



## **EFFECT OF NANO ZINC OXIDE ON TENSILE PROPERTIES OF NATURAL RUBBER COMPOSITE**

**Saja Q. Mohammed<sup>1</sup>, Abdulkareem A. Alhumdany<sup>2</sup> and Muhannad L. Al-Waily<sup>3</sup>**

<sup>1</sup> Mechanical Engineering Department, College of Engineering, Kerbala University,  
Email: [sajaqasim2@gmail.com](mailto:sajaqasim2@gmail.com)

<sup>2</sup> Mechanical Engineering Department, College of Engineering, Kerbala University, Email:  
[alhumdany@yahoo.com](mailto:alhumdany@yahoo.com)

<sup>3</sup> Mechanical Engineering Department, Faculty of Engineering, Al-Kufa University,  
Email: [muhanedl.alwaeli@uokufa.edu.iq](mailto:muhanedl.alwaeli@uokufa.edu.iq)

### **ABSTRACT**

This study investigates the effect of Nano-zinc oxide on tensile properties of natural rubber composites by replacing the conventional zinc oxide by Nano-zinc oxide as an activator. It has a small particle size and large surface area in comparison with conventional zinc oxide.

In this paper, one compound has a conventional zinc oxide as an activator with concentration 8phr (part per hundred rubber), and eight compounds have Nano-zinc oxide as an activator with concentrations of (0.2, 0.6, 1, 1.4, 1.8, 2.2, 2.6, and 4) phr. The tensile test sample carried out by using the Monsanto T10 Tensometer. Results showed that the maximum values of tensile strength and elastic modulus at 300% are found with Nano-zinc oxide at 1.8 phr. Replacing the conventional zinc oxide by Nano-zinc oxide decreased the price of the compounds because of reducing the amount of zinc oxide inside the compounds by 77.5%. It also reduced the contamination of the environment and improved the tensile strength by 38.31%.

**KEYWORDS:** Tensile strength; Modulus at 300%; Conventional zinc oxide; Nano-zinc oxide; Natural rubber

## تأثير أكسيد الزنك النانوي على خواص الشد لمتراكب من المطاط الطبيعي

سجى قاسم محمد<sup>1</sup>، عبد الكريم عبد الرزاق الحمداني<sup>1</sup>، مهند لفته الوائلي<sup>2</sup>

<sup>1</sup> قسم الهندسة الميكانيكية، كلية الهندسة، جامعة كربلاء

<sup>2</sup> قسم الهندسة الميكانيكية، كلية الهندسة، جامعة الكوفة

### الخلاصة

هذه الدراسة تبحث تأثير أكسيد الزنك النانوي على خواص الشد لمتراكبات المطاط الطبيعي باستبدال أكسيد الزنك الاعتيادي بأوكسيد الزنك النانوي كمادة منشطة. ذات حجم دقائق صغير ومساحة سطحية كبيرة مقارنة مع أكسيد الزنك الاعتيادي.

في هذا البحث، تم اخذ عجنت تحتوي على أكسيد الزنك الاعتيادي كمنشط بتركيز 8 PHR (جزء من مائة من وزن المطاط) وثمان عجنت تحتوي على أكسيد الزنك النانوي كمنشط بتركيز (0.2, 0.6, 1, 1.4, 1.8, 2.2, 2.6, 4) PHR. أجريت عملية فحص الشد باستخدام جهاز التنسومتر. بينت النتائج ان اعلى قيمة لمقاومة الشد ومعامل المرونة عند ال % (300) قد وجدت مع أكسيد الزنك النانوي عند 1.8 PHR. ان استبدال أكسيد الزنك الاعتيادي بأوكسيد الزنك النانوي سوف يقلل من سعر العجنت ، نتيجة انخفاض كمية أكسيد الزنك داخل العجنت بنسبة 77.5% . علاوة على ذلك فهو يقلل من تلوث البيئة ويحسن من قوة الشد بنسبة 38.31%.

## 1. INTRODUCTION

Rubber is generally called elastomers. They are used in many engineering applications due to their low cost, wide availability, dissipating energy, resiliency, long service life, light weight, and it can be simply molded into any shape. Applications of rubber are presently used in coatings, cables, medical/dental, tires, optical devices, engine mounts, and gaskets.

The tensile test includes the deforming of rubber on a single axis. When rubber is stretched, stresses and different elongations (typically 100, 200, 300% and at break,) are generated. A dumbbell specimen was used for determining rubber properties in tension according to ASTM D 412. The ZnO was used as an activator in rubber vulcanization and increased crosslink density. The zinc cations in ZnO react with organic accelerators to form an active zinc-accelerator complex. It is one of the main steps in the vulcanization process to form crosslinks between rubber chains. For industrial rubber, ZnO is used in about (50-60) % (Das et al., 2011). The ZnO has a negative effect on the environment. To solve this problem, it is necessary to reduce the ZnO level in rubber vulcanization (Heideman et al., 2005 and 2006). For this purpose, the Nano-ZnO is used as alternative to conventional ZnO. The efficiency of ZnO during vulcanization can be increased by maximizing the contact between ZnO particles and the accelerators in the rubber preparation. The average particles size of conventional ZnO is usually in the range (0.3-1.0)  $\mu\text{m}$ , and its specific surface area is correspondingly in a range of (4-6)  $\text{m}^2/\text{g}$ . Nano-ZnO presents high activity due to its small particle size and large surface area. Nano-ZnO has an average particle size less than 100 nm and a specific surface area greater than 15 $\text{m}^2/\text{g}$ . The equivalent replacement of conventional ZnO by nano-ZnO leads to an improvement of the properties of the rubber compound. This might be due to the fact that the higher specific surface area, and therefore a relatively higher amount of  $\text{Zn}^{2+}$  ions is compared to conventional ZnO. For this reason, a great reduction in the ZnO content in rubber compounds is achieved (Heideman et al., 2004).

Bhowmick et al. (2007) studied the effect of nano-ZnO on mechanical properties of Nitrile rubber (NBR) and natural rubber (NR), and they found that the tensile strength is improved by 70% for NBR and 80% for NR when replacing conventional ZnO by nano-ZnO as cure activator.

Kim et al. (2010) studied the effect of conventional ZnO and nano-ZnO with particle sizes of (30-40nm) and specific surface areas of (25-50  $\text{m}^2/\text{g}$ ) on the cure characteristics and mechanical properties of natural rubber/butadiene rubber (NR/BR) compound. When replacing conventional ZnO by nano-ZnO, they found that only 20% of nano-ZnO concentration gave the same level in cure characteristics and mechanical properties.

Bindu et al. (2013) studied the effect of 5phr conventional ZnO and (0.25, 0.3, 0.4, 0.5, and 1,2) phr nano-ZnO on cure characteristics of NR compounds. They found that the compound of 0.5 phr of nano-ZnO is faster in the vulcanization process than of that containing 5 phr of conventional ZnO. Also, it was found that nano-ZnO with a concentration of 0.5 phr accelerates the vulcanization process and increases the crosslink density.

Thomas et al. (2013) studied the effect of conventional ZnO and Nano- ZnO on the mechanical properties of NR. They found that these properties increased by using Nano-ZnO.

The main objective of the present research is to study and investigate the effect of nano-ZnO level on the tensile properties of the natural rubber compounds which is already used in Babylon tires factory. The test results will be a key factor for determining the best compound choice for the tire industry.

Hadi et al. (2015) studied the effect of replacing of conventional ZnO by nano-ZnO on tensile properties of the compounds of NR/SBR with a ratio (50/50). The concentrations of conventional ZnO is (0, 2, 4, 5, 6, and 8phr), and with nano-ZnO is (0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, and 1.6 phr). They found that maximum tensile properties are at 5 pphr of conventional ZnO and at 1.2 pphr of the nano-ZnO level. The replacing conventional ZnO by nano-ZnO increases tensile properties and crosslink density. Also, it is reduced the cost of the compounds by reducing the amount of ZnO inside the compounds.

## 2. EXPERIMENTAL

### 2.1. Materials

The materials used in the experiments are natural rubber (SMR20), conventional Zinc Oxide (purity=99%, Particle size=0.5-1 $\mu$ m, and surface area=3-5m<sup>2</sup>/gm.), Nano Zinc Oxide (Purity=99% and Particle size>80nm), phthalimide (CTP-100), stearic acid, phenolic tack resin, anti-ozinants (6PPD), carbon black, process oil, cobalt stearate, accelerator (DCBS), and sulfur. The concentrations of these materials are illustrated in the preparation method's section.

### 2.2. Preparation method

The formulation of the rubber compounds is illustrated in Table 1. (A) compound is standard using in State Company for Tire Industry in Najaf included 8phr conventional ZnO. (B) group included the compounds which are replaced conventional ZnO in (A) compound by Nano-ZnO and the concentration of other materials is not changed. Compounds were prepared by two-roll laboratory mill. The diameter of any roll is 150 mm, and face is 300 mm. The ingredients were added as follows:

1. The SMR20 was masticated in two roll mills several times with decreasing the distance between the rolls at a constant temperature at 70°C.
2. The ZnO is added to the SMR20 the the same procedure is followed in step 1.
3. The following additives are added to the mixture of SMR20 and ZnO in consequence. They are stearic acid, 6PPD, cobalt stearate and phenol tack resin, and the same procedure is followed in step 1.
4. Mixing half of carbon black (25 phr) with oil then adding to the homogeneous materials, and the same procedure is followed in step 1.
5. Adding the other half of carbon black alone and finally adding sulfur, CBS and CTP-100 and following the same procedure in step 1.

It is important to mention that the total mixing time is kept to minimum in order to avoid sticking of the rubber compound to the mill rolls. [Table 2](#) shows the time for all process according ASTM D15.

### **2.3. Vulcanization process**

The rubber in the original state is generally not very strong. It does not maintain its shape after a large deformation; it can be very sticky having even its consistency as gum. It cannot be made without vulcanization or curing.

Vulcanization is a process usually applied to rubbery or elastomeric materials. It can be defined as a process which increaseing the retractile force and reducing the amount of permanent deformation residual after removal the deforming force. Thus, vulcanization decreases plasticity while it increases elasticity ([Erman et al., 2013](#)).

The vulcanization process of the previously mentioned rubber compound was started by heating the hydraulic press which is used in the vulcanization process. It consists of two jaws used to generate a high pressure on the mold with dimensions of (150 x 150 x 2) mm as shown in [Fig.1](#). The mold was filled with 70 g of the compound. When the piston reached 150 °C, the mold was put between the jaws and pressed at 3.5 Mpa for 45 min to produce a thin sheet of rubber compound according to ASTM D3182 which can be used later to make the dumbbell specimens of all rubber compounds.

**Table 1. The formulation of the compound samples in phr**

<b>Material</b>	<b>A</b>	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>	<b>B5</b>	<b>B6</b>	<b>B7</b>	<b>B8</b>
SMR20	100	100	100	100	100	100	100	100	100
ZnO	8	-	-	-	-	-	-	-	-
Nano-ZnO	-	0.2	0.6	1	1.4	1.8	2.2	2.75	4
Stearic acid	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
6PPD	1	1	1	1	1	1	1	1	1
Phenol tack resin	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Carbone Blake	50	50	50	50	50	50	50	50	50
Oil Process	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
Cobalt stearate	1	1	1	1	1	1	1	1	1
DCBS	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulfur	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
CTP-100	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

**Table 2. Mixing schedule**

<b>NO</b>	<b>Operations</b>	<b>Time (minutes)</b>
1	Mastication of SMR20 rubber	4
2	Addition of zinc oxide	2
3	Stearic acid, 6PPD, cobalt stearate, phenol tack resin	2
4	Addition of carbon black + oil	6
5	Addition of carbon black	4
6	Sulfur, CBS, CTP-100	4
7	Sweep and dumb	3
8	Total	25



**Fig. 1. Mold of Sheets.**

#### **2.4. Tensile Test**

The vulcanized thin rubber sheet was released from the mold and left to cool down to the room temperature for a sufficient period of time. Finally, by using the Wallace test specimen cutting press, the dumbbell shaped specimens as shown in Fig. 2 were obtained according to ASTM D412 specifications for tensile test.

The device used in this test was Monsanto T10 Tensometer manufactured by Monsanto CO., England. This device is available in Babylon tires factory. The device consists of upper and lower grip positions which are used to hold both ends of the dumbbell specimen under consideration. The thickness of dumbbell was measured by a dial gauge to enter into controlled board of Tensometer with speed of moving grip is 500 mm/min. The results including elongation, tensile strength, modulus at (100%, 200%, and 300%), and elongation at break were recorded. This test is using of all rubber compounds, and three dumbbells for any compound were tested and took the average of the results.

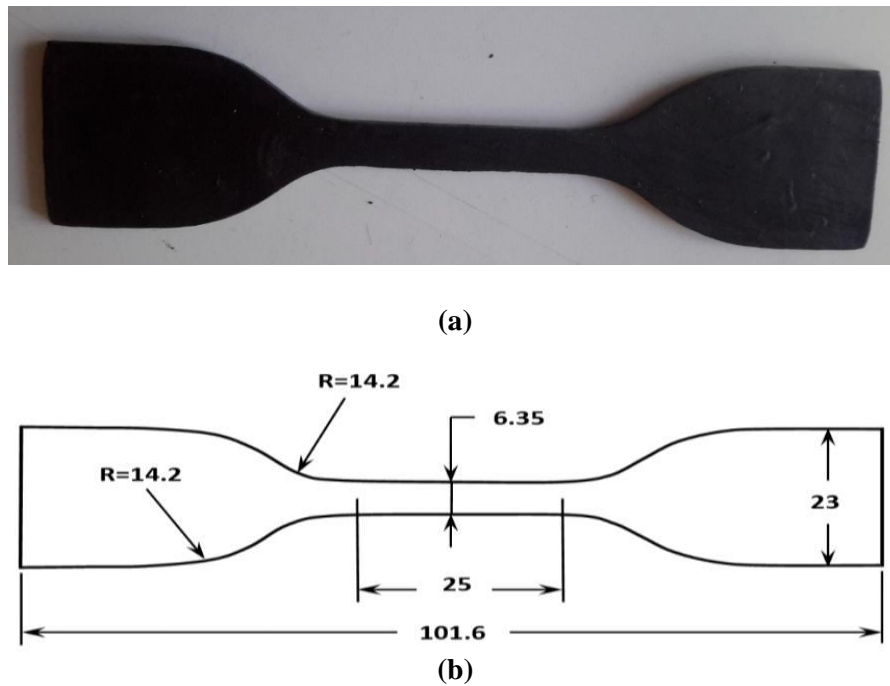


Fig. 2. (a) Actual Dumbbell specimen. (b) Dimensions of specimen (mm).

### 3. RESULTS AND DISSCUSION

#### 3.1. Tensile Strength

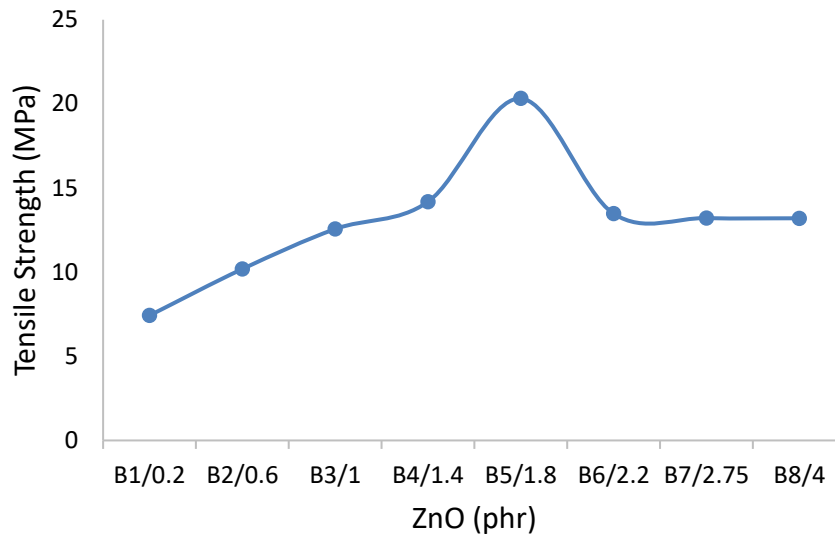
Referring to the Table 3 and Fig. 3, it is noted that the tensile strength increases progressively with increasing Nano-ZnO level from 0.2 phr up to a maximum value at 1.8 phr. This observation is attributed to the consolidation of the network structure of the rubber chains with increasing Nano-ZnO level due to increasing crosslink density.

But tensile strength decreases with increasing the concentration of Nano-ZnO beyond 1.8 phr due to decreasing of the crosslink density. The crosslink density is proportional to the concentration of ZnO. When the crosslink density increases, the elastomer becomes more elastic and the tensile strength increases and passes through a maximum as crosslink density at 1.8phr. When the crosslink density increases beyond 1.8 phr, the motion of rubber chains becomes restricted and the tight network is unable of dissipating much energy. This result is relatively good and brittle fracture at low elongation occurs. Therefore, tensile strength decreases with increasing ZnO beyond after 1.8 phr.



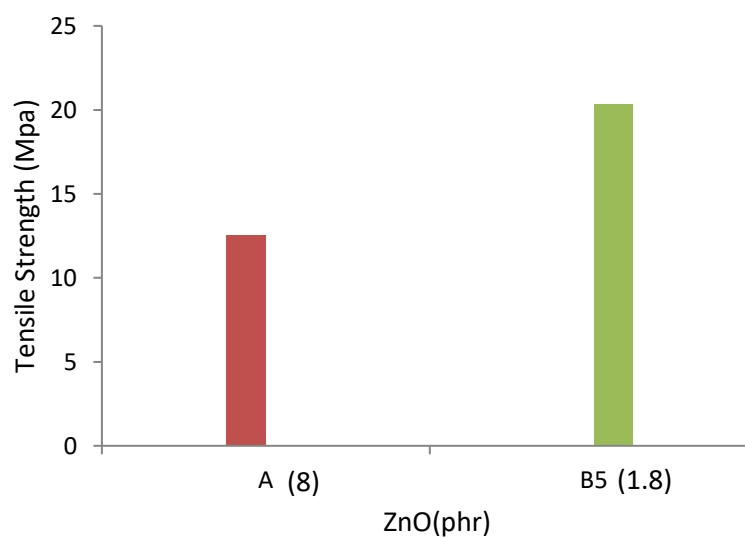
**Table 3. Results of tensile test compounds**

<b>Compound</b>	<b>Tensile strength (Mpa)</b>	<b>Tensile strength Average (Mpa)</b>	<b>Elongation at Break (%)</b>	<b>Elongation Average (%)</b>	<b>Modulus at 300% (Mpa)</b>	<b>Modulus at 300% Average (Mpa)</b>
A	12.238 12.988 12.582	12.602	336 374 297	336	11.256 10.312 8.006	9.858
B1	8.509 7.164 6.606	7.426	603 619 577	600	3.223 3.037 3.496	3.252
B2	10.146 9.929 10.488	10.187	512 460 469	495	3.847 3.863 3.383	3.697
B3	13.365 11.507 12.824	12.565	521 473 491	480	5.5 5.766 5.82	5.659
B4	14.559 13.095 14.899	14.184	526 483 521	454	6.526 6.658 6.687	6.623
B5	20.254 20.451 20.254	20.318	508 528 541	433	10.88 11.996 10.43	11.102
B6	12.984 13.687 13.750	13.475	444 324 432	445	9.387 8.957 8.795	9.046
B7	13.52 12.82 13.311	13.217	482 414 465	445	9.266 8.573 8.295	8.711
B8	13.412 12.915 13.28	13.202	453 377 490	460	7.742 7.663 7.134	7.513



**Fig. 3. Tensile strength of (B) compounds.**

To show the effect of Nano-ZnO on tensile properties comparison between (B5) compound (it is the best compound in group B compounds) and (A) compound (is used as standard in State Company for Tire Industry in Najaf) is made. Fig. 4 shows a comparison the tensile strength between two samples. Sample (A) represents a compound with conventional ZnO 8phr concentration. Sample (B5) represents a compound with 1.8 phr concentration of nano-ZnO. It is obvious that the tensile strength increased by 38.31% when using nano-ZnO. It is also noticed that reduction in ZnO by 77.5% occurs which is preferable in the contamination of the environment point of view. This result is due to high surface area and dispersion of nano-ZnO in comparing with conventional ZnO.



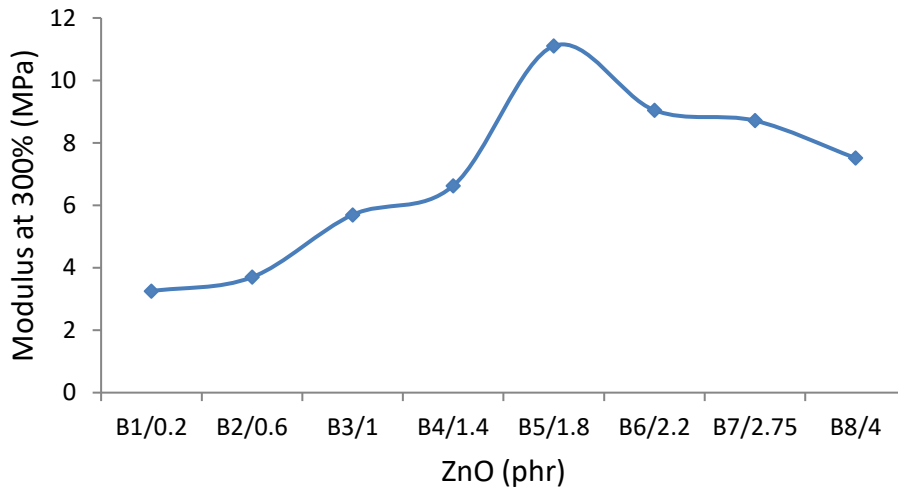
**Fig. 4. Tensile strength for A and B5 compounds.**

**3.2. Modulus at 300%**

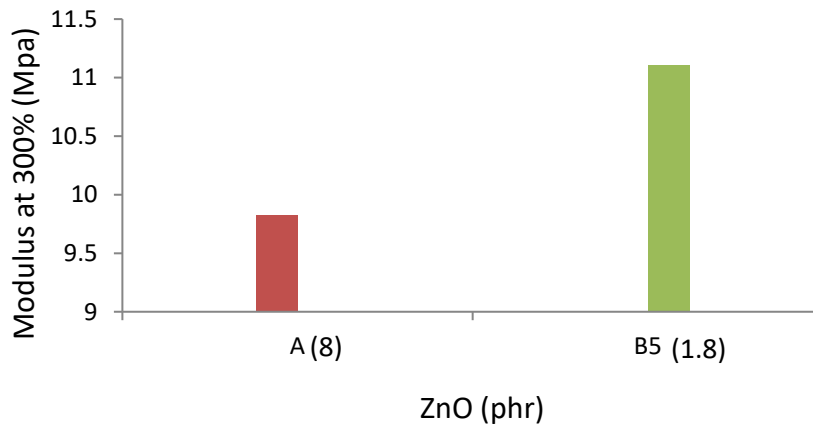
The results of B compounds group are presented in Fig. 5. As it was seen that the modulus at 300% increased progressively with increasing Nano-ZnO level from 0.2 phr up to a maximum value at 1.8 phr.

These results are due to increasing the crosslink density. But the modulus at 300% decreases with increasing Nano-ZnO beyond 1.8 phr. These results are due to the relation between zinc oxide and crosslink density and the negative effect of increasing the crosslink density on the elasticity of the compound after 1.8 phr of the concentration of Nano-ZnO.

Fig. 6 shows the effect of Nano-ZnO on modulus at 300% compared with the results of A compound. It is seen that the maximum modulus of B5 compound is 11.102 MPa where it is greater than the modulus at A compound which is 9.858 MPa. That means when using Nano-ZnO increased in modulus at 300% by 11.8% which is preferable from elasticity point of view.



**Fig. 5. Modulus at 300% for B compounds.**



**Fig. 6. Modulus at 300% for A and B5 compounds.**

### 3.3. Elongation at Break

Referring to the Fig. 7 of B compounds, the elongation at break decreases with increasing Nano-ZnO level. This observation is attributed to increasing in crosslink density with increasing Nano-ZnO level, leading to a reduction in molecular chain mobility. Also, in Fig. 8 the elongation at break for A compound is compared with that of B5 compound. It can be seen that the elongation in A compound was greater than B5 compound because the A compound material has less elasticity as compared with B5 compound which emphasized the fact mentioned in article 3.2.

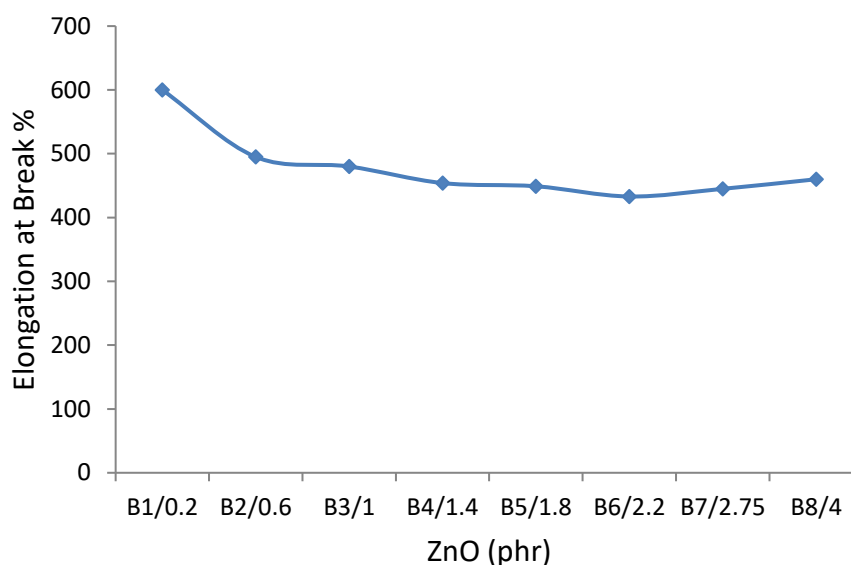


Fig. 7. Elongation at break for B compounds.

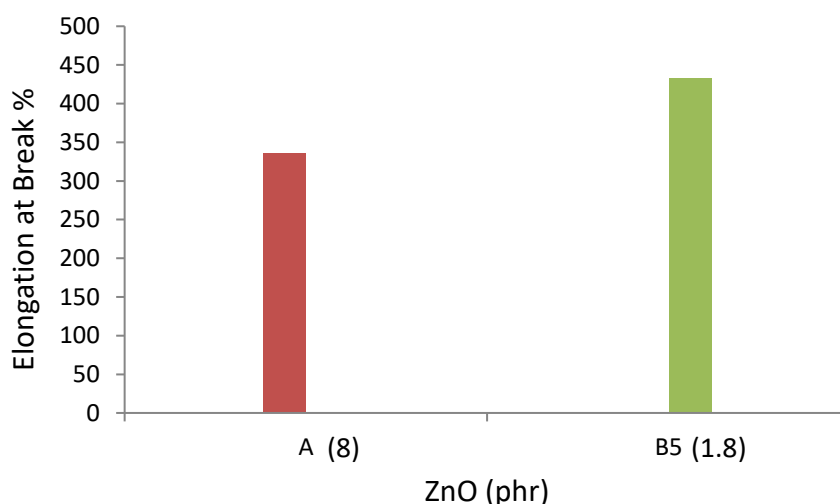


Fig. 8. Elongation at break for A and B5 compounds.

#### **4. CONCLUSIONS**

From the preceding articles, one can withdraw the following conclusions:

1. Nano-ZnO gives the SMR20 compound optimum tensile properties (tensile strength and modulus at 300%) at (1.8 phr).
2. Tensile strength with nano-ZnO at (1.8 phr) is greater than that of the conventional ZnO at (8 phr) with the percentage of 38.31%.
3. Modulus at 300% with nano-zinc oxide at (1.8 phr) is less than that of the conventional ZnO at (8 phr) with the percentage of 11.8%.
4. Elongation at break decreases with increasing nano-ZnO level.
5. Reduction the amount of ZnO by 77.5%. This reduction is preferable because the fact is that ZnO is harmful to the environments.

#### **5. REFRANCES**

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