A Study of the Influence of Zinc Oxide on Acid Resistance of Natural Rubber Composites

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Abstract. The natural rubber has good resistance for some acids such as hydrochloric acid. Therefore, natural rubber composites are used in the lining of acid containers. Acid resistance of the natural rubber improves by types and levels of additives such as zinc oxide level. This research focuses on the influence of traditional zinc oxide on the acid resistance of natural rubber composites against 37% (w/w) hydrochloric acid. Six rubber compounds were prepared with various levels of zinc oxide of (0, 2, 4, 5, 6, 8) phr (parts per hundred parts of rubber weight). This work includes tests of tensile properties, hardness (Shore A), compression set, tear resistance, and abrasion resistance. Test specimens of tensile properties and hardness immersed in hydrochloric acid for 70 hours at room temperature. After immersion, they dried and tested for determining acid resistance. The acid resistance of rubber composites increased by increasing the amount of zinc oxide and the best acid resistance of rubber composite was gotten at 5 phr of zinc oxide.

Keywords: Zinc oxide, Natural rubber, Acid resistance, Hydrochloric acid

1. Introduction
Corrosion occurs because of the chemical reaction between a metallic surface and its environment. When the metal surface is in contact with the acid, the metal is attacked or dissolved and hydrogen is evolved as a gas. The corrosion of metals can also occur in freshwater, seawater, salt aqueous solutions, and alkaline aqueous solutiones. The anticorrosive is very important to protect most products of modern technology [1].

One of the best ways to get rid of this problem is the lining of the surface of equipment by rubber composites, but the types of rubber don’t have the same chemical resistance. The natural rubber has low resistance to ozone, but butyl rubber has excellent resistance to ozone. Therefore, it must choose a suitable rubber for lining [2]. The chemical resistance of rubber can be improved by the levels of additives. Ji-Fang et al. added nano alumina to natural rubber for improving chemical resistance against hydrochloric acid aqueous solution and sodium hydroxide aqueous solution [3]. Mohammed et
al. added barium sulfate to natural rubber for improving chemical resistance against hydrochloric acid aqueous solution [4]. Chukov et al. used carbonization of nitrile butadiene rubber (NBR) by different carbon fillers, graphite, shungite fillers, carbon black, and silicon carbide for improving the chemical resistance of nitrile butadiene rubber composites which are used in the industry of oil pump impellers [5].

Zinc oxide is the best activator for sulphur vulcanization. It reacts with fatty acid such as stearic acid to form zinc stearate and liberates water before the onset of crosslinking. The zinc ions of zinc stearate salt has a number of functions in the compounds:

- Zinc ions react with most accelerators to form the active accelerator complexes [6].
- They increase the amount of sulphur atoms embedded in the active accelerator complexes to form polysulfide accelerator [7, 8].
- They are shorten the crosslinks between the polymer chains by their effect on the sulfur atoms of crosslink precursor [9].
- They creat new crosslink precursors [8, 10].

The role of zinc oxide in increase of crosslink density improves the acid resistance of natural rubber composites. The permeability of rubber composite reduces due to increasing the crosslink density. Therefore, the chemical resistance of rubber composite increases by increasing zinc oxide amount.

Natural rubber has good chemical resistance for hydrochloric acid. This acid reacts with the surface of natural rubber during chlorination process, and making impermeable film on the surface of natural rubber composite. When the hydrochloric acid stored inside container lined by natural rubber, it takes about three months for natural rubber crust formations with thickness of 1/64 (0.016”) and the hardness increases by 35 shore A. If hardness was 45 shore A, it becomes 80 shore A due to creating chlorinated rubber membrane. It is also destruct in later years when the acid penetrates the rubber and forming a new surface crust due to cracks which occur on the rubber surface. The period continues until complete lining dissolved and cracks reaches to surface of metal. The age of this lining ranges from 7 to 24 years [11].

Acid resistance of rubber composites can be measured by four ways [12]:

- Measuring the change of mass of vulcanized specimen by the following equation:
  \[ \Delta M = \frac{M_2 - M_1}{M_1} \times 100 \% \]  
  \( \Delta M \) is the percent change of mass, \( M_1 \) is initial mass of specimen in air, and \( M_2 \) is the mass of specimen in air after immersion.

- Measuring the change of volume of vulcanized specimen by the following equation:
  \[ \Delta V \% = \frac{(M_3 - M_1)}{d(M_1 - M_2)} \times 100 \% \]  
  \( \Delta V \) is the percent change of volume, \( M_1 \) is the initial mass of specimen in air, \( M_2 \) is the mass of specimen in immersion liquid, \( M_3 \) is the mass of specimen in air after immersion, and \( d \) is the density of immersion liquid.

- Measuring the change of tensile strength or elongation at break by the following equation:
  \[ \Delta P \% = \frac{P_1 - P_0}{P_0} \times 100 \% \]  
  \( P_1 \) is the property after immersion, \( P_0 \) is the original property before immersion, \( \Delta P \) is change rate of the property due to the immersion.

- Measuring the change rate of the hardness by the following equation:
  \[ \Delta H = H_1 - H_0 \]
$H_i$ is the hardness after immersion, $H_0$ is the original hardness before immersion, $\Delta H$ is change rate of the hardness due to the immersion.

Acid resistant rubber composites are prepared according to specifications which are included a range of values of mechanical properties. These specifications are determined by companies of rubber lining such as ASM International (American Society for Metals) [13].

2. Experimental

2.1. Materials

Traditional Zinc Oxide (purity =99%, Particle size=0.5-1μm, and surface area=3-5m²/gm, ChemTAL Sunnyjoint Chemicals CO. China), Carbon black (Type N326, Iran Carbon CO. Iran), Paraffinic Oil (Daura Refinery, Iraq), MBTS (Al-Kiubar CO. KSA), TMQ (Shenyang Sunnyjoint Chemicals CO. China), 6PPD (Shenyang Sunnyjoint Chemicals CO. China), Sulphur (Al-Meshrak CO. Iraq), Stearic acid (Acidchem-International CO. Malaysia), CTP-100 (produced by Shenyang Sunnyjoint Chemicals CO. China), and Natural rubber (SVR5 produced by Hoa Thuan CO. Vietnam).

2.2. Compounding

Compounding of rubber were prepared according to ASTM D 3182. Compounds were prepared by two roll mill mixing (300 mm × 150 mm) two roll mill. Compound formulas are listed in table (1) with different levels of zinc oxide.

**Table 1.** Recipes of rubber compounds with traditional zinc oxide.

| Material         | CO 1 (phr) | CO 2 (phr) | CO 3 (phr) | CO 4 (phr) | CO 5 (phr) | CO 6 (phr) |
|------------------|------------|------------|------------|------------|------------|------------|
| Natural Rubber   | 100        | 100        | 100        | 100        | 100        | 100        |
| Zinc oxide       | 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        |
| Sulphur          | 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        |

2.3. Characterization

The mechanical properties were selected according to specifications of ASM International documents [13]. Tensile properties were tested according to ASTM D 412. Tear resistance was tested according to ASTM D 624 by Monsanto tensometer. Hardness was tested according to ASTM D 2240 by durometer at scale shore (A). Abrasion resistance was tested according to GB/T1689-1998. Compression set was tested according to ASTM D 395.

Crosslink density was measured by Flory-Rehner method which is the common method to calculate the crosslink density. According to this method, vulcanized test-specimens have been weighted and immersed inside the solvent for seven days. They were directly weighted after removing them from the solvent. Volume fraction were calculated by the following equation [14]:

$$v_r = \left[1 + \frac{d(W_d-W_c)}{W_d} \right]^{-1}$$

(5)
\( v_r \) is the volume fraction, \( \rho_r \) is the mass density of rubber compound, \( \rho_s \) is the mass density of solvent, \( W_s \) is the weight of swollen sample after 7 days, and \( W_d \) is the weight of the dried sample before the immersion.

Crosslink density can be calculated by Flory-Rehner equation [14]:

\[
V_e = \frac{\ln(1-v_r)+v_r+Xv_r^2}{2v_r(v_r^{1/3}-\frac{1}{3}v_r)}
\]

\( V_e \) is the crosslink density of rubber composite, \( v_s \) is the molar volume of solvent, and \( X \) is parameter characteristic of interaction between the rubber network and the swelling agent (solvent). The value of this parameter depends on the type of polymer and the type of solvent. For natural rubber-toluene.

The value of \( X \) can be given by the following equation for natural rubber [15]:

\[
X = 0.44 + 0.18v_r
\]

Specimens of tensile properties were immersed inside 37 % (w/w) hydrochloric acid for 70 hours at room temperature according to ASTM D 471. After immersion, they were dried and tested for getting acid resistance [12].

3. Results and Discussion

3.1. Mechanical Properties

Figure (1) shows the influence of traditional zinc oxide level on tensile strength. This figure explains that tensile strength increases by increasing conventional zinc oxide amount up to maximum value at 5 phr and it decreases after that. The increasing of tensile strength occurred due to the effect of zinc oxide on crosslink density of rubber composites. The crosslink density increases when the rubber composite becomes more elastic and the tensile strength increases, and it reaches to maximum value at 5 phr. The motion of rubber chains becomes restricted when the crosslink density increases after 5 phr and the tight network is incapable of dispersing much energy. Therefore, the elastomer becomes brittle and can be break at low tensile strength; therefore, tensile strength decreases by increasing zinc oxide amount after 5 phr [10, 14]. This result agrees with the studies of Onyeagoro [16] and Habeeb [17], but maximum value is given at 5 phr of conventional zinc oxide according to Onyeagoro’s study [16] and 2 phr according to Habeeb’s study [17].

![Figure 1. Influence of traditional zinc oxide level on the tensile strength of rubber composite.](image-url)
Figure (2) shows the influence of traditional zinc oxide amount on modulus at 300% of natural rubber composite. It increases by increasing zinc oxide amount due to the effect of conventional zinc oxide on increasing crosslink density of rubber composite. This result agrees with Habeeb’s study [17], but it doesn’t agree with Onyeagoro’s study which explains that modulus at 300% increases by increasing the amount of conventional zinc oxide up to maximum value at 5 phr of traditional zinc oxide and decreases after that [16].

![Figure 2. Influence of traditional zinc oxide level on the modulus at 300% of rubber composite.](image)

Figure (3) shows the influence of traditional zinc oxide amount on elongation at break of natural rubber composite. This figure explains that the elongation at break reduces by increasing zinc oxide level. This result occurs due to the increasing of crosslink density by increasing zinc oxide amount. This result agrees with the studies of Onyeagoro [16] and Habeeb [17].

![Figure 3. Influence of traditional zinc oxide level on the elongation at break of rubber](image)
Figure (4) shows the influence of traditional zinc oxide on the tear strength of natural rubber composite. The tear strength increases by increasing traditional zinc oxide level up to maximum value at 4 phr and decreases after that due to the role of zinc oxide in increasing crosslink density. The tear strength increases by increasing crosslink density. The specimen becomes brittle and ruptures by low force after maximum value of the tear strength due to high value of crosslink density. This result agrees with Heideman’s study [10].

![Figure 4. Influence of traditional zinc oxide level on the tear strength of rubber composite.](image)

Figure (5) shows the influence of traditional zinc oxide amount on the hardness. This figure explains that the hardness increases by increasing zinc oxide amount due to the increasing of crosslink density. The resistance of the network of polymer chains against indentor when forced into rubber increases by increasing crosslink density [8]. The relation between the hardness and conventional zinc oxide amount is a positive relationship in all types of rubber composite because of the influence of zinc ions in creating crosslinks between polymer chains of rubber composites. This result agrees with the studies of Onyeagoro [16] and Habeeb [17].

Figure (6) shows the influence of traditional zinc oxide level on compression set of natural rubber composite. It decreases by increasing the amount of zinc oxide due to the influence of zinc oxide in increasing crosslink density. The high crosslink density between polymer chains reduces the effect of applied force on the test-specimen of rubber composite [8]. This result agrees with Habeeb’s study [17].

Figure (7) shows the influence of conventional zinc oxide on the abrasion loss of natural rubber composite. This figure explains that abrasion loss decreases by increasing conventional zinc oxide amount down to minimum value at 5 phr and increases after that. This result confirms that the abrasion resistance increases by increasing conventional zinc oxide amount up to maximum value at 5 phr and decreases after that. It is due the increasing crosslink density by increasing zinc oxide level. The rubber composite has high stiffness and it resists erosion due to high crosslink density. The decrease of abrasion resistance after maximum value due to the rubber becomes brittle, therefore, its abrasion resistance decreases. This result agrees with Onyeagoro’s study [16].
Figure 5. Influence of traditional zinc oxide level on the hardness of rubber composite.

Figure 6. Influence of traditional zinc oxide level on the compression set of rubber composite.
The curves of tensile strength, elongation at break, modulus at 300%, shore hardness, and tear strength are similar to the curves of these properties in the figure (8) which is suggested by Bateman, Hofmann, and Coran to explain the relation between crosslink density and the mechanical properties [8].

**Figure 7.** Influence of traditional zinc oxide level on the abrasion loss of rubber composite.

The similarities between the curves of mechanical properties against crosslink density and the curves of mechanical properties against the zinc oxide level because of the direct relationship between the crosslink density and the zinc oxide level.

**Figure 8.** Influence of crosslink density on the mechanical properties of rubber composite [8].
Figure (9) shows the direct relationship between the crosslink density and the zinc oxide level. The role of zinc oxide in shortening crosslinks and creating crosslink precursors between polymer chains is the main reason of the relationship between crosslink density and zinc oxide level [8, 9, 10].

![Figure 9. Influence of traditional zinc oxide level on the crosslink density of rubber composite.](image)

### 3.2. Acid Resistance
Figure (10) shows the influence of traditional zinc oxide on the change rate of tensile strength. This figure explains that the change rate of tensile strength increases by increasing the amount of zinc oxide up to maximum value at 5 phr and decreases after that. All values of this change rate are negative values. The crosslink density increases by increasing the amount of conventional zinc oxide. Therefore, the acid resistance and change rate of tensile strength increases by increasing crosslink density due to the effect of crosslink density on reducing the permeability of rubber and the penetration of hydrochloric acid into the rubber. The decreasing of the change rate after 5 phr of conventional zinc oxide occurs due to the effect of crosslink density on the rubber, it becomes brittle and the cracks can be created on the surface of rubber [18, 19, 20].

Figure (11) shows the effect of conventional zinc oxide on the change rate of elongation at break of natural rubber composite. This figure explains that the change rate of elongation at break increases by increasing conventional zinc oxide up to maximum value at 5 phr and decrease after that. All values of the change rate have negative values. The crosslink density increases the change rate of elongation at break due to the role of crosslink density in increasing the elasticity of rubber. The decreasing of the change rate after maximum value at 5 phr occurs due to the effect of crosslink density on the mobility of polymer chains. According to these figures, the acid resistance of natural rubber composites has best value at 5 phr of zinc oxide [21].
4. Conclusions

- The best mechanical properties are given by the addition of 5 phr of traditional zinc oxide into rubber composites.
- The best acid resistance against hydrochloric acid is given by the addition of 5 phr of conventional zinc oxide into rubber composites.
The mechanical properties of rubber composite at 5 phr are in the ranges of specifications of ASM International.

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