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Research article

Vulcanization kinetics and reinforcement behaviour of natural rubber-carbon black composites: Addition of Shea-butter versus aromatic oil as plasticizers

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ABSTRACT

This work is a comparative study between Shea butter (SB) and treated distillate aromatic extract oil (TDAE) as plasticizers in the vulcanization of natural rubber (NR)- carbon black (CB) vulcanizates (—CB—S—NR—). The plasticized —CB—S—NR— composites extended scorch (Ts2) and optimum (T90) curing times. The delays in crosslinking reaction were suspected to be due to the increased viscosity (ML) and insulation of the reacting species (NR, CB, Sulfur and other curing aids) by the films of plasticizers. This effect increased the activation energy (Ea (KJ/mol)) for vulcanization. The —CB—S—NR— without plasticizer SB (SBO), showed higher ML, crosslinking density index (ΔM), rheological strength (MH) and low cure reversion properties than others. In comparison, the SB loaded —CB—S—NR— composites showed improvement in ML, ΔM, T90, with lowers Ea (KJ/mol) than TDAE samples. Also, the SB compounds exhibited higher Young's modulus Eo(MPa) than SBO and TDAE compounds. For instance, the Eo(MPa) of SB5 was over 7 and 1200 % higher than SBO and STD5 respectively. However, —CB—S—NR— filled with TDAE generally showed higher strength(MPa), attributed to stronger CB—NR interactions. Therefore, environmentally friendly SB could replace petroleum based oils for compounding rubbers.

1. Introduction

Rubber matrices would be useless for most applications if filler reinforcements were not incorporated into them to form synergy compounds. Traditional reinforcements such as; carbon blacks (CB) [1–3], silica [4,5], nano-clays (NCL) [6,7] and the new ones like the carbon nanotubes (CNT) [8–10], graphene (G) [11,12] and boron nitrite nanotubes [13,14] etc others, have been used to form

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composites with elastomers. Usually, higher concentration (≤ ~ 5–70 phr (part per hundreds of rubber)) of the traditional fillers (CB, NCL etc.) is required to achieve high reinforcing action [1,15]. This is typically for rubber compounds intended for rubber products like automobile parts (sidewall, tread, gaskets) [1,16], and industrial hoses [17,18].

The reinforcement is defined by the level and mode of interactions between the filler and the matrix, which are explained in terms of the hydrodynamic effect (viscosity) [19], the filler-matrix [4,20] and filler-filler [21–23] interactions. The level and mode of reinforcement action in elastomeric composites, compounded using desired plasticizer in addition to higher degree of curing, have significantly been connected with the properties and the cost of the final product[1,15].

A number of elastomeric matrices including; ethylene propylene-diene monomer (EPDM) [24,25], acrylonitrile butadiene rubber (NBR) [6,26], styrene-butadiene rubber (SBR) [27–29], natural rubber (NR) [4,30–32] and their blends (NBR/EPDM [33–35], NR/EPDM [36] and NR/SBR [3,37] etc.); have been tailored for property enhancements, by incorporating into them various kind of reinforcements [1,38].

Highly filled rubber compounds usually exhibit high viscosity, leading to hardening/stiffening [1,15,38]. This result in difficulties in mixing the processing aids with the rubber matrix with the processing machines. Besides poor dispersions, high energy may be used for the mixing, thereby increasing the cost of production. These difficulties have been resolved by using softeners or plasticizers to reduce the viscosity, improve mixing and filler dispersions [1,39,40]. List of plasticizers used for this purposes include; dioctylphthalate (DOP), tricrecylphosphate (TCP), dioctyladipate (DOA) and the oils or petroleum based oils (PBO) like aromatic, naphthenic and paraffinic [39,40].

The PBO, like the Treated Distillate Aromatic Extracted (TDAE) and their derivatives are popularly used as plasticizers in the rubber manufacturing industries [1,41,42], probably due to their compatibility with various unsaturated rubber matrices such as; NR, SBR, bromo-isobutylene-isoprene rubber (BIIR) and filler dispersion efficiency [27,43].

However, it is preferable to use plasticizers from renewable sources rather than from fossil petroleum type. Such approach will be beneficial as it will lead to the limitations of the CO_2 emissions in the atmosphere [5,44]. Thus, an investigation for new plasticizer substitute, which is renewable, eco-friendly, effective and cheaper, should be a concern to rubber processing companies around the world (Vis; Goodyear, Cooper Tire, and Firestone etc.) who have been using the PBO in great quantities [39,40].

Petrović group [45] earlier explored the use of Soybean oils for compounding rubber and obtained interesting results. Pechurai et al. [46], reported that although, castor and jatropha oil caused a reduction in 100 % modulus and hardness in SBR compounds, however higher cure rates, abrasion resistance, and resilience were observed compared to those prepared with PBO. The recent review work by Sovtić et al. [47] on effect of vegetable oil (VO) on NR and the work of Roy and Ribeiro et al. [48,49] concluded that the VO may be the future plasticizer for rubber compounding, owing to the competitive properties exhibited over PBO. Shea-butter (SB) is another type of VO, which is a complex organic fat extract that comes from the nuts of the Shea trees, commonly grown in savannah region in West and East of Africa [50,51]. Market survey had indicated that exporters pay less than US$0.75 per kg (2.2 lbs) for traditional locally sold SB in Africa [50,51], thus making the material relatively cheaper than the PBO.

Earlier, the effect of palm oil vegetable oil in polar and non-polar rubber was explored by Mensah et al. [52], and it was observed that the palm oil was very compatible with polar matrix. Similarly, Doaa et al. showed that fruit and vegetable oils could replace petroleum-based hazardous oils in the rubber sector, as NBR rubber plasticized with fruit and vegetable oil demonstrated superior thermal stability relative NBR rubber plasticized using petroleum oil [53].

However, this present work seeks to investigate the influence of SB on the vulcanization properties/kinetics of natural rubber (NR)-carbon black (CB) vulcanizates (—CB—S—NR—) composites in comparison with those prepared with TDAE oil. The compounds were prepared by melt mixing technique using internal mixer and two-roll mill, after which they were vulcanized in a metal plate by using hot-press machine. The compounds were cut into standard dimension and characterized based on curing, morphology and bound rubber etc. The results obtained gives an insight on the possibility of using VO for compounding highly filled elastomeric composites materials for advanced applications.

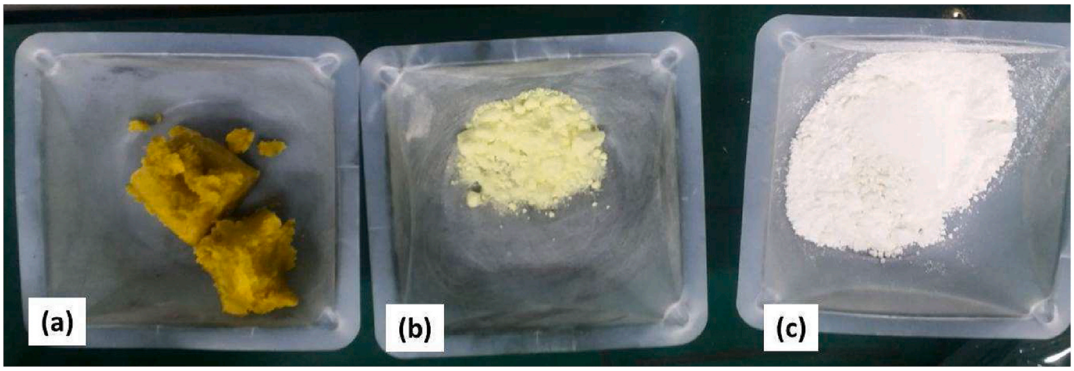

Fig. 1. Display of some of the processing ingredients for compounding the matrix; (a) hardened Shea butter (SB), (b) sulfur (S) and (c) *zinc oxide (*ZnO) powder.

2. Experimental

2.1. Materials used

Natural rubber (NR) was obtained from Doo Man Co. Ltd, South Korea, Carbon black N550 (with the specific surface of 95–105 m^2/g), and Aromatic oil (TDAE, dark brown, KUKDONG OIL & CHEMICAL CO. Ltd.) were obtained from IDONG TECH. The curing ingredients; zinc oxide (ZnO), Stearic acid (SA), Sulfur (S), tetramethyl thiuram disulfide (TMTD), and N-cyclohexile 2-Benzotiazole Sulfonamide (CZ) were all obtained from INFO CHEM CO. LTD. The Shea nuts were purchased from the local market in Ghana (Madina market) and the butter was extracted from the nuts in the laboratory following the same method earlier reported [50,51,54]. The hardened SB is as shown in Fig. 1a together with other processing aids.

2.2. Compounding process

The compounding of the composites was done in a kneader (model: QPBV-300, QMESYST, Yun Tech Co.Ltd., Seoul, South Korea) at 90 °C and 30 rpm. The natural rubber (NR) matrix was masticated in the kneader for 1 min, and all the processing ingredients were added one after the order and mixed for ~2 min. Later, the N550 was incorporated and mixed for additional 1 min. The composition was passed over a two-roll mill (QM300, QMESYSTEM, Yun Tech Co.Ltd., Seoul, South Korea) repeatedly whilst sulfur was gradually added. The roll mill mixing was done for ~9 min and then sheeted out. The cure rheometer was used to vulcanize the samples at 160 °C. The optimum curing time obtained from the rheo-curves was used to mold the samples in a rectangular metal mold with dimension 15 cm × 15 cm and thickness of 2 mm, by using electrical hot press machine at a pressure of 25 Tons. The samples were cut into standard shapes and subjected to further tests. The compounds prepared with the Shea butter oil, expressed as parts per hundred parts of rubber (phr) with their respective codes are listed in Table 1.

3. Characterization

3.1. 1Vulcanization behaviour of compounds based on cure rheometer curves

The —CB—S—NR— nanocomposites filled with different amounts of Shea butter (SB) were vulcanized at four different temperatures; 155, 160, 165 and 170 °C by using moving die oscillating-die rheometer (MDR, model: PDR2030, TESTONE, Yun Tech Co.Ltd., Seoul, South Korea). Later, the various curing parameters which include; maximum torque (M_H), minimum torque (M_L), change in torque ($\Delta M = M_H - M_L$), scorch time (t_{s2}), and optimum cure time (t_{90}) were determined from the rheo-curves. The curing rate index (CRI) was also computed by equation (1).

$$\mathrm{CRI} = 100/(t_{90}-t_{s2}) \tag{1}$$

3.2. Vulcanization kinetics based on autocatalytic model

The cure kinetic behaviours of the shea-butter (SB) compounds and representative samples prepared with the PBO (TDAE) were further studied using the autocatalytic model. The rheometer cure properties (torque and cure time) were used to compute the degree of curing (α), rate of curing (dα/dt), and the activation energies of the various cured compounds. The classical differential model for rubber curing reaction was proposed by equation (2) [55];

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $d\alpha/dt$ is the vulcanization rate, t the time, $k(T)$ the specific rate constant at temperature T, and $f(\alpha)$ is the function related to the phenomenological kinetic model. The degree of crosslinking, α, given by equation (3), was deduced from the cure rheometer study

Table 1
Compound formulation and their codes measured in (phr)[a].

Chemicals	SBO	SB5	SB10	SB20	SB40	STD5	STD40
NR	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5
TMTD	1	1	1	1	1	1	1
CZ	0.5	0.5	0.5	0.5	0.5	0.5	0.5
S/A	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	2.1	2.1	2.1	2.1	2.1	2.5	2.5
N550	50	50	50	50	50	50	50
Shea butter	–	5	10	20	40	5	40
Wax	1	1	1	1	1	1	1

[a] (parts per hundred parts of rubber).

[56];

$$\alpha = \frac{M_t - M_0}{M_\infty - M_0} \tag{3}$$

Where M_0 M_t, and M_∞ are the torque values at the time zero, at a given time t of curing, and at the end of crosslinking, respectively. equation (3) is based on the idea that crosslinking density is proportional to the stiffness of the rubber vulcanizates [57]. The function $k(T)$ in equation (2) is related to the activation energy, E_a(KJ/mol) by the Arrhenius equation (4);

$$k(T) = k_0 e^{-E_a/RT} \tag{4}$$

where k_0 is a pre-exponential factor, E_a, the activation energy, and R (8.314 J mol^{-1} K^{-1}) is the universal gas constant. The nth order kinetics of chemical reaction, $f(\alpha)$ based on Borchardt and Daniels, is given by equation (5) [58];

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where n is the order of reaction. For a multi-step curing reaction such as the vulcanization reactions in this present study, equation (4) can be written as;

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{5}$$

where m and n are both orders of reaction. Fitting equation (5) into equation (2) will yield the vulcanization kinetics for an auto-catalytic reaction used in this study;

$$\frac{d\alpha}{dt} = k(T)\alpha^m (1 - \alpha)^n \tag{6}$$

3.3. Morphology and state of dispersion of CB in NR by using scanning electron microscopy (SEM) analysis

The various compositions (SBO, SB5, SB10, SB20, SB40, STD5 and STD40) were fractured cryogenically by using liquid nitrogen. Their fractured surfaces were coated with platinum via sputtering technique. The effect of oil and the butter in the dispersion efficiency of carbon black (CB) in the natural rubber (NR) matrix were then observed with field emission SEM (JEOL, JSM 599, Japan) obtained from JBNU, South Korea.

3.4. Tensile properties

The tensile strength (MPa) of the various compositions (SBO, SB5, SB10, SB20, SB40, STD5 and STD40) was measured according to ASTM D412 standard by using (QM100s machine, QMESYSTEM, Yun Tech Co.Ltd., Seoul, South Korea) at a cross-head speed of 500 mm/min and at room temperature. Average of three samples for each composition tested was reported. The Young's modulus, E_o (MPa) for representative compositions (SBO, SB5 and STD5) were determined from the stress-strain curves at strain ~ 0.6 %. Also the ratio (E_o/E_1), which represents the initial modulus, E_o(MPa) and the steady-state or equilibrium modulus, E_1(MPa) for representative

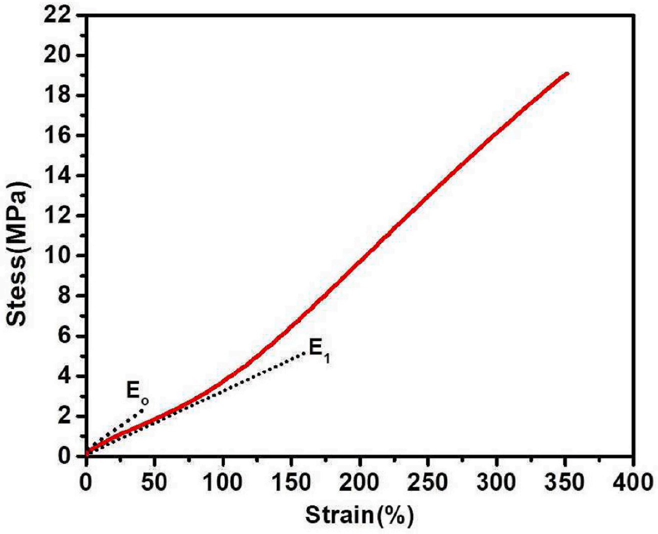

Fig. 2. Illustration of Young's modulus (E_o) and the steady-state slope (E_1).

compositions (SBO, SB5 and STD5) were determined from the stress-strain curve such as shown in Fig. 2.

The total crosslinking density (N_t), which include both chemical and physical interactions in the bulk compositions were determined for representative samples by using the following classical equation (7) [59].

$$E_o = 3N_tRT \tag{7}$$

where R is the universal gas constant ($8.314 JK^{-1}mol^{-1}$), T is absolute temperature (273K).

4. Results and discussion

4.1. State of dispersion of CB in NR in presence of SB/TDAE oil by using SEM analysis

To examine the state of the dispersion of CB within NR, in the presence of SB and TDAE, SEM images of representative samples SBO, SB5 and STD5 are shown in Fig. 3 (a-c). CB particles cannot be seen at the fractured surfaces, as the CB particles may be coated with rubber molecules or deeply embedded within the matrices. This makes it difficult to physically conclude on the nature of CB dispersions within the NR matrix. However, it can clearly be seen that, SBO shows relatively rougher surface morphology than the rest.

The rough surface may be due to difficulties encountered in cryo-fracturing of the samples, owing to strong CB—NR interactions [1]. Such surface morphologies are strain induced, and could be an indication of high mechanical strength behaviour [12,60]. The order of decreasing surface roughness is: SBO > SB5 > STD5. Generally, plasticizer increases the flow of the rubber matrices and therefore reduces filler-matrix interactions [46,61,62], hence this trend is expected. It is interesting to observe that SB5 is showing relatively rougher surface compared to STD5, suggesting that in the presence of SB, there may be tighter structures (CB—S_x—NR and/or CB—S_x—CB) than in the case of TDAE.

4.2. Effect of Shea-butter on cure-rheological properties

The effect of SB and TDAE on the curing properties of the representative composites (—CB—S—NR—) were studied with cure rheometer. The representative rheo-curves at 155 and 165 °C are shown in Fig. 4a and b respectively. The differences in curing properties like; on-set of curing, T_{s2} (min), optimum curing time, T_{90} (min), minimum torque or viscosity index (M_L) and maximum torque (M_H) etc., which were deduced from the rheo-curves have been discussed in detailed.

4.2.1. Scorch time (T_{s2})

The effects of Shea-butter (SB) and aromatic oil (TDAE) on T_{s2} (min) (on-set of curing) of natural rubber (NR)-carbon black (CB) composites (—CB—S—NR—), were deduced from rheo-curve at 155, 160, 165, and 170 °C and compared respectively in Fig. 5(a–d). The T_{s2} is seen increasing as loading of the SB increases with reference to the compound without SB (SBO). However, as temperature gets higher, T_{s2} (min) begins to decrease, although it still increases with respect to the loading of SB.

The initial delay (T_{s2}) of rubber nanocomposites is related to high viscosity, which slows down crosslinking reactions [63]. Although, the SB and TDAE oil lowers this viscosity, yet longer T_{s2} are observed. This indicates the SB and TDAE acted as cure retarders during the crosslinking process [46,64]. When compared, the SB based compounds have shorter T_{s2} (min) than the representative samples of the TDAE. However, delays in scorch time are usually good for the cure safety of the final product [1,52] as enough time is allowed for the curatives to melt well before initiating crosslinking reactions. The t_{s2} obtained for the SB/TDAE filled compounds are comparable to those obtained for standard tire and tread compounds earlier reported [1,44].

4.2.2. Optimum curing time (T_{90})

The results of the effects of Shea-butter (SB) and aromatic oil (TDAE) on the optimum curing time (T_{90} (min)) of natural rubber (NR)-carbon black (CB) composites (—CB—S—NR—), deduced from rheo-curves at 155, 160, 165, and 170 °C respectively are compared in Fig. 6(a–d). Increasing the content of SB and TDAE, generally increases the T_{90} (min) of the composites which is expected in rubber processing technology, when plasticizers effects are considered [1,27,44,46]. This is similar to the recent study on soybean oil fatty acid (SBOFA) loaded-NBR vulcanizates by Nun-Anan et al. [65], who observed an increment in T_{90} (min) compared to the

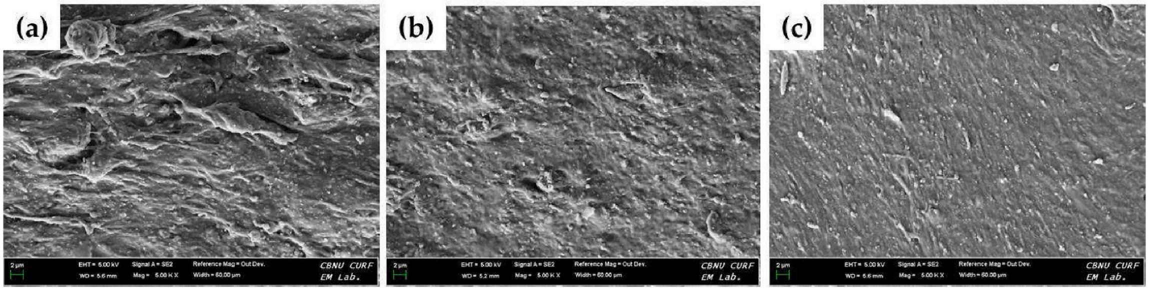

Fig. 3. Surface morphologies of representative samples; (a) SBO (b) SB5 and (c) STD5.

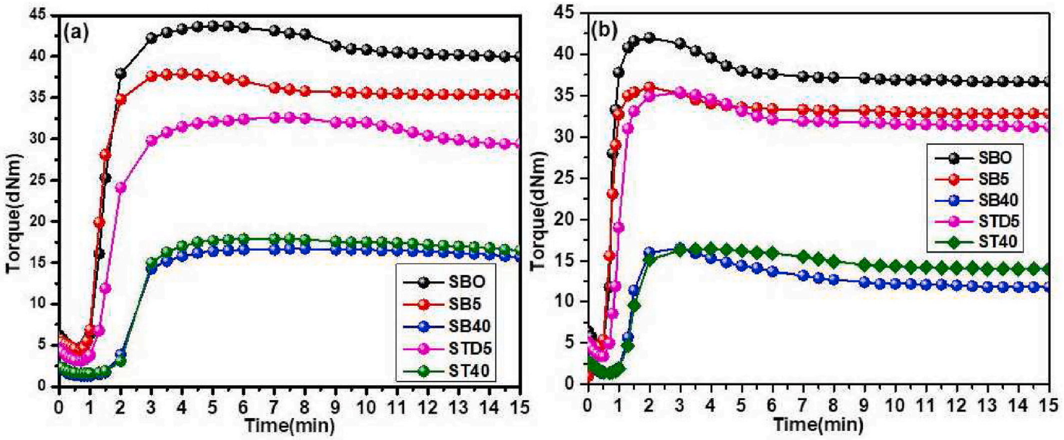

Fig. 4. Comparing the cure properties for the compositions(s) representative rheo-curves at 155° and (b) cure reversion at 155–177 °C.

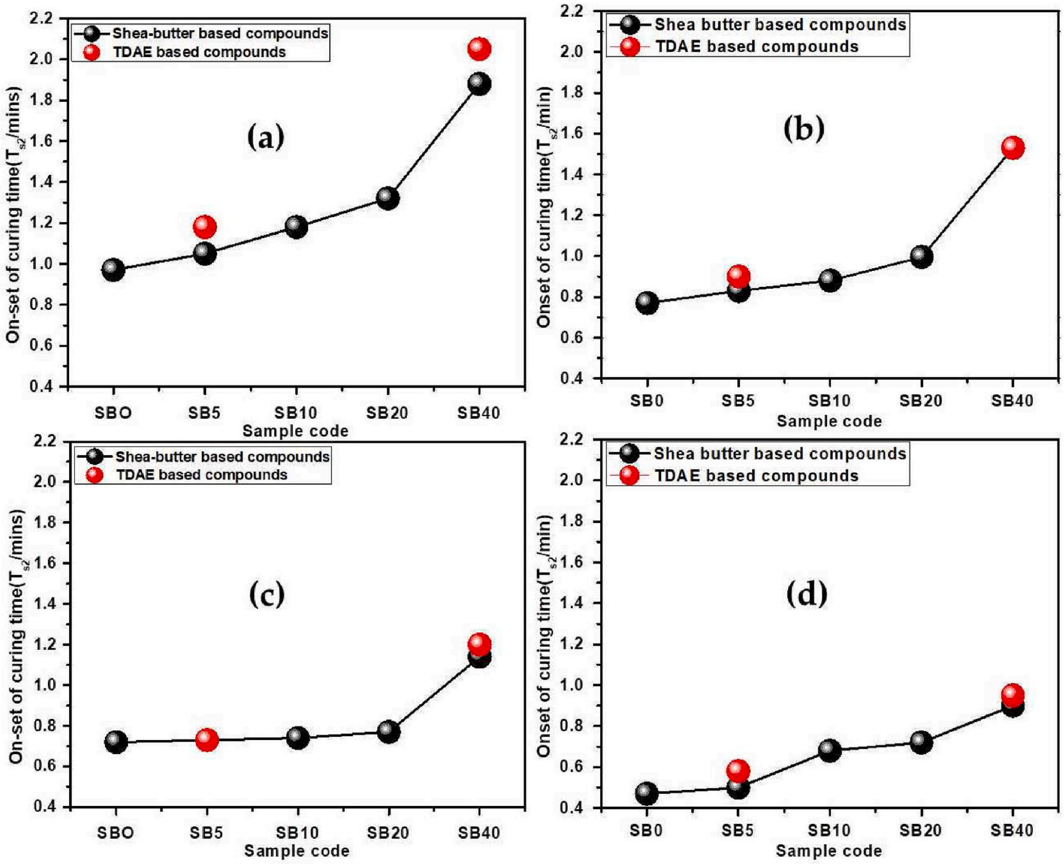

Fig. 5. Comparing the scorch time (T_{s2}) of compounds at difference temperatures; (a) 155 °C, (b) 160 °C (c) 165 °C and (d) 170 °C.

compound without SBOFA. From Fig. 6 (a-d), as temperature increases, the T_{90} (min) for all the samples drops, similar to those reported for DAE oil-filled NR by Hayichelaeh et al. [62].

The reduction in T_{90} (min) at higher temperatures may be linked to high reactivity of the curatives, the CB and the unsaturated NR, in the presence of SB or the TDAE oil [57,66]. With regards to delays of T_{90} (min) for plasticized rubber compounds, it is widely established that plasticizers (vegetable oils) contains fatty acids with unsaturated sites which can consume the sulfurating or cross-linking species [1,27,44,46,62,67], thereby lengthening T_{90} (min). Fig. 7 (a-d) is proposed in support of the explanation for the delays in T_{90} (min) for plasticized rubber compounds involving SB or TDAE. In the absence of plasticizer oils, a typical unsaturated sites

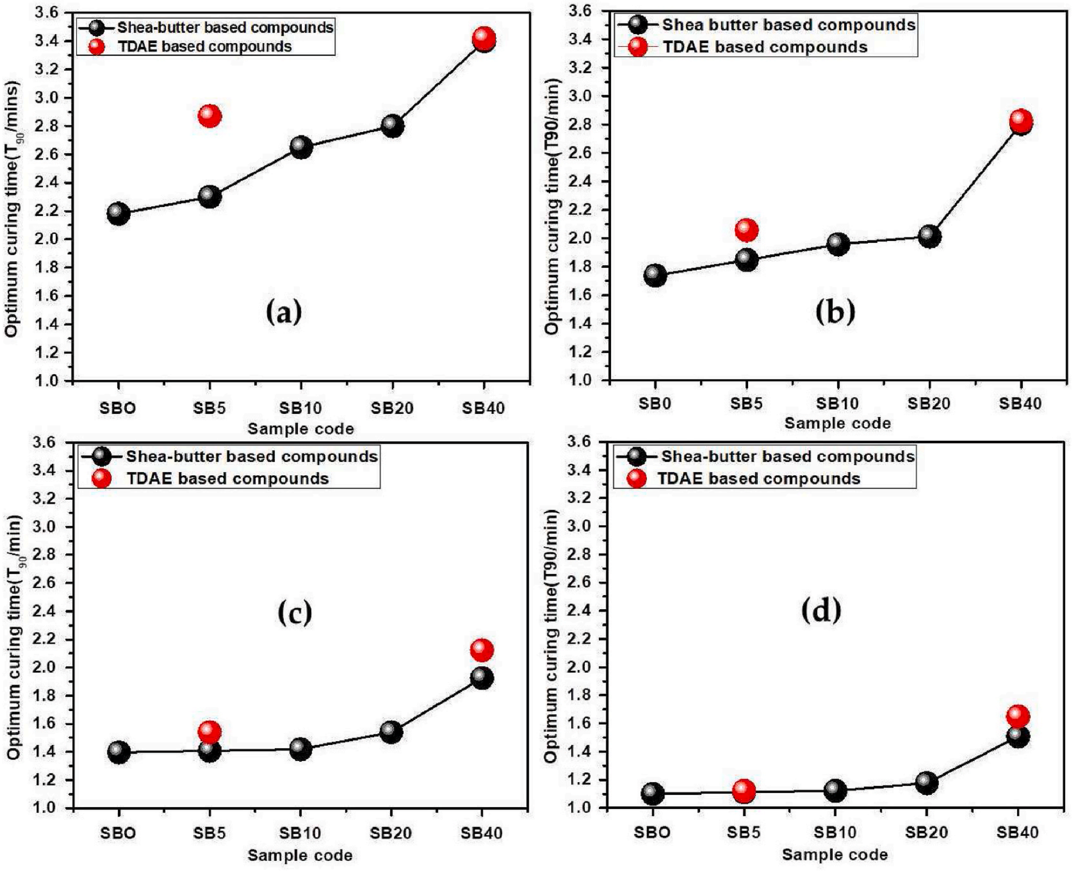

Fig. 6. Comparing the T_{90} (min) of compounds at difference temperatures (a) 155 °C, (b) 160 °C (c) 165 °C and (d)170 °C.

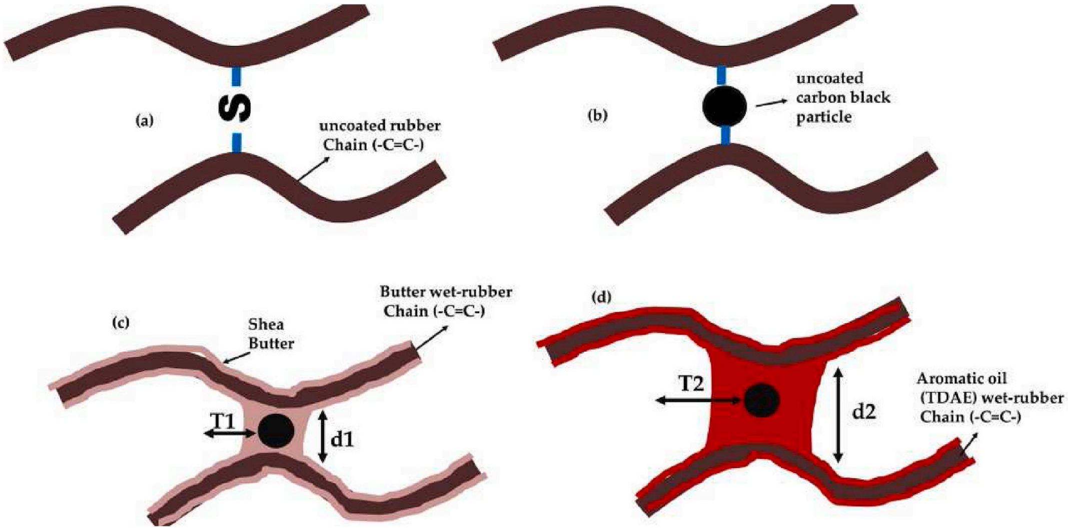

Fig. 7. A depiction of crosslinks formation in unsaturated rubber with CB; (a) crosslink of the virgin matrix (NR—S—NR) (b) crosslink of NR in presence of CB (CB–S—NR) (c) cross-section view of slightly SB-wetted CB interacting with –C═C— sites and (d) cross-sectional view of largely TDAE-wetted CB in-between adjacent (—C═C—) of the chains.

(—C═C—) of elastomers like NR or SBR can readily be attacked by sulfurating species at high temperatures, resulting in the formation of crosslinks (NR—S—NR or —C—S—C—), as depicted in Fig. 7a. It is also possible for the CB particles to bond with these (—C═C—) sites [21,22] forming CB—S—NR interactions and with themselves (—CB—S—CB— or —CB—CB—), leading to tighter structures [21, 22], as shown in Fig. 7b.

Moreover, the coating or oiling of either the curatives including the filler and the unsaturated sites (—C═C—) of NR by the SB and TDAE oil, could act as blockages for crosslinking reactions to progress. When compared, the SB based compounds exhibit shorter T_{90} (min) than the representative TDAE based compounds. Thus, it can be assumed that, much lighter or moderate coating of the CB particles or the –C═C— sites might have occurred (Fig. 7c) in the presence of SB than in the case of TDAE, probably due to viscosity difference. Therefore, it was relatively easier for the SB-coated curatives, –C═C— sites and the CB to undergo crosslinking reactions faster than in the case of TDAE (Fig. 7d), where coatings of these interacting species might have been be thicker (T2, d2 > T1, d1).

Evidence of oil-coated CB was earlier studied by Powell et al. [68]. It was observed that these oil-coated CB particles could actually coagulate or scatter, depending on the oil medium. In other words, the thermal breakdown of the curatives and NR during crosslinking reactions could be extended, as they seem to be insulted with SB or TDAE oil. Further, the differences in thermal conductivity behavior of the SB [69] and TDAE oil [70], could explain the differences in T_{90} (min) obtained for respective compounds. Comparatively, the current composition have exhibited shorter T_{90} (min) $< \sim 4$ min than the tire tread compounds consisting of rubber blends reinforced with CB and silica in the presence of TDAE oil, which recorded T_{90} (min) of ~8 min [1]. The —CB—S—NR— composites in the presence of SB or TDAE have exhibited lower T_{90} (min) than those reported for NBR-organo-modified and unmodified nanoclays, which recorded T_{90} within ~6–26 min, vulcanized at 160–170 °C [66]. They also exhibited shorter T_{90} properties compared to peroxide cured NR—CB composites which were prepared with Soybean oil [64] and that of NR—CB without plasticizer oil, reported by TK and Pal et al. [71,72]. Therefore, the present compounds have demonstrated high performances in terms of $T_{90,}$ even in the presence of the SB than TDAE oil.

4.2.3. *Effect of Shea-butter and curing temperature on cure rate index*

The effects of Shea butter (SB) and aromatic oil (TDAE) on the cure rate index (CRI) was computed with equation (1) for the various compositions as compared in Fig. 8(a–d). As seen, increasing the SB and TDAE content generally decreases the cure rate index (CRI), with reference to the compound without oils (SBO). As curing temperature increases, higher CRI are seen compared to the lower

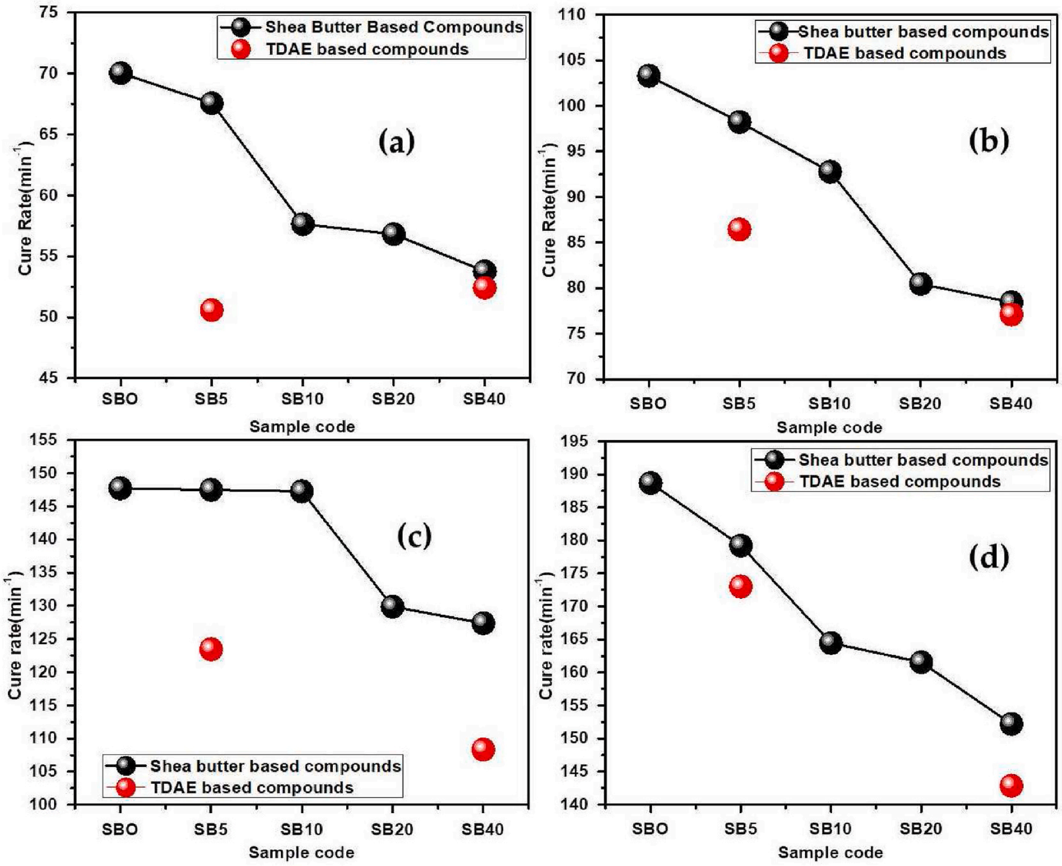

Fig. 8. Comparing the cure rate index (CRI) of the vulcanizates at different temperatures (a) 155 °C, (b) 160 °C (c) 165 °C and (d)170 °C.

temperature conditions. At this high temperature conditions, melting of the cure ingredients occurs together with the flow of the matrix, the reactivity and the interactions with backbone of NR (—C═C—) and with CB increases [1,54].

The SB based compounds, thus exhibit relatively high CRI compared to the representative samples of TDAE. The present compositions have exhibited high CRI than the tire tread compounds (ENR/SBR/polybutadiene rubber (BR)-CB-Silica composites) prepared with 10 phr TDAE oil, reported by Mensah et al. [1], peroxide cured NR-CB-Soybean oil [64] and that of NR—CB without plasticizer oil [71,72]. This confirms the competitiveness of SB as potential plasticizer for compounding rubber composites.

4.2.4. *Effect of Shea-butter and curing temperature on viscosity index (M_L)*

The influence of SB and TDAE oil on the minimum torque or viscosity index (M_L) of the various compounds at 155–170 °C, are compared in Fig. 9(a-d). Clearly, increasing the SB or the TDAE content significantly decreases the M_L of the respective compounds, especially when compared with the reference compound (SBO). By comparing SB and TDAE based compounds, the SB compounds exhibit higher M_L than the TDAE compounds, significantly at higher vulcanization temperatures for the low oil loaded samples (5 phr plasticizer oils). At higher oil content (40 phr), comparable results are generally observed except at 165 °C, where STD40 was higher than SB40, probably due to thermal instability and high reactivity of the compounds, just as observed for natural rubber-graphene composites [63].

Although, higher M_L is related to higher mechanical properties [15,54], the role of plasticizers is to lower viscosities for easy mixing of the ingredients (curatives and fillers) with the rubber matrix; hence the design of an optimised rubber compound must involve controlled M_L properties, in order not to compromise the physico-mechanical properties of the final product. For the same curing temperature, the M_L obtained by NR—CB loaded with 10 phr of Soybean oil and DAE [64] and those reported for NR—CB (35 phr) which does not contain plasticizer oil which recorded M_L of ~1.5 dNm [71] were lower compared to those reported in this current work.

4.3. *Curing kinetics study*

The plots of the dα/dt versus degree of conversion (α) for SBO are shown in Fig. 10a for temperatures 155, 160,170 and 170 °C

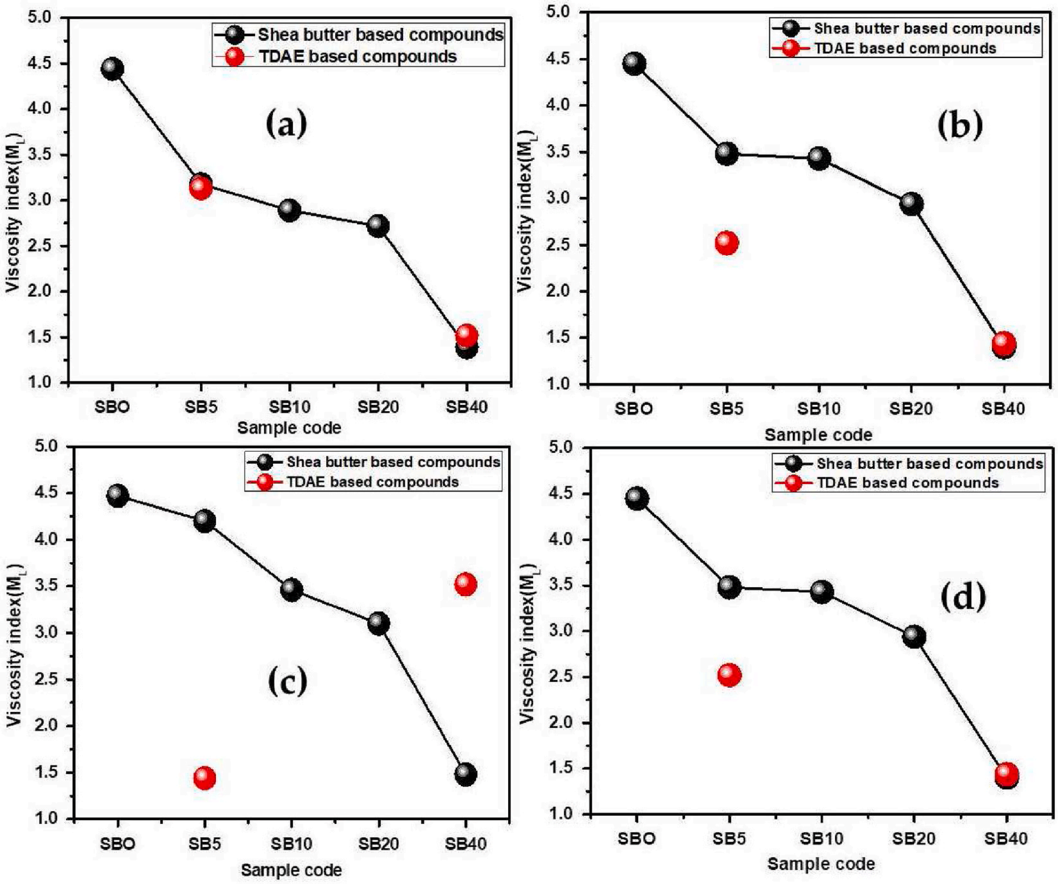

Fig. 9. Comparing the viscosity index (M_L) of the vulcanizates at difference temperatures (a) 155 °C, (b) 160 °C (c) 165 °C and (d)170 °C.

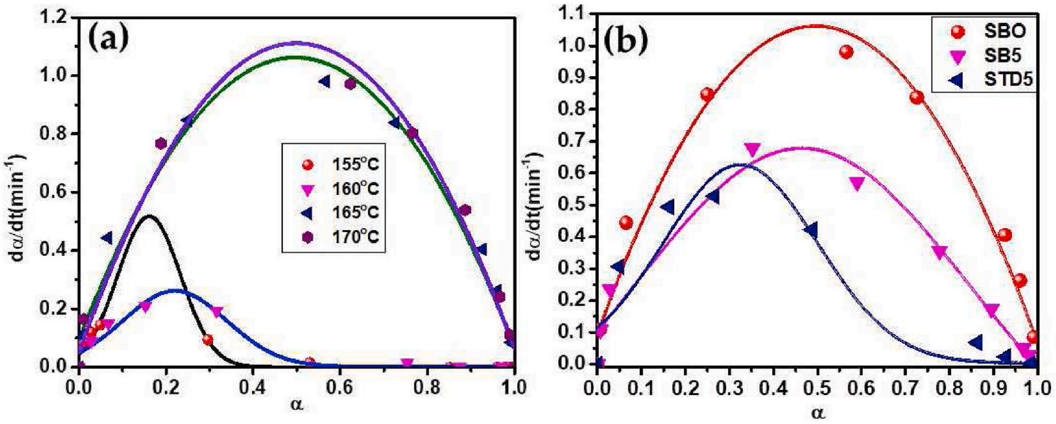

Fig. 10. The plots of dα/dt versus degree of conversion (α) for SBO at 155–165 °C and (b) comparing dα/dt versus α for SBO SB5 and STD at temperature of 165 °C.

respectively. The dα/dt generally increases with conversion (α) as temperature increases. The delay of conversion (α) at lower temperature is due to hindrance of crosslink formation between adjacent rubber chains as a result of high viscosity [66]. It was also observed that, the degree of conversion was associated with shorter curing times due to higher viscosities at higher temperatures. The plots of dα/dt versus degree of conversion (α) for representative samples; SBO, SB5 and STD5 at temperature of 165 °C are compared in Fig. 10b. It is clear from Fig. 10a that the dα/dt increases with the degree of conversion (α) and passes through maximum (0.5) points for the 165 °C, between 0.4 and 0.6. This simply suggests that the vulcanization reaction indeed follows the autocatalytic curing kinetic reactions, as described in equation (6).

The experimental data was fitted using a non-liner regression line with R^2 (correlation coefficient) ~0.96, indicting a very good agreement between experimental and theoretical data in Fig. 10a. In Fig. 10b, SBO shows higher α_{max} followed by SB5 and STD5 respectively. Thus, the decreasing order of faster curing nature of the composites can be written as; SBO > SB5 > STD5. This is in accordance with the scorch time (T_{s2}), optimum curing time (T_{90}) and consequently the cure rate index, CRI (min^{-1}).

The kinetics of vulcanization of the various composites prepared in the presence of SB or TDAE was further examined based on Arrhenius plot of ln$k$ versus 1/T (Fig. 11a), the slope of which is the activation of energy, E_a (KJ/mol) of vulcanization (Fig. 11b). In Fig. 11a, the experimental results fits well with theoretical predictions with strong correlation coefficient (R^2~0.99). The SBO shows intersections of the curve as temperatures increases, thus, curing of SBO seems to be best at lower temperatures.

From Fig. 11b it can generally be seen that, increasing either SB or TDAE content raises the E_a (KJ/mol). The SB compounds relatively lowered the E_a (KJ/mol) for vulcanization as compared to the TDAE based compounds. This observation may be due to the slightly SB-wetted CB and sulfurating species which relatively permits crosslinking reactions faster with the –C═C—sites. It appeared, the level of wetting by TDAE, made it difficult for the curatives, CB and adjacent chains to reach out to each other for faster crosslinking to ensue, hence higher E_a (KJ/mol) was significant. The order of increasing activation of energy E_a (KJ/mol) of Palm oil, Soybean oil and DAE was found to be Palm oil < Soybean oil < DAE by Hayichelaeh et al. [67]. This is in correspondence with the current findings

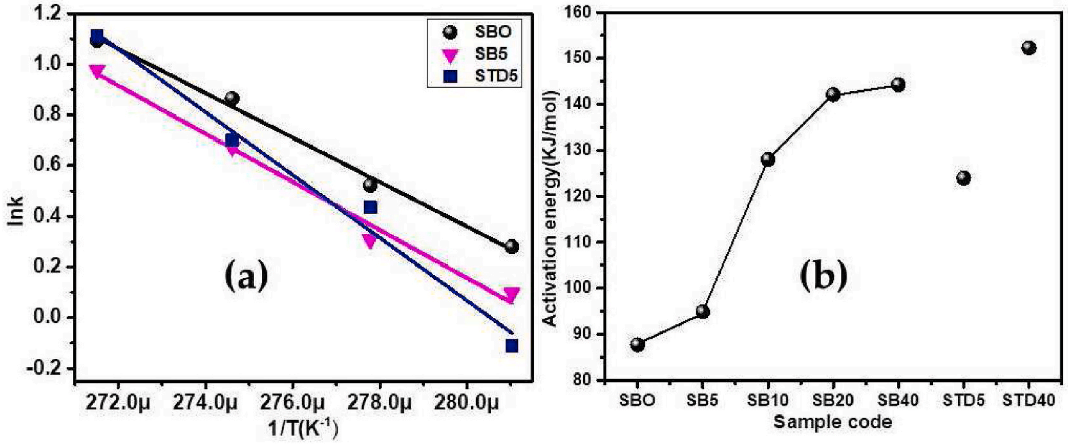

Fig. 11. Vulcanization behaviour of SBO and butter/oil based composites (a) Arrhenius plot of lnK versus 1/T for (b) activation of energy E_a (KJ/mol) for vulcanization for various compositions.

that vegetable oils such as SB, cures faster than aromatic based oil such DAE or TDAE [54].

4.4. *Effect of Shea butter and TDAE oil on physico-mechanical properties of compounds*

4.4.1. *Rheological strength behaviour of compounds*

4.4.1.1. Effect of Shea-butter on torque difference (ΔM) and cure reversion. The torque difference ($\Delta M = M_H$-M_L), which is also related to crosslinking density deduced from the rheo-curves for the various compositions at temperatures of 155–170 °C are compared in Fig. 12a. The effect of plasticizer on the percentage cure reversion for representative compounds at 155–170 °C, computed by using equation (8) [72,73] is shown in Fig. 12b.

$$\text{Reversion }(\%) = \frac{M_{H-M_\infty}}{M_{H-M_L}} \text{ x } 100 \tag{8}$$

Where M_H is the maximum torque, M_L is the minimum torque and M_t is the torque at the end of the vulcanization. As seen, increasing cure temperature decreases the ΔM with increase in the percentage cure reversion (Fig. 12b) of all the vulcanizates, with reference to the standard composition (SBO). Also, increasing the content of the plasticizers also increased the reversion percentage and caused a decreased in the ΔM. The declined ΔM and increased reversion was due to thermal degradation of the crosslinks [72,74,75]. Meanwhile, the cure reversion behavior of NR matrix is well known during vulcanization studies [72,74,75], and it was recently improved by compounding NR with a combination of zinc glycerolate and zinc laurate by Yang et al. [76].

The observed trend in ΔM is similar to those reported by Nun-Anan et al. [65] for NBR-soybean oil fatty acid and the various elastomers loaded with vegetable based plasticizers by Roy et al. [48]. At lower temperatures, the ΔM of TDAE and SB systems seemed comparable but at high temperatures the —CB—S—NR— filled with SB content (SB5 sample) and SB40 generally obtained higher ΔM values compared to their respective counterparts STD5 and STD40 compounds. Thus, SB seems to promote crosslink formation with relatively better anti-reversion behavior than the case of TDAE oil, even at high temperatures.

The present observation contradicts those observed for distillate aromatic extract (DAE) oil plasticized-NR, where higher ΔM was obtained than palm oil (PO) and Soybean oil, reported by Hayichelaeh et al. [62].

Although, the DAE is believed to be very compatible with unsaturated matrices like NR and SBR, DAE contains relatively high level of polycyclic aromatic hydrocarbons (PAHs) like; benzo(*a*)pyrene, benzo(e) pyrene, benzo(*a*)anthracene, chrysene, and benzo(*b*) fluoranthen etc, Some of these PAHs have been classified as carcinogens and therefore banned by European Union since 2010 [62]. The current ΔM results is comparable and mostly better than the those reported by Nun-Anan et al. [65], the recent industrial tire tread design, consisting of various blends of ENR/BR/SBR-filled with CB and Silica in the presence of 10 phr of TDAE oil by Mensah et al. [1], as well as a number of ΔM properties earlier reported for tire treads [5,44].

4.4.1.2. Effect of Shea-butter on mechanical strength index from the rheometer. The maximum torque (M_H), which corresponds to mechanical strength of the various rubber composites filled with She butter and TDAE deduced at 155–170 °C from the rheo-curve are compared in Fig. 13(a–d). As seen, at all levels of temperatures (155–170 °C) the reference sample (SBO) shows higher strength index compared to the butter/oil-filled compounds. This is a common observation with plasticized rubber based compounds, which tends to reduce mechanical related strength such as M_H of vulcanizates [49,62,65]. The M_H for the compounds containing SB and TDAE oil seems to be comparable, as no significant differences between them can be established. Compared to the current results, it is interesting and contradictory to observe that DAE-filled, NR exhibited higher M_H than those filled with or without vegetable oil (palm oil, and

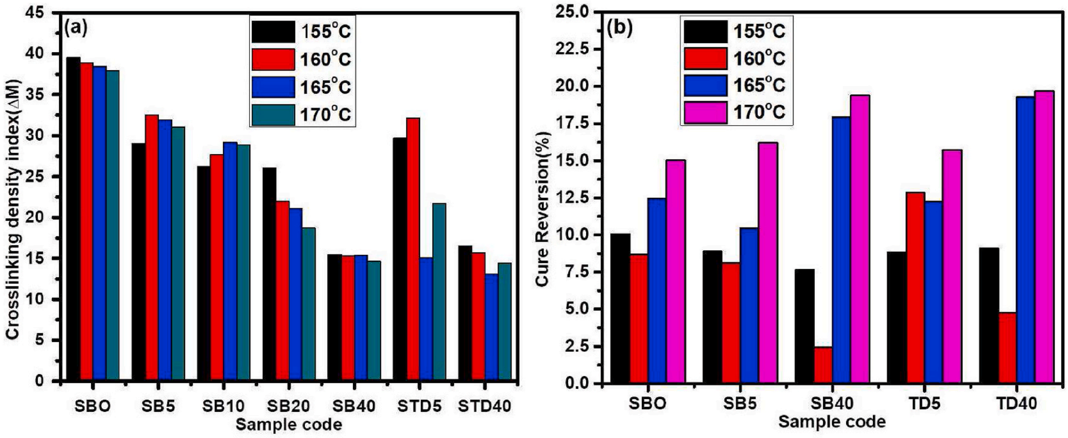

Fig. 12. Comparing cure properties; (a) the crosslinking density index (ΔM) of the vulcanizates at different temperatures 155–170 °C and (b) effect SB on cure reversion of compounds at 155–170 °C.

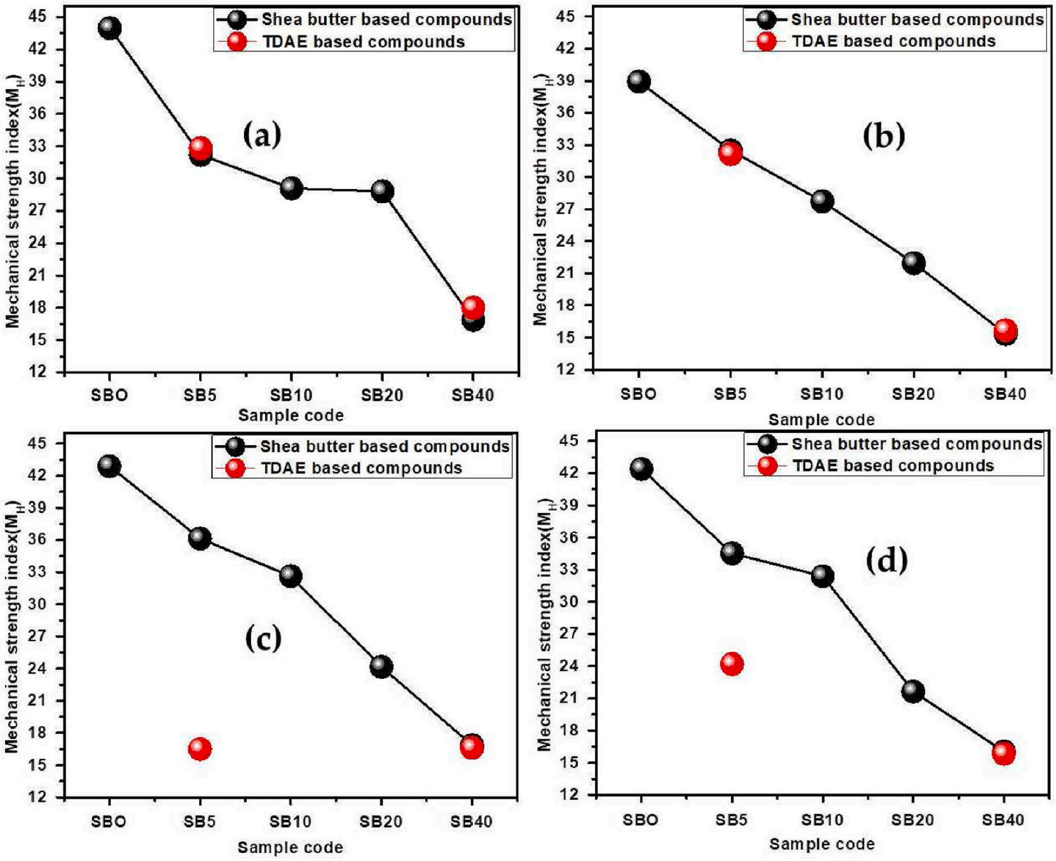

Fig. 13. Comparing the mechanical strength index of the vulcanizates at difference temperatures (a) 155 °C, (b) 160 °C (c) 165 °C and (d)170 °C.

soybean oil) [62,71].

The M_H and ΔM properties obtained in the present study outperforms those reported for peroxide cured NR—CB composites by Hayichelaeh et al. [64]. In cure rheometry analysis, ΔM is due to both physical and chemical interactions [4,21]; hence the controlling factor for the differences in M_H and subsequently ΔM can only be firmly established with successive mechanical tests like; tensile strength and cross-linking density measured by equilibrium swelling tests [54,77].

4.4.2. *Tensile strength behaviour of compounds*

Previously, the comparative study of the effect of Shea butter (SB) and aromatic oil (TDAE) on mechanical properties of (—CB—S—NR—) composites was studied in the previous report by Mensah et al. [54]. The SB based composites showed relatively better mechanical properties, compared to the TDAE based composites. Most of these observed properties were better than those reported for NR-CB-epoxidized vegetable oil reported by Chandrasekara et al. [78], rubber-CB-Soybean oil reported by Petrović et al. [45] and those reported by Jatropha oil-SBR and castor oil-SBR based systems by Roy et al. [48]. The composition without oil (SBO) generally dominated in all these properties, except that the oil/butter filled compositions significantly attained developments in properties like; rebound resilience, fatigue and reinforcement index or modulus ratio (M300/M100) [54]. It was also observed that the SBO showed comparable results in properties like hysteresis losses at lower SB and TDAE oil loading level. With regards to fatigue life study, irrespective of the content of SB or TDAE oil loaded into (—CB—S—NR—), the fatigue property improved compared to the sample void of SB [54].

To further understand the interactions of the CB in NR in the presence of the butter and oil, the tensile properties, Young's modulus, total network density and the ratio; Young's modulus (E_o) and the steady-state modulus (E_1) are presented in Fig. 14a– b, Fig. 14c and d, respectively.

There is no clear trend in the ultimate tensile strength, UTS (MPa), however it appears increasing the SB and TDAE oil generally decreases the UTS (MPa), with an increase in the elongation at break. On loading SBR with epoxidized palm oil, Young's modulus and strength dropped, with increased in elongation at break than the compounds without palm oil [61]. In Fig. 14a, the TDAE has exhibited higher tensile strength than the SB based compounds, significantly at lower loading level. For instance, STD5 obtained ~4 and ~11% higher tensile strength than SBO and SB5 respectively, whilst STD40 showed ~7 % growth in strength than SB40. In Fig. 14b the Young's modulus, E_o (MPa), related to combined effect of chemical and physical interactions, deduced at 0.006% strain increases in

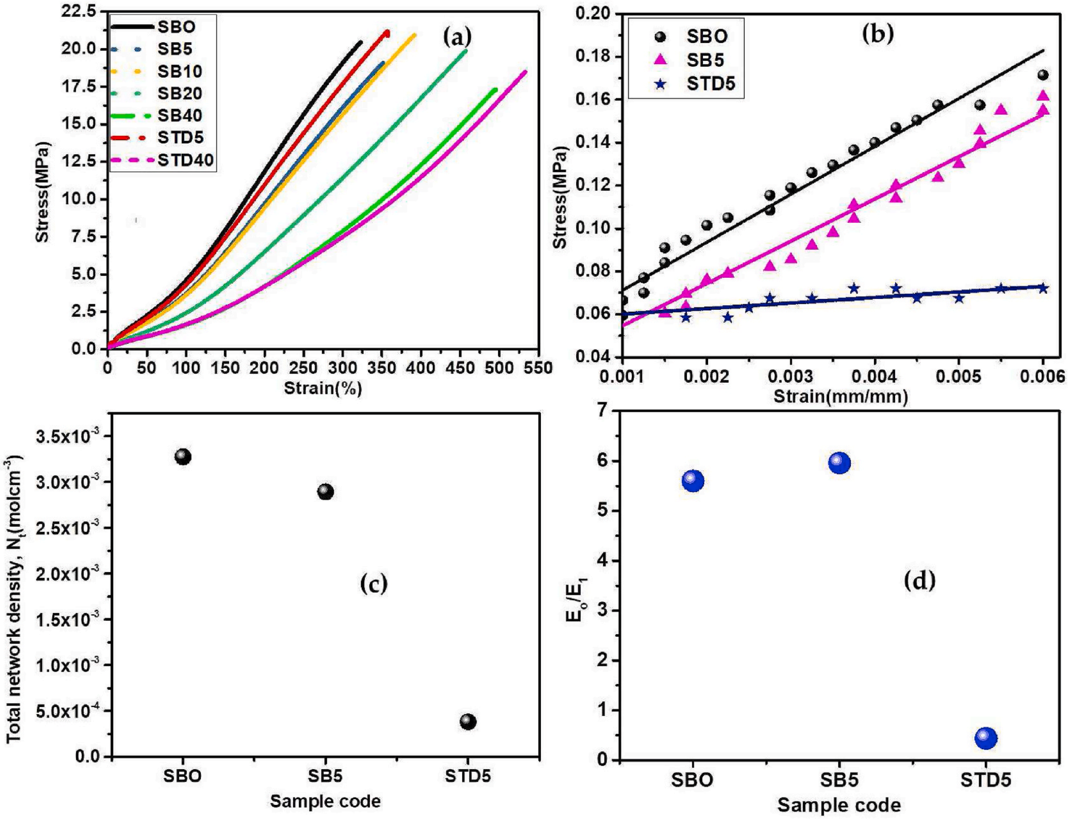

Fig. 14. Comparing the mechanical properties of representative samples cured at 160 °C; (a) stress-strain curves (b) Young's modulus determined at low strain (0.6%) (c) total network density and (d) modulus ratio (E_o/E_1).

the order of; STD5 < SB5 < SBO with corresponding values of ~2.6 MPa < ~19.7 MPa < ~22.3 MPa respectively. Here, the SB5 has exhibited extremely higher (~658 %) in E_o (MPa) than STD5.

In Fig. 14b, when the total crosslinking density (N_t (mol/cm^{-3}) of the composition was computed with equation (7), similar trend (STD5 < SB5 < SBO) can be seen. However, in Fig. 14b, when the calculated modulus ratio (E_o/E_1), which is mostly related to physical interactions (—CB—S—CB— or CB—O$^{\delta-}$———H $^{\delta+}$—CB), and which gets broken at higher strain by Payne's effect [23], it is interesting to observe that SB5 was over ~7 % higher than SBO and excessively over ~1200 % higher than STD5, respectively. By considering the differences of E_o/E_1 and E_1 or UTS (MPa), it is clear that the reinforcement mechanism of SB based compounds is dominated by CB—CB networks (—CB—S—CB— or CB—O$^{\delta-}$———H $^{\delta+}$—CB) with desired CB—S—NR interaction than TDAE oil compounds, which seems to be controlled by mainly CB—S—NR interactions with weaker CB—CB interactions. The strength of the reinforcing mechanism between CB—CB or —CB—S—CB— interactions in the presence of SB or TDAE oil is as depicted in Fig. 15 (a-f**).**

Despite the SB-film coating of the surfaces of the CB particles (Fig. 15a), the SB wetted-CB networks could still exhibit stronger interactions among themselves and with the NR matrix, during tensile deformation (Fig. 15b). This may be due to the fact that the thickness of SB wetted-CB particles (T1) shown in Fig. 15c was relatively thinner or moderate to permit enough physical interactions. Adversely, the TDAE oil wetted-CB particles seem to be separated far from each other (Fig. 15d), and thus, under tensile deformation (Fig. 15e), Payne effect may occur earlier than expected, owing to the relatively larger thickness or poor flow properties of TDAE oil wetted-CB particles (T2 > T1), as illustrated in Fig. 15f.

Li et al. [23] recently observed that with regards to carbonaceous fillers like CB, Payne effect, was highly dependent on high affinity of these fillers among themselves and to the rubber matrix. Hence, the weak interactions among TDAE oil wetted-CB particles (Fig. 15e) could account for the low Young's modulus and the differences in E_o/E_1 observed. Therefore, it is not a surprise that —CB—S—NR— loaded with SB showed better bound rubber content (filler-matrix interactions) [20] (SB5 > SB40 by ~9 % and SB40 > SDT40 by ~48 %), higher chemical crosslink density (SB5 > STD5 by ~13 % and SB40 ≈ STD40), fatigue life (SB5 > STD5 by ~31 % and SB40 ≈ STD40) and grater rebound resilience (%) behaviour (SB5 > STD5 by ~6.4 % and SB40 > STD40 by ~5.4%) than the TDAE based composites in the recent work reported by Mensah et al. [54].

5. Conclusion

The effect of Shea butter (SB) on natural rubber (NR)-filled with carbon black (CB) vulcanizates (—CB—S—NR—) was

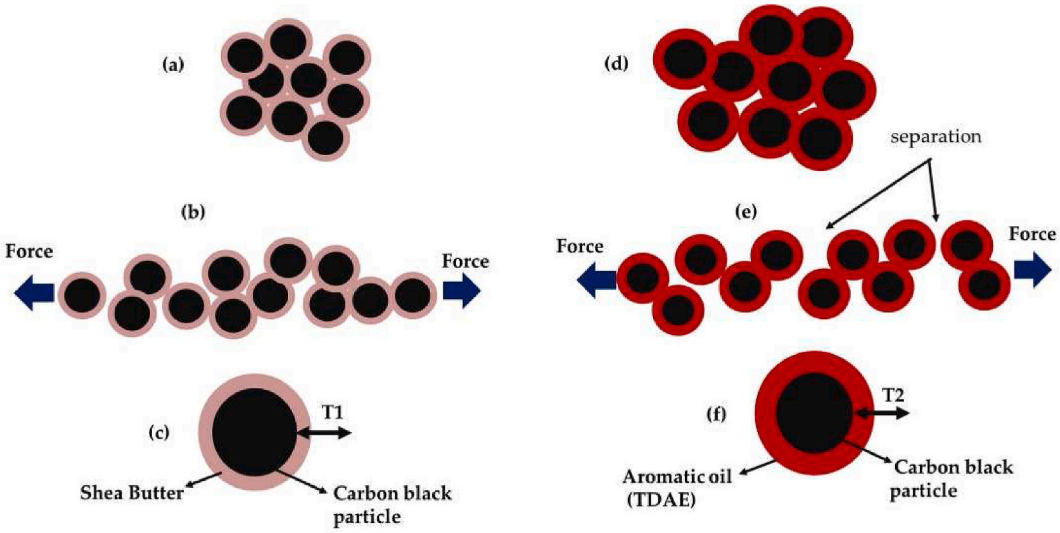

Fig. 15. illustrations of how CB—CB networks interacts with SB and TDAE oil in rubber matrix (a) SB wetted-CB particles unreformed (b) SB wetted-CB particles under uniaxial strain (c) size of SB wetted-CB particles (d) TDAE oil wetted-CB particles (e) TDAE oil wetted-CB under uniaxial deformation and (f) size of TDAE wetted-CB.

investigated. The results obtained on vulcanization properties, curing kinetics and tensile properties were compared with representative compositions prepared with petroleum-based oil (TDAE). Loading —CB—S—NR— with SB or TDAE generally resulted in lengthening scorch time (t_{s2}) and optimum curing time (T_{90}). Though, fatty acids in these plasticizers are reported to contain unsaturated sites which could absorb the sulfurating species, it was also observed that the separation or coating of the reacting species (NR, CB, Sulfur and other curing aids) by the films of the SB or TDAE oils during crosslinking reactions was suspected to be another cause. This effect could extend the time for the reacting species to reach out to each other to initiate and complete crosslinking reactions.

The activation energy E_a (KJ/mol) of curing of the compositions deduced by Arrhenius equation was in accordance with the T_{s2} and T_{90}. Again, the —CB—S—NR— without SB or TDAE showed higher viscosity index (M_L), crosslinking density index (ΔM) and mechanical strength properties (M_H) than the plasticized compounds, at all temperatures (155–165 °C), from the rheological studies. This observation is common with reinforced compounds without plasticizers. The SB also exhibited relatively lower anti-reversion behaviour than TDAE in —CB—S—NR—vulcanizates.

When compared, it was interesting to observe that, the SB loaded —CB—S—NR— composites showed improvement in $M_{L,}$ ΔM and M_H, with shorter T_{s2}, T_{90} and lower E_a (KJ/mol) than those loaded with TDAE. On the other hand, the —CB—S—NR— filled with TDAE showed higher ultimate tensile strength, (UTM) (MPa), possibly due to desired CB—NR than SB based compounds. To compare, STD5 and STD40 recorded ~11 and ~7 % higher UTS (MPa) than SB5 and SB40 respectively. Nonetheless, the SB loaded compounds exhibited higher Young's modulus than SBO and TDAE based systems. For example, SB5 obtained > ~7 % than SBO and over ~1200 % higher than STD5 respectively. This was suspected to be due to desired dispersions, chemical networks and the superior CB—CB interactions, as confirmed by WAXD peaks around ~26°, with the presence of crystalline structures (CB—CB).

It can be therefore be concluded that renewable, economical and environmentally friendly SB has exhibited better vulcanization and physico-mechanical properties in —CB—S—NR— composites, especially at lower loading level (~5–10 phr) compared to aromatic (TDAE) oil based systems.

Therefore, SB system is confirmed to be a suitable plasticizer to replace PBO for compounding non-polar rubber material like NR for the fabrication of rubber products in the future, upon further optimisation.

Data availability Statement

The data used to support the findings of this study are available from the corresponding author upon request.

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CRediT authorship contribution statement

Bismark Mensah: Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Boateng Onwona-Agyeman:** Writing – review & editing, Writing – original draft, Supervision. **Frank Nsaful:** Writing – review & editing, Validation, Software, Conceptualization. **Isaac Adjaye Aboagye:** Writing – original draft, Visualization, Validation, Formal analysis. **Nii Longdon Sowah:** Writing – original draft, Methodology, Formal analysis, Data curation. **Prosper Naah Angnunavuri:** Writing – review & editing, Writing – original draft, Visualization, Data curation, Conceptualization. **Vitus Atanga Apalangya:** Writing – review & editing, Writing – original draft, Validation, Investigation, Conceptualization.

Declaration of competing interest

NOTES: 1- The authors declare no competing financial interest.
2- Corresponding author has consent from all co-authors.

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