Potential of epoxidized palm oil as a green alternative to rubber processing oils

R. Saigal1, A. B. Chai1, N. S. Saad2, and Ch'ng Shiau Ying1,3

1 Department of Mechanical, Materials and Manufacturing Engineering, University of Nottingham Malaysia, Selangor, Malaysia
2 Sunrich Integrated Sdn Bhd, Seremban, Negeri Sembilan, Malaysia.
3 Mechanical Engineering and Aeronautics & Astronautics, University of Southampton Malaysia, Johor, Malaysia

Abstract. Sustainability is a growing concern in the rubber industry particularly due to the vast amount of environmental issues associated with the manufacturing process. The dependences of hydrocarbons as Rubber Processing Oils (RPOs) throughout the compounding process is an area that is being heavily researched in search for greener alternatives. This study aims to determine the viability of a naturally available vegetable oil, Epoxidized Palm Oil (EPO), as a substitute to the current petroleum-based rubber processing oils. Therefore, the processability, cure characteristics as well as mechanical properties of the rubber compounds with EPO were benchmarked with those of the standard rubber compounds prepared with selected petroleum oils; Paraffin Oil, Aromatic Oil and Naphthenic Oil. The finding from this report suggests that EPO is a viable substitute to petroleum-derived RPOs as it performs within the acceptable range as the compounds with the other RPOs.

1 Introduction

Rubber Processing Oils (RPOs), otherwise referred to as processing aids are plasticizers added to rubber compounds at low loadings during the mixing stage, to improve the processability of the compound without severely affecting the physical properties of said compound [1]. However, the conventional use of petroleum oils as RPOs has raised a few alarms due to their environmental and health effects. The extraction of petroleum oils has taken an enormous toll on the environment resulting in the destruction of ecosystems as well as increasing land and air pollution [2]. Furthermore, the use of these oils has been found to be highly carcinogenic.

Upcoming research looks at the viability of vegetable oils (VOs) as a green alternative to the petrochemically derived plasticizers, due to their environmental friendliness, low cost, biodegradability as well as stability [3]. These oils obtained from renewable resources are biodegradable, non-toxic and non-corrosive, thereby making them a viable alternative to their petroleum-derived counterparts [4]. Jayewardhana et al. [5] extended the study of VOs by looking at modification that can be made to their chemical composition to deliver more prominent results through processes such as epoxidation. Epoxidation converts unsaturated fatty acids into highly versatile intermediate epoxides via chemical and biotransformation. Amongst the other benefits of epoxidation, it is an efficient method to introduce new reactive groups to enhance chemical properties [6]. Epoxidized vegetable oils (EVOs) contain epoxy rings in their chemical structure and therefore may behave more similarly to PAH-rich extender oils as compared to their virgin counterparts [7]. Among these studies, it was found that Epoxidized Palm Oil (EPO) could be a feasible substitute as it improves the dispersion of fillers as well as increases the interaction between the fillers and elastomer.

Evidently, it is necessary to investigate the chemical and physical interactions of EPO with rubber to determine its viability as RPO. This will be done by looking at the processability, cure characteristics and effects on the mechanical properties of the rubber compounds and benchmarking it with those prepared with petroleum oils. The selected petroleum oils were Paraffin, Aromatic and Naphthenic Oils.

2 Experimental Methods

1Corresponding author: syclv16@soton.ac.uk
2.1 Materials

The materials used for this experiment were sourced through Sunrich Integrated Sdn. Bhd. The natural rubber used for this study was Standard Malaysian Rubber 10 (SMR10), whereas the styrene-butadiene rubber used was SBR1502. The RPOs used consist of paraffin oil (PO), aromatic oil (AO), naphthenic oil (NO) and epoxidized palm oil (EPO).

2.2 Preparation and mixing

The samples were prepared using the formulation in Table 1. A Banbury mixer was used to mix the masterbatch ingredients homogeneously according to the ASTM D3182 standard. Next, a two-roll mixing mill (MDXK-160) was used to incorporate curing agents of N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) and sulphur, both with the amount of 1.2 parts per hundred rubber (pphr) into the masterbatch following the ASTM D3184-80 standard. The nip size of the roll mill was adjusted to produce a 6 mm thickness of rubber sheet.

| Ingredients                  | Amount (pphr) |
|------------------------------|---------------|
| NR (SMR10)                   | 100 100 100 100 |
| SBR (1502)                   | 100 100 100 100 |
| Zinc Oxide                   | 5 5 5 5 5 5 5 5 |
| Steric Acid                  | 2 2 2 2 2 2 2 2 |
| Triallylamine (N235)         | 60 60 60 60 60 60 60 60 |
| 2,2,4-Trimethyl-1,2-Dihydroquinoline (TMQ) | 1 1 1 1 1 1 1 1 |
| PO                           | 10 10 |
| AO                           | 10 10 |
| NO                           | 10 10 |
| EPO                          | 10 10 |

2.3 Curing and moulding process

A moving-die rheometer (MDR 2000P) was used to determine the curing characteristics in accordance to the ASTM D2084 standards. Samples of 8-10 g were cut from the compounds and placed in the rheometer. The test conditions for the rheometer are 175°C for 10 minutes. The minimum torque (ML), maximum torque (MH), scorch time (tS20), and 90% of cure time (tC90) were determined from the rheometric data. The curing rate index (CRI) was calculated using Equation 1.

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\text{Cure Rate Index (CRI)} = \frac{100}{(t_{c90} - t_{52})}
\]

A Mooney viscometer (MV2000) was used in line with the ASTM D1646 standard to determine the Mooney viscosity of the rubber compounds. Using hydraulic press, the compounds were cut into dumbbell shape of 100 mm in length and 5 mm in width for tensile test, and button shape of 5 mm wide and 5 mm thick for hardness tests.

2.4 Testing

The Shore A hardness was measured using a TECKLOCK hand-held durometer following the ASTM D2240 standard. Tensile test was conducted using an Instron tensile machine at a crosshead speed of 500 mm/min following the ASTM D412 standard.

3 Results and Discussion

3.1 Curing characteristics

The comparison of scorch time and curing time with different RPOs were depicted in Fig. 1. It was found in general the result from EPO was comparable to petroleum oils, thus defending the notion that EPO has positive activator properties. For both SBR and NR, the scorch time of EPO was the highest. This shows that EPO demonstrated improved processing safety as higher scorch time prevent the compounds from being scorched before vulcanisation starts. Furthermore, longer scorch time is preferred as once the compound is scorched, the rubber compound does not flow properly due to presence of crosslinks.
Scorch time has a positive correlation with hardness, such that, when scorch time increases, hardness increases due to higher viscosity [8].

Fig. 1. Comparison of scorch time and curing time for (a) SBR and (b) NR with different RPOs.

Fig. 2. (a) and (b) show the maximum torque, MH and minimum torque, ML recorded from the rheograph of the tested compounds. The NR-EPO and SBR-EPO compounds recorded the highest and second highest values of minimum torque respectively. The minimum torque indicates the minimum viscosity of the rubber blend, reflecting how well the compound will flow during processing. Higher ML could be due to a delayed formation of crosslinks. Accordingly, the use of EPO results in slightly higher mastication rates when compared to the other processing oils. Both EPO compounds recorded the minimum maximum torque which measures the completion of crosslinking in the vulcanized rubber. Fig. 2. (c) shows that the EPO compounds have the highest CRI in both NR and SBR compounds. This demonstrates that the addition of EPO increases the activating site for vulcanization. The CRI is an important parameter that indicates the speed of with curing occurs as it measures the rate of vulcanization based on the difference between the optimum vulcanisation and the scorch time [4].

Fig. 2. Information obtained from rheograph: (a) minimum torque, (b) maximum torque and (c) calculated CRI.

Mooney viscosity is generally used as a characterising method to determine the processability of a compound [9]. The SBR-EPO and NR-EPO compounds recorded values within the acceptable range, with values in-between the other petroleum oils as shown in Fig. 3. The EPO compounds successfully reduced the Mooney viscosity and consequently the apparent shear
viscosity of the SBR and NR compounds. This could be attributed to the increase in filler and elastomer matrix due to epoxy groups by EPO, thus increasing cross-linking behaviour.

Fig. 3. Mooney viscosity of rubber compounds.

3.2 Mechanical properties

The hardness of the NR compounds was found to be within a small range whereas the SBR compound was recorded to be the lowest at 57 Shore A, being 14% lower than the SBR-NO compound as shown in Fig. 4. Hardness measures the elastomers response to stress applied onto small surfaces, therefore the harder the compound the greater the abrasion resistance as well as extrusion resistance. The hardness of the rubber compound is generally related to the filler loading and cross-link density [10].

Fig. 4. Hardness of rubber compounds.

Fig. 5. (a) depicts the tensile strength of rubber compounds whereby NR compounds showed no large difference whereas the SBR-EPO compound was found to be 32% lower than the compound with the highest tensile strength, the SBR-AO compound. From Fig. 5. (b), the elongation at break of the NR-EPO compound (521%) showed an improvement over the NR-NO compound (473%) but was still outperformed by the NR-AO and NR-PO compounds. A similar pattern was recorded for the SBR compounds whereby the SBR-EPO had an elongation at break of 555% and SBR-NO at 453%. However, the SBR-AO compound had the highest value being 23% higher than the EPO counterpart. The enhanced elongation showed by the EPO compounds relative to the NO compounds may be attributed to the improved dispersion of fillers in the EPO elastomer. This results in a restriction of motion among the elastomer chains, resulting in an improved interfacial adhesion amongst the fillers [9].
4 Conclusion

In conclusion, this study has demonstrated a holistic approach at determining the viability of EPO as a green alternative to current RPOs by encompassing the cure characteristics and mechanical properties of the vulcanizates. The EPO compounds recorded better curing times than the AO and NO compounds, lower desired maximum torques for the SBR compound relative to the PO and NO counterparts as well as lowest values for the NR compounds. The mechanical properties were in the accepted range as compared to the petroleum-derived rubber compounds. These findings conclude that EPO serves to be a viable green alternative to current petroleum-derived processing oils, showing positive effects as a processing aid as well as an activator.

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