# A New Processing Additive for Natural Rubber from Agricultural Waste

**Anti-oxidant · Adhesion · Waste · Rubber · Renewable resources.**

The leaves of the oil palm species *Elaeis Guineensis* were found to be a rich source of phenolic compounds. In an effort to dispose waste oil palm leaves usefully, our research team explored the antioxidant characteristics and tackifying ability of oil palm leaf extract (OPE) in a natural rubber-based formulation. After simulated ageing of the natural rubber (NR) compounds containing the OPE, the reduction in mechanical properties of the NR compounds was within acceptable limits. It was also observed that the OPE improves the tack strength of NR appreciably. The OPE could be a promising multifunctional additive in green polymer processing technology.

## Neue Verarbeitungshilfsmittel für NR aus landwirtschaftlichem Abfall

**Alterungsschutzmittel · Adhäsion · Abfall · Kautschuk · erneuerbare Ressourcen**

Die Blätter der Ölpalme *Elaeis Guineensis* enthalten höhere Mengen phenolischer Verbindungen. Um diese Blätter sinnvoll zu entsorgen hat unsere Arbeitsgruppe die Eigenschaften als Alterungsschutzmittel und Klebrigmacher des Extraktes (OPE) in NR Compounds untersucht. In Alterungsversuchen mit OPE wurde eine Abnahme der mechanischen Eigenschaften innerhalb akzeptabler Grenzen beobachtet. Es wurde ebenfalls gezeigt, dass durch OPE die Schälkraft von NR deutlich gesteigert wird. OPE kann ein multifunktionelles Additiv in der „grünen" Verarbeitungstechnologie werden.

Figures and Tables:
By a kind approval of the authors

Malaysia, being the world's largest producer of palm oil, generates a huge amount of oil palm waste. This is true in the cases of some other Asian countries as well. On an average, every year Malaysia generates 7.7 million tonnes of empty fruit bunches, 6.0 million tonnes of fiber, 2.4 million tonnes of palm shell. The fiber waste is used to generate energy to run the palm oil mill and for fertilizer purposes. There are more than 270 palm oil mills operating in Malaysia that utilize mainly fiber and partly shell in their boilers as fuel to generate power and steam required by the industry. About 30 % of the shell is utilized for this purpose [1]. On the other hand, almost whole of the oil palm leaves have been discarded as a waste.

Oil palm fruit shell has been reported to be a good source of phenolic compounds [2]. Previously some authors reported the presence of phenolic compounds in some natural food materials [3-5]. We have found out the leaves of oil palm to be a good source of phenolic compounds that can trap free radicals. Unsaturated polymers such as polyisoprene or polybutadiene undergo thermo-oxidative degradation readily at elevated temperatures [6,7]. Oxidative degradation usually leads to hardening, discolouration, as well as surface changes. Oxidative degradation involves formation of free radicals on polymer chain backbone followed by the formation of peroxy radical. The peroxy radical can attack the neighbouring segments, abstract hydrogen and form a hydroperoxide and a new free radical site. The hydroperoxide formed can lead to the formation of several new free radical sites. With so many free radicals being formed, their recombination can occur and result in the termination of the chain reactions [7]. Currently used rubber antioxidants can be classified into amines, phenols and thioesters. The main phenolic antioxidants belong to five types, namely, hindered phenols, hindered bisphenols, hindered thiobisphenols, polyphenols and polyhydroxyphenols [8].

The total antioxidant action would ordinarily involve three functions. First would be the absorption of UV light which catalyzes oxidation. Second would be the decomposition of initiating peroxides which are converted into non-radical products. It is believed that the phenolic antioxidants function in this way. The final one would be the stopping of the radical chain reaction. Synthetic antioxidants such as 2,2,4-trimethyl quinoline (TMQ) have been used widely in polymer formulations to prevent the thermo-oxidative degradation of polymers, but they are not environment-friendly. Also, their manufacture contributes significantly to carbon foot print.

From environmental point of view, instead of the synthetic antioxidants, natural ones could be used. Phenolic antioxidants are well known for trapping. Free radicals, such as peroxy radicals, to prevent oxidative degradation in organic materials such as plastics [9]. Even though there have been numerous reports on use of natural materials in rubber formulations, there have been only a few reports on the use of oil palm-based materials in rubbers. Ismail et al. studied the effects of palm oil fatty acid on curing characteristics, reversion and fatigue life of

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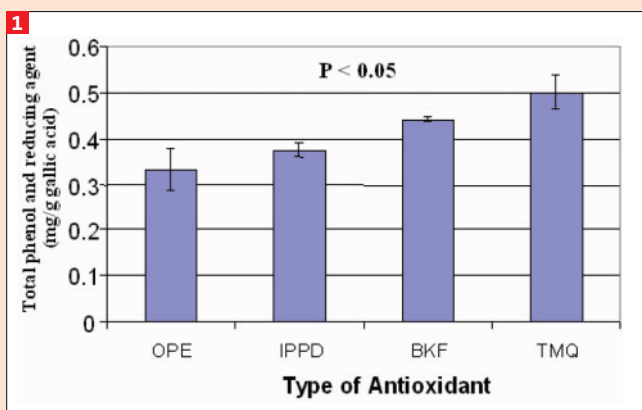Fax: +91-824-2474033
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**1** Phenolic and reducing agent content in various antioxidants
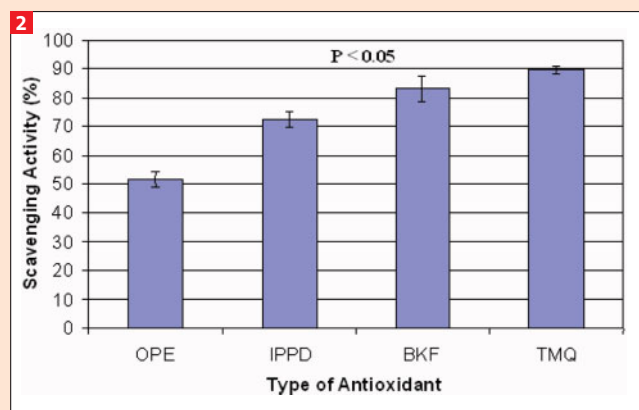


**2** Total radical scavenging activity of various antioxidants

various natural rubber compounds [10]. They also reported palm oil fatty acid as an activator in natural rubber gum compounds [11, 12]. Guhathakurta *et al.* [13] reported that Bahera gum, a natural material, can be used as a multifunctional additive for rubbers. Bahera gum was also used as an adhesion promoter in an adhesive formulation [14].

In an effort to dispose waste oil palm leaves usefully, our research team explored the antioxidant characteristics and tackifying ability of oil palm leaf extract in a natural rubber-based formulation. This was due to the abundance of phenolic compounds in oil palm leaves. To the best of the authors' knowledge, there has been no report(s) on the use of oil palm leaf extract in rubbers. In this paper, we report the results of our studies on the characterization of OPE, evaluation of the radical quenching ability of the OPE, and antioxidant characteristics and tackifying properties of the oil palm leaf extract in natural rubber.

## Experimental

### Materials

Oil palm leaves were collected at Semeling Oil Palm Estate, Malaysia. NR used in this study was SMR-5 with a Mooney viscosity of 86 (ML$_{1+4}$ at 100 °C = 86) and was procured from Revertex (Malaysia) Sdn. Bhd. The antioxidants IPPD(N'-phenyl-N-propan-2-yl-benzene-1,4-diamine), BKF (2-[(2-hydroxy-5-methyl-3-tert-butyl-phenyl) methyl]-4-methyl-6-tert-butyl-phenol) and TMQ (5-methyl-6-[[(3,4,5-trimethoxy-phenyl)amino]methyl]quinazoline-2,4-diamine) were procured from Bayer Malaysia. Other curatives were purchased from indigenous resources. Methanol of 99 % purity was obtained from Quick Lab Sdn. Bhd., Malaysia.

## Preparation of oil palm leaf extract

### Collection of oil palm leaves

Around 1 kg of the palm oil leaflets was collected. The leaflets were washed using tap water and then cut approximately into 1 cm$^2$ sized pieces. The thus obtained pieces were dried in an oven for about 5 to 7 days at 30-40 °C. The leaves were avoided from being exposed to excessive heat. Heat and air could destroy the beneficial natural products at above of 70 °C. After drying, the leaflets were ground using a heavy duty blender.

### Extraction of oil palm leaves with methanol

The extraction was done using the traditional soaking method. The leaves were finely powdered and put into a big container, covered with methanol. For about 100 g of the powder 250 mL of methanol was added. The plant material was left to soak in methanol for 5 days in a Quiet warm place and shaking was occasionally done. Then filtrate was separated out from the residue. Using a rotary evaporator (EYELA, USA) methanol was evaporated from the filtrate at 64.8 °C.

## Characterization of the oil palm leaf extract

### Determination of total phenolic (TP) and the reducing agent contents

The total phenolic content of the extracts was determined with the Folin–Ciocalteu method [15]. Briefly, 0.5 mL of diluted extract solution at 100 mg/mL was shaken for 1 minute with 100 µl of Folin–Ciocalteu reagent and 6 mL of distilled water. After the mixture was shaken, 2 mL of 15 % Na$_2$CO$_3$ was added and the mixture was shaken once again for about a minute.

Finally, the solution was brought up to 10 mL by adding distilled water. After 1.5 hour, the absorbance at 750 nm was taken using a visible spectrophotometer (Thermoscientific GeneSYS20, USA). The results were expressed as Gallic acid equivalents (Table 1). The Folin-Ciocalteu reagent is a mixture of phosphomolybdate and phosphotungstate used for the colorimetric assay of phenolic antioxidants and polyphenol antioxidants. It works by measuring the amount of a substance needed to inhibit the oxidation of this reagent. However, this reagent does not only measure total phenols and will react with any reducing substance. The reagent therefore measures the total reducing capacity of a sample, not just the level of phenolic compounds.

### DPPH Radical scavenging activity

Free radical scavenging activity was measured by 1,1-diphenyl-2-picrylhydrazyl (DPPH) by the method of Shimada etal. [16]. The antioxidant solution was kept in a universal bottle at 1 mg/mL. Then 5 mL of a 0.04 % solution of DPPH was added to antioxidant solution and was shaken vigorously. Then the bottles were incubated in the dark at room temperature for 30 minutes. A control sample was also prepared. The changes in the absorbance of the samples were measured at 517 nm (Table 2). Radical scavenging activity was expressed as the inhibition percentage and was calculated using the following formula [17]:

$$RSA(\%) = \frac{OD_C - OD_S}{OD_C} \times 100$$

Where, RSA = radical scavenging activity
OD$_c$ = Control optical density
OD$_s$ = Sample optical density

### EC$_{50}$ Determination

EC$_{50}$ index, defined as the concentration needed to reduce 50 % of DPPH. Time needed to reach the steady state at the concentration EC$_{50}$ is named TEC$_{50}$. EC$_{50}$ is inversely related to the antioxidant capacity of a compound, as it expresses the amount of antioxidant needed to decrease the radical concentration by 50 %. The lower EC$_{50}$, the higher the antioxidant activity of a compound is. The experiment was conducted using various concentration of the OPE (Table 3). Then a linear regression graph based on the percentage of the scavenging activity against the antioxidant concentration was plotted [18].

### Fourier transform infra red spectroscopy study of OPE

The OPE was mixed with KBr and made into a pellet by using a hydraulic press. The FTIR spectrum of this pellet was taken in transmission mode by using a Perkin Elmer FTIR spectrometer. The scans were made in a wave number range from 400 to 4000 cm$^{-1}$ and the average of 32 scans was recorded.

### Use of oil palm leaf extract in natural rubber

### Preparation of rubber compounds

The NR compounds were prepared by using a laboratory-sized two roll mill (GoeTech, Malaysia) (size: $6'' \times 11''$) following the ASTM procedure. Natural rubber formulations containing the synthetic antioxidants TMQ, BKF, IPPD and OPE were prepared as shown in Table 4.

### Cure characteristics

The cure characteristics of the rubber compounds were studied using a Monsanto moving die rheometer (MDR2000, USA) as per ASTM D5289-95. The rheometric studies were carried out at 150 °C with an arc oscillation of 0.5°. The optimum cure time of the compounds, t$_{90}$ obtained from their respective rheographs that correspond to an optimum torque, M$_{90}$, given by
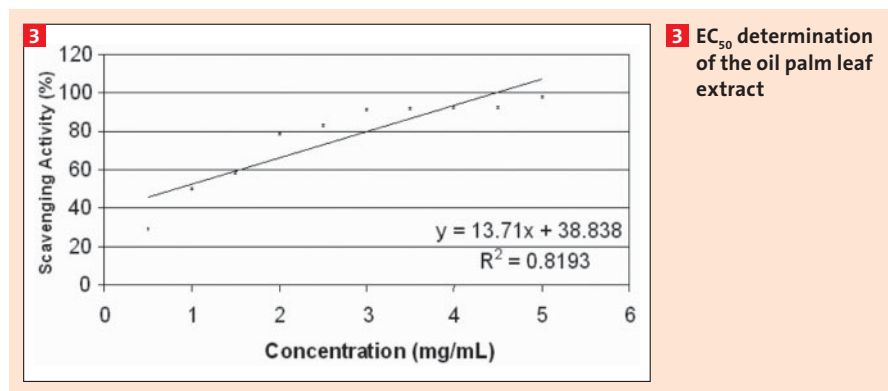
$$M_{90} = 0.9 \, (M_H - M_L) + M_L \qquad (1)$$

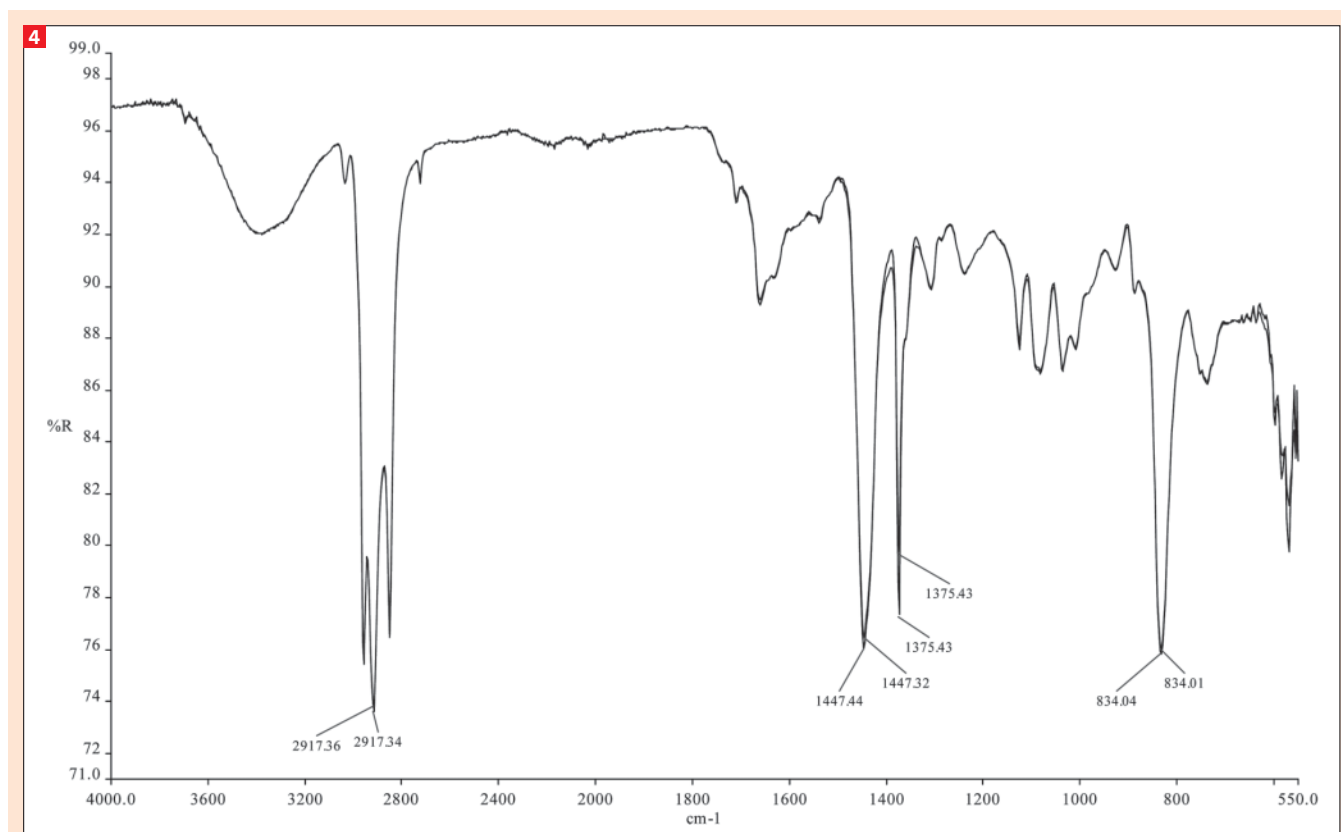Where, M$_H$ and M$_L$ are the maximum and minimum torques, respectively.
Cure rate was calculated using the following equation:

$$\text{Cure rate} = 100 / (t_{90} - t_2) \qquad (2)$$

Where, t$_2$ is the time corresponding to 2 unit rise in the torque above the minimum torque [13].



**3** EC$_{50}$ determination of the oil palm leaf extract



**4** FTIR spectrum of the oil palm leaf extract

## Molding

Test specimens were compression molded at 150 °C under a pressure of 10 MPa in an electrically heated hydraulic press. Optimum cure time $t_{90}$ as obtained from MDR for each compound was taken as the molding time [13].

## Measurement of mechanical properties

The stress–strain properties were determined as per ASTM-D-412-98a (method A, Die C). The measurements were done using a computerized Zwick Universal Testing Machine (model – 1445) at 25 °C. A grip separation rate of 500 mm/min was used in all cases. Properties such as tensile strength, elongation at break, Young's modulus, M100, M300 and toughness were evaluated. 5 test specimens were used for testing and the averages of values have been reported. Maximum deviations in the results of tensile strength, modulus, and elongation at break were ± 5 %.

## Ageing

The aging characteristics of the vulcanizates were studied according to ASTM D-412-98a (method A, Die C) standards. The ageing property of the OPE-containing rubber vulcanizate was compared with those having synthetic antioxidant in them. The mechanical properties were tested to evaluate the aging resistance of the vulcanizates. All the vulcanizates were aged at 70 °C in an air ageing oven (GoeTech, Malaysia) for 72 hours to initiate the thermo-oxidation and to see the changes in the properties of rubber [13].

## Measurement of tack strength

A practical definition of tack is the ability of two similar materials to resist separation after they are brought into contact for a short time under a light pressure [21]. Tackifiers are specialized types of softeners that
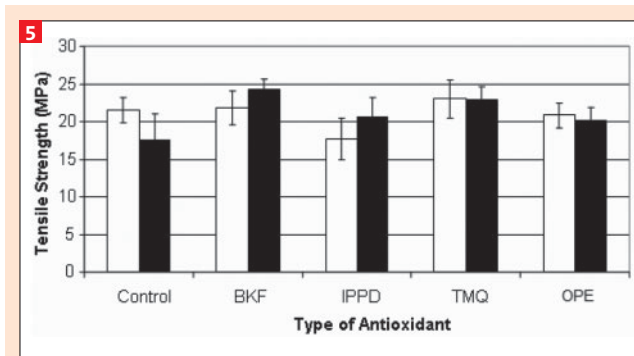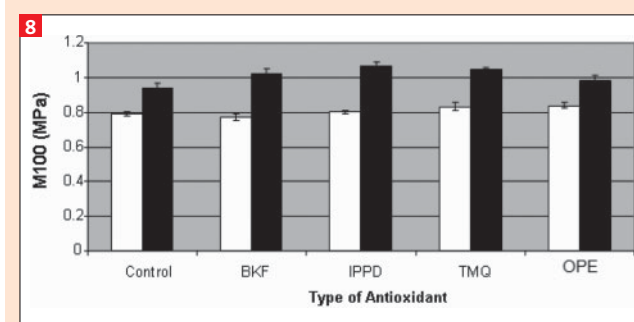


**5** Tensile strength of NR vulcanizates with different antioxidants
Key: (Applies as well to Figures 6-10)
☐ Befor Ageing
■ After Ageing
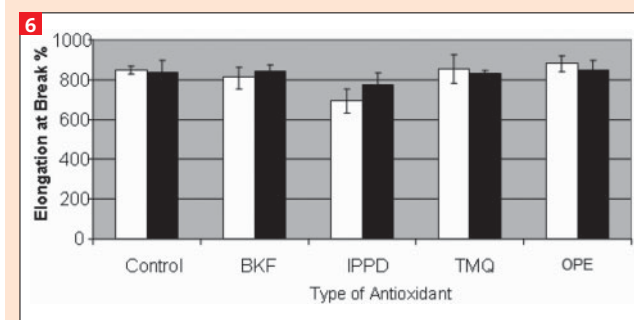


**6** Elongation at break of NR vulcanizates with different antioxidants
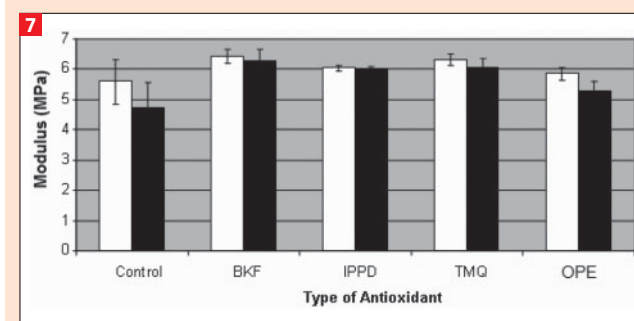


**7** Young's Modulus of NR vulcanizates with different antioxidants



**8** M100 of NR vulcanizates with different antioxidants

**1** Total phenol and reducing agent content

| Type of Antioxidant | Absorbance Replicates | | |
| --- | --- | --- | --- |
| | 1 | 2 | 3 |
| OPE | 0.417 | 0.436 | 0.347 |
| IPPD | 0.437 | 0.466 | 0.457 |
| BKF | 0.532 | 0.526 | 0.534 |
| TQ | 0.628 | 0.559 | 0.619 |

| Type of Antioxidant | Average Absorbance | Total Phenolic Content (mg/g Galic acid) | Standard Deviation |
| --- | --- | --- | --- |
| OPE | 0.4 | 0.333 | 0.046872167 |
| IPPD | 0.45 | 0.375 | 0.014843629 |
| BKF | 0.53 | 0.442 | 0.004163332 |
| TQ | 0.6 | 0.5 | 0.037509999 |
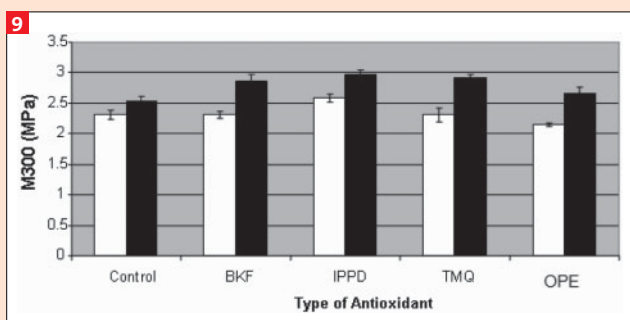
**9** M300 of NR vulcanizates with different antioxidants
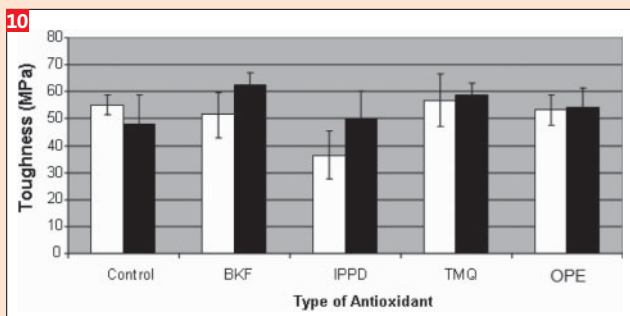


**10** Toughness of NR vulcanizates with different antioxidants



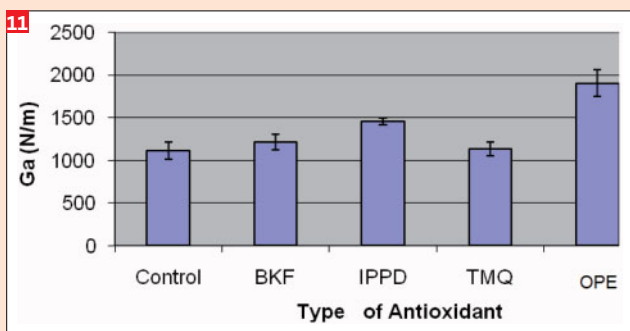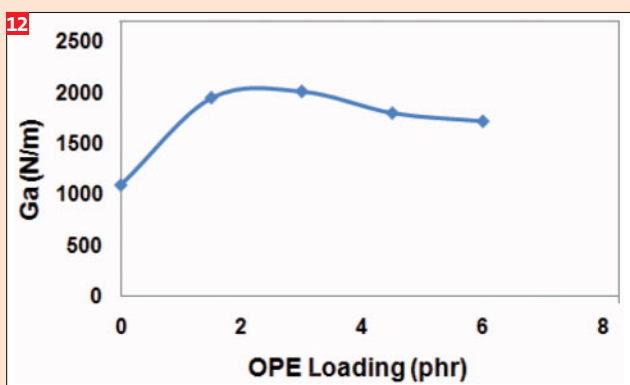**11** Tack strength of NR formulations with different antioxidants



**12** Variation of tack strength of NR with OPE Loadin

are used to increase the ability of uncured rubber formulations to form bonds with themselves or other surfaces under pressure by increasing the wettability or contact at the interface while maintaining or even increasing the green strength of the rubber formulation [22]. For the measurement of tack strength, mixes based on NR with 1.5 phr of TMQ, BKF, IPPD and OPE were prepared in a two-roll mill at roll temperature of 25°C. Also, NR compositions containing 3,

4.5 and 6 phr of OPE were prepared. One side of the rubber sheet was backed by cloth and the other side by aluminum foil. Narrow strips (2 cm × 7 cm) were cut from the molded rubber sheets. Just before the test, the aluminum foil was removed and the strips were allowed to come into intimate contact quickly. A load of 2 kg was applied for 30 s in each case. After the desired contact time, the average force required to peel off the two strips was measured in a Zwick Univer-

sal Testing Machine (model- 1445) at 25°C. A separation rate of 50 mm/min was used in all cases. The tack strength, $G_a$ (Nm$^{-1}$), was calculated using the following formula:

$$G_a = 2F/w \qquad (3)$$

Where, F is the average force (N) required for peeling and w is the width (m) of the sample. This test was reported in the literature [13 and 21] and had an error of ± 5 % in this investigation.

## Results and discussion

### Total extraction yield
Using the methanol soaking method, a satisfying amount of crude yield could be obtained. By using approximately 500 g of dried and ground oil palm leaves, the crude yield of around 19 g can be obtained. In each 2000 mL conical flask, 500 g of ground plant material can be retained. Seven of such conical flask were set up and the total yield of crude extract was around 137 g.

### Total phenolic and reducing agent contents
The antioxidant effect is mainly due to phenolic components, such as flavonoids [19], phenolic acids, and phenolic diterpenes [20]. The antioxidant activity of phenolic compounds is mainly due to their redox properties, which can play an important role in absorbing and neutralizing free radicals, quenching singlet and triplet oxygen, or decomposing peroxides.

The amount of phenolic and reducing agent content varied in different antioxidants and ranged from 0.33 to 0.5 mg GAE/100 mg extract (Table **1**). The highest total phenolic level was detected in TMQ and the lowest in OPE.

There is significant difference among all the antioxidants. The graph indicates that the antioxidant activity is better in TMQ compared to OPE, and IPPD and BKF have an intermediate effect when compared with the other two. The higher the phenolic content in a compound, the higher the antioxidant activity is. This fact is supported by the scavenging activity results (Fig. **1**).

### DPPH radical scavenging activity
2,2-Diphenyl-1-picrylhydrazyl (DPPH) is widely used to test the ability of compounds to act as free radical scavengers or hydrogen donors. It has also been used to quantify antioxidants in complex biological systems in recent years. The DPPH method can be used for solid or liquid samples and is not specific to any particular antioxidant

component, but applies to an overall antioxidant capacity of the sample.

The odd electron in the DPPH free radical gives a strong absorption maximum at 517 nm and is purple in colour. The colour turns from purple to yellow as the molar absorptivity of the DPPH radical at 517 nm reduces from 9660 to 1640 when the odd electron of DPPH radical becomes paired with hydrogen from a free radical scavenging antioxidant to form the reduced DPPH-H. The resulting decolourization is stoichiometric with respect to number of electrons captured.

The antioxidant activity of all of the solution were determined in terms of the proportion (%) of DPPH scavenged by 1 mg/mL. All of the fractions were able to scavenge the radical. There is significant difference between all the solutions. The lowest activity was found for the extract from oil palm leaves. This could be probably due to the presence of other compounds along with phenolics in this solution. This finding is consistent with its relatively low total phenolic content. The free radical scavenging activity decreases in the order of TMQ > BKF > IPPD > OPE (Fig 2). Overall, the antioxidant activities of the solutions correlate well with their total phenolic content.

### EC$_{50}$ Determination

The antioxidant ability of a compound may also be defined by the parameter antiradical power (ARP), which is related to the factor EC$_{50}$. EC$_{50}$ is the concentration of antioxidant necessary to decrease the initial concentration of DPPH by 50 % after 30 min. The EC$_{50}$ values were obtained by plotting the percentage of antioxidant activity against the various concentration of antioxidant. (Fig. 3). For OPE, the EC$_{50}$ is only 814 mg/mL. The EC$_{50}$ was determined using the formula Y = 13.71X + 38.383, that was obtained through the linear regression of the plotted graph, where Y represent the 50 % scavenging activity and X is value of concentration needed to reduce the 50 % of the free radical in the solution.

The amount needed is only a very small amount. It can be said that the more efficient the antioxidant, the smaller its EC$_{50}$ will be. Hence is can deduced that OPE is a good antioxidant because its EC$_{50}$ is very small.

### FTIR spectroscopy of OPE

Figure 4 shows the FTIR spectrum of the representative OPE. The strong broad band at 3200−3600 cm$^{-1}$ is attributed to the O-H stretching vibration for the absorbed moisture and hydrogen bonded hydroxyl groups present in the OPE. The adjacent absorption band at 2917 cm$^{-1}$ is due to C-H stretching. The band at 1645 cm$^{-1}$ is due to C=C stretching of the aromatic ring. Characteristic O-H in-plane deformation vibration gives rise to absorption band in the region of 1415 cm$^{-1}$, which is overlapped with the C-H deformation vibration in the same region. Absorptions due to O-H in-plane bending and out-of plane bending appear respectively at 1375 cm$^{-1}$ and 760 cm$^{-1}$. A peak due to C-O stretching is observed in the region of 970-1250 cm$^{-1}$. From the aforementioned peaks it can be understood that OPE contains phenolic compounds.

### Use of oil palm leaf extract in natural rubber

**Cure characteristics** The various cure parameters of the rubber compounds have been shown in Table 5. It can be deduced that with the addition of the OPE the minimum torque has reduced, meaning the modulus is reduced. This is beneficial because when the modulus is reduced it

| 2 | **Radical scavenging activity of various antioxidants** | | | |
|---|---|---|---|---|
| Type of Antioxidant | | Absorbance Replicates | | |
| | | 1 | 2 | 3 |
| Control | | 1.468 | 1.586 | 1.376 |
| OPE | | 0.692 | 0.742 | 0.710 |
| IPPD | | 0.396 | 0.399 | 0.421 |
| BKF | | 0.300 | 0.190 | 0.250 |
| TQ | | 0.168 | 0.138 | 0.149 |

| Type of Antioxidant | | Scavenging Activity (%) | | | | Standard Deviation |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | Average | |
| Control | | | | | |
| OPE | 52.86 | 53.22 | 48.40 | 51.49 | 2.682 |
| IPPD | 73.02 | 74.84 | 69.40 | 72.42 | 2.765 |
| BKF | 79.56 | 88.02 | 81.83 | 83.14 | 4.378 |
| TQ | 88.56 | 91.30 | 89.17 | 89.68 | 1.438 |

| 3 | **EC$_{50}$ Determination** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Concentration (mg/mL) | Absorbance Replicates | | | Scavenging Activity (%) | | | Average |
| | 1 | 2 | 3 | 1 | 2 | 3 | |
| Control | 0.913 | 0.922 | 0.928 | | | | |
| 0.5 | 0.655 | 0.65 | 0.651 | 28.26 | 29.5 | 29.85 | 29.2 |
| 1.0 | 0.438 | 0.473 | 0.467 | 52.03 | 48.7 | 49.68 | 50.14 |
| 1.5 | 0.360 | 0.375 | 0.418 | 60.57 | 59.33 | 54.96 | 58.29 |
| 2.0 | 0.216 | 0.195 | 0.169 | 76.34 | 78.85 | 81.79 | 79.00 |
| 2.5 | 0.130 | 0.195 | 0.155 | 85.76 | 78.85 | 83.30 | 82.64 |
| 3.0 | 0.093 | 0.075 | 0.067 | 89.81 | 91.87 | 92.78 | 91.48 |
| 3.5 | 0.067 | 0.068 | 0.081 | 92.66 | 92.62 | 91.27 | 92.18 |
| 4.0 | 0.063 | 0.079 | 0.069 | 93.10 | 91.43 | 92.56 | 92.36 |
| 4.5 | 0.068 | 0.071 | 0.069 | 92.55 | 92.30 | 92.56 | 92.47 |
| 5.0 | 0.014 | 0.029 | 0.022 | 98.47 | 96.85 | 97.63 | 97.65 |

| 4 | **Composition of the Natural Rubber Mixes in the Study of OPE as Antioxidant** | | | | |
|---|---|---|---|---|---|
| Ingredient | NR$_C$ | NR$_{TMQ}$ | NR$_{BKF}$ | NR$_{IPPD}$ | NR$_{OPE}$ |
| Natural rubber | 100 | 100 | 100 | 100 | 100 |
| ZnO | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 |
| CBS | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| TMQ | - | 1.5 | - | - | - |
| BKF | - | - | 1.5 | - | - |
| IPPD | - | - | - | 1.5 | - |
| OPE | - | - | - | - | 1.5 |
| Sulfur | 3 | 3 | 3 | 3 | 3 |

CBS      N-cyclohexylbenzothiazole-2-sulfenamide
TMQ     2,2,4-trimethyl-1,2-dihydroquinoline

**5** Effect of various antioxidants on the cure characteristics of NR compound

| Curing Parameters | $NR_C$ | $NR_{BKF}$ | $NR_{IPPD}$ | $NR_{TMQ}$ | $NR_{OPE}$ |
|---|---|---|---|---|---|
| Minimum torque (dNm) | 0.20 | 0.12 | 0.22 | 0.28 | 0.14 |
| Maximum torque (dNm) | 4.40 | 7.32 | 7.52 | 7.52 | 7.49 |
| Scorh time ($t_2$ min) | 5.00 | 6.15 | 5.52 | 5.52 | 5.13 |
| Optimum cure time ( $t_{90}$ min) | 8.70 | 11.70 | 10.65 | 11.24 | 10.49 |
| Cure rate (min$^{-1}$) | 27.02 | 18.01 | 19.49 | 17.48 | 18.66 |
| $M_{90}$ | 11.30 | 13.80 | 14.09 | 14.04 | 14.11 |

means the product is softer. Hence, it would not only be easier to do compounding in the two-roll mill, but, also would result in reduced energy requirement for processing. It is also expected to contribute to the improvement in adhesion properties. Furthermore, there is a slight increase in the scorch time and also in $M_{90}$.

**Oil Palm Leaf Extract as an Antioxidant** It is established that during aging, oxygen attacks the $\alpha$-methylenic carbon atom of the unsaturated rubber molecule, a hydrogen atom is abstracted and an oxidative chain reaction is initiated, which if unchecked, propagates auto-catalytically. Hydrogen donating antioxidants (AH) retard oxidation by competing with the polymer (RH) for peroxy radicals. Antioxidant inhibit the autocatalytic propagation either by (i) capturing the free radicals formed and/or (ii) ensuring that the peroxides and hydroperoxides produced decompose into harmless fragments without degrading the polymer chain.

$$R + AH \rightarrow RH + A$$
$$ROO + AH \rightarrow ROOH + A$$
$$ROOH + AH \rightarrow \text{harmless fragments}$$
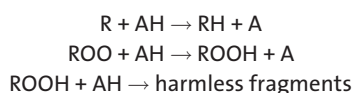
Palm oil was found to be a potential source of phenolic compounds. So it can act as an antioxidant. In the present study, to explore the aging resistance property of the OPE in NR; compounds were designed according to the formulations given in Table **3**. The mechanical properties were used to evaluate the aging resistance of the vulcanizates, and the results have been illustrated in Figures **5-10**.

Comparison was made with well-known commercial antioxidants TMQ, BKF and IPPD due to their better antioxidant activities than many polyphenols. It is known that in natural rubber and other diene rubbers, there is deterioration of mechanical properties upon aging [8].

From Figure 5, it can be seen that the vulcanizate with IPPD exhibits the lowest tensile strength and that with TMQ exhibits the highest amount of strength before ageing. The tensile strengths of the vulcani-

zates with BKF and OPE are intermediate to that with IPPD and TMQ. After ageing, the tensile strengths of the vulcanizates with BKF and IPPD have slightly increased, whereas, that of the vulcanizates with TMQ and OPE have marginally decreased. A similar trend has been observed for elongation at break (Fig. 6) of the vulcanizates. Figure 7 displays the Young's moduli of the vulcanizates before and after ageing. The Young's moduli of the vulcanizates decrease after ageing, but, the reduction is more pronounced in the case of the vulcanizate with OPE. The vulcanizate with OPE exhibits lower moduli before and after ageing in comparison to the moduli of the other vulcanizates. This could be due to the softening effect imparted by the OPE to NR. This observation is supported by the rheometric data (Table **5**). The stress at 100 % and 300 % strain (denoted respectively as M100 and M300) values of the vulcanizates exhibit an increase upon ageing (Fig. 8 and 9). The toughness of the vulcanizates with BKF and IPPD exhibit an appreciable increase where that with TMQ and OPE exhibit a marginal increase (Fig. 10). From the ongoing discussion, it can be understood that the antioxidant activity of the OPE in NR is comparable to that of commercial antioxidants. This is believed to be due to the polyphenolic compounds present in the OPE. Additionally the use of OPE is advantageous, because, the commercial antioxidants are: expensive, not-environmental-friendly and can cause staining of the rubber products. On the contrary, OPE is cheap, naturally abudant, environmental-friendly and non-staining.

*Oil palm leaf extract as a tackifier*
Compositions of the mixes used in this study contained only the natural rubber and the antioxidants alone. No other ingredient was added, as the purpose of the study was to investigate the effect of the synthetic antioxidants and OPE on tack strength. From Fig. 11, it can be seen that the synthetic antioxidants have not contributed significantly to the tack strength of NR, meanwhile, the OPE has improved the

tack strength of NR by about 40 %. This is due to enhanced flow due to softening of NR by OPE as revealed by the reduction in the minimum torque of NR compound. The influence of OPE loading on tack strength of NR is demonstrated in Fig. 12. The tack strength of NR has been improved to the maximum extent at OPE loadings of 1.5 and 3 phr. Beyond 3 phr of OPE, the tack strength of NR falls. It has been reported earlier that molecular contact, interdiffusion of polymer chains, and high cohesive strength are responsible for tack strength [13, 14, 21-26]. The enhancement in tack strength on addition of OPE be attributed to the lowering of viscosity of NR which results in interfacial diffusion of polymer chains at the interface, thus giving rise to good interfacial bonding.

**Conclusions**
The methanol extract from the leaves of *Elaeis Guineensis*, which is known as oil palm tree, possesses phenolic compounds. By using the methanol extraction method an acceptable amount of crude extract could be obtained. The OPE is not a pure phenolic compound, but contains some other compounds as well. The OPE might have compounds such as chlorophyll, fats, polysaccharides and other compounds which might have masked or interfered with the antioxidant property of the phenolic compounds during the evaluations. The OPE also proves to be a good multifunctional additive through the mechanical and tack strength evaluation. The change in mechanical properties after ageing of the NR vulcaniates containing the OPE is within acceptable limits. The rubber formulations containing the OPE also exhibit a very good tack strength. 1.5 phr of OPE is sufficient to increase the tack strength of NR by 40 %, which can be very good from industry point of view. The use of oil palm leaf extract in NR formulations could help in utilizing the abundant resource of oil palm waste in an economical manner as well as in reducing the carbon footprint of NR-based products.

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