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Contributed Paper

## Nanomodified ZnO in Natural Rubber and Its Effects on Curing Characteristics and Mechanical Properties

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### ABSTRACT

The wurtzite nanoparticles zinc oxide (n-ZnO) was prepared by using peroxide based route in this study. The effect of particle size of ZnO on cure characteristics and mechanical properties of natural rubber (NR) compounds were inquired. Two types of ZnO, commercial grade ZnO (c-ZnO) and n-ZnO, were used and compared. Masterbatches of ZnO particles were prepared by coagulation with formic acid of mixture between high ammonia latex with dry rubber and ZnO suspension. The dried masterbatches were mixed with vulcanizing ingredients on a two roll mill. The cure characteristic and tensile testing were determined. The n-ZnO filled compounds gave higher maximum torque and torque difference. The hardness of n-ZnO filled NR was higher. Moreover, the modulus at 300% elongation and tensile strength of n-ZnO filled compound were higher than that of c-ZnO filled rubber.

**Keywords:** Zinc oxide, natural rubber, mechanical properties

### 1. INTRODUCTION

Natural rubber (NR) is the most abundant natural polymer in the world. It is used widely in products such as tyres, condoms, and O-rings, due to its excellent tensile strength, damping properties, and elasticity [1]. The properties displayed by a particular rubber are determined by the compound composition, proper combination of chemicals and additives, and the vulcanization process. The vulcanization involves the conversion of raw rubber into a network through the formation of

crosslinks, a fluid material is transformed into an elastic rubbery product [2]. The desired property improvements obtainable through vulcanization include hardness, tensile strength, modulus and permanent set [3].

Zinc oxide (ZnO) is one of the basic components of rubber compounds. In natural rubber (NR), ZnO, stearic acid, accelerators and sulfur constitute the vulcanization system. The ZnO acts as an activator for rubber crosslinking by sulfur or sulfur donors [4-5],

it increases the amount of bound sulfur and the efficiency of the crosslinking system [6]. It can also be used as a good crosslinking agent in carboxylic rubbers [7-8], elastomers containing halogen groups [9], and also used as fillers in elastomers [10]. The physical properties of vulcanizates, namely heat buildup and abrasion resistance are influenced by ZnO.

In the vulcanization of NR, conventional ZnO (micro) is used as an activator and in general practice about 5 phr is the dosage. The reduction in the quantity of ZnO is worthwhile because it is relatively expensive pigment and has high density. Of late considering this problem, the use of nano ZnO in NR [11-13] and neoprene rubber was studied [14].

The aim of this study is to investigate the use of nano ZnO as cure activator in NR vulcanization instead of conventional micro ZnO.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The NR used in this study was high ammonia latex concentrate with 60% dry rubber content, supplied by Lucky Four Company (Nontaburi, Thailand). All other rubber ingredients used were commercial grade, supplied by Lucky Four Company (Nontaburi, Thailand). The compounding formulations are given in Table 1.

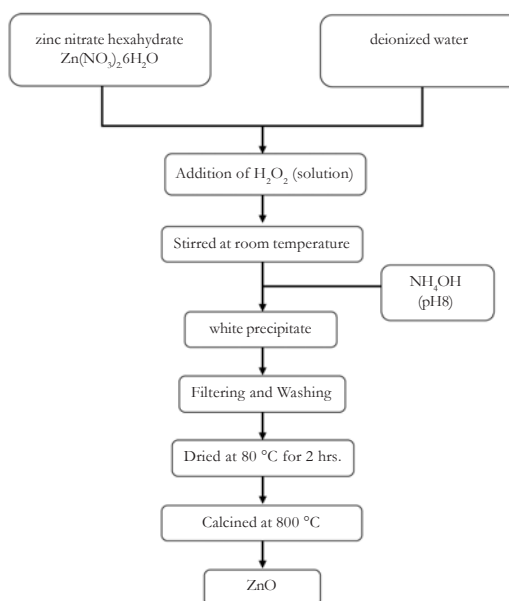
### 2.2 Preparation of Nano-zinc Oxide

The wurtzite n-ZnO was prepared by using peroxide based route as shown in Figure 1. In this synthesized method, zinc nitrate solution was prepared by dissolving 36.591 g of zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ) in 150.00 mL of deionized water. 12.53 mL of 30% hydrogen peroxide solution ( $H_2O_2$ ) was added to the zinc nitrate solution with vigorous stirring at room

temperature for 30 min. After that, the ammonium hydroxide ( $NH_4OH$ ) was added for adjusting the pH value which was taken to be 8 and the white precipitate was obtained. The precipitate was filtered using Büchner funnel and washed with deionized water several times. The obtained precipitate was dried at 80 °C for 2 hrs and then calcined at 800 °C for 3 hrs. The obtained wurtzite n-ZnO was collected and used for preparing of rubber compounding.

**Table 1.** Compounding formulations.

Chemical ingredients	phr
ZnO Masterbatch	101
Stearic acid	2.5
TBBS	1.8
Sulfur	1.2
TMQ	1
6PPD	1
Silica	20
Silane coupling agent	1.2
Paraffinic oil	5



**Figure 1.** Diagram of nano-ZnO synthesis.

### 2.3 Preparation of Rubber Compounding

The dried ZnO masterbatches were compounded by a Two-roll mill. The masterbatches were firstly masticated for 5 min at room temperature. The ingredients, silica, silane coupling agent, stearic acid, paraffinic oil, N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine (6PPD), Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), N-tert-butyl-2-benzothiazyl sulfenamide (TBBS) and sulfur were then sequentially added and mixed on the mill for 30 min. The compounds were then sheeted out and left at room temperature for at least 16 h before fabricating by compression molding at 150°C and testing.

### 2.4 Cure Characteristics

The cure characteristics of the compound were examined according to ASTM D 5289 at testing temperatures of 150 °C, using a moving die rheometer (MDR) (UR-2010, U-CAN Dynatex INC., Taiwan). The minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), torque difference ( $M_H - M_L$ ), scorch time ( $t$ ), cure time ( $t_{90}$ ) and cure rate index (CRI) were determined.

### 2.5 Mechanical Properties

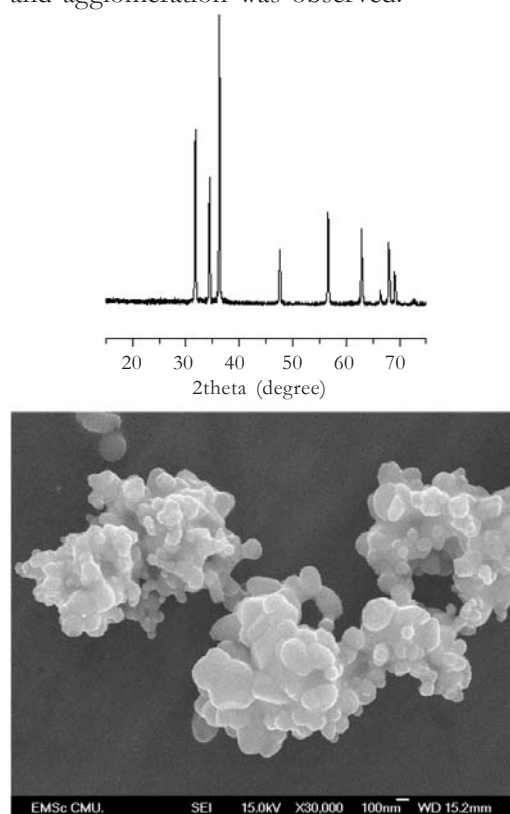
The hardness of the NR vulcanizate was measured in accordance to ASTM D2240 by using indentation durometer shore A. The resilience of the vulcanizate was determined by Schob pendulum rebound tester according to DIN 53512. The Tensile was carried out using the Universal testing machine (INSTRON 3366) according to ASTM D412.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of n-ZnO

XRD pattern of the wurtzite n-ZnO prepared by using peroxide based route (JCPDS No. 01-079-0206) was shown in

Figure 2. The clarification in the particle size of the prepared n-ZnO was given in the of SEM observation. SEM micrograph of the prepared n-ZnO (Figure 2.) displays the particles with size below 100 nm and exhibit regular sphere-like particles. The SEM image of the prepared n-ZnO also identified an individual particle, particle aggregation, and agglomeration was observed.



**Figure 2.** X-ray diffraction (XRD) pattern and scanning electron microscope (SEM) micrograph of nano-ZnO particle.

### 3.2 Cure Characteristics

Table 2 shows the cure characteristics of the compounds containing various processing oils. The scorch time generally defines the time to onset of vulcanization at a particular temperature and thus represents the limit time available for processing. Cure time is the time required during the vulcanization step for the required amount

of crosslinking to occur, yielding the desired level of properties. Minimum torque is related with the viscosity or plasticity of the unvulcanized stock, while maximum torque and torque difference (Delta torque) may give an idea upon maximum extent of cure (i.e. crosslink density). The results show that the nanoparticles ZnO (n-ZnO) filled compounds gave higher maximum torque and torque difference than that of commercial ZnO (c-ZnO). This is due to the higher interaction of n-ZnO particles in vulcanization process, leading to increase degree of crosslink density of rubber molecules. Moreover, the scorch time and cure time was lower for the compound prepared with n-ZnO. This is due to the n-ZnO particles increase the rate of vulcanization by activating the accelerator when compared with c-ZnO, which corresponds to higher cure rate index.

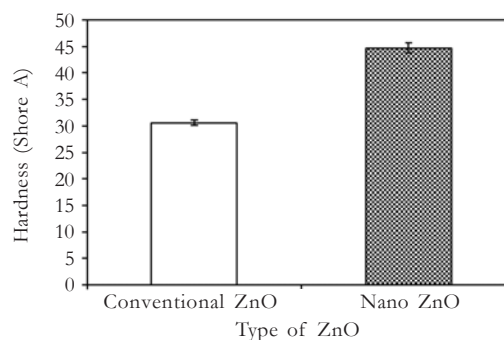
**Table 2.** Cure characteristics.

Properties	Unit	c-ZnO	n-ZnO
Minimum torque	dN.m	0.45	0.54
Maximum torque	dN.m	7.40	19.18
Torque difference	dN.m	6.95	18.64
Scorch time	min	4.42	3.15
Cure time	min	7.31	5.35
Cure rate index	1/min	43.01	47.37

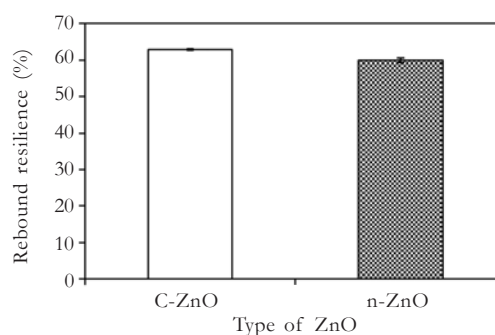
### 3.3 Mechanical Properties

Figure 3 shows hardness of NR vulcanizate. It was found that the hardness of n-ZnO was higher than that of c-ZnO. This is due to higher crosslink density of rubber molecules which corresponds to higher torque difference. The rebound is terms as ratio of the energy returned to the energy applied Figure 4. shows that the resilience of n-ZnO filled vulcanizate slightly lower than that of c-ZnO. Even though the n-ZnO has a higher crosslink density, the rebound resilience is low. This is probably due to the silica reinforcement of rubber that hinders

the elasticity of the vulcanizate and hence the energy is dissipated as heat. Higher rebound resilience value of c-ZnO indicated the ability of their molecules to store energy.



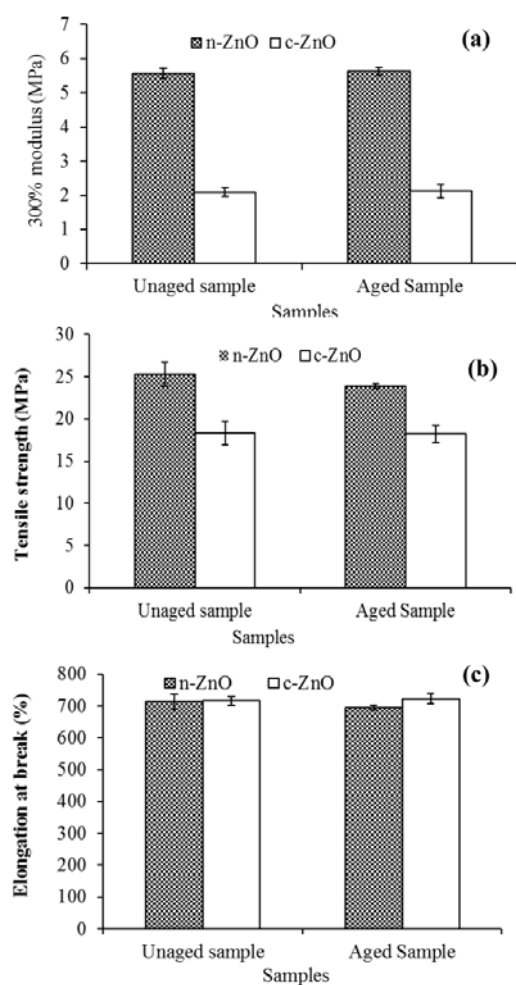
**Figure 3.** Hardness of NR vulcanizate with various types of ZnO.



**Figure 4.** Rebound resilience of NR vulcanizate with various types of ZnO.

The tensile properties are shown in Figure 5. (a) modulus at 300% elongation and (b) tensile strength (before and after aging) of n-ZnO filled vulcanizate were higher than that of c-ZnO. It can be explained that n-ZnO can be produced crosslinking of rubber molecules and strain-induced crystallization which also corresponds to higher maximum torque, torque difference and hardness. However, after aging, no distinctive variance in modulus at 300% elongation was observed for both of ZnO. Nevertheless, the tensile strength of n-ZnO filled vulcanizate was slightly decreased after aging but not changed in c-ZnO.

The %elongation at break of n-ZnO filled vulcanizate was lower than that of c-ZnO because n-ZnO filled vulcanizate has a higher crosslink density resulted in reduction of the deformability of rubber. In addition, elongation at break of n-ZnO filled vulcanizate after aging was decreased but in the case of c-ZnO filled vulcanizate was increased.



**Figure 5.** 300% modulus (a), tensile strength (b), and (c) elongation at break of NR vulcanizate with various types of ZnO.

#### 4. CONCLUSIONS

The improvement in curing characteristics and mechanical properties of NR was obtained by incorporation with n-ZnO into the NR matrix. By using of n-ZnO instead of c-ZnO, the compound requires a shorter cure time. In addition, the hardness, rebound resilience, modulus at 300% elongation and tensile strength were enhanced. The NR/n-ZnO composites also show better mechanical properties compared to the NR/c-ZnO composite at the same ZnO content.

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