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EFFECT OF CARBON BLACK/SILICA HYBRID REINFORCEMENT ON THE PROPERTIES OF SOLID TIRE TREAD COMPOUND CONTAINING GROUND TIRE RUBBER

[1]Ifeoma Janefrances Umunakwe, [1]Dosu Malomo, *[2]Reginald Umunakwe

[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 authors' email: reginald.umunakwe@fuoye.edu.ng Phone: +234 8135504894

ABSTRACT

The incorporation of ground tire rubber (GTR) in rubber compounds results to reduced strength of the rubber vulcanizates. The need to improve the properties of rubber vulcanizates containing GTR becomes necessary. This work evaluates the effect of hybrid filler reinforcement on the abrasion resistance, hardness, heat build-up, dynamic set and compression set of solid tire tread compound containing 10 phr and 20 phr of 60 mesh size GTR. The hybrid filler used was carbon black/silica (CB/SiO_2) in the ratio 60/0, 55/5, 50/10 and 45/15 phr respectively. The mixing followed two step mixing method and standard samples for testing were molded through compression molding technique at 150℃, under the pressure of 20 tons force and cure time based on the optimal cure time from rheometric measurement. Results show that abrasion volume loss was reduced with GTR addition while the samples containing hybrid filler showed slightly higher abrasion loss that than those containing GTR and filled with only carbon black. At 10 phr GTR loading, the desired reduction in the hardness of the vulcanizates containing GTR was achieved through the use of hybrid filler reinforcement; only small reduction was achieved at 20 phr GTR loading. At the optimal hybrid CB/SiO_2 reinforcement ratio (50/10), the properties of the solid tire tread vulcanizates were better than those of the samples filled with 55/5 and 45/15 hybrid CB/SiO_2 reinforcement. It is recommended that the use of hybrid CB/SiO_2 hybrid reinforcement at the optimal silica content be explored by tire industries exploring the incorporation GTR in solid tire tread vulcanizates.

Keywords: Ground tire rubber, recycling, hybrid filler, tire, properties

INTRODUCTION

The use silica as reinforcement in tire tread compound is very common. Silica reinforcement in tire tread vulcanizate contributes to improvement in tear strength, ageing resistance, and lowers the rolling resistance of the tire (Senthilvel *et al.*, 2016). Although, the addition of ground tire rubber (GTR) in rubber compounds is being explored and exploited by researchers and industry as means of removing tire waste from the environment while the GTR also contributes in cost reduction, the major drawback is that the addition GTR in rubber causes depreciation in the mechanical properties of the vulcanizate and increase in heat build-up and these can reduce the service life of rubber vulcanizates containing GTR (Fazli and Rodrigue, 2020; Hrdlička *et al.*, 2022). GTR is still in vulcanized state and lack the chain mobility to interact with rubber matrix due to the presence of cross-links in it. Possible improvement that may be achieved in tire tread compound containing GTR by use of hybrid carbon black and silica reinforcement is being explored in this research. Rattanasom *et al.* (2007) and Ulfah *et al.* (2015) gave an insight into the effect of utilization of hybrid carbon black /silica filler in vulcanized rubber; the major finding was that there is an optimal amount of silica in the hybrid filler at which the reinforcement ability of the hybrid filler supersedes those of the individual reinforcements. The advantage of using hybrid filler reinforcement is due to the synergistic effect of both fillers resulting to lower Payne effect, improve rubber filler interaction and improved the properties of the vulcanizate (Sattayanurak *et al.*, 2020). Using styrene butadiene rubber for their experimental research, Amrollahi *et al.* (2022) reported that hybrid carbon black/ silica reinforcement in rubber contributes to a synergistic effect resulting to filler network break down (lower Payne effect) which occurs at critical silica loading resulting to improvement of the overall properties of the vulcanizate. Report also suggested that the introduction of silica in carbon black reinforced elastomer results to improved ageing resistance and thermal stability in super specialty elastomers (Khanra *et al.*, 2020). In this work, the effect of carbon black and silica as the secondary filler on the hardness, abrasion resistance, dynamic set, heat build-up and compression set of solid tire tread compound containing GTR is reported. Earlier report has presented the rheology, tensile properties, tear strength and rebound resilience of the rubber compounds whose formulations are used for this study (YYYY *et al.*, 2023).

MATERIALS AND METHOD

Materials

Mechanically ambient ground 60 mesh size ground tire rubber (GTR) earlier characterized and properties reported (YYYY *et al.*, 2023) was used. The thermogravimetric analysis of the GTR gave about 8.5% volatile matters, 42% natural rubber, 15% synthetic rubber (BR and SBR), 29% carbon black and 5.6% residual mass. The particles size d distribution of the GTR was reported as 90% < 298.842 µm, 50% < 186.764 µm and 10% < 115.373 µm. The other materials used for the research were natural rubber (NR) grade STR 20 (L. C. E. H Bangkok (Thailand) Co. Ltd.), butadiene rubber (BR) (BR 01) (BST Elastomers Co., Ltd.), zinc oxide (ZnO) (Thai-Lysaght Co., Ltd.), stearic acid (Asia Chem Co., Ltd.), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (Eastman Chemical Switzerland LLC), poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (TMQ) (Monflex PTE Ltd.), aromatic oil (P. S. P. Specialties Public Company Limited), carbon black (N330) (Birla Carbon (Thailand) Public Company Limited), precipitated silica (Tokusil 255) (OSC Siam Silica Co. Ltd.), bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT or Si69 coupling agent) (Briture Co. Ltd.), sulfur (S)

(The Siam Chemical Public Company Limited) and (N-tert-butyl-2-benzothiazyl sulphenamide (TBBS) (Ningbo Actmix Rubber Chemicals Co., Ltd). Table 1 shows the formulation used for production of the samples and the codes given to each sample (YYYY *et al.*, 2023).

Table 1: Formulation used for the Production of the Vulcanized Rubber Samples

Chemical/Sample	**Amount (phr)**										
	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

Mixing

The mixing method followed two-step mixing as earlier described in the first part of the research (YYYY *et al.*, 2023). Samples “Control”, “F2” and “F7” followed the order of mixing presented in Table 2 for the step 1 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. Samples “F3 to F6” and “F8” to “F11” followed the mixing step presented in Table 3 using the same internal mixer, rotor speed and fill factor at starting temperature of 100 ℃ (Sattayanurak *et al*., 2020). After dumping from the internal mixer, the componds were allowed to cool to room temperature before they were transferred to two-roll mill for the step 2 of the mixing.The mixing step 2 was done on two-roll mill at 30℃ for 5 minutes for samples “Control”, “F2” and “F7” to achieve homogenization. The mixing step 2 for samples “F3 to F6” and “F8” to “F11” was also done on two-roll mill at 30℃ for 6 minutes and the curatives (TBBS and S) were added in the 3rd minute.

Table 2: Mixing Sequence in the Step 1 for Samples “Control”, “F2” and “F7”

Time (minute)	**Operation**
0	Loading STR 20, BR01 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: Mixing Sequence in the Step 1 for Samples “F3 to F6” and “F8 to F11”

Time (minute)	**Operation**
0	Loading STR 20, BR01 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

Production of the Rubber Vulcanizates

The molding of all the vulcanizates was carried out on a hydraulic compression molding press (Wabash MPI, USA) under a molding pressure of 20 tons-force at temperatures 150 ℃. The optimal cure time (t_{c90}) for each compound obtained from rheometric measurements have already been reported (YYYY *et al.*, 2023). The vulcanization time used for molding Akron abrasion testing samples (also used for hardness testing) having internal diameter of 12.77 mm, external diameter of 63.95 mm and height of 12.73 mm was $t_{c90} + 10$ minutes. The cure time for the production of samples used to measure heat build-up (having diameter 16.6 mm and height 24 mm) was $t_{c90} + 15$ minutes. The samples having diameter 3 mm and height 6 mm used to determine compression set were molded using $t_{c90} + 6$ minutes as the cure time. The vulcanized rubber samples were conditioned at room temperature for at least 24 hours before testing.

Testing of the Rubber Vulcanizates

Hardness testing was carried out with shore A digital micro hardness tester (Wallace Cogenix H17a/2, England) following ISO 48-4:2018 standard. The indentation on the surface of the sample was repeated 5 times at different locations on the surface and the average result was reported. The density of each vulcanizate sample was determined using electronic densimeter (Alfa Mirage model MD 200S, Japan) with resolution up 0.001g/cm^3 in line with ASTM D297-21 standard. Akron abrasion volume loss was determined with the testing machine (Gotech GT-7012-A, Taiwan) at room temperature (23℃) under a force of 45 N and counter weight of 6 lb (26.69 N) at an angle of 15° in line with BS 903-A9-2020 standard. The average of the weight loss of the 5 runs of 1000 revolutions was computed and used to calculate the volume loss (mm^3) using equation (1).

Volume loss, Δv (mm^3) $= \frac{weght\ loss,\ \ \Delta m\ (g)}{density\ of\ specimen,\ \ \rho\ (gcm^{-3})}$ (1)

The compression set of each rubber vulcanizate sample was measured following ASTM D395-18 standard using the compression set press (Gotech, GT-7049-1H, Taiwan). The height of the sample was initially measured before compression (H_1) with micrometer gauge (Mitutoyo, Japan) and installed in the compression set press, put in air circulating oven and the temperature raised at the rate of 5 ℃/min to 70℃ and held 24 hours before they were brought out, kept at room temperature (23℃) for 30 minutes and the height after compression (H_2) measured. 6 specimens of each vulcanizate sample were tested and the average result reported. Compression set was calculated from equation (2).

Compression set (%) $= \frac{H_1 - H_2}{H_1} \times 100$ (2)

Heat build-up and dynamic set of each rubber vulcanizate sample was measured with flexometer (BFGoodrich Model II, USA) under dynamic compressive force between the cross-section for 25 minutes, at constant frequency of 30 Hz, static force of 245 N, deformed distance of 3.19 mm and base temperature of 100℃ in line with ASTM D623-07(2019)e1 standard. Dynamic set was calculated using equation (3); H_A and H_B are the height of the specimen in mm before and after testing. Three specimens were tested for each sample and the average results were reported.

Dynamic set (%) $= \frac{H_A - H_B}{H_A} \times 100$ (3)

RESULTS AND DISCUSSION

Abrasion Loss

The Akron abrasion volume loss of the rubber vulcanizate samples are shown in Figure 1. The addition of 60 mesh size GTR in the rubber compounds decreased the abrasion volume loss of the vulcanizates and similar values were obtained at both 10 phr and 20 phr GTR loading (F2 and F7). Mixing at higher temperature further improved the abrasion resistance of the vulcanizate because of improved dispersion of the materials in the rubber matrix resulting to stronger bonds. At 10 phr GTR addition, the samples containing silica/carbon black hybrid filler showed slightly higher abrasion loss as the amount of silica increased. It has been reported earlier that high surface area of carbon black imparts abrasion resistance to rubber (Sattayanurak *et al.*, 2020). Therefore, when carbon black was reduced and silica increased, the abrasion loss slightly increased. At 20 phr GTR addition, samples F8, F9, F10, and F11 showed lower abrasion volume loss than sample F7 because of improved dispersion as a result of mixing at higher temperature and silica addition with coupling agent which improved filler-rubber interaction and formation of stronger bond. However, F9, F10 and F11 showed higher volume loss than F8 because carbon black was reduced when silica was added and further reduced as the amount of silica increased. All the vulcanizates containing GTR however exhibited lower abrasion loss than the control sample without GTR and this is desirable for tire tread application.

Hardness

The hardness results for the vulcanizates are shown in Figure 2. Increased hardness due to the the addition of GTR could be attributed to more carbon black in the mtrix from the GTR and the cross-linked state of the GTR promoting higher filler-filler interaction. Increased hardness due to the addition of GTR in the solid tire tread compound is not desirable (F2 compared to control) as very high hardness contributes to loss of elongation in rubber vulcanizates. The reduction in hardness for samples F3, F4, F5 and F6 can be attributed to reduced filler-filler interaction and improved filler-rubber interaction due to mixing at higher temperature and silane coupling of silica with elastomer. At 20 phr GTR addition, generally, the hardness reduced as the amount of carbon black was reduced with addition of silica similar to the trend earlier reported for hybrid silica/carobn black filled bagasse-SBR composites (Khalaf, 2023). The drop of hardness for sample F9 can be attributed to poor distribution of silica at small amount resulting to the formation of weak bond as earlier explained (YYYY *et al.*, 2023).

Compression Set

The compression set measures the ability of the rubber vulcanizates to retain their elastic properties when subjected to extended compression at a constant strain under specified conditions (Narupai *et al*., 2020). The compression set of the rubber vulcanizates is shown in Figure 3. Increase in compression set suggests that the elasticity of the rubber vulcanizate is impaired which could be as result of filler agglomeration, poor distribution or filler-filler interaction. It can be observed that the addition of GTR increased the compression set with further increase as the amount of GTR increased (F2, F3 and F7, F8) compared to the control sample. In our earlier report, it was pointed out that when silica was added at just 5 phr, it was trapped in between the bulk of the GTR and there was poor distribution and higher silica-silica interaction (YYYY *et al*., 2023),. The increase in compression set for samples F4 and F8 was due to high silica-silica interaction as a result of poor distribution. The positive effect of silica addition on the compression set was more manifest at 20 phr GTR addition as the compression set dropped with increase in the amount of silica and coupling agent.

Dynamic Compression Set and Heat Build-up

The effect of incorporating 60 mesh size GTR and hybrid carbon black/silica reinforcement on the dynamic compression set and heat build-up can be seen in Figures 4-5. The effect of poor distribution and high silica-silica interaction when silica was added at 5 phr showed in high dynamic compression set and high heat build-up of samples F4 and F9. Earlier report suggested that the optimal amount of silica in the hybrid carbon black/silica reinforcement for tire tread compound containing GTR is 50/10 (carbon black/silica) ratio as that is where the best dispersion and distribution were achieved (YYYY *et al.*, 2023). At that ratio, both dynamic compression set and heat build-up (Figures 4 and 5) were reduced at both 10 phr GTR loading (F5) and 20 phr GTR loading (F10) respectively, although not as low as the control sample. Similar observation was reported earlier by (Rattanasom *et al.*, 2007).

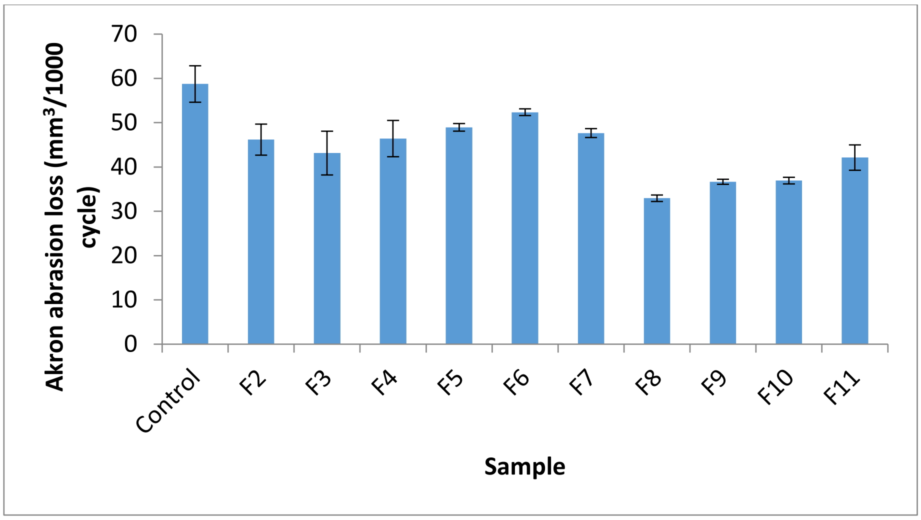

Figure 1: Akron abrasion volume loss

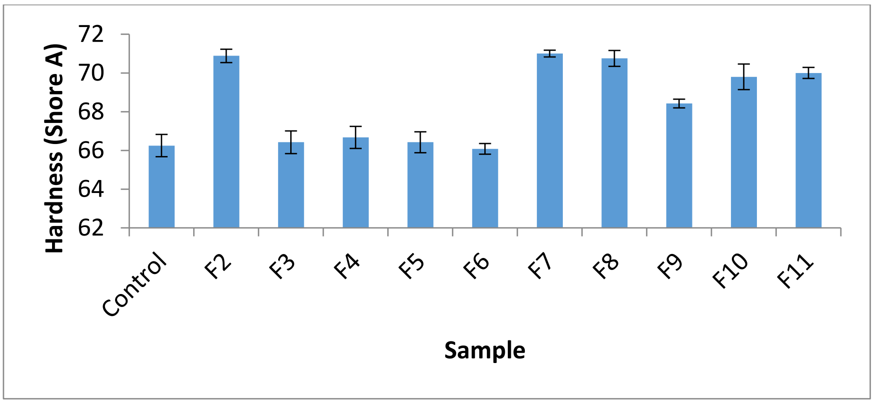

Figure 2: Hardness of the vulcanizates

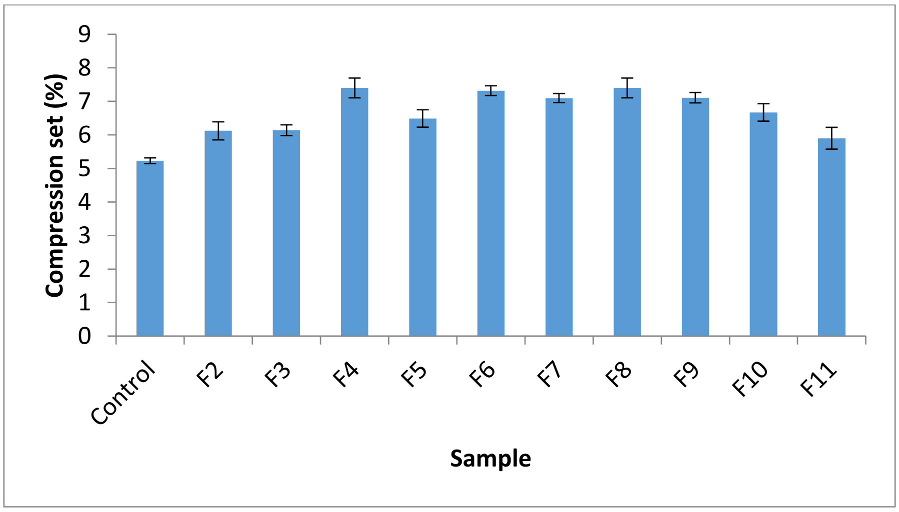

Figure 3: Compression set

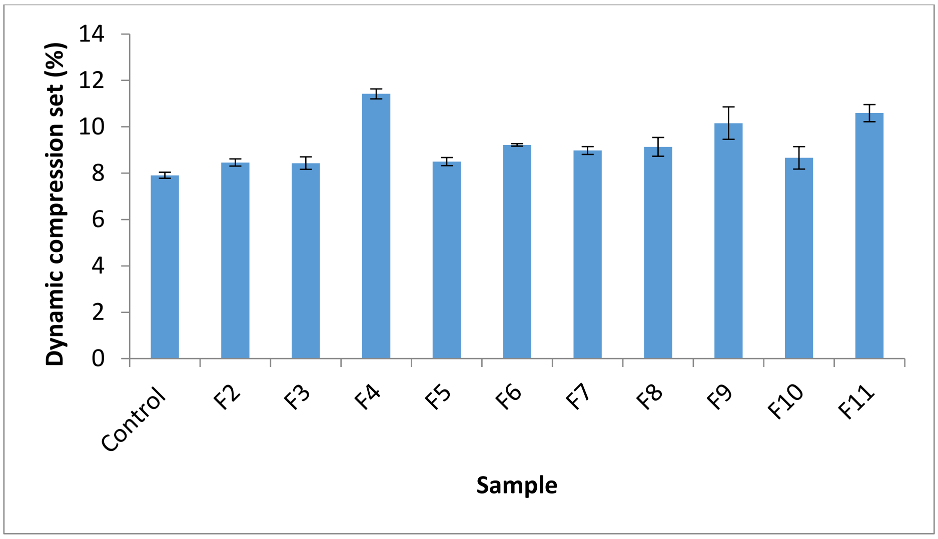

Figure 4: Dynamic set

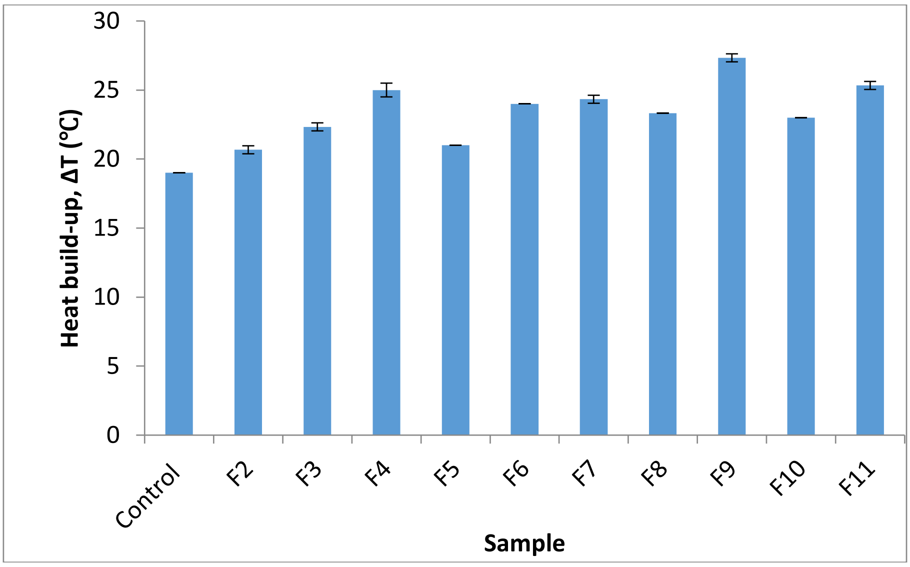

Figure 5: Heat build-up

CONCLUSIONS

In this work, the possibility of improving the properties of solid tire tread rubber vulcanizate containing 60 mesh size GTR at 10 phr and 20 phr loadings through hybrid carbon black/silica filler reinforcement was investigated. Generally, abrasion volume loss should not be worried about in tire tread compound containing GTR as the addition of GTR in the rubber lowered the abrasion volume loss. At 10 phr GTR addition, the attendant high hardness associated with rubber vulcanizate containing GTR was reduced by employing hybrid carbon black/silica reinforcement and mixing at higher temperature. At 20 phr GTR addition, only slight reduction in hardness was achieved through hybrid filler reinforcement. The results of the dynamic set and heat build-up suggest that at the optimal silica amount in the hybrid filler reinforcement (50/10 carbon black/silica), reduction in heat build-up and dynamic set could be achieved owing to good rubber-filler interaction in compound containing hybrid filler compared to the rubber vulcanizate containing GTR and single filler reinforcement. The compression set of the compounds that filled with hybrid filler were higher except at optimal ratio of the two fillers in the vulcanizate where effective results were achieved.

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