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EFFECTS OF POLYETHYLENE GLYCOL AS ALTERNATIVE ACTIVATOR IN A BAMBOO FIBRE FILLED NATURAL RUBBER COMPOSITE.

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Abstract

There is a growing interest in the research community of the possibility of reducing or total elimination of zinc oxide (ZnO) as activator in rubber compounds. This study therefore is an attempt in that direction to study the effect of polyethylene glycol (PEG) as an alternative activator in rubber compounds. Various levels of polyethylene glycol (0,2,3,4,5,6 phr) and zinc oxide (as reference) were compounded with 100phr of natural rubber and other compounding additives. The effects of both polyethylene glycol and zinc oxide were investigated on the mechanical properties of the composite. The results obtained shows that polyethylene glycol has the potential as an activator. But one significant phenomenon noticed in this study is that for modulus polyethylene glycol shows no effect of reversion cure unlike zinc oxide. It is our hope from evidence shown in this study that polyethylene glycol could provide alternative route for activation of natural rubber compounds.

Keywords: *Composite, Mechanical properties, Natural rubber, Polyethylene glycol, Zinc oxide,*

Introduction

As a result of increased environmental awareness and legislations regarding the use and application of heavy metals including zinc oxide and zinc containing compounds, it has become necessary to study the possibility of reducing or completely eliminating zinc oxide (ZnO) content in rubber products.

Zinc is released into the environment from rubber products during production, disposal and recycling of rubber products, also leaching in land-fill sites, and during service conditions through wear of automobile tyres. In most countries there are legislations and penalties concerning leaching of heavy metals into the environment as it concerns the use of zinc compounds in rubber products (Heideman, 2006).

From the above scenario, it is therefore necessary to reduce the zinc oxide content or if possible the total elimination of its use in rubber products. This has therefore made the replacement of zinc oxide as an activator an attractive area for further research. The road transport emission of zinc due to tyre wear is the main source of zinc pollution after iron steel production and non-ferrous metals manufacture. This arises from the zinc oxide content of the tyre-tread material, (Councell et al., 2004, Smolders et al.,2002). Some adverse environmental effects of zinc exposure have been reported (Maiti et. al., 2017).

It is desirable to keep the zinc oxide content in rubber compounds low. Various kind of activators like CaO, MgO, CdO, CuO, PbO have been used in order to replace conventional ZnO due to its toxic and fouling characteristics for acquatic flora and fauna. (Heideman et al.,2005).

Basu et al.,(2014) in their study asserted that layered double hydroxide (LDH) can be used as an alternative activator in place of zinc oxide and stearic acid combination in rubber vulcanisate and can provide a strong platform for reduction of ZnO level in elastomer vulcanisate system.

Several researchers have studied the replacement of conventional ZnO with nano-sized Zno particles. Bhowmicks and his coworkers (Sahoo,et al.,2007a,2007b,2008,) studied Zno nanoparticles as cure activator in natural rubber (NR), nitril rubber(NBR) carboxylated nitril rubber(XNBR) and chloroprene rubber(CR) for the replacement of conventional ZnO. Hadi et al.,(2015) studied the effect of nano zinc oxide on physical properties of NR/SBR composite. Similarly, Joseph et al (2008a, 2008b) also used it as cure activator in Natural Rubber and chloroprene rubber. Several other researcher, (Guzman et al., (2011), Heideman et al.,(2005), Kim et al(2010), Pryzbyszewska and Zaborski,(2010), worked along same line for the replacement of conventional zinc oxide in rubber compounding.

In another approach for the outright replacement of conventional zinc oxide in rubber compounding, Kim et. al., (2011) studied the effects of polyethylene glycol (PEG) on the properties of SBR/organoclay nanocomposite filled with Silica and carbon black.

From the above scenario, there is an interest from the research community to partially substitute or totally replace conventional zinc oxide with other material. Our effort here is also in that direction by trying to look at the effects of polyethylene glycol as alternative activator in a bamboo fibre filled natural rubber composite.

The aim of this work is to provide alternative route for activation of sulphur vulcanization without the use of zinc oxide with particular emphasis on the application of polyethylene glycol as alternative activator.

Experimental

Materials

Natural rubber conforming to SNR-10 was obtained for Rubber research institute of Nigeria, Stearic acid, sulphur, zinc oxide, polyethylene glycol (PEG 600) TMTD,CBS,MBT,TMQ, etc. were obtained from Merck, Aldrich, flexsy, Alfa-Bioch and British drug house (BDH) all were of analytical grades.

Methods

Sample preparation

Mixing and homogenization of the rubber and compounding additives was done on a laboratory two roll mill (size 12”x38inches) with a friction ratio of 1:1.5 in accordance with ASTM D3184-89. The nip was adjusted to review the nip and more passes were done until a firm band was formed around the roll. The temperature of the roll was maintained at 60±5ºC during mastication. The compounding ingredients were added as per sequence given in ASTM D3182. Before the addition of accelerator and sulphur, the batch was cooled. The compound was further homogenized to obtain a thorough mix and finally sheeted out on a nip gap of 3mm. Mixing time and temperature were controlled during the entire process to avoid scorch or premature vulcanization. Two different sets of material were prepared one containing different levels of PEG and another containing different levels of ZnO respectively.

Table1 1: Details of Formulation

Additives	**phr**
Natural rubber (SNR-10)	100.0
Bambooo fibre	40.0
Sulphur	3.0
Activator(PEG/ZnO)	0,2,3,4,5,6(*PEG*) 0,2,3,4,5,6(*ZnO*)
Stearic acid	2.0
CBS^{+}	0.5
MBT^{++}	1.0
TMQ*	0.5
Process oil	2.5

+ CBS = N-cyclohexyl-2-benzothiazolesulphenamide

++ 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^2)	Elongation@ Break (%)	Modulus (N/mm^2)	Abrasion resistance (mm^3/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

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Hardness

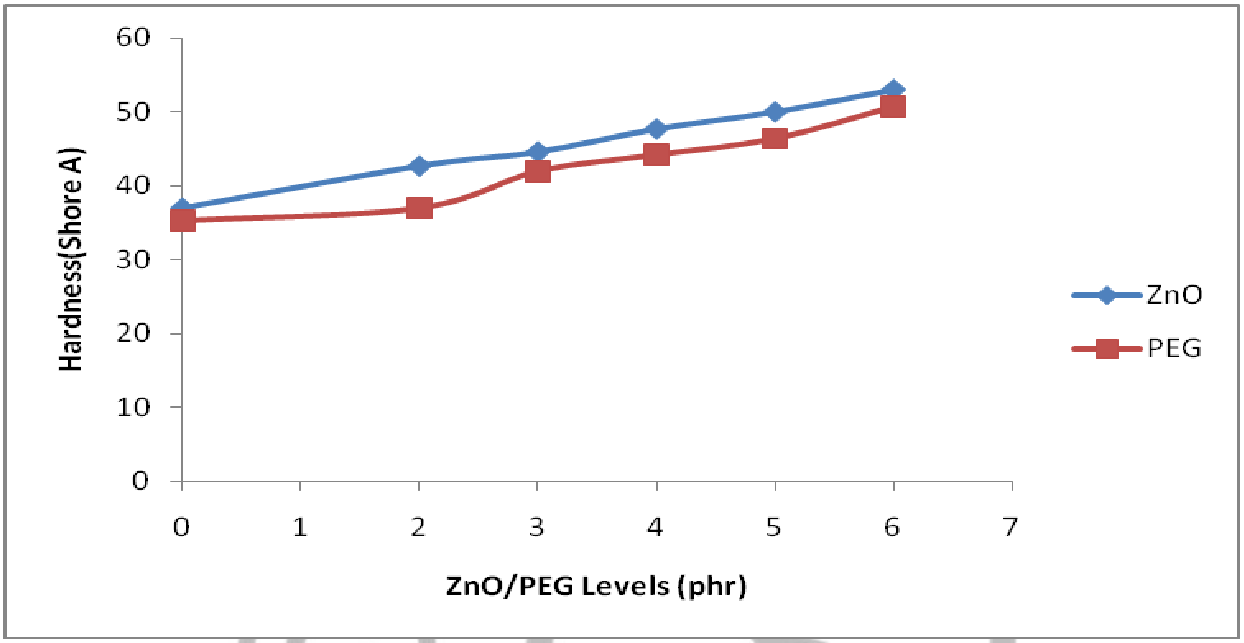

Fig. 1 Effect of ZnO/PEG level on Hardness

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).

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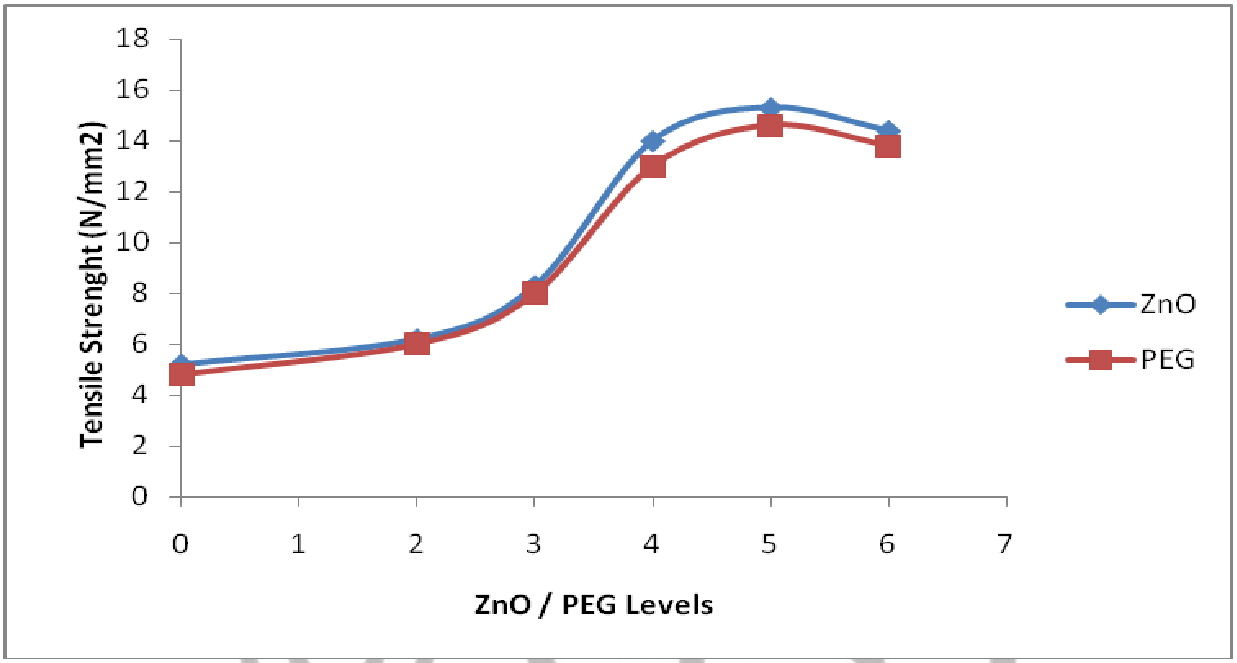
Tensile Strength.



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,

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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 5.0phr of Zinc Oxide/PEG levels as reflected in reduced tensile and elongation properties above 5.0phr respectively.

Elongation at Break.

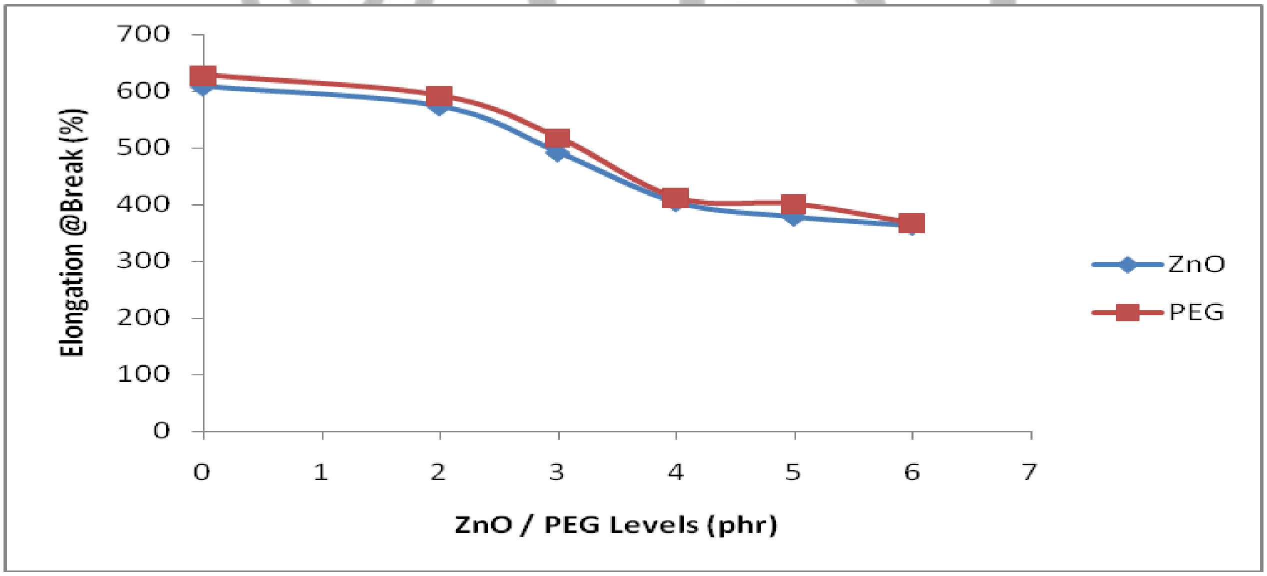

Fig. 3: Effect of ZnO/PEG levels on Elongation at Break

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.

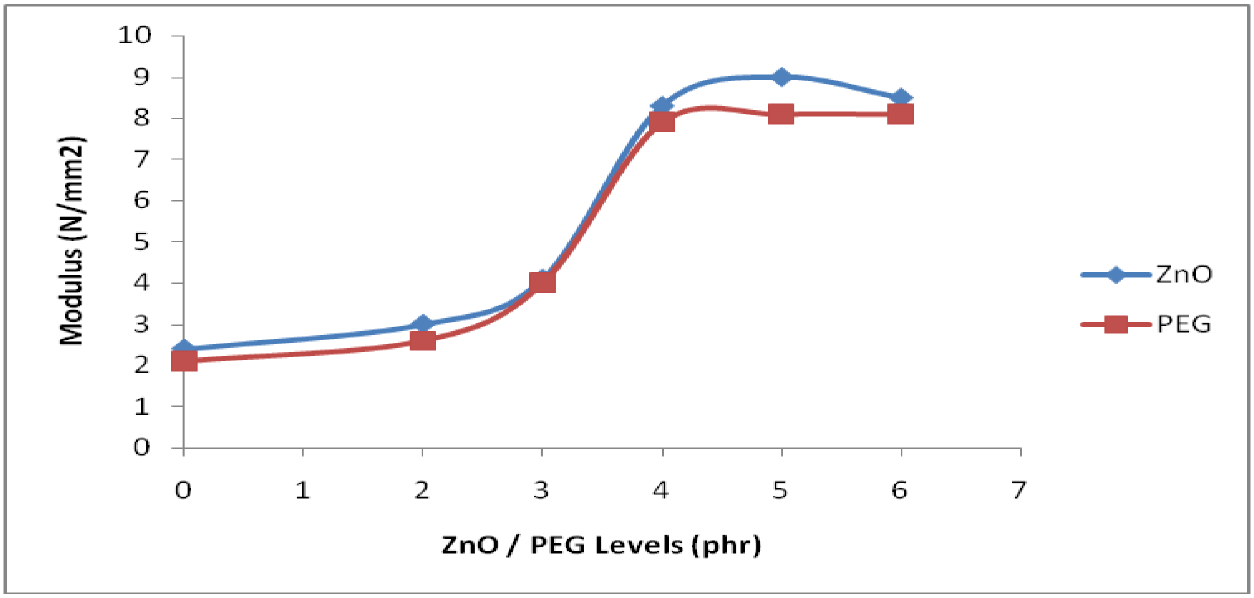

Fig. 4: Effect of ZnO/PEG levels on Modulus

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.

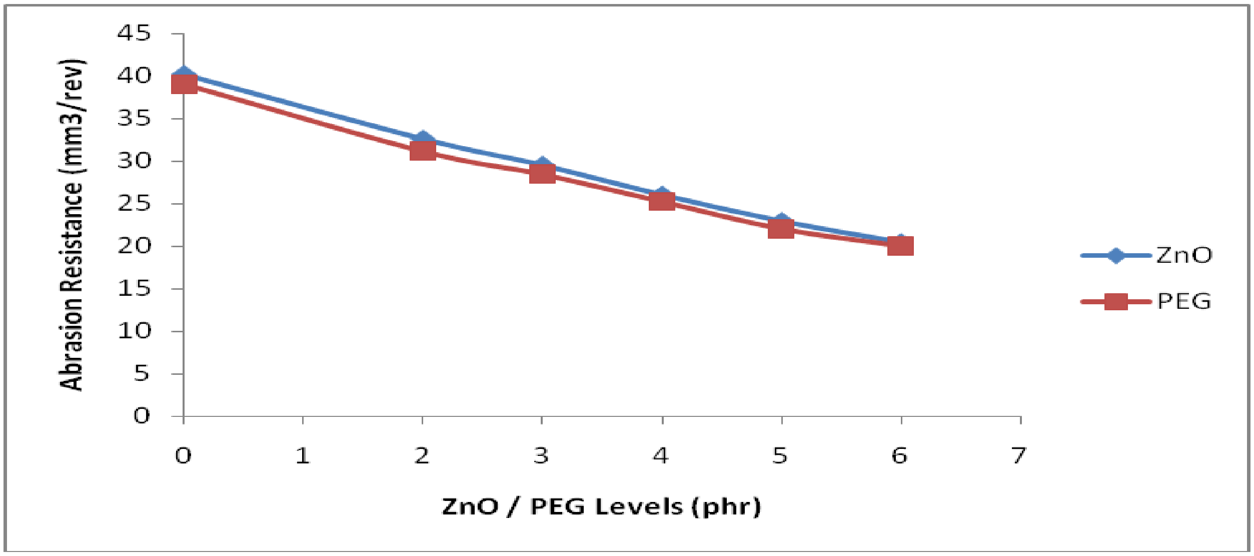

Fig. 5: Effect of ZnO/PEG levels on Abrasion Resistance

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.

Compresion set

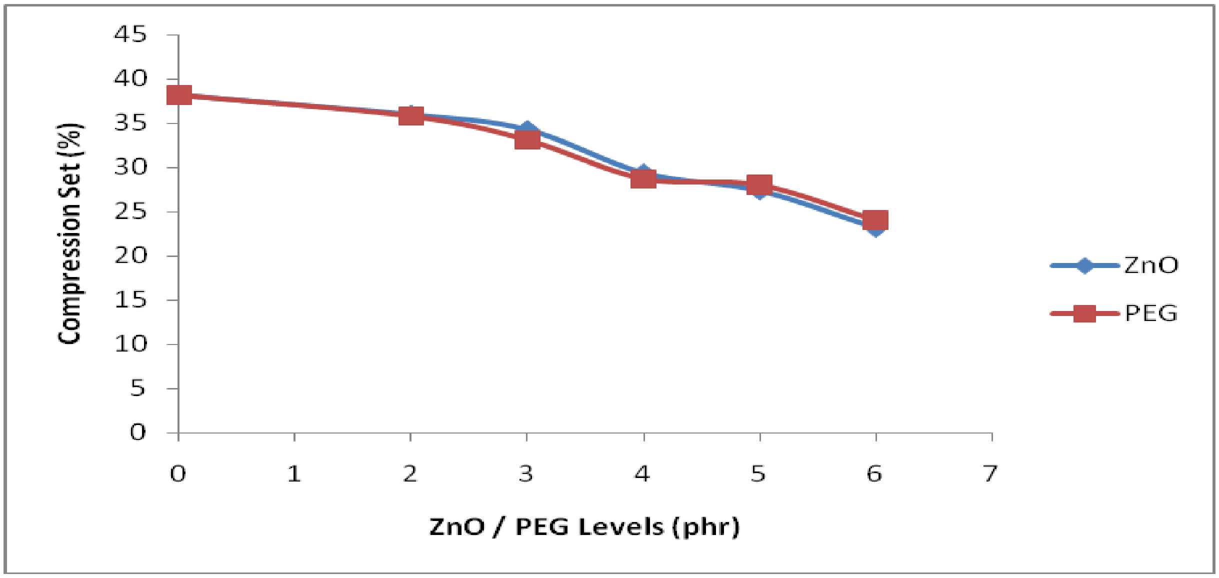

Fig. 6: Effect of ZnO/PEG levels on Compression Set

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 decreasd 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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