UJEAS

UNIZIK JOURNAL OF ENGINEERING
AND
APPLIED SCIENCES

UNIZIK Journal of Engineering and Applied Sciences 2(2), September (2023), 378-391
Journal homepage: https://journals.unizik.edu.ng/index.php/ujeas
PRINT ISSN: 2992-4383 || ONLINE ISSN: 2992-4391

Evaluating the Effect of Carbon Black and Silica Hybrid Reinforcement on the Rheological Behavior, Rebound Resilience, Tensile Properties and Tear Strength of Solid Tire Tread Compound Containing Ground Tire Rubber

Ifeoma Janefrances Umunakwe[1], Dosu Malomo[1], Reginald Umunakwe[2]*
[1] Department of Chemistry, Faculty of Science, Federal University Oye-Ekiti, Ekiti State, Nigeria
[2] Department of Materials and Metallurgical Engineering, Faculty of Engineering, Federal University Oye-Ekiti, Ekiti State, Nigeria
*Corresponding Author's E-mail: reginald.umunakwe@fuoye.edu.ng

Abstract

The generation of waste rubber and their disposal to the environment pose serious environmental problems. Researchers have shown interest in the incorporation of ground tire rubber (GTR) into rubber vulcanizates. The major challenge is that the addition of GTR in rubber vulcaniztaes reduces the strength and elongation of the vulcanizate. This work investigates effect of addition of precipitated silica to solid tire tread compound containing 10 phr and 20 phr of 60 mesh size GTR on the cure behavior, Mooney viscosity and Payne effect of the rubber compounds, and the tensile properties of the vulcanizates. The GTR and precipitated silica were initially characterized using optical microscope and particle size analyzer, while thermogravimetric analyzer was further used to characterize the GTR. In the formulation of the tire tread compound, silica was added at 5, 10 and 15 phr together with carbon black at 55, 50 and 45 phr respectively. The mixing followed two-step process. Results show that the 60 mesh size GTR particles were irregular and composed majorly natural rubber, synthetic rubber, fillers and additives. The silica aggregates were roughly spherical. The addition GTR in the rubber compounds resulted to increased viscosity, high Payne effect, reduced tensile strength, elongation, tear strength, rebound resilience and increased modulus. The optimal amount of silica found to achieve improved properties was 10 phr together with 50 phr of carbon black.

Keywords: Tire tread, recycling, hybrid filler, ground tire rubber, properties

1. Introduction

Man's use of products made with rubber such as tires, rubber automobile parts including seals, bearings and shock absorbing components, medical goods such as gloves and condoms as well as general rubber is indispensable. Rubber usually undergoes vulcanization during processing to form solid cross-linked network. The rubbers in these goods are in vulcanized state and therefore do not degrade after service life. They add to solid waste generation. The generation of rubber waste keeps increasing as the years pass. According to report (Alkadi *et al*., 2019), about 1.5 billion tire are produced annually throughout the world. The production of tires consumes about 70% annual global rubber productions (Forrest, 2019). Therefore, the annual generation of end-of-life tires which add to solid waste keeps increasing. It was reported that about 4 million scrap tires were generated in US alone in 2015 (Czajczynska *et al*., 2017). It has been estimated that the amount of end-of-life tires generated each year can reach up to 1.2 billion pieces in the year 2030 (Leong, *et al*., 2023). Due to the cross-linked nature of vulcanized rubber, rubber wastes are very difficult to recycle. Researchers and industries are therefore exploring several options to manage, use and recycle waste rubber products especially end-of-life tires. For example, polymer based recycled ground tire rubber (GTR) composites suitable for 3D printing was developed (Alkadi *et al*., 2019). He *et al*. (2016) investigated the effect of reinforcing cement concrete with oxidized and sulphonated GTR and reported that surface modified GTR improved the mechanical properties of the concrete when compared with unmodified ones by reducing the contact angle and improving the surface adhesion.

Recent work has suggested that the fracture toughness of cement concrete can be improved by reinforcing it with optimal amount (about 4%) of coarse grain recycled tire granules (Karimi *et al*., 2023). Another report suggested that the addition of up to 20% waste rubber powder in asphalt resulted to reduced viscoplastic damage deformation and residual viscoplastic damage deformation of the asphalt in service (Li *et al*., 2023). In poulyurethane, it was reported that H_2O_2 modified GTR offered better improvement as reinforcement than $KMNO_4$ modified GTR (Hejna *et al*., 2021). In polypropylene, the introduction of GTR as filler was reported to reduce the compressive strength and hardness of the composite compared to the unreinforced polymer; however, with the acid modified GTR, less reduction in the properties were reported compared to the use of the unmodified GTR (Elenien *et al*., 2018). The incorporation of waste rubber in rubber based compounds is also being explored. GTR is usually blended with natural rubber (NR), styrene butadiene rubber (SBR), polybutadiene rubber (BR), and acrylonitrile butadiene rubber (NBR) due to the high compatibility of ground tire rubber with these rubbers (Ramarad *et al*., 2015).

However, it has been reported that GTR is not as reinforcing as carbon black (HAF) as filler in rubber based compounds due the poor chain mobility in GTR resulting to poor interaction with rubber matrices (Fazli *et al*., 2020). As a result of poor reinforcing ability of GTR in rubbers, the need to further improve the properties of rubber vulcanizates containing GTR becomes very important. El Mogy and Lawandy (2023) have reported the possibility of improving the properties rubber vulcanizates based on waste tire rubber by incorporation of nanoclay as reinforcement in the rubber. The use of hybrid filler reinforcement to improve the properties of rubber based compounds containing GTR is currently being explored. The incorporation of silica in tire tread compound is presently very popular because silica imparts improved tear strength, ageing resistance and lower rolling resistance Senthilvel *et al*., 2016). In this work, the effect of replacing some portions of carbon black with silica in a solid tire tread compound containing GTR on the rheological behavior, rebound resilience, tear strength and tensile properties of the vulcanizate are presented. The research is geared towards environmental sustainability and improving the mechanical properties of rubber compounds containing GTR.

2.0 Material and methods

2.1 Materials - 60 mesh size ground tire rubber (GTR) was provided. Natural rubber (NR) grade STR 20 was gotten from L. C. E. H Bangkok (Thailand) Co. Ltd., butadiene rubber (BR) (BR 01) was from BST Elastomers Co., Ltd., zinc oxide (ZnO) was from Thai-Lysaght Co., Ltd., stearic acid was from Asia Chem Co., Ltd., N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) was from Eastman Chemical Switzerland LLC, poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (TMQ) was from Monflex PTE Ltd., aromatic oil was from P. S. P. Specialties Public Company Limited.

Table 1: Formulation of vulcanized rubber samples for outer layer (tread) of solid tire (Umunakwe *et al.*, 2023)

	Amount (phr)										
Chemical/Sample	**Control**	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**	**F9**	**F10**	**F11**
NR(STR20)	80	72	72	72	72	72	64	64	64	64	64
BR (01)	20	18	18	18	18	18	16	16	16	16	16
60 mesh size GTR	-	10	10	10	10	10	20	20	20	20	20
ZnO	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
6PPD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1	1	1	1	1	1	1
Aromatic oil	10	10	10	10	10	10	10	10	10	10	10
CB (N330)	60	60	60	55	50	45	60	60	55	50	45
Silica	-	-	-	5	10	15	-	-	5	10	15
Si69	-	-	-	0.5	1	1.5	-	-	0.5	1	1.5
S	2	2	2	2	2	2	2	2	2	2	2
TBBS	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

Carbon black (N330) was from Birla Carbon (Thailand) Public Company Limited, precipitated silica (Tokusil 255) was from OSC Siam Silica Co. Ltd., bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT or Si69 coupling agent) was from Briture Co. Ltd., sulfur was from The Siam Chemical Public Company Limited and N-tert-butyl-2-benzothiazyl sulphenamide (TBBS) was from Ningbo Actmix Rubber Chemicals Co., Ltd. The formulation used for production of the samples and the codes given to various samples for identification are presented in Table 1 (Umunakwe *et al,* 2023).

2.2 Methodology

2.2.1 Characterization of the GTR and precipitated silica - The morphology of the GTR and precipitated silica were studied with a high resolution optical microscope (Olympus BX53M, Japan) at magnification of × 1000. The particles size distribution of the particles were analyzed under dry mode with Mastersizer 2000 (Marvern Instruments, United Kingdom). Thermogravimetric analysis (TGA) was carried out on the GTR with TGA analyzer (NetzschTG 209 F1 Libra, Germany) by heating about 10 mg of the GTR sample in alumina pan under nitrogen atmosphere at a flow rate of 10 ml/min and heating rate of 20 ℃/min from room temperature (22℃) to 600℃ and then in oxygen atmosphere at the same flow rate and heating rate from 600℃ to 850℃.

2.2.2 Formulation and mixing - The recipe used for the production of the various samples of vulcanized rubber for the outer layer (tread) of solid tire is shown in Table 1. The mixing was carried out by two-step mixing method. The first step of the mixing for samples "control", "F2" and "F7" following the order of mixing presented in Table 2 was done using a 500 ml laboratory internal mixer (Brabender plasticoder lab station, Germany) at a starting temperature of 60℃, fill factor of 0.78 and rotor speed of 40 rpm. After dumping from the internal mixer, the compound was allowed to cool to room temperature before it was transferred to two-roll mill for mixing step 2 at 30℃ for 5 minutes to homogenize the compound. The mixing for samples "F3 to F6" and "F8 to F11" was carried out with the same internal mixer and also used the two-step mixing method as shown in the order presented in Table 3 at a starting temperature of 100℃ (Sattayanurak *et al*., 2020), fill factor of 0.78 and rotor speed of 40 rpm. After the compound removed from internal mixer cooled to room temperature, the second steps of mixing for the formulations were carried out on a two-roll mill at 30℃ for 6 minutes. The curatives (TBBS and S) were incorporated at the 3rd minute on the two roll mill and homogenized mixing was ensured. The rubber compounds were stored at room temperature for 24 hours before further processing.

Table 2: Order of mixing in the step 1 for samples "control", "F2" and "F7" (Umunakwe *et al*., 2023)

Time (minute)	Operation
0	Loading STR 20, BR150 and GTR (where applicable)
1st	ZnO, stearic acid, 6PPD, TMQ, ¼ of carbon black
3rd	¾ of the carbon black, aromatic oil
6th	Sulfur + TBBS
8th	Dumping

Table 3: Order of mixing in the step 1 for samples "F3 to F6" and "F8 to F11" (Umunakwe *et al*., 2023)

Time (minute)	Operation
0	Loading STR 20, BR150 and GTR (where applicable)
1st	ZnO, stearic acid, 6PPD, TMQ, ¼ of carbon black, silica and Si69 (where applicable)
3rd	¾ of the carbon black, aromatic oil
6th	Dumping

2.2.3 Determination of the Mooney viscosity, cure behavior and Payne effect of the rubber compounds - About 25 g of the uncured rubber sample was used to determine the Mooney viscosity (ML_{1+4}, 100℃) of each rubber compound at 100℃ after 4 minutes using the testing machine (Gotech, Taiwan) following ISO-289-1-2015 standard. 3 specimens of each compound were tested and the average value was reported. The cure behavior of each rubber compound was studied with a moving die rheometer (MDR-01, CGM Technology, Thailand) at 150℃ in line with ASTM D 2084-2019 standard using 5 g of the sample. The cure rate index (CRI) for each compund was calculated using the optimal cure time (t_{c90}) and scorch time (t_{s1}) from equation (1) (Zhao *et al*., 2019). 5g of each uncured rubber sample was used to determine the storage modulus at a temperature of 100℃, frequency of 0.5 Hz at varied strain amplitude sweep in the range of 0.1-300.065 using rubber process analyzer (RPA elite, TA instruments) (Sattayanurak *et al*., 2020). 3 repeated tests were carried out on each sample. The Payne effect of each sample was reported as the difference in storage moduli at low strain (0.096%) and high strain (100%).

$$\text{CRI} = \frac{100}{t_{c90} - t_{s1}} \tag{1}$$

2.2.4 Molding of the rubber vulcanizates - Compression molding process with hydraulic press (Wabash MPI, USA) was used to produced 2 mm vulcanized rubber sheets for tensile and tear tests, as well as cylindrical samples having 28.5 mm height and 12.5 mm diameter for rebound resilience measurement. The molding was carried out under a molding pressure of 20 tons-force at 150°C. The optimal vulcanization time (t_{c90}) of each sample gotten from the cure curve was the time used to produce 2 mm thick rubber sheets, while $t_{c90} + 6$ minutes was used to produce the samples for rebound resilience measurement.

2.2.5 Determination of tensile properties, tear strength and rebound resilience - Cutting die was used to cut dumbbell shaped specimens from the 2 mm thick sheet for tensile testing and the cut specimens were grouped into specimens for ageing and for non ageing. Room temperature (23℃) tensile testing of each specimen was carried out using the universal testing machine (Instron model 5566, USA) at cross-head speed of 500 mm/min according to ASTM D412-16 (2021) standard. Elongation was measured with extensometer attached to the testing machine and set at 2.5 mm gauge length. 5 repeated tensile tests were carried out on each sample and the average results reported to ensure reliability. Ageing was carried out on the prepared specimens inside an air circulating oven (Gotech GT-7017-EL, Taiwan) maintained at 100℃.for 22 hours before they were brought out and kept at room temperature for 24 hours (Zhou *et al*., 2023). The aged specimens were also subjected to tensile testing and ageing resistance of each sample was computed in terms of percentage retention of the tensile properties after ageing using equation (2) (Arayapranee and Rempel, 2013).

$$\text{Property retention (\%)} = \frac{Value\ obtained\ after\ ageing}{value\ obtained\ before\ ageing} \times 100\% \tag{2}$$

Also, cutting die was used to prepare samples from the 2 mm vulcanized rubber sheets for tear tests and the test was carried out on the universal testing machine at cross-head speed of 500 mm/min in line ASTM D624-00 (2020) standard. 5 repeated tests were carried out for each sample and the average results were reported. Rebound resilience of the rubber vulcanizates at 90° impact angle was measured with pendulum type rebound resilience tester (Gotech, GT-7042-RDA, Taiwan) utilizing 0.5 J impact according to ASTM D7121-05(2018). 3 specimens of each sample were tested and the average results were reported. Rebound resilience (or percentage rebound) was calculated from equation (3). α is the rebound angle.

$$\text{Rebound resilience (\%)} = \frac{1 - \cos\alpha}{1 - \cos 90} \times 100 = 1 - \cos\alpha \quad \times 100 \tag{3}$$

3.0 Results and Discussions

3.1 Properties of the GTR and Precipitated Silica – The results of the optical microscopy, particles size analysis, and thermogravimetric analysis are presented.

3.1.1 Optical micrographs of the GTR and precipitated silica - The optical micrograph of the 60 mesh size GTR is shown in Figure 1. The morphologies of the GTR particles are visibly irregular in shape and have rough surfaces. That is an indication that the GTR was mechanically ground at ambient temperature (Spanheimer *et al*., 2020). The optical micrograph of the precipitated silica used for the experiment is shown in Figure 2. Although, silica precipitated as particles during its production, the particles however formed aggregate and agglomerates outside the production system and while stored. Commercial precipitated silica packaged and sold rarely exists as particles. The particles seen in the micrograph are actually aggregates of many particulate silica. It can be seen from Figure 2 that the silica particles are roughly spherical in shape as each aggregate appear roughly spherical in shape. Similar morphology for precipitated silica has also been reported by Liu *et al.* (2009).

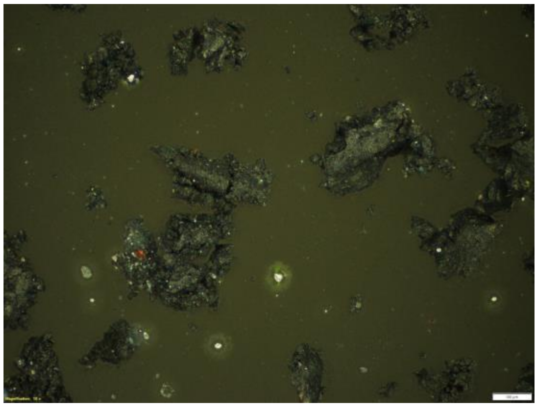

Figure 1: Optical micrograph of the 60 mesh size GTR

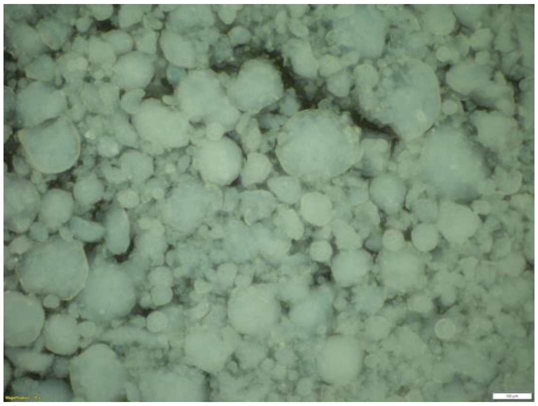

Figure 1: Optical micrograph of the 60 mesh size GTR

3.1.2 Particles size distribution of the GTR and precipitated silica - The particles size distribution of the 60 mesh GTR is shown in Figure 3. The particles size distribution is roughly 90% below 298.842 µm, 50% below 186.764 µm and 10% of the particle below 115.373 µm in size. The particles size (aggregate size) distribution of the precipitated silica as seen in Figure 4 are 90% below 177.730 µm, 50% below 47.505 µm while 10% of aggregate sizes are below 7.639 µm. Obviously, the sizes of the precipitated silica are finer than the particles of the GTR.

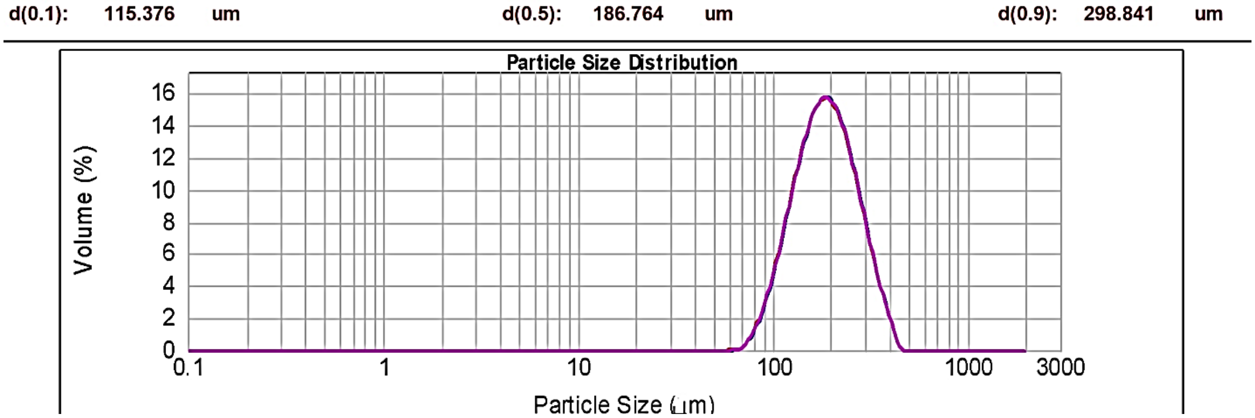

Figure 3: Particles size distribution of the 60 mesh size GTR

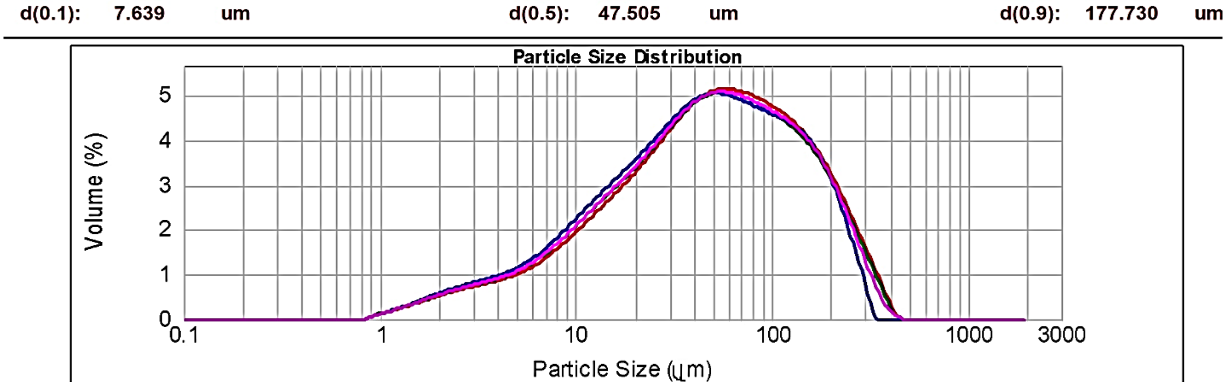

Figure 4: Particles size distribution of the precipitated silica

3.1.3 TGA and DTG curves of the GTR - The TGA and DTG curves of the GTR are shown in Figure 5. Similar thermogram for GTR was earlier reported (Wang *et al.*, 2020). The first stage of degradation in the TGA curve represents the degradation of volatile matters like moisture and plasticizers. It started at about 250℃ up to about 320℃ resulting to about -8.5% weight loss. The second stage roughly between 320℃ and 420℃ represents the degradation of natural rubber which recorded about -42% weight loss. The degradation of the synthetic rubber (SBR and BR) started thereafter and reached to about 490℃ resulting to about -15% weight loss. Carbon black decomposed at temperatures between 600℃ and 650℃ and recorded about 29% while the residual weight was about 5.6%. The major peaks from the DTG curves were observed at 386℃, 485℃ and 641℃ signifying the temperature at which the maximum rate of weight loss occurred. The first peak was the degradation of natural rubber while the second and third peaks were those of synthetic rubber and carbon black respectively.

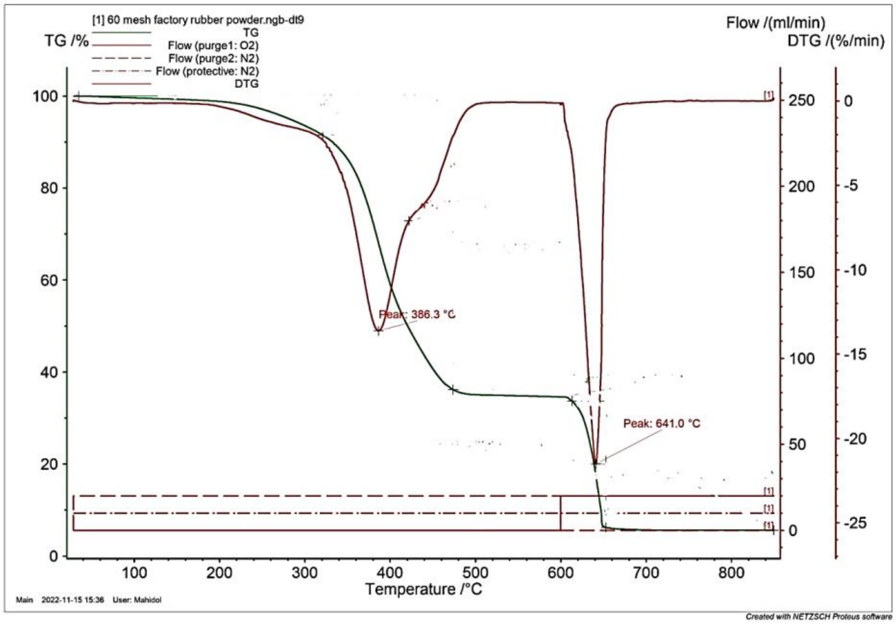

Figure 5: TGA and DTG curves of the 60 mesh size GTR

3.2 Rheological Properties of Rubber Compounds – The results of the Mooney viscosity, cure behavior, and payne effect of the rubber compounds are presented.

3.2.1 Mooney viscosity of the rubber compounds - The Mooney viscosity of the rubber compounds are presented in Table 4. The addition of GTR to rubber compound resulted to increased viscosity while the increase in the amount of the GTR from 10 phr to 20 phr resulted to further increase (see F2 and F7). The increase in viscosity due to the addition of GTR was reported to be due to the cross-linked nature of the GTR which does not allow chain mobility in the rubber compound (Hrdlička *et al.*, 2022). Also, more GTR in the matrix means increase in the amount of carbon black resulting to higher viscosity. When the same formulation containing GTR were mixed at a higher temperature (starting mixing temperature of 100℃), the viscosity further increased at both 10 and 20 phr of GTR addition (see F3 and F8). The increase in viscosity resulting from mixing at higher temperature could be said to be due to some cross-linking reaction as a result of small amount of accelerator and sulfur in the GTR added (Kaewsakul *et al.*,2012). The major observation when silica was added at 5 phr was further increase in the Mooney viscosity at both 10 phr and 20 phr GTR addition (see F4 and F9).

Upon increasing the silica to 10 phr and reducing carbon black, the viscosity significantly reduced (see F5 and F10), while further increase in silica addition to 15 phr (and reduction of carbon black from 60 phr to 45 phr) started pushing the viscosity up again. The initial increase in the addition small amount of silica could be attributed to poor distribution. At that amount, the small amount of silica could have been trapped in between the GTR resulting to poor distribution and dispersion, hence high viscosity. The hydroxyl groups on the surface of silica promotes filler-filer interaction and hence filler aggregates were formed when the small amount of silica added were trapped (Ulfah *et al*., 2015). When the silica increased, the interaction between rubber and silica improved, the silica aided the distribution and dispersion of fillers and GTR, hence the significant drop in the viscosity. The silane coupling agent helped in the coupling of silica to rubber. Beyond the optimal amount of silica in the rubber, the filler-filler interaction increased and hence the viscosity also increased.

Table 4: Mooney viscosity, MU (M_{L1+4}, 100℃)

Sample	Control	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
MU	58.87	66.04	72.9	76.07	61.49	83.41	69.83	81.69	99.14	63.65	84.07
Std. dev.	0.26	0.76	0.10	0.67	0.49	0.12	0.22	0.23	0.69	0.36	0.09

3.2.2 *Cure behvior* of the rubber compounds - The rheometric curves of the rubber compounds are shown in Figure 6 while the data from the rheometric curves are presented in Table 5. The minimum torque (M_L) followed similar trend as the Mooney viscosity. The addition of GTR in the rubber compounds (F2 and F7) resulted to reduced scorch time (t_{s1}) and cure time (t_{c90}) because of the migration of sulfur and accelerator from the GTR to the rubber matrix resulting to high cure rate (Formela & Haponiuk, 2014).

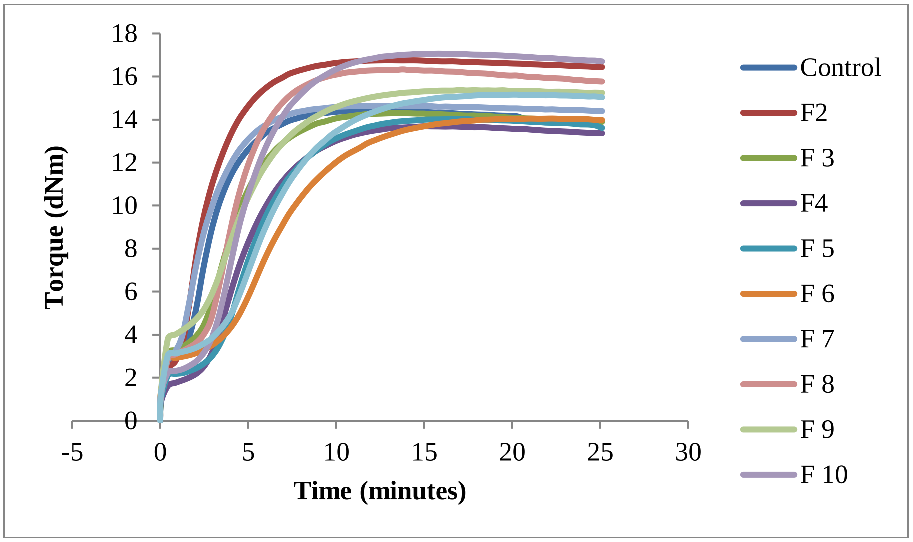

Figure 6: Cure curves of the rubber compounds

Table 5: Rheometric data of the uncured rubber samples

Sample	Maximum torque, M_H (dNm)	Minimum torque, M_L (dNm)	$M_H – M_L$ (dNm)	Scorch time, t_{s1} (min)	Optimal cure time, tc_{90} (min)	CRI
Control	14.72 (0.31)	2.23 (0.04)	12.49 (0.30)	1.72 (0.01)	6.56 (0.10)	20.66
F2	16.77 (0.35)	2.75 (0.14)	14.01 (0.34)	1.30 (0.01)	5.86 (0.11)	21.93
F3	14.3 (0.14)	3.28 (0.04)	11.02 (0.10)	2.34 (0.01)	7.43 (0.13)	19.65
F4	13.70 (0.11)	2.83 (0.13)	10.87 (0.09)	2.71 (0.06)	8.88 (0.09)	16.21
F5	14.02 (0.09)	2.18 (0.05)	11.85 (0.06)	3.08 (0.02)	9.37 (0.13)	15.90
F6	14.05 (0.05)	2.92 (0.05)	11.13 (0.02)	3.55 (0.03)	11.90 (0.02)	11.98
F7	14.65 (0.78)	3.23 (0.03)	11.43 (0.76)	1.33 (0.04)	5.57 (0.07)	23.58
F8	16.33 (0.21)	3.42 (0.10)	12.91(0.14)	2.55 (0.07)	7.24 (0.13)	21.32
F9	15.38 (0.04)	3.91 (0.17)	11.46 (0.20)	2.27 (0.10)	9.09 (0.04)	14.66
F10	17.03 (0.21)	2.31 (0.05)	14.76 (0.21)	2.58 (0.05)	8.46 (0.08)	17.01
F11	15.15 (0.07)	3.16 (0.03)	11.97 (0.06)	3.31 (0.04)	11.06 (0.13)	12.90

(The standard deviations are in the brackets)

The samples mixed at higher temperature (F3 and F8) did not have shorter t_{s1} and t_{c90} because the little accelerator and sulfur in the GTR may have reacted out during mixing while accelerators and sulfur were incorporated at lower temperature. The samples with silica reinforcement have longer t_{s1} and t_{c90} and the parameters increased as the amount of silica increased. This is because, silica has high density of silanol group on the surface which interfere with the vulcanization process due to their acidic nature and also have the tendency to absorb vulcanization accelerators, hence slowing down the cure rate (Sattayanurak *et al.*, 2019).

3.2.3 Payne effect - Filler-filler interaction which is referred to as Payne effect affects the properties of rubber vulcanizates. Payne effect is usually estimated as the difference in storage modulus (G') at low strain and that at high strain (Sattayanurak *et al.*, 2020). The graph of the G' against strain for the rubber compounds containing 10 phr GTR and 20 phr GTR is shown in Figures 7 (a-b). In both Figures 7a and 7b, the addition of GTR in the tire tread compound and 10 phr and 20 phr increased the storage modulus (F2 and F7) indicating a high filler-filler interaction. Mixing at higher temperature slightly reduced the storage modulus (F3 and F8), while silica addition with its attendant reduction in carbon black reduced the storage modulus. The samples containing 10 phr of silica exhibited the lowest storage moduli at both 10 phr and 20 phr GTR addition (F5 and F10) indicating that at the loading, the lowest filler-filler interaction was recorded which translated to good filler-rubber interaction. A higher Payne effect was observed at 5 phr silica addition, while Payne effect observed at 15 phr silica addition was also higher than the values at 10 phr silica addition. The results of the Payne effect correlate with the Mooney viscosity results.

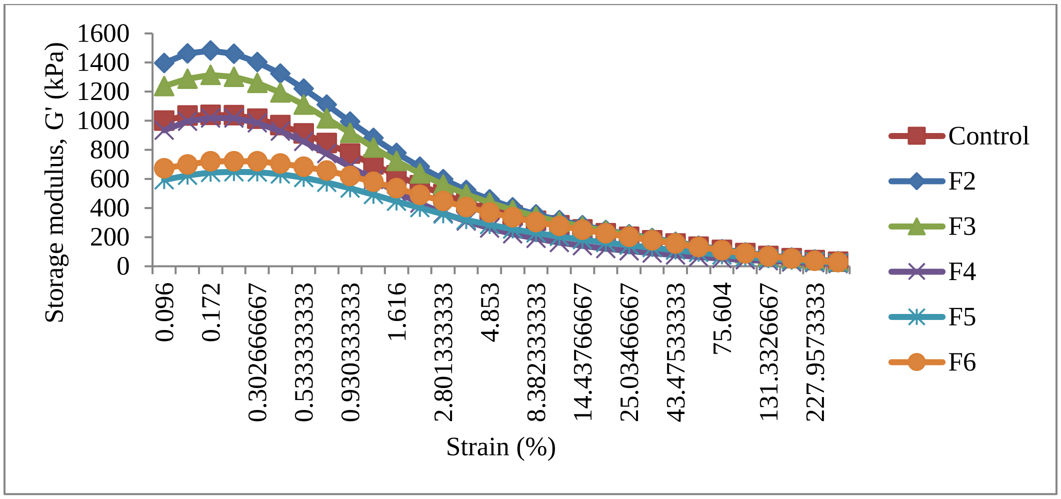

Figure 7a: Payne effect of the rubber compounds at 10 phr GTR loading

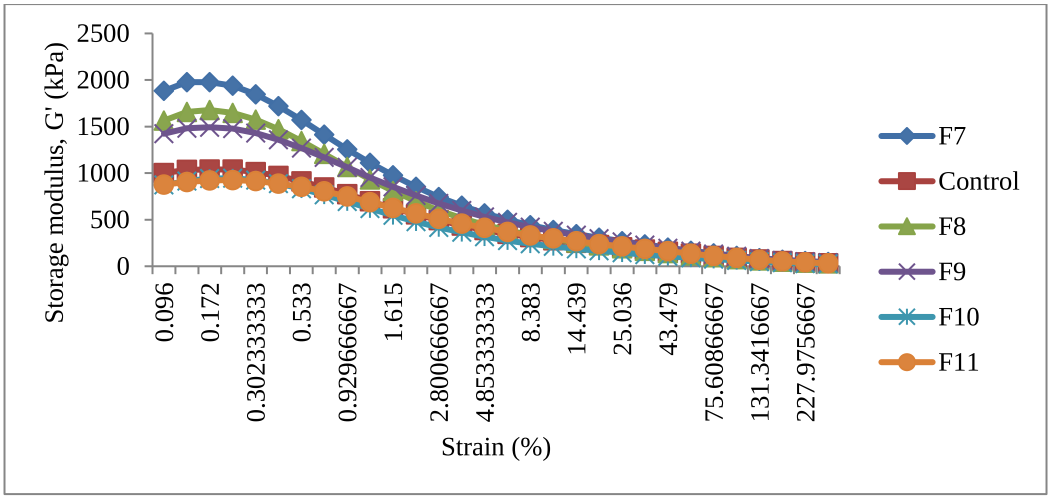

Figure 7b: Payne effect of the rubber compounds at 20 phr GTR loading

3.3 Mechanical Properties of the Vulcanizates –

3.3.1 Tensile properties - The results of the tensile strength of the compounds before and after ageing are shown in 8a while their tensile retention are shown in Figure 8b. While it was observed that the addition GTR to the tire tread compound resulted to reduced tensile strength with further reduction in strength as the amount of the GTR increased (F2 and F7) compared to the control sample in line with earlier reports (Mangili *et al*., 2015; Simon and Bárány, 2023), mixing at higher temperature slightly increased the strength compared to the samples mixed at lower temperature (F3 and F8 having higher strength than F2 and F7). The initial addition of silica at 5 phr further reduced the strength at both 10 phr and 20 phr of GTR loading (F4 and F9) due to higher filler-filler (silica-silica) interaction as a result of the filler being trapped in the bulk of the materials in its small quantity resulting to poor dispersion and high Payne effect. The best improvement in strength was achieved at 10 phr silica loading at both 10 phr and 20 phr GTR addition. About 12.94% and 16.97% increase in tensile strength was recorded at 10 phr silica addition at 10 phr and 20 phr GTR loading over the samples containing GTR without silica (F5 and F10 compared to F2 and F7). Beyond 10 phr silica loading, it was observed that the strength was still higher than those of the samples without silica, though it started reducing.

The improvement in strength due to silica addition can be attributed to improvement in filler-rubber interaction (lower Payne effect) and coupling of silica and rubber with silane resulting to production of vilcanizates with better cross-links. The samples containing 5 phr (F4 and F9) of silica recorded the lowest ageing resistance indicated by very low tensile retention due to its high viscosity resulting to poor distribution and high Payne effect. As expected, the addition of GTR in the tire tread compound resulted to reduced elongation (Figure 8c) and increased modulus (Figure 8 (e-f). Improvements in the elongation were achieved at 10 phr silica addition with further improvement at 15 phr silica addition. Rattanasom *et al*. (2007) has earlier reported that in hybrid carbon black/silica reinforcement of elastomers, increase in silica loading leads to higher elongation. The results obtained in this research followed the same trend. The ageing resistance also monitored using elongation retention (Figure 8d) shows that the sample containing 10 phr of silica showed the best ageing resistance among all saples containing GTR. The addition of GTR in rubber vulcanizates leads to increased modulus and this is not desirable (Figure 8 (e-f). Silica addition to the compounds containing 10 phr GTR effectively reduced the modulus because of the higher elongation recorded. Silica addition could not lower the modulus for the compounds containing 20 phr GTR until the silica was increased up to 15 phr. It is an indication that at 15 phr silica addition, the cross-link density of the rubber vulcanizate reduced resulting to higher elongation and reduced modulus.

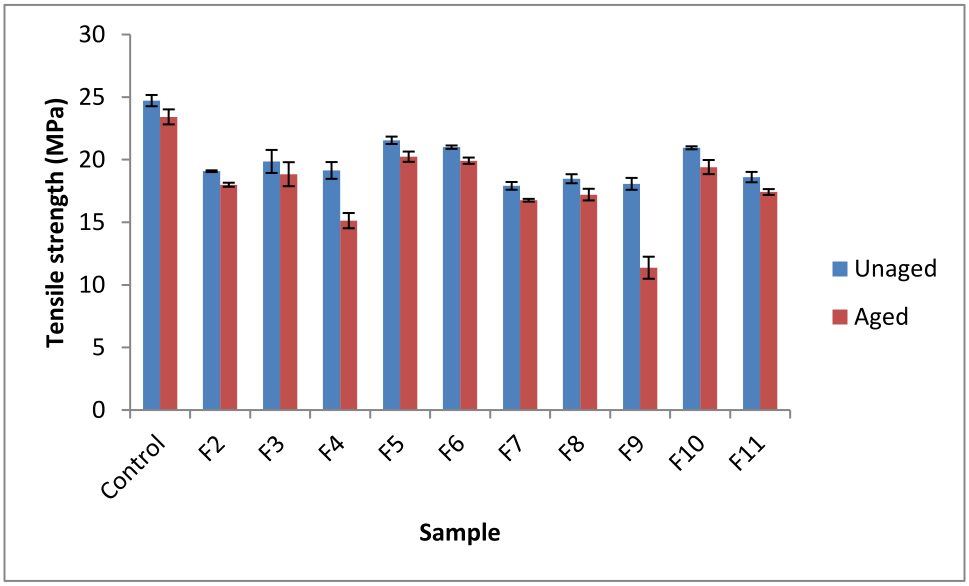

Figure 8a: Tensile strength of the rubber vulcanizates

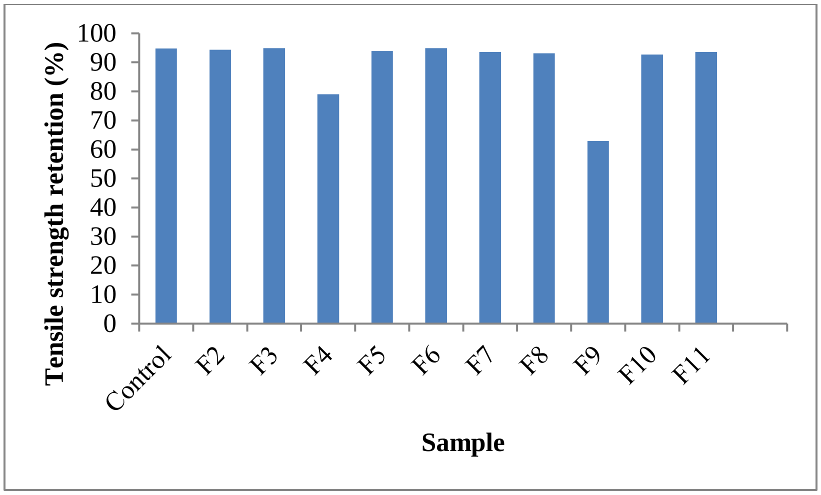

Figure 8b: Tensile retention of the rubber vulcanizates

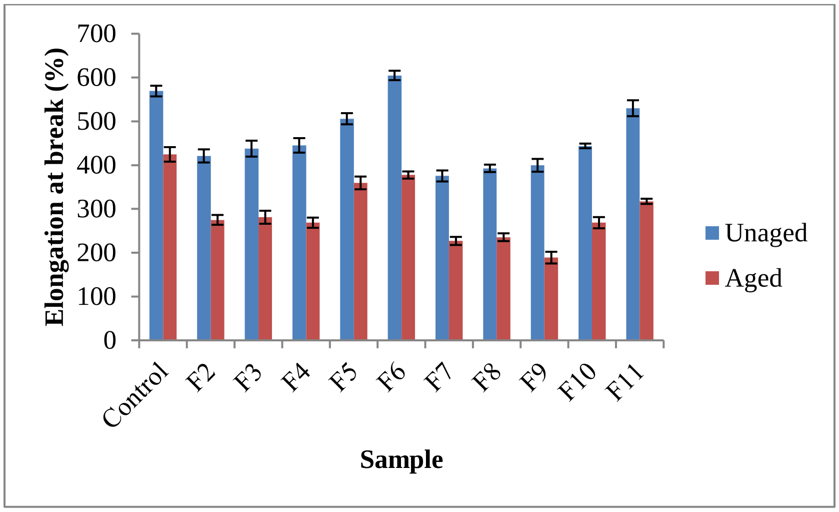

Figure 8c: Elongation at break of the vulcanizate samples

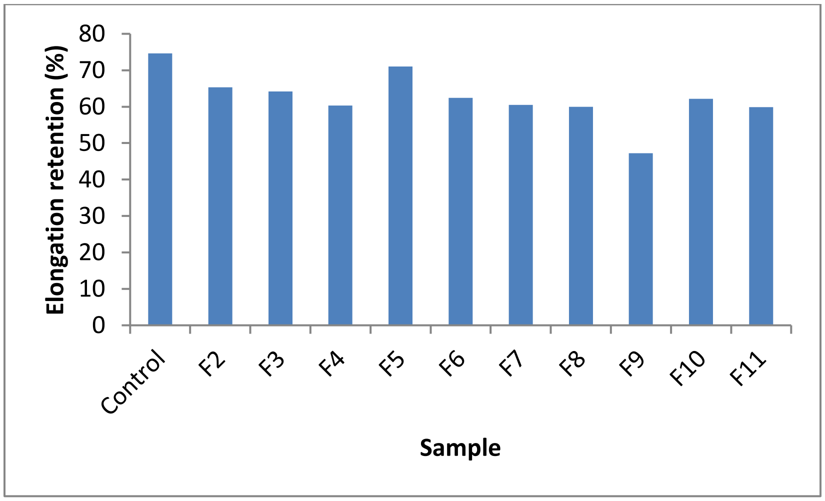

Figure 8d: Elongation retention of the vulcanizate samples

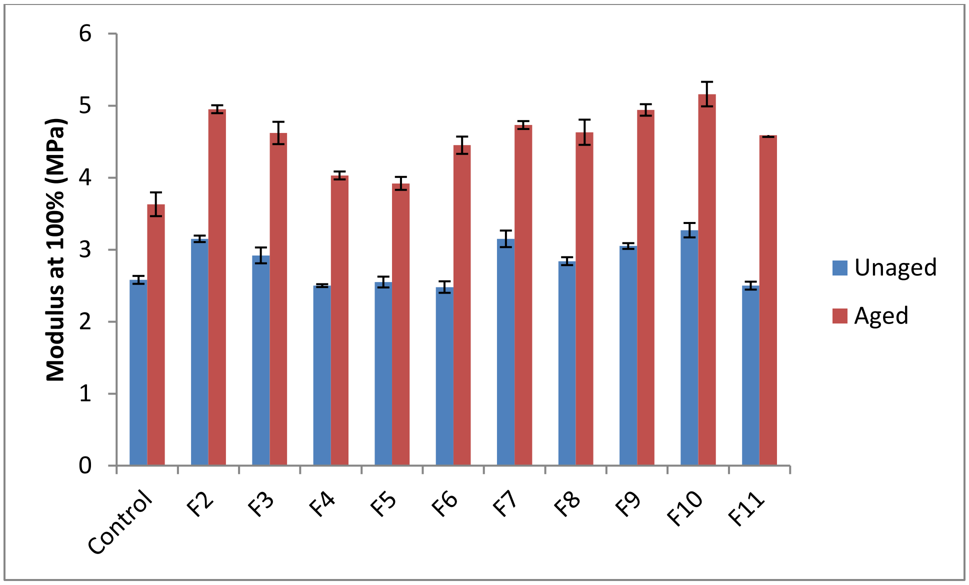

Figure 8e: Modulus at 100% of the vulcanizate samples

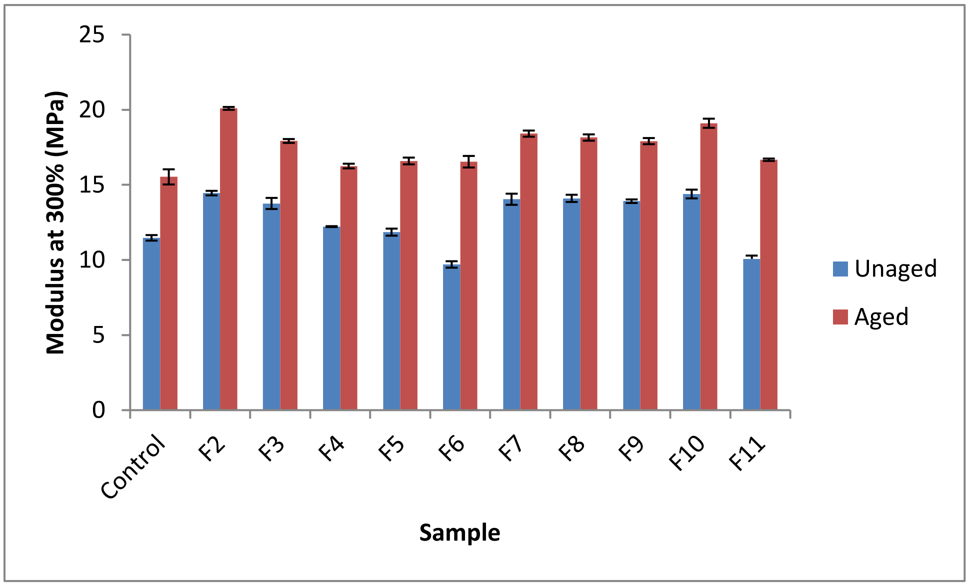

Figure 8f: Modulus at 300% of the vulcanizate samples

3.3.1 Tear strength - The tear strength of the rubber vulcanizates are shown in Figure 9. Also, GTR addition to the tire tread compound resulted to reduced tear strength (F2 and F7). Similar to tensile strength results, modification of the mixing method slightly increased the tear strength (F3 and F8) due to improved dispersion. 5 phr silica addition resulted to more reduced tear strength in agreement with the tensile strength. Increasing the silica to 10 phr and further to 15 phr significantly improved the tear strength for sample containing 10 phr GTR (up to 29.34% improvement of tear strength of F6 over F2). At 20 phr GTR loading, the best improvement was at 10 phr silica addition (up to 50.41% increase in tear strength of F10 over F7). Beyond that, silica-silica interactions increased and tear strength reduced. One of the attractive properties of silica as rubber reinforcement is its ability to improve the tear strength of vulcanizates as shown in the results.

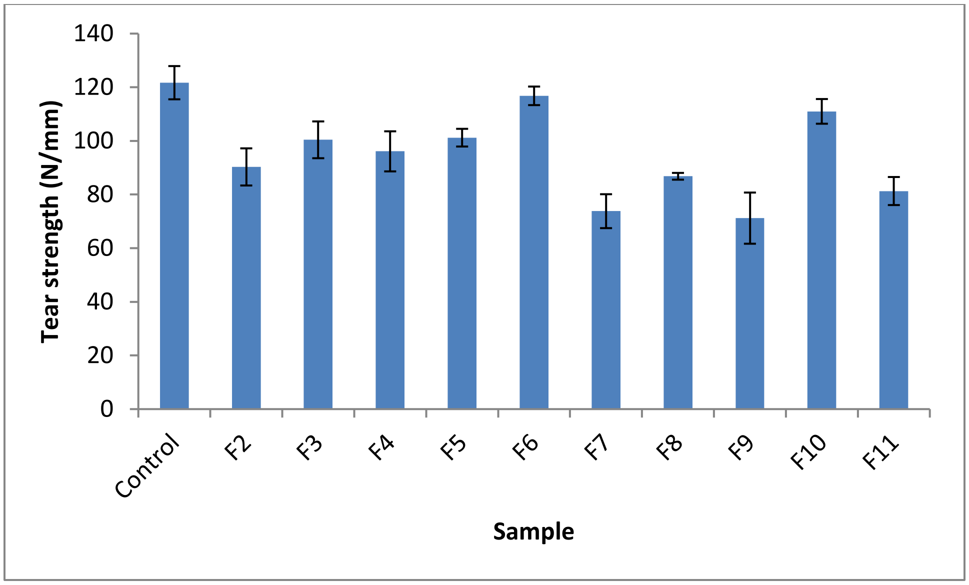

Figure 9: Tear strength of the vulcanizate samples

3.3.1 Rebound resilience - The results of the rebound resilience shown in Figure 10 also suggest that silica addition at the optimal amount will help to recover part of the elasticity of tire tread rubber vulcanizate containing GTR. The rebound resilience also showed similar trend with the elongation.

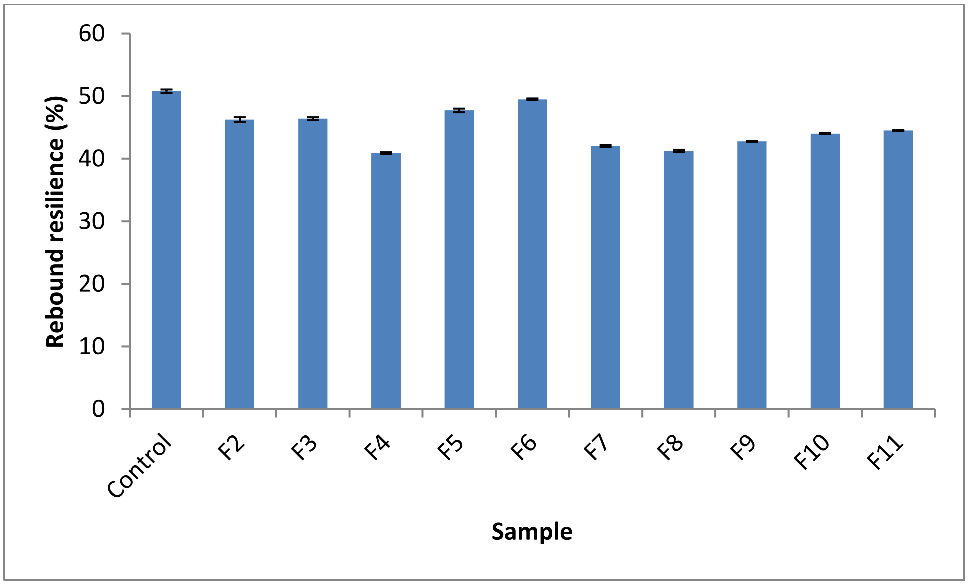

Figure 10: Rebound resilience of the vulcanizate samples

4.0. Conclusions

In this research, the possibility of improving the mechanical properties of solid tire tread compound containing GTR by incorporation of silica as secondary filler in carbon black reinforced solid tire tread compound has been explored. The results from the rheological studies show that silica addition at the optimal amount can reduce the viscosity and Payne effect thereby improving the filler-rubber interaction in the rubber compounds. When the silica loading exceeded the optimal level, silica-silica interaction increased and viscosity was higher. The incorporation of coupling agent was necessary. A correlation was observed between the rheological properties and mechanical properties. Although the addition of GTR in solid tire tread compound reduced the tensile strength, elongation, tear strength, rebound resilience and increased the modulus of solid tire tread compound, reduction of carbon black from

60 phr to 50 phr and incorporation of 10 phr of silica together with silane coupling agent helped in improving the filler-rubber interaction resulting to the recovery of some percentage of the lost mechanical properties in the rubber vulcanizate.

5.0 Recommendation

It is recommended that further studies be carried out on the incorporation of GTR of varied particles sizes at various amounts in tire tread compound reinfocrd with hybrid carbon black/silica reinforcement.

References

Alkadi, F., Lee, J., Yeo, J. S., Hwang, S. H., Choi, J. W. 2019. 3D printing of ground tire rubber composites. *International Journal of Precision Engineering and Manufacturing-Green Technology*, 6, 211–222.

Arayapranee, W., Rempel, G. L. 2013. Effects of polarity on the filler-rubber interaction and properties of silica filled grafted natural rubber composites. *Journal of Polymers*, 279529.

ASTM D 2084: 2019. Standard Test Method for Rubber Property—Vulcanization Using Oscillating Disk Cure Meter. American Society for Testing and Materials.

ASTM D412-16 (2021). Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension. American Society for Testing and Materials.

ASTM D624-00 (2020). Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers. American Society for Testing and Materials.

ASTM D7121-05(2018). Standard Test Method for Rubber Property—Resilience Using Schob Type Rebound Pendulum. American Society for Testing and Materials.

Czajczynska, D., Krzyzynska, R., Hussan, J., Spencer, N. 2017. Use of pyrolytic gas from waste tire as a fuel: a review. *Energy*, 134, 1121-1131.

Elenien, K. F., Abdel-Wahab, A., ElGamsy, R., Abdellatif, M. H. 2018. Assessment of the properties of PP composite with addition of recycled tire rubber. *Ain Shams Engineering Journal*, 9 (4), 3271-3276.

El Mogy, S. A., Lawandy, S. N. 2023. Enhancement of the cure behavior and mechanical properties of nanoclay reinforced NR/SBR vulcanizates based on waste tire rubber. *Journal of Thermoplastic Composite Materials*, https://doi.org/10.1177/08927057231180493.

Fazli, A., Rodrigue, D. 2020. Recycling waste tires into ground tire rubber (GTR)/rubber compounds: a review. *Journal of Composite Sciences*, 4 (103), 1-43.

Formela, K., Haponiuk, J. T. 2014. Curing characteristics, mechanical properties and morphology of butyl rubber filled with ground tire rubber (GTR). *Iranian Polymer Journal*, 23, 185–194.

Forrest, M. J. (2019). Recycling and Re-use of Waste Rubber. Berlin, Boston: De Gruyter.

He, L., Ma, Y., Liu, Q., Mu, Y. 2016. Surface modification of crumb rubber and its influence on the mechanical properties of rubber-cement concrete. *Construction and Building Materials*, 120, 403–407.

Hejna A, Olszewski A, Zedler Ł, Kosmela, P., Formela, K. 2021. The impact of ground tire rubber oxidation with H_2O_2 and KMnO4 on the structure and performance of flexible polyurethane/ground tire rubber composite foams. *Materials*,14 (3), 499

Hrdlička, Z., Brejcha, J., Šubrt, J., Vrtiška, D., Malinová, L., Čadek, D., Kadeřábková, A. 2022. Ground tyre rubber produced via ambient, cryogenic, and waterjet milling: the influence of milling method and particle size on the properties of SBR/NR/BR compounds for agricultural tyre treads. *Plastics, Rubber and Composites*, 51 (10), 497-506.

Zhou, M-Z., Wang, H-R., Guo, X., Wei, Y-C., Liao, S. 2023. Synergistic effect of thermal oxygen and UV ageing of natural rubber. *e-Polymers*, 23 (1), 20230016.

ISO 289-1:2015. Rubber, Unvulcanized — Determinations using a Shearing-disc Viscometer - Part 1: Determination of Mooney Viscosity. International Organization for Standardization.

Kaewsakul, W., Sahakaro, K., Dierkes, W. K., Noordermeer, J. W. 2012. Optimization of mixing conditions for silica-reinforced natural rubber tire tread compounds. *Rubber Chemistry and Technology*, 85 (2), 277–294.

Karimi, R., Aliha, M. R. M., Ebneabbasi, P., Salehi, S. M., Khedri, E., Haghighatpour, P. J. 2023. Mode I and mode II fracture toughness and fracture energy of cement concrete containing different percentages of coarse and fine recycled tire rubber granules. *Theoretical and Applied Physics*, 123, 103722.

Leong, S. Y., Lee, S. Y., Koh, T. Y., Ang, D. T. C. 2023. 4R of rubber waste management: current and outlook. *Journal of Material Cycles and Waste Management*, 25, 37-51.

Li, L., Wu, C., Cheng, Y., Wang, H., Liang J., Zhao, W. 2023. Synergistic effect of waste rubber powder on low-temperature toughness and high-temperature rheological properties of SBS modified asphalt. *Construction and Building Materials*, 365, 130112.

Liu, M.-C., Sheu, H.-S., Cheng, S. 2009. Anion-exchange induced Phase transformation of mesostructured silica. *Journal of the American Chemical Society*, A- H.

Mangili, I., Lasagni, M., Anzano, M., Collina, E., Tatangelo, V., Franzetti, A., Caracino, P., Isayev, A. I. 2015. Mechanical and rheological properties of natural rubber compounds containing devulcanized ground tire rubber from several methods. *Polymer Degradation and Stability*, 121, 369-377.

Ramarad, S., Khalid, M., Ratnam, C. T., Chuah, A. L., Rashimi, W. 2015. Waste tire rubber in polymer blends: A review on the evolution, properties and future. *Progress in Materials Science*, 72, 100-140.

Rattanasom, N., Saowapark, T., Deeprasertkul, C. 2007. Reinforcement of natural rubber withsSilica/carbon black hybrid filler. *Polymer Testing*, 26, 369-377.

Sattayanurak, S., Noordermeer, J. W., Sahakaro, K., Kaewsakul, W., Dierkes, W. K., Blume, A. 2019. Silica-reinforced natural rubber: synergistic effects by addition of small amounts of aecondary fillers to silica-reinforced natural rubber tire tread compounds. *Advances in Materials Science and Engineering*, 5891051.

Sattayanurak, S., Sahakaro, K., Kaewsakul, W., Dierkes, W. K., Reuvekamp, L. A., Blume, A., Noordermeer, J. W. M. 2020. Synergistic effect by high specific surface area carbon black as secondary filler in silica reinforced natural rubber tire tread compounds. *Polymer Testing*, 81, 106172.

Senthilvel, K., Vishvanathperumal, S., Prabu, B., John, B. L. 2016. Studies on the morphology, cure characteristics and mechanical properties of acrylonitrile butadiene rubber with hybrid filler (carbon black / silica) composite. *Polymers & Polymer Composites*, 24 (7), 473-480.

Simon, D. A., Bárány, T. 2023. Microwave devulcanization of ground tire rubber and its improved utilization in natural rubber compounds. *ACS Sustainable Chemistry & Engineering*, 11, 1797-1808.

Spanheimer, V., Jaber, G. G., Katrakova-Krüger, D. 2023. Ground tire rubber particles as substitute for calcium carbonate in an EPDM sealing compound. *Polymers*, 15, 2174.

Ulfah, I. M., Fidyaningsih, R., Rahayu, S., Fitriani, D. A., Saputra, D. A., Winarto, D. A., Wisojodharmo, L. A. 2015. Influence of carbon black and silica filler on the rheological and mechanical properties of natural rubber compound. *Procedia Chemistry*, 16, 258 – 264.

Umunakwe, I. J., Dosu, M., Umunakwe, R. 2023. Effect of carbon black/silica hybrid reinforcement on the properties of solid tire tread compound containing ground tire rubber. *FUDMA Journal of Science*, 7 (3), 232-237.