# Comparative Study on Natural Antioxidant as an Aging Retardant for Natural Rubber Vulcanizates

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**ABSTRACT:** The research aim is mainly to investigate the effectiveness of natural antioxidant (NA) obtained from oil palm leaves (*Elaeis guineensis*) as an aging retardant in natural rubber (NR) vulcanizates. Comparison of NA with other commercial antioxidants, trimethyl quinoline (TMQ) and butylated hydroxy toluene (BHT), is investigated. The effect of natural and commercial antioxidants on NR vulcanizates was explored before and after aging. Aging test was carried out at 70°C for three different periods, 4, 7, and 14 days to determine aging property by performing the tensile and tear tests. NA shows lower tensile properties, crosslink density, tack strength but high tear strength compared to the commercial antioxidants, BHT and TMQ. However, upon aging NR vulcanizates with NA retains its properties equivalent to that of commercial antioxidants, BHT and TMQ. Thus, NA can be used as an aging retardant for short-term protection in application requiring moderate tensile properties and can be used as alternative source for commercial antioxidant. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1490–1500, 2012

**Key words:** natural antioxidant; *Elaeis guineensis*; aging retardant; natural rubber (NR); commercial antioxidants

## INTRODUCTION

All around the globe, the quantity of waste materials is accumulating day by day. Thus, the use of waste materials has spurred the interests of many researchers to explore the possibility to use alternative sources. In rubber industry, the utilization of waste material in rubber compound becoming commercial and environmental interests.

Rubbers are used for various indoor and outdoor applications. Concerning about the outdoor application, the rubber goods should be protected from oxygen, ozone, light, and heat to extend the service life or prevent aging of the vulcanized rubber goods. Most natural and synthetic rubbers containing unsaturated backbones can be easily oxidized. For instance, natural rubber (NR) must be protected against oxygen.[1]

The principal mechanism of oxygen attack involves an autocatalytic, free radical reaction. The first step is the formation of macroradicals as a result of hydrogen abstraction from rubber chain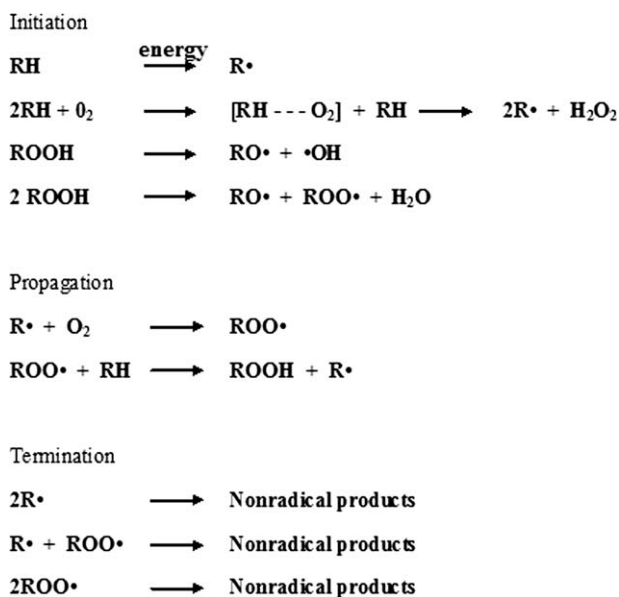s by proton acceptor. Oxidation continues by reaction of macroradicals with oxygen and the subsequent formation of peroxy radicals and hydrperoxides.[2] The mechanism of rubber degradation by oxidation under thermal energy is depicted as in Scheme 1.[1] The oxidative degradation results in aging which leads to the deterioration in the physical and mechanical properties of vulcanized rubbers. This becomes one of the major problems in rubber technology.[3]

To counteract the deterioration of the rubber, whether by natural or accelerated aging, these types of deterioration can be retarded but not completely avoided by the addition of antioxidants.[4] Antioxidants react with oxygen to prevent oxidation of vulcanized rubber and react with free radicals that degrade vulcanized rubber. A schematic chain termination or the stabilization of rubber chains by antioxidant is presented in Scheme 2.[1] The most common antioxidants for rubber are derivatives of aromatic amines and phenols. Amines are more effective in preventing long-term oxidative degradation for most of rubber systems. However, amine antioxidants usually discolor with aging and may not be correct choice for light and brightly colored rubber goods where color retention is important. In contrast to amine antioxidants, phenolic antioxidants do not discolor on aging but are generally less effective in preventing long-term oxidative degradation.[4]

Many commercial antioxidants such as trimethyl-quinoline (TMQ) and butylated hydroxy toluene (BHT)

Initiation

$$RH \xrightarrow{\text{energy}} R\bullet$$

$$2RH + O_2 \longrightarrow [RH \text{---} O_2] + RH \longrightarrow 2R\bullet + H_2O_2$$

$$ROOH \longrightarrow RO\bullet + \bullet OH$$

$$2\,ROOH \longrightarrow RO\bullet + ROO\bullet + H_2O$$

Propagation

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet$$

Termination

$$2R\bullet \longrightarrow \text{Nonradical products}$$

$$R\bullet + ROO\bullet \longrightarrow \text{Nonradical products}$$

$$2ROO\bullet \longrightarrow \text{Nonradical products}$$

**Scheme 1** Mechanism of rubber degradation by oxidation under thermal energy.

(BHT) have been used widely. In this study, natural antioxidant (NA) is used and the antioxidant activity is compared with the commercial antioxidants. NAs are primarily plant-phenolic and polyphenolic compounds that occur in all parts of the plant. Most naturally occurring phenolic compounds are present as conjugates with mono- and polysaccharides, linked to one or more of the phenolic groups, and many also occur as functional derivatives such as esters and methyl esters. However such structural diversity results in the wide range of phenolic compounds which can be categorized into several classes such as simple phenolics, benzoquinones, hydroxybenzoic acids, acethophenones, phenylacetic acids, hydroxycinnamic acids, phenylpropanoids, napthoquinones, xanthones, stilbenes, anthraquinones flavonoids, isoflavonoids, lignans, neolignans, biflavonoids, lignins, and condensed tannis. Of these, phenolic acids, flavonoids, and tannis are regarded as the main phenolic compounds.[5] Plant phenolics are multifunctional and can act as reducing agents (free radical terminators), metal chelators, and singlet oxygen quenchers. Some NAs have already been extracted from plant sources and are produced commercially as they proved to be potent antioxidants and free radical scavengers.[1,6]

The NA used in this study is extracted from oil palm leaves, *Elaeis guineensis* (*E. guineensis*). The oil palm tree, *E. guineensis*, is native to Africa. Although, it is native to Africa, Malaysia was the first country to embark on large-scale planting and processing. As Malaysia is the largest producer of palm oil, it is essential for us to exploit this abundant natural resource. The oil palm leaves can be used to extract

phenolic compounds to be used as antioxidant rather than discarded as waste material. *E.guineensis* methanolic extract has been identified as good source of phenolic compounds with potentially good antioxidant activity. The mechanism by which this NA exerts its effect may vary depending on the compositional characteristics of the antioxidants compounds. Method of extraction was adopted from Kawser and Nash.[7]

The study has been carried out to identify the antioxidant activity in oil *E. guineensis* extract. The effectiveness of NA obtained from oil palm leaves as an aging retardant in NR is evaluated by comparing the NA with the other commercial antioxidants TMQ and BHT. The comparisons of cure characteristics, crosslink density, tensile properties, tear strength, tack strength, and aging of NR compounds are investigated.
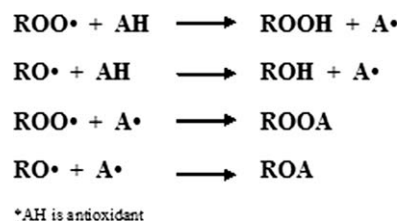
## EXPERIMENTAL

### Characterization of natural antioxidant

Fourier transform infrared spectroscopy analysis

The methanol extracts of *E. guineensis* was mixed with potassium bromide (KBr) using a mortar and pestle, and compressed into a thin pellet. Infrared spectra were recorded as KBr pellets on a Schimadzu FTIR Spectrometer 8000 series, between 4000 and 500 cm$^{-1}$. All determinations were performed in triplicate.

Gas chromatography–mass spectrometry analysis

The gas chromatography–mass spectrometry (GC/MS) analysis was done on a thermo gas chromatograph mass spectrometer (model Shimadzu 2010) equipped with DB-5 capillary column (30 m long, 0.25 mm i.d., film thickness 0.25 μm). The column temperature program was 50°C for 6 min, with 5°C increases per min to 250°C; which was maintained for 30 min. The carrier gas was helium at a flow rate of 1 mL/min (splitless mode). The detector and injector temperatures were both maintained at 250°C. The quadrupole mass spectrometer was scanned over the range 28–400 amu at 1 scan s$^{-1}$, with an

$$ROO\bullet + AH \longrightarrow ROOH + A\bullet$$

$$RO\bullet + AH \longrightarrow ROH + A\bullet$$

$$ROO\bullet + A\bullet \longrightarrow ROOA$$

$$RO\bullet + A\bullet \longrightarrow ROA$$

*AH is antioxidant

**Scheme 2** Schematic chain termination or the stabilization of rubber chains by antioxidant.

## TABLE I
### Formulations of Compounding Ingredients Based on Part Per Hundred (pphr)

| Ingredients | Control | NA (pphr) | TMQ (pphr) | BHT (pphr) |
|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 |
| Zinc oxide | 5.0 | 5.0 | 5.0 | 5.0 |
| Stearic acid | 2.0 | 2.0 | 2.0 | 2.0 |
| CBS | 0.8 | 0.8 | 0.8 | 0.8 |
| Antioxidant | – | 1.5 | 1.5 | 1.5 |
| Sulfur | 3.0 | 3.0 | 3.0 | 3.0 |

BHT, butylated hydroxy toluene; CBS, N-cyclohexyl-2-benzothiazolsulfenamide; NA, natural antioxidant; TMQ, trimethyl quinoline.

ionizing voltage of 70 eV, an ionization current of 150 Ma and an ion source temperature of 200°C. To determine the Kovats index of the components, a mixture of alkenes (C9–C24) was added to the crude extract before injecting in the GC–MS equipment and analyzed under the same conditions as above. The compounds were identified by computer searches in commercial libraries of NIST (National Institute of Standard and Technology) and by their Kovats retention indexes.

## Compounding ingredients and formulation

Table I shows the formulation used in this study. NR grade SMR CV60 was supplied by Rubber Research Institute, Malaysia. Other compounding ingredients such as sulfur, zinc oxide (ZnO), stearic acid, N-cyclohexyl-2-benzolthyazolsulfenamide (CBS), TMQ, and BHT were purchased from Bayer (M) Ltd. NA was extracted from oil palm leave in our Polymer Lab according to Kawser and Nash.[7]

## Sample preparation

Mixing was carried out in a laboratory model "two roll mill" according to method described by ASTM D 3184-80. The cure characteristics of the rubber compounds were studied using a Monsanto Rheometer, model MDR 2000 at 160°C. From the rheographs, cure time ($t_{90}$), scorch time ($t_{s2}$), minimum torque ($M_L$), and maximum torque ($M_H$) were obtained. The optimum cure time of compounds, $t_{90}$ obtained from the rheograph corresponding to an optimum torque, $M_{90}$, is given by:

$$M_{90} = 0.9(M_H - M_L) + M_L$$

Cure rate index was calculated using the following equation:

$$\text{Cure rate index (CRI)} = 100/(t_{90} - t_{s2})$$

where $t_{s2}$ is the time corresponding to two units rise in the torque above the minimum torque.

The rubber compounds were compression molded into sheets at temperature of 160°C to respective cure time, $t_{90}$ using Hot Press Machine.

## Measurement of tensile properties and tear strength

Tensile and tear tests were carried out according to ASTM D 412 at a constant rate of 500 mm/min and ASTM D 624 standard at constant rate of 100 mm/min, respectively, by Universal testing machine (Tensometer). Dumbell and trouser tear piece specimens were cut from vulcanized rubber sheets and conditioned at temperature of 23°C.

### Aging test

Aging test was carried out according to ASTM D 573. Test specimens of vulcanized rubber were exposed to the deteriorating influence of air at temperature of 70°C in an oven, for interval time of 4, 7, and 14 days. Then, their physical properties were determined by comparing these specimens with the properties determined on the original specimens and changes noted. The determination of tensile properties and tear strength was carried out in accordance with D 412 and ASTM D 624, respectively. The percent retention (%) of tensile properties and tear strength were calculated using the equation[8]:

$$\text{Propertiesretention } (\%) = [(P_u - P_a)/P_u] \times 100$$

where $P_u$—properties (tensile properties and tear strength) of unaged sample, $P_a$—properties (tensile properties and tear strength) of aged sample.

### Swelling test

The crosslinking efficiency of the cured vulcanizate was evaluated in terms of crosslink density using an equilibrium solvent swelling test method, ASTM D 471. The specimens 10 mm × 5 mm × 2 mm were accurately weighted ($W_1$) and immersed in toluene and allowed to swell in closed bottles for 22 h at room temperature. Then, the specimen was removed and the surface of the swollen samples was quickly wiped and weighed ($W_2$). Flory–Rehner equation was used to calculate crosslink density[9]:

$$-[\ln(1 - v_r) + v_r + \chi v_r^2] = \rho V_o M_c^{-1} v_r^{1/3}$$

where, $V_o$—molecular volume of the swelling liquid (105.7 cm$^3$), $v_r$—volume fraction of the original rubber network in the swollen gel, $\chi$—polymer–solvent interaction parameter (often depending on $v_r$ for a particular rubber–solvent system and normally given as 4.2), $M_c$—crosslink density.
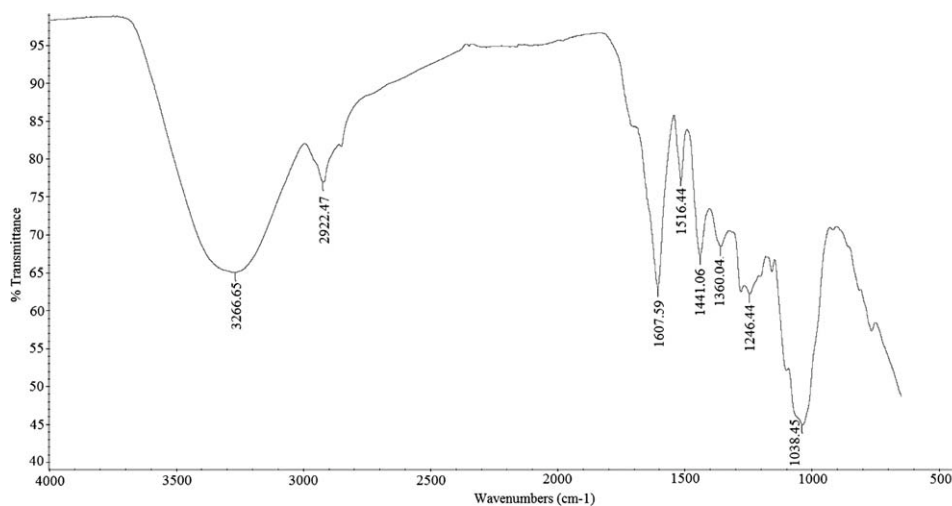
**Figure 1** FTIR spectrum of methanol extract from *E. guineensis* leave.

The volume swelling can be used to determine the crosslink density. The volume fraction of rubber at equilibrium, $v_r$, was calculated using the following relationship:

$$v_r = \frac{\frac{x_r}{\rho_r}}{\frac{x_r}{\rho_r} + \frac{x_s}{\rho_s}}$$

where, $\rho_r$, $\rho_s$ were the densities of swelling solvent and density of the raw rubber and $x_r$, $x_s$ were the mass fractions of solvent and rubber given by:

$$x_s = [\text{weight at equilbrium swelling})$$
$$- (\text{original weight})]/(\text{weight at equilbrium swelling}$$
$$x_r = 1 - x_s.$$

Tack (adhesion) test

The test method used to determine the tack (adhesion) strength or adhesion of rubber layer. Tack strength, $G_a$ (N/m) was calculated using the following formula:

$$G_a = 2F/w$$

where, $F$—average force (N) required for peeling, $w$—width (m) of the sample.

For measurement of tack strength, the rubber was mixed with antioxidant without any other compounding ingredients. The test specimen was prepared between sheets of smooth aluminum foils by hot press at temperature of 80°C for 3 min. Narrow strips of 20 mm width and 70 mm length with thickness of 2.0 ± 0.05 mm test specimens were prepared. Before the test, the aluminum foil at one side of strip removed and the strips allowed coming into intimate contact quickly. A load of 2 kg was applied for 30 s. After preferred contact time, the force required to peel off the strips was measured using Universal Testing Machine. A separation rate of 50 mm/min was used.[10]

## RESULTS AND DISCUSSION

### Characterization of natural antioxidant (*E. guineensis* methanolic extract): FTIR and GC–MS analysis

The results of FTIR spectrum of NA obtained from oil palm leaves, *E. guineensis* extract is shown in Figure 1. The results of functional group analysis using FTIR demonstrated that the existence of various characteristic functional groups in the *E. guineensis* extract. The FTIR spectrum of fresh *E. guineensis* extract as shown in Figure 1 is in the wave length range of 100–1700 cm$^{-1}$ and 2900–3500 cm$^{-1}$ and there are eight functional compounds found. In the spectrum, the presence of broad bands at 3406.05–3436.91 cm$^{-1}$ can be attributed to (OH) stretching vibrations from phenols. The presence of bands with strong to medium intensities are also observed at 2983.67–2870.84 cm$^{-1}$ which is confirmed as carboxylic acid group. Some other bands appeared at 1514.00–1450.00 cm$^{-1}$ and 1038.45 cm$^{-1}$ which might be due to presence of C=C aromatic, alkena, alchohol primer, and phenol group, respectively. In general, free radical scavenging and antioxidant activity of phenolics (e.g., flavonoids, phenolic acids) mainly depends on the number and position of hydrogen-donating hydroxyl groups on the aromatic ring of the phenolic molecules. It is also affected by other factors such as glycosylation of aglycones, other H-donating groups (-NH, -SH) and, etc.[11] The antioxidant properties of *E. guineensis* are suspected to be associated with hydrogen-donating hydroxyl groups on the aromatic ring of the phenolic molecules which is detected by the FTIR analysis.
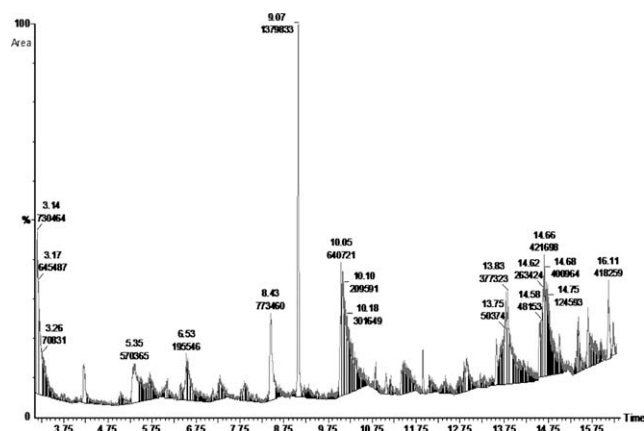
**Figure 2** GC–MS chromatogram of methanol extract from *E. guineensis* leave.

Further confirmation of the antioxidant compound in crude *E. guineensis* extract was found from GCMS analysis and presented as in Figure 2 and Table II. Each of the peaks at a retention time may represent one or more compounds present in the crude extract. Retention time is the time between sample injection and appearance of a solute peak or known as the amount of time that a compound is retained in the GC column. Typically chromatographically separated peaks would contain a single major component. The components are identified as dimethyl sulfoxide; 3,4-furandiol, tetrahydro-, trans-; 1-Amino-2,6-dimethylpiperidine; 4*H*-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6methyl; 3-cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-; 3-*tert*-butyl-4-hydroxyanisole; 2(1*H*)-isoquinolinecarboximidamide,3,4-dihydro-; 5-isopropenyl-2-methylcyclopent-1-enecarboxaidehyde; 2-furancarboxaldehyyde, 5-(hydroxymethyl)-; D-mannose; 1,6-Anhydro-a-D-glucopyranose (Levoglucosan), illustrated in Figure 3. The antioxidant properties of *E. guineensis* are suspected to be associated

with the dimethyl sulfoxide; 2,3-dihydro-3,5-dihydroxy-6methyl; 4*H*-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6methyl; 3-cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-; D-mannose; 3-*tert*-butyl-4-hydroxyanisole; and 5-isopropenyl-2-methylcyclopent-1-enecarboxaidehyde which are detected by GC-MS analysis in this study. Dimethyl sulfoxide; 2,3-dihydro-3,5-dihydroxy-6methyl; 4*H*-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6methyl; 3-cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-; D-mannose; 3-*tert*-butyl-4-hydroxyanisole; and 5-isopropenyl-2-methylcyclopent-1-enecarboxaidehyde have been tested previously and was reported to have a significant antioxidant activity.[12–16] It is possible that these compounds are mainly responsible for the observed antioxidant effects in this study. There are also minor peaks observed in GC-MS graph. These peaks might be due to the presence of impurity molecules in the crude *E. guineensis* extract, which most likely introduced during the leaf extraction process.

### Cure characteristics

The results of cure characteristics; minimum torque ($M_L$), maximum torque ($M_H$), optimum torque ($M_{90}$), scorch time ($t_{S2}$), optimum cure time ($t_{90}$), and curing rate index (CRI) are listed in Table III. It can be seen from Table III that there was not much variation in the cure characteristics of natural compounds (NR) comparing with the control compound. It is evident that the addition of NA extracted from oil palm leave has no adverse effect on the cure characteristics where the cure values obtained are comparable to those of control, BHT, and TMQ vulcanizates. Kuriakose and Rajendran[17] also conducted similar research by extracting phenol from rice husk. They reported that the rice bran oil can be used as a substitute for antioxidant in rubber compounding due the presence of natural phenols and rice bran

**TABLE II**
**Chemical Composition of Phenolic Compounds in *E. guineensis* Methanolic Extract Detected by GC–MS**

| No. | Compound | Retention time (min) |
|---|---|---|
| 1 | Dimethyl sulfoxide | 3.14 |
| 2 | Dimethyl sulfoxide | 3.17 |
| 3 | 3,4-Furandiol, tetrahydro-,trans- | 5.35 |
| 4 | 1-Amino-2,6-dimethylpiperidine | 6.53 |
| 5 | 4*H*-Pyran-4-one,2,3-dihydro-3,5-dihydroxy—methyl- | 8.43 |
| 6 | 3-Cyclohexen-1-ol,4-methyl-1-(1-methylethyl)- | 9.07 |
| 7 | 3-tert-Butyl-4-hydroxyanisole | 15.42 |
| 8 | 2(1*H*)-Isoquinolinecarboximidamide,3,4-dihydro- | 15.65 |
| 9 | 5-Isopropenyl-2-methylcyclopent-1-enecarboxaldehyde | 16.11 |
| 10 | 2-Furancarboxaldehyde,5-(hydroxymethyl)- | 10.05 |
| 11 | D-Mannose | 13.83 |
| 12 | 1,6-Anhydro-á-D-glucopyranose (levoglucosan) | 14.66 |
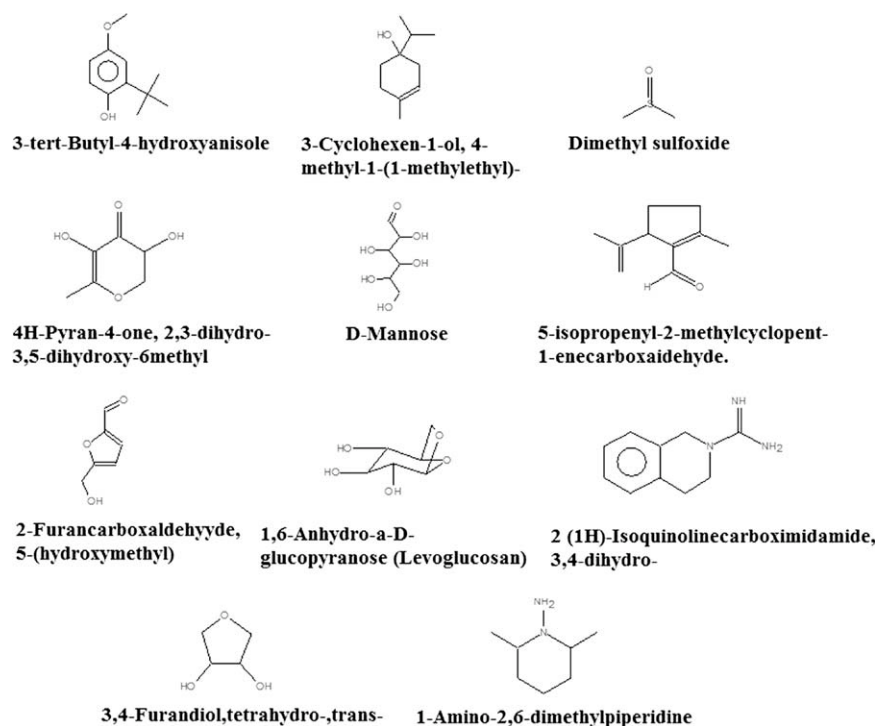
**Figure 3** Chemical structure of compounds present in methanol extract from *E. guineensis* leave.

oil does not affect much the cure characteristic in both carbon black and silica filled systems.

## Crosslink density

The crosslink density values of the NR vulcanizate containing NA obtained from oil palm leaves and those contains commercial antioxidant were evaluated. This crosslink density values are compared with the control NR vulcanizate and the results are given in Figure 4. Basically, crosslink density refers to the degree of crosslinking which determines the state of cure of a compound. Since, it is a conventional vulcanization system; the majority of crosslinking formed are polysulphidic linkages.

From the results, it can be seen that the crosslink density values for the three NR vulcanizates are almost nearer to the control. TMQ shows similar value to that of control and BHT slightly higher crosslink density than control. On the other hand,

NA shows a slightly lower value compared to control. As discussed in GC-MS analysis, the lower crosslink density can be attributed to the presence of certain impurity molecules from the leaf extraction process which obstructs the formation of crosslinking. Bag et al.[18] reported that the use of plant polymers as antioxidant in rubber compound has low crosslink density. This is due to the interference of other molecules in the formation of crosslink by sulfur. The molecules incorporated between the rubber chains, where it results in formation of rubber chains with one chain saturated and unsaturation in neighboring rubber chain. Then the formation of crosslink between these chains is difficult.

## Tensile properties before aging

Tensile properties of vulcanizate containing NA extracted from oil palm leave are compared with control and two other commercial antioxidants,

**TABLE III**
**Cure Characteristics of Natural Rubber Compounds Containing Various Types of Antioxidant**

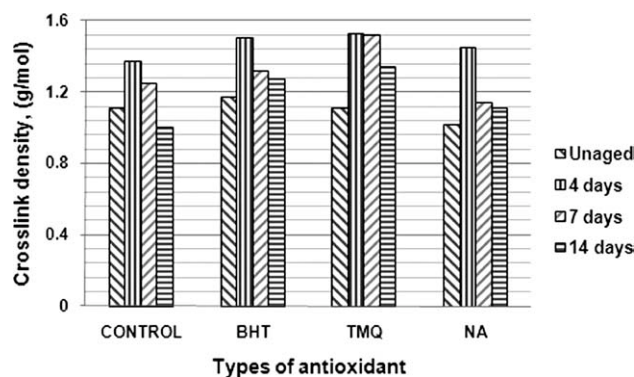| Compound cure characteristics | Control | TMQ | BHT | NA |
|---|---|---|---|---|
| $M_L$ (dNm) | 0.13 | 0.09 | 0.05 | 0.12 |
| $M_H$ (dNm) | 7.44 | 7.47 | 7.68 | 7.39 |
| $M_{90}$ (dNm) | 6.71 | 6.76 | 6.92 | 6.66 |
| $t_{S2}$ (min) | 3.07 | 3.19 | 2.53 | 2.21 |
| $t_{90}$ (min) | 5.28 | 5.35 | 5.27 | 5.21 |
| Curing rate index (CRI) | 45.25 | 46.30 | 36.50 | 33.33 |

**Figure 4** Crosslink density of control and NR vulcanizates with various types of antioxidant before and after aging.

TMQ and BHT. Tensile strength, elongation at break, modulus at 100% elongation (M100), and modulus at 300% elongation (M300) are the properties that investigated for each vulcanize with different antioxidants. Tensile properties are used to indicate the ability of rubber to react to the forces being applied in tension. The results obtained are tabulated in Table IV and presented in Figures 5–8.

Tensile strength is an important characteristic among the other tensile properties because it indicates the limit of final stress in most applications. Basically NR has a good tensile strength due to its ability to crystallize on extension. Bhowmick et al.[9] describe that strain induced crystallization at high stored energies causes the bonds to rupture and to be reformed according to the preferred configurations. Consequently, more energy is required to affect the final rupture. According to Table IV, it is clearly shown that the tensile strength of control vulcanizate is higher, followed by BHT, TMQ, and NA is the lowest. NR vulcanize with NA shows lower tensile strength. As mentioned for crosslink density, the lower strength might be due to the presence of impurities in the NA which is expected to weaken the interaction between the rubber chains hence requires less energy to rupture.

The elongation at break obtained for control and NR vulcanizes with different types of antioxidants are as given in Table IV. Elongation at break is

referred as percent of extension at the point of break. As for tensile strength, the elongation at break of NA vulcanizate is the lowest compared to control, BHT, and TMQ. Modulus value at 100 and 300% elongation are identified as M100 and M300 gives the tensile values at a given strain. Referred to Table IV, M100 of control is greater than of TMQ, BHT, and NA. The similar trend is observed for M300 as shown in Figure 8. The lowest value of elongation at break for NA vulcanizate might be due to the NA which gives softening effect leading to reduction of the stiffness of the NR vulcanizate.

From the result obtained, it is verified that the tensile properties obtained for control vulcanizate, TMQ, and BHT are more or less the same. However, decrement in tensile properties is observed when the commercial antioxidants are replaced with NA which extracted from oil palm leaves. Although NA vulcanizate gives slightly lower tensile properties compared to commercial antioxidant, it still exhibits a reasonable tensile values due to NR which is capable of strain-induced crystallization. This result is also supported by Kuriakose and Rajendran.[17] Extracted phenol from husk as an antioxidant in vulcanization study of NR gives antioxidant protection to the rubber comparably to a commercial antioxidant. These phenols do not show any adverse effect on tensile properties of the vulcanizates.

## Tear strength

Table IV and Figure 9 illustrate tear strength of control and NR vulcanizates with the addition of various types of antioxidants. Tear strength measures the maximum force or ability of rubber to resist tearing. The result shows that NR vulcanize with NAs exhibits the highest tear strength compared to control and other two commercial antioxidants, TMQ and BHT. Kuriakose and Rajendran[17] also observed that higher tear strength for rubber vulcanize with NA contains phenols obtained from husk compared to other commercial antioxidants.

It is known that tear resistance depends on degree of vulcanization. This is supported by Bhowmick et al.[9] and Coran that slightly undercured compounds claims for highest tear strength. Thus, the

**TABLE IV**
**Mechanical Properties and Tack Strength of Control and Natural Rubber Vulcanizates with Various Types of Antioxidants Before Aging**

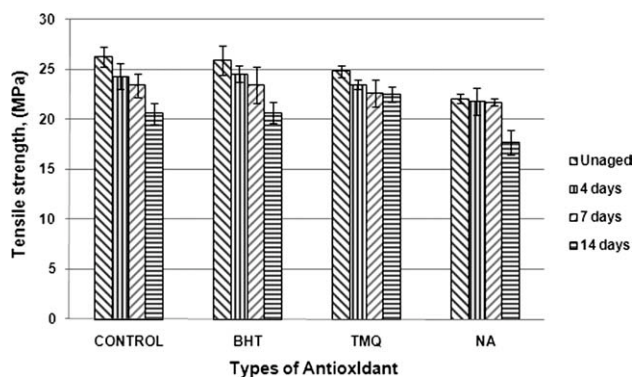| Properties and compound | Crosslink density ($10^{-4}$ g/mol) | Tensile strength (MPa) | Elongation at break (%) | M 100 (MPa) | M 300 (MPa) | Tear strength (kN/m) | Tack strength (N/m) |
|---|---|---|---|---|---|---|---|
| Control | 1.11 | 26.28 ± 1.0 | 989 ± 25.4 | 0.85 ± 0.01 | 2.13 ± 0.02 | 8.84 ± 1.6 | 1490 ± 0.02 |
| BHT | 1.17 | 25.95 ± 1.5 | 992 ± 26.4 | 0.83 ± 0.01 | 2.10 ± 0.04 | 7.96 ± 1.3 | 1510 ± 0.02 |
| TMQ | 1.11 | 24.84 ± 0.6 | 945 ± 13.9 | 0.84 ± 0.01 | 2.12 ± 0.01 | 6.87 ± 0.8 | 1910 ± 0.02 |
| NA | 1.02 | 22.08 ± 0.5 | 929 ± 12.2 | 0.80 ± 0.01 | 1.95 ± 0.02 | 9.44 ± 1.0 | 1170 ± 0.01 |

**Figure 5** Tensile strength of control and NR vulcanizes with various types of antioxidant before and after aging.

higher tear strength of NA vulcanizate might be due to undercure of the vulcanizate which results in low crosslink density. This is further supported by results obtained from crosslink density and cure time.

## Aging

The resistance of the rubber vulcanizates to the thermal aging is considered as an essential requirement for better service performance of products. Crosslink density, tensile properties and tear strength were used to evaluate the ability of NA to retard aging of NR vulcanizates. These properties of vulcanizates are compared with NR vulcanizates of commercial antioxidants which are TMQ, BHT, and control, NR vulcanizate without antioxidants. TMQ is identified as aromatic amine antioxidant which is used for long-term protection while, BHT is phenolic antioxidants used for short-term protection. The results obtained are as presented in Figures 4–9.

### Crosslink density

Figure 4 illustrates the effect of aging of NR vulcanizates with and without antioxidant on crosslink density. A similar trend is observed for all the vulcanizates where the crosslink density increases when
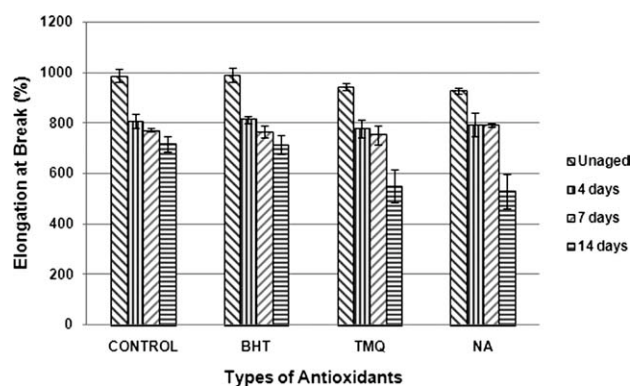


**Figure 6** Elongation at break of control and NR vulcanizates with various types of antioxidant before and after aging.
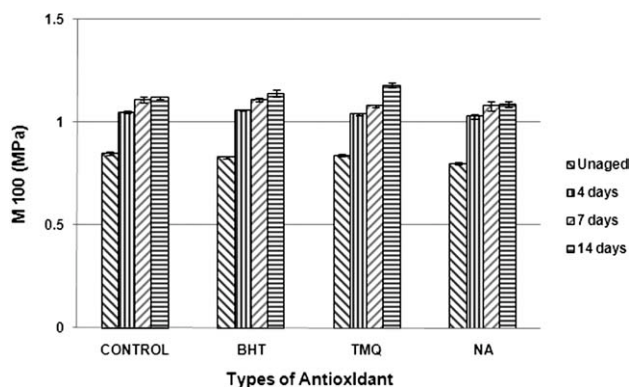


**Figure 7** M100 of control and NR vulcanizates with various types of antioxidant before and after aging.

aged for 4 days, and then decreases as the aging time increased to 7 and 14 days. The increase in crosslink density is due to the presence of free sulfur content which leads to further crosslinking during the aging period. The decrease in crosslink density after 7 and 14 days is due to decomposition of crosslinks. It is also supported by Choi[19] that formation of new crosslinks takes place in the case of undercured vulcanizate which has free-sulfur content. Fundamentally, the crosslink densities of rubber vulcanizates cured by a sulfur accelerator system are changed by thermal aging where changes occur by formation of new crosslinks and dissociation of existing crosslinks.[19]

NR vulcanizate with TMQ exhibits highest crosslink density after aging compared to other NR vulcanizates. It is then followed by BHT, control, and NA. It is also noted that the crosslinking density of all unaged vulcanizates are lower than aged except for control. This is due to the absence of antioxidant to retard aging. The crosslink density of 14 days aged control vulcanzate is lower than unaged.

### Tensile properties and tear strength

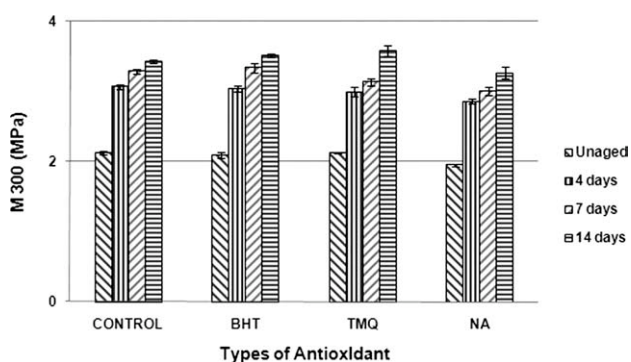As mentioned earlier, Figures 5–9 illustrate the tensile properties and tear strength of NR vulcanizates



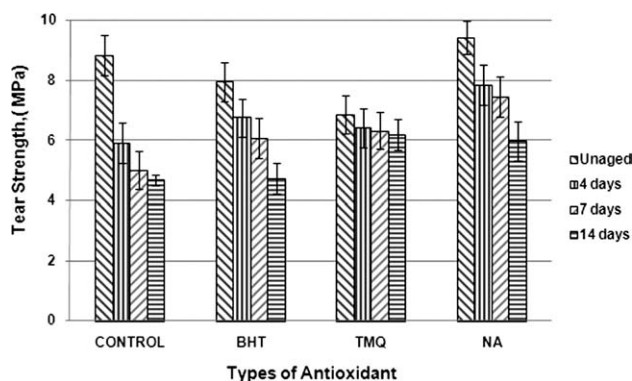**Figure 8** M300 of control and NR vulcanizates with various types of antioxidant before and after aging.

**Figure 9** Tear strength of control and NR vulcanizates with various types of antioxidant before and after aging.



**Figure 11** Percentage of retention (%) of elongation at break of control and NR vulcanizates with various types of antioxidant.

after aging process. All the vulcanizates shows a reduction in tensile strength and elongation at break after aging excluding modulus where it increases with aging. The changes in the tensile properties indicate that rubber has undergone degradation.

Under temperature of 70°C, rubber chains cleaves where the polysulphidic crosslinks are destroyed and new crosslinks such as monosulphidic are formed. This crosslinks are low resistance to heat or thermal aging. Thus, tensile strength decreases with time due to breakdown of polysulphidic crosslinks. The decrease in elongation at break with aging is due to decrease of uncoiling and slipping nature of rubber chain. Meanwhile, modulus increases due to the stiffness of the rubber matrix brought about by a reduction in the number of double bonds.

A similar trend as tensile strength and elongation at break is observed for tear strength, Figure 9. Control vulcanizate shows a drastic drop in tear strength, BHT and NA exhibits a gradual decrease while TMQ shows a small reduction in tear strength. Basically, tear strength of all vulcanizate give a decreasing trend.

To quantify the effect of aging on the various properties investigated, percent retention (%) of property was carried out. The percentage of reten-
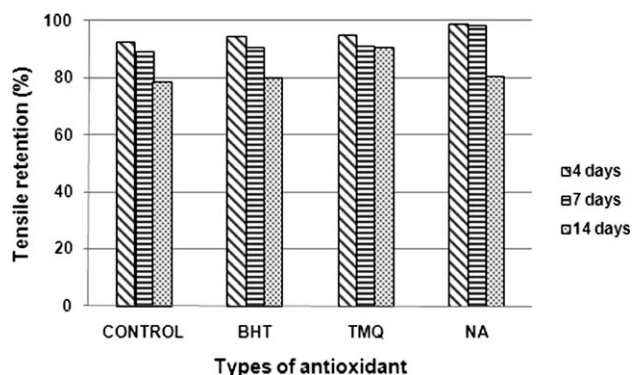
tion (%) of tensile properties and tear strength of the NR vulcanizate of control, TMQ, and BHT after aging process are compared with NA and plotted as shown in Figures 10–14. Comparison was made with commercial antioxidants such as TMQ and BHT.

Figure 10 shows the plot of retained tensile strength for three different time of aging for NR vulcanizates without antioxidants and with antioxidants, BHT, TMQ, and NA. As the duration of aging are increased from 4 days to 7 and 14 days, the percent of retention of tensile strength decreases. It proves that duration of aging has remarkable effect on the tensile strength of all vulcanizates due to the degradation. The best retention in tensile properties after aging for 14 days was displayed by TMQ due to their property to provide long-term protection by inhibiting radicals and retard aging. Whereas, NA vulcanizate show the second best followed by BHT and control. Retention of tensile strength for control is slightly lower due to the absence of antioxidant.

A similar trend as retention tensile strength is observed for retention of elongation at break where it decreases as the aging time increased from 4 days to 14 days. Figure 11 shows the percent retention



**Figure 10** Percentage of retention (%) of tensile strength of control and NR vulcanizates with various types of antioxidant.
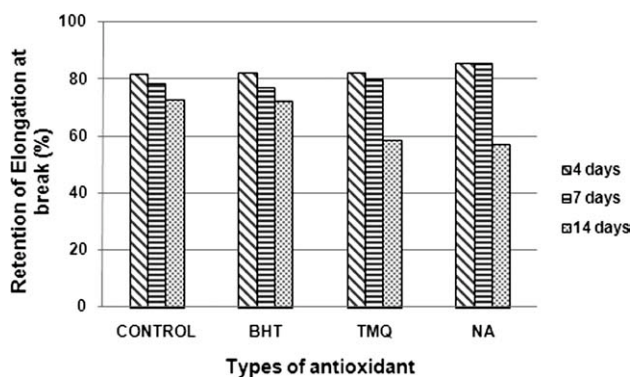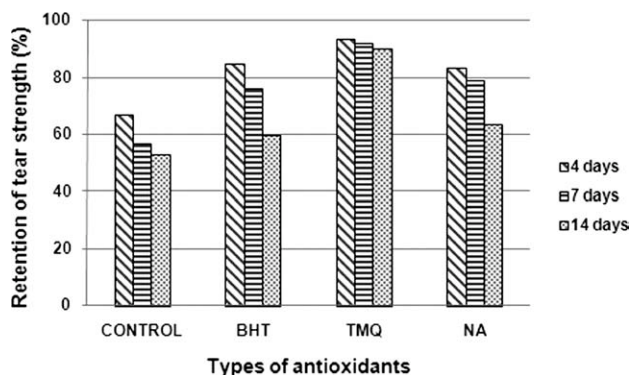


**Figure 12** Percentage of retention (%) of tear strength of control and NR vulcanizates with various types of antioxidant.
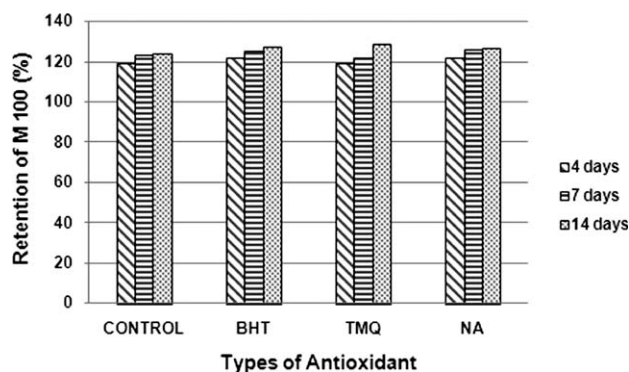
**Figure 13** Percentage of retention (%) of M100 of control and NR vulcanizates with various types of antioxidant.

(%) of elongation at break. Vulcanizate of NA antioxidant shows highest retention of elongation at break for 4 and 7 days and lowest retention for 14 days compared to the other vulcanizates. Control, BHT, and TMQ have a gradual decrease in retention (%). Vulcanizates control, BHT, and TMQ for 4 days aging shows almost similar retention values. After aging for 7 days, NA shows highest retained value followed by TMQ, control, and BHT. After 14 days aging, retention of control is higher followed by BHT, TMQ, and NA.

Aging also decrease the retention of tear strength which resulted from the thermal degradation of the rubber network. The percent retention (%) of tear strength is depicted in Figure 12. The lowest retention is observed for tear strength of control vulcanizate after aged for 4, 7, and 14 days. Whereas, TMQ retained significantly higher tear strength above 90% after aging. BHT and NA vulcanizates shows almost similar trend. The addition of antioxidants to the NR vulcanizate improved the retention in the tear strength.

Figures 13 and 14 present the percent retention of M100 and M300 for all four vulcanizates, control, BHT, TMQ, and NA. Both figures show similar trend where the properties increases as the duration of aging increased. This is due to slight increase in hardness during aging. BHT, control, and NA vulcanizates shows a gradual increase in retention of M100 and M300, whereas, TMQ exhibit sudden increase in retention after 14 days of aging. As for tensile and tear retention, vulcanizate of TMQ shows the highest retention of M100 after aged for 14 days. Whereas, control has the lowest percent of retention after being aged for 14 days compared to other vulcanizates. Meanwhile, BHT and NA vulcanizates show a gradual increment in percent retention of M100.

The percent (%) retention of M300 is presented in Figure 14. As mentioned earlier, it shows increment trend in percent of retention. Among the vulcani-

zates aged for 4 days, NA shows good retention followed by BHT, control, and TMQ. Meantime, after aging for 14 days, percent of retention of NA is higher than control and comparable retention with BHT and TMQ.

From the result, it is clear that NR with the addition of TMQ antioxidants exhibits better antioxidant activity. This is due to the characteristic of antioxidant which provides a good and long-term protection to the rubber against aging. Vulcanizate with NA inhibits radical formation and retards aging comparable to BHT antioxidant. This is because the NA extracted from oil palm leave contains antioxidant compounds (phenolic compounds) as in BHT for the antioxidant activity. However, it is found that the NA give slightly better protection compared to BHT even though it provides lower tensile properties compared to BHT.

According to Bag et al.[18] plant polymer can act as an antioxidant in rubber due to the presence of antioxidant moieties even they have drawback such as slight decrease in tensile properties which may be compensated by increasing small amount of sulfur level. Basically, phenolic compounds in herbs or plants act as antioxidants due to their redox properties allowing them to act as reducing agents and free radical quenchers.[20]

## Adhesion/tack strength

Figure 15 shows the effect of different antioxidants on tack strength of NR compound. According to Figure 15, TMQ exhibits higher tack strength. It is followed by BHT, control, and NA. The result is tabulated in Table IV. The variation in the result obtained is due to the effect of molecular weight of antioxidant. NR has superior tack strength but due the influence of molecular weight of antioxidant can detract it from this advantage.[21]

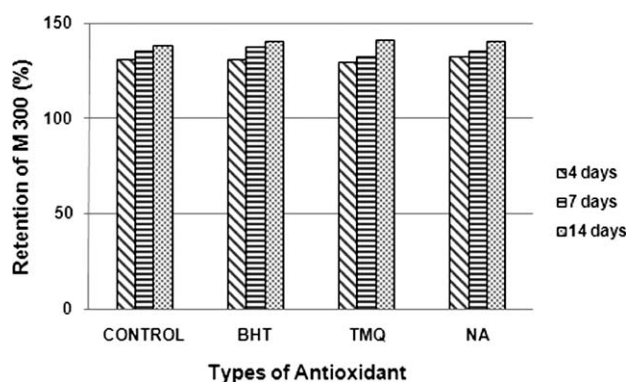If two rubber surfaces were in sufficiently close contact, part of the long chain molecules on the



**Figure 14** Percentage of retention (%) of M300 of control and NR vulcanizates with various types of antioxidant.
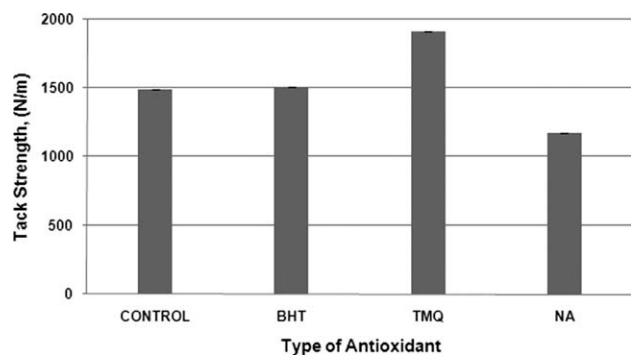
**Figure 15** Tack strength of control and NR vulcanizates with various types of antioxidants.

surface would diffuse across the interface, surface molecules will interpenetrate and eventually the interface will disappear and the two parts become one.[22,23] For such interdiffusion to take place the molecules must be relatively mobile which should not have any appreciable degree of crosslinking in either of them. Stacer and Stacer[22] account tack strength as energy required to pull these molecules out of the surrounding physical entanglements and backing across the interface. The deeper the interpenetration distance, the greater will be the energy to pull.

The diffusion of the rubber molecules across the interface increases as the molecular weight decreases.[22,23] The molecular weight of antioxidant TMQ is lower than BHT. Thus NR vulcanizate with TMQ shows higher tack strength compared to NR vulcanizate of BHT. However, control NR vulcanizate exhibits lower tack strength although it has low molecular weight than the NR vulcanizates with two commercial antioxidants. A rubber compound having low molecular weight which can easily diffuses across the interface, cannot develop a good tack due to poor cohesive strength.[21] NR vulcanizate with NA has the lowest tack strength than control; BHT and TMQ NR vulcanizate due to the various molecular compounds present in NA which inhibits the interdiffusion between rubber chains consequently requires less energy to pull apart the chains. Thus, the tack strength is the lower.

## CONCLUSIONS

From the research, the results indicate that NA posses lower tensile properties, crosslink density, tack strength but high tear strength compared to the commercial antioxidants, BHT, and TMQ. However, the NA does not show any adverse effect on the tensile and other properties of the vulcanizates before aging. It does show comparable value of crosslink density but least value compared to other antioxidants. Tear strength of NA is the highest with lower

tack strength. There is also no adverse effect on cure characteristics evaluated.

However, as the NR with and without antioxidants is aged, a decrease in tensile and tear properties is observed due to the effect of degradation of the rubber network. NR with TMQ exhibits better antioxidant activity to retard aging compared to BHT. Percent retention (%) of tensile strength and tear strength due to aging shows that the phenolic component in NA gives antioxidant protection to the rubber comparably to commercial antioxidant BHT.

As a result, NA from oil palm leaves can be used as aging retardant in rubber compounds. It will be more significant if used as aging retardant for short-term protection in application requiring moderate tensile properties. Being natural, NA can be used as alternative source for commercial antioxidants to retard aging.

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