A Study of the Effect of Nano Zinc Oxide on Cure Characteristics and Mechanical Properties of Rubber Composites

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Abstract. This study investigates the effect of nano zinc oxide on cure characteristics and mechanical properties of natural rubber composites in comparison with the effect of conventional zinc oxide. Six rubber compounds were prepared with nano zinc oxide (particle size = (10-30) nm and surface area = (30-60) m²/g) and levels of (0, 0.4, 0.8, 1.2, 1.6, 2) phr (parts per hundred parts of rubber weight). Six rubber compounds were prepared with conventional zinc oxide levels of (0, 2, 4, 5, 6, 8) phr. The cure rate index was improved by 48.29% and torque difference was improved by 4.77%. The tensile strength was improved by 7.37% and the modulus at 300% was improved by 3.27%, while the hardness was decreased by 5.73%. The using of nano zinc oxide instead of conventional zinc oxide reduced the amount of zinc oxide inside rubber composites by 75%.

Keywords: Nano zinc oxide, Natural rubber, Cure characteristics, Mechanical properties

1. Introduction
Nowadays, there are many studies on the addition of nano additives instead of conventional additives such as zinc oxide to rubber composites due to them have nano particle size and great surface area in comparison with conventional additives. Nano additives have high diffusion inside the rubber composite and high contacting with the atoms of cross-link precursors between the polymer chains during compounding and vulcanization processes, therefore, they can improve the physical properties of the vulcanized rubber, in addition to that, they can be added to rubber with low amounts.

Some researchers studied the addition of calcium carbonate as a reinforcing filler to rubber composites such as: S Mishra and N Shimpi added conventional calcium carbonate and nano calcium carbonate at the same levels to styrene-butadiene rubber composites, and they found that tensile strength and modulus at 300% were improved by 58% and 94% Respectively due to replacing conventional calcium carbonate by nano calcium carbonate (particle size = 9 nm) [1].
Other researchers studied the addition of nano silica as a reinforcing filler to the rubber composites such as: M Lay et al. added nano silica to natural rubber composites with different levels (1-5) phr, and they found that the natural rubber composite has the highest tensile strength and shortest cure time at 3 phr [2]. J Ahmed et al. added nano silica (less than 100 nm) to styrene-butadiene rubber composites, and they found that the mechanical properties decreased at high levels of nano silica (greater than 10 phr), while they increased at low levels of nano silica (less than 5 phr), tensile strength, tear resistance, fatigue resistance, and abrasion loss had maximum values at 1 phr [3]. A Sultani et al. added nano silica (50-84) nm with carbon black of 50 phr to rubber compound of tire sidewall, and they found that tensile strength, modulus at 300% and tear strength were improved by 18%, 43% and 29% respectively at 1 phr of nano silica [4].

Other researchers studied the addition of nano zinc oxide as an activator instead of conventional zinc oxide to rubber composites such as: S Sahoo et al. added nano zinc oxide (30-70) nm to natural rubber and nitrile rubber composites, and they found that tensile strength was improved by 80% for natural rubber composites and 70% for nitrile rubber composites [5]. Maiti et al. added nano zinc oxide (particle size (7-12)) nm to SBR/BR composites, and they found that cure rate index and tensile properties improved by adding nano zinc oxide instead of conventional zinc oxide [6]. P Pornprasit et al. added nano zinc oxide (less than 100 nm) to natural rubber composites, and they found that tensile properties, hardness, rebound resilience, cure rate index and torque difference improved [7].

These studies and other studies refer to that the addition of nano additives improves cure characteristics and mechanical properties of rubber composites and it reduces the amounts of the nano additives. According to Council Directive 2004/73/EC Zinc oxide was classified as N “Dangerous for the Environment” [8], therefore, reducing zinc oxide amount inside the rubber products is important for reducing the environmental pollution.

2. Experimental

2.1. Materials
Natural rubber (SVR5 produced by Hoa Thuan CO. Vietnam), Conventional Zinc Oxide (purity =99%, Particle size=0.5-1μm, and surface area=3-5m²/gm, produced by ChemTAL Sunnyjoint Chemicals CO. China), CTP-100 (produced by Shenyang Sunnyjoint Chemicals CO. China), Carbon black (Type N326, Iran Carbon CO. Iran), Paraffinic Oil (Daura Refinery, Iraq), MBTS (Al-Kiubar CO. KSA), Sulfur (Al-Meshrak CO. Iraq), TMQ (Shenyang Sunnyjoint Chemicals CO. China), 6PPD (Shenyang Sunnyjoint Chemicals CO. China), Stearic acid (Acidichem-International CO. Malaysia), Nano zinc oxide (Assay=99%, Particle size=10-30 nm, Surface area=30-60 m²/gm, Skyspring Nano materials, Inc. USA).

2.2. Compound recipes
Compound recipes are listed in table (1) with conventional zinc oxide and in table (2) with nano-zinc oxide.

2.3. Equipment
Electronic balance with (± 0.001 gm) accuracy, two-roll mill, electronic press machine, Monsanto Rheometer (ODR-2000), Monsanto T 10 Tensometer, and Dead load hardness Tester.

2.4. Compounding Process
The compounding process carried out in State Company for Rubber Industry and Tires in Najaf, and according to ASTM D 3182. The natural rubber and additives mixed on a two roll mill (size 15 cm x 30 cm), Starting temperature was 60 ⁰C.

2.5. Vulcanization Procedure
The specimens of hardness and tensile properties were prepared in the State Company for Rubber Industry and Tires in Najaf, and according to ASTM D 3182.
• The temperatures and pressures of the press machine were determined according to the type of test, where the temperature for preparing the specimens of hardness test was 175°C and pressure was 24 MPa for 15 minutes while, the temperature for preparing the specimens of tensile test was 145°C and pressure was 32 MPa for 45 minutes;
• Cure characteristics of the rubber compounds were tested by the Rheometer in State Company for Rubber Industry and Tires in Najaf, and according to ASTM D 2084 (48);
• Preparing of specimens and tests were carried out at temperatures (23±3) °C.

Table 1. Recipes of rubber compounds with conventional zinc oxide.

| Material                  | A1  | A2  | A3  | A4  | A5  | A6  |
|---------------------------|-----|-----|-----|-----|-----|-----|
| SVR5                      | 100 | 100 | 100 | 100 | 100 | 100 |
| Conventional ZnO          | 0   | 2   | 4   | 5   | 6   | 8   |
| Stearic acid              | 2   | 2   | 2   | 2   | 2   | 2   |
| TMQ                       | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| 6PPD                      | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Carbon black N326         | 45  | 45  | 45  | 45  | 45  | 45  |
| Paraffinic oil            | 3   | 3   | 3   | 3   | 3   | 3   |
| MBTS                      | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| Sulfur                    | 3.25| 3.25| 3.25| 3.25| 3.25| 3.25|
| CTP-100                   | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |

Table 2. Recipes of rubber compounds with nano zinc oxide.

| Material                  | B1  | B2  | B3  | B4  | B5  | B6  |
|---------------------------|-----|-----|-----|-----|-----|-----|
| SVR5                      | 100 | 100 | 100 | 100 | 100 | 100 |
| Nano ZnO                  | 0   | 0.4 | 0.8 | 1.2 | 1.6 | 2   |
| Stearic acid              | 2   | 2   | 2   | 2   | 2   | 2   |
| TMQ                       | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| 6PPD                      | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Carbon black N326         | 45  | 45  | 45  | 45  | 45  | 45  |
| Paraffinic oil            | 3   | 3   | 3   | 3   | 3   | 3   |
| MBTS                      | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| Sulfur                    | 3.25| 3.25| 3.25| 3.25| 3.25| 3.25|
| CTP-100                   | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |

3. Results and Discussion

3.1. Cure Characteristics
The testing results of cure characteristics of rubber compounds with conventional zinc oxide and nano zinc oxide are explained by the following tables.

Table 3. Cure characteristics of rubber compounds with conventional zinc oxide.

| CO  | t82 (minute) | t90 (minute) | ML (Lb.In) | MH (Lb.In) | MH-ML (Lb.In) | Cure Rate (minute⁻¹) |
|-----|--------------|--------------|------------|------------|---------------|-----------------------|
| A1  | 0.78         | 1.66         | 3.5        | 25.38      | 21.88         | 113.366               |
| A2  | 0.69         | 1.44         | 2.67       | 33.45      | 30.78         | 133.333               |
| A3  | 0.66         | 1.23         | 2.83       | 33.76      | 30.93         | 175.438               |
| A4  | 0.64         | 1.17         | 2.93       | 34.46      | 31.53         | 188.679               |
| A5  | 0.63         | 1.11         | 3.18       | 34.57      | 31.39         | 208.333               |
| A6  | 0.58         | 0.98         | 2.48       | 34.76      | 32.28         | 250                   |
Table 4. Cure characteristics of rubber compounds with nano zinc oxide.

| CO | $T_{s2}$ (minute) | $T_{90}$ (minute) | ML (Lb.In) | MH (Lb.In) | MH-ML (Lb.In) | Cure Rate (minute$^{-1}$) |
|----|-----------------|-----------------|-----------|-----------|---------------|------------------------|
| B1 | 0.78            | 1.66            | 3.5       | 25.38     | 21.88         | 113.636                |
| B2 | 0.73            | 1.32            | 2.94      | 27.5      | 24.56         | 169.492                |
| B3 | 0.7             | 1.19            | 3.06      | 29.44     | 26.38         | 204.082                |
| B4 | 0.66            | 1.07            | 2.93      | 32.36     | 29.43         | 243.902                |
| B5 | 0.63            | 0.93            | 3.18      | 34.86     | 31.68         | 333.333                |
| B6 | 0.61            | 0.88            | 2.48      | 36.3      | 33.82         | 370.370                |

The cure rate index can be expressed as an indicator of the vulcanization speed. It can be calculated by the following equation [9]:

$$CRI = \frac{100}{(t_{90} - t_{s2})}$$

(1)

Where:

$CRI$ is the cure rate index, $t_{90}$ is the cure time and $t_{s2}$ is the scorch time.

Figure 1. (a) Influence of conventional zinc oxide level on cure rate index. (b) Influence of nano zinc oxide level on cure rate index.
The cure rate index increased with increasing of zinc oxide level due to the role of zinc oxide in creating of cross-links between the polymer chains of the rubber. The figure 1 shows that the cure rate index increased with the increasing of zinc oxide levels. Chemically, zinc oxide reacted with stearic acid and formed hydrocarbon-soluble zinc stearate and liberated water molecules and the accelerator reacted with the sulfur atoms and formed poly sulfide accelerator at the same time under the action of the heat, but poly sulfide accelerator created cross-link precursors by the bonding of it with a double bond carbon atom of the polymer chain [10, 11].

Zinc ions (Zn+2) of zinc stearate were chelated by cross-link precursors. Under the effect of zinc ions (Zn+2), the cross-link precursors were broken and leaved a small number of sulfur atoms and formed cross-link (bridge) with adjacent polymer chain, while the residual polysulfide accelerator created another cross-link precursor. This process increased the cure rate index and the cross-link density [10,11,12].

The effect of zinc oxide on the cross-link density can be explained by the (figure 2), this figure explains that the comparison between the vulcanization process with and without zinc oxide. The effect of zinc oxide on cross-link density and cure rate index can be enhanced by increasing the dispersion of the particles of zinc oxide inside the rubber during the compounding process and the contacting between zinc ions and cross-link precursors. Dispersion of the particles of zinc oxide and contacting between zinc ions and cross-link precursors depend on the sizes of zinc oxide particle, their shape and their specific surface area, so that, the efficiency of nano zinc oxide is greater than the efficiency of conventional zinc oxide. The cure rate index was 370 minutes\(^{-1}\) at 2 phr of nano zinc oxide (figure 1 (b)), but it was 250 minutes\(^{-1}\) at 8 phr of conventional zinc oxide (figure 1 (a)). The improving of the cure rate index was 48.29% by using nano zinc oxide [10].

The torque difference which equals the difference between the maximum and minimum torques and it can be expressed as an indicator of the cross-link density, it increased with increasing of zinc oxide level due to the relationship between zinc oxide level and cross-link density figures (3) [9]. In comparison between (figure 3 (a)) and (figure 3 (b)), we found that the torque difference with nano zinc oxide improved by 4.38%.

![Figure 2](image.png)

**Figure 2.** Comparison between two vulcanization processes with and without zinc oxide[10].
3.2. Mechanical Properties
There are many mechanical properties of rubber compounds, but we focused on the hardness and tensile properties. They are explained in the tables (5) and (6). These results are due to the relation between zinc oxide and cross-link density. The effect of zinc oxide on mechanical properties can be summarized into two ways [10,11]:
1- Shortening of the cross-links between the rubber chains.
2- Increasing of the cross-link density.
The increasing of the cross-link density and the shortening of the cross-links are directly affect on mechanical properties. The retractile force against a deformation of the polymer chains increases with increasing of the cross-link density and shortening of the cross-links, therefore, the mechanical properties improve with increasing zinc oxide level.

**Table 5.** The mechanical properties of the rubber compounds with conventional zinc oxide.

| CO  | Tensile strength (Mpa) | Tensile strength Rate (Mpa) | Elongation (%) | Elongation Rate (%) | Modulus at 300% (Mpa) | Rate of Modulus at 300% (Mpa) | Hardness (IRHD) | Rate of Hardness (IRHD) |
|-----|------------------------|----------------------------|----------------|---------------------|------------------------|-------------------------------|----------------|------------------------|
| A1  | 15.820                 | 16.320                     | 15.650         | 15.930              | 655                    | 611                          | 628             | 631.333                | 5.572                   | 6.125                    | 5.663                    | 36          | 37                      | 35                      | 36          |
| A2  | 18.437                 | 16.220                     | 15.638         | 16.765              | 526                    | 542                          | 623             | 563.667                | 6.633                   | 6.367                    | 5.553                    | 6.184       | 55                      | 57                      | 56          |
| A3  | 14.171                 | 20.062                     | 19.748         | 17.994              | 465                    | 459                          | 432             | 452                    | 8.249                   | 6.716                    | 7.05                     | 7.338       | 61                      | 62                      | 60.667      |
| A4  | 18.765                 | 18.084                     | 22.418         | 19.756              | 421                    | 410                          | 486             | 439                    | 8.511                   | 7.885                    | 9.005                    | 8.476       | 64                      | 61                      | 61          |
| A5  | 18.589                 | 16.85                      | 21.01          | 18.816              | 406                    | 390                          | 429             | 408.333                | 7.776                   | 9.654                    | 9.91                     | 9.113       | 63                      | 64                      | 63          |
| A6  | 21.010                 | 16.647                     | 14.253         | 17.303              | 429                    | 431                          | 344             | 401.333                | 10.331                  | 9.928                    | 11.337                   | 10.532      | 65                      | 64                      | 63          |

**Table 6.** Mechanical properties of rubber compounds with nano zinc oxide.

| CO  | Tensile strength (Mpa) | Tensile strength Rate (Mpa) | Elongation (%) | Elongation Rate (%) | Modulus at 300% (Mpa) | Rate of Modulus at 300% (Mpa) | Hardness (IRHD) | Rate of Hardness (IRHD) |
|-----|------------------------|----------------------------|----------------|---------------------|------------------------|-------------------------------|----------------|------------------------|
| B1  | 15.820                 | 16.320                     | 15.650         | 15.930              | 655                    | 611                          | 628             | 631.333                | 5.572                   | 6.125                    | 5.663                    | 36          | 37                      | 35                      | 36          |
| B2  | 18.437                 | 16.220                     | 15.638         | 16.765              | 597                    | 602                          | 587             | 595.333                | 5.478                   | 6.311                    | 6.573                    | 6.121       | 44                      | 42                      | 42.333      |
The hardness is the relative resistance of the surface of the material to indentation[9]. The hardness was increased with increasing zinc oxide level, but its values with conventional zinc oxide were greater than the values with nano zinc oxide (figures 4 (a) and (b)). It increases with increasing of the cross-link density due to the role of the cross-links in reducing the permeability of rubber composite.

|   | 22.829 | 20.062 | 20.748 | 486  | 499  | 473  | 486  | 9.124 | 6.548 | 8.567 | 8.080 | 51  | 53  | 49  | 51  |
|---|--------|--------|--------|------|------|------|------|-------|-------|-------|-------|-----|-----|-----|-----|
| B3| 21.213 | 458    | 433    | 462  | 451  | 7.542| 8.221| 10.369|       |       |       | 8.711| 53  | 56  | 57  | 55.333|
| B4| 19.756 | 423    | 411    | 429  | 421  | 9.365| 8.998| 10.564|       |       |       | 9.642| 55  | 58  | 59  | 57.333|
| B5| 18.816 | 431    | 408    | 415  | 418  | 11.368|10.478|10.765|       |       |       |10.876| 61  | 62  | 58  | 60.333|

The hardness was increased with increasing zinc oxide level, but its values with conventional zinc oxide were greater than the values with nano zinc oxide (figures 4 (a) and (b)). It increases with increasing of the cross-link density due to the role of the cross-links in reducing the permeability of rubber composite.
Tensile properties of the rubber composites can be classified into three properties:

- Tensile strength
- Elongation
- Modulus at 300%
In addition to that, modulus at 100% and modulus at 100%, but we focused on modulus at 300% due to it is the common property among the researchers. Tensile strength can be defined as the maximum tensile stress applied in stretching a specimen of rubber compound to rupture. It is expressed by Pascal or pound per square inch of the cross section. The tensile strength was increased and it had a maximum value at 5 phr with conventional zinc oxide and at 0.8 phr with nano zinc oxide, (figures 5 (a) and (b)), but it decreased with increasing the level of zinc oxide after the maximum value.

After the maximum value of the tensile strength, the motion of rubber chains became confined, and the distances between the chains became narrow due to the cross-link density increased, therefore, the rubber composite became brittle and it fractured at low elongation, therefore, tensile strength decreased with increasing of zinc oxide level. Nano zinc oxide improved tensile strength by 7.37% and reduced zinc oxide level 84% due to its role in increasing of the cross-link density [13].
Elongation is the ability of a rubber compound to stretch without breaking. It is equal to the ratio of difference between the final and initial lengths and initial.

\[ E_L = \frac{L - L_0}{L_0} \times 100\% \]  

(2)

Where: \( E_L \) is the elongation, \( L \) is the final length and \( L_0 \) is the initial length.

The elongation at break decreased with increasing zinc oxide level due to the relation between zinc oxide level and cross-link density too (figures 6 (a) and (b)).

**Figure 6.** (a) Influence of conventional zinc oxide level on the elongation. (b) Influence of nano zinc oxide level on the elongation.
Modulus is the required stress for a given elongation (frequently 300%), and it is used in comparison between the rubber composites. Modulus at 300% was increased with increasing zinc oxide level, figures 7 (a) and (b)) due to the relation between zinc oxide and cross-link density. The nano zinc oxide has improved modulus at 300% by 3.18 % and reduced zinc oxide level 75%. The using nano zinc instead of conventional zinc oxide in rubber industry can be improved cure characteristics and mechanical properties and reduce the zinc oxide level in rubber composites. In the world markets, nano zinc oxide and conventional zinc oxide are sold at close prices, therefore, the costs of rubber products and environmental pollution can be reduced by using nano zinc oxide in rubber industry [13].

The results and figures of the tested mechanical properties are identical to the relations between mechanical properties and the cross-link density, which are explained in the following figure and taking into consideration the relationship between the cross-link density and zinc oxide level. The following figure was designed by Coran [11].
4. Conclusions
The following observations were gotten when nano zinc oxide (particle size (10-30) nm and surface area (30-60) m²/g) was used as a cure activator instead of conventional zinc oxide in the vulcanization process of natural rubber composites.
- Cure rate index was improved by 48.29%;
- Torques difference was improved by 4.77%;
- Tensile strength was improved by 7.37%;
- Modulus at 300% was improved by 3.27%;
- Hardness was decreased by 5.73%;
- Zinc oxide level was decreased by 75%.

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*Figure 8. Effect of the cross-link density on mechanical properties of rubber composite [10].*
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