The Effect of ZnO Modification on Rubber Compound Properties

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Abstract: This work paper evaluates the influence of modified zinc oxide (ZnO) particles on different rubber compound properties. Considering that ZnO is the most widely used activator of vulcanization its function, influence on the vulcanization rate, and its influence on the final rubber product properties were analyzed. Based on the actual tendency to minimize the level of ZnO in rubber compounds because of its toxicity for aquatic organisms, the new promising method of modification is introduced. The experiment itself was divided into three main parts. In the first stage, ZnO particles were treated and zinc complex was synthesized. Secondly, different types of vulcanization activators were incorporated into the rubber compounds. In the final step, process and material properties were measured.

Key-Words: Activator of vulcanization, ZnO particles modification, Zinc-m-glycerolate, Activator, Sulfur vulcanization, Zinc oxide.

1 Introduction

The influence of ZnO on the crosslinking network in rubber vulcanizates has been known widely for years. ZnO particles can raise the effectiveness of sulfur vulcanizing system applied in rubbers by more than 60 percent and thus together with stearic acid within sulfur vulcanization play particular role.

Although, zinc is one of the less harmful heavy metals, according to European Council Directive 2004/73/EC, the reduction of zinc level in environment has become an important task because of its toxic effect on aquatic organisms. ZnO is classified as N "Dangerous for the Environment" with the risk phrase R50/53 "Very toxic for aquatic organisms, may cause long-term averse effects in the aquatic environment"[1].

the aquatic environment"[1]. Nevertheless, zinc is 17th most common element in the earth's crust and an essential element for humankind, fauna and flora and its deficiency can bring about many negative effects. These facts are pursued by International Zinc Association (IZA), which stated that the problem of zinc deficiency is on the fifth position among the causes of diarrhea, pneumonia, memory loosing and problems with reproduction [1].

Based on all these information, the International Programme on Chemical Safety (IPCS) under the auspices of the World Health Organization (WHO) constituted a Task Force on Zinc to establish Environmental Health Criteria for Zinc. Among the conclusions, the Task Force states: "Zinc is an essential element in the environment. The possibility exists for both a deficiency and excess of this metal. For this reason it is important that regulatory criteria for zinc, while protecting against toxicity, are not set as low as to drive zinc levels into the deficiency area" [2].

The release of zinc into the environment can arise in several different ways. Firstly, various amounts of zinc are released during its production by wastewater and emissions. In the next phase, zinc is released within its secondary use, especially by the production, use and recycling of rubber products, particularly tires. In to the ground waters, zinc is released by rubber dust wearing off tires and recycled rubber granulates used as a substrate for artificial sport grounds [3]. The task of effective control of the performance of ZnO activator with respect to processing and final properties of rubbers, thus decreasing the ZnO level in rubber products, is important as for environmental as for economic reasons.

Many experiments were carried out in this field. Experiments including use of various metal oxides, nano ZnO, zinc complexes and zinc filled clays as a vulcanization activators are described in several experimental papers [3–11].

The intention of this paper is to introduce a new method for the reduction of potential harmful environmental impact caused by rubber compounds.

A simple and easily applicable method of ZnO's activity control would be useful towards above defined goals. The aim of ZnO particles modification is to change their size, morphology and composition of their active surface which influence the main parameters of vulcanization process and the final properties of rubber compounds as well. Experimental work done within this research paper introduces new modification procedures and compares the effects of modified zinc oxide with standard zinc oxide and zinc-m-glycerolate (Zn-glycerolate).

The structure of the paper is divided into three stages. Within the first stage of the experiment, ZnO particles are treated and Zn-glycerolate is synthesized. In the second part, the different types of activator are incorporated into six different rubber compounds. In the last stage, rubber compounds are vulcanized and characterized.

2 Experimental

2.1 Activators Synthesis

Original ZnO particles (Zinkweiss Rotsiegel, WIEHART, Pernhofen, BET 5.0–6.5 m².g⁻¹) were modified by four different types of solutions: 0,1M-HCl, 1M-HCl, 1M-NaOH and mixture of 1M-HCl and HMTA (molar ratio 1:0.1). A specified amount of ZnO particles were poured into beaker and one of the solutions was added. The suspension was stirred using a magnetic stirrer for defined time at 250 rev.min⁻¹. The wide range of treatment times was applied (from 5 min to 24 hours).

In next step, mixture was filtered and properly rinsed using the Sartorius set and a nitrocellulose filter with pores of size 230 nm. Collected particles were dried in a laboratory oven at 60 °C for 24 hours. A white powder of modified ZnO particles was obtained and inspected by the SEM.

The synthesis of Zn-glycerolate proceeded according to Heideman et al. [5]. Glycerol (150 g), ZnO (25 g) and zinc acetate (2 g) were mixed for

approximately 15 minutes to obtain an uniform slurry. The mixture was then heated to 105 °C for 90 minutes under vigorous stirring. After cooling to approximately 40 °C, isopropanol (75 g) was added and the slurry was mixed for 15 minutes before it was centrifuged. The washing and centrifuging procedure was repeated three times. The final centrifuge residue was dried in a hot air oven at 80 °C for 8 hours. A white powder was obtained [5].

The thermogravimetric analysis has showed that the content of ZnO in prepared Zn-glycerolate is 53 percent, which is in accordance with Zn-glycerolate stechiometry. For that reason also a doubled amount of Zn-glycerolate in one of the rubber compounds was used.

2.2 Rubber Mixing

Six filler free master batches were prepared at twin cylinder (at room temperature) in order to get a homogeneous mixture. The compounds were sheeted off at a thickness of approximately 2 mm.

The composition of a basic rubber compound and the time schedule of mixing are provided in Table 1. The amount of added activator was the same for all the compounds, except the one with amount recalculated according to the result from thermogravimetry analysis of Zn-glycerolate.

Table 1. The composition of a rubber compound.

Component	Amount	Weight	Time
	[phr]	[g]	[min]
SBR 1500	100	181.16	0
Filler	0	0	
ZnO	5	9.06	3
Stearic acid	1	1.81	6
MBTS	1.2	2.17	7
MBT	0.7	1.27	8
DPG	0.5	0.91	9
Sulfur	2	3.62	10
Σ	110.4	200	15

2.3 Curing

The cure characteristics of the different compounds were measured at 150 °C, frequency 1.67 Hz and oscillation amplitude 6.97 % with a Rubber Process Analyser RPA2000 (Alpha Technologies). The optimal vulcanization time (t90) and scorch time (t_s2) of the compounds were determined. The compounds were cured in a hydraulic laboratory press at 150 °C, according to the t90 of the specific compounds.

Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37 using Tensometer 2000 (Alpha Technologies).

3 Results and Discussion

3.1 Activators Synthesis

Various modified ZnO particles of different shapes and sizes were obtained during the synthesis. Whilst, particles modified by 0.1M-HCl and 1M-NaOH show only very small change in their shapes with respect to the original ZnO, during modification by 1M-HCl (see the upper right SEM scan in Fig.1) and by the mixture of 1M-HCl and HMTA the changes in the shape and also the size were significant. Hexagonal disc-shaped particles were produced.

The influence of HMTA on the particle growth is significant especially for longer time periods. After two hours of modification, using the mixture of HMTA and 1M-HCl, ZnO particles increased in size more than in case of pure 1M-HCl solution, with final particle edge length about 4 μ m and thickness 0.5 μ m, while after two hours of modification by 1M-HCl the particle edge length was 1.5–2 μ m and thickness was 0.3–0.4 μ m.



Fig. 1. Particles of ZnO incorporated into rubber compounds: a) non-modified; modified by: b) 1M-HCl, c) 1M-NaOH, d) mixture of 1M-HCl and HMTA. SEM magnification was 10kx.

For the incorporation into the rubber compounds, four different types of ZnO were selected according to the type and time of the treatment. Sample codes and description are given in Table 2. SEM scans of the selected ZnO particles are compared in Fig. 1. As seen in Fig. 1, particles modified by 1M-HCl for half an hour have the biggest size among materials incorporated into the rubber compounds. Particles shape is hexagonal, edge length is $1-1.5 \mu m$ and thickness 0.25 μm .

Among particles modified by mixture of 1M-HCl and HMTA were selected those that were treated for 1 hour only, which are slightly bigger than particles modified by 1M-NaOH.

Particles modified by 1M-NaOH have irregular shapes and single particle size is smaller than 1 µm.

The smallest particles appear the non-modified ones.

3.2 Rubber Mixing

In the stage of a rubber mixing, six different types of rubber compounds were prepared according to the type and the amount of activator used. The prepared compounds are described below, in Table 2.

Table 2. Review of prepared compounds.

Compound	Activator	Description
SBR01	KK000	Non-modified ZnO
SBR02	KK013	ZnO modified by 1M-HCl for 30 min
SBR03	KK022	ZnO modified by mixture of 1M-HCl and HMTA for 1 h
SBR04	KK034	ZnO modified by 1M-NaOH for 30 min
SBR05	Zn- glycerolate	Amount 9.06 g
SBR06	Zn- glycerolate	Amount 17.09 g

3.3 Compounds characterization

Vulcanization characteristics and tensile tests were used for description of the modified ZnO effects in rubber compounds.

Vulcanization curves are plotted in Fig. 2, where the dependence of the torque (S') on the vulcanization time is showed. The saturation plateau of the curves shows the value of maximal torque (M_H) that corresponds to the highest level of sulfur crosslinking.

Maximal torque values are summarised in Fig. 3 where the highest level of crosslinking obtained for compound SBR06, containing Zn-glycerolate as an activator can be clearly recognized thus the crosslinking level can be altered over the range of \pm 15 % of M_H value of standard ZnO (10 dN.m for SBR01).



Fig. 2. The dependence of the torque (S') on the vulcanization time.

The comparison of vulcanization rates u, defined according to the eq. (1), is showed in Table 3.

$$u = \frac{1}{t90 - t_s 2}$$
, [min⁻¹] (1)

t90 is time to reach 90 % of the maximal torque and t_s2 represents the scorch time of a compound, i.e. time till two torque units rise above the minimum.

According to this definition, vulcanization rate shows how fast the curing process is and can be used to determine the press time required during production since *t90* represents the optimal vulcanization time.



Fig. 3. The comparison of maximal torque values obtained for each compound.

Comparing the vulcanization rates (u) in the Table 3, compound SBR01 containing standard ZnO appears to have the highest vulcanization rate being followed by SBR04 in which ZnO modified by

1M-NaOH was used as an activator. The vulcanization rate appears to be closely dependent on the size of particles and thus on the surface area.

Table 3: The vulcanization rate used compounds.

Compound	Vulcanization rate u [min ⁻¹]
SBR01	0.235
SBR02	0.050
SBR03	0.131
SBR04	0.212
SBR05	0.163
SBR06	0.143

Aside the widely used and useful definition of the vulcanization rate (u), another approach was additionally chosen for a more detailed analysis of vulcanization rate. Fig. 4 shows first derivatives of vulcanization curves, i.e. vulcanization rate (v).

$$v = \frac{\mathrm{d}S'}{\mathrm{d}t}, \quad [\mathrm{dN.m.min}^{-1}] \qquad (2)$$

There is almost no difference in curing kinetics between SBR01 and SBR04 in Fig. 4 which means that reactivity of ZnO material was not changed by the modification procedure. The maximum v is nearly 2.5 dN.m.min⁻¹. On the other hand, strong influence was confirmed for acidic modification. Re-crystallisation of the ZnO activator in 1M-HCl lead to increase of size of the particles and decrease of its activity thus the maximum v is about 0.7 dN.m.min⁻¹ for SBR02. The addition of HMTA strongly influenced the re-crystallisation process in HCl solution as it was manifested by change of particle morphology and yielded a moderate effect on v having the maximum of $1.6 \,\mathrm{dN.m.min}^{1}$.



Fig. 4. Vulcanization rates v obtained for each compound by differentiation of vulcanization curves. Only first 15 min is shown.

Another easily recognisable pair of curves in Fig. 4 that almost eclipse each other is the case of Zn-glycerolate. Reaction kinetics is not influenced by concentration as there is no difference between SBR05 and SBR06 vulcanization rate v curves. The maximum v is about 2.3 dN.m.min⁻¹, which is a value close to that of standard ZnO. Moreover, the vulcanization rate v increases from 0.2 dN.m.min⁻¹ to its maximum in approximately 2.5 min for both highly reactive materials. Thus non-modified ZnO and Zn-glycerolate differ in start time of the reaction rate increase and it seems that glycerolate needs induction period (see Fig. some 2 also). Nevertheless, since the process starts and reaches certain value once, the rise to maximum rate takes almost the same time. After maximum, the vulcanization rate v for ZnO steeply decreases and the crosslinking process completes although there must be more sulfur available as higher level of crosslinking can be achieved with Zn-glycerolate. The reaction rate decreases slower for Znglycerolate than for ZnO. According to the results of [5], it was expected that molecular form of zinc should be more readily available than that coming from solid particles embedded in this material. Here, presented observation indicates that this is not the case.



Fig. 5. Scorch time evaluation.

Although some onset time of curing is observable in Fig. 4, the evaluation of initial delay before curing was performed by the use of scorch time t_s2 which concept is standardised and closer to the practical point of view followed here as well. The values of scorch times are plotted in Fig. 5. The type of used modification of ZnO showed a very pronounced effect. The highest value of scorch time was gained for the compound SBR02 containing ZnO modified by 1M-HCl, while the lowest scorch time was gained for the standard ZnO. The scorch time values for compounds comprising Znglycerolate are moderately prolonged.



Fig. 6. Values measured for the modulus at 100 % elongation.



Fig. 7. Values measured for tensile strain represent the highest measured strain at break.

Three representative mechanical properties were chosen for evaluation of modification effects on final rubber properties: modulus at 100 % elongation (Fig. 6), tensile strain (Fig. 7) and elongation at break (Fig. 8). Modulus at 100 % shows very good repeatability as it can be seen from error bars in graph in Fig. 6 and perfectly follows the trend of maximal torque achieved at the end of vulcanization. On the other hand, only reductive effects on modulus value were observed while enhancement of modulus was not confirmed as the error limits of moduli of SBR01 and SBR06 slightly overlap. Tensile strain and elongation at break are closely related together and have worse statistics than previously discussed data. Tensile strain values overlap within the error limits with standard compound for all but the one material, i.e. SBR03 that has the lowest tensile strain. Small effects are visible also in Fig. 8 where SBR02 and SBR05 have

slightly higher values of elongation at break than SBR01 without overlapping error bands.



Fig. 8. The comparison of values measured for elongation at break.

4 Conclusion

The modification of standard ZnO by tested methods has a large influence on a curing process but relatively small impact on the final properties of rubber compound. Generally, the biggest dependency on the modifications was observed for scorch time and vulcanization rate.

Neither size nor activity of ZnO material was changed by NaOH treatment yet it slightly decreased the modulus at 100 % elongation and resulted into the larger standard deviation of obtained values in almost all tests. In contrast to that, an acidic treatment slowed down vulcanization and caused relatively small but observable softening of the material. The HMTA acidic modification gives moderate results in all parameters.

The use of Zn-glycerolate led to higher crosslink density compared to the reference compound, but with a longer scorch delay and prolonged activity in the final phase of curing.

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- International Zinc Association (IZA), "Zinc in the Environment" [online]. [cit 2011-04-20]. Available on WWW: http://www.zincworld.org/publications.html>.
- [2] World Health Organisation (WHO), "Environmental Health Criteria 221: Zinc" [online].[cit 2011-04-21]. Available on WWW: <http://whqlibdoc.who.int/ehc/>.
- [3] Pysklo, L., Pawlovski, P., Parasiewicz, W., Study on Reduction of Zinc Oxide Level in Rubber Compounds Part I, KGK-Kautschuk Gummi Kunstsoffe, Vol. 60, No. 10, 2007, pp. 548–553.
- [4] Heideman, G., Datta, R. N., Noordermeer, J. W. M., et al., Various Ways to Reduce Zinc Oxide Levels in S-SBR Rubber Compounds, *Macromolecular Symposia*, Vol. 245–246, No. 1, 2006, pp. 657–667.
- [5] Heideman, G., Noordermeer, J. W. M., Datta, R. N., et al., Effect of Zinc Complexes as Activator for Sulfur Vulcanization, in Various Rubbers, *Rubber Chemistry and Technology*, Vol. 78, No. 2, 2005, pp. 245–257.
- [6] Nieuwenhuizen, P. J., Zinc Accelerator Complexes - Versatile Homogeneous Catalysts in Sulfur Vulcanization, *Applied Catalysis A: General*, Vol. 207, No. 1–2, 2001, pp. 55–68.
- [7] Wei A.-L., Wei T.-X., Yang F.-W., et al., *Effect* of Nano ZnO on Rubber Properties, Vol. 48, No. 9, 2001. [online].[cit 2011-03-15]. Available on WWW:<http://www.fhnm.com>.
- [8] Przybyszewska, M., Zaborski, M., The Effect of Zinc Oxide Nanoparticle Morphology on Activity in Crosslinking of Carboxylated Nitrile Elastomer, *eXPRESS Polymer Letters*, Vol. 3, No. 9, 2009, pp. 542–552.
- [9] Heideman, G., Noordermeer, J. W. M., Datta, R. N., et al., Zinc Loaded Clay as Activator in Sulfur Vulcanization – A New Route for Zinc Oxide Reduction in Rubber Compounds, *Rubber Chemistry and Technology*, Vol. 77, No. 2, 2004, pp. 336–355.
- [10] Ducháček, V., Kuta, A., Přibyl, P., Efficiency of Metal Activators of Accelerated Sulfur Vulcanization, *Journal of Applied Polymer Science*, Vol. 47, No. 4, 1993, pp. 743–746.
- [11] Heideman, G., Noordermeer, J. W. M., Datta, R. N., et al., Effect of Metal Oxides as Activator for Sulphur Vulcanisation in Various Rubbers, *KGK-Kautschuk Gummi Kunstsoffe*, Vol. 58, No. 1–2, 2005, pp. 650–656.