and the efficiency of the accelerator, which can vary from 10 to 30 min. (Alam *et al*., 2024). This process relies on the thermal-induced formation of mono, bi and polysulfide bridges between polymer chains in the presence of sulfur. ZnO and especially Zn(II) centers play a main role on both the kinetics of the curing reaction and the properties of vulcanized rubber (Mostoni *et al*., 2021). Accelerators (Coleman *et al*., 1974) activators (Ducháček *et al*., 1993; Heideman, 2004) and co-activators, have been employed to enhance processability, increase the vulcanization rate and improve cross-linking efficiency. These additives are used to meet productivity demands while reducing energy and time consumption,

ultimately improving the mechanical properties of the cured materials (Krejsa & Koenig, 1993; Morrison & Porter, 1984). Among activators, ZnO is regarded as the most efficient for sulfur vulcanization and is widely used in the global rubber industry (Mostoni *et al*., 2019). In fact, it accounts for more than 50% of the world's annual ZnO production (25 million tons reported in 2010 (IRSG, 2017) is used in rubber manufacturing (IRSG, 2017; Perl, 1997; IZA, 1997). Due to the highly hydrophilic nature of ZnO, which contrasts with the hydrophobic character of rubber, large amounts of zinc oxide are typically used in tire formulations. This is done to counteract its tendency to agglomerate and to ensure uniform cross-link formation throughout the rubber matrix (Mostoni *et al*., 2021).

Although zinc is a naturally occurring element and generally considered one of the less harmful heavy metals, it can become toxic when its concentration exceeds certain thresholds. During the production, use, disposal and recycling of rubber products, zinc is released into the environment. In the case of tires, zinc leaching primarily occurs through tread wear, potentially leading to elevated concentrations in surrounding ecosystems. Some aquatic species are particularly sensitive to zinc ions and several soluble zinc compounds have been identified as toxic to aquatic life. Acknowledging these environmental concerns, the European Union classified zinc oxide as hazardous to the environment in April 2004 and introduced regulations to restrict and monitor its use in rubber technology (Chapman & Johnson, 2005), with the aim of mitigating potential ecological harm. Minimizing ZnO content in rubber products has become a top priority. As a result, researchers and technologists are actively exploring ways to reduce its usage or replace it with alternative zinc compounds that deliver similar performance with significantly lower zinc ion concentrations (Maciejewska *et al*., 2021).

Zn^{2+} ion complexes with accelerators are thought to be far more reactive than the accelerators alone, speeding up sulfur insertion during vulcanization (Coran, 2003). These complexes interact with sulfur or sulfur donors to create powerful sulfurating agents, which then target the allylic sites on rubber chains kick starting the formation of crosslink precursors and driving efficient network formation (Heideman, 2005). The detailed mechanism of natural rubber vulcanization is still a controversial issue, it is widely accepted that the vulcanization reaction consists of three stages. Firstly, vulcanization accelerators react with themselves, sulfur and vulcanization activators to form polysulfide intermediates Secondly, these intermediates react with unsaturated double bonds of NR molecular chains to form crosslinking precursors. Finally, crosslinking precursors react with of NR molecular chains to form the crosslinking network, thus endowing rubber with high strength and elasticity (Wei *et al*., 2023).

This study explores two innovative zinc complexes one from an azo dye and the other from a Schiff base as activators for the sulfur vulcanization of Indian Standard Natural Rubber (ISNR-5). Their performance was evaluated through mechanical testing of the rubber before and after aging, offering fresh insights into their promise as eco-friendly alternatives to traditional ZnO activators.

2. Experimental

2.1. Materials and methods

All chemicals and solvents used in this experiment were of analytical reagent (AR) grade, purchased from Merck and used without further purification. The natural rubber (ISNR-5, Mooney viscosity ML (1+4) 100^{o}C-82) was received from the Rubber Research Institute of India, Kottayam. The compounding ingredients, ZnO, stearic acid, naphthenic

oil, TDQ (Polymerized 2,2.4-trimethyl-1.2-dihydroquinoline), HAF (High abrasion furnace), TBBS(N-t-butyl benzothiazole-2-sulfenamide) and sulphur were of commercial grade.

The IR spectra of RABA, FAMP and the Zn complexes were recorded in KBr pellet method in the range 400-4000cm^{-1} on a Perkin Elmer FT-IR model 2 spectrophotometer, at MG College, Kesavadasapuram, Thiruvananthapuram. Electronic absorption spectra of the ligand and complexes in methanol were obtained using a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer. The ^{1}H NMR spectra of the compounds were recorded in DMSO-d_6 using a 400 MHz FT-NMR spectrometer, with TMS as the internal reference, at SAIF, Cochin University of Science and Technology. ESI mass spectra of all five compounds were acquired using an FTMS mass spectrometer at NIIST, Trivandrum.

2.2. Preparation of ligands

The azo dye (E)-4-((2,6-dihydroxyphenyl)diazenyl)benzoic acid [RABA] was synthesized by diazotizing 4-aminobenzoic acid and coupling it with resorcinol (Mini & Aravind, 2018), while the Schiff base Furan-2-ylmethylene-(4-methoxyphenyl)amine [FAMP] was obtained by refluxing 4-methoxyaniline with furan-2-carbaldehyde (Mini & Darsana, 2017).

2.3. Preparation of Zinc complexes

The zinc complexes were synthesized by combining methanolic solutions of zinc chloride and the respective ligands in a 1:1 molar ratio. The mixture was refluxed on a water bath for 2-5 hours, leading to the gradual formation of solid products upon cooling. These were then filtered, washed with a methanol-water mixture, recrystallized from methanol and finally dried over anhydrous calcium chloride to obtain pure, crystalline complexes.

2.4. Characterization of ligand and the Zinc complexes

The ligand and the complexes were characterized by micro analytical method, metal estimation, conductance measurements, electronic spectra, IR spectra, NMR and Mass spectral analysis. Based on the experimental results, the ligand and its corresponding metal complexes were assigned the following molecular formulae, RABA- $C_{13}H_{10}N_2O_4$, $[Zn(RABA)(H_2O)_2]Cl$ (Mini & Aravind, 2018) and FAMP- $C_{12}H_{11}NO_2$, $[Zn(FAMP)_2]Cl_2$ (Mini & Darsana, 2017). The stoichiometry of the ligands and the complexes are shown in table 1 and their structures are shown in Figures 1 and 2.

Table 1. Data of Ligands and the Zn(II) complexes

Compound	Molecular formule	Molecular wt.	Metal %	Conductance (methanol)
RABA	$C_{13}H_{10}N_2O_4$	258	-	-
FAMP	$C_{12}H_{11}NO_2$	201	-	-
$[Zn(RABA)(H_2O)_2]Cl$	$Zn(C_{13}H_{10}N_2O_4)(H_2O)_2Cl$	395	18.2	85
$[Zn(FAMP)_2]Cl_2$	$Zn(C_{12}H_{10}NO_2)_2Cl_2$	536	13.8	152

2.4.1. Infrared spectra

In the ligand FAMP azomethine group (C=N) has a characteristic stretching frequency. A strong band at 1610 cm^{-1} shown by the ligand FAMP is attributable to the C=N stretching (Madhu *et al*., 2000) is shifted in the Zn complex to 1588 cm^{-1} indicating the coordination of azomethine nitrogen to the metal ions. This is supported by the appearance of new band in the region 468 cm^{-1} in the complex due to ν_{M-N} (Abdallah *et al*., 2010). The formation of new bands in the regions 541cm^{-1} attributed to ν_{M-O} bands respectively (Sujamol *et al*., 2010).

The IR spectral data of the ligand RABA and complexes with Zn(II), are in agreement with an expected range. The band at 1477cm^{-1} in the ligand is attributed to azo group. This is shifted to 1417cm^{-1} in Zn complex, suggesting a coordination of metal ion to nitrogen of azo group. The band at 1242cm^{-1} in the ligand is attributed to C-O stretching. This is shifted to 1236cm^{-1} in Zn complex. The carbonyl absorption of ligand and complex are given by the bands at 1602cm^{-1} (in ligand), 1597cm^{-1} (in Zn complex). The very weak bands observed around 553cm^{-1} and 578cm^{-1} in the complexes can be assigned to bands for M-N and M-O absorptions. These bands are absent in ligand. The IR spectral data is given in Table 2.

Table 2. IR Spectral dats of the ligands and the Zn complexes

FAMP (cm^{-1})	$[Zn(FAMP)_2]Cl_2$ (cm^{-1})	RABA (cm^{-1})	$Zn(RABA)(H_2O)_2]$ (cm^{-1})	Assignment (cm^{-1})
------	------	3423	3350	$\nu_{OH\ str}$
2999	2925	2912	2865	$\nu_{C-H\ Str}$
1610	1590	------	------	$\nu_{C=N\ Str}$
------	------	1477	1417	$\nu_{N=N\ str}$
		1602	1597	$\nu_{C=Ostr}$
------	528	-----	578	ν_{M-O}
------	459	------	553	ν_{M-N}

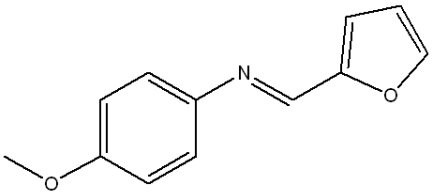


Figure 1. Structure of FAMP

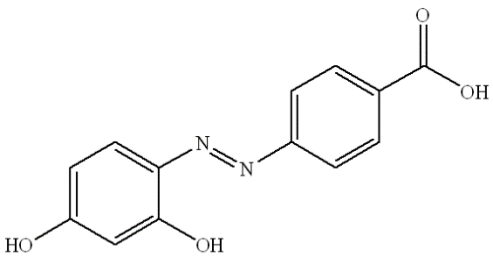


Figure 2. Structure of RABA

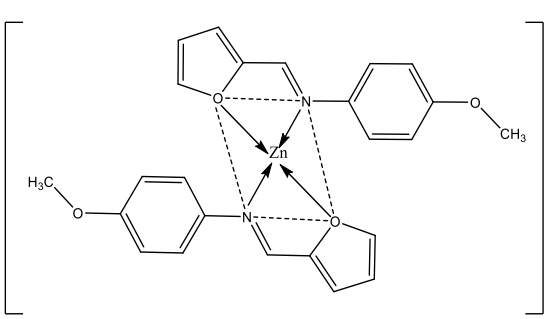


Figure 3. Structure of $[Zn(FAMP)_2]^{2+}$

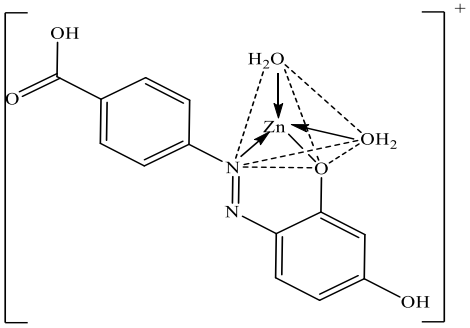


Figure 4. Structure of $[Zn(RABA)(H_2O)_2]^{+}$

2.5. Preparation of Rubber Compounds

Table 3. Composition of rubber compounds

	Control	**compound-1**	**compound-2**
ISNR-5	100	100	100
ZnO	5	-	-
$[Zn(RABA)(H_2O)_2]Cl$	-	5	-
$[Zn(FAMP)_2]Cl_2$	-	-	5
Stearic acid	3	3	3
TDQ	2	2	2
HAF	35	35	35
Naphthenic oil	4	4	4
TBBS	0.9	0.9	0.9
Sulphur	2.25	2.25	2.25

The rubber compounds were prepared according to ASTM D 3182 in an internal mixer. Internal mixer used was model Kointermix MK3 Francis Shaw & Co. (Manchester) Ltd. Manchester, England. The master batch is prepared by internal mixer and the compound (with curatives) is prepared in two roll mill. 5 gm each of the prepared chelates, $[Zn(RABA)(H_2O)_2]Cl$ and $[Zn(FAMP)_2]Cl_2$ were mixed with 100gm ISNR-5 and other ingredients in correct proportion to get a homogenous mixture of two new rubber compounds. ZnO is used as inorganic activator, stearic acid is used as organic activator, naphthenic oil as plasticizer, carbon black (High abrasion furnace, HAF) is used as reinforcing filler, TBBS (N-t-butyl benzothiazole-2-sulfenamide) is used as accelerator and sulphur is used as the vulcanizing agent. The addition of vulcanization mixture will promote the formation of more crosslinking structures in natural rubber (Fang *et al*., 2024). The compositions of other vulcanizing agents including sulphur are shown in Table 3.

2.6. Working procedure

The rubber compound including the vulcanizing system is shaped on the mill as 6-8 mm thick sheets. The samples were cured at 150^{o}C. Cure time is measured using Moving Die Rheometer (M.D.R) under isothermal condition with constant strain and frequency conforms to ASTM D 5289/ ISO 6502. The optimal vulcanization time t_{90} (time to 90 % of maximum torque, optimum cure) of the compounds was determined.

Physical testing was performed on samples cured in a press to t_{90} times at the same temperature. Tensile strength, modulus, elongation at break and hardness of the new compounds, before and after ageing was also determined.

The tensile strength of the newly formulated rubber compounds was evaluated according to IS 3400 Part 1-1977. Using the same standard, the modulus at 300% elongation and elongation at break (%) were also determined. Hardness measurements were carried out as per ASTM D-2240 guidelines using a Shore a type Durometer.

To assess ageing characteristics, the samples were subjected to thermal ageing at 70°C for 72 hours. After ageing, the specimens were removed from the oven, cooled to room temperature on a flat surface and allowed to rest for a period of 16 to 96 hours or longer before evaluating their physical properties. The mechanical properties of the rubber compounds were measured both before and after ageing to determine their durability and performance over time.

3. Results and discussion

The performance of the two newly synthesized Zn(II) chelates was evaluated against the conventional ZnO/stearic acid activator system in ISNR-5 rubber using the methods described above. As established in previous studies, the zinc content plays a crucial role in determining activator efficiency during vulcanization, directly influencing the cure characteristics of rubber compounds (Chapman & Johnson, 2005; Heideman *et al*., 2005).

The cure behavior of the rubber samples was assessed using rheometric analysis. Figure 1 presents the cure time curves for Compound-1 and Compound-2, compared to the standard formulation. The results reveal that the Zn chelates exhibit cure rates comparable to those reported for other zinc-based activators (Przybyszewska *et al*., 2009), highlighting their potential as effective and eco-friendlier alternatives to conventional ZnO systems.

The addition of $[Zn(FAMP)_2]Cl_2$ to the rubber compound was found to retard the curing process, whereas $[Zn(RABA)(H_2O)_2]Cl$ did not exhibit such an effect. The lower efficiency of $[Zn(FAMP)_2]Cl_2$ may be attributed to the high stability of its chelate structure, which potentially limits the release of free Zn^{2+} ions needed to form Zn–accelerator complexes. When zinc ions remain tightly bound within a stable complex, they are rendered unavailable for effective crosslinking.

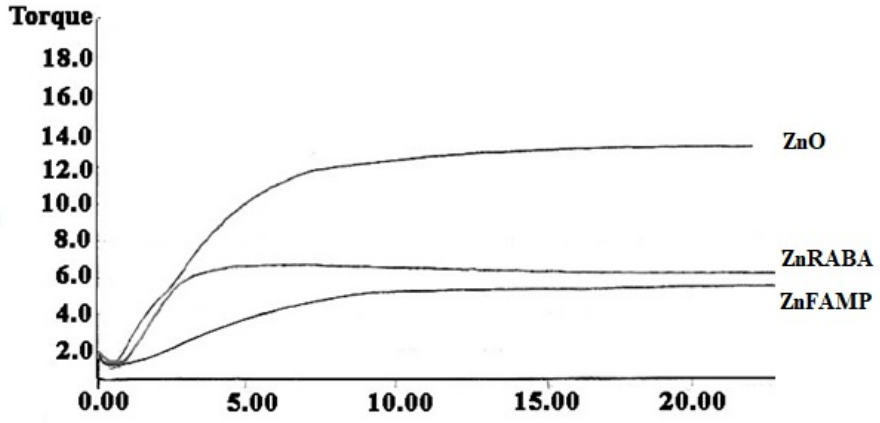


Figure 5. Rheometer isotherms of $[Zn(RABA)(H_2O)_2]Cl$ and $[Zn(FAMP)_2]Cl_2$

Based on the ZnO lattice parameters (Yin *et al*., 2000), the Zn^{2+} ion availability in a single crystal is estimated at 1.8 mmol/g of ZnO. Therefore, for a zinc-based compound to function effectively as an activator, the accessible Zn^{2+} content must exceed this threshold (Vidya *et al*., 2016). The observed variation in the reactivity of these complexes could also be linked to their basicity, as more alkaline activators tend to enhance sulfur vulcanization (Heideman *et al*., 2005). The weaker cure performance of $[Zn(FAMP)_2]Cl_2$ is likely due to reduced crosslinking density and limited Zn^{2+} availability. This availability is influenced by multiple factors, including the complex's molecular structure, the strength of Zn-ligand bonding, the stability of the chelate and the amount of activator used.

Evaluating the mechanical properties of these rubber compounds is crucial, as they directly determine the quality and applicability of the final rubber products. The physical properties of the tested formulations both before and after ageing are presented in Tables 4 and 5 along with the standard.

Table 4. Processing and physical properties of mixes before ageing

Test parameter	Method	Control	Mix-1	Mix-2
Optimum cure time t_{90} at 150°C	ASTM D 5289-1979	7:55	13:33	3:98
Tensile strength (kg/cm^2)	IS 3400 Part 1-1977	329.3	97.5	96.3
Modulus 300% (kg/cm^2)	IS 3400 Part 1-1977	85.7	34.3	34.2
Elongation at break %	IS 3400 Part 1-1977	670	632	616
Hardness, Shore	ASTM D 2240-2004	52	39	39

Table 5. Processing and physical properties of mixes after ageing

Test parameter	Method	Control	Mix-1	Mix-2
Tensile strength (kg/cm^2)	IS 3400 Part 1-1977	359.2	170.8	141
Modulus 300% (kg/cm^2)	IS 3400 Part 1-1977	108.7	30.3	27.3
Elongation at break %	IS 3400 Part 1-1977	662	654	653
Hardness, Shore	ASTM D 2240-2004	58	42	40

Tensile strength in vulcanized rubber is closely linked to the chemical crosslinking density. In this study, the tensile strength of the vulcanizates showed no significant improvement when compared to the conventional ZnO system. This limited performance, particularly for the $[Zn(FAMP)_2]Cl_2$ complex, may be attributed to steric hindrance, which restricts the availability of Zn(II) ions necessary for effective crosslink formation.

Interestingly, an increase in tensile strength after thermal ageing was observed for all compounds. This is likely due to the curing being performed at the optimum cure time (t_{90}), where residual crosslinks could continue to form during the ageing process. As reported by Hernandez et al. (1992), vulcanizates with more homogeneous crosslink networks tend to exhibit higher tensile strength.

While only a reductive effect was seen in the modulus at 300% elongation, the elongation at break remained comparable to the standard formulation. Modulus values are indicative of the elastic recovery of the material, which in turn is supported by the crosslink density (Aprem *et al*., 2003). According to Vilgis and Heinrich (1992), the

heterogeneity of the network significantly impacts vulcanization behavior under high strain, influencing key mechanical properties such as tensile strength and elongation. Under stress, microcracks may form; however, a well-structured network can hinder their propagation, thereby enhancing elongation at break - a reflection of the material's elasticity.

Overall, the results indicate that the use of zinc chelates did not significantly enhance the tensile strength of the vulcanizates when compared to conventional ZnO. However, $[Zn(RABA)(H_2O)_2]Cl$ showed notably better performance than $[Zn(FAMP)_2]Cl_2$, likely due to its higher Zn^{2+} ion content and greater ion availability, making it a more effective alternative activator in sulfur vulcanization.

Hardness, one of the most fundamental mechanical properties of rubber, reflects the modulus of elasticity at low strain (Ferrigno, 1978). The rubber compounds prepared in this study exhibited hardness values comparable to those reported for other zinc chelates (Todorova *et al*., 2014). A higher degree of crosslinking typically results in greater resistance to deformation in sulfur-vulcanized rubbers (Li *et al*., 2008).

The compounds were subjected to thermal ageing at 70°C for 72 hours. Post-ageing analysis showed increased tensile strength, modulus at 300% elongation, elongation at break and hardness, suggesting that the zinc chelates promote a gradual vulcanization process. The slight increase in hardness after ageing may indicate enhanced interactions between the chelates and the rubber matrix over time.

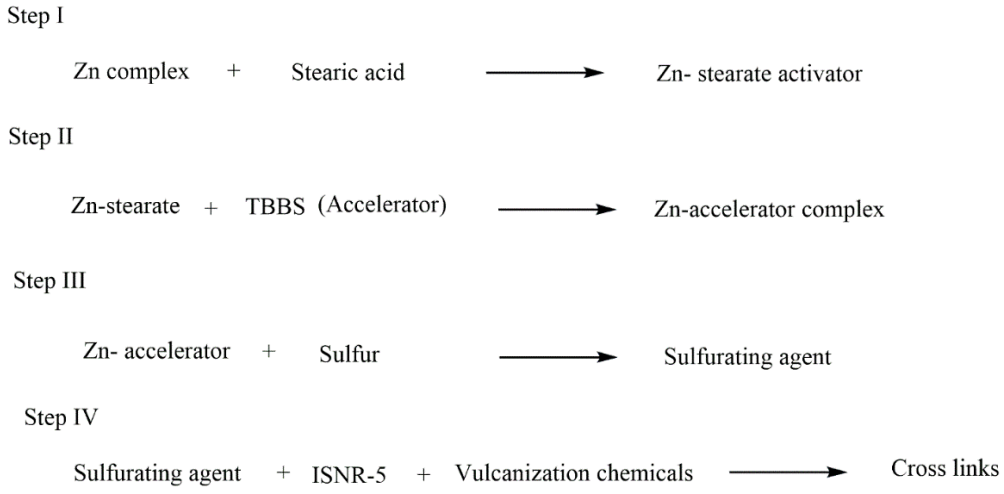
However, it's important to note that heterogeneous distribution of crosslinks, irregular spatial arrangement and structural defects in the elastomer matrix can adversely affect the mechanical properties of vulcanizates. Such inconsistencies may lead to weak spots in the rubber network, reducing uniformity and overall performance despite the apparent increases in measured values.

3.1. Catalytic activity of Zinc complexes

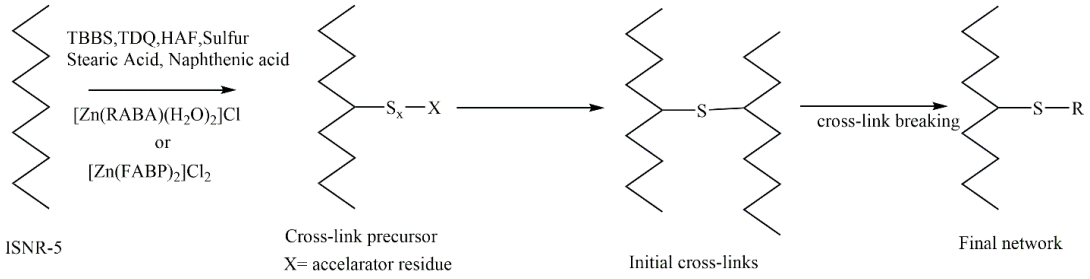
During vulcanization, zinc complexes play a vital role in forming chemical crosslinks between rubber molecules, leading to a stronger and more elastic network. These new complexes release Zn^{2+} ions into the rubber matrix, where they interact with the accelerator (TBBS) to form zinc-accelerator complexes. These intermediates then react with sulfur to produce sulfurating species that promote efficient crosslink formation.

Zinc compounds significantly accelerate the vulcanization process, reducing the time needed to achieve optimal material properties. The efficiency of crosslinking and the structure of the resulting network directly influence key physical attributes of vulcanized rubber, such as tensile strength, elasticity and wear resistance.

The zinc content is a critical factor in determining the effectiveness of activators. While newly synthesized zinc complexes generally contain less zinc than conventional ZnO-based systems, their performance depends heavily on how well they release Zn^{2+} ions and how uniformly they are dispersed within the elastomer matrix. Structural modifications to the zinc complexes can help to optimize these properties, leading to better performance in vulcanized rubber products. The mechanism of the catalytic activity of zinc complexes are shown in the Schemes I and II.



Scheme I. catalytic activity of zinc complexes in vulcanization



Scheme II. Mechanism of accelerated vulcanization

4. Conclusion

This study highlights a new generation of zinc-based activators for sulfur vulcanization, presenting a sustainable and effective alternative to conventional ZnO systems. The synthesized Zn(II) complexes display distinct vulcanization behaviors - $[Zn(RABA)(H_2O)_2]Cl$ significantly boosts crosslinking efficiency, while $[Zn(FAMP)_2]Cl_2$ moderates the cure rate due to its structural stability. Notably, both complexes deliver activation performance on par with established zinc chelates, without compromising the thermal ageing resistance of the vulcanizates. The findings underscore the potential of molecularly engineered zinc chelates to revolutionize rubber technology. By fine-tuning ligand design and metal-ligand interactions, even greater enhancements in curing behavior and material performance can be achieved. This opens exciting possibilities for next-generation, eco-friendly vulcanization systems tailored to meet both industrial demands and environmental regulations.

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