EFFECT OF ZINC OXIDE LEVEL AND BLEND RATIO ON VULCANIZATE PROPERTIES OF BLEND OF NATURAL RUBBER AND ACRYLONITRILE-BUTADIENE RUBBER IN THE PRESENCE OF EPOXIDIZED NATURAL RUBBER

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ABSTRACT

Effect of Zinc Oxide level and blend ratio on vulcanizate properties of natural rubber (NR)/acrylonitrile-butadiene rubber (NBR)/epoxidized natural rubber (ENR) blend was studied. NR/NBR/ENR vulcanizates with compositions of 100/100/0 ; 100/90/10 ; 100/70/300 ; 100/50/50 ; 100/30/70 ; and 100/10/90 wt. %, respectively were each prepared with Zinc Oxide level of 0, 2.0, 4.0, 5.0, 6.0, 7.0, and 8.0 phr. The effect of Zinc Oxide level and blend ratio on tensile strength, modulus, elongation at break, hardness, abrasion resistance, compression set, and swelling behaviour of the vulcanizates were investigated. Results obtained show that the use of lower or higher than recommended level of Zinc Oxide in rubber vulcanization can lead to inferior or poor quality vulcanizate. Zinc Oxide level of 5.0 phr gave vulcanizates with optimum tensile strength, modulus and abrasion resistance. Further addition of Zinc Oxide was accompanied by a steady decrease in these properties. Of all blend systems studied, blend sample with composition NR/NBR/ENR: 100/70/30 produced the highest value of these properties. Hardness and compression set showed an increasing trend with increase in Zinc Oxide level due to increase in crosslink density; whereas elongation at break decreased with increase in Zinc Oxide level for the same reason. All vulcanizates exhibited a decreasing trend in swelling ratio as Zinc Oxide level increased up to 5.0 phr, and then increased with further increase in Zinc Oxide. The values of Gibbs free energy (ΔG) and volume fraction of NR in all vulcanizates studied increased with increase in Zinc Oxide level, reaching a maximum at 5.0 phr Zinc Oxide. This signifies progressive improvement in the interfacial interaction between blend components. These interactions lead to an increase in the effective degree of crosslinking, which improves the mechanical properties of the vulcanizates.

Keywords: Zinc oxide level, blend ratio, vulcanizate properties, natural rubber, acrylonitrile-butadiene rubber, epoxidized natural rubber.

INTRODUCTION

The primary motivation for blending polymers is to create materials with combinations of properties superior to the components (Ultracki et al, 1998). Rubber blends make up one class of polymeric materials that have assumed prominence in many areas of application including engineering works. Expectedly, the demand for rubber blends has continued to experience a steady growth over the years. Rubbers in their raw state are not good enough for any useful application, except in their vulcanized state. The desired property improvements obtainable through vulcanization include hardness, tensile strength, modulus and permanent set (Koshy et al, 1992). These vulcanizate properties can be optimized when rubbers are compounded with suitable property-enhancing additives.

Among these additives, Zinc Oxide (ZnO) in conjuction with Stearic acid acts as an activator (or activating system) during sulphur vulcanization (Findik et al, 2004). Sulphur vulcanization alone is a very slow process; hence the essence of activating the vulcanization process is to increase the efficiency of crosslink formation and consolidation of crosslink density (Ramesan, 2004). The use of Zinc Oxide/Stearic acid as activating system is a standard practice in any rubber compounding operation (Kraus, 1978). The object of compounding is to select the most suitable combination of additives in their correct proportion in order to enhance the vulcanization or processing characteristics and/or the end use performance of the vulcanizate (Kurian et al, 1995). Every compounding recipe contains a number of additives, each having a specific function to perform either during processing, vulcanization or end use.

Low or excess level of compounding additives could lead to compromise of vulcanizate properties (Medalia and Kraus, 1994). Previous investigation reports (Barlow, 1993 ; Brydson, 1987 ; Barnhart, 1982) have indicated that some rubber compounders use Zinc Oxide, a basic compounding additive, in quantities higher than the recommended dosage of 4.5 – 5.0 Phr (parts per hundred weight of rubber)(Ciullo and Hewitt, 1999). The arbitrary use of ZnO as against the recommended level by rubber compounders could lead to inferior or poor quality vulcanizate which may fail to satisfy the intended end use requirements. Therefore, formulation design and material selection in their appropriate ratio, must take into account, necessary features which may contribute to failure of end product.

Natural rubber (NR) is the most abundant natural polymer in the world. It is used widely in products such as tyres, condoms, and O-rings, due to its excellent tensile strength, damping properties, and elasticity (Riyajan and Sakdapipanich, 2009). Although, NR is inexpensive and largely abundant in most countries of the world like Nigeria, with its excellent physical properties due to its ability to crystallize on stretching, yet it is immiscible with polar rubbers such as acrylonitrile-butadiene rubber, causing phase separation when blended with such rubbers due to difference in polarity. To address this problem, epoxidized natural rubber (ENR) is considered a potential compatibilizer for this blending system. ENR has epoxide groups along the double bond of the NR polymer chain, which impart excellent oil resistance, gas barrier, good wet grip, and high damping characteristics, while inducing high polarity and promoting miscibility with with polar polymers (Varghese et al, 1995).

In the present study, the effect of Zinc Oxide and blend ratio on vulcanizate properties of blend of NR and NBR in the presence of ENR was investigated. Varying compositions of NR/NBR/ENR containing varying levels of ZnO were prepared. The vulcanizate properties of the blend samples, such as tensile strength, modulus, and elongation at break, compression set, hardness, abrasion resistance and crosslink density were evaluated. The effect of Zinc Oxide level and blend ratio on the vulcanizate properties of blend of NR and NBR in the presence of ENR has not been reported in the scientific literature to my knowledge. However, in my recent study (Onyeagoro, 2012) the influence of carbonized Dika (Irvialgia Gabonensis) nutshell powder on the vulcanizate properties of NR/NBR blend was reported. The study revealed a decreasing trend in elongation at break with decrease in carbonized Dika nutshell filler, whereas a higher elongation at break was shown by NR and NR-rich blends, an observation which is attributed to greater chain mobility of NR matrix over that of NBR matrix due to lower T_g of NR (-72^0c) compared to that of NBR (-40^0c). The report also show an increasing trend in crosslink density for NR and NR-rich blends due to greater chain regularity of NR over NBR which improves on reinforcement.

MATERIALS AND METHODS

Materials

The acrylonitrile-butadiene rubber (NBR, Nipol – produced by Japan Suynthetic Rubber Co. Ltd) was purchased from a chemical store in Lagos, Nigeria. Natural rubber (NR) conforming to Standard African Rubber grade 3 (SAR-3), and the epoxidized natural rubber (ENR) used were kindly provided by Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City. The rubber compounding chemicals, also provided by RRIN, Iyanomo, Benin City were of commercial grades. The basic characteristics of NR (SAR-3), NBR and ENR are given in table 1 at next page.

Preparation of Rubber Blends

NR/NBR/ENR blends with compositions of 100/100/0, 100/90/10, 100/70/30, 100/50/50, 100/30/70, and 100/10/90 wt. %, respectively, were prepared with varying levels of ZnO (Phr) of 0, 2.0, 4.0, 5.0, 6.0, 7.0, and 8.0. The formulation used in preparing the rubber blends is given in Table 2. Weighed amounts of the compounding ingredients with the exception of vulcanizing agent and accelerators were first introduced into a Banbury mixer already preset at 145-150^{0}c for the mastication of the ingredients, and the rubber blend produced was later transferred to a two-roll mill which converted it from an irregularly shaped mass to suitable sheets. The temperature of the mill was reduced from

170^{0}c to 90^{0}c before the introduction of the vulcanizing agent and accelerators to prevent premature curing of the compound mix. The rubber blends were calendared and allowed to condition for seven hours after which they were cured at 5MPa pressure and heating temperature of 145^{0}c for 20min

Table 1: Characteristics of ^{a}NR (SAR-3), ^{b}NBR and ^{c}ENR

Material	Parameter	
Natural rubber, NR (SAR-3)	Dirt content retained on 45µm sieve (%)	0.02
	Ash content (%)	0.32
	Volatile matter (%)	0.40
	Nitrogen (%)	0.23
	Initial Plasticity (P^0)	36
	Plasticity after aging for 30min @ 140^{0}c (P^{30})	24
	Plasticity retention index (PRI)	67
	Mooney viscosity, ML (1+4), 100^{0}c	70
	Glass transition temperature, T_g (^{0}c)	-72
Acrylonitrile-butadiene rubber (NBR, Nipol)	Acrylonitrile content (%)	33
	Density (g/cm^3)	0.98
	Volatile matter (%)	0.75
	Ash content (%)	0.5
	Mooney viscosity, ML(1+4), 100^{0}c	77.5
	Glass transition temperature, T_g (^{0}c)	-40
Epoxidized natural rubber (ENR-33)	Epoxy group (%)	33
	Density (g/cm^3)	0.953
	Glass transition temperature, T_g (^{0}c)	-23.5
	Volatile matter (%)	0.55
	Ash content (%)	0.50
	Mooney viscosity, ML (1+4), 100^{0}C	58.5

I. Professional Assoc. of NR in Africa, 1998.
II. Nipol – Japan Synthetic Rubber Co. Ltd.
III. Rubber Research Institute of Nigeria (RRIN).

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Table 2: Compounding recipe of NR/NBR/ENR blend (parts per hundred weights of rubber, (phr)) using varying levels of Zinc Oxide

Compounding Ingredients (phr)	Blend Sample						
	A	B	C	D	E	F	G
NR	100	100	100	100	100	100	100
NBR	100	90	70	50	30	10	0
ENR	0	10	30	50	70	90	100
Stearic Acid	2	2	2	2	2	2	2
Wax	4	4	4	4	4	4	4
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	1	1	1	1	1	1	1
Sulphur	3	3	3	3	3	3	3
Carbon black (330 HAF)	55	55	55	55	55	55	55
Zinc Oxide	0	2.0	4.0	5.0	6.0	7.0	8.0

MBT: mercaptobenzoylthiazole.
TMTD: tetramethylthiauramdisulphide.

MEASUREMENT OF VULCANIZATE PROPERTIES

Tensile Property Test

Tensile properties were determined on a Monsanto Tensile Tester (Model ¼) with a crosshead speed of 500mm/min using dumbbell test pieces measuring 45mm x 5mm x 2mm according to ASTM D412 – 87 method A. The recorded value for each tensile parameter is the average of three measurements.

Compression Set Test

Compression Set is the residual strain left in a rubber sample when subjected to tensile stress (force) for a given time and allowed to recover on removal of the deforming force. Wallace Compression Set Machine with serial No. C84025/2 was used, and procedure adopted for measurement was based on ASTM 385. The test pieces were compressed between two parallel plates under a specified load and the test assembly was conditioned for 22 hours at 70^0c, after which the samples were removed and allowed to recover at room temperature for 30 min. The difference between the original thickness and the final thickness gave the compressibility as a percentage of the original thickness, according to the following equation:

Compression Set (%) = $(t_o – t_f)/t_o$ x 100 -- (1)

Where t_o and t_f are the original thickness and final thickness of the test samples, respectively.

Hardness Test

Hardness is the relative resistance of the surface of a test sample of specified dimension to indentation by an indenter under a specified load. It is recorded as International Rubber Hardness Degree (IRHD). In the present study hardness of blend sample was determined in accordance with the method prescribed by ASTM D1415.

Abrasion Resistance Test

Abrasion resistance of a rubber vulcanizate is its resistance to wear when in contact with another moving surface. Abrasion resistance test was done in Akron Abrasion Machine by employing the method of BS 903 – part A9. The abrasion resistance index (ARI) which is a measure of the abrasion resistance of the test sample was determined by using the following equation:

Abrasion Resistance Index (ARI) (%) = (S/T) X 100 ------------------------------- (2)

Where S is the standard sample volume loss and T is the volume loss of the test sample.

Swelling Measurements

Swelling test in toluene solvent was conducted for the blend systems. Samples of 25 mm x 15 mm x 2 mm were used to determine the swelling behaviour of the vulcanized blends according to ASTM D 471-06. Initially, the dry weight of the samples was measured. Then, the samples were immersed in toluene at 25^0C for 72 hours; the swollen weight of the samples was recorded for the determination of the swelling ratio and crosslink density. The samples were periodically removed from the test bottles, the adhering solvent was cleaned from the surface, and the samples were weighed immediately. The degree of equilibrium can be used to quantify swelling ratio, crosslink density, and chemical interaction between a polymer and its blend/composites (Shah et al, 2009). The swelling ratio can be calculated by the following equation: (Ismail et al, 2001).

$$\text{Swelling Ratio} = \frac{m_s - m_d}{m_d} \quad \text{-- (3)}$$

Where m_d and m_s are the initial weight of the dry rubber blend and the weight of solvent adsorbed by the sample, respectively. The volume fraction of blend sample (v) and the crosslink density (μ) was calculated by using data from equilibrium swelling and Flory–Rehner equation as follows: (Pojanavaraphan and Magaraphan, 2008 ; Sperling, 2006)

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$$v = \frac{\qquad}{1 + [(m_s - m_{ex})/m_{ex}]\ [\rho_r/\rho_s]} \qquad \text{---} \ (4)$$

$$\mu = \frac{-[\ \ln(1-v) + v + \chi v^2\ ]}{V\ [v^{1/3} - (v/2)\ ]} \qquad \text{--} \ (5)$$

Where m_{ex} is the sample dried weight after swelling, ρ_r and ρ_s are the densities of the blend samples and solvent (0.86 g/cm^3 for toluene), respectively, V is the molar volume of the solvent (106.3 cm^3/mol for toluene) (Pojanavaraphan and Magaraphan, 2008). The thermodynamic parameters such as Gibbs free energy (ΔG) and entropy change (ΔS) can be determined from the Flory-Huggins equation and from the statistical theory of rubber elasticity: (Lopez-Manchado et al, 2003 ; Hwang and Wei, 2004 ; Bao Lei et al, 2006)

$$\Delta G = RT\ [\ \ln(\ 1-v + v + v\chi^2)] \qquad \text{---} (6)$$

$$\Delta G = -T\Delta S \qquad \text{---} (7)$$

Where R and T are the universal gas constant and the absolute temperature, respectively.

RESULTS AND DISCUSSION

The effects of Zinc Oxide level and blend ratio on vulcanizate properties of NR/NBR blends prepared in the presence of ENR are discussed below:

Tensile Properties

In a study by Fairclough and Swift, 1993, it was reported that the use of Zinc Oxide/stearic acid as activating system in sulphur vulcanization improves the dispersion of other compounding ingredients by exerting a plasticization action on the stock compound. Previous reports have also shown that the use of Zinc Oxide/stearic acid during sulphur vulcanization of rubber increases the efficiency of the penetration and consolidation of the elemental sulphur at the anchoring points of the network (Barnhart, 1982) referred to as internal lubrication effect (Wang, 1994).The dependence of tensile strength, elongation at break and modulus of elasticity on Zinc Oxide level for various NR/NBR/ENR compositions is presented in Figures 1, 2 and 3 respectively. The results show that for all NR/NBR/ENR compositions, the tensile strength and modulus of elasticity increased progressively with increase in ZnO level from 0 phr up to a maximum value at 5 phr. This observation is attributed to consolidation of network structure of the rubber chains with increasing ZnO level, which results to increase in crosslink density. Further addition of ZnO was accompanied by a steady decrease in tensile strength and modulus. This decrease is attributed to over-cure of the blend samples which decreases the tensile strength and modulus. This result is consistent with the report of Kuriakose, 1993 in his study on the effect of high temperature vulcanization on the physical properties of pre-cured retread compounds. In an independent study on the effect of high temperature vulcanization on the physical properties of pre-cured retread compounds, the author reported a reversion (over-cure) in crosslinking efficiency resulting in lower tensile strength and modulus of natural rubber vulcanizate for stearic acid (a saturated fatty acid used in conjunction with Zinc Oxide as activators in sulphur vulcanization) level above 4.0 phr. In a corroborative report by Simpson, 2002, it was revealed that all rubber compounds in which elemental sulphur is the crosslinking agent are subject to reversion in crosslinking efficiency, usually accompanied by reduction in tensile strength and modulus.

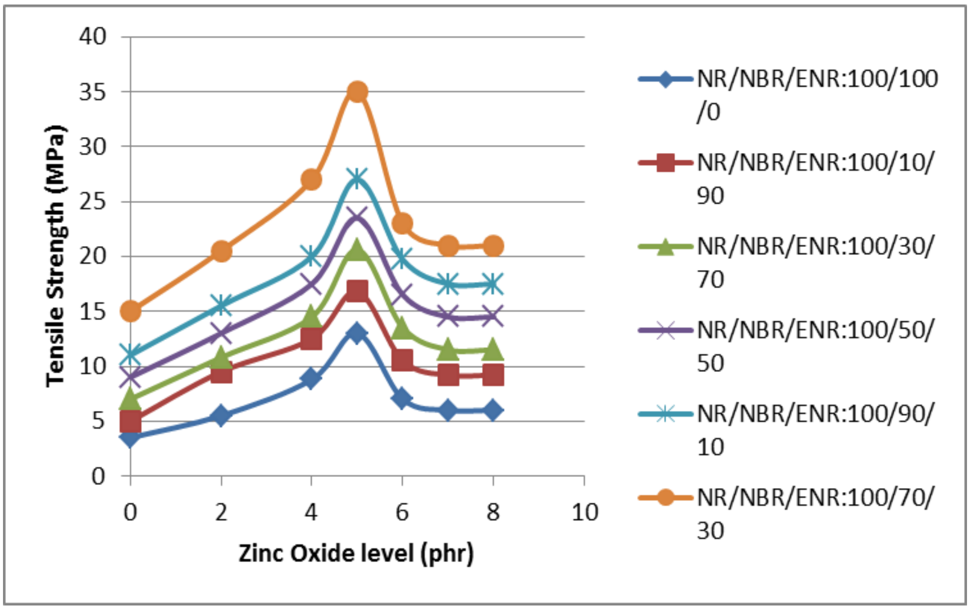

Figure 1: Dependence of Tensile Strength on Zinc Oxide level for various NR/NBR/ENR compositions

For all blend samples studied, highest values of tensile strength and modulus were obtained at blend ratio of NR/NBR/ENR: 100/70/30 due to optimal polar-polar interaction between NBR and ENR at this blend composition. Elongation at break (Figure 2) decreased with increasing ZnO level. This observation is attributed to increase in crosslink density with increase in ZnO level leading to reduction in molecular chain mobility. The highest elongation at break obtained at blend ratio of NR/NBR/ENR: 100/70/30 is due to optimal polar-polar interaction between NBR and ENR at this blend composition. This observation is consistent with the findings of Kraus, 1978, Wolf et al, 1993 and Wolf et al, 1994. The authors in their independent studies reported that the reinforcement of rubber particles by the incorporation of carbon black is due to the presence of active polar groups such as phenol, carboxyl, quinine and lactones on the carbon black. They reported that these polar groups on the carbon black surfaces interact with rubber and the interaction is higher with polar rubbers than hydrocarbon rubbers, which is due to polar-polar interaction. Medalia and Kraus, 1994, further reported that the interaction between hydrocarbon rubber and carbon black can be improved by the introduction of polar groups in the rubber through blending and/or addition of some particular additives.

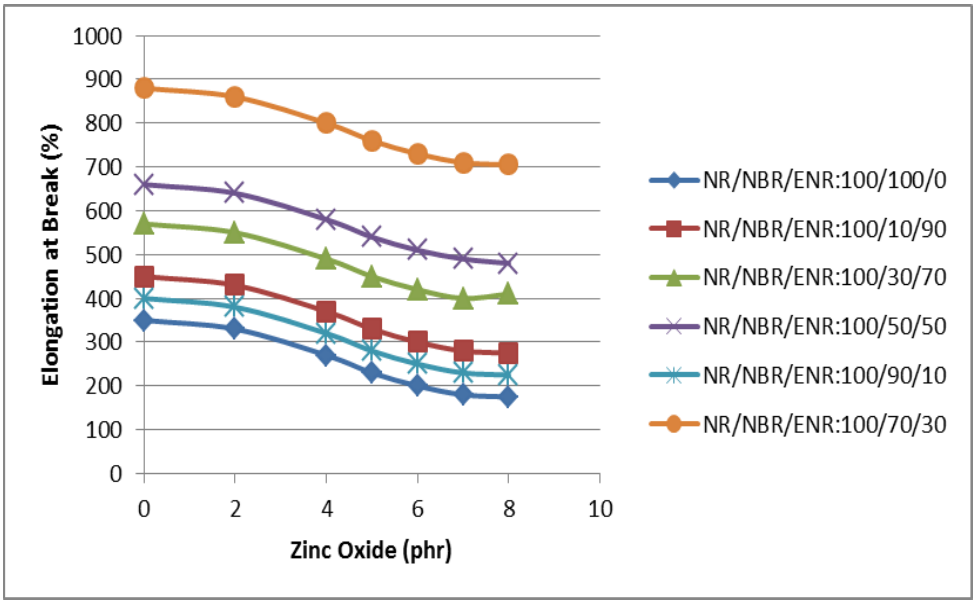

Figure 2: Dependence of Elongation at Break on Zinc Oxide level for various NR/NBR/ENR compositions

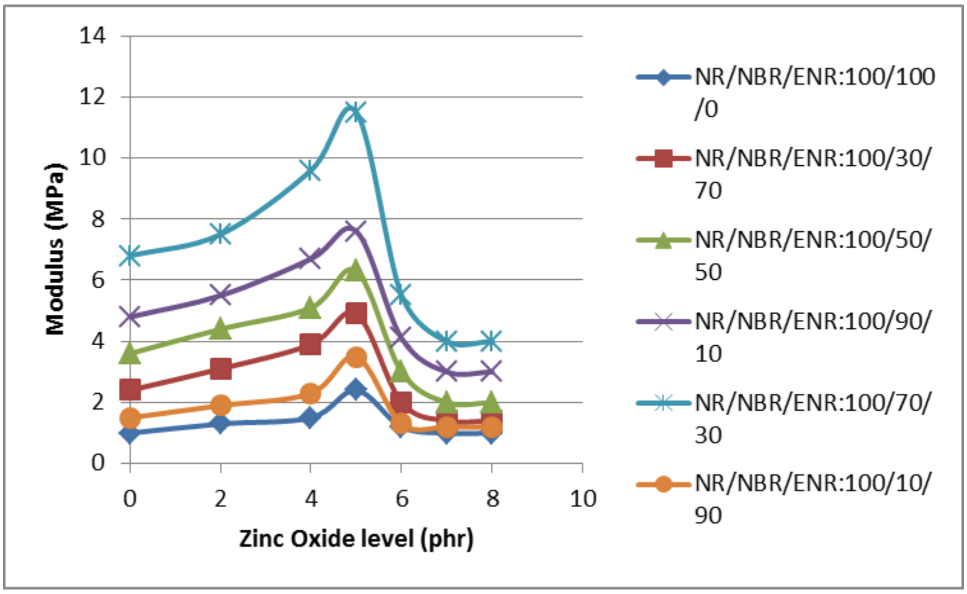

Figure 3: Dependence of Modulus on Zinc Oxide level for various NR/NBR/ENR compositions

Compression Set

The dependence of compression set on Zinc Oxide level and blend ratio is presented in Figure 4. The results show an increasing trend in compression set with increase in Zinc Oxide. Increasing the Zinc Oxide content decreases the chain mobility due to increase in crosslink density which increased the compression set. Blend composition of NR/NBR/ENR : 100/70/30 gave the highest values of compression set for all blend samples studied. This is due to optimal polar-polar interaction between NBR and ENR at this blend composition. Absence of polar ENR in blend sample NR/NBR/ENR : 100/100/0 caused a wider difference in polarity between hydrocarbon NR and polar NBR, which is responsible for the lowest value of compression set obtained at this blend composition.

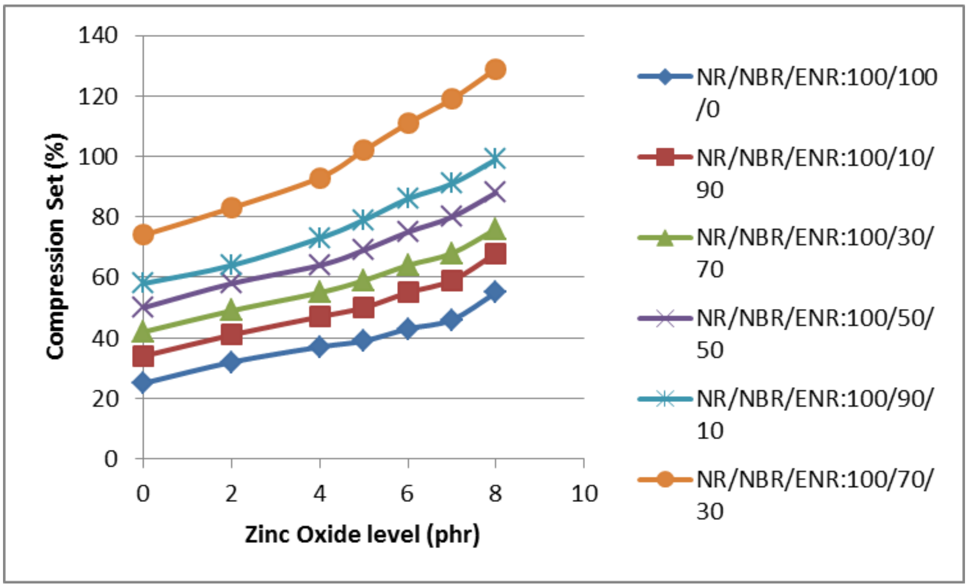

Figure 4: Dependence of Compression Set on Zinc Oxide level for various NR/NBR/ENR compositions

Hardness Test

The effect of Zinc Oxide level and blend ratio on hardness of the blend samples is shown in Figure 5. The results show that hardness increased with increase in Zinc Oxide due to increase in crosslinking efficiency and crosslink density with increase in Zinc Oxide content (Wang, 1994). The blend sample with composition NR/NBR/ENR: 100/70/30 exhibited the highest hardness, indicating optimal polar-polar interaction between NBR and ENR at this blend composition. Similarly, absence of ENR in blend sample NR/NBR/ENR: 100/100/0 caused weak interfacial interaction between NR and NBR due to difference in polarity between NR and NBR, which resulted in the lowest hardness obtained at this blend composition.

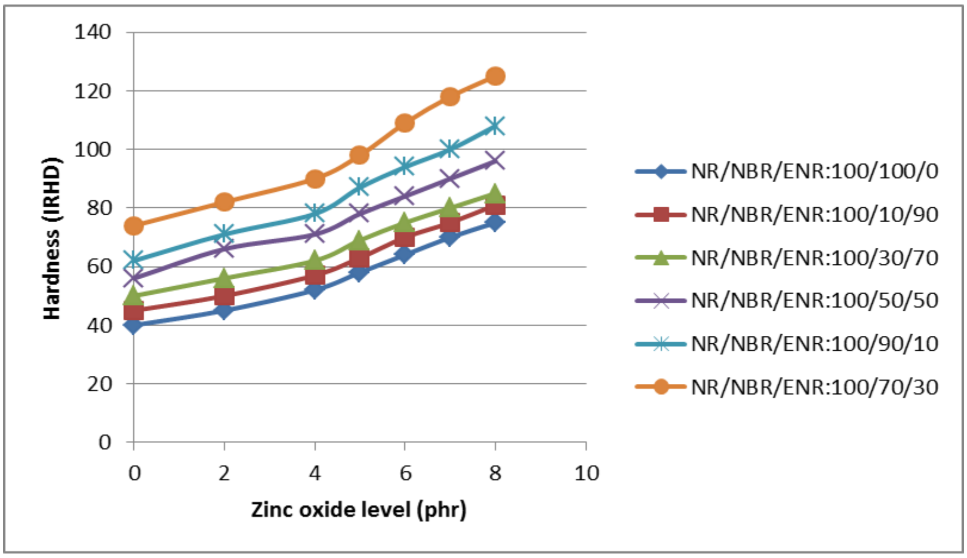

Figure 5: Dependence of Hardness on Zinc Oxide level for various NR/NBR/ENR compositions

Abrasion Resistance

The effect of Zinc Oxide level and blend ratio on abrasion resistance is shown in Figure 6. For all blend samples, the results show an initial decrease in abrasion resistance from 0 - 2 phr ZINC Oxide content. Thereafter, it increased to a maximum value at 5.0 phr Zinc Oxide level, followed by a sharp decrease. The initial decrease in abrasion resistance is expected since at low level of Zinc Oxide (0 – 2 phr), particles of Zinc Oxide tend to act as flaws instead of as activators. This reduces the abrasion resistance due to decrease in crosslink density. This result is consistent with the reports of Wang, 1994, who revealed that normal levels of stearic acid (stearic acid is used in conjuction with Zinc Oxide as activator in rubber vulcanization) lead to significant improvement in abrasion resistance. The decrease in abrasion resistance above 5.0 phr Zinc Oxide content is attributed to reversion in crosslinking efficiency which caused a decrease in crosslink density. The blend sample with composition NR/NBR/ENR: 100/70/30 gave the highest abrasion resistance due to optimal polar – polar interaction between NBR and ENR at this blend composition. Similarly, blend sample NR/NBR/ENR: 100/100/0 (i.e,without ENR) exhibited the lowest abrasion resistance due to weak interfacial interaction between NB and NBR because of difference in polarity between NR and NBR.

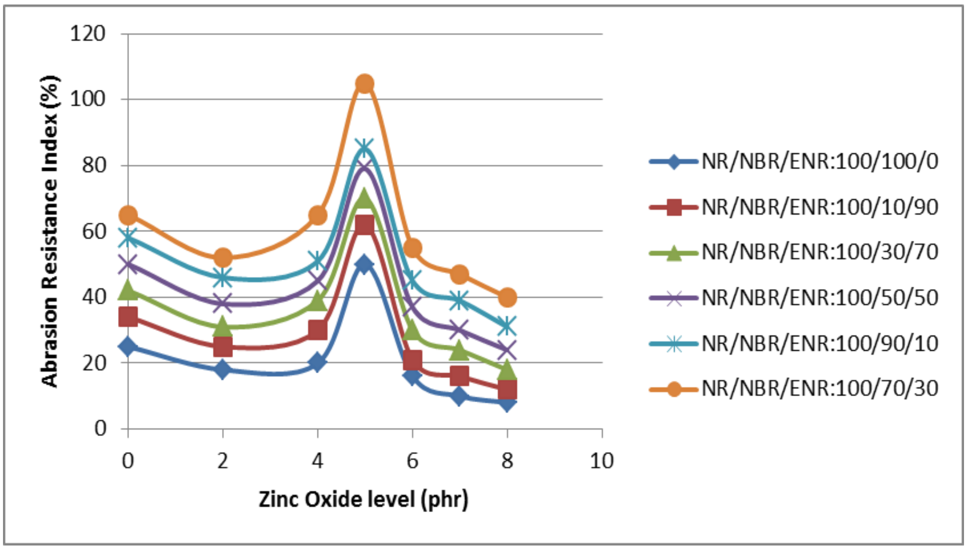

Figure 6: Dependence of Abrasion resistance on Zinc Oxide level for various NR/NBR/ENR compositions

Swelling Behaviour of Blend Systems

The degree of adhesion between blend components can be evaluated from equilibrium swelling of the blend samples in good solvents. The extent of swelling at equilibrium is reduced with increase in Zinc Oxide level up to a maximum at 5.0 phr Zinc Oxide (Table 3).This decrease in swelling ratio is attributed to increase in crosslink density due to increase in interfacial interaction between blend components, which decreased the rate of solvent transport by lengthening the average diffusion path in the blend sample (Jacob et al, 2008; Mathew and Kuriakose, 2007). Above 5.0 phr Zinc Oxide content, the swelling ratio increased due to a negative effect of poor crosslinking efficiency that reduces the crosslink density. Blend sample NR/NBR/ENR: 100/70/30 produced the lowest swelling ratio of all blend systems studied, due to higher crosslink density.

Table 3: Effect of Zinc Oxide level on Swelling Ratio for various NR/NBR/ENR compositions

Zinc Oxide Level (phr)	Swelling Ratio					
	NR/NBR/ENR					
	100/100/0	100/10/90	100/30/70	100/50/50	100/90/10	100/70/30
0	3.85	2.83	2.44	1.98	1.35	0.95
2	3.52	2.70	2.21	1.76	1.10	0.70
4	3.20	2.52	2.08	1.57	0.90	0.55
5	3.03	2.39	1.86	1.34	0.75	0.35
6	3.37	2.60	1.99	1.65	0.88	0.60
7	3.55	2.88	2.28	1.82	0.97	0.76
8	3.90	2.96	2.36	1.95	1.14	0.85

The volume fraction (v) of NR in the swollen blend vulcanizates has a direct relationship with the crosslink density. The v – value of the blend vulcanizates is an estimate of the crosslinking efficiency of Zinc Oxide and is presented in Table 4.

Table 4: Effect of Zinc Oxide level on Volume Fraction (v) of natural rubber (NR) for various NR/NBR/ENR compositions

Zinc Oxide Level (phr)	Volume Fraction (v)					
	NR/NBR/ENR					
	100/100/0	100/10/90	100/30/70	100/50/50	100/90/10	100/70/30
0	0.25	0.33	0.48	0.55	0.60	0.74
2	0.38	0.47	0.56	0.65	0.73	0.80
4	0.46	0.54	0.67	0.74	0.79	0.88
5	0.52	0.63	0.75	0.88	0.82	0.98
6	0.40	0.50	0.54	0.62	0.70	0.82
7	0.32	0.41	0.47	0.53	0.62	0.75
8	0.20	0.32	0.38	0.44	0.50	0.60

As expected, the volume fraction of NR increased with increase in Zinc Oxide content up to a maximum at 5.0 phr Zinc Oxide, due to increase in crosslinking efficiency and good interfacial interaction between blend components. These interactions lead to an increase in the effective degree of crosslinking, which in turn enhances the mechanical properties of the vulcanizates. Above 5.0 phr Zinc Oxide content, the volume fraction (v) decreased due to decrease in crosslink density. Blend system with composition NR/NBR/ENR : 100/70/30 had the highest volume fraction of all blend systems studied, and thus gave the highest value of crosslink density. The thermodynamic parameter (Gibbs free energy, ΔG) of the vulcanizates is reported in Table 5. The results show that ΔG increased with increase in Zinc Oxide content up to a maximum at 5.0 phr Zinc Oxide content, and decreased thereafter. ΔG is closely related to the elastic behavior of the vulcanizates, i.e, the vulcanizates show a better elasticity than the pure NR (Jacob et al, 2008). The higher crosslink density and interfacial interaction between blend components is responsible for the noticeable increase in ΔG with increase in Zinc Oxide content. Again, blend sample with composition NR/NBR/ENR : 100/70/30 gave the highest volume fraction of all vulcanizates studied, and thus exhibited the highest value of crosslink density.

Table 5: Effect of Zinc Oxide level on Gibbs free energy (ΔG) of blend systems for various NR/NBR/ENR compositions

Zinc Oxide Level (phr)	Gibbs Free Energy (ΔG)					
	NR/NBR/ENR					
	100/100/0	100/10/90	100/30/70	100/50/50	100/90/10	100/70/30
0	-114	-98	-85	-73	-66	-54
2	-102	-84	-78	-65	-59	-42
4	-90	-72	-67	-52	-47	-30
5	-81	-65	-56	-44	-36	-20
6	-88	-70	-62	-55	-45	-35
7	-97	-86	-71	-67	-55	-48
8	-108	-92	-82	-75	-64	-50

CONCLUSION

The following conclusion can be drawn from this work:

1. The use of lower or higher than the recommended level of Zinc Oxide in rubber vulcanization can lead to inferior or poor quality vulcanizate which may not perform the intended desired function in service.
2. Zinc Oxide level of 5.0 phr gave vulcanizates with optimum tensile strength, modulus and abrasion resistance. Further addition of Zinc Oxide was accompanied by a steady decrease in these properties. Of all blend systems studied, blend sample with composition NR/NBR/ENR: 100/70/30 produced the highest value of these properties. Hardness and compression set showed an increasing trend with increase in Zinc Oxide level due to increase in crosslink density.
3. Swelling ratio is a measure of the degree of adhesion between blend components. It decreases with increase in crosslink density. All blend vulcanizates studied, showed a drcreasing trend in swelling ratio with increase in Zinc Oxide level up to 5.0 phr Zinc Oxide content. Further addition of Zinc Oxide was accompanied by an increase in this property. On the other hand, the Gibbs free energy (ΔG) of the vulcanizates and volume fraction of natural rubber in all the vulcanizates studied, increased with increase in Zinc Oxide level, reaching a maximum at 5.0 phr Zinc Oxide due to improvement in the interfacial interaction between the blend components. These interactions lead to an increase in the effective degree of crosslinking, which enhanced the mechanical properties of the vulcanizates.

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