The Effect of Natural Based Oil as Plasticizer towards
Physics-Mechanical Properties of NR-SBR Blending for Solid Tyres

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Abstract. Petroleum derivatives oil has been used dominantly as a primary plasticizer in rubber compounding for tyre industries. Despite its harmful effect to the environment, it is also a nonrenewable resources that need to be replaced. This research would study the effect of natural based oil such as castor oil, palm oil, fried - palm oil as an alternative plasticizers to replace petroleum based oil like white oil and minarex oil in Natural Rubber and Styrene Butadiene Rubber (NR-SBR) composites for rubber solid tire. The rubber compounding applied the same amount of each plasticizers which was 8,75 phr in 90/10 phr of NR-SBR composites filled by 64 phr Carbon Black N330 and 34 phr CaCO₃. Physical mechanical properties of 5 formulas were examined, the hardness values range from 68 - 74 ShoreA; tensile strength 118 - 136 kg/cm²; modulus 200% 19,25 – 31,16; density 1,22 - 1,29 g/cm³, abrasion resistance 102,37 - 135,64 mm³, compression set (tested in 25% defl, 70 °C, 22 hours) range from 65,44 to 72,35; and there were no crack for ozone resistance (tested in 50 ppdm, 20% strain, 24 hours, 40 °C). To sum up, it is indicated that there is no significant difference in physical mechanical properties of composites using either natural or petroleum based oil as plasticizers.

Keywords: natural based plasticizers, petroleum based plasticizer, NR-SBR composites, solid tyres.

1. Introduction

Plasticizers for rubber industry primarily used petroleum or mineral oils derivates. On the one hand, the mineral resources has depleted recently, while the petroleum based plasticizer experienced constant competition with many other petroleum consumers [1, 2]. Mineral oils are made from crude petroleum which are effective, tightly controlled for quality, inexpensive and easy to use for rubber compounding. The necessity of releasing the polymer industry from its dependence on depleting resources represents a major concern. On the other hand, plant oils represent a renewable resource that can be used as reliable starting material to access new polymer products [3]. Its availability and relatively low cost becomes a competitive advantages of an industrial material for plastic or polymer industries [4]. The largest sources of vegetable oils are annual plants such as corn, castor oil, cottonseed, peanut, linseed, palm oil, soybean as well as oil bearing perennials such as palm, oil or coconut.
Plasticizers are added in rubber compounding process in order to soften or as lubricant in rubber milling, mixing, and extrusion process and increase dispersion of fillers as well as extend the rubber giving a larger volume of elastomer [5]. The type of plasticizers such as naphthenic, paraffinic petroleum-based, and natural oils could affect the physical properties namely hardness, fleck life, low temperature performance, abrasion resistance, and tensile strength [1, 3].

SBR has good wear resistance and traction performance, it is the primary rubber for passenger car tire tread compounds. While Natural rubber has good properties in tensile properties [6]. Various types of oil can be added into the rubber compound in order to reduce its viscosity, get better processing properties, increase low temperature flexibilities and decrease cost [5]. Producing of oil-extended rubbers has been industrialized since 1950s in the United States using petroleum based extender oils such as aromatic oil, naphthenic oil and paraffinic oil. Aromatic/ Mineral oil is the most widely used extender oil in modern tire manufacturing due to its good compatibility with tire rubbers, such as SBR and natural rubber. However, in 1994 a report by Swedish National Chemicals Inspectorate showed that polycyclic aromatic hydrocarbon (PAH), which is the main constituent of aromatic oil, is highly carcinogenic. Hence, plasticizer from mineral oil also not eco-friendly, corrosive, and irritate stated that natural / plant oils could be developed in polymer industry due to its availability, low cost, eco-friendly and less toxic for nature and human being [4].

The research on utilize the commercial brown factices of castor oil at temperature 170°C, then use it in rubber compounding of natural rubber and EPDM 6250, and the results showed that the compounding energy and modulus of torque were decreasing [7]. The addition of castor oil as a plasticizer with a 5 phr ratio has a positive effect towards the mechanical properties which is increasing tensile strength, elongation at break, and fracture resistance. The other vegetable oil utilizations were the vegetable oil and epoxidized palm oil (EPO), the addition of 2-3 phr vegetable oil and EPO in natural rubber compounding and yielded the increasing of cross linking density, hardness, modulus but decreasing tensile strength and elongation at break [8]. While, EPO improved the carbon black dispersion in the matrix polymer as well as increase its heat resistance. However, research on the utilization of natural based oil as plasticizers for Natural Rubber and Styrene Butadiene Rubber composites filled with Carbon Black and Calcium Carbonates is still limited. Hence, the effect of using natural based oil as a greener plasticizer towards its properties of rubber products is an urgency to be investigated.

Bearing in mind the importance of searching new alternative mineral plasticizers and with regard to some weakness of using petroleum based oil for rubber compounding in solid tires industries, it is a necessity to do this research. The objective of this research was to study the effect of natural plasticizers namely castor oil, palm oil, fried-palm oil towards it physic-mechanical and tensile properties. Comparison those properties with commercial extended petroleum based oil such as white oil and minarex oil was evaluated to determine the feasibility using natural based plasticizers. Consequently, the research would contribute new information about the characteristics of natural plasticizers that potentially could replace the petroleum oil in rubber compounding of NR-SBR composite in solid tyres industries

2. Materials and Methods

2.1 Materials
Natural Rubber/ NR (Standard Indonesian Rubber/SIR 20) and Styrene Butadiene Rubber/ SBR were used as polymer. Other chemicals used were Zinc Oxide (NC 105 Global Chemical Co, Ltd), Stearic Acid
(SA 1806, Oleochemicals Industry, PT Sumi Asih), Carbon Black (CB N330 or HAF VULCAN, CABOT), Calcium Carbonate (400 mesh, SK Product). While, MBTS, Diphenyl Guanidine (DPG), Paraffin Wax, N-(1,3-dimethylbutyl)- N’-phenyl-p-phenylene diamine 6 PPD, Sulphur were bought from Brataco Chemical. Three types of natural based oils namely castor oil, palm oil, fried-palm oil, while the petroleum based oils were industrially commercial white oil, and minarex oil.

2.2 Methods

2.2.1 Rubber Compounding for Solid Tyre

The rubber compounding process were conducted based on the standard procedure of ASTM D3182 using laboratory two roll mill XK-160, Shanghai Rubber- Machine Worker, China. The formulations are given in Table 1. The five different types of plasticizes oils were in the same quantity of 8.75 phr. The composites were vulcanized and pressed for 14 minutes at 160 °C. Three replication for each formulas were compounded in order to obtain an accurate data.

Table 1. Formulation of NR-SBR Composites for Rubber Solid Tyre

| Ingredients                  | Formula |
|------------------------------|---------|
| NR (SIR 20)                  | 90      |
| SBR                          | 10      |
| ZnO                          | 4.75    |
| Stearic Acid                 | 2.25    |
| Carbon Black N330            | 62      |
| CaCO₃                        | 34      |
| Fried Palm Oil               | 8.75    |
| Palm Oil                     | 8.75    |
| Castor Oil                   | 8.75    |
| Minarex Oil                  | 8.75    |
| White oil                    | 8.75    |
| MBTS                         | 1.65    |
| DPG                          | 0.87    |
| Paraffin Wax                 | 1.55    |
| 6PPD                         | 1.37    |
| Sulfur                       | 2.65    |

2.2.2 Physical-Mechanical Properties Testing

The five formulas of solid tyres were tested for parameters as follows hardness Shore A (ASTM D 2240); tensile strength (ASTM D 412); modulus 200% (ASTM D 412); density (ASTM D 624); abrasion resistance (ASTM D 5963); compression set, 25% defl, 70°C, 22h (ASTM D 395); and ozon resistance, 50 pphm, 20% strain, 24 h, 40°C (SNI.7655-2010). Each replication was tested for those parameters, the data presented in this results are the average of 3 replications.

3. Results and Discussion

3.1 Physical Properties
Table 1 shows the physical properties of SBR-NR composites filled by CB and CaCO₃ using castor oils, palm oil, fried-palm oil, minarex oil, and white oil. It shows that composites using fried-palm oil as plasticizer yield the lowest hardness of 68 ShoreA, while minarex oil could yield 74 ShoreA. It could be said that the natural oil based could plasticize the composites well, even though the value of hardness smaller than the petroleum based oil. Natural based oil has different fatty acid that could soften the interaction between NR, SBR, CB, and CaCO₃ during the mixing process. However, the compatibility between the types of plasticizers could effect the cross linking reaction in rubber matrix [9]. Thus, different plasticizer influence the speed of insertion filler into rubber matrix and the homogeneity between reinforcing and non-reinforcing filler [10]. Thus, it could yield the different level of hardness.

| No | Parameter       | Testing Results |
|----|----------------|-----------------|
|    |                | Unit           | A Castor Oil | B Palm Oil | C Fried-Palm Oil | D Minarex Oil | E White Oil |
| 1  | Hardness       | ShoreA         | 71           | 70         | 68              | 72            | 74          |
| 2  | Density        | g/cm³          | 1,28         | 1,27       | 1,22            | 1,26          | 1,29        |

The effect of using different natural and petroleum based plasticizers on the density of vulcanized rubber is not significant. The density ranges from 1,22-1,28 g/m³. The composites using free palm oil has the lowest density among others. It is stated that the hardness and density is directly influceed by the volume of reinforcing filler, but in order to obtain homogeneous and fine dispersion, plasticizer plays an important roles along with the type and particle size of the fillers [11]. Furthermore, the rheological analysis would be beneficial in order to know the effect of different plasticizers on rubber mixing and vulanization. Based on the data as listed in Table 1, it is indicated that hardness have linear relationship with density. Similarly, those relationship also connected to the abrasion resistance [12].

3.2 Tensile Properties

The value of tensile strength and modulus of each composites using various plasticizer depicted in Figure 1. Compared to other formulas, minarex oil could give the highest tensile strength 145 kg/cm², while the lowest is formula C (fried-palm oil) 118 kg/cm². Aforementioned, the phenomena could be explained as follows. Each plasticizer has different ability to stretch rubber matrix during the chemicals dispersion and also compatibility between polymer matrix and filler [5]. Its ability depends on the fatty acid and other components contained in the plasticizers [11].
It is stated that increasing of plasticizer loading gradually reduces the bounding rubber contents of the compounds, but the bound rubber content is insignificantly influenced by the types of plasticizers [1]. The more saturated rubber shows less bonding to the same type of carbon black than unsaturated rubber. The composites in this research used 90 phr NR and 10 phr SBR. NR that possesses a higher un-saturation than SBR shows a higher bound rubber content than SBR at the same carbon black loading. In comparison with the un-plasticized compound, the addition of plasticizer remarkably decreases the bound rubber content for the filled SBR compounds, whereas the filled-NR and NR/SBR compounds show a narrower range of reduction in bound rubber content with increasing plasticizers loading [13]. This indicates a different level of interaction strength in NR and SBR because of their difference in chemical structure. In addition to their different unsaturation levels, the chain break-down of NR during mixing generates free radicals which may lead to strong interactions with the filler surface [6]. Similarly, the bounding rubber could affect the tensile strength properties.

Modulus 200% for the given formulas range from 19 - 31 MPa. Similarly, the minarex oil could give indirectly insignificant effect to the tensile properties rather than the natural based oil. As expected, an increase of plasticizers volume reduces the hardness and modulus of the vulcanizes since the rubber molecules can deform easier due to an increase of the free volume and the lubrication effect of the each plasticizers [14]. Thus, at the same plasticizers content, NR/SBR composites filled CB and CaCO₃ display the slightly same modulus irrespective of the plasticizer types.

### 3.3 Physical-Mechanical Properties

Similarly with the tensile properties minarex oil is able to soften the rubber mixing and yield the highest abrasion resistance as shown in Figure 2. The 90/10 phr of NR/SBR composites would be beneficial for the rubber product since NR has a good tensile, tear strength, flexing and fatigue resistance, and elastic properties [9]. In addition, rubber compounding has advantage such as reduced rolling resistance, low temperature flexibility and enhances adhesion between components [15]. However, filler are practically added into NR composites to enhance properties like stiffness, abrasion and skid resistance [16]. Hence, the plasticizers type in the same volume could not give significant different of abrasion resistance of each composites. This results was highlighted that particle size of filler influence the 3 dimensional networking in rubber polymer matrix in a very fine dispersion, not the plasticizers yet.

![Figure 1 Tensile Properties of NR-SBR Composites filled by CB and CaCO₃ using Various Plasticizer](image-url)
Figure 2. Physical-Mechanical Properties of NR-SBR Composites filled by CB and CaCO₃ using Various Plasticizer

The compression set (25% deflation, temperature 70 °C, 22 hours) for each formulas shown in Figure 2. It depicts that using fried-palm oil yield the compression set approximately 65%, while the about 72% using minarex oil. Some researchers concluded that the compression set is dominantly influenced by the presence of reinforcement fillers within the rubber polymer matrix. The incorporation of fillers (silica – quartz) into rubber increases both the dynamic storage modulus and the phase angle [17]. The filled-rubber compounds are highly complex systems in which various solid and liquid ingredients are dispersed in a rubber matrix. In such a system, the reinforcing filler develops strong interactions that lead to the development of a structural material and the associated specific flow properties [14]. Filler-rubber interactions give rise to additional cross links in the network structure, and the immobilized elastomeric layers on the filler surface have an influence on the dynamic response of the material [3]. Thus, the plasticizers type doesn’t give any massive impact on the physical mechanical properties like compression set as well as modulus.

The test results showed that there is “no crack” after expose of 50 pphm ozone, 20% strain for 24 hours at 40°C. It is implied that the plasticizers type does not influence the abrasion resistance of the vulcanizates. The abrasion resistance is closely related to the chemical of anti-degradation quantity and types in rubber compounding. Aforementioned, the plasticizers activity dominantly play as lubricant role not for protect rubber polymer matrix from ozone, oxidant attack or even flex cracking. Therefore, the same amount of MBTS (1.65phr) is in appropriate to yield the solid tyres which has a good ozone resistance.

4. Conclusion
In summary, the research showed that natural based oil namely castor oil, palm oil, fried palm oil were a potentially alternative plasticizer to substitute naphthenic/ petroleum basedoil in NR-SBR composites filled with CB and CaCO₃ for rubber solid tyres industries. It is indicated that the physical mechanical properties of rubber vulcanizates using castor oil, palm oil, fried-palm oil are not significantly different from using minarex oil and white oil as plasticizers. However, using minarex and white oil yielded a little bit better physical properties for tensile strength, modulus, and abrasion resistance.

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