ISSN: 2621-4709 E-ISSN: 2621-2528
Journal of Applied Agricultural Science and Technology
Vol. 9 No. 2 (2025): 239-254

Esterified Illipe Butter-Based Fatty Amine as a Bio-Based Multifunctional Additive for NR/BR Blends Reinforced with a Silica/Silane System in Green Tire Tread Development

Mohamad Irfan Fathurrohman [a], Santi Puspitasari [a,*], Norma Arisanti Kinasih [a], Dewi Kusuma Arti [b]

[a] Indonesian Rubber Research Institute, PT Riset Perkebunan Nusantara, Bogor, Indonesia
[b] Research Center for Advanced Material, National Research and Innovation Agency (BRIN), South Tangerang, Indonesia

Abstract. *The sustainable rubber industry, particularly in the tire sector, is supported by the use of biomaterials such as multifunctional additives. Fatty amine, derived from the esterification of illipe butter, is considered a promising bio-based multifunctional additive for the development of green tires. This research aimed to investigate the effect of varying dosage of fatty amine on the properties of green tire treads based on NR/BR blends reinforced with a silica/silane system. DPG and unmodified illipe butter were used as comparative references. The "magic triangle of tire performance" was employed as a benchmark for evaluating green tire tread performance. The result indicated that both unmodified illipe butter and fatty amine functioned as bio based multifunctional additives, specifically serving as a bio-plasticizer (filler dispersant) and fast-delayed bio-accelerator, respectively. Therefore, they have the potential to substitute DPG in rubber formulations. The combination of unmodified illipe butter and fatty amine at dosages of 2.5 and 1.25 phr, respectively, exhibited similar behavior by enhancing rubber-filler interaction. Consequently, they meet the desirable criteria outlined in the magic triangle of tire performance.*

Keywords: *biomaterials; green tire; multifunctional additive; rubber blends; silica/silane.*

Type of the Paper: Regular Article.

1. Introduction

The production of rubber goods involves three essential stages: rubber compounding based on a specific formulation, shaping into a defined form, and vulcanization. The formulation of the rubber compound plays a strategic role, as it significantly influences the quality of the final product to meet the intended performance requirements. A rubber compound is a mixture of a base elastomer and various additive ingredients, commonly referred to as rubber chemicals. The types of rubber chemicals typically included in the formulation consist primarily of anti-aging agents, fillers, plasticizers, activators, accelerators, and vulcanizing agents [1]. Recent developments aimed at achieving a more economical and sustainable rubber industry, particularly in the green tire manufacturing sector, have promoted the use of essential bio-based multifunctional additives.

A bio-based multifunctional additive is defined as a specialized group of rubber chemicals derived from biomaterial or biological source, combining two or more functions of conventional

https://doi.org/10.55043/jaast.v9i2.357
Received October 8, 2024; Received in revised form April 14, 2025; Accepted May 25, 2025; Published May 25, 2025

*First corresponding author.
Email: santi.puspitasari.ppk@gmail.com

rubber additives. Recent research has focused on the development of promising bio-based multifunctional additives. For example, phenol-functionalized 1,2-polybutadiene (1,2-PB-g-CA) has been synthesized by grafting bio-based cardanol onto 1,2-polybutadiene rubber (1,2-PB) via olefin metathesis and applied as plasticizer for silica filled styrene butadiene rubber (SBR) compounds [2]. Additionally, natural waste gum from *Moringa oleifera* has shown potential as an accelerator activator and plasticizer in SBR compounds [3]. Gallate ester derived from castor oil functions as an accelerator activator and antioxidant, while also enhancing the swelling resistance of natural rubber composites filled with carbon black [4]. Moreover, aminated epoxidized soybean oil has been reported to promote rubber vulcanization, improving rubber mixing, and enhancing mechanical properties of rubber products [5].

Indonesia possesses a vast biomaterial resource that has the potential to be used as raw material for the synthesis of bio-based multifunctional additives for rubber. Illipe butter is a type of vegetable butter extracted from the nuts of the tengkawang tree (*Shorea stenoptera*), an endangered and endemic plant that grows exclusively in West Borneo. Illipe butter has a cream to dark yellow solid appearance at 15°C. It also has a high melting point of 30–338°C, making it ideal for producing solid products. The native people of Borneo traditionally use illipe butter as a cosmetic to moisturize the skin, heal sores or sunburn, and as flavor-enhancer for dishes.

Chemical modification through esterification with an alkanolamine compound converts illipe butter into fatty amine. Fatty amine is formed by attaching the amine group of the alkanolamine to the fatty acid chain of illipe butter. The fatty acid profile of illipe butter includes 14–22% palmitic acid, 36 –50% stearic acid, 30–42% oleic acid, and a maximum of 6% linoleic acid. Due to the high content of stearic acid, illipe butter is regarded as potential to be used as a rubber chemical which is involved in the vulcanization reaction. Heideman et al. [6] proved that amine contributes to accelerate curing of SBR compounds. Additionally, fatty acids enhance the process-ability of uncured rubber compounds. Consequently, fatty amine is expected to function as a bio-based multifunctional additive, acting simultaneously as plasticizer and an accelerator.

Heavy vehicles, such as buses and large trucks, generally require tires with excellent mechanical performance. Natural rubber or a blend of natural rubber and polybutadiene rubber is preferred as the matrix material for heavy-duty vehicle tires. Natural rubber possesses desirable properties, particularly low heat build-up and high wear resistance [7-9]. Polybutadiene rubber, on the other hand, exhibits superior abrasion resistance. The present study investigates the performance of fatty amine derived from the esterification of illipe butter as a novel bio-based multifunctional additive for use in the production of green tire treads composed of natural rubber and polybutadiene rubber blends reinforced with a silica/silane system. Fatty amine was introduced as a substitute for diphenyl guanidine (DPG). Therefore, the results of this experiment are expected to expand the potential applications of pure or modified illipe butter across various sectors, including but not limited to the pharmaceutical, cosmetic, and food industries.

2. Materials and Methods

2.1. Materials

This study used two types of rubber blended together: natural and synthetic rubber. The natural rubber, Ribbed Smoked Sheet 1 (RSS 1) grade, was supplied by PT Nyalindung, Padalarang, West Java, Indonesia. The synthetic rubber, specifically polybutadiene rubber of the Nd-BR CB24 type, was obtained from Lanxess Germany. Various rubber chemicals were used in the experiment, including high-dispersion (HD) silica (Zeosil 1165 MP, Solvay, China), carbon black (CB N330, OCI, South Korea), bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT silane, JHS69, Jianghan Fine Chemical Co. Ltd, China), treated distillate aromatic extracted oil (TDAE ARMAX 500, Enerco, Indonesia), zinc oxide (ZnO, Lanxess, Germany), stearic acid (Aflux 52, Rhein Chemie Rheinau Mannheim GmbH, Germany), N-cyclohexyl-2-benzothiazole sulfonamide (CBS OCP, Kemai Chemicals Co. Ltd, China), diphenyl guanidine (DPG, Kemai Chemical Co. Ltd, China), tetrabenzylthiuram disulfide (Rhenogran TBzTd-70, Rhein Chemie Rheinau Mannheim GmbH, Germany), sulfur (Midas SP-325, Miwon Chemicals Co. Ltd, Korea), 2,4-trimethyl-1,2-dihydroquinoline (TMQ Vulkanox HS/LG, Rhein Chemie Rheinau Mannheim GmbH, Germany), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD, Sirantox Vulkanox 4020, Lanxess, Deutschland GmbH, Germany) and paraffin wax (Antilux 654A, Lanxess, Deutschland GmbH, Germany).

The bio-based fatty amine investigated in this study was previously synthesized by the Bogor Getas Research Unit through the esterification of illipe butter with triethanolamine. The proposed structure of the resulting fatty amine is illustrated in Fig. 1. Illipe butter was produced by PT Forest Wise Wild Keepers, Sintang, West Kalimantan, Indonesia, through the extraction of tengkawang nuts. Triethanolamine (pro analysis grade, Millipore) was supplied by Merck, Germany. The rubber compound formulations are detailed in Table 1. As shown, the fatty amine was incorporated at dosages of 2.5 parts per hundred rubber (phr) (code: FA) and 1.25 phr (code: FA*). Rubber compounds containing DPG (code: DPG) and unmodified illipe butter (code: TKG) served as reference samples.

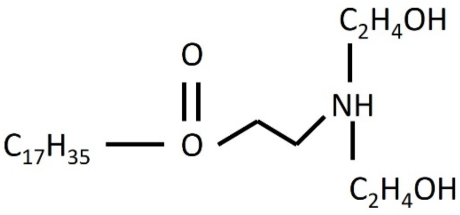

Fig. 1. Possible structure of bio-based fatty amine [10]

Table 1. Rubber compound formulation design

Material	Quantity (phr)				Function
	DPG	TKG	FA	FA*	
Natural rubber (RSS 1)	70	70	70	70	Base elastomer
Polybutadiene rubber	30	30	30	30	Base elastomer
High Disperse Silica	60	60	60	60	Reinforcing filler
Carbon Black N 330	5	5	5	5	Reinforcing filler
TESPT	4.5	4.5	4.5	4.5	Coupling agent
TDAE Oil	10	10	10	10	Plasticizer
ZnO	3	3	3	3	Activator
Stearic acid	2	2	2	2	Activator
CBS	1.6	1.6	1.6	1.6	Accelerator
TBzTD	0.2	0.2	0.2	0.2	Accelerator
Sulfur	2	2	2	2	Vulcanizing agent
TMQ	1.5	1.5	1.5	1.5	Antioxidant
6PPD	2	2	2	2	Antioxidant
Paraffin wax	2	2	2	2	Antiozonant
DPG	2.5		-	-	Silanization promoter
Illipe butter		2.5			Multifunctional Additive
Fatty Amine	-		2.5	1.25	Multifunctional Additive

2.2. *Method*

The rubber compound was prepared at laboratory scale using a Banbury mixer (David Bridge Co Ltd, England), operating at a fill factor of 70% of the mixer's total capacity (1500 cm^3). Rubber compounding was performed in two stages, as outlined in Table 2. In the first stage, both rubbers were masticated into a softened mass, followed by the addition of half of the filler, silane, and plasticizer. Mixing was conducted for 5 minutes at a chamber temperature of 110°C and a rotor speed of 80 rpm. The rubber compounding was continued by adding the remaining half of the filler, silane, plasticizer, activator, antioxidant, antiozonant, and either DPG, fatty amine or a combination of DPG and fatty amine. After all the materials from the first stage were fed into the Banbury mixer, the rotor speed was increased to 100 rpm, causing the chamber temperature to rise and reach a dump temperature of 110°C. Under these conditions, the silanization reaction occurred [11]. Subsequently, the dump temperature was measured before the rubber compound was discharged from the Banbury Mixer. The compound was then sheeted using a two roll open mill (Berstorf, Germany) to achieve a more homogenous distribution of filler within the rubber matrix. Rubber sheet was matured for 24 hours prior to further processing in the next compounding stage.

The second stage of rubber compounding began with pre-heating the cold rubber sheet compound obtained from the first stage. Unlike the first stage, the fill factor in the second stage was set at 65%, and the initial chamber temperature was maintained at 50°C. Accelerators and the vulcanizing agent were added to the heated rubber compound in the mixing chamber and mixed for 2 minutes. The mixing process was completed by passing the rubber compound through a two roll open mill to enhance the dispersion of the rubber chemicals. The homogenized rubber sheet compound was stored at room temperature for 24 hours prior to testing and vulcanization to produce the rubber vulcanizate.

Table 2. Mixing stages during rubber compounding

No	Stage	Ingredients	Mixing time (minute)
1.	1st	RSS 1 and BR	1
2.		½ filler + ½ silane + ½ plasticizer	5
3.		½ filler + ½ silane + ½ plasticizer + ZnO, Stearic acid, TMQ, 6PPD, DPG or fatty amine or combination DPG/fatty amine	5
4.		Isothermal mixing at 110 °C	
5.		Dump, check weight, sheet out and storage 24 h	
1.	2nd	Add batch stage 1	1
2.		Add CBS, TBzTD, Sulfur	2
3.		Dump, check weight, sheet out and storage 24 h	

2.3. Characterization the Rheology and Chemicals Properties of Rubber Compound

Rubber compound was analyzed for its rheological and chemical properties including the following parameters: Payne effect and bound rubber, which represent chemical properties. Meanwhile, rheological properties were studied through curing characteristic analysis. The payne effect test of rubber compound without addition of vulcanizing curative was measured in accordance with ASTM D 8059 using a Rubber Processing Analyzer (RPA Elite, TA Instrument, USA) in oscillating shear mode. The RPA was operated at an oscillating frequency of 0.5 Hz under a varying strain range from 0.56% to 100% at 100°C. Payne effect was calculated based on the difference of storage modulus (denoted as G'), according to the equation developed by Jin et al. [12], as follows: G'(0.56%) – G'(100%).

Bound rubber evaluation was conducted in three categories, i.e., total, chemical, and physical bound rubber. Chemical bound rubber was analyzed by placing a small piece of rubber compound in a metal cage, followed by immersion in toluene (Merck, Germany) and exposure to ammonia solution (Merck, Germany). Ammonia cleaved the physical linkage between rubber chains and filler particles. Meanwhile, total bound rubber was determined by immersing approximately 0.2 g of rubber compound in excess toluene without any ammonia exposure. The bound rubber test was conducted at room temperature for 168 hours. At the end of the test, rubber specimens were dried at 105°C for 24 hours. Bound rubber content was calculated based on Eq. 1.

$$\text{Bound rubber content} = \frac{m - m_s}{m_r} \times 100 \qquad (1)$$

Where m is the weight of the test piece after extraction, m_s is the weight of filler in the uncured rubber sample, and m_r is the weight of the rubber component contained in the sample. Physical bound rubber is the difference between total and chemical bound rubber.

Rubber compound with the addition of vulcanizing curatives obtained from the 2nd stage of mixing was used as the curing characteristic test specimen. The curing characteristic test procedure followed ISO 6502-3 and was conducted at a temperature of 150°C for 30 minutes, with a frequency of 1.67 Hz and a strain 0.5°, using a Moving Die Rheometer (MDR Alpha 2000, Alpha Technology, USA). The test result of the curing characteristic analysis was presented as a rheometer curve, which plotted torque against cure time. The curve served as the basis for calculating curing rheometric parameters.

Mooney Viscosity (ML 1+4) test of the rubber compound was performed using a Mooney viscometer (RPA Elite, TA Instrument, USA), following the test procedure specified in ISO 289. The testing temperature was set at 100°C, and a small rotor size was selected to measure the Mooney viscosity of the rubber compound over a duration of 5 minutes.

2.4. Characterization the Properties of Rubber Vulcanizate

Rubber vulcanizate was prepared by press-curing the rubber compound using a hot press hydraulic machine (KMC, Kobe Machinery Co Ltd, Japan). The curing conditions were set at 150°C and a pressure of 100 kgf/cm^2. The curing time depended on the optimum curing time (tc$_{90}$) obtained from the curing characteristic analysis. The dimensions of the rubber vulcanizate were adjusted to match the test specimen requirements for each mechanical and dynamic test parameters evaluated in the study.

Apparent crosslink density was assessed by immersing the rubber vulcanizate in toluene for 72 hours at room temperature. After equilibrium swelling was reached, the test piece was removed and air dried at room temperature for 24 hours. Swelling value (Q) was identified as the amount of nonpolar solvent absorbed by rubber vulcanizate (in grams) per gram of rubber vulcanizate, while the formula weight was defined as the total weight of all rubber compound ingredients. Accordingly, the apparent crosslink density was calculated as the reciprocal of the swelling value (1/Q). Eq. 2 was used to calculate the Q value.

$$Q = \left(\frac{\text{swollen weight - dried weight}}{\text{sampel weight}}\right) \text{ x } \frac{\text{formula weight}}{100} \tag{2}$$

Mechanical properties testing parameters of the rubber vulcanizate included hardness, tensile properties, modulus elasticity, tear strength, and abrasion resistance. The hardness testing procedure followed ISO 48-4 and was conducted using Frank Durometer Shore A (Karl Frank GmbH, Germany). Tensile properties, consisting of tensile strength and elongation at break, were determined through static uniaxial tensile tests in accordance with ISO 37-2, using a Universal Testing Machine (UTM E43, MTS, USA) at a crosshead speed of 500 mm/min under room temperature and humidity conditions. Modulus elasticity was measured using UTM MTS under slightly different conditions, i.e., crosshead speed of 100 mm/min, following the ASTM E 111-17 standard test procedure. The UTM MTS was also used for tear strength analysis based on ISO 34. Specifically, hardness and tensile properties were evaluated under conditions before and after aging (ISO 188). The aging process was conducted at 70°C for 168 hours in an oxygen environment using an oven (Model 4081, Inventum, Netherland). Abrasion resistance was tested in accordance with ASTM D 5963 using a Rotary Drum Abrader (DIN Abrasion, Model Karl, Frank, Germany). Volume loss of rubber vulcanizate in mm^3 per 40 m, represented as abrasive action.

Dynamic mechanical properties, along with Payne effect and abrasion resistance, were used to predict the “magic triangle properties” of a green tire. Dynamic mechanical analysis was conducted using Dynamic Mechanical Analyzer (DMA, DMA 7100, Toshiba, Japan) under the following test conditions: a heating rate of 2°C/min, a fixed deformation frequency of 10 Hz, and 0.1% strain, with tension measuring mode and a temperature sweep ranging from -80 to 80°C. The loss factor (tan δ) at 0°C and 60°C was recorded during the test.

3. Results and Discussion

Payne effect indicates filler networking and agglomeration in rubber composites, and therefore has a close relation to tire performance. Generally, the Payne effect is represented by the variation in the apparent storage modulus (G’) with strain amplitude [13]. The pattern of the Payne effect curve is characterized by a reduction in storage modulus with increasing strain amplitude, as shown in Fig. 2. Meanwhile, the Payne effect value is accessible in the legend.

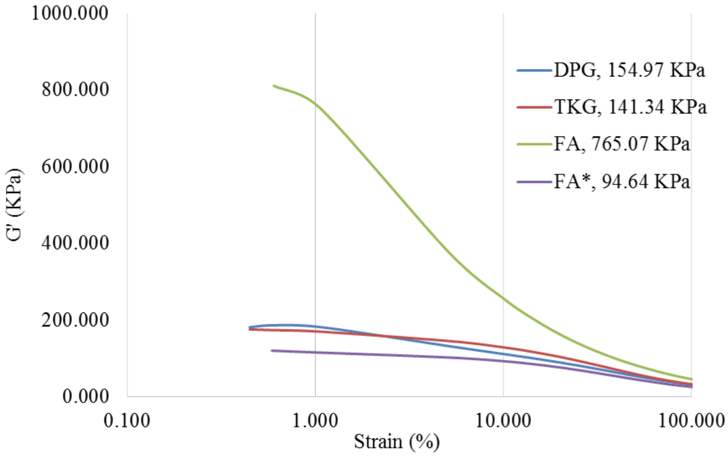

Fig. 2. Storage modulus vs strain amplitude (Payne effect) of thread compound

As shown in Fig. 2, the Payne effect curve of rubber compound coded with FA exhibits the sharpest G’ curve and results in the highest Payne effect value. However, the Payne effect curve of the FA rubber compound also shows a significant reduction in G’ value with increasing strain amplitude. Meanwhile, DPG, TKG, and FA* the rubber compound also shows a significant reduction in G' value with increasing strain amplitude. The lowest Payne effect value was obtained from the FA* rubber compound, which contains 1.25 phr of fatty amine.

A high Payne effect value signifies strong filler-filler interaction or filler agglomeration. In contrast, a low Payne effect value indicates better filler dispersion in the rubber matrix, leading to improved rubber-filler interaction. Based on this characteristic, it can be concluded that fatty amine, synthesized from the esterification of illipe butter at a concentration of 1.25 phr, acts as filler dispersant in the rubber compound formulation. Filler dispersant, like plasticizer, helps improve filler dispersion in the rubber matrix and enhance rubber-filler interaction. The NH- group of fatty amine molecules forms hydrogen bonds with the silanol groups of the silica particles, thereby accelerating the silanization reaction and strengthening the rubber-filler interaction, as proposed in Fig. 3. However, an excess of fatty amine loadings in the rubber compound leads to rubber particles surfaces being covered with fatty amine, which inhibits the interaction between the rubber and the filler.

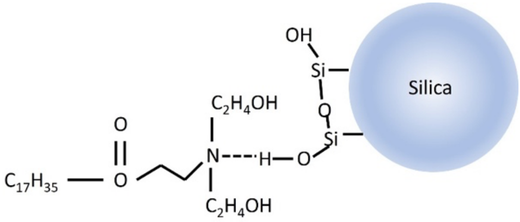

Fig. 3. Proposed interaction between silica and esterified illipe butter

Another parameter used to evaluate rubber-filler interaction in rubber compounds containing fatty amine is the bound rubber content, as shown in Fig. 4. According to Fig. 4, bound rubber content is categorized as chemical, physical, and total bound rubber. The TKG, FA, and FA* rubber compounds show the chemical bound rubber is greater than physical bound rubber. In contrast, DPG rubber compound exhibits a different behavior, with a higher physical bound rubber, indicating ongoing interaction between the silanol groups on the silica surface, as DPG does not act as a dispersion agent. The high chemical bound rubber in TKG, FA, and FA* compounds are attributed to the presence of fatty acid and fatty amine materials, which function as filler dispersant, especially at the appropriate dosage. Filler dispersant enhances filler distribution in the rubber matrix, thereby improving the rubber filler interaction, as indicated by the higher chemical bound rubber value.

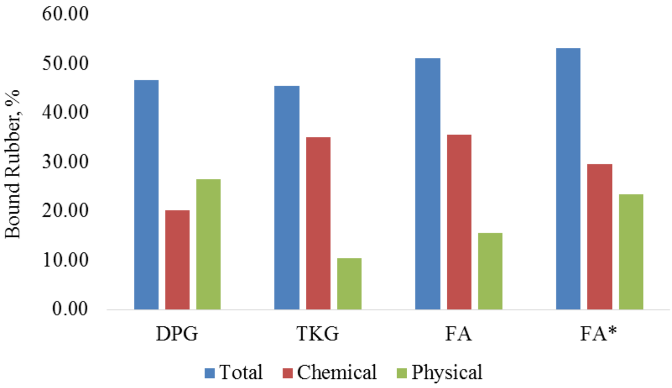

Fig. 4. Bound rubber of rubber thread compound

The curing characteristic of the rubber compound was also analyzed in this study. The results were presented as a rheometer curve, as displayed in Fig. 5. According to Fig. 5, the rheometer curves of TKG and FA* compounds exhibit a similar pattern. During the induction stage, both TKG and FA* showed a longer delay before reaching the curing phase compared to DPG and FA. This performance indicates that the presence of illipe butter and fatty amine at concentrations of 2.5 and 1.25 phr, respectively, delayed the onset of curing reaction. In contrast, DPG and fatty amine at 2.5 phr accelerated the curing reaction. Commonly, DPG functions as a secondary accelerator in sulfur vulcanization. Additionally, the excess amine from 2.5 phr fatty amine is also believed to contribute to the acceleration of the curing reaction.

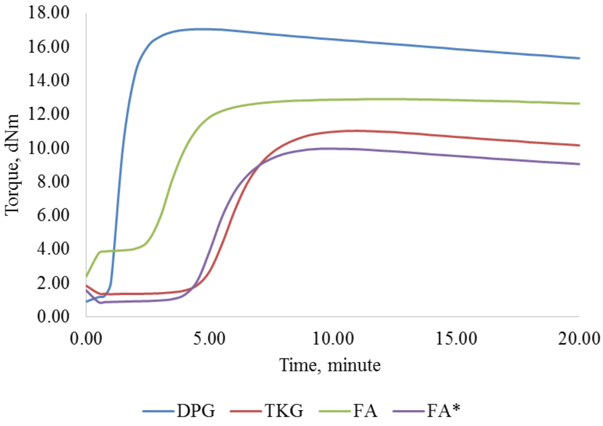

Fig. 5. Rheometer curve of rubber thread compound

Table 3. Curing rheometric parameters of rubber thread compound

No	Rubber Compound	Maximum torque (M_H, dNm)	Minimum torque (M_L, dNm)	Torque difference (ΔM, dNm)	Optimum curing time (tc_{90}, minute)	Scorch time (ts_2, minute)
1	DPG	17.08	0.60	16.48	2.14	1.03
2	TKG	11.05	1.36	9.69	7.52	5.14
3	FA	12.92	2.32	10.60	5.01	2.22
4	FA*	9.99	0.88	9.11	7.06	4.45

Curing rheometric parameters obtained from curing characteristic calculations are summarized in Table 3. The data in Table 3 exhibit that DPG resulted in the highest maximum torque (M_H), followed by FA, TKG, and FA*, respectively. M_H is closely related to filler-filler interactions, rubber networks formations, and rubber-filler interactions. A high M_H value is primarily attributed to strong filler-filler interaction and dense rubber networks. However, as shown in Fig. 2, the Payne effect value of DPG is relatively low, indicating weaker filler-filler interaction. Therefore, the high MH value in DPG rubber compounds is mainly influenced by the dominance of rubber network formation. In contrast, M_H value of the FA* rubber compound is the lowest, as it exhibits better rubber-filler interaction and a lower Payne effect value due to enhanced plasticization. The findings align with research conducted by Menezes et al. [14], which reported that lowest torque modulus values in curing rheometric parameters result from increased plasticization effects.

From the perspective of tc_{90}, the fastest curing time is obtained in the DPG rubber compound due to its function as a secondary accelerator. Furthermore, both TKG and FA* compounds exhibit longer curing periods. The safety period of curing reaction, as identified by ts_2, is also relatively longer for TKG and FA* compared to DPG and FA rubber compounds. Fatty amine at an appropriate dosage is considered to function similarly to sulfonamide-type rubber accelerators. Sulfonamide types are characterized by a long induction period (delayed action) and a rapid cross-linking reaction (fast curing rate). The addition of 2.5 phr of fatty amine in the rubber compound results in slightly longer curing time. Unreacted fatty acid contained in the fatty amine is expected to contribute to accelerating the curing reaction. The combination of ZnO and fatty acid is known to be an effective activator system for sulfur vulcanization [15].

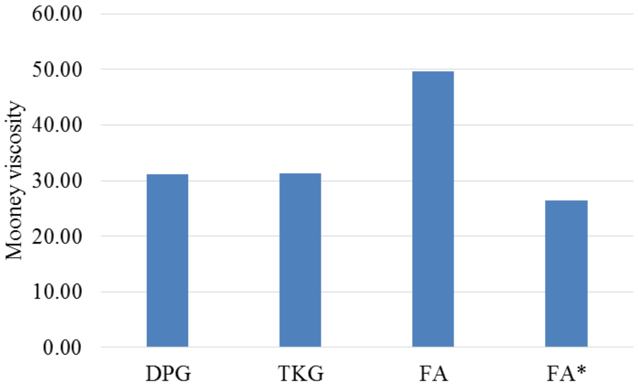

Fig. 6. Mooney viscosity of rubber compound

The Mooney viscosity measurement results of the rubber compound, as shown in Fig. 6, indicate a positive correlation between Mooney viscosity and M_L. FA* rubber compound exhibits low M_L and Mooney viscosity, while the FA rubber compound shows the opposite trend. The significant plasticizing effect of fatty amine at a concentration of 1.25 phr results in a softened rubber compound, leading to improved processability, as indicated by the low Mooney viscosity and ML values. The TKG compound demonstrated a similar performance.

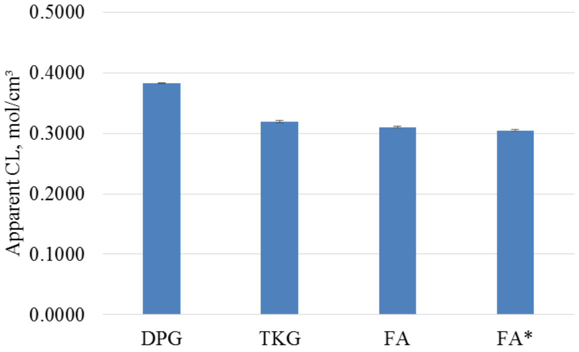

Fig. 7. Apparent crosslink density of rubber vulcanizate

Fig. 7 illustrates the apparent crosslink density of the rubber vulcanizate. As shown in Fig. 7, the addition of illipe butter and fatty amine decreased the apparent crosslink density of the rubber vulcanizates. The most significant reduction was observed in the FA* compound, followed by FA and TKG, respectively. The strong plasticizing effect of 1.25 phr fatty amine promoted a more homogenous filler within the rubber matrix, resulting in improved rubber-filler interaction. Consequently, rubber network formation or rubber-rubber interaction was hindered, as reflected by the reduction in apparent crosslink density.

Mechanical properties were evaluated under the conditions before and after accelerated aging. Table 4 summarizes the result of the mechanical properties testing of the rubber vulcanizates before aging. According to Table 4, the FA* and TKG compounds generally exhibited comparable properties. Interestingly, the DPG and FA vulcanizates show similar trends. The reduction in hardness and modulus elasticity observed in the TKG and FA* compounds were attributed to plasticizing effect of illipe butter and fatty amine at appropriate dosage of 2.5 and 1.25 phr, respectively.

Table 4. Mechanical properties of rubber vulcanizate at condition before aging

No	Rubber Compound	Hardness (Shore A)	Modulus elasticity (MPa)	Tensile strength (MPa)	Elongation at breaks (%)	Tear strength (kN/m)
1	DPG	65	0.0242	22.9	500	87.1
2	TKG	56	0.0167	21.2	550	60.0
3	FA	66	0.0158	23.8	660	91.7
4	FA*	56	0.0153	18.8	550	66.4

Lubricity concept defines that plasticizers reduce intermolecular friction between rubber chains, thereby decreasing the polymer stiffness and increasing molecular chain mobility [16-17]. Consequently, introduction of 2.5 phr of illipe butter or 1.25 phr of fatty amine resulted in reduction of modulus elasticity, tensile strength, and tear strength, while slightly increasing elongation at break. A study conduction by Park et al. [18] found that fatty acid reduced both viscosity and hardness in silica-filled rubber compounds. As explained previously, fatty amines may contain unreacted fatty acids, which could act as filler dispersant or plasticizing agents in addition to the amine component. Furthermore, Dutta [19] reported that plasticizers at optimal dosage reduce the effective diameter at the tip of the tear, thereby decreasing the tear strength of rubber vulcanizates.

Table 5. Mechanical properties of rubber vulcanizate at condition after aging

No	Rubber Compound	Hardness (Shore A)	Tensile strength (MPa)	Elongation at breaks (%)
1	DPG	69	21.0	370
2	TKG	61	18.0	440
3	FA	67	22.9	580
4	FA*	60	19.8	450

Meanwhile, under post-aging conditions, as presented in Table 5, all rubber vulcanizates exhibited similar trends, namely an increase in hardness value, accompanied by a reduction in tensile property. This behavior may be attributed to post-vulcanization reactions occurring in rubber polymers during the accelerated aging process, which promote the formation of the additional three-dimensional of rubber crosslinks.

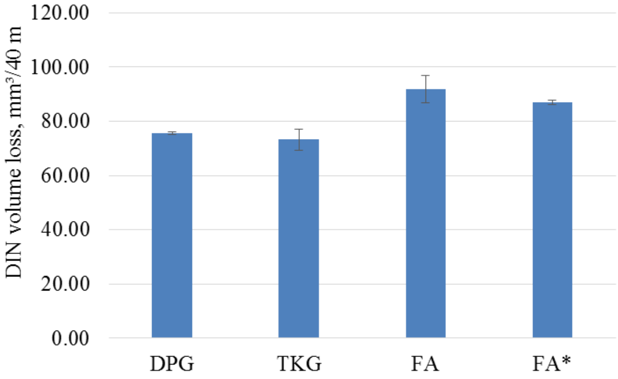

Fig. 8. DIN volume loss of rubber vulcanizate

Good abrasion resistance is indicated by low DIN volume loss value. Fig. 8 shows the DIN volume loss of the rubber vulcanizates. As illustrated in Fig. 8, the addition of 2.5 phr illipe butter resulted in improved abrasion resistance. In contrast, the same dosage of fatty amine yielded the lowest abrasion resistance, as indicated by the highest DIN volume loss. In addition to the type of rubber, abrasion resistance is also influenced by rubber-filler interactions [20]. Effective dispersion of filler particles within the rubber matrix enhances rubber-filler interaction (indicated by a low Payne effect value), thereby improving the vulcanizate's resistance to abrasive forces. As a result, tires exhibit a longer service life.

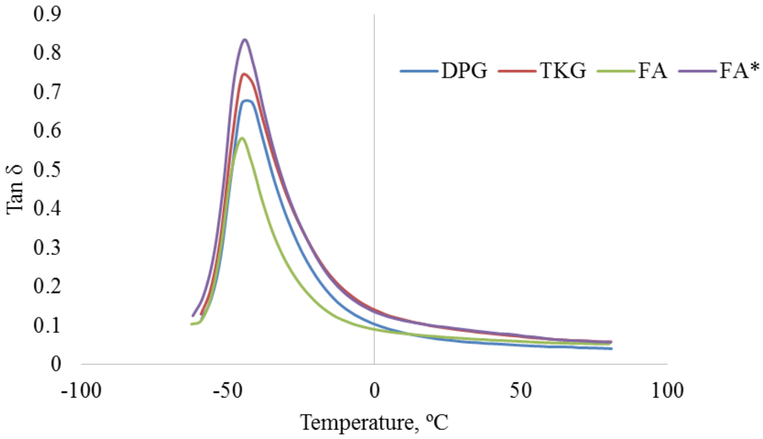

Fig. 9. Tan δ vs temperature of DMA analysis of rubber vulcanizate

The loss factor (tan δ) as a function of temperature at a fixed frequency for all tested rubber vulcanizates is illustrated in Fig. 9. Based on Fig. 9, the sharpest and highest tan δ peak (tan δ max) was observed in the FA* compound, followed by TKG, DPG, and FA, respectively. The higher tan δ max of the FA* rubber compound can be attributed to a greater proportion of rubber segments participating in the glass transition, resulting from improved silica dispersion in the rubber matrix, an important factor governing rubber-filler interaction [21-22]. In contrast, a lower tan δ max peak, as seen in the FA compound, indicates poor filler dispersion. This is consistent with its high Payne effect value, which reflects strong filler–filler interactions and reduced rubber–filler compatibility.

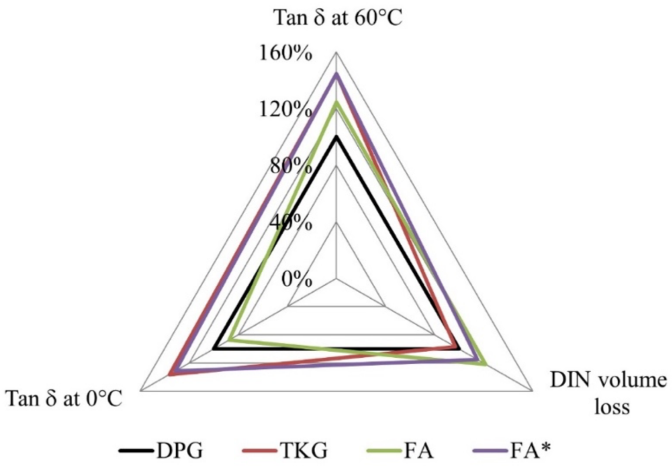

Fig. 10. Magic triangle principles of rubber vulcanizate

The core principles in the development of green tire technology are fuel efficiency and driving safety [23]. These principles are represented by the "magic triangle" of tire performance, which consists of three correlated parameters: low DIN volume loss (indicating high abrasion resistance) and rolling resistance, combined with high wet grips. Abrasion resistance corresponds to DIN volume loss [24], while rolling resistance and wet grips are reflected by the tan δ values at 60ºC and 0ºC, respectively, as evaluated through DMA testing [25-26]. Fig. 10 illustrated the magic triangle principles of all rubber vulcanizates investigated in this study, each designed for use as green tire tread. The TKG and FA* vulcanizates demonstrate favorable magic triangle characteristics, as they exhibit the highest tan δ values at 0ºC—indicating superior wet grip—despite slightly elevated tan δ values at 60 °C, which correspond to rolling resistance. Their overall performance is further supported by relatively low DIN volume loss and high tensile properties.

4. Conclusions

Based on the experimental result, it can be concluded that both unmodified illipe butter and its esterified illipe form, fatty amine, function as bio-based multifunctional additives in rubber compounds. These additives act specifically as bio-plasticizer, enhancing filler distribution within the rubber matrix, and as bio-accelerators, delaying the induction period during curing. Therefore, they present a potential alternative to DPG in rubber compound formulations. The dosage of these bio-based multifunctional additives significantly influences the characteristics of the rubber compound and vulcanizate. The arrangement of unmodified illipe butter and fatty amine at concentrations of 2.5 and 1.25 phr, respectively, showed similar performance and was determined as a favorable additive system for the production of green tire treads composed of NR/BR blends reinforced with silica/silane. This formulation enhances rubber – filler interaction, thereby fulfilling the requirements of the tire performance "magic triangle."

Abbreviations

DIN	deutsches institute fur normung
DMA	dynamic mechanical analyzer
MDR	moving die rheometer
PHR	part per hundred rubbers
RPA	rubber processing analyzer
RSS	ribbed smoke sheet
SBR	styrene butadiene rubber
TKG	illipe butter

Data availability statement

Authors confirm that raw and processed data that support the findings of this current study are available from the corresponding author, [MIF], upon reasonable request.

Authorship contribution statement

Mohamad Irfan Fathurrohman: performed on the project supervisor, conceptualization of the research study, analysis of the experiment and testing result, also on the paper writing (review and editing). **Santi Puspitasari**: contributed to the conceptualization of the research study, analysis tools and experimental methods, and writing the original draft of the paper. **Norma Arisanti Kinasih** and **Dewi Kusuma Arti**: played role on the analysis of the testing result.

Declaration of Competing Interest

The Authors clearly state no conflict of interest.

Acknowledgement

Authors gratefully Indonesia Endowment Fund for Education Agency (LPDP) and National Research and Innovation Agency (BRIN) for the financial support within the research grant scheme Riset Inovasi Indonesia Maju (RIIM) Batch 2 Year 2022 with contract number 86/IV/KS/11/2022. Authors also thank to Ms. Woro Andriani, Mr. Jaenal, Mr. Winda Dahri, Mr. Aos Kosasih, Mr. M. Rey Dandi, Mr. Regi Ferdian and Ms. Azka Ghaisanni for the assistance during the research activity.

References

[1] Zhu K, Liu Y, Wang H, Guo X, Liao S, Wang Z, Fang L. Xanthate-modified silica as novel multifunctional additive for properties improvement of natural rubber. Compos Sci Tech. 2021;203:108567. https://doi.org/10.1016/j.compscitech.2020.108567

[2] Gao W, Zhang W, Liu J, Hua J. Multifunctional and anti-migration plasticizers based on bio-based phenol-functionalized liquid 1,2-polybutadiene. Polym Test. 2023;118:107917. https://doi.org/10.1016/j.polymertesting.2022.107917

[3] Koley R, Kasilingam R, Sahoo S, Chattopadhyay S, Bhowmick AK. Waste moringa oleifera gum as a multifunctional additive for unfilled SBR compound. Rubber Chem Technol 2021;94:248-267. https://doi.org/10.5254/rct.21.79998

[4] Kandil H, Samy M, El-Nashar DE. Gallate ester of castor oil as a multifunctional additive in HAF carbon black-filled natural rubber composite. J Vinyl Add Tech 2021;28:331-342. https://doi.org/10.1002/vnl.21886

[5] Sarma AD, Federico CE, Nzulu F, Weydert M, Verge P, Schmidt DF. Multipurpose processing additives for silica/rubber composites: synthesis, characterization, and application. Polym 2021;13:3608. https://doi.org/10.3390/polym13213608

[6] Heideman G, Noordermeer JWM, Datta RN, van Baarle B. Multifunctional additives as zinc-free curatives for sulfur vulcanization. Rubber Chem Technol 2006;79:561-588. https://doi.org/10.5254/1.3547952

[7] Chollakup R, Suethao S, Suwanruji P, Boonyarit J, Smitthipong W. Mechanical properties and dissipation energy of carbon black/rubber composites. Compos Adv Mat 2021;30:1-6. https://doi.org/10.1177/26349833211005476

[8] Boden J, Bowen CR, Buchard A, Davidson MG, Norris C. Understanding the effect of cross-linking density on the self-healing performance of epoxidized natural rubber and natural rubber. ACS Omega 2022;7:15098-15105. https://doi.org/10.1021/acsomega.2c00971

[9] Chae E, Yang SR, Choi SS. Test method for abrasion behavior of tire tread compounds using the wear particles. Polym Test 2022;115:107758. https://doi.org/10.1016/j.polymertesting.2022.107758

[10] Park SH, inventor. Silica dispersion agent of amine type for producing tire. Korean Patent KR101409502B1. 2014-06-18. https://patents.google.com/patent/KR101409502B1/en

[11] Brinke JWT, Debnath SC, Reuvekamp LAEM, Noordermeer JWM. Mechanistic aspects of the role of coupling agents in silica-rubber composites. Compos Sci Technol 2003;63:1165-1174. https://doi.org/10.1016/S0266-3538(03)00077-0

[12] Jin J, Noordermeer JWM, Blume A, Dierkes WK. Effect of SBR/BR elastomer blend ratio on filler and vulcanization characteristics of silica filled tire tread compounds. Polym Test 2021;99:107212. https://doi.org/10.1016/j.polymertesting.2021.107212

[13] Narayan SPA, Palade LI. Modelling Payne effect with a framework of multiple natural configurations. International J Eng Sci 2020;157:103396. https://doi.org/10.1016/j.ijengsci.2020.103396

[14] Menezes F, Passador FR, de Mello SAC. Effect of phthalate-free plasticizer addition on thermal, mechanical, and aging properties of nitrile rubber (NBR). J Elas Plas 2024;56:293-308. https://doi.org/10.1177/00952443241236912

[15] Junkong P, Morimoto R, Miyaji K, Tohsan A, Sakaki Y, Ikeda Y. Effect of fatty acids on the accelerated sulfur vulcanization of rubber by active zinc/carboxylate complexes. RSC Advances 2020;10:4772-4785. https://doi.org/10.1039/C9RA10358A

[16] Eslami Z, Elkoun S, Robert M, Adjalle K. A review of the effect of plasticizer on the physical and mechanical properties of alginate-based films. Mol 2023;28:6637. https://doi.org/10.3390/molecules28186637

[17] De Carvalho AP, Dos Santos HF, Ribeiro GD, Hiranobe CT, Goveia D, Gennaro EM, Paim LL, Dos Santos RJ. Sustainable composites: analysis of filler-rubber interaction in natural rubber-styrene-butadiene rubber/polyurethane composites using the Lorenz-Park method and scanning electron microscopy. Polym 2024;16:471. https://doi.org/10.3390/polym16040471

[18] Park SS, Kil SG, Jang BM, Song KC. Influence of amine base dispersing agent on properties of silica filled rubber compounds. Polym Korea 2001; 25:503-511. https://www.researchgate.net/publication/297473393_Influence_of_amine_base_dispersing_agent_on_properties_of_silica_filled_rubber_compounds

[19] Dutta NK. Effect of plasticizer concentration on the hysteresis, tear strength and stress-relaxation characteristics of black-loaded rubber vulcanizate. Colloid Polym Sci 1991;269:331-342. https://doi.org/10.1007/BF00654580

[20] Sae-oui P, Suchiva K, Sirisinha C, Intiya W, Yodjun P, Thepsuwan U. Effects of blend ratio on SBR type on properties of carbon black-filled and silica-filled SBR/BR tire tread compounds. Adv Mat Sci Eng 2017;1:2476101. https://doi.org/10.1155/2017/2476101

[21] Wen Y, Yin Q, Jia H, Yin B, Zhang X, Liu P, Wang J, Ji Q, Xu Z. Tailoring rubber-filler interfacial interaction and multifunctional rubber nanocomposites by usage of grapheme

oxide with different oxidation degrees. Compos Part B: Eng 2017;124:250-259. https://doi.org/10.1016/j.compositesb.2017.05.006

[22] Moretto E, Stoffels C, Federico CE, Roge V, Staropoli M, Imiete IE, Audinot JN, Steiner P, Duez B, Lenoble D, Thomann JS. Interplay of region-selectively modified dendritic silica particles with styrene-butadiene rubber: the route towards better tires with lower rolling-resistance and higher grip. Chem Eng J 2023;461:141964. https://doi.org/10.1016/j.cej.2023.141964

[23] Kim MC, Adhikari J, Kim JK, Saha P. Preparation of novel bio-elastomers with enhanced interaction with silica filler for low rolling resistance and improved wet grip. J Clean Prod 2019;208:1622-1630. https://doi.org/10.1016/j.jclepro.2018.10.217

[24] Bernal-Ortega P, van Elburg F, Araujo-Morera J, Gojzewski H, Blume A. Heading towards a fully sustainable tire tread compound: use of bio-based resin. Polym Test 2024;133:108406. https://doi.org/10.1016/j.polymertesting.2024.108406

[25] Araujo-Morera J, Santana MH, Verdejo R, Lopez-Manchado MA. Giving a second opportunity to tire waste: an alternative path for the development of sustainable self-healing styrene-butadiene rubber compounds overcoming the magic triangle of tires. Polym 2019;11:2122. https://doi.org/10.3390/polym11122122

[26] Bernal-Ortega P, Gaillard E, van Elburg F, Blume A. Use of hydrocarbon resins as an alternative to TDAE oil in tire tread compounds. Polym Test 2023;126:108168. https://doi.org/10.1016/j.polymertesting.2023.108168