Using bio-based plasticizers, alternative rubber

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Executive summary

Plasticizers such as treated distillate aromatic extracts and aromatic oils commonly are used in tread compounds because of their chemical compatibility and ability to improve rubber processing. Alternative sources to these petroleum-derived plasticizers, such as oils extracted from crops, were evaluated in model tread compounds.

Select bio-based oils with varying fatty acid compositions and functionality were used to replace part of the petroleum oil and compounded into silica-based tread formulations. These bio-based plasticizers were evaluated in rubber compositions with 80/20 blends of solution styrene-butadiene rubber and natural rubber, as well as blends with an alternative bio-derived rubber, guayule.

Effects of these bio-based plasticizers and rubber on the material's cure kinetics and key physical properties are discussed. Dynamic mechanical thermal analysis results are correlated to on-vehicle performance predictors for rolling resistance and traction by assessing tangent delta in various temperature regions.

This study shows that use of bio-based materials provides a promising alternative to standard oil and rubber matrices, as supported by comparable mechanical properties and performance predictors. Key technical challenges and the potential future outlook for using sustainable raw materials in tread compounds are discussed.

Organic plasticizers, such as polycyclic aromatic hydrocarbons (PAH) and treated distillate aromatic extracts (TDAE) are important ingredients in rubber compound formulations.

These extender oils are used to improve the processing of rubber compounds during the mixing, extruding and molding stages. Plasticizers also are used to improve the physical properties of elastomers by increasing elongation, decreasing hardness, increasing tack and improving low temperature elasticity. By modifying the ratios of oil, filler and elastomer content, the physical properties of the rubber compound can be adjusted according to the targeted application.

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Plasticizers are selected according to their chemical compatibility with the elastomer matrix and glass transition temperature, Tg, which affects the compounded rubber's dynamic mechanical properties. In tire tread formulations, oils such as MES (mild extraction solvate), TDAE, RAE (residual aromatic extract) or naphthenic extenders commonly are used. These oils are compounded with rubber matrices such as styrene-butadiene rubber (SBR), polybutadiene rubber (BR), natural rubber (NR), or blends of these types.

In addition to petroleum-derived plasticizers, naturally occurring oils from agricultural sources such as plants, nuts, seeds and fruit have been investigated for several years[1]. Alternative sources to petroleum-based chemicals provide an opportunity to improve environmental impact and increase renewable content of industrial products[2]. Renewable oils currently are used within the chemical industry for applications including paints, coatings and cosmetics.

Investigation of these eco-oils has expanded into the rubber industry as well, with recent reports of limited usage in commercial tire applications[3,4].

Researchers have studied a wide variety of natural oils, including soy, sunflower, corn, canola and castor oils for compatibility and performance in rubber compounds[5,6]. With diverse options of natural sources available, sustainable oils may vary in degree of polarity, molecular weight, transition temperatures and unsaturation sites[7]. Further research is necessary to develop compound formulations and oil-rubber compatibility for widespread usage in high performance rubber applications.

A previous study by the authors comparing sustainable oils in SBR tread compounds indicated that bio-oils showed promising results for both physical and dynamic mechanical properties[8]. In this paper, four additional bio-plasticizers were selected for evaluation in model tread rubber with a blend of SBR/NR: palm oil, flaxseed oil, cashew nut shell liquid and low saturated soybean oil.

Additionally, an alternative, bio-derived rubber called guayule was used to replace polyisoprene in the rubber blends to increase the potential of sustainable content in the compounded tread.

Guayule is a shrub grown in arid climates of Mexico and the southwest region of the U.S. By extracting rubber particles from its bark, producers are able to collect high molecular weight rubber that provides similar characteristics to natural rubber from *Hevea brasiliensis* (para rubber tree)[9].

According to a 2011 report on alternative rubber and latex sources, an estimated 10 million tons of natural rubber and latex are produced per year, with 70 percent of the supply supporting the tire industry[10]. With high demands and price spikes of up to $6/kg for natural rubber, alternatives to imported latex and natural rubber from *Hevea* trees have gained attention.

This paper explores the technical merits and challenges of using guayule as a substitution for *Hevea* natural rubber and in combination with bio-derived plasticizers in silica-based, model tread compounds.

Experimental

Materials selection

Dry guayule natural rubber (GNR) in bale form was supplied by the Ohio Agricultural Research and Development Center) in Wooster, Ohio. The noted elasticity and softness of guayule rubber has made it an interesting choice for replacing the cis-1,4-polyisoprene rubber in this study.

Guayule (*Parthenium Argentatum*), a perennial shrub grown in desert regions, accumulates latex rubber particles in its bark.

By drying or coagulating these natural latex particles, GNR is produced. **Fig. 1** shows a photograph comparing chopped bales of SMR natural rubber and GNR used in this study.

The bio-plasticizers used in the study include palm oil, flaxseed oil, cashew nut shell liquid (CNSL) and low-saturated soybean oil (SBO), as shown in **Fig. 2**. Palm oil was supplied by Cargill Industrial Oils & Lubricants Inc. Nulin flaxseed oil was provided by Viterra Inc. and is bred with higher levels of linolenic acid than traditional flaxseed and is expeller crushed.

Modified cashew nut shell liquid was supplied by Composite Technical Services, under the product name XFN-50. The low-saturated soybean oil is a product of Zeeland Food Services Inc., and has been refined, bleached and deodorized.

These bio-plasticizers were selected

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Table I. Fatty acid profile of select bio-oils.

Chemical Structure (Carbon-Carbon Double Bonds)	Fatty Acid	Palm Oil	High Linolenic Flaxseed Oil	Low Saturated Soybean Oil
C 16:0	Palmitic	44	4.89	4.07
C 18:0	Stearic	4.5	2.23	3.21
C 18:1	Oleic	39	9.54	21.71
C 18:2	Linoleic	10	12.75	60.36
C 18:3	Linolenic	1	69.08	8.7

Table II. Recipe formulation, parts per hundred rubber (phr), by weight.

Formulation	
Component	phr
S-SBR, OE[a]	84.78
S-SBR, clear	18.34
Natural Rubber or Guayule	20.00
N234 Carbon Black	10.00
Zeosil® 1165 MP	60.00
TESPT[b] coupling agent	4.80
Processing Oil	10.00
Microcrystalline Wax	2.00
Antiozonant	2.00
Antioxidant	0.50
Zinc Oxide	1.90
Stearic Acid	1.50
Processing Aid	2.00
Sulfur	1.50
Sulfenamide Accelerator	1.30
Guanidine Accelerator	1.50
Total phr	222.12

[a] oil extended
[b] bis(triethoxysilylpropyl) tetrasulfide

Table III. Mixing protocol.

Stage 1 Mixing	
Start temperature	76.7°C
Starting rotor speed, rpm	65
Fill factor	70%
Ram pressure, psi	40
Mix sequence	at 0' add elastomers
	at 1' add 2/3 silica + TESPT
	at 2' add 1/3 silica + others
	at 3' sweep
Dump conditions	hold 4' at 160-165°C (total mix time = 7')
Stage 2 Mixing	
Start temperature	76.7°C
Starting rotor speed, rpm	65
Fill factor	70%
Ram pressure, psi	50
Mix sequence	at 0' add first pass masterbatch
	at 30 seconds add ZnO, stearic acid and process aid
	at 1.5' sweep
Dump conditions	hold 2-4' at 160°C
Stage 3 Mixing	
Start temperature	50°C
Starting rotor speed, rpm	60
Fill factor	68%
Ram pressure, psi	50
Addition order	at 0' add 1/3 second pass masterbatch, at 30" add sulfur, accelerator and 2/3 second pass masterbatch, sweep at 1'
Dump conditions	110°C or 2' 30"

Table IV. Rubber compound cure kinetics.

		t_{s2} (minutes)	t_{c50} (minutes)	t_{c90} (minutes)	Max Torque, MH (lb-in)
1	Control	3.99	8.61	17.96	53.61
2	Palm Oil	3.87	7.73	16.56	49.42
3	Flaxseed Oil	3.75	6.93	16.91	49.30
4	CNSL	3.24	6.16	17.17	49.44
5	SBO	3.46	6.58	16.03	49.43
6	Guayule	4.11	7.86	17.65	48.92
7	Guayule / Palm Oil	3.84	7.05	16.70	47.79
8	Guayule / SBO	3.92	6.98	16.95	47.02

Plasticizers

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based upon their range in saturation or unique chemical structure.

In contrast to the combination of aromatic rings characterizing PAHs, many of the plant-based oils are triglycerides, containing fatty acids comprised of long unbranched aliphatic tails attached to a carboxyl group.

Plant oils can be characterized by their fatty acid distributions, which determine the relative level of unsaturation in the oil. **Fig. 3** shows the chemical structures of five of the prominent fatty acids: palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid.

These plant-based oils are triglyceride-based esters of glycerol and three fatty acid chains, as shown in **Fig. 4**. The composition of fatty acids will vary the number of alkane groups (single carbon bonds), alkene groups (double carbon bonds) and alkyne groups (triple carbon bonds) in the oil. Palm oil, for example, has a high concentration of palmitic and oleic acid, whereas low-saturated soybean oil has over 60 percent linoleic acid in its fatty acid distribution.

The distribution of fatty acids in these oils also varies based upon the crop source and processing methods. **Table I** provides a comparison of the percentage of main fatty acid constituents for each oil type. Low saturated soybean oil was selected based upon promising results of degummed soybean oil used in a previous study[8]. The low-saturated soybean oil has a level of saturation of about 7 percent, compared to traditional soybean oil with a saturation level of approximately 15 percent. The flaxseed oil that was selected for this study has a unique fatty acid profile compared to traditional bulk flaxseed oil and is from a specialized breeding program which yields oils with approximately 82 percent polyunsaturated fatty acids compared to 72 percent for traditional flaxseed oil[11].

While triglyceride based oils are often extracted from plants or seeds, additional agricultural based plasticizers may include other chemical structures. Essential oils such as d-limonene, commonly known as orange oil, have cyclic terpene structures and cashew nut shell liquids are based upon aromatic rings with long aliphatic hydrocarbon tails, as illustrated in **Fig. 5**.

The modified cashew nut shell liquid in this study is a polymeric material produced from the natural resins of cashew shells, which are byproducts of the nut industry.

Iodine number can be used as an indicator of available unsaturation or sites for bonding opportunities within the chemical. Reported iodine numbers for these bio-oils provide a ranking from high unsaturation to high saturation: CNSL, flaxseed oil, low saturated SBO, palm. Two of the four bio-plasticizers, palm oil and low saturated soybean oil, were selected for evaluation with the guayule rubber due to their anticipated compatibility with the rubber matrix.

Characterization of plasticizers

Oils were evaluated using differential scanning calorimetry (DSC), with a TA-3000 Mettler thermo-analytical instrument. Bio-oil samples of 10 mg were placed in standard Al crucibles and compared to the heat flow in empty crucible reference cells at a heating and cooling rate of 0.17°C/second. Melting thermograms were obtained by cooling samples to -50°C, holding temperature for 10 minutes, and then heating samples to 100°C. Heat flow was recorded in W/g during the segments.

Compound formulations and mixing

The rubber compound used in this study is a model passenger tire tread formulation with 80/20 blend of styrene-butadiene rubber and natural rubber. **Table II** provides the compound formulation, expressed in parts per hundred rubber (phr) by weight. Solution styrene-butadiene rubber was a blend of oil extended and clear grade rubber from Lanxess, Buna VSL 5025-2 HM SBR (50% Vinyl/25% Styrene) and Buna VSL 5025-0 HM SBR (50% Vinyl/25% Styrene), respectively. The natural rubber used in the rubber compounds was a controlled viscosity NR from para rubber trees, CV-60, or when indicated, 20 phr of guayule derived natural rubber was used.

Precipitated silica, Zeosil 1165MP with BET of 165 m2/g, was supplied by Rhodia and used as the primary filler in addition to 10 phr of N234 carbon black filler. Processing oil in the control rubber was TDAE, Tudalen 4192 by Hansen-Rosenthal Oils. In the experimental rubber compounds, bio-plasticizers were used to replace TDAE oil at 10 phr loading levels. Additional chemicals included standard rubber formulation ingredients such as antioxidants, antiozonants, activators, accelerators and sulfur.

Two distinct sets of rubber compounds were formulated and compounded: natural rubber with alternative bio-oils and guayule rubber with alternative bio-oils. In total, eight tire tread formulations were compounded in a Farrel Model 2.6 BR Banbury mixer using a three pass mixing approach. **Table III** details the mixing protocol. In the first stage, the elastomers, fillers, processing oil, silane coupling agent and antidegradants were mixed, followed by the addition of cure activators and processing aid in the second pass. During the first two mixing stages, rotor speed was adjusted after the addition of each set of ingredients to raise the batch rubber temperature to 160°C for completion of the silanization reaction. In the final, productive pass, the sulfur and accelerators were mixed with the rubber. The Banbury mixing process used a 68-70% fill factor with ram pressure ranging from 40-50 psi as noted. Rubber compounds were sheeted out on a Farrel two-roll mill after each Banbury mixing stage.

Processing properties

An oscillating disc rheometer (Monsanto Rheometer ODR 2000) was used to determine cure kinetics of the rubber compounds, following ASTM D 2084[12]. An oscillating shearing action of constant amplitude was applied while the sample was held under pressure at 160°C. As is typical for SBR vulcanization curves, the torque plateaued at maximum torque and no significant reversion was evident. From the torque versus time graphs, the time needed to achieve 90% maximum torque, t_{c90}, was noted. Rubber charges were compression molded at 160°C with molding times equal to t_{c90}+5 minutes.

Physical and heat-aged properties

An Instron dual column testing system equipped with a 5-kN load cell and a long-travel extensometer was used to evaluate key physical properties: tensile strength, elongation and tear resistance. Under ASTM D 412[13] guidelines, Test Method A, Die C, five dumbbell-shaped tensile specimens per sample were die-cut from a 2-mm thick test plaque using a hydraulic die press. Tensile samples were tested at 500 mm/min cross-head speed with gage length of 25 mm. Tear resistance was evaluated according to ASTM D 624 Die B, razor-nicked method[14]. Hardness was measured as directed in ASTM D 2240[15] using a Shore A Durometer.

Aged rubber physical properties were obtained after conditioning samples in an air oven at 70°C for 168 hours, fol-

Fig. 1. (a) Para rubber tree natural rubber; (b) guayule natural rubber.

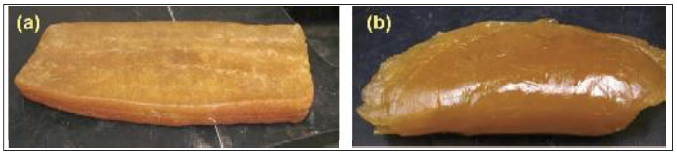

Fig. 2. Selected bio-plasticizers used in model tire tread compounds: (a) palm oil; (b) high linolenic flaxseed oil; (c) cashew nut shell liquid; and (d) low-saturated soybean oil.

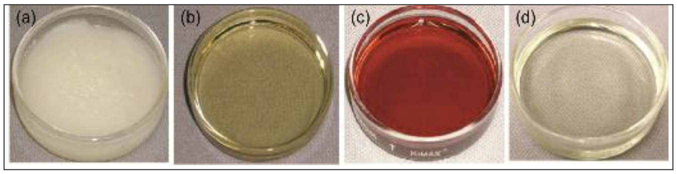

Fig. 3. Fatty acid chemical structures of natural oils.

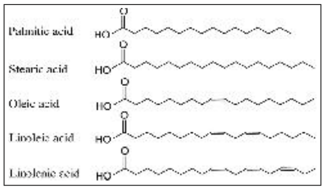

Fig. 4. Chemical structure of triglyceride-based oils.

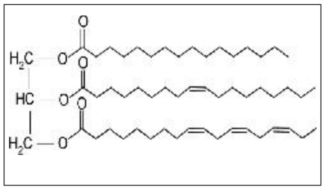

Fig. 5. Chemical structure of cashew nut shell liquid.

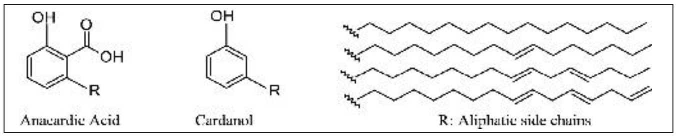

Table V. Physical properties of bio-oil compounds and guayule compounds.

	1	2	3	4	5	6	7	8
Compound	Control	Palm Oil	Flaxseed Oil	CNSL	SBO	Guayule	Guayule/ Palm Oil	Guayule / SBO
Tensile Strength[a] (MPa)	19.54 (0.69)	22.30 (1.17)	22.66 (0.80)	22.80 (0.52)	23.93 (0.45)	19.66 (1.00)	22.30 (0.89)	23.87 (0.96)
Elongation[a] (%)	401.40 (10.11)	458.00 (18.43)	477.40 (19.27)	528.60 (17.90)	543.40 (11.28)	423.8 (22.93)	491.36 (17.35)	526.75 (18.15)
Modulus at 100% Elongation[a] (MPa)	2.75 (0.03)	2.67 (0.17)	2.58 (0.06)	2.38 (0.05)	2.25 (0.04)	2.74 (0.05)	2.29 (0.05)	2.34 (0.02)
Modulus at 300% Elongation[a] (MPa)	13.38 (0.15)	12.95 (0.82)	12.29 (0.34)	11.09 (0.29)	10.84 (0.07)	12.70 (0.30)	11.51 (0.34)	11.46 (0.09)
Reinforcement Index (M300/M100)	4.87 (0.04)	4.85 (0.04)	4.77 (0.05)	4.65 (0.02)	4.83 (0.08)	4.64 (0.10)	5.03 (0.08)	4.89 (0.02)
Tear Strength[b] (kN/m)	45.26 (1.11)	42.58 (2.91)	45.72 (2.47)	48.88 (4.67)	48.02 (5.09)	52.02 (8.73)	44.40 (7.85)	44.90 (4.21)
Shore A Durometer[c]	64.88 (0.69)	61.90 (0.47)	60.56 (0.34)	61.34 (0.37)	58.75 (0.30)	64.68 (0.52)	61.54 (0.42)	60.22 (0.19)

[a] ASTM D 412 Die C, 500 mm/min
[b] ASTM D 624 Die B razor-nicked, 500 mm/min
[c] ASTM D 2240, Shore A Model 717 Micro Hardness tester

Table VI. Heat-aged physical properties of bio-oil compounds and guayule compounds.

	1	2	3	4	5	6	7	8
	Control	Palm Oil	Flaxseed Oil	CNSL	SBO	Guayule	Guayule/ Palm Oil	Guayule/ SBO
Percent change after aging[a]	%	%	%	%	%	%	%	%
Tensile Strength	8.05	-4.81	-9.43	-10.82	-2.59	-2.50	-6.18	-1.69
Elongation	3.74	-7.95	-16.51	-23.27	-10.75	-8.82	-5.30	-1.51
Modulus at 100% Elongation	13.24	9.58	16.37	28.86	20.04	14.32	14.28	10.39
Modulus at 300% Elongation	6.60	8.29	17.29	27.33	17.70	10.94	4.27	6.53
Tear Strength	8.79	-8.64	-0.96	3.85	1.92	-17.34	8.92	-9.04
Shore A Durometer	0.36	4.90	5.44	6.18	4.67	3.40	1.38	2.14

[a] ASTM D 573, 70°C for 7 days

lowed by room temperature exposure for 12 hours on a flat surface. Per ASTM D 573[16], five tensile, tear and durometer specimens from each set were tested for tensile strength, tensile modulus, elongation at break and Shore A hardness.

Dynamic viscoelastic properties

Viscoelastic rubber properties and responses were characterized using a Rheometrics RSA II machine, with 1 Hz frequency, 0.25% strain and tensile geometry. Dynamic mechanical analysis (DMA) was used to evaluate storage modulus (E'), loss modulus (E"), complex modulus (E*) and tan δ (ratio of loss to storage modulus) with temperature sweeps from -100°C to 100°C.

Results and discussion

Characterization of plasticizers

Bio-plasticizers were selected primarily according to their range in saturation, from low saturation of CNSL and chosen grades of soybean oil and flaxseed oil to high saturation in the palm oil. **Fig. 6** compares the DSC melting thermograms of five processing oils used in the study: TDAE, palm, flaxseed, cashew nut shell liquid (CNSL), and low saturated soybean (SBO)

The low saturated soybean oil exhibited a transition temperature on heating around -29.6°C, whereas two transition peaks were noted in the palm oil, at 6°C and 32°C range. Unsaturated fatty acids are characterized by carbon chains having one or more double bonds, which provide opportunities for bonding with the rubber or other additives. Low saturated soybean oil is liquid at room temperature, whereas the palm oil is in a solid form. In palm oil, the high saturation indicates structures with long chain carboxylic acids that are saturated with hydrogen with limited or no carbon-carbon double bonds. The two noted peaks correspond to the low and high solidification segments within the palm oil, caused by fractions of Olein and Stearin.

The degree of saturation and indicative transition temperatures can affect the oils' compatibility with the rubber matrix. Highly polar polymers are more miscible with processing oils with a higher level of unsaturation. For lower polarity polymers, compound miscibility is likely to be improved by choosing oils with lower polarity which is expressed by fewer areas of unsaturation.

Compound processing

Rheological curves are compared for the two sets of samples using either bio-oils or guayule derived natural rubber, shown in **Fig. 7**. As compared to control rubber with TDAE oil and 20 phr natural rubber (**Fig. 7a**), substitution of TDAE oil with bio-oils accelerated the rubber cure slightly from 17.96 minutes to 16.03 minutes with SBO. A similar result was noted for guayule-based compounds using bio-oils as compared to guayule control sample, in **Fig. 7b**. Control rubber had the highest maximum torque, indicating potential for higher cross-linking and hardness of the rubber compound. Compounds using bio-oils plateaued to maximum torque values that were lower than the control but similar to each other.

Table IV provides a summary of the scorch time (t_{s2}), cure times at 50% and 90% maximum torque, t_{c50} and t_{c90}, respectively, as well as the maximum torque of the rubber compound after curing. One noted advantage of the guayule compound compared to the control rubber was the increase in scorch time with slight decrease in time for curing the rubber formulation.

The formulation containing 20 phr natural rubber and 10 phr SBO (compound 5), exhibited enhanced processing ability compared to the other compounds. Formulations with 20 phr guayule (compounds 6-8) experienced high tack in the Banbury and on the two-roll mill, making it difficult to obtain a smooth sheet. Of the three compounds containing guayule, the addition of palm oil (compound 7) reduced tack and improved the ability to process the masterbatch. The CNSL formulation bagged on the two-roll mill after the second and third mixing passes. Overall, the SBO and palm oil compounds provided processing advantages compared to the control formulation. Blooming of the processing oil after cure was not observed in any of the compounds in this study.

Physical and heat-aged properties

Physical properties of the molded tread compounds were compared for tensile performance, tear resistance and hardness. Use of guayule rubber in place of 20 phr natural rubber provided compounds with similar physical attributes including tensile strength, modulus at 100% elongation and Shore A durometer. **Fig. 8** compares the stress-strain behavior of this alternative rubber to the control as well as a comparison of palm oil and low saturated soybean oil as plasticizers. In these samples, use of SBO with guayule increased the percent elongation of the molded rubber compound from 401% to 526%, while increasing the tensile strength from 19.54MPa in the control compound to 23.87MPa in guayule/SBO compound.

An overview of the key physical properties is presented in **Table V**, where average values and standard deviations are reported for the eight tread compounds. Comparison of rubber tensile strengths indicate that use of bio-based plasticizers increased the percent elongation of the rubber, while maintaining tensile strength. In particular, cashew nut shell liquid and low saturated soybean oil significantly increased ultimate elongation of the rubber. Modulus at 300% elongation was highest for TDAE/-natural rubber compounds (control) and decreased significantly for SBO based

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Fig. 6. Melting thermograms of bio-processing oils at a heating rate of 0.17°C/sec.

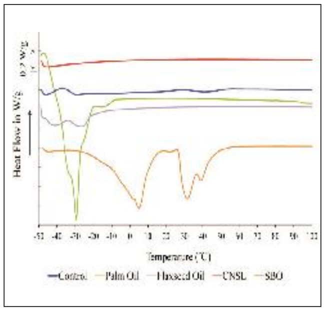


Fig. 7. Rheological curves of a) bio-oil compounds; b) guayule compounds (measured torque while curing rubber at 160°C).

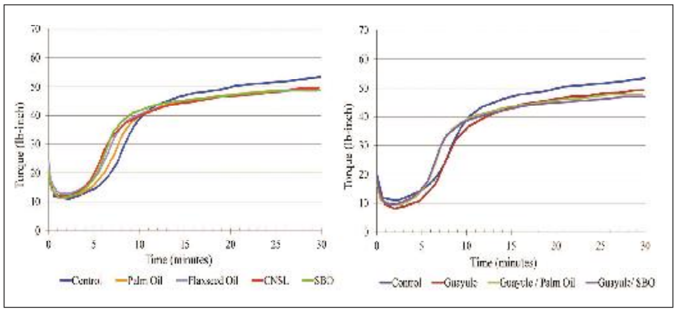


Fig. 8. Comparison of stress-strain behavior of select bio-oil and guayule compounds.

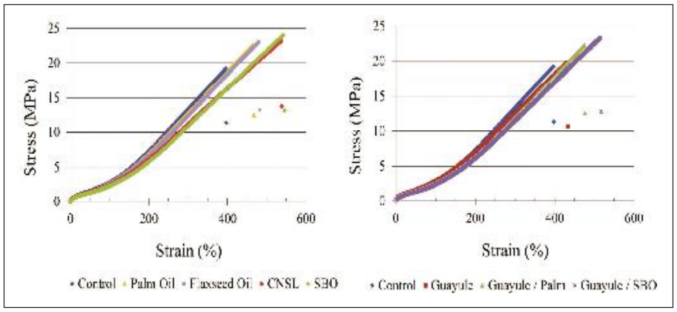


Fig. 9. (a) Normalized physical properties of bio-oil compounds; (b) normalized physical properties of guayule compounds.

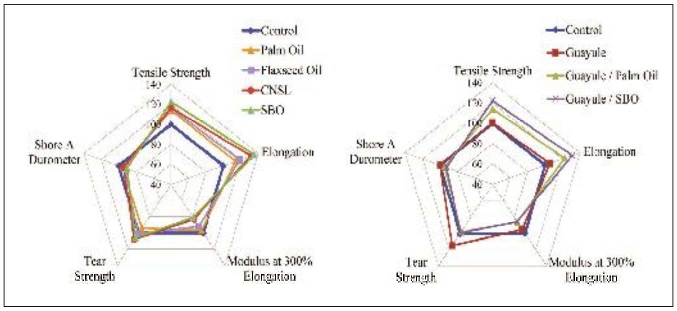
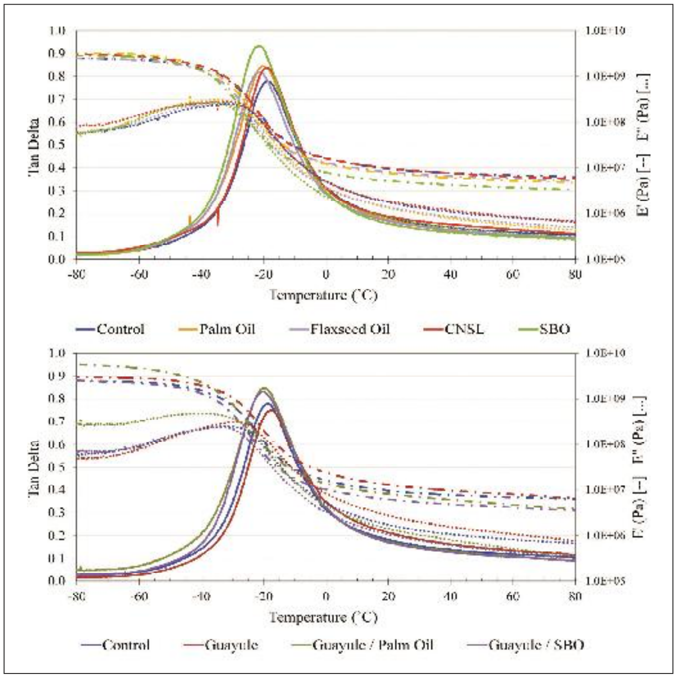


Fig. 10. (a) Tangent delta, E' and E" versus temperature of bio-oil compounds; (b) tangent delta, E' and E" versus temperature of guayule compounds.



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rubber.

Tear strength resistance was similar for all eight compounds, within one standard deviation of the reported average. Shore A durometer ranged from approximately 59 to 65, with control samples and guayule samples having the same hardness value. Use of soybean oil decreased the hardness to 58.75 Shore A.

Table VI compares the percent change of heat aged physical properties of the eight compounds using bio-oil plasticizers and/or guayule derived rubber, versus the as-molded compounds. As expected, control rubber specimens showed a slight increase in modulus, tensile strength and elongation to break after heat aging. Cashew nut shell liquid samples and soybean oil samples exhibited 17-28% change in either modulus at 100% elongation or modulus at 300% elongation. These changes were consistent with the increase in durometer for each of the compounds. Due to the increased number of carbon-carbon double bonds in highly unsaturated oils, rubber using low saturated processing oils is more likely to be susceptible to oxidative aging.

Normalized values of key physical properties are compared in **Figs. 9a** and **9b**, with the control compound used as the baseline. Graphs are presented so larger values are preferred for each attribute. **Fig. 9a** shows that CNSL and SBO affected the rubber compound properties to a similar degree, in which durometer was decreased slightly and a significant improvement in tensile strength, tear strength and elongation were noted. Use of palm oil and flaxseed oil also showed interesting performance in terms of increased elongation and tensile strength, while maintaining modulus at 300% elongation.

This selection of bio-oils has a range of reactive carbon-carbon double bonds that may influence the curing process, and therefore, the reactivity of sulfur between elastomer chains. This mechanism is consistent with the noted decrease in durometer and increase in elongation. For example, low saturated soybean oil increased the rubber's elongation from 400% in the control sample to over 540%, but decreased Shore A durometer by 6 points. One of the highly saturated oils, palm oil, provided an increase in elongation of 57% compared to the control with only a 3 point drop in hardness. For SBO and CNSL, the increase in elongation is reflected in a reduction in tensile modulus at 300% extension.

In **Fig. 9b**, guayule rubber had very similar overall physical performance characteristics to the natural rubber control formulation. Combinations of guayule and soybean oil or palm oil extended the elongation and tensile strength, while decreasing the modulus at 300% elongation.

Dynamic viscoelastic properties and tire performance predictors

Evaluating the viscoelastic response of rubber through different temperature regimes has been used extensively in rubber compound development to predict its performance in tire tread applications[17, 18, 19]. Dynamic mechanical analysis (DMA) provides an opportunity to compare the effects of different chemicals and rubber, such as plasticizers or base compounds, on resulting performance properties. Using this approach, **Figs. 10a** and **10b** provide temperature sweeps from -80°C to 80°C versus E' (storage modulus), E" (loss modulus) and tangent delta, ratio of loss modulus to storage modulus for the two sets of samples.

In **Fig. 10a**, use of the bio-plasticizers in the model compounds resulted in an increase in the tan delta curve peak height and a shift to a slightly lower glass transition temperature. Comparison of the guayule to natural rubber control compound in **Fig. 10b** showed higher tan delta for the guayule compound relative to the control in the temperature regime of 5°C to 80°C, with lower values for the guayule/bio-oil combinations.

It may be noted that the S-SBR in these formulations had a glass transition temperature of -22°C for the clear grade and -29°C for the oil extended grade. The glass transitions of the compounded rubber ranged from -17.6°C for the guayule formulation to -21.7°C for the SBO formulation. The relatively high compound Tg makes this particular recipe more suited for a summer tire application instead of a tire exposed to cold weather conditions. In future studies, base polymers with lower glass transition temperatures may be chosen in order to provide a formulation more suited to all-season use.

As reported previously[20], tangent delta and storage moduli values at a given strain and frequency may be used as predictors for tire tread performance for different conditions. **Fig. 11** provides normalized radar graphs of performance predictors of tread compounds compared to the control rubber, presented with higher values indicating desired performance. In this figure, tangent delta values of the tread compounds at 10°C and 60°C are used to assess the predicted performance for wet traction and rolling resistance, respectively. Lower tan delta values are preferred as indicators for lower rolling resistance, whereas higher tan delta values reflect prediction of improved wet traction of the tread compounds. Dry handling is assessed by measuring the storage modulus, E', at 30°C in tension and snow traction is predicted by comparing tan delta values at -10°C. Tan delta values at 30°C are used as performance predictors for dry traction.

The rolling resistance indicators suggest that use of guayule/palm oil, guayule/SBO, SBO, palm oil and flaxseed oil may be desirable in tread compounds where fuel economy is a key attribute. However, performance predictors for dry handling, dry traction and wet traction indicate that this benefit may result in a tradeoff for these key attributes. **Fig. 11a** compares the predicted performance of the influence of bio-oils on compound properties and **Fig. 11b** compares DMA predictive response for guayule compounds. As shown in **Fig. 11a**, use of cashew nut shell liquid as processing oil provided a compound with similar performance predictors as the control rubber, but with less desirable rolling resistance. Compounds using flaxseed oil showed an improvement in predictors for snow traction, slight improvement in rolling resistance and detriment to dry handling.

For closer examination of the influence of bio-plasticizers and alternative natural rubber on tread properties, **Fig. 12** provides a comparison of the typical trade-off performance attributes for rolling resistance and wet traction. In this graph, lower rolling resistance predictors (tan delta at 60°C) and higher wet traction predictors (tan delta at 10°C) are preferred. Compared to the control rubber, guayule rubber performance shows the typical trade-off of improvement in wet traction at the detriment of rolling resistance. Use of low saturated soybean oil and flaxseed oil decreased rolling resistance but reduced wet traction, according to the DMA predictors. Combinations of guayule and palm oil or SBO showed an optimization of the properties indicated by each of the chemical constituents.

Tire researchers often refer to the "magic triangle" of tire performance, including impact on fuel economy, all season traction and wear resistance. As a

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Fig. 11. Normalized laboratory predictors for key tire performance attributes using DMA data from (a) bio-oil compounds; (b) guayule compounds.

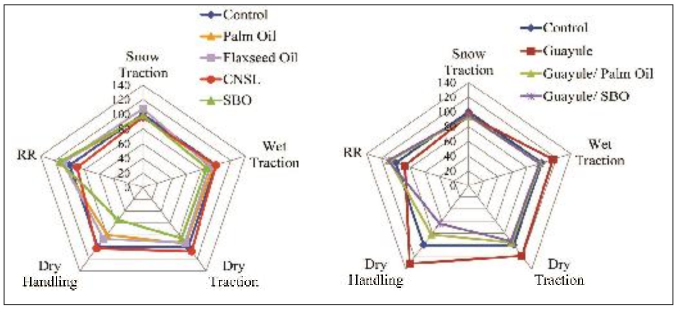


Fig. 12. DMA performance predictors for rolling resistance and wet traction predictors.

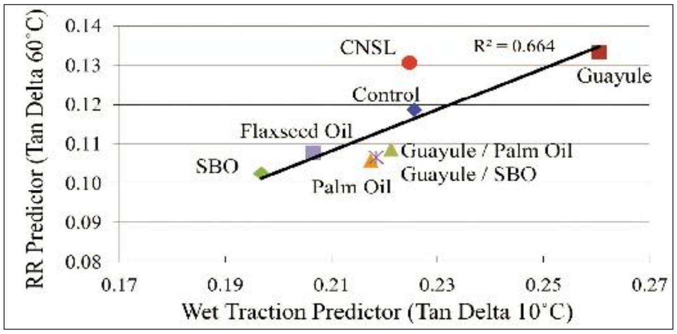
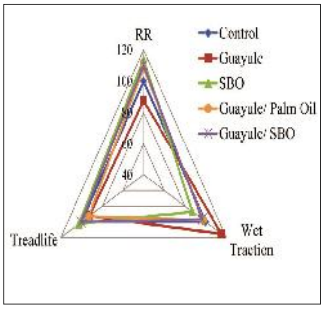


Fig. 13. Normalized laboratory predictors for rolling resistance, wet traction and wear resistance of select bio-oil and guayule compounds.



Appendix A. Tire tread formulation expressed as phr (parts per hundred rubber, by weight).

Component	1 Control	2 Palm Oil	3 High Linolenic Flaxseed Oil	4 Cashew Nut Shell Liquid	5 Low Saturated Soybean Oil	6 Guayule	7 Guayule & Palm Oil	8 Guayule & Low-Sat Soybean Oil
S-SBR, OE^a	84.78	84.78	84.78	84.78	84.78	84.78	84.78	84.78
S-SBR, clear	18.34	18.34	18.34	18.34	18.34	18.34	18.34	18.34
Natural Rubber, CV-60	20.00	20.00	20.00	20.00	20.00			
Guayule						20.00	20.00	20.00
N234 Carbon Black	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Zeosil® 1165 MP	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
TESPT^b	4.80	4.80	4.80	4.80	4.80	4.80	4.80	4.80
TDAE	10.00					10.00		
Palm Oil		10.00					10.00	
High Linolenic Flaxseed Oil			10.00					
Cashew Nut Shell Liquid				10.00				
Low Saturated Soybean Oil					10.00			10.00
Microcrystalline Wax	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Antiozonant	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Antioxidant	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Zinc Oxide	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90
Stearic Acid	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Processing Aid	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Sulfur	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
TBBS	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30
DPG	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Total phr	**222.12**	**222.12**	**222.12**	**222.12**	**222.12**	**222.12**	**222.12**	**222.12**

[a] oil extended
[b] bis(triethoxysilylpropyl) tetrasulfide

PRODUCTS

VMI Group Extrusion is marketing its Shark 90 multisystem that provides final mixing, straining, preform and profile capabilities, all coupled with optional vacuum.

The company said its gear pump systems are comprised of a single screw extruder in conjunction with a gear pump. The extruder is used to achieve effective plasticization of the compounding while ensuring sufficient feeding to the gear pump, VMI said.

More information is available at the firm's website, www.vmi-az.com.

ContiTech A.G. has introduced its Conti Secur Premium adhesive for cold bonding on conveyor belts.

The single-component adhesive—unlike typical two-component products—is ready for immediate use and will provide long service life, ContiTech claims. The product, which was created in collaboration with **H.B. Fuller Co.**, is based on polychloroprene. The company said it can be used in rubber-to-rubber and rubber-to-metal bonding.

Visit www.contitech.de for more information.

Cabot Corp. has released a fumed silica tailored toward applications requiring transparency and mechanical reinforcement.

Cab-O-Sil Duramold 2150 is a high-temperature vulcanizing silica that can be useful for clear HTV silicone applications such as medical tubing and consumer goods, Cabot said. With 30 percent less measured grit, it delivers levels of performance achieved through higher structure products, according to the company.

The new silica is aimed at such markets as automotive seals, gaskets, electrical insulating tubing and cable seals, industrial seals, bushings and hoses. Cabot provides more data on the product at its website, www.cabot-corp.com.

Wacker Chemie A.G. is offering a tin-free catalyst for two-part, room-temperature-curing silicone rubber mold-making compounds.

Elastosil Catalyst NEO is formulated to provide a long pot life and ensure it cures within 24 hours, the company said. The catalyst has been tailored with condensation-curing components of Elastosil M rubber grades. Visit www.wacker.com for more information on the product.

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laboratory predictor for wear resistance, DIN abrasion was measured for the tread compounds. **Fig. 13** provides a normalized plot of laboratory predictors for rolling resistance, wet traction and abrasive wear for selected bio-based compounds. Selection of oils and natural rubber type influences the laboratory predictors for these three key attributes. Use of soybean oil predicted improvement in rolling resistance and treadlife but with reduction of wet traction. The compound using guayule rubber to substitute *Hevea* natural rubber in the 80/20 SBR/NR blend showed an increase in wet traction with degradation in predicted tread wear and rolling resistance.

Replacing the *Hevea* natural rubber with guayule in conjunction with the use of sustainable processing oils helped to mitigate some of the predicted performance trade-offs. In particular, use of guayule rubber with soybean oil containing low saturation or highly saturated palm oil provided well balanced attributes for predictors of rolling resistance, treadlife and wet traction. Guayule/palm oil based rubber and guayule/SBO based rubber showed an improvement of 8% and 10% in rolling resistance compared to the control rubber, respectively. This result is promising given that the reduction of wet traction was only 2% in guayule/palm oil and 3% in guayule/SBO based rubber compared to the control.

While combinations of guayule rubber and bio-oil were evaluated for SBO and palm oils, it would be interesting to evaluate oils with increased number of potential reactive sites, such as flaxseed or CNSL. However, it should be noted that heat aged physical properties suggest oxidative stability issues with compounds using highly unsaturated oils. For example, percent change in elongation and durometer were greatest for rubber compounds using CNSL, followed by flaxseed oil. SBO and palm oil had lower overall percent change of these properties.

This study examined the DMA performance predictors for use of bio-plasticizers and alternative natural rubber in model, silica-based tread compounds. While physical and viscoelastic properties are useful in the development of new material systems, they are not intended to be a substitute for tire testing or on-vehicle evaluation. Additionally, other attributes including noise, wet handling and wear need to be assessed prior to further developments in this area.

Conclusions

This study evaluated the usage of sustainable raw materials in high performance, silica-based tread compounds. The scope of this experimental evaluation included agricultural-based processing oils, guayule rubber obtained from desert shrubs, and combinations of bio-oils with this alternative source to Hevea natural rubber. The purpose of the paper was to evaluate the potential of using sustainable materials in model tread compounds by determining key processing parameters, physical properties and tire performance predictors.

Selected bio-plasticizers were chosen based upon their range of saturation and miscibility with the base rubber compounds. Low saturated soybean oil, palm oil, cashew nut shell liquid and flaxseed oil were evaluated in silica-based tread compounds. Since oils derived from agricultural resources vary in their chemical structures, molecular weight and compatibility with different rubber matrices, the use of selected bio-oils influences the resulting rubber properties.

Experimental evaluations indicated that these bio-oils provided ease in rubber processing while demonstrating similar physical properties to the TDAE control rubber. Each of these bio-oils increased the compound's elongation but in some cases, decreased durometer and reduced modulus at higher extensions.

Dynamic mechanical analysis was used to predict tire tread performance in various conditions, including rolling resistance, wet traction and dry handling. These results showed that selected bio-plasticizers influenced rubber performance, with typical trade-offs between rolling resistance and wet traction.

Rubber using cashew nut shell oil had similar, overall performance predictors to that of the control with TDAE processing oil. Similarly, use of flaxseed oil and palm oil provided tread compounds with well balanced attributes but with a predicted decrease in dry handling. Low saturated SBO provided a low hysteretic rubber compound, but with significant trade-offs for dry handling and dry traction predictors.

Additionally, guayule rubber was assessed as an alternative to Hevea natural rubber for 20 parts in blends of 80/20 styrene butadiene rubber/natural rubber. Use of guayule rubber in the tread compound resulted in similar properties to that of natural rubber, with the benefit of increased tear resistance. Performance property indicators from DMA analysis showed that guayule rubber enhanced wet traction, dry traction, and dry handling performance of the tread compounds, with equivalent predicted snow performance to the control rubber. The trade-off to these performance benefits was a reduction in predicted fuel economy, as determined through DMA predictors for rolling resistance.

By combining low saturated soybean oil or palm oil with guayule rubber, the balance between fuel economy and wet traction was adjusted to provide performance attributes similar to the control rubber. Blending two or more sustainable processing oils in guayule formulations in order to further refine compound chemistry may yield additional performance improvements. Based upon processing, physical and performance predictor results, future studies are recommended to further optimize use of palm oil, soybean oil, blends of sustainable oils and guayule rubber in SBR/NR or NR compounds.

Overall, the use of bio-plasticizers and alternative natural rubber provides a promising material choice compared to standard oil and rubber matrices, as supported by comparable mechanical properties and performance predictors. These materials provide opportunities to reduce the environmental footprint of rubber products and in some cases, increase domestic availability of raw ingredients. The sustainable plasticizers show promise in replacing part or all of petroleum derived processing oils such as TDAE oil for use in low rolling resistance tread compounds. Potential future outlook for using these types of sustainable raw materials in tread compounds is dependent upon economies of scale, availability and further evaluations for optimizing tire performance during vehicle usage. The recent expansion of research into agricultural, raw materials for rubber compounds provides new choices for developing high performance products with increased sustainable content.

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