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Evaluation of suitability of sesame oil as an alternative for aromatic processing oil in natural rubber composites

A D Wickramapala*, D G Edirisinghe**, P K I L Jayarathna**,
A M W K Senevirathna* and C G Bandara*

* *Faculty of Animal Science and Export Agriculture, Uva Wellassa University of Sri Lanka, Badulla, Sri Lanka*

** *Rubber Technology and Development Department, Rubber Research Institute of Sri Lanka, Telawala Road, Ratmalana, Sri Lanka*

Abstract

Polycyclic aromatic oils, high in aromatic content are used in tyre compounds as processing aids and these have been found to be carcinogenic. Therefore, it is necessary to find processing aids consisting of a low content of aromatics which would help to overcome the problem associated with the use of petroleum-based aromatic oils.

The main aim of this research was to develop carbon black filled natural rubber (NR) composites using environmentally friendly sesame oil as the processing aid. Initially sesame oil was characterized using Fourier Transform Infra-Red analysis. Thereafter, a series of NR based tyre tread compounds was prepared by varying the sesame oil loading from 3-9 phr at 2 phr intervals. Cure characteristics, physico-mechanical and swelling properties of these composites were evaluated and compared with those of the composite prepared with the aromatic processing oil, Dutrex-R (control). Dispersibility of carbon black in all the NR composites was assessed.

Viscosity, processing safety and cure rate of the composite produced with 5 phr sesame oil were higher compared to the control and indicated that the oil behaves as a co-activator in rubber compounds. Hardness, modulus at 100% elongation and abrasion volume loss of the vulcanizates prepared with more than 5 phr sesame oil were lower, whereas tensile strength, elongation at break and resilience were higher than those of the control. Tear strength and compression set of the vulcanizates prepared with 5 phr sesame oil were comparable to those of the control. Further, the former vulcanizate showed a higher and lower swelling indices in toluene and water, respectively compared to the control. Furthermore, the vulcanizates prepared with sesame oil showed better ageing resistance in comparison to the control. Hence, sesame oil could be a suitable alternative for Dutrex-R in tyre tread compounds at 5 phr level.

Key words: cure characteristics, physico-mechanical properties, polycyclic aromatic oils, sesame oil, swelling index, thermal ageing

Introduction

Petroleum-based aromatic oils, widely used in the tyre industry as processing aids have a greater aromatic content than petroleum-based naphthenic and paraffinic oils. Higher aromatic content indicates the presence of polycyclic groups in the oils. Aromatic oils have aliphatic hydrocarbon surface groups as aromatic substituent. Paraffinic and naphthenic oils have aliphatic hydrocarbon as short chain compound or substituent and all the natural oils including sesame oil have aliphatic carboxylic acid ester, alkyl long-chain and long chain aliphatic carbonyl compound surface groups. These aromatic oils containing polycyclic aromatic hydrocarbons have been found to release carcinogenic compounds to the environment (Dasgupta *et al.,* 2007). Hence, there is a growing interest for the search of processing aids low in aromatic content namely natural oils as alternatives for polycyclic aromatic (PCA) oils.

The focus nowadays in the rubber industry is towards identifying eco-friendly materials such as plant-based materials to substitute the harmful petroleum oils. As a result, markets for plant-based sustainable and biodegradable oil materials are growing and use of these oils is gaining popularity. If these oils can be used to replace petroleum based carcinogenic processing oils in natural rubber composites, it would help in the reduction of generation of carcinogenic compounds to the environment safeguarding the lives of human beings.

Sesame oil contains considerable amounts of linoleic, oleic, stearic, and palmitic acids. Some natural oils including sesame oil show flash and fire points higher than 200℃, whereas these points are higher than 160℃ in the case of petroleum oils. Flash and fire points are one of the important criteria for determining the processing safety, whilst handling the rubber compound during mixing, calendaring, extrusion, etc. Higher flash and fire points of oils always indicate good processing safety. High flash and fire points of natural oils may be due to the presence of carbonyl groups, alkaloids groups, etc. Such groups are absent in the case of petroleum-based oils, where the major groups are long chain alkyl type (Dasgupta *et al.,* 2007).

Early work reported that some petroleum oils show higher aniline point values, whereas natural oils including sesame oil show lower values. Aniline point indicates the presence of aromatic rings in the oils. As all the natural oils show very low aniline points, the compatibility of these oils with the general-purpose polymers like NR, styrene-butadiene rubber (SBR), and polybutadiene rubber (BR), was found to be better (Dasgupta *et al.*, 2007).

Studies have been conducted in the past using plant-based vegetable oils as processing aids in rubber composites. Palm oil, soybean oil and rapeseed oil are the globally important vegetable oils because of their high worldwide production and reasonable cost for large-scale industrial applications (Zhang *et al.*, 2017). Soybean oil, palm oil and sunflower oil were found to be better alternative processing aids than petroleum based aromatic oils. In addition, soybean oil was found to behave as a co-activator in carbon black filled NR composites (Jayewardhana *et al.,* 2009). Some of these vegetable oils were modified in the past with the aim of improving the processing behavior and properties of rubber composites. In one of these studies, effect of epoxidized vegetable oils as processing aids and activators in carbon black filled NR composites have been evaluated (Chandrasekera *et al.*, 2011). In another study, the plasticizing effect of epoxidized palm oil (EPMO) was compared with that of virgin palm oil and petroleum-based aromatic oil (AO) in carbon black (CB) filled SBR composites. At 3 phr loading of processing oil, the tensile strength of an EPMO-plasticized SBR/CB composite was comparable to that of an AO-plasticized SBR/CB composite (Lee and Song, 2019). Kumarjyoti *et al.* (2021) have reviewed the advancements in the application of renewable vegetable oils instead of non-renewable petroleum-based oils as processing aids for manufacture of commercially suitable sustainable rubber products. However, effect of sesame oil on physico-mechanical properties of NR composites has not been reported in literature. Hence, this research was conducted to assess the suitability of sesame oil as an alternative for petroleum-based aromatic processing oil, Dutrex R in carbon black filled NR composites in relation to physico-mechanical properties.

Experimental

Materials

Ribbed Smoked Sheet (RSS) rubber was provided by the Dartonfield Estate, Agalawatta. Organic virgin sesame oil was purchased from Coconut Miracle Ltd, Sri Lanka. Dutrex-R and CBS (N-cyclohexyl benzthiazyl sulphenamide) was supplied by Samson Compounds (Pvt.) Ltd., Galle. The other compounding ingredients namely carbon black, zinc oxide, stearic acid, IPPD (N-isopropyl–N'–phenyl–p-phenylenediamine), sulphur and toluene were purchased from Glorchem Enterprises, Colombo, Sri Lanka.

Methods

Initially, Fourier Transform Infra-Red (FTIR) analysis was conducted on virgin sesame oil and Dutrex-R and the two spectra were compared. Thereafter, five NR composites were prepared with the aid of a laboratory two-roll mill according to the tyre tread formulation given in Table 1. The composites were designated according to the content of the processing aid (Table 2). The mixing cycle employed in the preparation of these composites is given in Table 3.

Table 1. *Tyre tread formulation used in the preparation of NR composites*

Compounding Ingredient	Quantity (phr)
RSS	100
ZnO	5
Stearic acid	2
Carbon black (N330)	50
Processing oil (Dutrex-R/Sesame oil)	5/3, 5, 7 or 9
IPPD	1.5
CBS	1.5
Sulphur	2.5

phr = parts per hundred parts of rubber

Table 2. *Amount of processing oil used in the preparation of NR composites*

Compound No.	Name of processing aid	Amount (phr)
T0	Dutrex R (Control)	5
T1	Sesame oil	3
T2	Sesame oil	5
T3	Sesame oil	7
T4	Sesame oil	9

Table 3. *Mixing cycle used in the preparation of NR composites*

Compounding ingredient	Total mixing time (minutes)
Added RSS	0
Added ZnO + stearic acid	3
Added IPPD	4
Added ½ (HAF-N330 + Processing Oil)	5
Added ½ (HAF-N330 + Processing Oil)	6
Added CBS	7
Added sulphur	8
Dumped	9

Dispersibility of carbon black in the NR composites was analyzed using a dispergrader (Future Foundation, India). Cure characteristics, physico-mechanical properties, ageing resistance and swelling properties of the composites were determined as given below.

Determination of cure characteristics of NR composites

Cure characteristics namely, minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}), optimum cure time (t_{90}), cure rate index (CRI) and delta cure (M_H-M_L) of the five NR composites were obtained from the rheographs of MonTech D-RPA 3000, Germany according to ISO 6502-3 Part 3 at 150 ^{o}C.

Preparation of vulcanised test pieces

The five NR composites were placed in test piece moulds and pressed between the platens of a hydraulic hot press (Shiran Rubber Industries, Sri Lanka). The composites were cured at 150 ^{o}C temperature and applied pressure of 0.25-0.35 MPa according to respective optimum cure times obtained from the rheographs. After curing, the test pieces were removed from the moulds and immediately cooled under tap water to prevent further curing. The test pieces were conditioned at room temperature for 16 hours before carrying out testing.

Measurement of physico-mechanical properties of NR vulcanisates

An Instron tensile testing machine was used to measure the tensile properties of the rubber vulcanisates in accordance with ISO 37: 2017 at room temperature (27±2 ^{o}C) at a grip separation rate of 500 mm/min. Tear strength of the vulcanisates was measured using angle (Die B) test pieces with the aid of the same machine as per ISO 34-1: 2022. Hardness of the vulcanisates was measured by a "Digi Test" hardness tester for hardness in the IRHD N-scale as per ISO 48: 2018. Resilience of the vulcanisates was measured by a Wallace Lupke pendulum in accordance with ISO 4662: 2017. Abrasion volume loss of the vulcanisates was determined using a DIN abrasion tester in accordance with DIN 53516. Compression set of the vulcanisates was determined using a compression set apparatus (Wallace Instruments, UK) according to ISO 815-1: 2019**.** The test-pieces were compressed for 72 hours at room temperature. In addition, equilibrium swelling measurements were conducted and percentage swelling in toluene as well as in water was determined.

Determination of thermal ageing resistance of NR vulcanisates

Tensile and tear strengths were evaluated after ageing. Ageing was carried out in an air circulating oven at 100 ^{o}C (Sanyo Gallenkamp, UK) for 22 h according to ISO 188: 2011.

ONE WAY-ANOVA statistical analysis using Minitab 17 was employed to measure the impact of different sesame oil quantities on each of the above-mentioned properties at 0.05 significance level. Mean comparison was done using Tukey's test at 95% confidence level for each of the properties and identified the best treatment in comparison to the control.

Results and Discussion

FTIR spectra of oils

The peaks shown in the highlighted area of Figure 1 is due to the presence of polycyclic aromatic hydrocarbons. The two peaks observed for sesame oil at 693.18 and 720.89 cm^{-1} arise from the presence of 1% of monosubstituted aromatic groups such as phenols (Dasgupta *et al.*, 2007; Hossam *et al*., 2022), whilst the peaks observed at 728.72, 748.11, 810.51 and 855.49 cm^{-1} for the aromatic oil Dutrex-R correspond to monosubstituted aromatic, ortho disubstituted aromatic, para disubstituted aromatic and meta disubstituted aromatic, respectively. According to Dasgupta and co-workers (2007), aromatic content of petroleum based aromatic oil, low PCA oil, power oil TDAE_A and power oil TDAE_B are 36, 18, 30 and 29, respectively and that of the natural oil, sesame oil is 1 %. Hence, Figure 1 confirms that the aromatic content of sesame oil is low compared to that of petroleum-based aromatic oil, Dutrex-R.

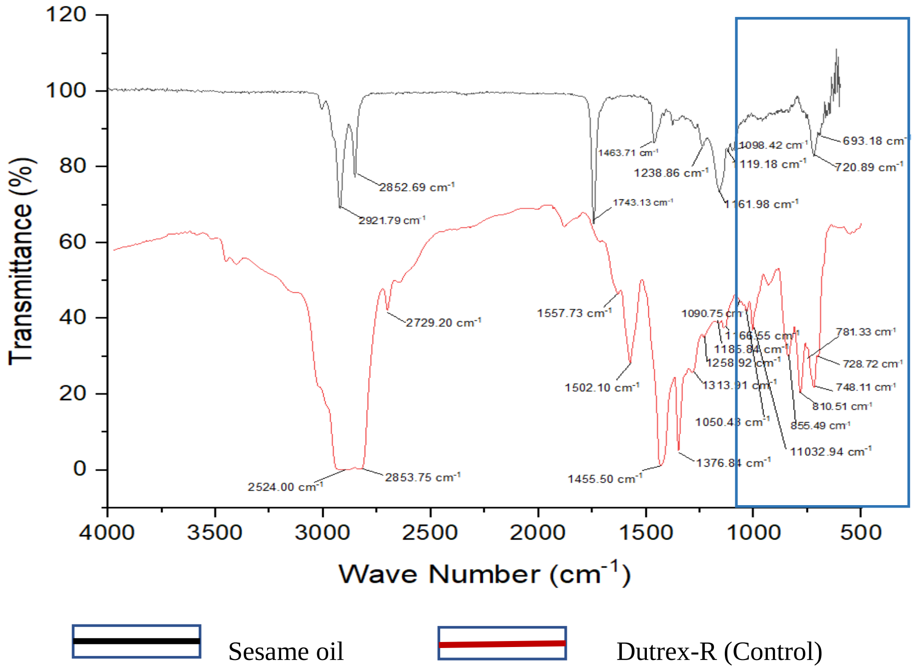

Fig. 1. FTIR spectra of sesame oil and Dutrex-R

Carbon black dispersion analysis

The filler dispersion images of the five NR vulcanisates are shown in Figure 2. The results are tabulated in Table 4.

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Table 4. *Filler dispersion results of NR vulcanisates*

Compound No.	Dispersion rating	Maximum size of agglomerates (Sq Pixel)
T0 (control)	9	5
T1	9	65
T2	9	24
T3	8	55
T4	9	63

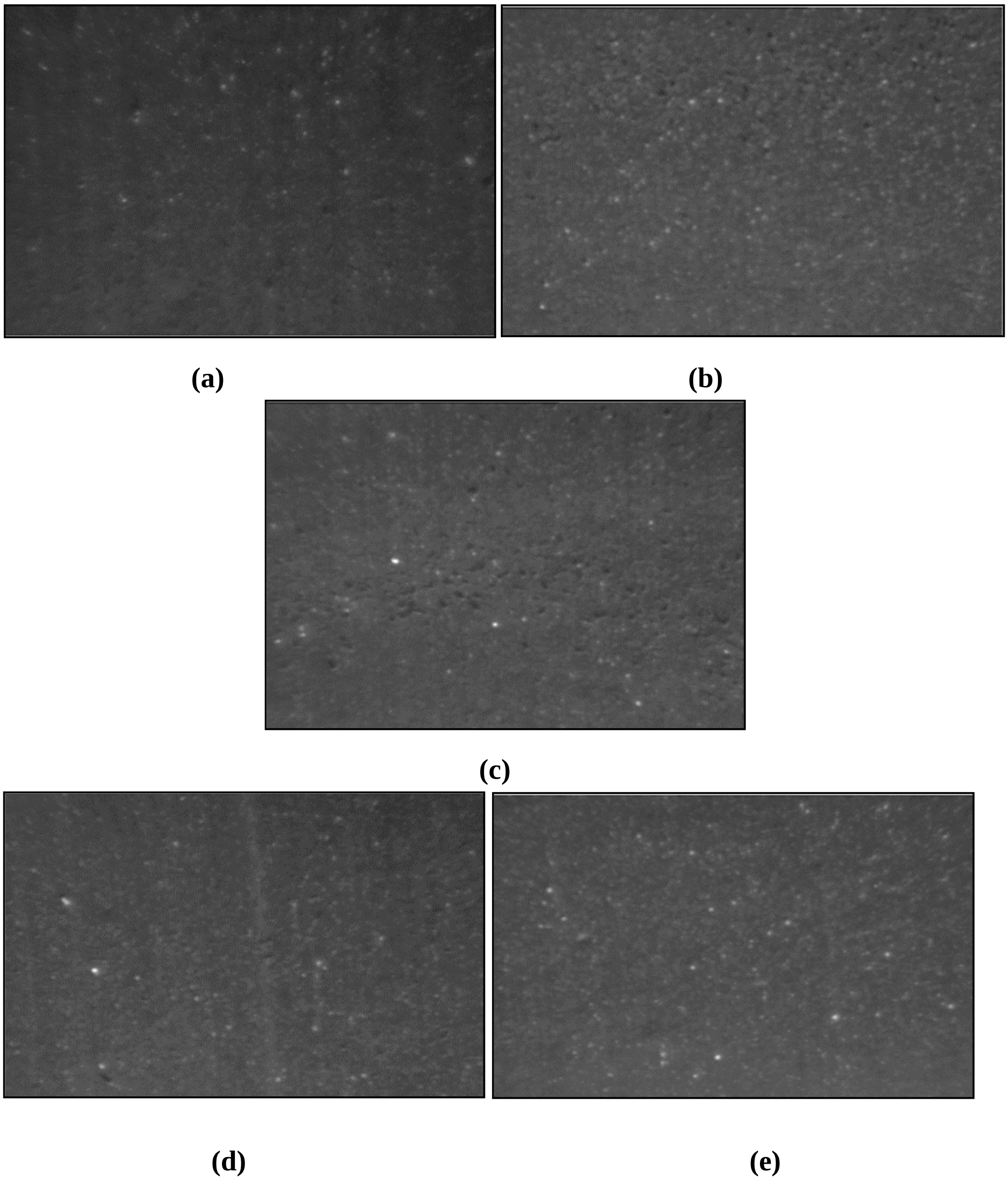

Fig. 2. Filler dispersion images of carbon black filled NR vulcanisates produced with Dutrex-R–5 phr **(a)** and sesame oil–3 phr **(b),** 5 phr **(c),** 7 phr **(d)** and 9 phr **(e)**

The results of dispersion rating indicate that carbon black is well dispersed in the NR matrix of all five vulcanisates. Further, dispersion rating of the sesame oil incorporated vulcanisates are almost the same as that of the control.

However, maximum size of carbon black agglomerates present in the vulcanisates produced with sesame oil is very much higher than that of the control.

Cure characteristics

The cure characteristics of the NR composites are given in Table 5.

The lower minimum torque shown by the composites prepared with Dutrex-R (control) compared to that of the composites produced with sesame oil can be attributed to reduction in viscosity due to ease of dispersion of ingredients in NR (Abbas and Ong, 2019). Maximum torque and hence state of crosslinking of composites prepared with aromatic oil is higher than that of the composites prepared with sesame oil and could be mainly attributed to the presence of sulphur in aromatic oil. Additionally, sesame oil contains ester groups and these can cause hydrolysis at curing temperature in the basic medium and release free acid groups which would retard curing reducing the state of crosslinking. Further, maximum torque decreases with the increase of sesame oil loading. This is probably due to the increase in the amount of aliphatic carboxylic acid ester and long chain aliphatic carbonyl groups (Dasgupta *et al.*, 2007) which may restrict formation of crosslinks.

Most of the composites produced with sesame oil show a higher scorch time in comparison to the control. This is attributed to higher flash and fire points of sesame oil in comparison to petroleum-based oils due to the presence of carbonyl and alkaloid groups (Dasgupta *et al.*, 2007). 0.5-4 % sulphur present in petroleum oils may be another reason for the lower scorch time of the control (Dasgupta *et al.*, 2007). 90% cure time of the composite produced with 5 phr sesame oil is markedly lower than that of the control and agrees with the results of the study conducted by Dasgupta and co-workers. As expected, the trend in the variation of CRI is opposite to that of cure time.

Table 5. *Cure characteristics of the NR composites*

Processing aid	**Scorch time (min)**	**90% Cure time (min)**	**Cure rate index (min^{-1})**	**Maximum torque (d Nm)**	**Minimum torque (d Nm)**	**Delta cure (d Nm)**
Dutrex -R (5 phr) (control)	1.88	3.92	49.02	20.57	2.22	18.35
Sesame oil (3 Phr)	1.91	3.82	52.36	18.98	2.73	16.25
Sesame oil (5 Phr)	2.00	3.31	76.34	16.02	2.94	13.08
Sesame oil (7 Phr)	1.76	3.06	76.92	15.41	3.02	12.39
Sesame oil (9 Phr)	2.15	3.43	78.13	14.94	3.03	11.91

The trend in the variation of delta cure is similar to that of maximum torque. The results of delta cure indicate that crosslink density is higher in the composite prepared with Dutrex-R compared to the composites prepared with sesame oil.

Physico-mechanical properties

Hardness of the control is markedly higher than that of the vulcanisate prepared with 5 phr sesame oil (Fig. 3) and is in agreement with the results of modulus at 100% elongation (Fig. 4) and can be attributed to higher crosslink density (Pechurai *et al.,* 2015). Hardness decreases with the increase of sesame oil loading due to the decrease in crosslink density and softening effect of oil at higher loadings. As expected, variation of tensile strength (Fig. 5) is similar to that of elongation at break (Fig. 6). Elongation at break of the control is lowest and it could be due to the highest hardness achieved by better dispersibility of filler (Dasgupta *et al.*, 2007).

Resilience is higher (Fig. 7), hence heat build-up is lower and abrasion volume loss is also lower (Fig. 8) in the composites produced with sesame oil compared to the control. Lower abrasion volume loss of the former vulcanisates is advantageous in tyre treads and could be attributed to the presence of larger carbon black agglomerates as evident from carbon black dispersion analysis. Higher % swelling in toluene (Fig. 9) shown by the composites produced with sesame oil is due to lower crosslink density. In contrast, these composites show lower values for % swelling in water (Fig. 10) which is an added advantage for tyre treads.

Compression set (Fig. 11) and tear strength (Fig. 12) of the vulcanizates prepared with 5 phr sesame oil are comparable to those of the control.

The alphabetical letters A, B, C and D provide information on the source of the overall difference that was detected and detailed information on which groups differ from one another.

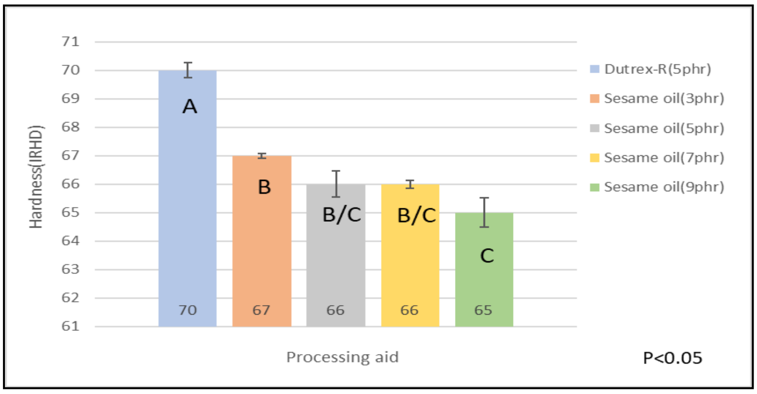

Fig 3. Variation of hardness of the NR vulcanisates

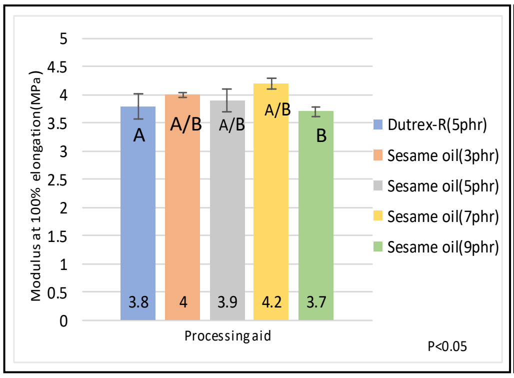

Fig. 4. Variation of modulus at 100% elongation of the NR vulcanisates

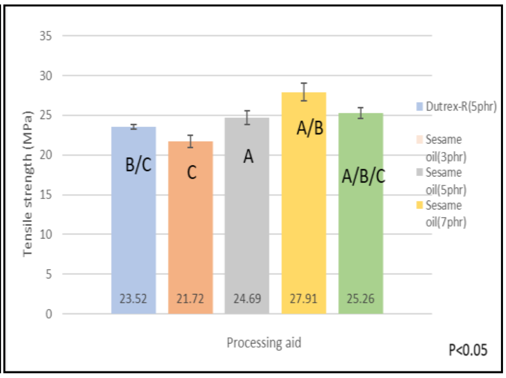

Fig. 5. Variation of tensile strength of the NR vulcanisates

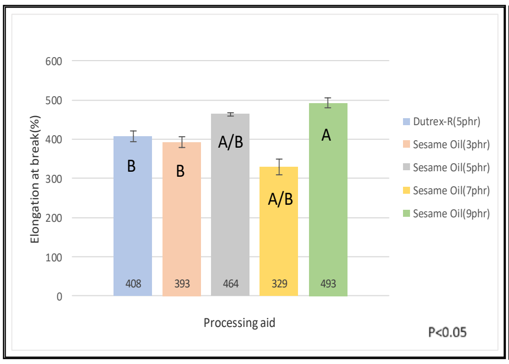

Fig. 6. Variation of elongation at break of the NR vulcanisates

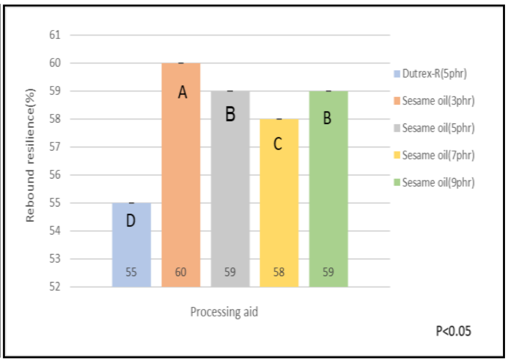

Fig. 7. Variation of resilience of the NR vulcanisates

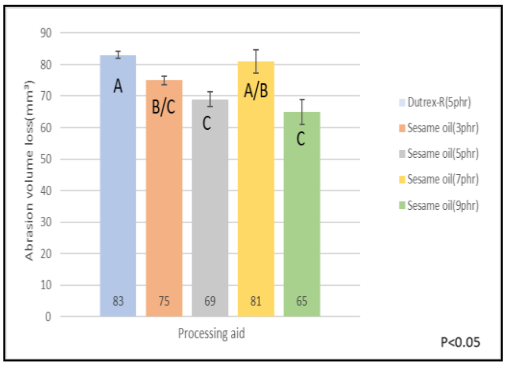

Fig. 8. Variation of abrasion volume loss of the NR vulcanisates

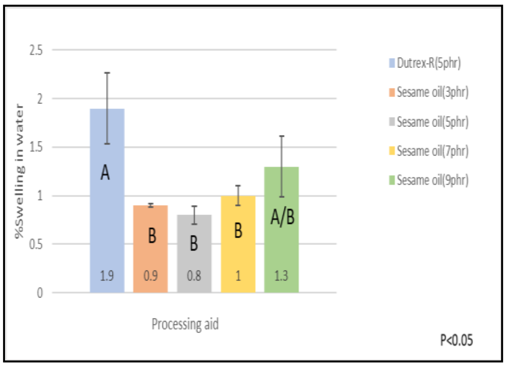

Fig. 9. Variation of % swelling in water of the NR vulcanisates

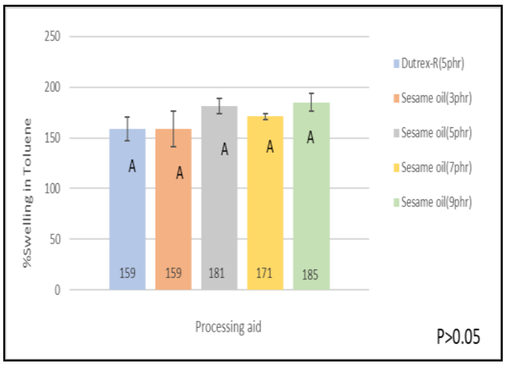

Fig. 10. Variation of % swelling in toluene of the NR vulcanisates

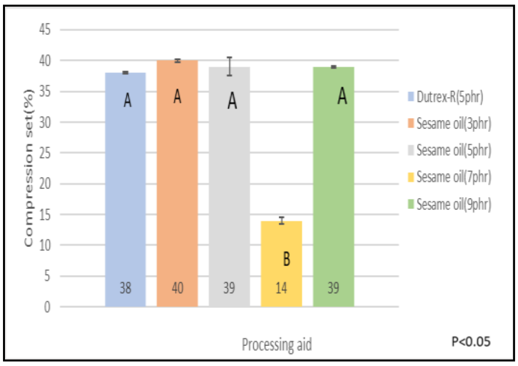

Fig. 11. Variation of compression set of the NR vulcanisates

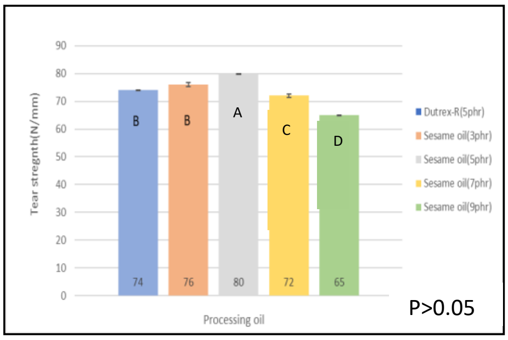

Fig. 12. Variation of tear strength of the NR vulcanisates

Resistance to thermal ageing

The vulcanisates prepared with sesame oil show better resistance to thermal oxidation compared to the control in regard to modulus at 300% elongation, tear strength and comparable with the other ageing properties of the control (Table 6). This could be attributed to the presence of natural antioxidants in sesame oil (Lucy and Hwang, 2005).

Table 6. *Percentage retention of mechanical properties after ageing*

Property	Dutrex-R (5 phr)	Sesame oil (3 phr)	Sesame oil (5 phr)	Sesame oil (7 phr)	Sesame oil (9 phr)
%Retention of tensile strength	82±4.80AB	104±12.14 AB	63±9.99B	85±19.03AB	86±5.38AB
%Retention of tear strength	68±11.76B	78±23.85AB	88±4.11AB	81±14.54AB	113±16.87A
%Retention of modulus at 100% elongation	147±25.41A	147±20.12A	133±8.88AB	111±10.49B	113±9.54B
%Retention of modulus at 300% elongation	91±14.35B	131±9.82A	109±20.68AB	111±5.76AB	108±3.22AB
%Retention of elongation at break	67±9.36A	85±12.07A	63±13.23A	83±18.63A	85±4.60A

Values in each column represent the mean of replicate ± SD (Standard deviation)
The means followed by the same letter within each row are significantly different at $p< 0.05$, except in the case of % retention of elongation at break.

According to Tukey's mean comparison, it was identified that for physico-mechanical properties, each of the sesame oil quantity shares the same grouping frequency when compared with the control. However, 5 phr was selected as the most suitable treatment since the control was also prepared with 5 phr Dutrex-R. Further, the former vulcanisate showed a lower swelling index in water (0.8 ± 0.16%) compared to the control (1.9 ± 0.63%). Furthermore, the former vulcanisate showed higher retention of tear strength after ageing (88 ± 4.11%) in comparison to the control (68 ± 11.76%). There is a statistically significant difference ($p < 0.05$) between each of the treatments, when tested in regard to physico-mechanical properties.

Conclusion

Sesame oil incorporated NR composites have shown an enhancement in most of the properties in comparison to the control NR composite prepared with Dutrex-R aromatic processing oil. Out of the NR composites produced with sesame oil, the composite produced with 5 phr sesame oil could be a suitable alternative for the composite produced with the same amount of Dutrex-R in tyre tread compounds.

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Address for correspondence: Dr (Mrs) D G Edirisinghe, Acting Additional Director, Rubber Research Institute of Sri Lanka, Telewala Road, Ratmalana, Sri Lanka.
email: *dilharae@yahoo.com*