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REBOUND RESILIENCE AND HEAT BUILD-UP OF HYBRID CARBON BLACK/SILICA-REINFORCED SOLID TIRE TREAD COMPOUND CONTAINING GROUND TIRE RUBBER OF DIFFERENT PARTICLE SIZES

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ABSTRACT

The effect of addition of 20 phr ground tire rubber (GTR) of 40, 60, 80 and 100 mesh sizes in hybrid carbon black/silica (CB/SiO_2) reinforced solid tire tread compound on the rebound resilience and heat build-up was investigated. The hybrid filler reinforcement was in the ratio of 50/10. Two-step mixing utilizing an internal mixer and two-roll mill was employed for the mixing, while vulcanization was carried out at 150℃. Results show that additional GTR lowered the rebound resilience and increased the heat build-up of the vulcanizates with the 100 mesh size GTR impacting the most adverse effect on the vulcanizates. The use of hybrid CB/SiO_2 reinforcement helped in the recovery of some of the lost rebound due to the addition of GTR in the matrix. The use of hybrid CB/SiO_2 reinforcement contributed to only a slight reduction in the heat build-up of solid tire tread compound containing 20 phr of GTR.

Keywords: *Ground Tire Rubber, Heat Build-Up, Hybrid Filler, Rebound Resilience, Vulcanizate*

INTRODUCTION

The global generation of end-of-life tires (ELTs) is quite enormous. End-of-life tires adversely impact the environment as solid waste. They pollute the water, occupy the landfill and constitute a fire hazard. As of 2010, it was reported that 1.5 billion tires were produced each year and about 5.7 million tonnes of waste tires were generated in Europe (Banar 2015). The global generation of waste tires in 2012 was reported to be about 18 million tonnes (Kordoghli *et al*., 2014), and it continues to increase each year. It has been projected that about 5 billion tires will be discarded by the end of 2030 (Thomas and Gupta, 2016; Grammelis *et al*., 2021). ELTs constitute about 70% of the rubber waste generated globally (Leong *et al*., 2023). The disposal of ELTs into landfill has been banned in many countries (Banar 2015; Kordoghli *et al*., 2014). Continuous efforts are being made to effectively manage ELTs and utilize them for diverse applications to reduce their impacts to the environment. Some of the technologies being explored by researchers and industries include downsizing or grinding of ELTs to rubber crumbs called ground tire rubber (GTR) through technologies such as dry ambient grinding, wet ambient grinding and cryogenic method (Leong *et al*., 2023). Some researchers have reported that the incorporation of GTR in rubber compounds reduces the strength and elongation of the vulcanizate while increasing the hardness and heat build-up (Wisniewska *et al*., 2022; Liu *et al*., 2022). CB/SiO_2 hybrid reinforcement is being utilized in tire tread compounds because silica imparts improved tear and aging resistance and the hybrid filler imparts low hysteresis and good abrasion resistance (Wang *et al*., 2021; Narupai *et al*., 2020). A report has suggested that the use of hybrid CB/SiO_2 reinforcement in rubbers can improve the properties of the vulcanizates (Narupai *et al*., 2020). Hybrid CB/SiO_2 reinforcement in rubber has been reported to lower the filler network due to the synergistic effect of the two fillers thereby improving the properties of vulcanizate by improving the rubber filler interaction (Sattayanurak *et al*., 2020). We are currently exploring the possibility of improving the properties of solid tire tread rubber vulcanizate containing GTR through hybrid filler reinforcement. In this work, the effect of hybrid CB/SiO_2 reinforcement on rebound resilience and heat build-up of solid tire tread compound containing GTR of varied mesh sizes are presented.

MATERIALS AND METHOD

Materials

40, 60, 80 and 100 mesh sizes of GTR from truck tires ground at ambient temperature were provided by the Rubber Technology Research Centre, Mahidol University, Thailand. Thermogravimetric analysis of the GTR gave the approximate composition of volatile matter (7.6%), natural rubber (40%), synthetic rubber (BR and SBR) (15%), carbon black (30%) and residual mass (7.4%) in the GTR. The other compounding ingredients used include natural rubber (NR) grade STR 20 (L. C. E. H Bangkok (Thailand) Co. Ltd.), butadiene rubber (BR) (BR 150) (Thai Synthetic Rubber Company Limited), zinc oxide (ZnO) (Thai-Lysaght Co., Ltd.), stearic acid (Asia Chem Co., Ltd.), N-(1,3-dimethyl butyl)-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 (The Siam Chemical Public Company Limited) and N-tert-butyl-2-benzothiazyl sulphenamide (TBBS) (Ningbo Actmix Rubber Chemicals Co., Ltd). The formulation used for the production of the vulcanized rubber samples is shown in Table 1. CB and CB/SiO_2 represent the samples filled with only carbon black and those filled with hybrid carbon black/silica respectively.

Mixing of the rubber compounds

A two-step mixing method was used to mix the rubber compounds. The first step of the mixing was carried out using a 500 ml laboratory internal mixer (Brabender plasticoder lab station, Germany), a fill factor of 0.78 and a rotor speed of 40 rpm. In the first step of the mixing for the ***control sample***, NR and BR were first loaded in the mixer when it attained the set temperature of 60℃ after the rotor was already rotating at the set speed. Then, ZnO, stearic acid, 6PPD, TMQ, and ¼ of carbon black were loaded in the 1st minute, while ¾ of the carbon black, and aromatic oil were added in the 3rd minute, followed by the addition of sulfur and TBBS in the 6th minute and the compound dumped from the mixer on the 8th minute. After cooling to room temperature, the compound from the internal mixer was transferred to a two-roll mill for step two of the mixing at 30℃ for 5 minutes to homogenize the compound. The starting mixing temperature for the first step of the mixing for the samples containing GTR of different mesh sizes and filled with carbon black or hybrid CB/SiO_2 was 100℃ at the same fill factor and rotor speed. The higher temperature selected for the mixing was to ensure the coupling of silica with rubber with the help of Si69.

Table 1: Formulation of Vulcanized Rubber Samples for The Outer Layer (Tread) of Solid Tire

	Sample code		
	Control	**CB**	**CB/SiO_2**
Chemical		(phr)	
NR(STR20)	80	64	64
BR (150)	20	16	16
GTR(40 or 60 or 80 or 100 mesh size)	-	20	20
ZnO	4	4	4
Stearic acid	2	2	2
6PPD	1.5	1.5	1.5
TMQ	1	1	1
Aromatic oil	10	10	10
CB (N330)	60	60	50
Silica	-	-	10
Si69	-	-	1
S	2	2	2
TBBS	1.2	1.2	1.2

The mixing time was 6 minutes. At the 0 minute, NR, BR and GTR were loaded. ZnO, stearic acid, 6PPD, TMQ, ¼ of carbon black, silica and Si69 (in the hybrid systems) were loaded on the 1st minute, while ¾ of the CB and aromatic oil was loaded on the 3rd minute and the rubber compounds were dumped on the 6th minute. After each compound had cooled to room temperature, the second step of the mixing was carried out on a two-roll mill at 30℃ for 6 minutes. The curatives TBBS and S were added in the 3rd minute and the compounds were properly homogenized. The rubber compounds were kept at room temperature for 24 hours to attain equilibrium before further processing.

Molding of the rubber vulcanizates

A hydraulic press compression molding machine (Wabash MPI, USA) was used to produce the vulcanized rubber samples under a molding pressure of 20 tons-force at 150℃. The cure time (t_{c90}) used for the vulcanization process was based on the values obtained from the rheometric measurements for each compound. The cure time for the specimens having a diameter of 16.6 mm and height of 24 mm used for determination of heat build-up and dynamic set was t_{c90} + 15 minutes. The cure time for the specimens having a diameter of 28.5 mm and height of 12.5 mm for the rebound resilience test was t_{c90} + 6 minutes.

Determination of rebound resilience and heat build-up of the vulcanizates

The rebound resilience of each rubber vulcanizate sample was measured with the pendulum type rebound resilience testing machine (Gotech, GT-7042-RDA, Taiwan) utilizing a 0.5 J impact cap at 90° impact angle according to ASTM D7121-05(2018) standard. The 3 specimens of each sample were tested and the average results were computed. Equation (1) (α is the rebound angle) was used to calculate the rebound resilience (percentage rebound).

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

$$= (1-\cos\alpha) \times 100 \qquad (1)$$

Heat build-up of the rubber vulcanizates was measured with a flexometer (BFGoodrich Model II, USA) under dynamic compressive force between the cross-section for 25 minutes, at a constant frequency of 30 Hz, static force of 245 N, deformed distance of 3.19 mm and base temperature of 100℃ according to ASTM D623-07 (2019)e1 standard.

RESULTS AND DISCUSSION

The results presented and discussed are the rebound resilience and heat build-up.

Rebound resilience

The rebound resilience of the vulcanizate samples is shown in Fig. 1. The code 40 MS GTR represents the samples containing 40 mesh size GTR based on the formulation in Table 1. Similar codes are used to identify the other samples containing different mesh sizes of the GTR. The rebound resilience is a measure of the elastic recovery of the vulcanizates after deformation. The percentage rebound represents part of the energy input during deformation that is returned, while the remaining percentage is converted to heat (Indrajati and Setyorini, 2020).

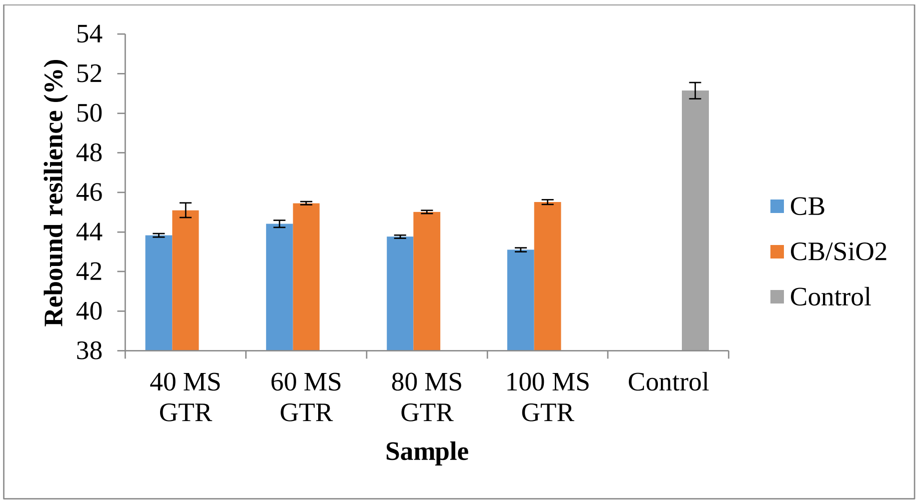

Fig. 1: Rebound resilience of the vulcanizate samples

Table 2: Percentage decrease of the rebound resilience of the vulcanizate samples

	Decrease in rebound resilience (%) compared to control sample	
	CB	**Hybrid CB/SiO_2**
Mesh size of GTR/Filler type		
40	14.29	11.81
60	13.16	11.11
80	14.43	11.99
100	15.72	11.01

Generally, the introduction of GTR reduced the rebound resilience of the vulcanizates. This is an indication of the decreased elastic response of the vulcanizates containing GTR. Variations in the mesh sizes of GTR had little or no effect on the rebound resilience of the rubber vulcanizates. The rebound resilience of the control sample was 51.14%, while those of samples 40 MS GTR, 60 MS GTR, 80 MS GTR and 100 MS GTR filled with only CB were 43.83%, 44.41%, 43.76% and 43.1% respectively; and the values for the samples filled with hybrid CB/SiO_2 were 45.1%, 45.46%, 45.01% and 45.51% respectively. The percentage decrease in the rebound resilience of the rubber vulcanizates filled with different mesh sizes of GTR when compared with the control sample is presented in Table 2. The results show that the compound containing 60 mesh size GTR exhibited the lowest percentage loss of rebound compared to the control sample. Quantitatively, the sample containing 100 mesh size GTR had the lowest value of rebound resilience. The least value of rebound exhibited by the vulcanizates containing 100 mesh size GTR could be as a result of agglomeration of the GTR in the matrix due to their fine particles. It is difficult to distribute very fine particles of GTR in the matrix. Contrarily, coarse particles of GTR in the rubber matrix introduced a bigger stress factor, the rubber vulcanizate containing 60 mesh size GTR exhibited a lower decrease in rebound resilience than the sample containing 40 mesh size GTR.

The addition of silica and reduction of the amount of CB in the rubber vulcanizates resulted in improved rebound resilience of the hybrid CB/SiO_2 reinforced vulcanizates over those of the samples filled with only CB. All the vulcanizates containing different mesh sizes of the GTR showed similar values of rebound resilience after the addition of 10 phr silica and reduction of CB from 60 phr to 50 phr in hybrid filler reinforcement of the tire tread compound containing up to 20 phr GTR. This is an indication that the silica addition at that amount improved the rubber filler interaction and helped the rubber vulcanizate containing GTR to recover some of its elasticity.

Heat build-up

The heat build-up of the vulcanizate samples is shown in Fig. 2. The samples containing GTR showed higher heat build-up than the control sample.

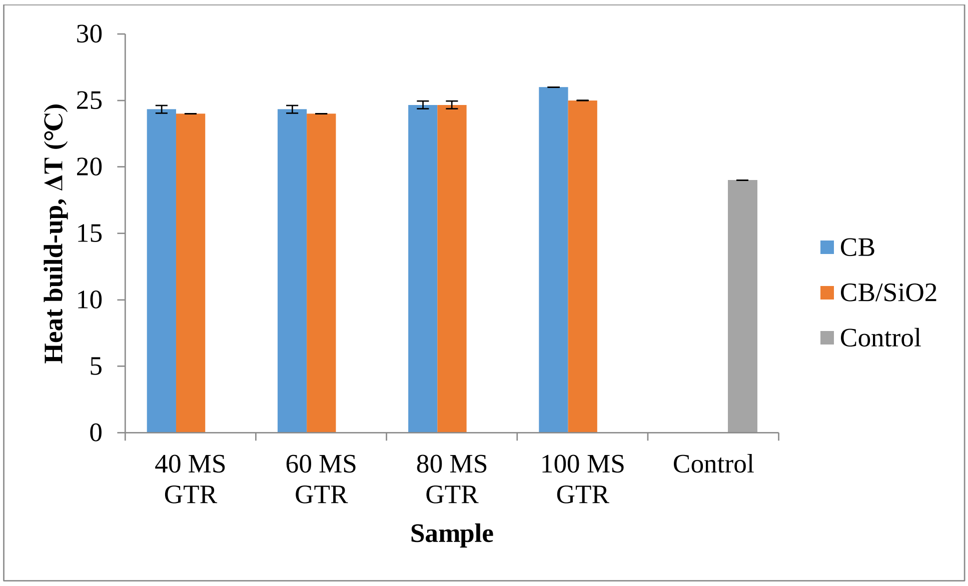

Fig. 2: Heat build-up of the vulcanizate samples

This is because the addition of GTR also increased the CB content resulting in higher filler loading. Higher filler loading will give rise to higher heat generation during cyclic testing due to the breakage of the carbon black structure and the formation of anteraggregate bonds (Park *et al*., 2000). Sample 100 MS GTR filled with only carbon black exhibited higher heat build-up than the other sample because it exhibited the lowest rebound thereby converting most of the energy input during deformation to heat. The samples containing GTR and filled with hybrid CB/SiO_2 exhibited just slightly lower heat build-up because of their higher rebound which implies that they recovered most of the energy input during deformation and therefore do convert lower energy to heat as compared to the samples filled with only CB.

CONCLUSIONS

This work has evaluated the effect of hybrid CB/SiO_2 reinforcement of solid tire tread compound containing 20 phr GTR of different mesh sizes on the rebound resilience and heat build-up of the vulcanizates. All the rubber vulcanizates containing GTR exhibited lower rebound resilience than the control sample that was not filled with GTR. The vulcanizates containing GTR of different mesh sizes and filled with hybrid CB/SiO_2 reinforcement exhibited higher rebounds than those filled with only CB. The addition of 60 mesh size GTR imparted higher rebound in the vulcanizates when compared with the values of rebound resilience obtained in the vulcanizates containing 40, 80 and 100 mesh sizes of GTR. Generally, the incorporation of GTR of different mesh sizes in the tire tread compound increased the heat build-up, and the vulcanizates containing 100 mesh size GTR exhibited the highest heat build-up. The heat build-up of the vulcanizates containing 20 phr GTR of different mesh sizes and filled with hybrid CB/SiO_2 (50/10) reinforcement was slightly lower than those of similar samples filled with only CB. While we are currently working on the optimization of the incorporation of GTR in tire tread compounds, the results from this research show that the properties of the vulcanizates containing 60 mesh size GTR are better than those containing either 40, 80 or 100 mesh size GTR.

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DECLARATION OF CONFLICTING INTERESTS

The authors declared that there is no conflict of interest.

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