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EFFECT OF ZINC OXIDE LOADING LEVELS ON THE CURE CHARACTERISTICS, MECHANICAL AND AGING PROPERTIES OF THE EPDM RUBBER

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ABSTRACT

This paper attempts to show that, the ethylene-propylene-diene monomer (EPDM) activated by adding different loading levels of zinc oxide (ZnO). A two-roll mill used to mix and distribute the elements of the rubber compound. MV-ODR-PROPERTIES rheometer employed to determine the properties of the rubber compound at 180°C for 6 min. The curing process carried out using the hot press at a temperature of 180°C and pressure of 10 bars. Results show that the addition of the (2,4,6,8,10)Part per hundred parts of rubber (phr) ZnO into the EPDM elastomer guides to reduce the scorch time ,curing time with increasing the Max.Torque and cure rate index (CRI), particularly at 2 and 4 phr. Furthermore, an improvement in the tensile strength and modulus of elasticity at 300% elongation, hardness and compression set seen. 2 and 4 phr represent the best loading level of the ZnO, which had more effect on the aging and mechanical properties. In addition, the rubber compound becomes more stiffness, especially when the retention percentage of the properties after thermal aging is low.

Key words: EPDM, Zn, Mechanical Properties, Cure Characteristics, Aging Properties.

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1. INTRODUCTION

Ethylene-Propylene-Diene Monomer (EPDM) is one of the rapid growing elastomers in recent years. It can be attributed to this monomer has a good electrical properties and high resistance to thermal aging [1-3]. It has great effect on sound absorption and noise [4] However, it requires some activators such as zinc oxide (ZnO) to improve its mechanical and thermal properties, and curing characteristics, especially when the sulfur is used in the vulcanization process of rubber[5,6]. It has high resistance against oxygen, UV lights, chemicals, and ozone [7, 8]

It has high cross-links density when it is vulcanized using sulfur at a high-temperature. Activators that include ZnO, are used to reduce the curing time and increase the curing rate by combining ZnO with the stearic acid in the rubber to form (soap-zinc stearate) [9,10]. ZnO is an organic material and widely used in the production of natural and industrial rubber compounds, and the best loading levels of the ZnO in the rubber compounds are between 2 and 5 phr [10]. ZnO gives a stable state of curing by activating the sulphur vulcanization, increases the torque, and reduces the cure time and scorch time [11,12].ZnO surface acts as a reactive substance and a catalyst reaction guide by stimulating and connecting the reactants, sulfur, accelerators and the fatty acids that are diffusing easily within the matrix, and absorbed on the surface of the ZnO to form a complicated compound. During this case, the location of the S-S bond is a change, and there is possibility to break the bond. Nevertheless, the range of the generated cross-links improved, additionally to the vital role that plays the surface area of the ZnO to increase the cross-links [12, 13]. The addition of the ZnO into EPDM rubber enhances the mechanical properties such as the tensile strength and modulus of elasticity, and increases crystalline properties of composite rubber [14]. Mu et al, 2007 reported that the mechanical properties like tensile strength, hardness increased with increasing the ZnO content until 12 phr. to reinforce the silicone rubber [15]·The aim of the paper is to provide a conceptual theoretical framework based on the influence of the ZnO loading on the curing, thermal and mechanical properties of the EPDM rubber.

2.1. Materials

EPDM rubber (Keaton, 4802) was purchased from DSM Elastomers B.V., European nation, includes 52%wt. of ethylene parts and 4.3%wt. of ENB; it is a relatively slim relative molecular mass allocation and a standard "Mooney viscosity, mL (1+4) at 125°C". "Carbon black N326 with surface area seventy-six m^2/g, average particle size 45µm obtained from (MAKROchem S.A.)". "ZnO with surface area six m^2/g , pureness of zinc oxide ninety nine Min, , SP. Gravity 5.6 with a particle size 300-1000µm obtained from Merck B.V. stearic acid with SP. Gravity 0.85, Ash at 550°C 0.1% Max. , Volatile matter at 65°C 0.5% Max", "Insoluble in sulfur with SP.Gravity1.57 obtained from J.T. Baker, sulfur content 80±2%, Ash at 550°C 0.2% Max, volatile matter at 80°C 0.5% max obtained from J.T. Baker", " 2-Mercaptobenzothiazole obtained from (Perkacit MBT) and "Tetramethylthiuram-disulphide (Perkacit TMTD)" obtained from (Flexsys B.V.).

2.2. Rubber Combining

The EPDM-master batch is prepared by using a 6-inch dual-roll mill at ~ 50°C according to ASTM D 3182 witha uniform mix and lessen the impact of blending conditions. In the rubber mixing system, the different loading levels of the ZnO added to rubber compound using a dual-roll mill. The blends laminated to a thickness of roughly 2mm, which appropriated for the following production of check examples. The component of the ethylene-propylene-diene monomer with various percentage of ZnO illustrated in Table 1.

Table 1: Rubber compounds for different ZnO loading levels.

Ingredient	**Recipe, phr[a]**
Rubber [b]	100
Stearic acid	1.0
Zinc oxide	0,2,4,6,8,10
Carbon black (N326)	70
TMTD	1.0
MBT	0.5
Sulfur	1.5

[a]Part per hundred parts of rubber, [b] EPDM

2.3. Curing Properties

The curing properties of the various components were tested at 160°C and 180°C with a "MV-ODR-PROPERTIES rheometer (Micro vision Enterprises-India)" according to ASTM D2705. The cure time (T_C) and scorch time (T_S) of the components specified. It found that the best cure time and scorch time were 90% of the cure time (T_{C90}) and 2min after the scorch time (T_{S2}), respectively. The compounds were cured in the labs of polymers and petrochemical industries department using XLB-D 350 X 350 electrically heated press(Huzhou, East machinery- China) at 180°Cwith the optimum cure time T_{C90} under pressure of 10 bar .

2.4. Characterization

2.4.1. Tensile Test

The tensile inspection was carried out on dumb-bell samples according to the ASTM D 412 using " (Time group Inc –Chain) with model WDW-5E microcomputer controlled electronic universal testing machine". The dumb-bell samples with 2mm thickness cut off from the molded layers using a Wallace die cutter. The speed test, that used, was 500 mm/min at 25± 3°C. and 5 specimens were tested for each case.

2.4.2. Thermal Aging

The thermal aging properties of the cured rubber were studied by aging for 4 days at 100°C according to ASTMD573.

2.4.3. Hardness

Hardness of the specimens was tested using Hardness-meter Shore A tester" TH200 (Beijing time technology Ltd) according to ASTM D2240-02 test method. It was recorded 5 readings on different places at room temperature for each specimen.

2.4.4. Compression Set

The compressive set examination of the rubber samples must carried out according to the standard (ASTM D395-03 (2008). The sample have to be cylindrical, 20 mm diameter and 15 mm thickness. The steps of the test showed as following:

The sample placed between the plates of the compression equipment to reduce the thickness of 25% of the initial thickness.

The compressed sample was then set in an oven at 100°C for 24 hours.

The sample cooled for 30 minutes.

The thickness of the final sample measured to determine the compression set of the samples.

3. RESULTS AND DISCUSSION

3.1. Curing Properties

The rheological behavior of the uncured elastomer after addition of (0, 2, 4, 6, 8, 10) phr of the loaded ZnO to the EPDM Rubber is presented in **Table 2**. The results show that the curing time (T_{C90}) of the vulcanized EPDM rubber at temperatures 160°C and 180°C decreases with increasing the ZnO content. The vulcanization properties of the rubber compound greatlyimproved at 180°C, especially the torque characteristic. The lowest cure time and scorch time with the highest cure rateindex (CRI) are observed at 2 and 4 phr. The EPDM rubber exhibits longer T_{C90} than the EPDM rubber reinforced with the ZnO particles. This result will be linked with the fact that when the ZnO particles are added to rubber compounds, they enhance sulfur vulcanization performance and cure properties by combining ZnO and the stearic acid within the rubber matrix to make (soap-zinc stearate)[9,10] . On the other hand, the CRI helps in raising the speed of the cure reaction [16, 17], this relation is given in the following equation:

$$CRI = 100 / (T_{C90} - T_{S2}) \quad (1)$$

Where the T_{C90} is 90% of the cure time and T_{S2} is 2min after the scorch time. CRI increases with increasing the ZnO content. The best activation of the cure reaction is at 2 and 4 phr. In spite of the increasing the torque at higher loading, the curing time decreases slightly with increasing the ZnO loading until 4 phr. This can attributed to the high interference between the elastomer matrix and the ZnO surface, this confirms the tendency of the rubber compounds to create agglomerations at higher loading of ZnO resulting in decreasing the cross-links formation [12, 13].

Table 2 Rheometric properties of the EPDM rubber reinforced with ZnO at 160°C and 180°C for 6 min.

ZnO	**CRI [a](min^{-1})**		**(T_{C90}) [b] (min)**		**(T_{S2}) [c] (min)**		**(D_{max})[d](Ib-in)**	
(phr)	**160°C**	**180°C**	**160°C**	**180°C**	**160°C**	**180°C**	**160°C**	**180°C**
0.0	28.5	33.4	5.5	4.5	2.0	1.50	80.00	85.000
2.0	34.88	56.81	3.95	2.53	1.25	0.77	100.16	100.99
4.0	32.752.08		4.2	2.78	1.33	0.86	103.33	104.34
6.0	30.4646.94		4.62	3.13	1.55	1.00	111.54	118.21
8.0	30.4643.47		4.60	3.32	1.52	1.02	114.27	117.99
10.0	30.9344.85		4.58	3.18	1.52	0.90	116.27	120.15

[a] Cure rate index CRI = 100 / ($T_{C90} - T_{S2}$), [b] Cure time, [c] Scorch time , [d] Max. Torque

3.2. Mechanical Properties

The effect of addition of (0, 2, 4, 6, 8, 10) phr of the ZnO on the tensile strength, modulus of elasticity at 300% elongation, elongation at the break, hardness shore-A and compression set are illustrated in the **Figures 1-5**. The mechanical properties show a direct correlation with the characteristics of curing, in particular, the properties of curing at 180°C. The tensile strength and modulus of elasticity at 300% elongation of the EPDM rubber reinforced with the ZnO particles increase with increasing the ZnO content compared with the mechanical properties of the EPDM rubber (in the absence of the ZnO in the EPDM rubber), especially at the low loading levels 2 and 4 phr (**Figures 1 and 2**). This confirms the important role that the low loading levels of the ZnO play in obtaining a homogenous mixture resulting from good dispersion in the rubber matrix. On the others hand, the torque of the rubber mixtures increased with increasing the znic oxide loading levels (6,8 and 10 phr) which lead to the heterogeneity of the rubber mixture, particle aggregations and reduction in the formation of cross-links at high znic oxide [14,15].Furthermore, the elongation at break decreases with increasing the ZnO loading levels as compared to the EPDM rubber compound without ZnO (**Figure 3**).

Overall, these results indicate that theZnO particles that play as a good activator in the rubber curing by sulfur and combination with the stearic acid to form good bonding with the rubber [10]. The improvement of the Cure rate index and interference between the ZnO particles and the elastomer matrix, lead to a slight improvement in hardness of rubber compounds with increasing the ZnO content (**Figure 4**). On the other hand, the results of the compression set presented in (**Figure 5**) which shows that low loading levels give the best results for a compression set. Because the compression set represents the ability of vulcanized rubber to maintain elasticity specifications after removing applied stresses for long times under certain conditions. Therefore, the weak performance of the rubber compound can attributed not form a sufficient cross-link, leading to relaxation during the examination of compression set [17].

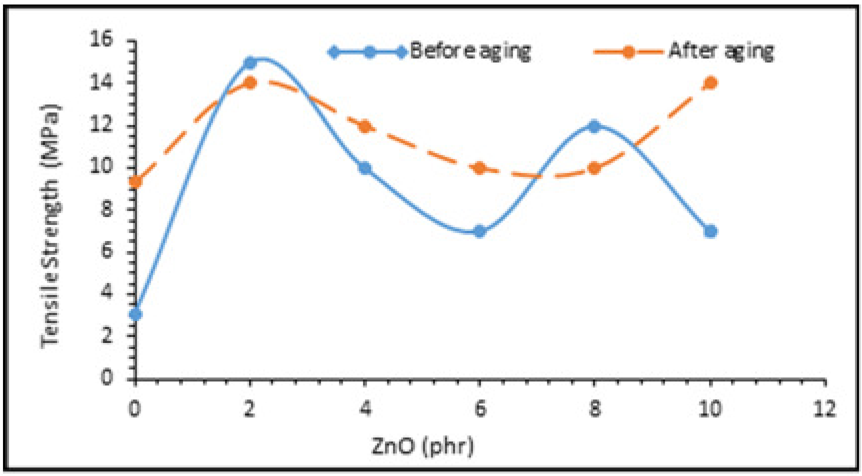

Figure 1 Tensile strength of the EPDM rubber with different ZnO loading levels (phr).

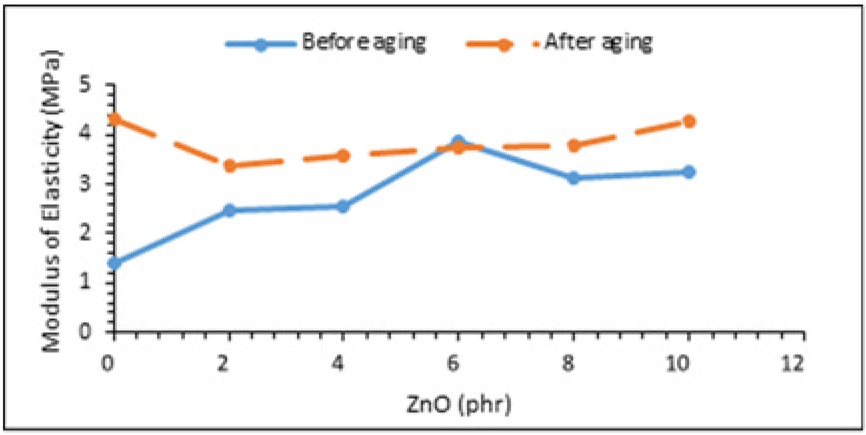

Figure 2 Modulus of elasticity at 300% elongation of the EPDM rubber with different ZnO loading levels (phr).

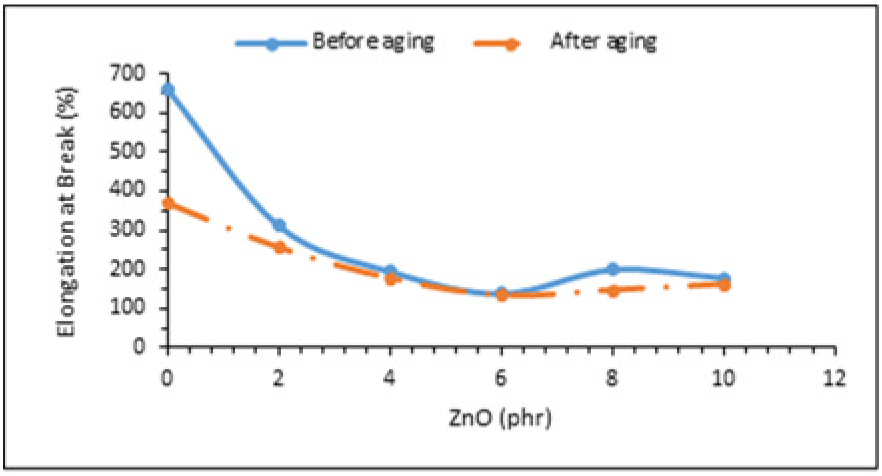

Figure 3 Elongation at break (%) of the EPDM rubber with different ZnO loading levels (phr).

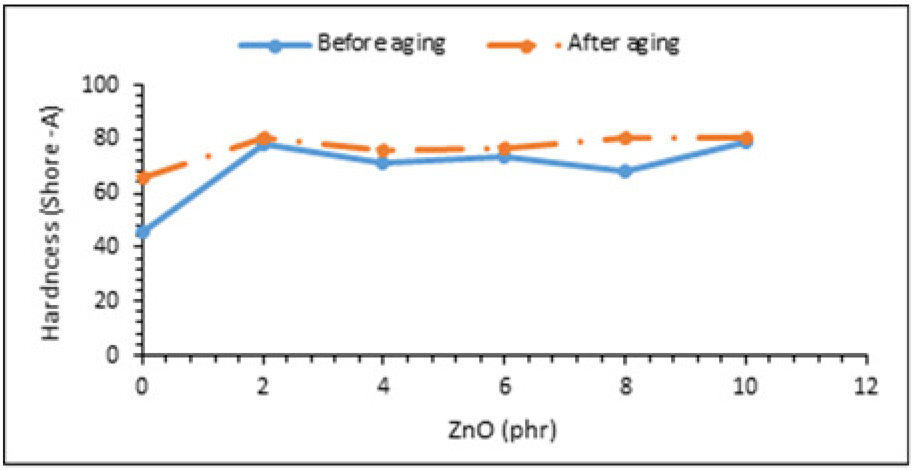

Figure 4 Hardness (Shore-A) of the EPDM rubber with different ZnO loading levels (phr).

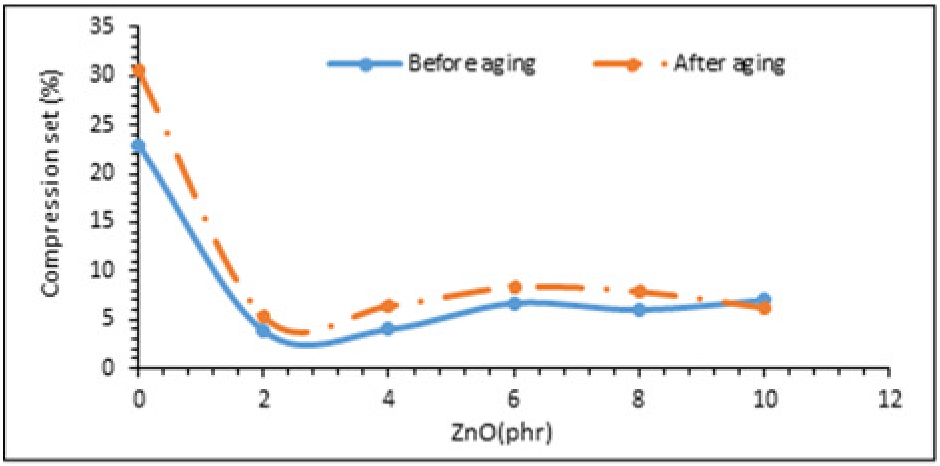

Figure 5 The compression set (%) of the EPDM rubber with different ZnO loading levels (phr).

3.3. Thermal Aging

The results in this part indicate that the influence of thermal aging at 100°C for 4 days on the mechanical properties of the EPDM rubber reinforced with ZnO particles (0, 2, 4, 6, 8 and 10 phr), which represented in **Figures (1-5)**. The results display that the rubber compound at 2 phr of ZnO presents higher tensile strength, hardness, and lower compressive set for both before and after aging. The thermal aging lead to enhancement the hardness, tensile strength and the reduction in the compression set for the rubber compounds having a low cure rate index (CRI) [18].On the other hand, the tensile strength, modulus of elasticity at 300% elongation, elongation at the break, hardness shore-A and compression set of accelerated aging measured after one day of an aging check to estimate aging resistance of the EPDM rubber compoundsas described in (**Table 3**). The percentage retention of the above properties calculated according to the following equation [17, 19].

$$\textbf{Retention}\% = \frac{\textbf{Value once aging}}{\textbf{Value before aging}} \boldsymbol{x}\ \textbf{100} \qquad (2)$$

In general, the retention percentage of the mechanical properties of the EPDM rubber after the aging is good, Therefore, the properties after again do not rely on the network structure or the character of the cross-links [20]. It can see in **Table 3** that the percentage of retention after the aging of the tensile strength, the modulus of elasticity at 300% elongation and hardness are reduced at 2 and 4 phr and so raised with high amounts of ZnO. In contrast, the retention percentage of elongation at the break and the compression set promoted with increasing the amounts of ZnO. This may be due to the reduction in the elasticity of rubber chains after aging, giving more plasticity with the addition the ZnO particles [17]. Thus, the property that has the lowest percentage of retention after aging, it has a low aging resistance.

Table 3 Percentage of retention of the mechanical properties of EPDM rubber with different loading levels of ZnO after thermal aging at 100°C for 4 days

ZnO (phr)	(T.S) [a](%)	(M)[b] (%)	(E)[c] (%)	(H)[d] (Shore-A)	(C.S)[e] (%)
0.0	300	307	56	143	133
2.0	93	137	72	104	139
4.0	83	120	90	107	160
6.0	120	97	96	104	124
8.0	143	121	73	105	131
10.0	200	131	91	81	91

[a] Tensile Strength , [b] Modulus of elasticity at 300% elongation , [c] Elongation at break ,
[d] Hardness , [e] Compression set

4. CONCLUSION

The present study designed to determine the effect of the amount zinc oxide on the cure characterization; the mechanical and thermal properties of the EPDM rubber compound rely on the temperature of the curing. The loading levels of the ZnO such as 2 and 4 phr display a big effective on the cure characterization such as a high cure rate index, torque, low scorch and cure time. In accession, holding the most effective mechanical properties like high tensile strength, hardness with low compression set but low resistance for thermal aging.

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