

# Effect of CaCO<sub>3</sub> nanoparticles and synthesized ZnO nanoparticles on the properties of natural rubber

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**Abstract.** The effect of the synthesized zinc oxide nanoparticles (sZnO) and calcium carbonate nanoparticles (NCC) on the cure characteristics and mechanical properties of natural rubber were investigated. The sZnO synthesized by microwave assisted aqueous precipitation method using zinc nitrate hexahydrate and sodium hydroxide as a precursor. The morphology of the sZnO is a spherical shape with the average primary size of 46.63 nm and the specific surface area of 38.87 m<sup>2</sup> g<sup>-1</sup>. For the NCC is a commercial grade with the average primary size of 66.67 nm and the specific surface area of 28.97 m<sup>2</sup> g<sup>-1</sup>. Based on the obtained results, in the unfilled natural rubber, sZnO can be reduced successfully from 5 to 1 phr compared to conventional ZnO (cZnO) and increase tensile strength, 300% modulus and elongation at break by 11%, 9% and 11%, respectively. In case of sZnO and NCC filled with natural rubber, it increases tensile strength, 300% modulus and tear strength by 19%, 19% and 18%, respectively compared to conventional grade (cZnO and CC) in microparticles. This benefit is due to small grain size and large specific surface area of nanoparticles.

## 1. Introduction

Zinc oxide (ZnO) uses as an activator to the sulphur vulcanizing system and play an important role in rubber crosslinking [1]. In generally, the conventional ZnO always used in natural rubber or synthetic rubber formulation at 5 parts per hundred parts of rubber (phr) with stearic acid 1 phr for the optimum cure state. Nowadays, there is currently a tendency to reduce the dosage of ZnO in rubber compound because it is suspected to negative environmental effects. The nanomaterials may be improved the rubber properties and reduce the dosage due to small grain sizes and large specific surface area for the example nanoclays, nanocalcium carbonate and carbon nanotubes [2, 3]. For ZnO nanoparticles, aqueous precipitation is widely method for synthesis of ZnO nanoparticles with various morphologies by changing conditions such as precursor, pH, temperature and reactive time [4, 5]. This method is a simple, low cost and environmental friendly. For reactive time can be shortened by microwave heating. The microwave-assisted heating has various advantages such as rapid and selective heating [6]. Additionally, calcium carbonate (CaCO<sub>3</sub>) is a type of filler which always load to compound for cost reduction because it is a non-reinforcing filler. Thus, calcium carbonate is being developed to replace of silica or carbon black for improve rubber properties. As is well known, nanotechnology is the science that makes materials on the nanometer scale. Therefore it increases interface area between rubber and filler. This is significantly causes to improve in the rubber properties. The aim of this research is studied the effect of CaCO<sub>3</sub> nanoparticles (NCC) and synthesized ZnO nanoparticles (sZnO) by microwave-assisted precipitation method on the rubber properties; as compared to conventional CaCO<sub>3</sub> (CC) and conventional ZnO (cZnO).

## 2. Experimental

ZnO nanoparticles (sZnO) were synthesized by precipitation method using NaOH (Qrec) aqueous solutions and aqueous solution containing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Qrec) and polyacrylic acid (PAA, Sigma-Aldrich). The solution was put in a microwave oven (Sharp, 220 V 50Hz) for 5 min. The precipitates were calcined at 200°C for 2 h. Morphology of sZnO and NCC was observed by transmission electron microscopy (TEM, JEM 2010, JEOL). The specific surface areas were investigated by Brunauer-Emmett-Teller (BET) technique.

Rubber formulations of the unfilled natural rubber were illustrated in table 1. Natural rubber, ZnO and stearic acid were masticated in the mixer for 2 min. The rubber accelerator (MBTS and TMTD) and sulphur were added on a two roll mill at room temperature (35°C) and sheeted off to a thickness of 8 mm. The cZnO was purchased from Univentures. Preparation of NCC filled with natural rubber used the NCC was purchased from Nano Materials Technology, Ltd. The CC was obtained from Formosa Plastic, Ltd. The compounds were mixed following the formulations in table 2. Natural rubber, ZnO and stearic acid were masticated in the mixer for 2 min. The  $\text{CaCO}_3$  and rubber antioxidant (TMQ) were then added and continuously mixing for 4 min. The rubber accelerator (MBTS and TMTD) and sulphur were added on a two roll mill and sheeted off to a thickness of 8 mm.

The cure characteristics of the rubber compounds were measured at 170°C for 10 min with a MDR2000. The  $M_H-M_L$ , the  $t_{10}$  and the  $t_{90}$  were determined. The mechanical properties such as hardness, tensile strength, 300% modulus, elongation at break and tear strength were determined. The hardness test was performed using a hardness tester (Teclock) using a Shore A durometer. An Instron Universal testing machine was used to determine tensile strength, 300% modulus and elongation at break of the samples at  $23 \pm 2^\circ\text{C}$ , with an extension speed of  $500 \text{ mm min}^{-1}$ . The tear strength was measured with a universal testing machine.

## 3. Results and discussion

Figure 1 shows TEM image of sZnO and  $\text{CaCO}_3$  nanoparticles (NCC, commercial grade). The morphology of sZnO exhibited a spherical shape with the average primary size of 46.63 nm. The morphology of NCC exhibited a nearly spherical shape with the average primary size of 66.67 nm. The specific surface area of sZnO and NCC are 38.87 and  $28.97 \text{ m}^2/\text{g}$ , respectively.

The cure characteristics of the unfilled natural rubber which is filled cZnO at 5 phr compared to sZnO at various contents by 0.5, 1 and 5 phr and summarized in table 3. It can be observed that the  $M_H-M_L$ , the  $t_{10}$  and the  $t_{90}$  are slightly increased with the increasing sZnO content. The  $M_H-M_L$  is indirectly related to the crosslink concentration of rubber vulcanized. The relative torque shows an increasing value which is probably due to small grain size and large specific surface area of sZnO. As same loading, sZnO shows the improvement of cure state higher than cZnO. Note that the natural rubber filled cZnO at 5 phr is same degree of crosslinking compared to sZnO at 1 phr. This test result related to the fact that small grain size lead to increase the crosslink density in the rubber vulcanized.

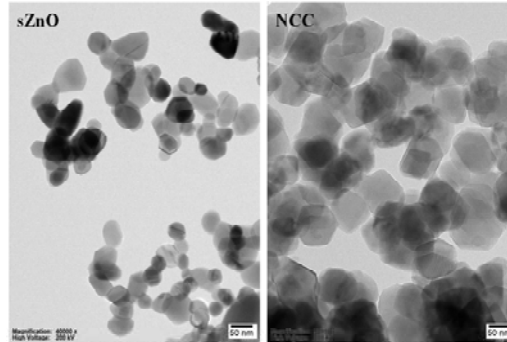
The effect of ZnO type on the mechanical properties is also given in table 3. It can be seen that the hardness, tensile strength and 300% modulus are increased with the increasing sZnO content. A similar trend is previously observed in the  $M_H-M_L$  of the rubber compound. This is attributed to increase in the crosslink density and can be seen in enhanced the rubber properties. Whereas, the elongation at break shows a decreasing trend with the increasing sZnO content. This phenomenon is due to the increasing crosslink density and it is indicated that the compound exhibits more rigid behavior than the elastic behavior; as previously reported by Sahoo et al [1] and Kim et al [3], enhancement of the rubber properties depend on the increment of specific surface area of sZnO leads to an increase in the degree of crosslinking. In particular, the tensile strength, 300% modulus and elongation at break of rubber compound which uses sZnO at 1 phr are  $169 \pm 3 \text{ kgf cm}^{-2}$ ,  $16.22 \pm 0.04 \text{ kgf cm}^{-2}$  and  $800 \pm 10 \%$ , respectively. It is improved by 11%, 9% and 11%, respectively compared to the rubber compound uses the cZnO at 5 phr. Therefore, the large specific surface area and smaller grain size of sZnO can be reduced successfully from 5 to 1 phr when compared to cZnO.

**Table 1.** Formulations of the unfilled natural rubber.

Materials	cZnO- 5 phr	sZnO- 0.5 phr	sZnO- 1 phr	sZnO- 5 phr
Natural rubber	100	100	100	100
cZnO	5	-	-	-
sZnO	-	0.5	1	5
Stearic acid	1	1	1	1
MBTS	1	1	1	1
TMTD	0.3	0.3	0.3	0.3
Sulphur	2.5	2.5	2.5	2.5

**Table 2.** Formulations of CaCO<sub>3</sub> filled with natural rubber.

Materials	cZnO-5/ CC-80 phr	sZnO-1/ CC-80 phr	sZnO-1/ NCC-60 phr	sZnO-1/ NCC-70 phr	sZnO-1/ NCC-80 phr
Natural rubber	100	100	100	100	100
cZnO	5	-	-	-	-
sZnO	-	1	1	1	1
CC	80	80	-	-	-
NCC	-	-	60	70	80
Stearic acid	1	1	1	1	1
TMQ	1	1	1	1	1
MBTS	1	1	1	1	1
TMTD	0.3	0.3	0.3	0.3	0.3
Sulphur	2.5	2.5	2.5	2.5	2.5

**Figure 1.** TEM images of sZnO and NCC.**Table 3.** The cure characteristics and mechanical properties of the unfilled natural rubber.

Properties	Unit	cZnO-5 phr	sZnO-0.5 phr	sZnO-1 phr	sZnO-5 phr
The differential torque ( $M_H-M_L$ )	lb in	4.50	3.96	4.52	4.95
The cure time ( $t_{10}$ )	Min	0.75	0.65	0.72	0.76
The optimum cure time ( $t_{90}$ )	Min	1.29	1.11	1.26	1.32
Hardness	Shore A	39±1	36±1	40±1	41±1
Tensile strength	kgf cm <sup>-2</sup>	152±5	132±4	169±3	182±5
300% Modulus	kgf cm <sup>-2</sup>	14.89±0.05	12.21±0.03	16.22±0.04	17.37±0.05
Elongation at break	%	720±10	820±20	800±10	760±20

According to previously studied about effect of sZnO on the cure characteristics and mechanical properties of the unfilled natural rubber. The test results show at 1 phr of sZnO is minimize content that provide superior properties when compared to cZnO. Therefore, we fixed the content of sZnO at 1 phr to study the properties of natural rubber vulcanizates filled with NCC compared to CC. The influence of the NCC on the cure characteristics and mechanical properties can be seen in table 4. The results show that when NCC increased, the  $M_H-M_L$  also increased but the values of the  $t_{10}$  and the  $t_{90}$  slightly decreased. This is indicated that increase in the interaction between filler and rubber. For the cure time is significantly decreased due to increment of viscosity of the rubber compound. When

considering the NCC loading on mechanical properties such as hardness, tensile strength, 300% modulus and tear strength. It can be observed that all properties are increased with the increasing NCC content. This may be caused an increment in reinforcement of nanoparticles which correspond to increase in the  $M_H$ - $M_L$ . On the other hand, it is also found that the elongation at break gradually decreased because it disrupt to extension of the rubber chains. Furthermore, the evaluation of sZnO-1/NCC-80 phr compared to sZnO-1/CC-80 phr; as same loading content. The results of tensile strength, 300% modulus and tear strength revealed that NCC enhances the rubber properties higher than CC. The TEM images of NCC; as see in figure 1. The NCC shows that its small grain size and large surface area which may be attributed to highly interaction with rubber chains and provide to the superior rubber properties. Additionally, we evaluated the effect of sZnO-1/NCC-80 phr on the rubber properties to compare with cZnO-5/CC-80 phr in the natural rubber vulcanizates. It can clearly see that the nanotechnology which conducted at the nanoscale will enhance the rubber properties such as the tensile strength, 300% modulus and tear strength are  $203 \pm 4$  kgf cm<sup>-2</sup>,  $31.01 \pm 0.05$  kgf cm<sup>-2</sup> and  $41.66 \pm 0.04$  kgf cm<sup>-1</sup> (increased by 19%, 19% and 18%, respectively) compared to conventional grade.

**Table 4.** The cure characteristics and mechanical properties of the natural rubber vulcanizates.

Properties	Unit	cZnO-5/ CC-80 phr	sZnO-1/ CC-80 phr	sZnO-1/ NCC-60 phr	sZnO-1/ NCC-70 phr	sZnO-1/ NCC-80 phr
The differential torque ( $M_H$ - $M_L$ )	lb in	6.69	6.72	6.52	6.91	7.17
The cure time ( $t_{10}$ )	min	0.58	0.56	0.61	0.60	0.59
The optimum cure time ( $t_{90}$ )	min	1.06	1.02	1.14	1.08	1.03
Hardness	Shore A	48 $\pm$ 1	49 $\pm$ 1	45 $\pm$ 1	47 $\pm$ 1	49 $\pm$ 1
Tensile strength	kgf cm <sup>-2</sup>	170 $\pm$ 5	182 $\pm$ 3	166 $\pm$ 4	188 $\pm$ 5	203 $\pm$ 4
300% Modulus	kgf cm <sup>-2</sup>	25.99 $\pm$ 0.03	27.13 $\pm$ 0.05	25.54 $\pm$ 0.04	29.11 $\pm$ 0.04	31.01 $\pm$ 0.05
Elongation at break	%	690 $\pm$ 20	700 $\pm$ 30	740 $\pm$ 20	700 $\pm$ 30	650 $\pm$ 30
Tear strength	kgf cm <sup>-1</sup>	35.05 $\pm$ 0.05	37.20 $\pm$ 0.04	34.87 $\pm$ 0.05	39.22 $\pm$ 0.05	41.66 $\pm$ 0.04

#### 4. Conclusions

In the unfilled natural rubber, the cure characteristics and mechanical properties such as hardness, tensile strength and 300% modulus are increased but elongation at break is decreased with the increasing sZnO content. However, sZnO at 1 phr can improve the tensile strength, 300% modulus and elongation at break by 11%, 9% and 11%, respectively compared to cZnO at 5 phr. This is due to large specific surface area and smaller grain size lead to enhancing the crosslink density. Therefore, sZnO can be reduced successfully from 5 to 1 phr when compared to cZnO. In case of sZnO and NCC filled with natural rubber, we fixed the content of the sZnO at 1 phr because minimize dosage that provide superior properties. The cure characteristics and mechanical properties of rubber compound are improved when compared to conventional grade (cZnO and CC). The sZnO and NCC can improve the tensile strength, 300% modulus and tear strength by 19%, 19% and 18%, respectively.

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