Evaluating Performance of Magnesium Oxide at Different Sizes as Activator for Natural Rubber Vulcanization

Siti Nor Qamarina M., and S. Kawahara

***Abstract*—** It is generally known that activator containing zinc-compounds has been extensively used in the rubber industry due to its outstanding ability in promoting beneficial effects to the rubber products. Ever since these compounds were identified having negative environmental effects as well as contributing to mould fouling during rubber products manufacturing, various approaches have been considered by the rubber manufacturers in reducing its utilization. Among all the alternatives proposed, an approach of utilizing magnesium oxide (MgO) seems to be promising. A lot of research has been conducted on the performance of the typical MgO in affecting natural rubber (NR) vulcanizates, but limited works had been performed in evaluating the activating properties of the nano-sized MgO in NR. Therefore, in this study, affects MgO sizes at various loadings on the vulcanization reaction and vulcanizates properties of NR are investigated. The normally used zinc-containing compound was employed as an activator in the vulcanization of NR for comparison purposes. Gauging on the cure characteristics, it was found that nano-sized MgO performed better; as it exhibited faster onset time, lower cure time (t_{90}) with greater physical properties, as compared to the typical MgO. Morphological observations on images taken from scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis demonstrated that nano-sized MgO appeared in smaller aggregates with even aggregates distributions throughout the rubber matrix, in comparison to the aggregates behavior of the typical MgO. The aggregates for both sizes of MgO particles were found intensified with higher amount of MgO present in the vulcanization system, which accounted for reversion in the NR vulcanizate performances. Although the overall performance of the nano-sized MgO in NR vulcanization surpassed the typical MgO used in the similar discipline; nevertheless, the findings obtained were to some extent lower in comparison to the NR vulcanizate performance containing normally used zinc-containing compound. On the whole, MgO has some ways behaved as the zinc-containing compound, but the role of the MgO as an alternative activator for NR vulcanization should be further investigated, specifically for the nano-sized MgO in enhancing its reactivity within the NR compounds.

***Index Terms*—** Magnesium Oxide, Particle Size, Natural Rubber, Vulcanization, Physical Performances, Morphology

I. INTRODUCTION

Magnesium oxide (MgO) is a well-known material to be thermally stable due to its stoichiometric-crystalline form, which is like a simple sodium chloride structure. It is anticipated that its presence in nano-sized may impose greater potential as the nano-sized MgO particles may offer larger surface area as compared to the conventional MgO [1-2]. The nano-size MgO crystalline-like structure will exhibit remarkable reactivity in accelerating reactions as a catalyst, for instance in rubber manufacturing besides enabling them to act as filler for rubber products [2]. Specifically, the nano-sized MgO will form active sulfurating agents and activate the crosslinking formation between the rubber particles during vulcanization, as the normally used activator executed in the rubber vulcanization process. While offering greater sites for acceleration reactions during rubber vulcanization, the nano-sized MgO might exhibit as a potential suitable alternative metal activator for the rubber vulcanization.

Availability of boundless source of MgO from seawater and brine has made it identified as the third most abundant element. Therefore, exploiting the beneficial properties of the MgO is useful for many areas, including rubber technology. Generally, fabricating nano-sized MgO for rubber products manufacturing was initiated attributed to the increase concern in protecting the environment. Previously, zinc oxide (ZnO) was used to catalyze rubber vulcanization process. Its mechanism during vulcanization process [4,8,9,12] and its effects on the properties of the vulcanizates [3-7,9,11] has long been known and investigated. However, ZnO release into the environment that occurs during production, disposal and recycling of rubber products, which is in soluble zinc compounds is classified as ecotoxic to aquatic organisms [5,7,9-10]. Moreover, usage of ZnO is also associated with a problem related to mold fouling that occurs during rubber manufacturing [9,13-14]. There is evidence that during vulcanization, a considerable amount of ZnO is consumed and transformed into zinc sulfide (ZnS), which is a by-product of the vulcanization reactions. Distributions of un-dissolved ZnS particles formed inhomogeneity within the rubber matrix [15]. These inhomogeneities have been reported lead to mold fouling of the rubber products. As consequences, many efforts have been put into considerations in minimizing the ZnO content in rubber products manufacturing to ensure low pollution impact, nonetheless at tolerable manufacturing cost.

Among numerous numbers of investigations comparing different metal oxides as rubber vulcanization activators, considering the usage of MgO as an environmentally friendly activator for rubber vulcanization is worthwhile. It is anticipated that replacement of the ZnO with the MgO resulted in promising characteristics, since Zn^{2+} and Mg^{2+} have equal charges. Furthermore, the MgO presence in nano-sized particles will offer greater surface area for vulcanization reaction. Therefore, in this study, the effects of the nano-sized MgO in curing, mechanical properties and morphology of the rubber vulcanizates are evaluated in order to understand the

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nano-sized MgO effectiveness in the sulfur vulcanization process while elucidating a relationship between the hierarchal structure and the vulcanizates properties achieved.

II. EXPERIMENTAL

A. Material

Natural Rubber (NR) grade of SMR 20, obtained from Yokohama Rubber Japan was used throughout this study. Other compounding ingredients such as sulfur and ZnO was purchased from Nacalai Tesque Inc. Tetramethyl thiuram disulphide (TMTD) and stearic acid from TCI/EP; N-tertiary butyl-2- benzothiazole sulfonamide (TBBS) and conventional MgO (micro-sized) were from Wako Chemicals; while Tokuyama Soda Co. Ltd supplied the nano-sized MgO. All the materials were of commercial grades and used as such.

B. Preparation of Rubber Compounds

The rubber compounds contained various loadings of different MgO, as activator was prepared, as tabulated in Table I. The control rubber compound containing fixed amount of normally used ZnO as activator was used as control. All the NR batches were prepared using laboratory internal mixer (Toyoseiki Labo Plastomill 4M150). The rubber mixings were carried out in accordance to ASTM D-3192. The internal mixer was set to working at 50˚C with rotor speed of 60 rpm.

TABLE I
COMPOSITION OF RUBBER COMPOUNDS (IN PHR)
A: *2, 4, 12, 20*

Composition	Nano-size	Typical-size	Control
SMR20	100	100	100
ZnO	-	-	2.0
Stearic acid	1.5	1.5	1.5
TBBS	1.9	1.9	1.9
TMTD	0.9	0.9	0.9
MgO	a	a	-
Sulphur	2.2	2.2	2.2

C. Analysis of Rubber Vulcanizates

Cure Characteristic: The cure characteristics of rubber compounds were measured using Toyoseiki Rotorless Rheometer RLR-4 at 150˚C. The optimal vulcanization time, t_{90} were determined. The compounds were cured using laboratory press at 150˚C according to t_{90} for the specific compounds. The compounds were sheeted off at a thickness of 1 mm.

Physical Properties Analysis: Dumbbell-shaped samples were cut from the mould sheet according to JIS K6251 (type 7). Tensile properties were determined via an Instron 3300 testing machine with a crosshead speed of 200 mm/min.

Morphological Observation: Observation on the rubber vulcanizates compositional difference was carried out using focused ion-beam/scanning electron microscopy (FIB/SEM) technique (JEOL Ltd. Japan; Model SMI 3050 SE). The FIB is first used to ion mill a trench on the vulcanizates surface, of which the thickness is around 100nm will be removed; followed by SEM imaging on the exposed area to obtain its morphological information. In order to understand the rubber vulcanizate internal characteristic, transmission electron microscopy (TEM) of JEOL JEM-2100 at an accelerating voltage of 20kV was used. Ultrathin sections with a thickness about 50-100 nm were first prepared at -90°C using a Richert-Nissei FC S-Ultracut before conducting the observation.

III. RESULTS AND DISCUSSION

Cure curves for various NR compounds at different sizes of MgO were illustrated in Fig. 1a and 1b. Overall, the cure curves for the nano-sized MgO and the typical MgO were lower in comparison to the normally used ZnO, as represented in Fig. 1a and Fig.1b, respectively. Both of the cure curves agreed that increased content of the MgO would increase the torque value for a specific period of time before truncated. In conjunction with that, it was also noticed that the cure time (t_{90}) of the NR compounds in the presence of the MgO were found to some extent lower than the NR compound with ZnO utilization. It was reported that MgO possess slightly slow rate of cure during vulcanization reaction [2-6], hence lower t_{90} values achieved for NR compounds with MgO loadings were much expected.

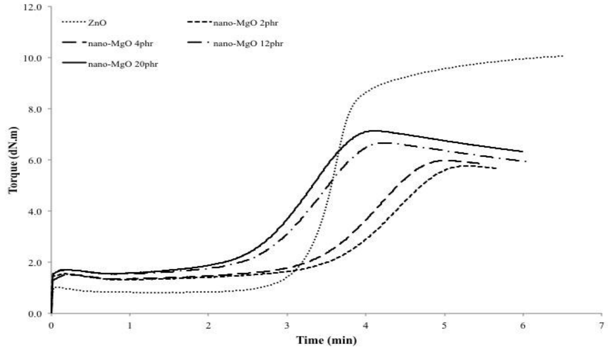


Fig. 1a. NR compounds cure curves with nano-sized MgO at various loadings

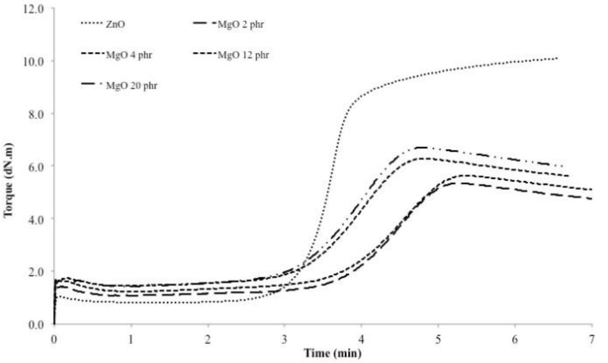


Fig. 1b. NR compounds cure curves with typical MgO at various loadings

Meanwhile, the MH, which can be regarded as a measure of modulus were found increased with increased of the MgO loadings and similar trend was observed on the ML values, which represent the rubber compounds' viscosity behavior. Furthermore, it was apparent that the cure curves of NR compounds with MgO contents showed significant shift once the NR vulcanizate contained 12 and 20 phr of the MgO loadings. The results might suggest that higher amount of MgO is necessary to catalyze an enhancement in the vulcanization reaction.

The sudden increased or defined as the onset time for vulcanization was found faster in the NR vulcanizate with nano-sized MgO as activator. It was appeared at 2 minutes, while the NR vulcanizatess with typical MgO and the normally used ZnO activator have an onset time after 3 minutes. These results showed the ability of the MgO in activating the vulcanization process of the NR compounds besides suggesting that nano-sized MgO attained faster onset time due to greater sites offered for the vulcanization interaction to take place.

Stress-strain (σ/γ) curves of rubber compounds activated by the nano-sized MgO and the typical MgO were shown in Fig. 2a and Fig. 2b, respectively. Apparently, NR vulcanizates with nano-sized MgO has 15% longer strain, as compared to the NR vulcanizates with the typical MgO. Overall, NR vulcanizates demonstrated a recoverable extension within $\gamma < 5$ before ruptured. The σ/γ curves between low and high loading amount of the nano-MgO demonstrated a big gap between the curves (Fig. 2a). The significant disparity was anticipated due to the effect of strain-induced crystallization [16]. Greater amount of the nano-sized MgO available during vulcanization might offer better interaction between the chemicals during vulcanization, which in the end affect the elongation of crosslinks formed in the vulcanizates. On the other hand, NR vulcanizates with the typical MgO illustrated limited vulcanizates extension. The size of the MgO was presumed to be one of a factor that restricted the extensibility of the vulcanizates to elongate, hence causing a breakage at relatively small deformation [17].

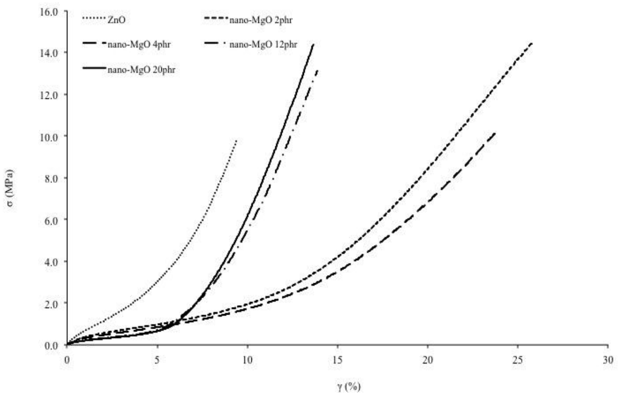


Fig. 2a. Stress-strain curves contained nano-sized MgO at various loadings

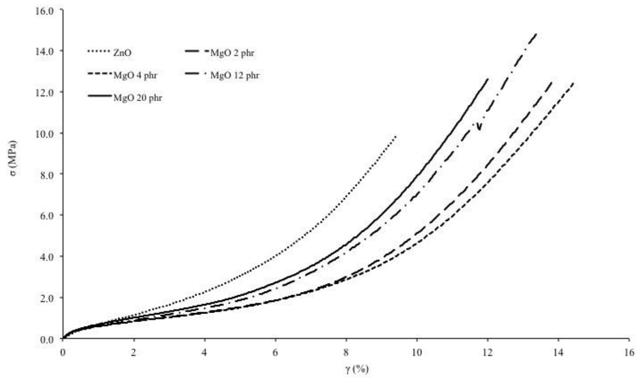


Fig. 2b. Stress-strain curves contained typical MgO at various loadings

The physical properties of the NR vulcanizates, which contained different type of activator at varied loadings, were listed in Table II. Although NR vulcanizates contained MgO illustrated lower physical performances as compared to the NR vulcanizates with ZnO as activator; it's worth affirmed that the NR vulcanizates with MgO portrayed longer extension before ruptured. Low tensile strength and M_{300} values of NR vulcanizates achieved in the presence of MgO could be related to low activation energy of the MgO. Due to this, greater heterogeneities have been created during the vulcanization reaction, which in the end intensified the ruptured potential of the NR vulcanizates [18].

TABLE II

PHYSICAL PROPERTIES OF RUBBER VULCANIZATES WITH DIFFERENT TYPE OF ACTIVATOR AT VARIED LOADINGS

Activator	Tensile strength (MPa)	M_{300} (MPa)	Elongation at break (%)
Control	17.5	2.74	59
Nano-size MgO			
• 2 phr	12.7	0.75	251
• 4 phr	13.7	0.68	245
• 12 phr	14.3	0.41	139
• 20 phr	15.0	0.39	135
Typical-size MgO			
• 2 phr	12.4	0.95	138
• 4 phr	12.4	1.03	141
• 12 phr	12.7	1.14	136
• 20 phr	12.4	1.33	109

In order to understand the distribution of the activator within the rubber matrix, morphological observation through FIB/SEM technique was conducted. Fig. 3 represents the inner structure of NR vulcanizate in the presence of 2 phr ZnO. The bright domains, which is known as ZnO-aggregates complexes were found apparently distributed within the rubber matrix. Comparison of inner structure between the NR vulcanizates in the presence of ZnO and nano-sized MgO showed that NR vulcanizate with nano-sized MgO portrayed better interaction with the rubber matrix (Fig. 4a). However, greater aggregates complexes were observed distributed within the rubber matrix once the nano-size MgO were abundantly present in the system (Fig. 4b).

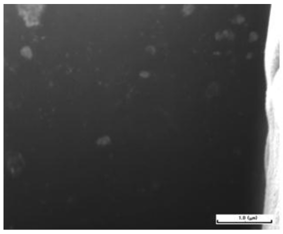
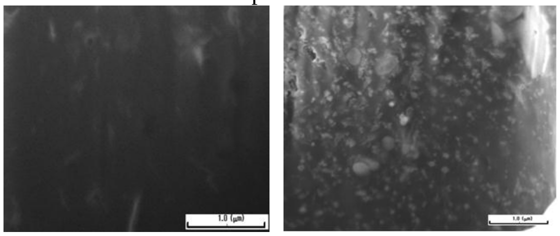


Fig. 3. FIB/SEM image of NR vulcanizate in the presence of ZnO at 2 phr



(a) (b)

Fig. 4. FIB/SEM images of NR vulcanizate in the presence of nano-sized MgO at (a) 2 phr and (b) 20 phr

In contrast, the inner surface of the NR vulcanizates contained typical MgO were found to comprise noticeable amount of bright domains within the rubber matrix even at 2 phr loading (Fig. 5a). The aggregates complexes were intensified and grow in size at higher typical MgO content (Fig. 5b). These aggregates were responsible to the decrease in the mechanical properties of the NR vulcanizates as they will act as sources of fracture, which led to the elasticity disturbance of the NR.

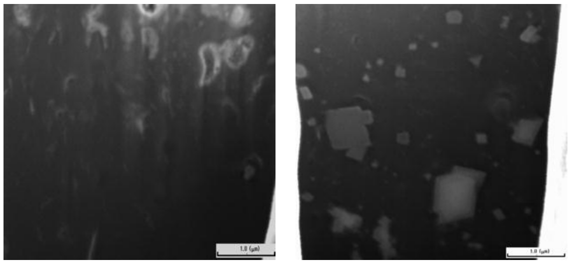

(a) (b)

Fig. 5. FIB/SEM images of NR vulcanizate in the presence of typical MgO at (a) 2 phr and (b) 20 phr

TEM images for the NR vulcanizate in the presence of ZnO, nano-sized MgO and typical MgO were shown in Fig. 6-Fig. 8, respectively. The bright domain represents the rubber matrix, while the dark domains were the activator-complexes aggregates. It was appeared that size of activator-complex aggregates dependent on the size and the loading amount of the activator. The images obtained from TEM technique were well agreed with the SEM images and the physical properties achieved.

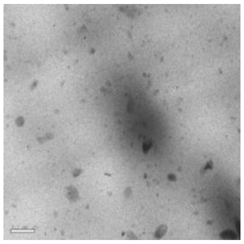


Fig. 6. TEM image of NR vulcanizate in the presence of ZnO at 2 phr

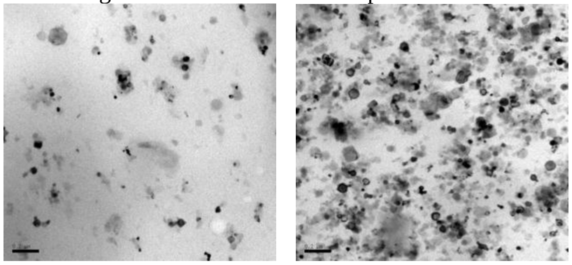

(a) (b)

Fig. 7. TEM images of NR vulcanizate in the presence of nano-sized MgO at (a) 2 phr and (b) 20 phr

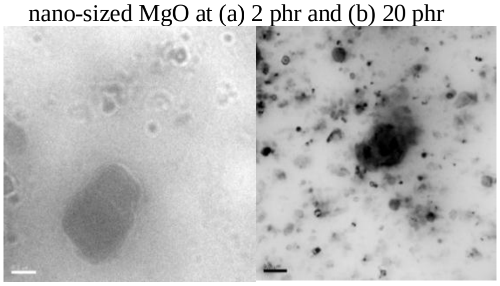

(a) (b)

Fig. 8. TEM images of NR vulcanizate in the presence of typical MgO at (a) 2 phr and (b) 20 phr

IV. CONCLUSION

The utilization of nano-sized MgO as an activator for NR compound was found performed better in curing with acceptable physical properties values and portrayed a good particle distribution in the rubber matrix, in comparison to the typical MgO. Even though the final NR vulcanizates properties of this material were to some extent lower than the ZnO vulcanizates, nevertheless the findings obtained proved that this nano-sized MgO is still capable to activate the vulcanization process with faster onset time. At present, the nano-sized MgO can be considered as an alternative activator for NR vulcanization. However, exploring approaches in optimizing the nano-sized MgO functionality for NR vulcanization, with an aimed replacing ZnO utilization shall be thoroughly conducted for our future benefits.

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