

# Preliminary Comparison of the Effects of N-(1, 3 dimethylbutyl)-N- phenyl-p-phenylene diamine (DPPD), Galic Powder (GP) and N-isopropyl-n-phenyl-p-phenylene diamine (DPPD) on the Properties of Natural Rubber Compound

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## Abstract

The effects of N-(1,3-dimethyl butyl)-N- phenyl-p-phenylene diamine, DPPD (anti-oxidant), garlic powder, GP and N-isopropyl N- phenyl-p-phenylene diamine, PPPD (anti-degradant) have been examined. Garlic powder shows comparable tensile strength, hysteresis, (heat build-up) hardness, scorch time (resistance to pre-vulcanization), crosslink density and reversion resistance to the DPPD (anti-oxidant), but better tensile strength, cure time, hysteresis and hardness compared to the PPPD (anti degradant). Garlic powder exhibits comparable ability to resist pre-vulcanization and reversion to both the antioxidant and the antidegradant.

## 1. INTRODUCTION

Degradation in polymer is taken to mean any process leading to deterioration of polymer properties (Grassie, 1996). There are two general type of polymer degradation processes, random degradation (where chain rupture or scission occurs at random points along the chain, Leaving fragment which are usually large compared to a monomer unit) and chain depolymerization (which involves the successive release of monomer units from a chain end in a depropagation or unzipping reaction). These two types which may occur separately or in combination, may be initiated thermally or by ultraviolet light, oxygen, ozone, or other foreign agent and may occur entirely at random or preferentially at chain ends or at other weak links in the chain (Billmeyer, 1971). Chain scission is common in natural rubber, which becomes soft and sticky and loses tensile strength on degradation in styrene butadiene rubber (SBR). The predominant reaction is cross linking and so it becomes hard and brittle when attacked by oxygen. With either chain scission or cross linking, the intermediates are free radicals, which set in motion many repetitive reaction cycles (Harrison and Bronk, 1977).

Attempts have been made to prevent polymer degradation by the introduction of antioxidants and antidegradants in the compounding formulation of polymer material (Elliot, 1986; Bristow, 1986, Saltman, 1965, Maassen 1965, Robin 1969, Cox 1965). These are chemicals that protect rubber from being attacked by oxygen and ozone. They combine with the rubber and interrupt the free radical chain reaction that brings about rubber degradation. Commercially, antioxidants are of two types (i) phenolic containing type and (ii) nitrogen and or sulphur containing type (Sybil, 1982). Examples include 4-tert-butyl catechol (TBC), N-isopropyl-N-phenyl-P-phenylene diamine and phenol thiazines.

It has been reported that the addition of garlic extract can inhibit the oxidation process of some vegetable oils (Harrison, and Bronk, 1977). It is of interest therefore to compare the effect of the conventional natural rubber antioxidant DPPD, the conventional natural rubber antidegradant PPPD and garlic powder on the mechanical and rheological properties of the resultant NR vulcanizate. The result of this preliminary investigation might spark off a comprehensive study on the antioxidation/ antidegradation ability of garlic in natural rubber processing.

## 2. MATERIALS AND METHODS

1. The natural rubber used in this work was crumb rubber produced at the Michelin, Plantation, Araromi Obu, Ondo State Nigeria. The rubber was characterized on the basis of the following properties: dirt content, ash content volatile matter. These properties were determined as reported in Standard Malaysian Rubber (SMR) Bulletin No 7 (1970). Results are contained in table 2.
2. Garlic was purchase at the Erekesan market. Ado Ekiti, Nigeria. It was crushed fresh in a grinder and sun dried for seven days. The proximate (AOAC) and the elemental compositional determined with AAS using 306 Perkins Elman's model (AOAC, 1980, Vogel, 1961) analyses and the result are shows in Table 3 and 4 respectively.
3. Chemicals used for compounding as indicated in Table 1 are BHD products collected from Dunlop laboratory, Ikeja Lagos.

## 2.1 COMPOUNDING AND CURING

- (i) Formulation: These are as shown in Table 1.
- (ii) Mixing: A standard mixing procedure summarized in Table 7 (Bateman 1963, Adu, 1991) was used for each compounding batch. This was performed on a water cooled two-roll laboratory mill. The times of milling of rubber during the incorporation of other compounding ingredients are as shown in table.
- (iii) Curing: curing was done at 185°C using a Monsanto Rheometer model 100 in accordance with the method recommended and report by the British Standard Organization (BSO No 903, 1969,1971). Cure properties were evaluated from the rheograph produce from the rheometer (Table 6).

## 2.2 DETERMINATION OF MECHANICAL PROPERTIES:

Rectangular mould was filled with compounded sample and the compound cured at 142°C for 35 minutes in an hydraulic operated steam press. After dropping vulcanizate in chilled water, it was allowed to cool for 48 hours in the water before dumbbell shaped test pieces were cut for the determination of mechanical properties. The tensile strain were determined using Universal Tensiometer 4301 following the methods recommend and reported by BSO No 903, 1971. The stress strain curves from the Instron machine provided values for tensile strength, and elongation at break (Figure 1, Table 5)

Circular shaped test pieces for hardness determination/measurement was cured at 152°C for 15 minutes, in an hydraulic operated steam press, dropped into chilled water and allowed to cool for 48 hours in the water. The test pieces were then tested for hardness using Rubber Hardness Tester (BSO No 903, 1995). Table 5

## 2.3 DATA ANALYSIS

- a. Cross link density was evaluated as the difference between maximum and minimum torque rise (Bristow, 1986).
- b. Hysteresis was evaluated as the reciprocal of resilience
- c. The method used by Bristow (1986) was adopted in which Reversion resistance was evaluated as being equal to

$$\frac{\text{Time to 5(10) decrease from maximum torque}}{\text{Time to 90(95)\% torque rise from minimum}} = \frac{t_{R5}(t_{10})}{t_{05}(t_{90})}$$

- d. Cure rate index was evaluated using the relation

$$\frac{100}{\text{Cure time} - \text{scorch time}} \quad \text{OR} \quad \frac{100}{t_{95} - t_{s2}}$$

(Asarifar and Jain, 1999)

**Table 1: COMPOUNDING FORMULATION OF SAMPLES**

	A	B	C	D
Natural Rubber	100	100	100	100
Zinc Oxide	5	5	5	5
Stearic Acid	3	3	3	3
MBT	1	1	1	1
Sulphur	3	3	3	3
Antioxidant	-	-	2	-
Antidegradant	-	2	-	-
Garlic	-	-	-	2
Carbon Black	40	40	40	40

## 3.0 RESULTS AND DISCUSSION

It is observed from Table 2 that the natural rubber used contains 5.78% protein, 2.19% carbohydrate and ash 1.03%. The major elements are potassium and manganese with traces of sodium, copper and iron. Garlic used contains 63.06% water Table 3 close to the 60% reported for garlic by Zalejska Fiolka (2001). The protein content of the garlic used (12.13% is higher while carbohydrate content of 6.50% and 30.00% respectively reported by Zalejska Fiolka, (2001) while other elements show significant variation. The variation in both proximate and elemental composition of garlic might not be unconnected with the difference in geographical location of cultivation and agriculture practices.

From the result of tensile strength of the four systems in Table 1, it is observed that the conventional MBT antioxidant system shows strength than both the conventional MBT and the MBT antidegradant systems. The MBT garlic system shows a comparable strength to the MBT antioxidant system better than both MBT and MBT antidegradant system. Better strength of antioxidant and garlic systems might be due to better compatibility of natural rubber/garlic and natural rubber/antioxidant which results in property synergy.

Table 5 contains the mechanical properties of the systems. The MBT-antioxidant and MBT-garlic systems show comparable resilience slightly lower than for the MBT-antidegradant system. Conversely the MBT antioxidant and MBT garlic systems show comparable hysteresis slightly higher than for the MBT antidegradant system. The implication of the value of hysteresis of the system is twofold. Relatively higher hysteresis value makes the system better as a trunk tyre in temperate roads. The elongation at break ( $E_B$ )% of the garlic system (44.59) is higher than the MBT system (32.83) but lower than the antioxidant and the antidegradant which are fairly comparable.

The scorch times of the MBT antioxidant and MBT antidegradant are better than the MBT and the MBT (garlic system table 6) but MBT and MBT antidegradant systems show comparable cure times economically disadvantage than the MBT garlic and the MBT antioxidant systems. The MBT garlic system shows a slightly better cure time compared with the MBT antioxidant system.

Cross link density was measured as the difference between maximum and minimum torque values, which is an indication of how dense the C-S bond of the mix. The cross link densities of the MBT and MBT-antidegradant systems are comparable but higher than for MBT garlic system, which shows a comparable density to the MBT antioxidant system. The ability of the system to resist reversion was evaluated as reported by Bristow (1986). All system show comparable reversion resistance and hardness.

#### 4.0 CONCLUSION

- Garlic system shows comparable tensile strength, hysteresis, hardness, scorch time (resistance to pre-vulcanization), cross link density and reversion resistance to the conventional antioxidant system, DPPD.
- Garlic system shows better strength and cure time but comparable hysteresis, hardness, scorch time, and reversion resistance compared to the conventional anti degrading PPD.
- Garlic system shows comparable ability to resist pre-vulcanization (scorch time) and reversion to the conventional antioxidant, DPPD and the anti degradant IPPD systems, the two properties closely connected with oxidation of polymer.
- In the light of above garlic and DPPD are comparable in strength and cure time but better than PPD in both properties.
- Garlic and conventional antioxidant DPPD being observed to show similar properties can be classified to be in the same group antioxidant.

The following investigation directly linked with oxidation and degradation of a polymer are already being examined for more facts to emerge on the properties of garlic power to allow its classification as an antioxidant or otherwise in natural rubber compounding

- a. Plasticity retention index (PRI) of the compounds under examination
- b. The effect of temperature on the properties of the compounds under investigation
- c. The effect of weathering on the properties of the compounds under investigation

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**TABLE 2: CHARACTERIZATION OF NATURAL RUBBER**

Dirt content	0.08
Volatile matter	0.79
Ash content	1.03
Protein content	5.78
Carbohydrates	2.19

**TABLE 3: PROXIMATE ANALYSIS OF GARLIC USED IN THIS WORK (%)**

Water	Ash	Protein	Crude Fibre	Fat	Carbohydrate
63.06	1.24	12.13	2.52	4.61	16.45

**TABLE 4: ELEMENTAL ANALYSIS OF GARLIC USED IN THIS WORK**

Element	Iron (Fe)	Magnesium (mg)	Potassium (K)	Phosphorus (P)
Content mg/100g	1.68	17.87	16.58	7.71

**TABLE 5: MECHANICAL PROPERTIES OF THE VULCANIZATES EXAMINED**

	A	B	C	D
Elongation at break ( $E_B$ )%	32.83	60.86	69.23	44.59
Resilience (%)	52	55	52	53
Hysteresis (IHRD)	1.92	1.82	1.92	1.89
Tensile strength $KNm^{-2}$	6.38	6.11	9.27	8.96

**TABLE 6 RHEOLOGICAL PROPERTIES OF THE COMPOUNDS EXAMINED**

	A	B	C	D
Hardness	81	79	80	79
Scorch time (Sec)	18	19.8	19.2	18
Cure time (Sec)	2.08	2.25	1.8	1.15
Maximum torque (a)	90	88.5	78	79
Minimum torque (b)	5	3.5	2.5	5
Cross link density (a-b)	85	85	75.5	74
Reversion resistance				

**TABLE 7: MIXING CYCLE**

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Maximum temperature	70 <sup>0</sup> C
Mixing speed	24rpm
Roll ratio (slow to fast)	1 to 1.4
Natural rubber (NR)	60sec
NR + 2/3 of carbon black	60-120sec
Incorporation of stearic acid and zinc oxide	120sec
Incorporation of remaining 1/3 of carbon black	30-60sec
Incorporation of MBT, sulphur and garlic	240sec
Total time (seconds)	510-600sec

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