Synthesis of nano zinc oxide and its effect on the cure characteristic and properties of natural rubber vulcanizates

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Abstract. In this work, nano ZnO was synthesized by a simple method using a polymeric substance as a dispersing agent. Characterization of the synthesized ZnO by XRD and SEM confirmed the ZnO was nanometric in size and had a wurtzite structure. The synthesized nano ZnO was used as an activator for natural rubber vulcanization. Different amount of ZnO, 1, 2, and 3 phr, was investigated in the rubber formulation and compared to conventional ZnO at a typical amount (6 phr). The sample with 3 phr nano ZnO showed the lowest curing induction time with the highest (M_L-M_H) at all studied temperatures. Furthermore, the rubber sample with 3 phr ZnO achieved the best properties, i.e., crosslink density, rebound resilience, and hardness compared to the rubber sample with 6 phr conventional ZnO. Interestingly, the properties of rubber sample with 2 phr nano ZnO were probably equivalent and comparable to that of 6 phr conventional ZnO. Thus, it suggested that the synthesized nano ZnO could replace the conventional ZnO as an activator for rubber vulcanization even at a lower amount.

1. Introduction

Vulcanization is one of the most critical technologies that has been explored and utilized to bring about the practical application for rubber materials. After vulcanization, the inherent elasticity of unvulcanized rubber becomes more durable under the severe conditions. The crosslinking between rubber particles plays a vital role in making the polymer to be more elastic and durable [1]. There are many types of crosslinking, such as peroxide crosslinking [2-4], irradiation crosslinking [5], sulfur crosslinking or so-called vulcanization [6]. Sulfur vulcanization uses sulfur as a crosslinking agent. However, sulfur vulcanization takes place at a very high temperature and needs a long time to accomplish. Thus, some additives such as accelerator, activator (ZnO), fatty acids, and antioxidants have been used to promote the rubber vulcanization’s efficiency.

Zinc oxide (ZnO) is one of the chemical compounds that was widely used for rubber vulcanization. It serves as an activator that improving the curing and providing short sulfide crosslink junction [7]. In
the presence of ZnO, the vulcanization is expected to generate a high crosslink density. ZnO could react with accelerator to form zinc chelates which subsequently interact with sulfur to form zinc polysulfide complexes. These polysulfide complexes will react with rubber molecules to generate a sulfide crosslink structure. Unfortunately, zinc compounds are known to be harmful to the ecological environment, as reported [8]. Thus, the amount of zinc used for rubber technology should be decreased as much as possible. To solve this problem, nano ZnO has arisen as a prominent candidate for replacing micro ZnO in rubber vulcanization [9,10]. Since the small size of ZnO could enhance the contact with accelerator and bring about the increase in vulcanization efficiency even at a small dosage of ZnO.

Nano ZnO was synthesized by different methods, such as chemical precipitation [11], sol-gel [12], hydrolysis [13], solid-state pyrolytic [14], solution-free mechanochemical method [15], and biological method [16]. Chemical precipitation is one of the most straightforward strategies to produce nano ZnO with high efficiency. There are a great variety of methods for synthesizing the ZnO in nanoscale. To obtain the nano size of ZnO with the precipitation method, stabilizing or dispersing agents are used to prevent the agglomeration and formation of large ZnO particles. The role of dispersive agents is to maintain the stability of the reaction and thus enhance the homogeneity of ZnO particles.

In the present work, we aim to synthesize the nano ZnO particles using a chemical precipitation method assisted with polyacrylamide (PAA) as a dispersing agent. Effect of various conditions on the preparation of nano ZnO such as reaction temperature, pH, maturation time, amount of PAA dispersing agent was studied to find out the optimum condition. The synthesized nano ZnO was characterized by XRD and SEM. The rubber vulcanization using the synthesized nano ZnO as an activator was investigated. The effect of ZnO dosages on the curing characteristic and properties of rubber vulcanizates were also discussed.

2. Experimental

2.1. Materials
Zinc sulfate (ZnSO₄·7H₂O 98%) was from Krins, Chian, and sodium hydroxide solution (NaOH, 98%) was purchased from Sigma. Polyacrylamide N101 was purchased from Merck. STA (99.9%) was formed Origin, Malaysia. SVR3L was provided by a Vietnam rubber company. Sulfur, TBBS, micro conventional ZnO were brought from China. The other chemicals are analytical grade.

2.2. Synthesis of nano ZnO
ZnO nanoparticles were synthesized by precipitation method assisted with a dispersive agent, polyacrylamide (PAA) grade N101. First, a sodium zincate solution (0.5M) was prepared from zinc sulfate solution (0.5M) with sodium hydroxide solution. Then zincate solution and zinc sulfate were added to the reaction flask at the same time as the PAA solution, and the pH of the reaction was adjusted in the range from 8 to 10 by changing the flowing rate of zincates and zinc sulfate solution. The PAA (with different amounts from 2, 4, 6, and 8 ppm) was continuously injected during the reaction. The reaction was prolonged for about 5 min under stirring at different temperatures (30, 40, 50, and 60°C) and then kept for different maturation times (0.5, 1, 2, and 3 hours). After that, the appeared white precipitates were filtered by centrifugation and washed with distilled water, assisted with ultrasonication for 15 mins until SO₄²⁻ was removed entirely. The removal of SO₄²⁻ was confirmed by BaCl₂ reagent until no BaSO₄ was formed. The precipitates were dried at 80°C for 4 hours and 120°C for 5 hours to remove water completely. The dried ZnO sample was calcinated at 600°C for 5 hours in a muffle furnace, and the nano ZnO was obtained.

The synthesized nano ZnO was characterized by X-Ray diffraction spectrometer (Bruker D8 Advance, Germany) at \( \lambda = 1.540 \ \text{Å} \) with the angle ranging from 10° to 80°, angle increment of 0.05°. The ZnO sample powder was deposited on the sample holder before the measurement.
Morphology of ZnO particles was observed with scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan). The sample was deposited on the substrate and coated with Pt before the observation.

2.3. Compounding and vulcanization

Compounding and vulcanization were performed in an internal mixer, Baopin 8412 (China), for 8 mins at 70°C and 30 rpm. The formulation for rubber vulcanization is given in Table 1. The formulation used is typical for rubber vulcanization. The amount of nano ZnO used is 1, 2, and 3 phr, lower than a conventional dosage of 6 phr. The compounded rubber was tested with a Rheometer (MDR 2020) according to ASTM D5289 at various temperatures, i.e., 140, 145, 150, 155, 160°C. The $t_{90}$, $M_R$, and $M_L$ were determined to study the kinetic of rubber vulcanization.

| Ingredients (phr) | Sample name |
|-------------------|-------------|
|                   | NR-nn1      | NR-nn2 | NR-nn3 | NR6 |
| NR (SVR3L)        | 100         | 100    | 100    | 100 |
| Sulfur            | 3.5         | 3.5    | 3.5    | 3.5 |
| TBBS              | 0.7         | 0.7    | 0.7    | 0.7 |
| Stearic acid      | 0.5         | 0.5    | 0.5    | 0.5 |
| Nano ZnO          | 1           | 2      | 3      | -   |
| Micro ZnO         | -           | -      | -      | 6   |

2.4. Characterizations

The swelling test was performed according to ASTM D471-12a. The rubber samples were cut in a dimension of (25±2) x (25±2) mm with a thickness of (2±0.2) mm. Then it was immersed in toluene for 72 hours. The swelling degree was calculated from the weight difference of the sample before and after swollen as shown in equation (1). From the swelling degree, the crosslinking density was calculated, followed by the Flory-Rehner equation.

$$\text{swelling degree (\%)} = \frac{m_1 - m_0}{m_0} \cdot \frac{1}{m_1}$$

$$- \left[ \ln(1 - V_r) + V_r + \chi V_r^2 \right] = 2V_s \left( V_r^{1/3} - \frac{V_r}{2} \right)$$

where, $m_0$ and $m_1$ are the mass of the sample before and after immersion in toluene, $\rho_1$ and $\rho_2$ are the density of solvent and rubber, $V_s$ is the partial molar volume of solvent; $V_r$ is the volume fraction of the sample at the saturated swelling and $\chi$ the solubility parameter. The value of $\chi$ is found to be 0.43 for the NR-toluene system [17].

Hardness (shore A) for rubber samples was determined using a Durometer tester (TFCLOCKGS 790N, Japan) following by ISO 7619-1. The samples were prepared with a thickness of (6±0.2) mm.
Measurement of compression set was carried out according to ASTM D395-03:2008 at room temperature and 70°C, and rebound resilience property was estimated according to ASTM D2632-01.

3. Result and Discussion

3.1. Characterization of synthesized nano ZnO

Figure 1 shows the XRD pattern of nano zinc oxide (ZnO). There are characteristic peaks that appeared at 2θ = 31.7°, 34.5°, 36.2°, 47.5°, and 56.6°. These sharp and intense peaks confirmed the high crystallinity and purity of the synthesized ZnO. Furthermore, these peaks are consistent with the characteristic peak of standard ZnO and confirmed that the synthesized ZnO is of wurtzite hexagonal structure [18]. From the XRD result, the peak at 2θ = 47.5° was selected to calculate the ZnO crystal size following the Scherrer equation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where, D is crystallite size, β is the full-width at half maximum of the diffraction peak, K is constant (0.89), λ is the wavelength of X-ray radiation (0.154 nm), and θ is the Bragg’s angle. The size of ZnO crystallite was evaluated from the full-width at half maximum of the most intense peak, that is, at 2θ = 47.5°.

Table 2 shows the results of XRD at various pH and temperatures. It can be seen that the crystal size of ZnO increased as the pH of the reaction increased. However, the size of the ZnO crystal decreased when the temperature increased from 30°C to 40°C, and it increased as temperature increased from 40°C to 60°C. The optimum temperature and pH were 40°C at pH=8.

| Temperature | pH=8 | pH=9 | pH=10 |
|-------------|------|------|-------|
|             | β(°) D(nm) | β(°) D(nm) | β(°) D(nm) |
| 30°C        | 0.339 25.31 | 0.309 27.78 | 0.272 31.55 |
| 40°C        | 0.386 22.23 | 0.385 22.59 | 0.319 26.90 |
| 50°C        | 0.368 23.32 | 0.342 25.09 | 0.310 27.69 |
| 60°C        | 0.350 24.52 | 0.332 25.85 | 0.306 28.05 |
The effect of maturation time on the formation of small ZnO particles was investigated at pH=8, temperature 40°C, and 2 ppm of N101. Table 3 illustrates the effect of maturation time on the ZnO crystal size. As the time for the maturation process increase, the size of the crystal produced seems to increase. Therefore, the suitable calcination time was determined to be 1 hour.

**Table 3. Crystallite size of nano ZnO prepared at different maturation time (pH=8; 40°C, 2 ppm of N101)**

| Crystallite size | Maturation time (h) |
|------------------|-------------------|
|                  | 0.5 | 1  | 2  | 3  |
| β(°)             | 0.345 | 0.381 | 0.338 | 0.284 |
| D (nm)           | 24.87 | 22.53 | 25.39 | 30.22 |

The amount of N101 dispersant significantly affects the precipitation method since it prevents the agglomeration of Zn(OH)₂ and produces good dispersion of Zn(OH)₂. Thus, it helps to generate more fine ZnO particles. The result for crystal ZnO size prepared at the various amounts of N101 was given in Table 4. It was seen that the higher amount of N101, the smaller the size of ZnO. Therefore, the suitable amount of N101 was 6 ppm.

**Table 4. Crystallite size of nano ZnO prepared at various amounts of N101 (pH=8; 40°C; maturation time 1 h)**

| Crystallite size | Amount of N101 (ppm) |
|------------------|---------------------|
|                  | 2 | 4 | 6 | 8 |
| β(°)             | 0.381 | 0.443 | 0.557 | 0.551 |
| D (nm)           | 22.53 | 19.40 | 15.43 | 15.58 |

Overall, the optimum condition for ZnO synthesis was as follows: pH=8; 40°C; maturation time 1 h and 6 ppm of N101. Under this optimum condition, the size of the nano ZnO obtained was 15.43 nm. This sample has the smallest size of ZnO. The morphology of the nano ZnO particles observed with SEM (Figure 2) illustrated that the ZnO crystals are hexagonal, with sizes ranging from 50 ÷ 100 nm. This morphology is consistent with the result from XRD pattern of ZnO particles. The result obtained from the XRD and SEM confirmed the successful synthesis of nano ZnO by precipitation method supported with N101 as the dispersing agent.

**Figure 2. SEM images of nano ZnO at 30,000 and 100,000 magnification**
3.2. Cure characteristics

The effect of synthesized nano ZnO as a cure activator for NR was studied. Figure 3 shows the cure characteristic of NR at 140°C. The sample with 1 and 3 phr of nano ZnO, NR-nn1 and NR-nn3, started to vulcanize earlier than the samples 6 phr of conventional ZnO (NR6) and 2 phr of nano ZnO (NR-nn2). It may be because of the nanosize of ZnO, which could form the complex with accelerator more efficiently. The sample NR-nn1 had the lowest $M_L$, indicating that 1 phr was not enough to promote the vulcanization. The difference in minimum ($M_L$) and maximum ($M_H$) torque ($\Delta M = M_H - M_L$) increased as the amount of nano ZnO increased. Also, the ($M_H - M_L$) for NR-nn2, NR-nn3 samples were higher than that for NR6. The increase in ($M_H - M_L$) indicates that the decrease in NR chain mobility due to the formation of crosslinking junctions between rubber particles when the amount of ZnO used increased.

![Rheometer profile of NR containing different ZnO amounts at 140°C](image)

Figure 3. Rheometer profile of NR containing different ZnO amounts at 140°C

The vulcanization characteristic of NR using nano ZnO as an activator at various temperatures such as 145°C, 150°C, 155°C, 160°C were also investigated, and the results are shown in Table 5. As the amount of nano ZnO increased, the $M_H$ values and ($M_H - M_L$) values increased. Interestingly, the NR-nn2 and NR-nn3 had higher torque values higher than NR6. This evidence demonstrated that the nano ZnO had better efficiency in forming crosslink points for NR than conventional ZnO, even at lower amount. Furthermore, the ($M_H - M_L$) values for NR seem to decrease as increasing temperatures. The highest value of ($M_H - M_L$) and $M_H$ was obtained at 140°C.

| Samples  | Temperature (°C) | Min torque, $M_L$ (lb-in) | Max torque, $M_H$ (lb-in) | $\Delta M = M_H - M_L$ (lb-in) |
|----------|-----------------|--------------------------|--------------------------|--------------------------------|
| NR-nn1   | 140             | 1.32                     | 11.83                    | 10.51                          |
| NR-nn2   |                 | 1.8                      | 16.09                    | 14.29                          |
| NR-nn3   |                 | 1.26                     | 16.77                    | 15.51                          |
| NR-6     |                 | 2.27                     | 15.63                    | 13.36                          |
| NR-nn1   | 145             | 1.38                     | 11.72                    | 10.34                          |
According to Arrillaga [19], the kinetics of rubber vulcanization could be considered as a pseudo-first order chemical reaction. The rate equation is shown as: \( \ln(\alpha-x) = -kt + \ln\alpha \). Since the torque values obtained from rheology curves are proportional to the modulus of rubber, we have \((\alpha-x) \sim (M_{H} - M_{L})\), with \( M_{t} \) is the torque at time \( t \). Thus, we got the equation: \( \ln(M_{H} - M_{L}) = -kt + \ln\alpha \). From the rheometer profile, the value of time \( t \), \( M_{t} \), \( M_{H} \) at various temperatures was used to calculate the kinetics constant such as \( k \) constant and activation energy.

Plots of \( \ln k \) versus \( 1/T \) for vulcanization of the NR-nn1, NR-nn2, NR-nn3, and NR6 were shown in Figure 4. In addition, the linear curves of \( \ln k = f(1/T) \) were validated with the \( R^2 \) values of nearly 1. From these curves, the activation energy \( (E_{a}) \) of the vulcanization was obtained and shown in Table 6. The activation energy of NR-nn1, NR-nn2, NR-nn3 varied with different in ZnO content and almost higher than that of NR6.
Figure 4. Dependence of $\ln k$ versus temperatures

Table 6. Kinetic constant and activation energies for rubber vulcanization

| Sample names | $\ln k = f(1/T)$ | $R^2$ | $E_a$ (kJ/mol) |
|--------------|------------------|-------|----------------|
| NR-nn1       | $\ln k = -10956.1/T + 25.76$ | 0.9967 | 91.0           |
| NR-nn2       | $\ln k = -11676.1/T + 26.93$ | 0.9804 | 97.1           |
| NR-nn3       | $\ln k = -12223.1/T + 28.06$ | 0.9932 | 102.0          |
| NR-6         | $\ln k = -11130.1/T + 26.14$ | 0.9969 | 92.5           |

3.3. Properties of NR vulcanizates

The efficiency of vulcanization is evaluated by determining the swelling degree of the rubber in the toluene solution. The result of swelling degree for NR-nn1, NR-nn2, NR-nn3, and NR6 are shown in Figure 5. It was seen that the swelling degree of vulcanized natural rubber decreased as the ZnO content increased. The swelling degree is proportional to crosslinking junctions made from sulfide bridges. It suggested that the increase in ZnO content used in rubber vulcanization gives rise to crosslinking junctions. It is noteworthy that the crosslinking density obtained for NR-nn2 was equivalent to that for NR6. It demonstrated that the nano ZnO with 2 phr can produce a comparable crosslink density to the micro conventional ZnO with 6 phr. This result is consistent with the previous literature that nano ZnO could react with accelerator to produce more crosslink in g junctions than the micro ZnO. It is one of the advantages of using nano ZnO compared to that of micro ZnO.

Table 7 shows the compression set value measured at room temperature and 70°C, the rebound resilience and hardness shore A for the NR-nn1, NR-nn2, NR-nn3, and NR6 samples. The compression set values at room temperature for NR vulcanizates decreased as increasing ZnO content. The compression set represents the fail in the recovery of the sample to its original height. When crosslinking is high, it helps the sample adhere to each other more strongly and reduce the deformation after compression. The compression set value of NR-nn3 is the lowest, indicating the best interaction between rubber particles in this sample. It is consistent with the highest crosslinking density of NR-nn3. However, the compression set value obtained at 70°C were higher than those at room temperature. It is due to the sulfide crosslink may be broken under deformation at high temperatures. Another possible reason is that the ZnO nanoparticles in the rubber may get inclusion more closely to the rubber matrix during compression at high temperatures.
A successful synthesis of nano ZnO by the chemical precipitation method was performed in this work. The optimum condition to prepare nano ZnO was pH 8, reaction temperature 40°C, maturation time 1 h, and 6 phr of N101. The nano ZnO obtained at the optimum condition has the morphology of the wurtzite structure and the size of about 15.43 nm, which was estimated from the XRD spectrum. The

Table 7. Properties of NR vulcanizates

| Sample names | Compression set at room temp (%) | Compression set at 70°C (%) | Rebound resilience (%) | Hardness (shore A) |
|--------------|---------------------------------|-----------------------------|------------------------|-------------------|
| NR-nn1       | 5.26                            | 29.93                       | 63.7                   | 39                |
| NR-nn2       | 3.51                            | 33.20                       | 68                     | 44.2              |
| NR-nn3       | 2.78                            | 39.33                       | 71                     | 46.5              |
| NR-6         | 3.81                            | 35.60                       | 61                     | 43.5              |

As seen in Table 7, the rebound resilience for the samples using nano ZnO got higher values than the micro ZnO. The rebound resilience is determined by the return height of the rubber sample to the drop height. It is expected to be inversely proportional to the hysteresis loss: the more elasticity, the more rebound resilience. The highly rebound resilience of NR-nn3 sample may be explained to be due to the presence of more crosslinking junctions in NR-nn3. The more linkings between rubber particles, the more energy to be stored in the samples.

The hardness shore A of the NR vulcanizates is shown in Table 7. The hardness was seen to increase when increasing the ZnO content. The NR-nn3 had the highest hardness value. The high value of hardness could be related to the crosslinking junctions in the rubbers. The higher the crosslink density, the higher hardness shore A and vice versa.

Overall, the properties of NR vulcanizates were closely related to the amount of crosslinking junctions. The higher crosslinks junctions, the higher properties for NR. It was noted that the properties of NR-nn2 were nearly those of NR6 despite the low amount of ZnO used. This evidence indicates that nano ZnO could replace conventional micro ZnO in acceleration for rubber vulcanization and improvement of NR properties.

4. Conclusion
A successful synthesis of nano ZnO by the chemical precipitation method was performed in this work. The optimum condition to prepare nano ZnO was pH 8, reaction temperature 40°C, maturation time 1 h, and 6 phr of N101. The nano ZnO obtained at the optimum condition has the morphology of the wurtzite structure and the size of about 15.43 nm, which was estimated from the XRD spectrum. The
synthesized nano ZnO was used as an activator for rubber vulcanization at various dosages. The vulcanization is confirmed to occur faster with the higher torque values at 3 phr of nano ZnO than 6 phr of micro ZnO. It proves that the kinetic of rubber vulcanization followed the first-order reaction with different activation energies at different dosages of nano ZnO. The NR vulcanized with 3 phr of nano ZnO achieved the best properties, and it was higher than micro ZnO at 6 phr. It concludes that the nano ZnO synthesized by the precipitation method could accelerate the rubber vulcanization and, at the same time, improve the NR properties.

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