Effect of synthesized ZnO nanoparticles on thermal conductivity and mechanical properties of natural rubber

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Abstract. Zinc oxide (ZnO) is widely used in rubber industry as a cure activator for rubber vulcanization. In this work, comparison of cure characteristic, mechanical properties, thermal conductivity and volume swell testing in oil no.1 and oil no.3 between natural rubber (NR) filled synthesized ZnO nanoparticles (sZnO) by precipitation method and NR filled conventional ZnO (cZnO). The particle size of sZnO is 41.50 nm and specific area of 27.92 m²/g, the particle size of cZnO is 312.92 nm and specific surface area of 1.35 m²/g. It has been found that NR filled sZnO not only improves rubber mechanical properties, volume swell testing but also improves thermal conductivity and better than NR filled cZnO. Thermal conductivity of NR filled sZnO increases by 10.34%, 12.90% and 20.00%, respectively when compared with NR filled cZnO in same loading content (various concentrations of ZnO at 5, 8 and 10 parts per hundred parts of rubber). This is due to small particle size and large specific surface area of sZnO which lead to an increase in crosslinking in rubber chain and enhance heat transfer performance.

1. Introduction

Natural rubber (NR) is an unsaturated hydrocarbon or called cis-1,4 polyisoprene. The mechanical properties of vulcanized natural rubber are dependent on several factors such as degree and type of crosslinking, type and amount of fillers, degree of filler dispersion [1]. The important properties of NR are high elasticity and abrasion resistance, good tensile strength, good resilience, low heat build-up and excellent dynamic property, insoluble in water, alcohol and acetone. Due to the presence of a double bond in each repeat unit, ozone in the air will attack double bond in rubber chain and affect to degradation. It is always used in many applications such as automotive part, tires, footwear and engineering products. In addition, NR has a low thermal conductivity 0.135-0.150 W/m-K and then fine electrical insulating property. This is weakness to completely vulcanized of the surface and inner of the thick rubber product due to poor heat transfer. In fact the increment of the thermal conductivity leads to an increase in heat transfer performance. Zinc oxide (ZnO) is a type of material that used as an activator in vulcanizing with accelerators, reinforcement, aiding in heat dissipation [2] and other fillers such as aluminum nitride [3] and graphite [4] also enhance thermal conductivity. Generally, the conventional rubber grade uses ZnO particle size in range of 0.1-0.4 μm, the specific surface area around 10-20 m²/g and thermal conductivity of 34 W/m-K [5]. The reduction of particle size and increment of specific surface area may have important contribution to improve thermal conductivity [6]. The objective of this research is studied the effect of synthesized ZnO nanoparticles (sZnO) by precipitation method comparing with conventional ZnO (cZnO) which is usually used in rubber industry on thermal conductivity. Additionally, cure characteristic, volume swell testing and mechanical properties are also carried out.
2. Materials and Methods

2.1. Synthesis of sZnO
Zn(NO$_3$)$_2$·6H$_2$O and NaOH are used as precursors in precipitation method. Polyacrylic acid (PAA) is used as a polymeric additive. The process of synthesis sZnO is followed by the previous studied [7]. The morphology and primary size of sZnO and conventional ZnO (cZnO) are observed by a transmission electron microscope (TEM). The specific surface areas are investigated by a Brunauer-Emmett-Teller (BET) technique.

2.2. Preparation of rubber compound
The formulations of rubber compound are showed in table 1. Compound is prepared in an internal mixer 3 liter with rotor speed of 30 rpm. STR 20 is first masticate for 2 min, N-330, N-550, aromatic oil, 6PPD, stearic acid and ZnO are then added and mixed continued up to 5 min. The accelerator (CBS and DPG) and sulphur are added on a two roll mill at room temperature (35°C) and sheeted off a thickness at 8 mm.

2.3. The cure characteristics and mooney viscosity testing
The cure characteristics of rubber compound are measured at 170°C for 10 min with a Moving Die Rheometer (MDR2000, Alpha Technologies). The differential torque (M$_H$-M$_L$), cure time (T$_{10}$) and optimum cure time (T$_{90}$) are determined. Mooney viscosity (ML 1+4) at 125°C for 10 min are measured by Mooney Viscometer (MV2000, Alpha Technologies).

2.4. The mechanical properties and volume swell testing
The mechanical properties such as hardness, tensile strength, elongation at break and modulus are determined. The hardness test is performed using a Hardness tester (Teclock), according to ASTM D2240. Tensile strength, elongation at break and modulus are performed at 23±2°C with a crosshead speed of 500 mm/min using an Autograph (AG-IS, Shimadzu), according to ASTM D412.

2.5. The thermal conductivity testing
The specimen is prepared by compression molding at 165°C for 8 min, into rectangular sheets (100 mm × 100 mm × 10 mm). Thermal conductivity of the rubber is measured by Thermal Constants Analyser (TPS 2500S), according to ISO 22007-2.

| Table 1. The formulation of rubber compound. |
|--------------------------------------------|
| Materials   | Chemical name                  | phr (part per hundred of rubber) |
|             |                               | 5 phr | 8 phr | 10 phr | 5 phr | 8 phr | 10 phr |
| STR 20      | Natural rubber                | 100   | 100   | 100    | 100   | 100   | 100    |
| N-330       | Carbon black                  | 35    | 35    | 35     | 35    | 35    | 35     |
| N-550       | Carbon black                  | 50    | 50    | 50     | 50    | 50    | 50     |
| Aromatic oil| Aromatic oil                  | 5     | 5     | 5      | 5     | 5     | 5      |
| 6PPD        | N’phenyl-p-phenylenediamine   | 1     | 1     | 1      | 1     | 1     | 1      |
| Stearic acid| Stearic acid                  | 1     | 1     | 1      | 1     | 1     | 1      |
| cZnO        | Conventional ZnO             | 5     | 8     | 10     | -     | -     | -      |
| sZnO        | Synthesized ZnO nanoparticles| -     | -     | -      | 5     | 8     | 10     |
| CBS         | N-cyclohexyl-2-benzothaiazole| 1     | 1     | 1      | 1     | 1     | 1      |
|             | sulf enamide                  |       |       |        |       |       |        |
| DPG         | Diphenyl guanidine           | 1     | 1     | 1      | 1     | 1     | 1      |
| Sulphur     | Sulphur                       | 2     | 2     | 2      | 2     | 2     | 2      |
3. Results and discussion

3.1. The morphology of ZnO particles
TEM images of sZnO and cZnO are showed in figure 1. The sZnO exhibits a spherical shape with the average primary size of 41.50 nm and specific surface area of 27.92 m²/g. The particle size of cZnO is 312.92 nm and specific surface area of 1.35 m²/g.

3.2. The cure characteristics and mooney viscosity
The comparison of cure characteristics and mooney viscosity of NR filled sZnO and cZnO are presented in table 2. Mooney viscosity (ML1+4), the differential torque (M₉₀-M₅₉), cure time (T₁₀) and optimum cure time (T₉₀) are increased with increasing ZnO content. It is indicated that increasing degree of crosslink density or stiffness of the rubber compound. This phenomenon is occurred in both types of ZnO. In the case of NR filled sZnO, the experimental results showed that the M₉₀-M₅₉ is higher than NR filled cZnO in all loading content. This may be attributed to small particle size (nanoparticles) and large specific surface area of sZnO [8]. Furthermore, the ML1+4 of NR filled sZnO higher than filled cZnO due to fast curing because of a lower T₁₀ and T₉₀ are observed.

3.3. The mechanical properties
The mechanical properties of the NR filled with the various types and loading content of ZnO are showed in table 3. Results indicated that hardness, tensile strength and 100% modulus are gradually increased with increasing ZnO content [9]. The increment in these properties is due to enhancing degree of crosslink density in rubber chain. This phenomenon is confirm by M₉₀-M₅₉ result which is a measure of shear modulus and degree of crosslinking. Whereas the elongation at break show a decreasing trend when the content of ZnO increases. This is due to the increasing crosslink density and it is indicated that the rubber exhibits hardly extension. At similar loading content, the mechanical properties of NR filled sZnO are higher than NR filled cZnO. It is clearly demonstrated that small grain size and grain boundaries of sZnO improve rubber mechanical properties more than cZnO.

3.4. The thermal conductivity
The effect of NR filled with the various types and ZnO loading on thermal conductivity are showed in figure 2. It can be seen that the thermal conductivity for both types of ZnO are increased with increasing ZnO content. This is possibly due to increase metal oxide content and attributed to the enhancement of heat transfer performance. In addition the fixed ZnO loading, NR filled sZnO shows a higher thermal conductivity than NR filled cZnO. While the thermal conductivity of NR filled sZnO increases by 10.34%, 12.90% and 20.00%, respectively when compared with NR filled cZnO in same loading content. The higher thermal conductivity of NR filled sZnO is due to large specific surface area and enhance the heat transfer ability, thus the reduction of particle size leads to an increase in thermal conductivity.

3.5. The mechanical properties
The mechanical properties of the NR filled with the various types and loading content of ZnO are showed in table 3. Results indicated that hardness, tensile strength and 100% modulus are gradually increased with increasing ZnO content [9]. The increment in these properties is due to enhancing degree of crosslink density in rubber chain. This phenomenon is confirm by M₉₀-M₅₉ result which is a measure of shear modulus and degree of crosslinking. Whereas the elongation at break show a decreasing trend when the content of ZnO increases. This is due to the increasing crosslink density and it is indicated that the rubber exhibits hardly extension. At similar loading content, the mechanical properties of NR filled sZnO are higher than NR filled cZnO. It is clearly demonstrated that small grain size and grain boundaries of sZnO improve rubber mechanical properties more than cZnO.

3.6. The volume swell testing
Figure 3 summarizes the volume swell value in oil no.1 and oil no.3. It can be seen that the volume swell value is decreased with increasing ZnO content in both oil types. The decreasing of volume...
swell value with higher ZnO content is associated mainly with the degree of crosslinking in rubber chain. This result is correlated with the higher differential torque (M_H-M_L); as previously reported in table 2. In addition, the effect of nanoparticles size of sZnO on volume swell is also investigated. It is showed that the volume swell value of NR filled sZnO in oil no.1 and oil no.3 lower than NR filled cZnO. Because of nanoparticles size significantly enhance crosslink density higher than microparticles size which leads to a decrease in the volume swell.

![Figure 1. TEM images of (a) sZnO and (b) cZnO.](image)

**Table 2.** The cure characteristics and mooney viscosity.

| Properties          | cZnO 5 phr | cZnO 8 phr | cZnO 10 phr | sZnO 5 phr | sZnO 8 phr | sZnO 10 phr |
|---------------------|------------|------------|-------------|------------|------------|-------------|
| ML1+4 (MU)          | 65.78      | 72.71      | 76.02       | 67.33      | 74.83      | 79.20       |
| M_H-M_L (lb-in)     | 20.70      | 21.96      | 22.02       | 21.40      | 22.65      | 23.52       |
| T_10 (min)          | 1.71       | 1.80       | 1.81        | 1.65       | 1.74       | 1.78        |
| T_90 (min)          | 4.15       | 4.28       | 4.36        | 4.06       | 4.11       | 4.21        |

**Table 3.** The mechanical properties of the NR filled with various ZnO types.

| Properties          | cZnO 5 phr | cZnO 8 phr | cZnO 10 phr | sZnO 5 phr | sZnO 8 phr | sZnO 10 phr |
|---------------------|------------|------------|-------------|------------|------------|-------------|
| Hardness (Shore A)  | 78         | 79         | 80          | 79         | 80         | 82          |
| Tensile strength (MPa) | 19.70      | 20.40      | 22.10       | 21.70      | 22.70      | 23.20       |
| Elongation (%)      | 266        | 254        | 231         | 275        | 254        | 247         |
| 100% modulus (MPa)  | 7.19       | 8.43       | 8.88        | 7.82       | 8.62       | 9.12        |

![Figure 2. Thermal conductivity of NR filled with the various types and content of ZnO.](image)
4. Summary
This work is studied the effect of sZnO which is synthesized by precipitation method and compared with cZnO on cure characteristics, mechanical properties, thermal conductivity and volume swell in oil no.1 and oil no.3. The test results found greatly improve all rubber properties such as higher tensile strength and modulus, reduce volume swell in oil no.1 and oil no.3. This is due to nanoparticles size enhances the degree of crosslinking in rubber chain which confirm by the differential torque (\(M_H-M_L\)) result. Furthermore, the small particle size and large specific surface area of sZnO also improve heat transfer performance or thermal conductivity.

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6. References
[1] Ismail H and , Freakley P K 1997 Polym-Plast Technol. 36 873
[2] Sim L C, Ramanan S R, Ismail H, Seetharamu K N and Goh T J 2005 Thermochim. Acta. 430 155
[3] Namitha L K, Ananthakumar S and Sebastian M T 2015 J. Mater. Sci: Mater. Electron. 26 891
[4] Song S H, Jeong H K, Kang Y G and Cho C T 2010 Korean J. Chem. Eng. 27 1296
[5] Lee B and Dai G 2009 J. Mater. Sci. 44 4848
[6] Jeong J, Li C, Kwan Y, Lee J, Kim S H and Yun R 2013 Int. J. Refrig. 36 2233
[7] Suntako R 2017 Key. Eng. Mat. 748 79
[8] Kim I J, Kim W S, Lee D H, Kim W and Bae J W 2010 J. Appl. Polym. Sci. 117 1535
[9] Suntako R 2014 Adv. Mater. Res. 1044-1045 23