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Investigation of Crude Palm Oil as an Alternative Processing Oils in Natural Rubber : Effect of the Unsaturated Fatty Acid

Khaliesah Abbas[1] and S.K. Ong[1]

[1] Universiti Kuala Lumpur, Malaysian Institue of Chemical and Biengineering Technology (UniKL MICET), Lot 1988 Kawasan Perindustrian Bandar Vendor, Taboh Naning, 78000 Alor Gajah, Melaka

E-mail: skong@unikl.edu.my

Abstract. Petroleum based processing oils is the hydrocarbon oils derived from petroleum refining process and commonly used as extender or processing oils to improve the rubber processability. Hydrocarbon oils can be classified as paraffins, aromatics, naphthene and olefins oil based on their molecular structure. The studies on replacement of hydrocarbon oils with natural processing oils had been studied by vast number of researchers due to finite resources and the toxicity of the hydrocarbon oils which enhanced awareness in using natural based oils. These natural processing oils are from vegetable or animal. The vegetable oils contain mainly unsaturated fatty acids. Studies showed that the unsaturated fatty acids affect the cure characteristics and the mechanical properties of the filled vulcanizates as these fatty acids took part during the vulcanization and promote the filler-rubber interaction. In this study, natural rubber (NR) of grade Standard Malaysian Rubber 20 (SMR 20) with the loadings of paraffin oil (PO) and crude palm oil (CPO) between 1 to 5 phr was investigated. Within the loadings of PO and CPO studied, the unsaturated fatty acid in CPOs were reported to results in plasticizing effect which results in lower minimum and maximum torques. Though that the unsaturated fatty acid which took part during the vulcanization prolonged the cure time, it resulted in higher CB-SMR 20 interaction. The tensile properties, tear strength, hardness and abrasion resistance of the CPO recipes were affected by combination of plasticizing effect and better CB-SMR 20 interaction.

1. Introduction

Over the past 20-30 years, the tire and rubber industry has focused on using renewable sources of raw material, recycling materials or used materials for its new application. There is significant potential to use crude palm oil (CPO) as an alternative for processing oils in rubber compound to replace petroleum-based processing oils. CPO is one of the four leading vegetable oils traded on the world market. Malaysia has a rich oil palm industry that generates excess CPO, in vast quantities for consumption [1]. The use of natural processing oils in rubber compounds has already been commercially demonstrated by the incorporation of *d*-limonene, sunflower oil, castor oil, orange oil, and olive oil by three manufacturers in the large, high performance application of passenger car [2].

Hydrocarbon processing oils can be classified into four types which are paraffins, aromatics, naphthene and olefins [3]. The classification is based on the molecular structure. Paraffins are also available with both normal and iso-paraffins which the former is alkanes while the latter is the branched paraffins [3]. The normal paraffins oil (PO) is used in this study.

CPO are obtained from the mesocarp of the oil palm fruit (*Elaeis Guineensis*) and consists of 49.91% saturated fatty acids (0.93 % myristic, 45.48 % palmitic and 3.49 % stearic) and 50.9 % unsaturated fatty acids (40.17 % oleic and 9.92 % linoleic) [4]. Lai *et al.* also reported that in general, palm oil contained approximately 50 % saturated, 40 % monounsaturated fatty acids and

10 % polyunsaturated fatty acids [5]. The fatty acids are a long stearic chains compounds containing an even number of carbon atoms C_{10} to C_{18} [6]. Like others vegetable oils, the main component of palm oil is triacylglycerol. It also contains a minor amount of monoacylglycerols and diacylglycerols. Apart from that, CPO is rich with phytonutrients such as tocopherols, tocotrienols and phytosterols [5].

Some studies evaluated several vegetable oils in comparison with hydrocarbon processing oil. Kukreja *et al*. used castor oil (loading: 1–5 phr) and cashew nut shell liquid (CSNL) (loading: 1 phr) in natural rubber/polybutadiene (NR/BR) blends and found that with an increasing amount of castor oil and CSNL, the modulus at 300 % elongation (M300), tear strength and tensile strength increased up to optimum oil loading [7]. The presence of unsaturated fatty acid in castor oil and CSNL was suggested to assist the interaction between carbon black (CB) and the rubbers which resulted in better reinforcement. Dasgupta *et al*. also studied the effect of various natural oils in comparison to aromatic, naphthenic and paraffinic oils at 8 phr [8]. They observed that the mechanical properties, particularly with the use of soybean oil, exhibited a reduction in M300 and tensile strength but increased in the elongation at break because the elastomer molecular chains have greater mobility when vegetable oils was employed. Fernandez *et al.* studies on incorporation of linseed oils of (loading: 2–10 phr) in Nitrile rubber/Expandable Graphite (NBR/EG) and found that the linseed oil (LO) compound showed higher maximum torque with the LO loading. This is due to esters and double bond presence in LO which enhanced the physico-chemical interaction between EG and polymer matrix. However, decrement of cure time with the increased of LO loading was reported as the unsaturated fatty acid interrupted the vulcanization [9]. Khalaf *et al.* studies the effect of orange and olive oil as multipurpose additives in NBR and concluded that the physico-mechanical results indicated that olive and orange oils (loading: 5 phr) impart good mechanical properties to NBR vulcanizates due to the polar characteristic of the oils which improve compatibility with NBR [10]. Based on the studies carry out, natural oils improved the properties of the filled rubber vulcanizate up to its optimum loading. However, there are limited study on the effect of CPO on CB filled vulcanizate. To date there are no study carried out on the effect of CPO on CB filled NR vulcanizate.

In this study, the effect of vegetable oil; i.e. CPO in comparison with PO was investigated. Since CPO is rich with unsaturated fatty acid, better performance of the filled vulcanizate in comparison with CB filled NR vulcanizate prepared using PO is hypothesized.

2. Materials and Method

2.1. Materials

NR of grade SMR 20 was supplied by Lembaga Getah Malaysia, CPO was obtained from Sime Darby Plantations Sdn.Bhd, PO and CB of grade N330 were purchased from Sah Petroleum Ltd, Daman, India and Cabot Corporation Sdn.Bhd., respectively. Sulphur was supplied by Orice Australia Ptd. Ltd Australia, zinc oxide is manufactured by Sigma-Aldrich (M) Sdn. Bhd, stearic acid is by Fisher Scientific USA, 6PPD (N-cyclohexyl-2-benzothiazyl sulphonamide) is by Flexys America L. P USA and CBS (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) is by Rongcheng Chemical General Factory Co. Ltd.

2.2. Recipes
The recipes used in this study are show in Table 1. The loading of PO and CPO were varied between 1 to 5 phr while the other compounding ingredients were constant. The recipes used were adopted from the standard tire tread recipe [11].

Table 1 : Rubber compounding recipes

Compounding Ingredients	PO_1 (phr)	PO_3 (phr)	PO_5 (phr)	CPO_1 (phr)	CPO_3 (phr)	CPO_5 (phr)
SMR 20	100.0	100.0	100.0	100.0	100.0	100.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic Acid	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1.0	1.0	1.0	1.0	1.0	1.0
6PPD	1.5	1.5	1.5	1.5	1.5	1.5
N330	50.0	50.0	50.0	50.0	50.0	50.0
PO	1.0	3.0	5.0	-	-	-
CPO	-	-	-	1.0	3.0	5.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

2.3. Rubber Compounding
SMR 20 compounds were prepared using two roll mills (Model: SLIMC SXK-160A) at room temperature. The compounding ingredients were added to SMR 20 according to the order in Table 1. N330 with either PO or CPO were added into the rubber compound alternately. Finally, the sulphur was incorporated into the rubber compound. The rubber compounds were kept in the freezer for 24 hours.

2.4. Cure Characteristics
Cure characteristics was carried out using Monsanto Rheometer (Model: Monsanto 100) according to ASTM D2084-01. A sample sealed in a temperature-controlled die cavity surrounds a rotor. The test temperature of 160 °C and torque ranges from 0 to 100 lb-in were used. The test was conducted for 30 minutes and data for cure characteristics such as minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}),cure time (t_{c90}) and cure rate index (CRI) were obtained. For CRI measures the rate at which cross-linking and the development of stiffness of the compound occur after the scorch point. The CRI was calculated using the equation below:

$$\mathrm{CRI} = \frac{100}{t_{c90} - t_{s2}} \text{ (ASTM D2084-01)}$$

2.5. Compression Moulding
The test specimens were prepared by compression moulding of model 4129-039 under pressure 10 MPa at 160 °C according to the cure time, t_{c90} reported in cure characteristics result.

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2.6. Mechanical Tests

a) *Tensile Test:* The test was performed using INSTRON universal testing machine according to ASTM D638-14. The test specimen dimension is 165 mm x 19 mm. Cross head speed of 500 mm/min was employed. Average of 5 test specimens was reported.

b) *Tear Test:* The INSTRON universal testing machine was used to carried out the test as outlined in ASTM D1004-13. The test specimens of Die C were extended with the crosshead speed of 500 mm/min. Average of 5 test specimens was reported.

c) *Hardness Test:* The hardness test was conducted by using the Shore A Durometer according to ASTM D2240-15. Average of 5 test specimens was reported.

d) *Abrasion Resistance Test:* The test is evaluated using Akron Abrasion Tester according to ASTM D1630-00. The test is carried out for 5000 revolutions. The average in abrasion resistance index (ARI) for 3 test specimens were reported. The ARI was calculated according to the following equation :

$$ARI = \frac{V_s}{V_t} \times 100\%$$

Where, V_t is the original volume of the test specimen (in mm^3) and V_S is the volume loss of the test specimen (in mm^3) determined under the same test conditions.

3. Results and Discussion

3.1. Cure Characteristics

The processability of rubber compounds can be determined by evaluating the cure characteristics such as minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}),cure time (t_{c90}) and cure rate index (CRI) as shows in Table 2.

Table 2: Cure characteristic of different loading of PO and CPO in SMR 20

Materials	PO_1 (phr)	PO_3	PO_5	CPO_1	CPO_3	CPO_5
M_L (dNm)	3.70	4.00	4.20	4.90	3.60	2.00
M_H (dNm)	31.22	35.70	36.5	32.3	38.7	34.5
M_H-M_L (dNm)	27.52	31.7	32.3	27.4	34.1	32.5
t_{s2} (min)	4.00	3.21	3.38	4.13	3.52	4.03
t_{c90} (min)	11.23	10.91	11.39	12.47	12.56	12.15
CRI (min^{-1})	13.83	12.98	12.48	11.99	11.06	12.32

The value of M_L measures the compound viscosity before vulcanization [12]. It gives an indication on the ease of rubber flow during processing [13]. M_L results in Table 2 shows that increased amount of PO exhibit an increased amount of M_L. This result shows a lower plasticizing effect happened in rubber compound of NR and PO due to the lack of different polarities in PO resulting in low interactions with NR [10]. For M_L results of CPO shows that the increased of CPO loadings resulted in decrement in M_L. The results indicate that higher plasticizing effect is due to the unsaturated fatty acids presence in CPO which had facilitated the rubber compound processability [14].

The M_H value is related to molecular stiffness of rubber compounding [12]. From the results in Table 2, it shows that the M_H increased with the increased of PO loading. These results are attributed to the cross-linking in NR increased with PO loading [15]. For CPO loading, M_H is highest at 3 phr CPO loading and lowest at 1 phr CPO loading. The results suggested that CPO improved the CB-NR interface at 3 phr loading [16].

t_{s2} indicates the period of time before vulcanization starts. No significant difference on the t_{s2} for both PO and CPO was observed. The results suggested that neither PO nor CPO affects the t_{s2}.

The results for t_{c90} shows that recipes with PO had slightly faster cure time compared to CPO. The results indicated that CPO which contained higher unsaturation fatty acids had caused sulphur dilution effect due to interaction between sulphur and double bond in CPO molecules as well as promoting the CB-rubber interaction [17]. Therefore, lower cure rate and the higher cure time were observed for CPO loadings in NR compared to PO.

From the results, it shows that CPO cured slightly slower compared to PO. The present of fatty acid groups react with ingredients presented in rubber compounds reduced the cure rate at increase loading of CPO [8] [18].

3.2 Mechanical Properties

The results for tensile strength are shown in Fig. 1. Processing oils has plasticizing effect, thus decrement in tensile strength with the increase of CPO loading is expected. Increase of PO loading does lead to plasticizing effect. This might be due to the amount of PO studied is low. The filled vulcanizate with CPO has lower tensile strength as compare to the filled vulcanizate with PO at the same loading. The results are attributed to the capability of CPO to undergo self-vulcanization to form factice which will results in the decreased value of tensile strength [19].

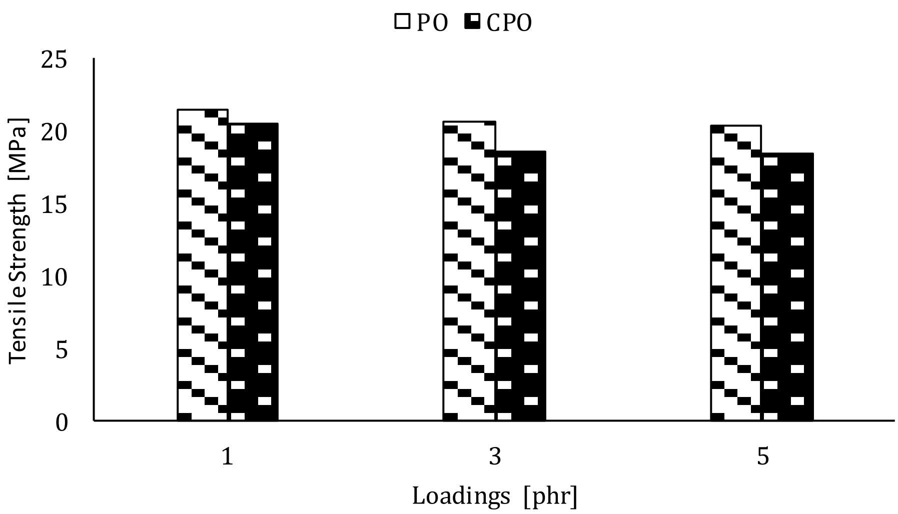

Fig. 1. Effect of PO and CPO loadings on the tensile strength of the CB filled vulcanizates

In Fig. 2, it shows the results for elongation at break for PO and CPO are consistent with the tensile strength trend, the presence of PO does not show plasticizing effect on the PO recipes. The decrement of elongation at break with the increment of CPO loadings was probably due to coupling action, which happened between CB and NR molecular chains. CPO which had unsaturated fatty acid takes part in dual interactions. The polar end of the chain could interact with CB surface while the non-polar unsaturation rich ends could interact with rubber molecules. Although higher stress is applied, the entanglement that happened inside rubber compounds prevents freedom of the molecular chains to move thus, lowered the elongation at break was observed [7] [20].

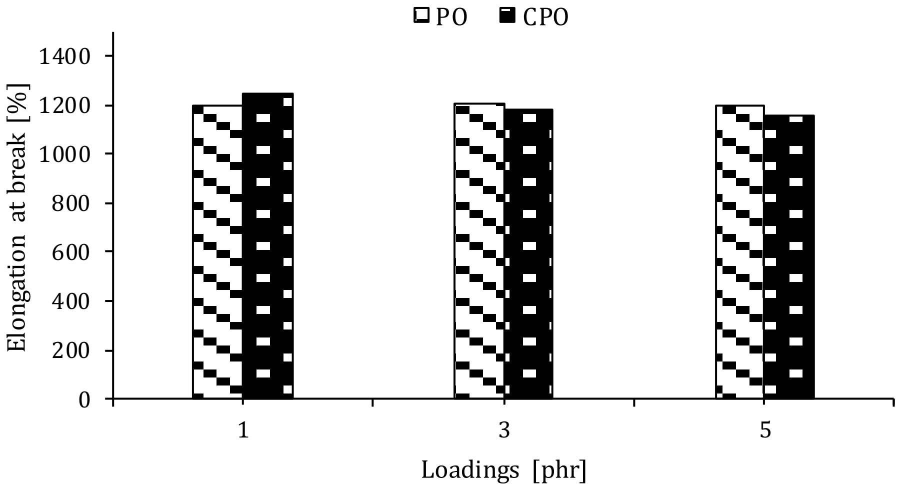

Fig. 2. Effect of PO and CPO loadings on the elongation at break of the CB filled vulcanizates

Tear strength results for PO and CPO filled vulcanizates are show in Fig. 3. The results showed that the incorporation of CPO had resulted in higher tear strength as compared to the recipes with PO. The is because PO had low degree of unsaturation as compared to CPO, thus, lower tear strength was reported [7]. The CPO recipes consistently had higher tear strength as compared to the PO recipes at the same processing oil loading. The highest tear strength was reported at CPO loading of 5 phr. This is due to the high amount of unsaturated fatty acid which actively participated in curing and coupling at the CB-rubber interface resulted in higher tear strength [7].

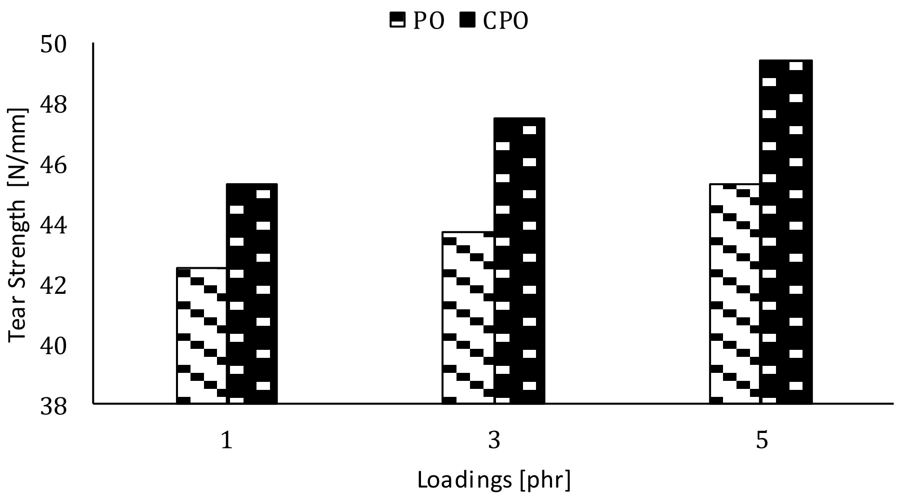

Fig. 3. Effect of PO and CPO loadings on the tear strength of the CB filled vulcanizates

The hardness results for PO and CPO filled vulcanizates were show in Fig. 4. The results do not show the significance differences on the hardness of the filled vulcanizate within the loading of PO studied, and similar results were observed for CPO_1 and CPO_3. A slight increment in the hardness of CPO_5 in comparison with CPO_1 and CPO_3 was reported. Chandrasekara *et al.* reported that longer cure time of CPO recipes implies good CB-rubber interaction and resulted in higher hardness in CPO recipes [21]. Consistently Kukreja *et al.* reported similar trend which is due to the dual interactions of CPO with CB and rubber is more significant at higher loading [7].

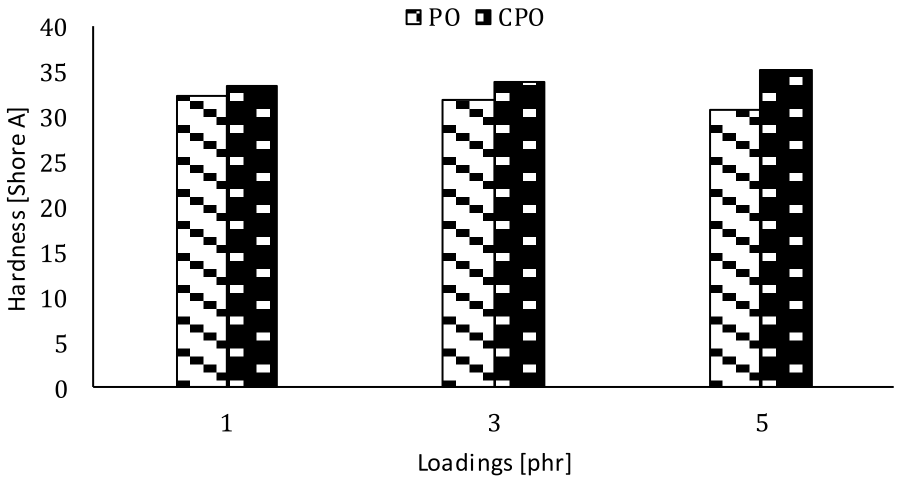

Fig. 4. Effect of PO and CPO loadings on the hardness of the CB filled vulcanizates

Fig. 5 shows the results on the Abrasion Resistance Index (ARI) for PO and CPO recipes studied. From the results, it was observed that the difference of ARI between PO recipes are insignificant. The ARI depends on the softness of the rubber surface, the CB dispersity and the rubber vulcanizates crosslink density [7]. Thus, within the range of PO studied, the CB dispersity and the rubber vulcanizate crosslink density does not differs. The slight decrement in the abrasion resistance was reported on CPO_3 and CPO_5 which due to the high amount unsaturated fatty acid in CPO. The CPO which participated in the vulcanization and the CB-rubber interaction leading to lower ARI [14].

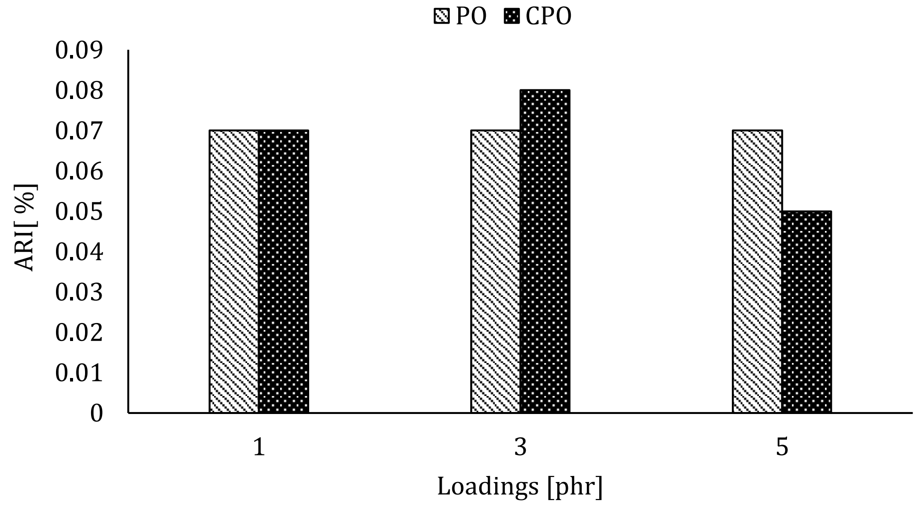

Fig. 5. ARI of the PO and CPO recipes

4. Conclusions

As a conclusion, the presence of unsaturated fatty acid in CPO resulted in plasticizing effect and facilitated the CB-rubber interaction. This resulted in lower M_l and M_H, longer t_{c90} as well as lower tensile strength and elongation at break. Harder and better tear strength of the CB filled vulcanizates were also observed when CPO was employed as the processing oil. Thus, CPO can be a potential and alternative processing oils for CB filled SMR 20 vulcanizates within the CPO loadings studied.

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