Review - The Importance of Zinc Oxide (ZnO) in Rubber Technology

Introduction
ZnO occupies a unique position in rubber industry. ZnO is an essential rubber compounding ingredient in vulcanization process [1]. Zinc oxide is used as an activator to speed up the vulcanization process. The action of accelerators is effective only in the presence of inorganic activators. The most important and commonly used inorganic activator in this regard is ZnO.

ZnO is added in the form of dispersion to protect natural rubber latex from premature cure. A composite preservation system comprising 0.2 - 0.3 per cent ammonia along with 0.013 per cent each of TMTD and ZnO, known as LATZ system has been introduced in 1975 [2]. LATZ system of preservation can be applied to both field latex and concentrated latex. The reaction of zinc soaps with a curing system consists of mercapto accelerators enhances the physical properties of the rubber vulcanize such as tensile strength, modulus and hardness.

ZnO is an outstanding UV absorbing material and hence it serves as an effective stabilizer of white and tinted rubber compounds under prolonged exposure to the destructive rays of the sun [3]. There should be an optimum amount of ZnO for vulcanization. The use of high or low quantity than the recommended level can lead to poor quality vulcanizates [4].

ZnO can be prepared by different methods. French process zinc oxide, made from metallic zinc, is preferred for rubber formulations. The major reason is that they have nearly spherical particle shape and have narrow particle size distribution. Global production of ZnO is 105 tonnes per year and rubber industry holds the major share of usage of ZnO for the manufacture of various rubber products [5]. The important role played by zinc oxide in rubber industry is given below [6].

Activation
In the curing process of natural rubber and most types of synthetic rubbers, the chemical reactivity of ZnO is utilized to speed up the rate of cure with the organic accelerator. The unreacted share of the ZnO remains available as a basic re-

Die Bedeutung von Zinkoxid (ZnO) in der Kautschuktechnologie: Eine kleine Übersicht


Figures and Tables: By a kind approval of the authors.

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Role of metal oxides in tetramethylthiuram disulphide (TMTD) vulcanization is explained by Dogadkin and Shershnev [8]. They found that vulcanization in the presence of MBT (mercaptopbenzothiazole) or DPG (diphenylguanidine) as accelerators; activators have almost no effect on the rate of addition of sulphur to rubber, but have a significant influence on the rate and degree of crosslinking of the rubber molecules. Special interest attaches to studies of the action of metal oxides in vulcanization with TMTD. In the absence of ZnO this accelerator does not bring about vulcanization. Manik and Banerjee [9] studied about the salient features of both non-elemental sulphur vulcanization by TMTD and elemental sulphur vulcanization promoted by TMTD both in presence and absence of ZnO and stearic acid. They found that the entire course of the reaction can be altered by ZnO or ZnO-stearic acid. Both the crosslink formation and TMTD decomposition are much higher in presence of ZnO or ZnO-stearic acid, but stearic acid seems to have no effect.

Mechanism of the gelling of Hevea latex by zinc compounds were studied [10]. The effect of zinc distribution on the mechanical stability of NR latex concentrations were studied by Davies and Pendle [11]. They found that the mechanical stability of latex concentrates, particularly for LATZ latices can be increased by using dithiothreitol (DTT). Zinc ions tend to destabilize latex by neutralizing some of the fatty acid anions on the rubber particle surface and DTT increases the stability of latex by removing a large proportion of these zinc ions.

Tack retention
One of the unique properties of ZnO is its ability to retain the tack of uncurd rubber compounds for adhesive tapes on storage.

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To study the accelerating power of zinc-salts of organic accelerators as well as to find the relation between these Zn-salts and ZnO, zinc-salts of mercapto-benzothiazole and tetramethylthiuram disulphide were synthesized and vulcanization tests were carried out [12]. It has been found that in the absence of ZnO, Zn-salts had no accelerating power. Saijo and Kaneko [13] reported that rubber to brass bonding can be improved by increasing the ZnO content up to 40 phr. It is suggested that bonding is promoted by the formation of zinc-copper sulphide from acidic copper sulphide and basic ZnO. Finely divided ZnO is treated with normal zinc propionate which provides easy dispersion in rubber and improved physical properties [14].

Action of ZnO in Rubber Vulcanization (Mechanism)
It is believed that metal oxides activates the function of accelerator by transforming them into a more soluble salt-like compound [15]. Frenkel and Kuz’minskii in 1963 studied the role of ZnO in thiuram (TMTD) based vulcanization [16]. Thermal dissociation of thiuram may follow two routes: 1) in the absence of zinc oxide, thiuram disintegrates with principal formation of carbon disulphide and amines. This does not lead to the formation of cross-links, and, consequently, it is of no use for vulcanization; 2) the free-radical dissociation of thiuram, which occurs in the presence of zinc oxide and leads to the development of a three-dimensional spatial network for the vulcanize. Besides this, the ZnO may also react with the dithiocarbamic acid formed during the vulcanization, which also promotes vulcanization. They have concluded that the principal role of ZnO as an activator of the process, consists in accelerating the effect on the free-radical dissociation of the thiuram. The chemistry of thiuram accelerated vulcanization is complex as it contains 13 per cent sulphur available for crosslinking. During TMTD accelerated vulcanization in the presence of ZnO, dimethyl dithiocarbamic acid (DMDCA) is formed as a by-product [17].

The mechanism of the crosslinking process in the presence of ZnO is well known: ZnO reacts with accelerators to form highly active accelerator complex. Complexes of Zn+2 ions with accelerators are more reactive and the complexes interact with sulphur or sulphur donors or other activators generating the active...
sulphurating agent. This reacts with allylic sites of rubber chains to form crosslink precursors. The crosslink precursor can react with another rubber bound intermediate or with another polymer chain to generate a crosslink [18, 19]. (Scheme 3)

The general scheme of sulphur vulcanization can be explained under the following headings:[20]
1. Active accelerator complex
2. Active sulphurating species
3. Crosslink precursor
4. Polysulphidic crosslinks
5. Formation of shorter crosslinks or cyclic sulphides

Zinc-salts of fatty acids are generally regarded as indispensable activators in conjunction with ZnO to solubilize the ZnO and the accelerator to form the actual catalyst [21, 15]. The role of activators also depends on the type of rubber, vulcanization accelerator and active filler used [15].

The mechanism of reaction of ZnO with the accelerator TMTD is as follows: [18] (Scheme 2)

ZnO has the greater influence on the degree of crosslinking, while stearic acid has the greater influence on the rate of the crosslinking reaction [21, 22].

The presence of Zn⁺⁺ in benzothiazole-accelerated vulcanization, were explained as follows: [23] (Scheme 3)

**Importance of ZnO for other polymers (synthetic) - Mechanism**

ZnO is used as a crosslinking agent for rubbers like polychloroprene (CR), chlorosulphonated polyethylene, etc. [17]. A combination of 5 phr ZnO along with 4 phr MgO yields vulcanizates having stronger crosslinking with good scorch safety [17]. Mechanism for the vulcanization of CR by the action of zinc oxide and magnesium oxide is as follows [24]. (Scheme 4)

The crosslinking mechanism of halobutyl rubber with zinc oxide was reported by Vukov in 1984 [25].

Carboxylic elastomers can be cured by standard compounding recipes utilizing sulphur and zinc oxide. The zinc oxide, besides aiding the sulphur cure, also gives a secondary cure through an ionic bond with the carboxyl groups. However, because of the affinity of the ZnO for the carboxyl group, the stocks tend to have an excessive scorch and a short shelf-life. To prevent this excessive scorch, the ZnO must be isolated from the carboxyl group.
until the desired cure temperature is reached. Heat and light stability of ethylene propylene ter polymers containing ZnO and titanium dioxide were studied [26]. Oven ageing properties at 350° F and 300° F of EPT polymers were substantially improved with additions of ZnO up to 10 and 20 phr. The Gibbs free energy (ΔG) of the vulcanizates and volume fraction of natural rubber in NR/NBR/ENR blends increased with increase in ZnO level, reaching a maximum at 5.0 phr [4].

Silicone rubber filled with thermally conductive, but electrically insulating fillers such as Al_2O_3 or ZnO were investigated to be used as elastomeric thermal pads, a class of thermal interface materials by Sim et al. [27]. The effect of Al_2O_3 or ZnO fillers on the thermal conductivity and coefficient of thermal expansion (CTE) of the silicone rubber were investigated, and it was found that with increasing Al_2O_3 or ZnO, the thermal conductivity of the thermal pads increases, while the coefficient of thermal expansion (CTE) decreases. The effects of alumina (Al_2O_3) and ZnO fillers on the curing characteristics, thermal and mechanical properties of silicone rubber were studied [28]. Comparison of mechanical strength between the two silicone rubber hybrids indicates that ZnO is a better reinforcing filler, as evidenced in the tensile strength, elongation at break, and modulus at 300 per cent elongation. The thermal conductivities of silicone rubber filled with ZnO in a wide volume range were studied [29].

Problems with ZnO (environmental pollution, ZnO thickening, lack of transparency etc.)

Since 2004, European Union classified ZnO as a hazardous chemical and excess release of which is toxic to the environment particularly, to the aquatic species. For humans the recommended intake should not exceed 12-15 mg/day. To minimize the usage of ZnO in rubber products, “Eco Zinc” concept has been set up by the European Union (EU). Large amount of ZnO is released to the environment by the wear and tear of tyres and from other rubber products. Thus, from ecological point of view, there is a pressure from Government Organizations and Environmental Protection Agencies to minimize its usage in rubber formulations.

When ZnO is added to ammonia preserved latex, the viscosity of the latex increases. This can be accelerated by increasing the temperature and sometimes results in coagulation of latex. The thickening is due to the solubilization of zinc oxide and the formation of positively charged complex ions, which destabilizes the latex. The factor’s that influences the zinc oxide stability of latex has been presented in 1950’s [30].

When transparency of the finished product is required, concentration of the ZnO should be 0.5 phr (max.). The high tinting power of ZnO is responsible for the reduction of transparency [31]. The transparency of NR latex films also depends on the particle size of ZnO. As the particle size decreases, transparency increases.

Johnson and Scott made experiments on the preparation of transparent vulcanized rubbers [32]. Tests with other activators zinc carbonate, zinc oleate, and zinc stearate with magnesium carbonate showed that these are less effective than zinc oxide and the vulcanizates obtained had inferior mechanical properties. Results indicated that in most cases vulcanizates containing 1 per cent of ZnO were transparent, but were not so when cured with Zn salts of organic acids [33]. Though it is necessary to use ZnO as an adjuvant in curing with organic accelerators but when transparent products are required, it is practicable to use only 1 per cent ZnO or lower.

Alternative measures (partial/full replacement of ZnO, use of novel chemicals etc.)

The effect of zinc resinate on the properties of NR vulcanizates were reported [34]. The effect of reducing zinc oxide level in rubber compounds on the amount of zinc leached from rubber granulates and powder was investigated [35]. The amount of zinc leached increases with increase of zinc oxide level up to around 3 phr and then levels off. It has been reported that, replacement of 5 phr...
conventional ZnO with 1 phr nano magnesium oxide (MgO) as a cure activator resulted significant reduction in optimum cure time and 400 per cent increase in cure rate index [36].

Dzikowicz invented a method for vulcanizing latex compounds without the use of metal oxide activators or a zinc based accelerator. The inventor used a zinc based antioxidant synergist material, which functions as an activator for a curing system for latex compounds [37]. Replacement of ZnO with various organic oxidizing agents on the cure characteristics of rubber were reported [38].

Zinc acetylacetonate and zinc complexes with 1,3-diketones were used as good substitutes for sulphur vulcanization of NBR rubber, without any detrimental effects on the crosslinking rate or physical properties [19]. Hiedeman et al. studied the effects of different zinc complexes on the cure and physical properties of EPDM and s-SBR [39]. The effect of various metal oxides as activator in thiram-accelerated vulcanization of EPDM and s-SBR are also reported.

**Importance of nano-ZnO (Advantages, property enhancements etc.)**

To minimize the usage of ZnO without compromising technological properties, the nano concept has come into existence. The author’s synthesized ZnO nanoparticle through solution-free mechano-chemical route and studied their effects on pre-vulcanized natural rubber latex properties [40]. It has been found that compared with micro ZnO, incorporation of nano ZnO results in better retention of mechanical properties after ageing.

To reduce the ZnO levels in rubber compounds, mixed metal oxide nanoparticles of zinc and magnesium (Zn$_{1-x}$Mg$_x$O) have been synthesized and used as activator [41].

Nano ZnO at different levels were incorporated into NR latex the properties of the vulcanize films were examined and compared with conventional micro ZnO incorporated films [42]. The thermal stability of nano ZnO incorporated films were found to be superior as evident from ageing studies. The antifungal activity of the films also found to be good [42].

Compared with the addition of 5 phr of ordinary ZnO in NR, the tensile strength and elongation of NR vulcanize filled with 2 phr of in situ surface-modified nano-ZnO increased by 0.55% and 10.34%, respectively [43].

Zinc oxide (ZnO) nanoparticles of size 20 – 90 nm were synthesized and used as cure activator and reinforcing filler in NR [44]. The dispersion of ZnO plays a crucial role in vulcanization process. The use of high surface area ZnO nanoparticles undergoes agglomeration and impedes the activity at the nano level. Thomas et al. synthesized ZnO nanoparticles and surface modified with suitable capping agents and studied their effect on NR vulcanization. The capped nano ZnO improved the scorch safety and mechanical properties compared to conventional ZnO.

Layered Double Hydroxides (LDH) was synthesized by a one-step process and employed as filler to rubber [45]. The author’s claims that this method can be used for the preparation of rubber vulcanizates containing lesser Zn content with improved transparent properties. The silica-filled NR/BR compounds containing 0.3 – 3.0 phr of nano-ZnO showed improved cure characteristics and mechanical properties compared to the compound with 5 phr of conventional ZnO. The optimum amount of nano ZnO required is 1 phr only [46]. The tensile strength of NR/SBR blends (50:50) with 1.2 phr nano-ZnO is greater than that with conventional zinc oxide at 5 phr [47].

The optimum cure time of SBR/BR blends decreased by 5 min using PEG coated nano-ZnO compared with that containing standard rubber grade ZnO [48]. The effect of nano-ZnO and conventional ZnO on natural rubber (NR)/butadiene rubber (BR) and NR/styrene–butadiene rubber (SBR) blends was reported [49]. The swelling results showed that the compounds containing nano-ZnO absorb less solvent and offers greater cross-link density in comparison with compounds containing conventional ZnO.

Addition of highly dispersed nano-ZnO in natural rubber can improve the

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**Fig. 3(a-b): Photographs showing fungal growth in the medium and in vulcanized latex films.**

|M5 represents films containing 0.5 phr micro ZnO, N5 - 0.5 phr nano ZnO, N3 - 0.3 phr nano ZnO, N1 - 0.1 phr nano ZnO.|

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**Fig. 4: Percentage of swelling of nano and micro ZnO filled NR/SBR composites.**

![Graph showing swelling ratio percentage for nano and micro ZnO filled NR/SBR composites.](image-url)
From the above discussion, it is obvious that replacing the conventional micron-sized ZnO with nano in rubber formulation can make a tremendous impact on the performance and quality of rubber vulcanizates. The inclusion of high surface area nano-ZnO in rubber formulation can significantly reduce the cure time and improves the technological properties as well.

Conclusion

The mechanism of chemistry of vulcanization is very complex. Though a number of different rubber processing chemicals and compounding ingredients are required for rubber product manufacturing, ZnO deserves a unique position. ZnO along with other chemicals such as MgO is used as a crosslinking agent for chloroprene rubber. The particle size and dosage of ZnO is very important as it can determine the end properties of the vulcanize. In latex technology, the excessive usage of ZnO can cause latex thickening. It can reduce the transparency of latex products also. The excess release of ZnO is hazardous and large amount of ZnO is released to the environment by the wear and tear of tyres and from other rubber products. To minimize its usage, researchers are working on alternate methods or chemicals to replace ZnO. The effects of various metal oxides and zinc complexes on vulcanizate properties were reported. With the advancements in nanotechnology, replacement of conventional ZnO with lower amount of high surface area nano-ZnO in rubber technology is widely discussed nowadays. Results reveal that when nano-ZnO is used, the release of zinc ions in the effluent will be minimum. Usage of nano-ZnO reduces the cure time, offers good thermal stability and improves the technological properties. In short, the use of nano-ZnO in polymer research opens new avenues for the development of novel functional elastomeric products.

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References


EVENTS/VERANSTALTUNGEN

Seminar: TPE - Grundlagen und Praxis


13th Fall Rubber Colloquium / 13. Kautschuk Herbst Kolloquium

DIK The 13th Fall Rubber Colloquium will take place from 6th to 8th of November, 2018 in Hannover (Germany). It is the 13th conference in rubber technology every two years in this series. The previous conferences were highly successful and attracted delegates from a variety of disciplines from around the world. Delegates are encouraged to register both from outside and within Germany. The conference highlights the latest and most important scientific concepts and advanced processing techniques in rubber and polymer science and technology. Experts from all over the world will give keynote presentations. Recognized industrial experts will identify future trends in the rubber industry. Basic researchers will present studies to understand, and therefore, predict the properties of final products. Contact: Trinidad Rodriguez Gallegos, Phone: +49 511 84201-17, khk@dikautschuk.de

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