









++ MBT = 2-Mercaptobenzothiazole

\*TMQ = Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline

## Assessment of vulcanisate properties

Vulcanisate properties such as Hardness, Tensile strength, Modulus Elongation at break, Compression set and Abrasion resistance were assessed according to standard methods. (ASTM D1415, ASTM D1456, ASTM D 385, BS 903 part A9, BS 903 part A6) respectively.

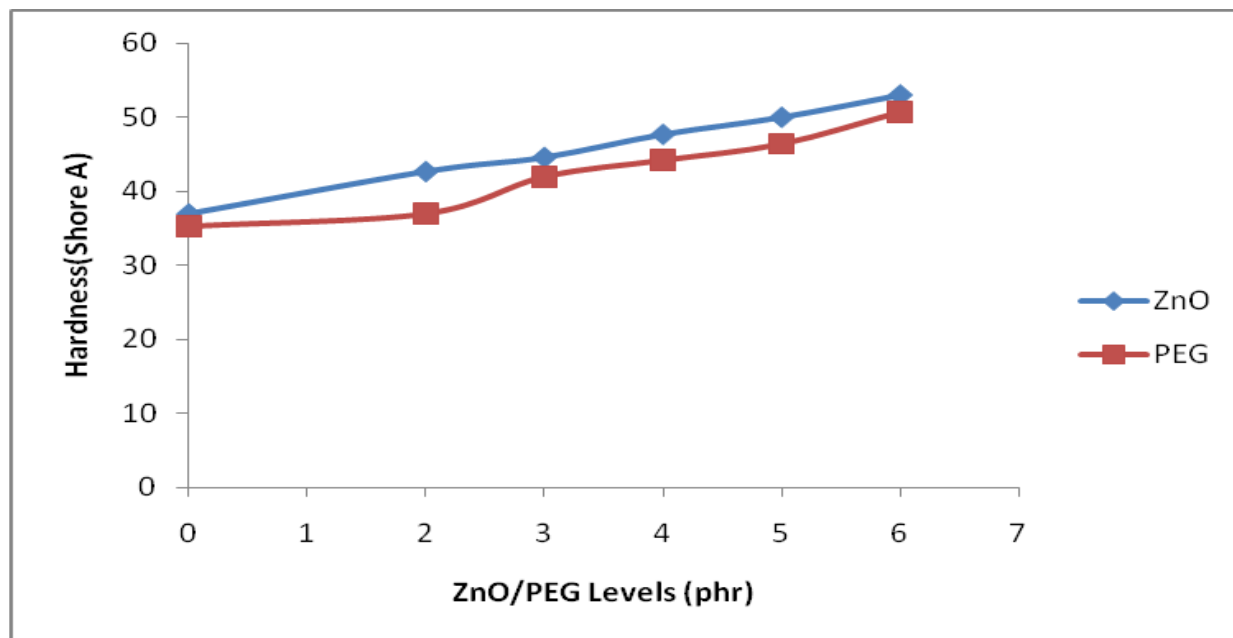
## Results and Discussion.

**Table 2: Effect of ZnO/PEG levels on the Mechanical Properties.**

S/No	ZnO	PEG	Hardness (Shore A)	Tensile Strenght (N/mm <sup>2</sup> )	Elongation@ Break (%)	Modulus (N/mm <sup>2</sup> )	Abrasion resistance (mm <sup>3</sup> /rev)	Compression set (%)
1	0.0	0.0	(37.0) [35.3]	(5.2) [4.8]	(608.2) [628.1]	(2.4) [2.1]	(40.2) [39.0]	(38.2) [38.2]
2	2.0	2.0	(42.7) [37.0]	(6.2) [6.0]	(573.0) [591.8]	(3.0) [2.6]	(32.6) [31.1]	(36.0) [35.8]
3	3.0	3.0	(44.6) [42.0]	(8.3) [8.0]	(492.3) [518.0]	(4.1) [4.0]	(29.5) [28.4]	(34.3) [33.1]
4	4.0	4.0	(47.7) [44.2]	(14.0) [13.0]	(404.4) [412.0]	(8.3) [7.9]	(26.0) [25.2]	(29.4) [28.7]
5	5.0	5.0	(50.0) [46.4]	(15.3) [14.6]	(378.8) [401.4]	(9.0) [8.1]	(22.9) [22.0]	(27.4) [28.0]
6	6.0	6.0	(53.0) [50.7]	(14.4) [13.8]	(363.1) [367.0]	(8.5) [8.1]	(20.4) [20.0]	(23.2) [24.0]

() ZnO [ ]PEG

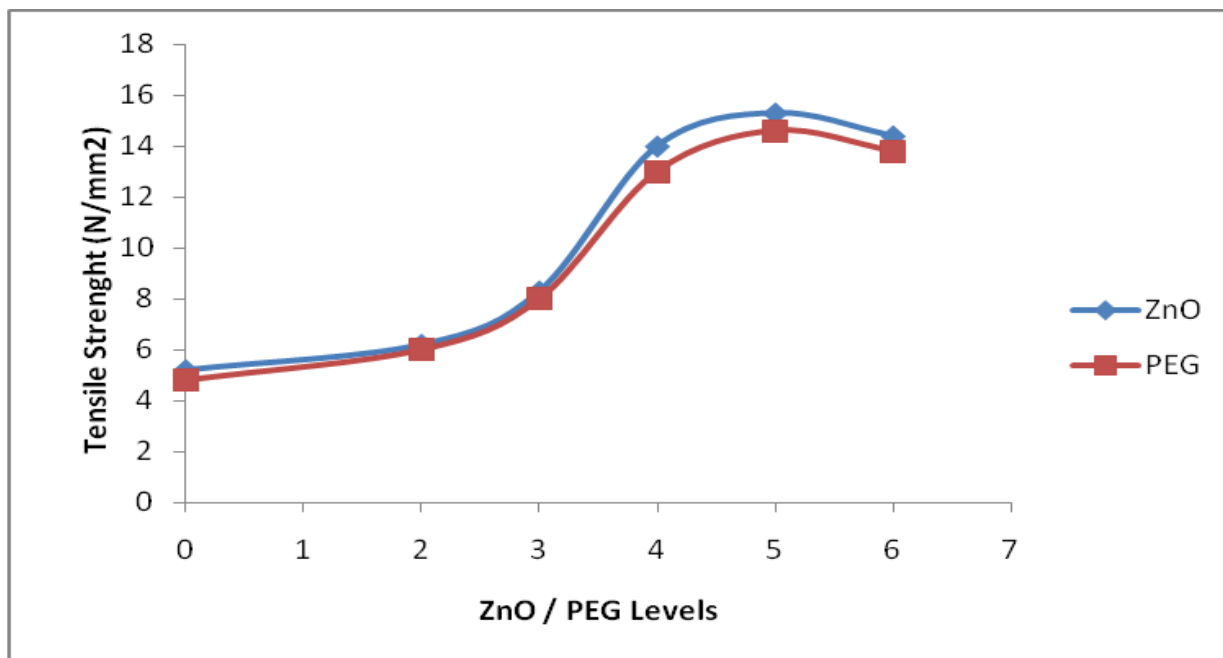
## Hardness



**Fig. 1 Effect of ZnO/PEG level on Hardness**

Hardness is determined by the amount and type of reinforcement, degree of dispersion and extent of crosslink density formation as a result of vulcanization (Erman, 2013). Figure 1 shows that hardness increase with increase in both Zinc Oxide and PEG levels respectively but much better with ZnO than PEG, due to increase in crosslink efficiency and crosslink density formation. A number of studies on the activation process (Heidemann et al, 2004, 2005, 2006), (Maiti et al, 2017) has revealed that with ZnO an active sulphurating complex is formed by the reaction of ZnO and MBT to produce ZMBT, which eventually is converted into the active sulphurating complexes that enhances the formation of more crosslink densities. Qi et. al., (2014) observed that the crosslink density increased with increasing zinc stearate concentrations. Maiti et. al., (2017) asserted that due to the presence of long – chain organic PEG molecules that there is good compatibility with elastomeric matrix leading to better dispersion. Hardness is a factor of crosslink density; the higher the crosslink density produced during vulcanization, the harder the material. (Sahoo, et al. 2017).

### Tensile Strength.



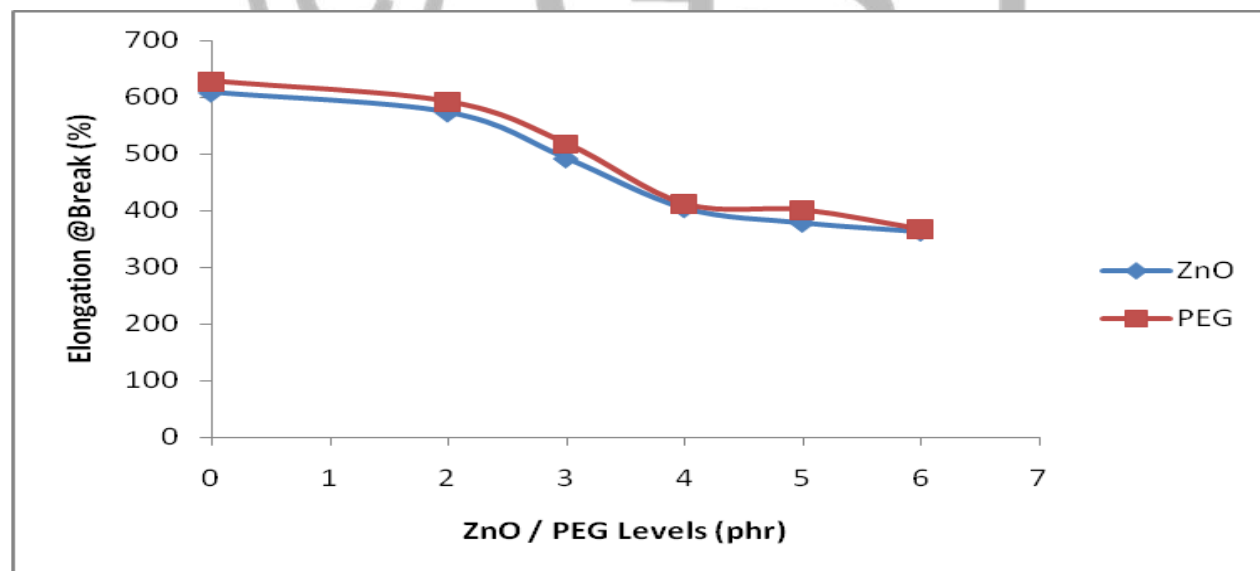
**Fig. 2: Effect of ZnO/PEG on Tensile Strength.**

Figure 2 above shows that tensile strength increased progressively with increase in Zinc Oxide and PEG levels respectively from 0phr up to a maximum at 5phr. This increase is attributed to consolidation of network structure of the rubber chains as a result of increase crosslink density (Muhammad et. al, 2018). Further increase in ZnO/PEG levels was accompanied by decrease in tensile strength. Heideman et al. (2004) observed that the crosslink density increased with increasing zinc stearate concentration up to a level until reversion occurs which led to reduction in mechanical properties. Also Simpson, (2002) asserted that all rubber compounds in which elemental sulphur is the crosslinking agent are subject to reversion usually manifested by reduced tensile strength and modulus. This trend was also observed by Chukwu et al. (2011) in their independent work “effect of stearic acid level on the physical properties of natural rubber vulcanizate”. The noticeable decrease in tensile properties at 6.00phr can equally be explained as reported by Samarzija-Jovanovic et al., (2014) they postulated that the initial polysulphide crosslink formed from the conventional vulcanization system reacts further to form weak mono,

di and cyclic sulphide bonds during vulcanization via the dissociation, recombination and rearrangement of the sulphure linkages. The above reactions are possible because the initial polysulphidic crosslinks formed are thermally unstable and hence undergoes homolytic scission of the sulphure bonds and thermal decomposition and desulphuration leading to weaker bonds. The above assertion was also earlier been made by Lewis, (1986) in his seminal work “Vulcanizate structure and its effects on properties”. As a result of the formation of these weaker bonds at higher stresses, these chains breaks and greater stress will be imposed on neighbouring chains with the eventual result of catastrophic rupture leading to decrease in tensile strength as the force increases.

Heideman et al. (2005) observed that there is increased reversion above 7.0pphr of Zinc Oxide level which is reflected in reduced physical properties such as tensile strength, elongation at break, modulus, and hardness. In this study, we equally noticed the same phenomenon of reversion but at 5.0pphr of Zinc Oxide/PEG levels as reflected in reduced tensile and elongation properties above 5.0pphr respectively.

### Elongation at Break.



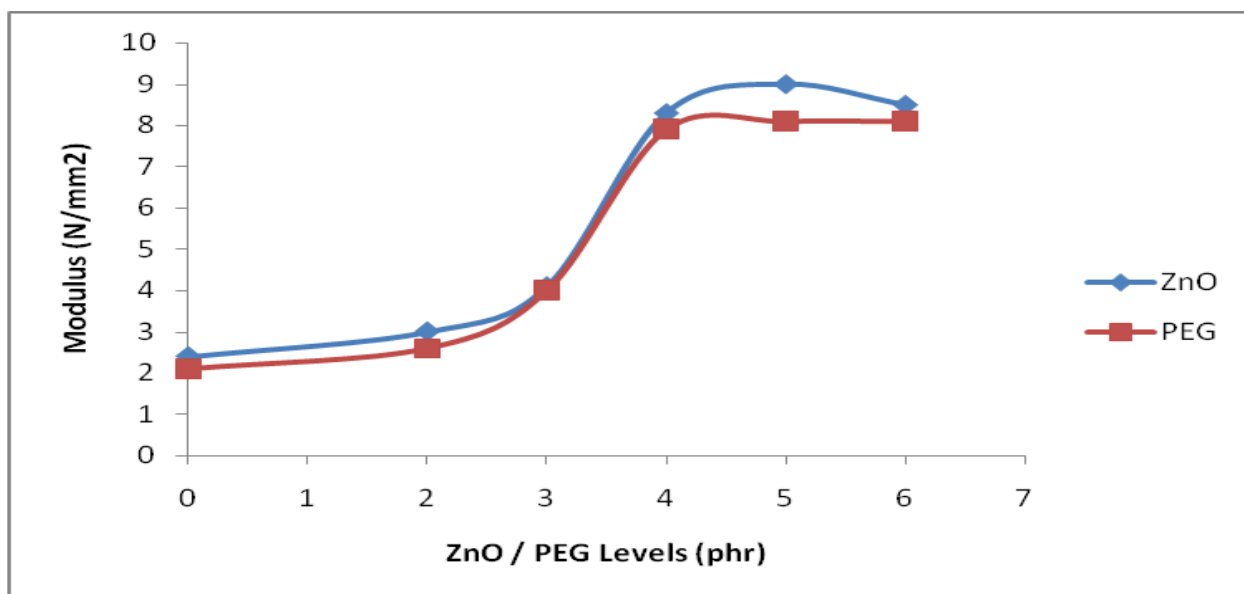
**Fig. 3: Effect of ZnO/PEG levels on Elongation at Break**

The Figure above shows that PEG has more effect on elongation at break than zinc oxide. Elongation at break decreased with increasing PEG/ ZnO level. This observation is



attributed to increase in crosslink density with increased PEG/ZnO levels as a result of consolidation of network structures. The reduction in elongation at break is due to stiffening of the polymer matrix as a result of high crosslink density formation and stiffening of the polymer chains leading to decrease in molecular chain mobility due to extensive formation of physical bonds in the polymer chain (Samarzija-Jovanovich et. al., 2014). The decrease in elongation at break is as a result of corresponding increase in the efficiency of crosslink formation leading to less elastic material. Note that elongation is extension between benchmarks produced by tensile force (Simpson, 2002).

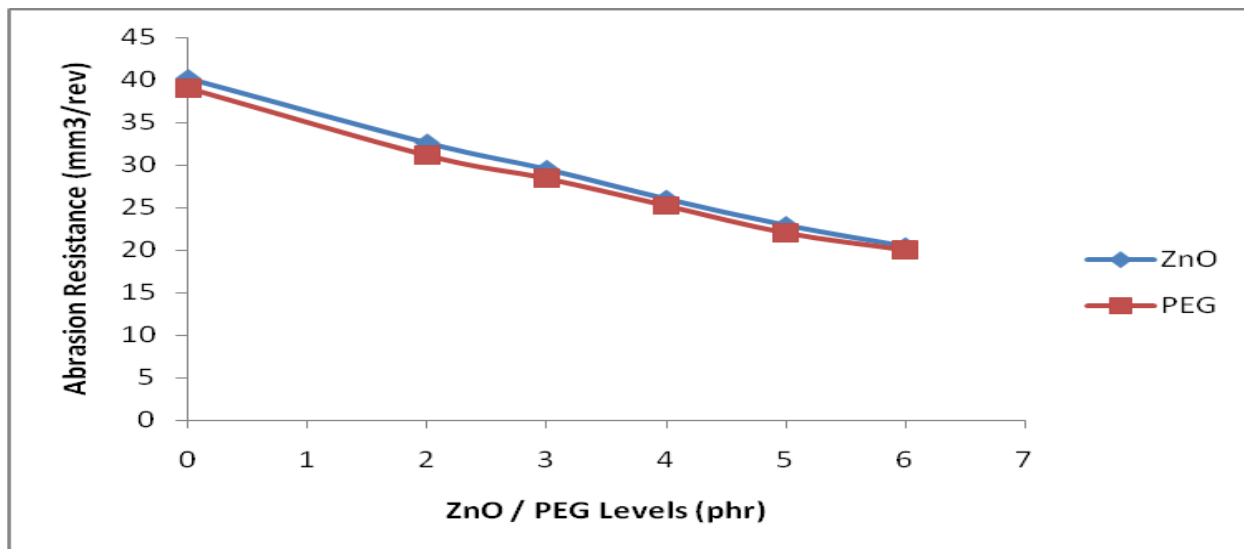
**Modulus.**



**Fig. 4: Effect of ZnO/PEG levels on Modulus**

Modules increased progressively with increase in ZnO/PEG levels from 0phr to a maximum at 5.0phr. This observation is attributed to consolidation of network structure of the vulcanisate as a result of increase in crosslink density as reported earlier (Samarzija-Jovanovich et al 2014). Further addition of zinc oxide after 5.0phr was accompanied by a decrease in modulus, showing sign of reversion cure. At reversion there is reduction in crosslink density formation resulting in less stiff material (Scheirs, 2000). But further addition of PEG above 5.0phr shows no reduction in modulus signifying that there was no reversion but rather an optimization of the property.

### Abrasion Resistance.

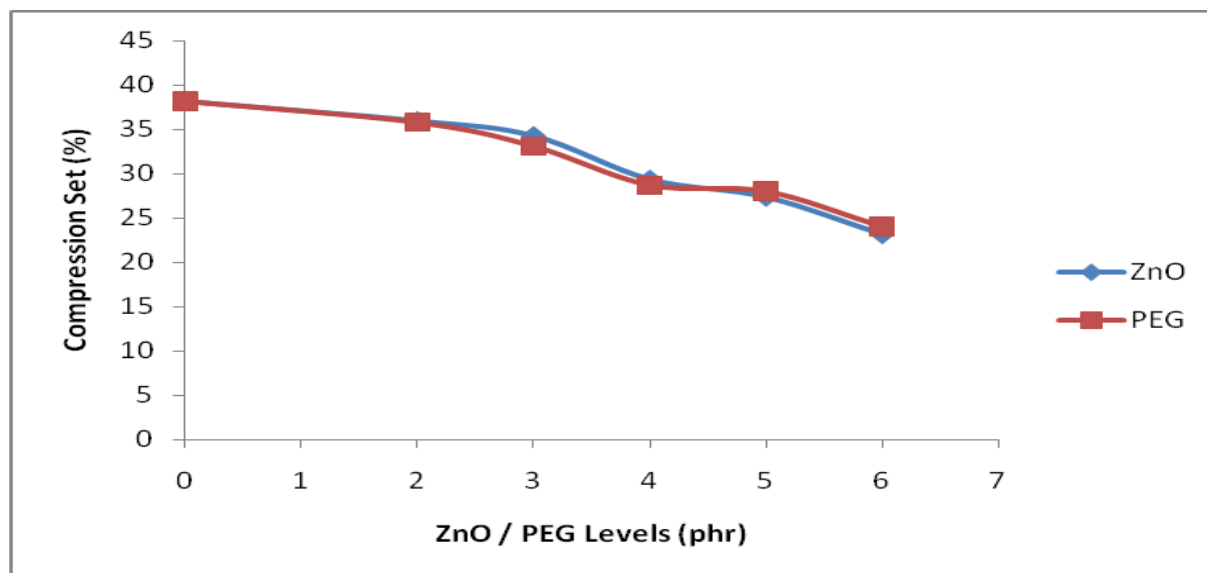


**Fig. 5: Effect of ZnO/PEG levels on Abrasion Resistance**

Abrasion resistance is the resistance of a rubber composition to wearing away by contact with a moving surface or an abrader (Simpson, 2002).

There is a reduction in the abrasion resistance as the ZnO/PEG levels increased; this is as a result of the consolidation of network structures leading to increase in crosslink density formation which results to stiffer material. As the stiffness increased, there is the tendency to resist abrasion, hence the reduction in the abrasion resistance.

## Compression set



**Fig. 6: Effect of ZnO/PEG levels on Compression Set**

Compression set is a useful property of vulcanisates in predicting the service life performance where a rubber article is under load or a compressive force. A high percentage of compression set means high deformation, while lower compression set signifies low deformation (Nagdi, 1992).

The extent of compression set depends on temperature, the amount of load applied and the duration of the deformation. A low compression set at service temperature is an essential requirement for seals, O-rings and gaskets (Scheirs, 2000). If an elastomer is compressed under specified load and conditions, the residual decrease in its thickness after complete release of the compressive force is known as compression set (Simpson, 2002). It is important that compression set should be low for load bearing applications.

Figure 6 shows the effect of compression set on ZnO/PEG levels. The Compression set decreased as the level of ZnO/PEG increases. Both ZnO and PEG have almost the same effect on the compression set of natural rubber vulcanisate at 0 to about 2.0phr, between 2.0 to 4phr there is a marginal increase in the compression set of ZnO against that of PEG, at about 4.0phr both ZnO/PEG have same effect on compression set, but above 5.0phr there is a marginal increase in PEG compression set against ZnO. This could be explained from our earlier observed reversion

of ZnO at 5.0phr in fig.5 and also reflected in fig.6, but this phenomenon (reversion) was not much noticeable in compounds containing PEG as activator.

## **Conclusion**

From this study it has been shown that polyethylene glycol(PEG) can serve as an effective activator in natural rubber compounds.

Complete elimination of zinc compounds in sulphur vulcanisation seems interesting and ambitious. Nevertheless, alternative activation system without zinc or metal species will contribute much regarding the role of activators in sulphur vulcanisation and also to safe guard the environment. Polyethylene glycol is environmental friendly. The aim of this work is to provide alternative route for activation of natural rubber compounds without the use of zinc oxide compounds as a result of its reported environmental effects and legislations involving zinc containing rubber compounds. The work is mainly on the extent of activation of polyethylene glycol on natural rubber compounds, the chemistry and mechanistic details of polyethylene glycol activation process is a subject of another study.

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