Study of non-negligible chemical reduction of ZnO in the rubber industry

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Abstract. Although the presence of small portion of zinc in the tire industry has been employed as activator, it should be concerned as the non-negligible chemical toxics and risks. The aim of this work was to study the effect of zinc oxide (ZnO) on physical and mechanical properties of tire rubber compound. The control characteristics of the composites were determined by the composites of practical compounds and curing of a hot press machine. The properties of the composites, i.e. Mooney viscosity, curing time, tension, etc, were characterized. Generally, ZnO could work coupled with stearic acid (SA), the experimental was prepared by reducing ZnO at 20% and reducing stearic acid at approximately ratio to prevent excessive amount. The comparative data revealed the trend of the changes in the physical and mechanical properties just not lower at the same percentage. This recognized study supports the high possibilities in enhancing low ZnO and stearic acid content typical.

1. Introduction

Natural and synthetic rubber contains long polymeric chain with a high degree of flexibility and mobility since the molecules could be extensively movable and extendable in materials matrix excellently against applied load. Its high elasticity is most required property to be transformed to rubber compounding when have been modified into a network structure by crosslinking process. Sulfur crosslinking or so called ‘vulcanization’ is the most common and continued developing curing for unsaturated elastomers application, particularly in tire manufacturing industry. To gain desirable properties, i.e. high torque, high load aspect ratios, low rolling resistance, high wear resistance and good braking performance [1].

Zinc oxide has been applied as an activator supporting the vulcanization process among other rubber compounds to permit the 3D crosslinking network. ZnO, combined with SA, reduces the vulcanization time and improves rubber properties, even in the case of unaccelerated vulcanization [2]. The major industry for ZnO is rubber compounding, agriculture and ceramics, meanwhile zinc oxide is accounting for 59% of the zinc chemicals above zinc sulfate (36%) and zinc chloride (5%) [3]. The momentum of growing environmental awareness has become emphasized throughout toxicity of Zn possibly occurred in both acute and chronic forms [4]. The toxicological profile for Zinc [5] provided sample laboratory experiments indicated that a significant fraction of zinc may be released from tire rubber debris. S. Loranger et al. [6] collected zinc levels in snow on soil near an expressway in Montréal, Québec (Canada) at 15 m from expressway, the concentration of zinc in snow was 0.143 mg/L, while at150 m from the expressway, the mentioned concentration 0.029 mg/L. These conditions indicated a significant fraction of zinc dissolved in snow would be possibly released from tire rubber of vehicle using the
expressway. A. Szwalec et al. [7] studied the impact of roads with various conditions of traffic and period of use on the distribution of Zn in the arable roadside topsoil. The concentrations of Zn, regardless of the distance from the road were 40.31 m/kg dry mattering topsoil of the road with 10 years of use and 18,000 vehicles/day and 63.97 mg/kg dry matter in topsoil of the road with 50 years of usage and 20,000 vehicles/day. The higher concentrations of Zn depended on traffic intensity, road type and distance from the road statistically were another evidence for non-negligible chemical loading by dust from the road.

Zinc compounds may be applied in the manufacturing and later be found as hazardous waste such zinc chloride, zinc oxide, zinc sulfate, and zinc sulfide. To protect workers, the Occupational Safety and Health Administration of the United States (OSHA) has set an average legal limit of 1 mg/m$^3$ for zinc chloride fumes and 5 mg/m$^3$ for zinc oxide (dusts and fumes) in workplace air during an 8-hour workday, 40-hour work week. Furthermore, a kind of community right-to-know regulations was issued to be guidance for industry’s use and release of hazardous substances to prepare communities for and protect communities from chemical accidents. For instance, USA has implemented Emergency Plan and Community Right-to-know Acts (EPCRA) Section 313 for Reporting Guidance for Rubber and Plastics Manufacturing [8] particularly. This guidance states a sample step to identify, to transfer and to release the total amount of ZnO in process during the year determined by the annual throughput of the rubber mixture.

Several researches have been investigated over the decades in efforts to reduce ZnO, but further challenges of this complex chemical process are remaining significant in different solutions. For instance, the commercial grade of ZnO might be concerned about its low surface area, it further caused low ability to disperse the rubber matrix. [9] L. Pysklo et al. novel proposed novel such as active ZnO produced in a wet chemical process with smaller particle size and larger specific surface area to obtain the higher efficiency to be able to decrease ZnO loading. M. Guzmán et al. [10] proposed the use of nano-sized ZnO particles couple with more alternative metal oxides of Mg by the method consisted on the preparation of a polymer/metal salt complex. Despite previously explained novel or complex alternative, this study intended to provide the affordable green solution for reducing ZnO and reduce time to market as much as possible.

The main objective of this work was to investigate and adjust the rubber compounds to keep desired properties in the controlled compound from commercial sample could be. Basically, ZnO was used about 2-5 phr. Therefore, the middle of range was selected to be control sample in this study.

2. Experimental
2.1. Materials and preparations
Natural rubber (NR) type STR20 and butadiene rubber (BR) were used as the base materials for preparation of rubber composite with other substances following the formulation as shown in Table 1. Carbon black is fillers or reinforcement aids added to rubber formulations to meet application targets such as tensile strength and abrasion resistance 3 typical components for vulcanizing system are vulcanizing agents, activators and accelerator. This experimental used sulfur for vulcanizing, zinc oxide stearic acid for activating and then N-cyclohexyl-2-benzothiazyl sulfenamide (CBS) for accelerating. Another organic chemical was N-1,3-Dimethylbutyl-N'-phenyl-para-phenylenediamine (6PPD) used as an antiozonant [11].
All materials supplied from Thailand. The compounds were mixed in a two roll-mill mixer (Model R11-3FF; Kodaira Seisakusho; Japan) at a temperature of 70°C for 25 min by adding ingredients as following stage:

1. NR and BR 8 min.
2. ZnO and stearic acid 3 min
3. 6-PPD and carbon black and then aromatic oil 8.5 min.
4. CBS 1 min.
5. Sulphur 4.5 min.
6. Final Mix 2 min.

Each sample rubber compounds were then left 24 h prior to testing for which determine cure time (t90) and scorch time. The rubber composites were molded into sheets with respective cure time, t90, at 150°C using a hot press machine.

2.2 Characterization
The Mooney viscosity of the rubber compounds was determined using a Mooney viscometer in compliance with Standard ISO 289-1:2015. The cure characteristics were analyzed using a moving die rheometer (MDR) for 30 min at 50°C according to ASTM D5289-19. The vulcanized rubber sheet of each recipe was prepared 5 dumbbell shape samples with dimensions 115 mm x 25 mm x 2 mm. The mechanical properties were collected, according to ASTM D412-16, consisting of the tensile modulus, tensile strength and elongation at break.

3. Results and Discussion

| Table 2. Properties of rubber composites. |
|------------------------------------------|
| Mechanical and Physical Properties      | Recipe A | Recipe B |
| Mooney viscosity (+/- 5 a.u.)            | 31.60     | 34.60     |
| t90 at 150°C (+/- 1 min)                 | 17.61     | 16.64     |
| Tensile Stress at Preset Point: Tensile strain 100% (MPa) | 0.60     | 0.70     |
| Tensile Stress at Preset Point: Tensile strain 300% (MPa) | 2.10     | 2.10     |
| Tensile Stress at Preset Point: Tensile strain 500% (MPa) | 4.90     | 4.90     |
| Tensile Stress at Break (MPa)            | 7.60      | 8.00      |
| Elongation to Break (+/- 10%)            | 637.00    | 654.00    |
The experimental results of reducing ZnO and stearic acid in rubber compounds, that represented tire rubber component, could be determined in 2 groups of properties for exploring macrostructure of unvulcanized rubber compounds. Another important property of vulcanizates was mechanical characteristics.

Mooney viscosity is the resistance of uncured rubber to flow under stress depended on deforming temperature measured by rotational viscometer techniques. Recipe B, which mixed with less ZnO and stearic acid, took slightly higher viscosity than Recipe A within the same uncertainty measurement. It should be noted that fewer zinc in Recipe B could keep generating adequate rate of vulcanization growth.

According to the ration of amount of accelerator and amount of sulfur in this control recipe or Recipe A was equal to 1, the curing system could be defined as the semi-effective vulcanization (SEV) [12]. When the accelerator activities rise more than conventional system, the reactions took place more actively, the monosulfide crosslinks increase, and the degree of effective crosslinking of sulfur increases. Since couple of ZnO and stearic acid would form as zinc soap, then it further improved the solubility of ZnO in the rubber compound and with the accelerator to form a complex. This complex is very lively, reacting with sulfur to produce an extremely strong vulcanizing agent. As a results of Recipe B’s top or curing time was almost the same time with that of Recipe A. The reduced of ZnO level in recipe B were not affect the curing time in this study.

Tensile stress of both Recipes at preset point of tensile strain 300%, which are frequently interested among researchers for determining effect of reinforcing with carbon black in rubber matrix, was 2.1 MPa for both recipes. And also 100% and 500% point could be reported as same increasing from 0.6 to 4.9 MPa. So, there were no significant differences of mechanical properties between 2 recipes, even less ZnO of Recipe B.

4. Conclusion
This study focused on simply reduce zinc content in tire and to discover the effect of less activator on rubber compounds characteristics. The experimental recipe adopted from practical tire rubber ingredients with less 20% of ZnO. As results of viscosity, curing time and mechanical properties, those results were not change within the same uncertainty magnitude. It should be noted that amount of ZnO was adequate to activate reactions initially in this study. Anyway, further steps responded by ZnO and stearic acid together as zinc-soap to facilitate by increase solubility with accelerator to increase rate of sulfur crosslinking, the less amount of ZnO would affect the accelerating rate. However, the efficiency of reduced ZnO recipes were not as high as the control recipes. So, reduced ZnO recipe could be a good alternative to the control recipe when determine its properties at general working range for contributing to eco-friendly productions.

Acknowledgement
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