Effect of Mg Oxide Nanoparticles on Sulphur Vulcanisation of Natural Rubber

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Magnesium oxide (MgO) nanoparticles were introduced in natural rubber (NR) as an activator to investigate its effect on NR vulcanisates. The MgO nanoparticles were mixed in a ratio of 0−20 p.h.r. before curing at 150°C. Results of cure time and torque showed that at 12 and 20 p.h.r. loadings, acceptable cure characteristics to that of the control compound, 2 p.h.r. zinc oxide (ZnO) were exhibited. Crosslink density of the vulcanisates, determined by the swelling method confirmed that the MgO nanoparticles intensified the formation of crosslinking. Dispersion of the MgO nanoparticles observed by focused ion-beam/scanning electron microscopy (FIB/SEM) and transmission electron microscopy (TEM) indicated that aggregates of complexes distributed throughout the rubber matrix is consistent with the MgO nanoparticle loadings and were well correlated to the mechanical properties achieved. These findings offer an alternative route for vulcanisation formulation of NR.

Keywords: MgO nanoparticles; activator; rubber; sulphur vulcanisation; characterisation

Magnesium oxide (MgO) nanoparticles may have superior potential as catalyst in rubber manufacturing\(^1\)^\(^2\). The MgO nanoparticles are known to be stable thermally and stoichiometrically due to its crystalline form, which is a simple sodium-chloride type structure. It is anticipated that reactivity of the MgO nanoparticles is more prominent as compared to conventionally prepared MgO, as the MgO nanoparticles have a larger surface area. The crystalline MgO nanoparticles exhibit remarkable reactivity in accelerating reactions as a catalyst and they are able to act as a filler\(^2\). The MgO nanoparticles possess the ability to form active sulphurating agents, particularly for decomposition of accelerators during vulcanisation. The presence of MgO in the nano-meter scale offered greater sites to accelerate reactions, making MgO nanoparticles a suitable alternative metal activator for rubber vulcanisation.

Besides being known as an environmentally friendly metal oxide, MgO is basically the end product produced by precipitation of magnesium hydroxide from seawater or brine sources, which amounts to about 14% of world magnesia production\(^1\). Availability

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of boundless non-toxic sources of MgO, along with its size in the nano-meter scale introduces MgO as a potential activator for rubber compounding, after zinc oxide (ZnO). This nano-sized MgO may have a great impact on the vulcanisation activity and final product performances. Even though MgO is less reactive, its nano-sized particles will offer more reactive sites for vulcanisation. These greater-site-interactions may form more accelerator-complexes, which contribute to the higher formation of crosslinks, and subsequently improve the final vulcanisates properties.

Numerous investigations have been carried out in comparing different metal oxides as vulcanisation activators. However, the reactivity of these metal oxides is dependent on type of activators and type of polymer used. From a historical point of view, ZnO is a well established activator that has been extensively used and studied in the rubber industry. Its outstanding ability to promote vulcanisation, results in many beneficial effects on the properties of the vulcanisates. The mechanism of the crosslinks process is well known: ZnO reacts with an accelerator to form highly active complexes. The reactions of these complexes with other complexes or through the reaction with polymer chains generate polysulphidic crosslinks. The formations of the polysulphidic crosslinks are basically catalysed by the Zn$^{2+}$ ion.

Although zinc is generally considered as one of the least harmful heavy metals, it is also one of the most widespread in the environment, especially during production, disposal and recycling of rubber products. Release of zinc through the leaching process, for instance, drive soluble zinc levels into surplus and consequently leads to adverse effects on aquatic organisms. Apart from that, it has been reported that utilisation of zinc during rubber manufacturing is also associated with a problem related to mould fouling. There was evidence that during vulcanisation, a considerable amount of ZnO is transformed into zinc sulphide (ZnS), which is a by-product of the vulcanisation reactions. Distribution of undissolved ZnS particles formed inhomogeneity within the rubber matrix. Most of all, ZnO used nowadays has limited availability since at present, ZnO is produced only from the mining process. Increasing demand of rubber products will lower ZnO levels in the earth’s crust and this situation will have an effect not only on rubber production but also from an economic point of view.

In view of the disadvantages exposed by ZnO and zinc containing compounds, different approaches have been considered for reducing the zinc level, such as the use of nano-sized ZnO particles and zinc complexes, as well as reducing ZnO content to 2 p.h.r. It has been reported that the reduction of ZnO content to a minimum of 2 p.h.r. resulted in shortening of scorch time and optimal vulcanisation, besides giving similar curing level as the traditionally used ZnO content (3–8 p.h.r.) in rubber formulations. Another approach considered for reducing zinc levels is the use of other oxides as activator for rubber vulcanisation. Although several metal oxides have been used, at present there is still no research reported on the use of MgO nanoparticles. Thus, the accelerating properties of the MgO nanoparticles in vulcanisation of NR were considered worthwhile. Previous studies suggested that replacement of ZnO with MgO resulted in promising characteristics, since Zn$^{2+}$ and Mg$^{2+}$ have equal charges.

In this paper, MgO nanoparticles will be used as activator for sulphur vulcanisation of natural rubber (NR) at different loadings, ranging between 0 to 20 p.h.r. Control compound, which contained ZnO was fixed
at 2 p.h.r. This is due to the comparable physical properties of conventionally used ZnO at 3–8 p.h.r.\textsuperscript{4,9}, besides aiming to lower the environmental impact. Measurements of rheological and mechanical properties, as well as morphological observation of the vulcanisates were performed in order to understand the role and effectiveness of MgO nanoparticles in sulphur vulcanisation and to elucidate a relationship between hierarchical structure and vulcanisate properties.

**EXPERIMENTAL**

**Materials**

Natural rubber of SMR 20 grade, a product from Yokohama Rubber, Japan was used throughout this study. The MgO nanoparticles were supplied by Tokuyama Soda Co. Ltd., Japan. Other compounding ingredients such as sulphur and ZnO were purchased from Nacalai Tesque Inc. Tetramethyl thiuram disulphide (TMTD) and stearic acid from TCI/EP; and N-tertiary butyl-2-benzothiazole sulphonamide (TBBS) was from Wako Chemicals, Japan. All the chemicals were used as supplied. The compounding formulation is shown in Table 1.

**Sample Preparation**

In this work, the contents of MgO nanoparticles incorporated into rubber were varied from 0–20 p.h.r. In each case, mixings were carried out using a laboratory internal mixer (Toyoseiki Labo Plastomill 4M150) in accordance to ASTM D-3192. The internal mixer was set at 50°C with a rotor speed of 60 r.p.m. The cure characteristics of the mixes were determined by Toyoseiki Rotorless Rheometer RLR-4 at 150°C. The compounds were then compression moulded at 150°C for cure time, $t_{90}$ respectively which were determined by the rheometer test in obtaining sheets with approximately 1 mm thickness.

**Characterisation**

**Mechanical Testing.** Dumbbell-shaped samples were cut from the mould sheet according to JIS K6251 (type 7) for tensile and stress-strain analyses. Tensile properties were determined via an Instron 3300 testing machine with a crosshead speed of 200 mm/ min. As for stress-strain measurements, the sample is strained at a traction rate of 1 mm/min. For tear properties measurement, trouser tear samples were cut according to JIS K6252 by using a sharp razor blade. The tear test was

**TABLE 1. COMPOSITION OF RUBBER COMPOUNDS WITH DIFFERENT TYPES OF ACTIVATOR**

<table>
<thead>
<tr>
<th>Activator (p.h.r.)</th>
<th>No activator</th>
<th>ZnO</th>
<th>MgO nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR 20</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TBBS</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Activator</td>
<td>-</td>
<td>2</td>
<td>2, 4, 12, 20</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

TBBS : tert-butyl-2-benzothiazole sulphenamide
TMTD : tetra methyl thiuram disulphide
carried out with a crosshead speed of 100 mm/minute.

**Crosslink Density Measurement.** Cured test pieces with a diameter of 12 mm and 1 mm thickness were swollen in toluene for three days at room temperature. At the end of the immersion period, samples were removed, the solvent was quickly blotted off, weighed and then dried to a constant weight. The swelling data were then utilised to estimate the molecular weight between crosslinks, $M_c$, by applying the Flory-Rehner expression:

$$-\ln[(1-V_r) + V_r + \chi V_r^2] = \frac{\rho V_s M_c}{V_r^2} - \frac{V_r}{2} \ldots 1$$

where $V_r$ is the volume fraction of rubber in the swollen gel at equilibrium, $\chi$ is the rubber-toluene interaction parameter (0.34), $V_s$ is the molar volume of toluene, $M_c$ is the number average molecular weight between crosslinks and $\rho$ is the density of rubber. The crosslink density, defined as $\frac{1}{2} (M_c)$ can therefore be calculated.

**Morphology Observation.** Inner morphological observation of the vulcanisates were carried out using FIB/SEM technique (SII; Model SMI 3050 SE). Prior to observing the inner morphology, the vulcanisate was immersed in osmium tetra-oxide ($\text{OsO}_4$) solution for seven days and dried in vacuum. For incision, the Ga-ion was charged at about 50 pA onto the surface of vulcanisates. The cutting sections were observed through SEM to study the chemical distribution and morphology of the vulcanised rubber. Distribution of the MgO nanoparticles in the rubber matrix was investigated via TEM (JEOL JEM-2100) at an accelerating voltage of 15kV. Ultrathin sections with a thickness about 100 nm were prepared at -90°C using a Richert-Nissei FC S-Ultracut, placed onto copper-grids of 100 meshes before being observed under an electron beam.

**RESULTS AND DISCUSSION**

Cure curves in a plot of torque ($\tau$) versus time ($t$) represent fingerprints of rubber processing: that is, mixing, maturing, moulding and vulcanising. Figure 1 shows cure curves of NR compounds activated by the MgO nanoparticles and ZnO particles. Overall, the cure curves for the MgO nanoparticles compounds were lower than the ZnO control compound. At a prolonged curing time, decreased or reversion curves occurred in the MgO-activated compounds. However, it is worthy to note that at higher MgO nanoparticle loadings, particularly at 12 and 20 p.h.r., significant shift in the cure curves were observed. Besides that, these amounts also showed faster scorch time as compared to the 2 p.h.r. ZnO compound. Thus, these results proved the ability of the MgO nanoparticles to catalyse the vulcanisation reaction in NR, especially at higher loadings, although the curing level were to some extent lower than the 2 p.h.r. ZnO compound. The possibility of the MgO nanoparticles to substitute ZnO as activator could be due to its large surface area, which offers greater sites for interactions with the curing agents during the vulcanisation mechanism. Since the MgO nanoparticles have in some ways behaved as the ZnO, specific experimental optimisation should be further investigated in ensuring the competitiveness of the MgO nanoparticles as activator for the NR vulcanisation.

The crosslink density, $\frac{1}{2} (M_c)$, at varied activator contents is showed in Figure 2. Based on the figure, the catalytic behaviour of the MgO nanoparticles is confirmed as at larger amounts of the MgO nanoparticle loadings, formations of crosslink density intensified. In comparison to the ZnO-activated compound, crosslink density of the MgO nanoparticles compounds was lower. This is possibly due to the low activation energy of the MgO, which caused the formation of short chain crosslinks throughout the MgO activated compounds.
Figure 1. Cure characteristics for rubber compounds with varied contents of metal oxides as activator

Figure 2. Crosslink density for rubber compounds with varied contents of metal oxides as activator
and consequently weakened the elastomeric strength. This result is parallel with the curing characteristics achieved and mechanical properties obtained, which will be detailed out at a later stage.

Figure 3 represents stress-strain ($\sigma/\gamma$) curves for NR vulcanisates activated by the MgO nanoparticles and the ZnO particles. Generally, all the NR vulcanisates demonstrated recoverable extension within $\gamma < 5$ before rupture, whereby vulcanisates without activator content had typical stress-induced crystallisation behaviour, as compared to the 2 p.h.r. ZnO vulcanisate, which exhibited sudden increased in stress before rupture. As for the MgO nanoparticle vulcanisates, the stress-strain curves at 12 and 20 p.h.r. loadings showed abrupt increase in stress before rupture. It was anticipated that significant shifts might be due to the effect of strain-induced crystallisation\textsuperscript{18}. This occurrence can enhance the degree of intermolecular correlations as the crystallites formed would act as additional crosslinks in the polymer network and subsequently correspond to a significant toughening of the vulcanisates.

The mechanical properties for NR vulcanisates at varied activator contents are tabulated in Table 2. Generally, 2 p.h.r. of ZnO-activated vulcanisate performed better, as compared to the varied loadings of the MgO nanoparticle vulcanisates. Nevertheless, it should be highlighted that with larger amounts of the MgO nanoparticle loadings, gradual increase in tensile and tear properties was observed. These indicate good

![Figure 3. Stress-strain ($\sigma/\gamma$) curve for rubber vulcanisates with varied contents of metal oxides as activator](image-url)
interactions between the MgO nanoparticles with chemicals in the polymer matrix. On the other hand, the modulus at 100% ($M_{100}$), modulus at 300% ($M_{300}$) and elongation at break decreased with increasing content of MgO nanoparticles. This may be due to low activation energy of the MgO, which caused heterogeneities in the rubber matrix$^{19,20}$. This phenomenon leads to the formation of weak points or flaws within rubber chains, consequently reducing the vulcanisates’ strength and extensibility.

In order to understand the relationship between the properties and morphology, SEM images of inner structure of the NR vulcanisates after incising through FIB technique were captured. SEM images for the sliced surface of the vulcanisates are illustrated in Figure 4. The bright domain represents aggregate complexes, while the dark denotes the rubber matrix. In Figure 4a, no visible aggregate was observed in the absence of an activator, but the aggregate complexes were observable once the activator is present in the rubber compounds (Figure 4b, 4c and 4d). It was also noticed that the 2 p.h.r. ZnO-control vulcanisate tended to create micro-sized aggregates, while MgO nanoparticle vulcanisates were having smaller aggregates that distributed throughout the rubber matrix. Low activation energy of the MgO nanoparticles could be accounted for this occurrence, which is well correlated with the curing and mechanical properties achieved.

Figure 5 shows the TEM images for rubber vulcanisates with different activator contents. The bright domain represents the rubber matrix, while the dark domain denotes the aggregate complexes. The micrographs showed that amount of aggregate complexes in the rubber matrix increased with increasing content of MgO nanoparticles and these findings were consistent with the FIB/SEM analysis.

**CONCLUSION**

MgO nanoparticles could be considered as a potential alternative activator for sulphur vulcanisation of NR. Its catalytic behaviour in some ways is comparable to ZnO during the vulcanisation reaction of NR, but its performance is to some extent lower to that of ZnO due to its low activation energy. Nevertheless, its positive effect in enhancing the vulcanisation efficiency and improving vulcanisate properties, especially at 12 and 20 p.h.r. loadings is a worthy consideration. In view of the current results, comprehensive research should be further explored with MgO nanoparticles if its substitution of ZnO is preceded. Overall, this work is particularly
relevant as reducing the use of ZnO is an important ecological goal for the rubber industry.

ACKNOWLEDGEMENTS

All the research work reported here was part of the author’s masters study, conducted at Nagaoka University of Technology, Japan. The author would like to thank the Director General of Malaysian Rubber Board for the financial support and permission to publish this paper. The authors’ acknowledgement also goes to all other respective persons who contributed towards successful completion of her study.

Date of receipt: May 2013
Date of acceptance: October 2013

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