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MICROSTRUCTURE OF CB/SIO_2 HYBRID REINFORCED SOLID TYRE TREAD COMPOUND CONTAINING GROUND TYRE RUBBER AND THEIR EFFECT ON FATIGUE RESISTANCE

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Abstract The possibility of improving the properties of rubber compounds containing ground tyre rubber (GTR) is an active research area. This study investigates the microstructure of carbon black filled tyre tread compound containing 20 phr GTR and compares the microstructure with those of similar compounds reinforced with hybrid carbon black/precipitated silica (CB/SiO_2). In the compounds reinforced with hybrid filler, amount of the GTR was maintained at 20 phr, while the amount of the hybrid filler (CB/SiO_2) were in the ratios 55/5, 50/10 and 45/15 respectively. The compounds were mixed by two-step mixing method using internal mixer and two-roll mill. The vulcanisation of each rubber compound was carried out on a compression moulding machine at 150℃. Results obtained from scanning electron microscopy of the fractured surfaces showed that the ingredients in the control sample that was not filled with GTR were well dispersed and distributed. The micrograph of the sample containing GTR and mixed at 60℃ showed that GTR was not very compatible with the matrix. Improved mixing was achieved with increased mixing temperature. The addition of precipitated silica at 5 phr resulted in poor dispersion. The dispersion improved as the amount of silica increased to 10 phr and 15 phr respectively. Results obtained from flex fatigue test show that the compounds filled with hybrid CB/SiO_2 in the ratios 50/10 and 45/15 phr exhibited no crack after 1000 cycles due to good dispersion. It is recommended that hybrid CB/SiO_2 reinforcement at optimal amount of silica should be utilised to fill rubber compounds containing GTR in order to improve the properties of the vulcanisates.

Keywords: Tyre, ground tyre rubber, recycling, scanning electron microscopy

I. INTRODUCTION

The use of tyres is indispensable in the automobile industry. The number of new automobile tyres for passenger cars, trucks and other machines produced globally exceed 1.6 billion per annum [1]. China is the world largest producer of automobile tyre. In 2019, global production of tyres was estimated to be 16.86 million tons [2]. The production of tyres requires the use of so many materials, but rubber is the major component of tyres. The rubber in tyres are in vulcanized state. The chains are highly cross-linked and therefore very stable to the environment. As a result of their cross-linked nature, they do not degrade when disposed after the service of the tyre. The rubber in tyre takes about 800-1000 years before it will degrade naturally in soil [3]. End-of-Life Tyres (ELTs) constitute environmental problems. According to report [3], about 14.6 million tons of ELTs were generated and discarded in 2018. ELTs add to solid waste. The combustion of waste tyres contributes to atmospheric pollution. The pollutants from combustion of waste tyres include SO_2, NO_x, doxins, dibenzofurans, etc. Heavy metals in the

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ash after combustion such as manganese (Mn), chromium (Cr) and lead (Pb) can lead to soil and water pollution. Researchers and industries are therefore exploring the various options such as tyre retreading, rubber reclaiming, the use of waste tyres as fuels, waste tyre pyrolysis and the grinding of waste tyres and subsequent utilisation as fillers in composites in order to reduce the number of end-of-life tyres in the environment. Recently, some research effort focused on the addition of GTR in tyre tread compounds as part replacement of the rubber [4-5]. It has been reported in literature that the addition of GTR in rubber compounds reduced the mechanical properties such as tensile strength, elongation and tear strength of the vulcanisates, and increased the heat build-up, hardness and stiffness [6-8]. This work is focused on incorporating GTR in solid tyre tread compound and improving the properties of the vulcanisates through hybrid filler reinforcement. The microstructure and flex fatigue resistance of the compound containing 20 phr GTR is reported.

II. MATERIALS AND METHODS

A. Materials

60 mesh size GTR was provided by the Rubber Technology Research Centre, Mahidol University, Thailand. The base elastomers are natural rubber (NR) grade STR 20 supplied by L. C. E. H Bangkok (Thailand) Co. Ltd., and butadiene rubber (BR) grade BR 01 supplied by BST Elastomers Co., Ltd. The other compounding ingredients and their suppliers are as listed in Table 1. The recipe used to produce the various vulcanisate samples are presented in Table 2.

Table 1: Rubber compounding ingredients and their suppliers

S/N	Rubber compounding Ingredient	Supplier
i	Zinc oxide (ZnO)	Thai-Lysaght Co. Ltd.
ii	Stearic acid	Asia Chem Co., Ltd.
iii	Poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (TMQ)	Monflex PTE Ltd.
iv	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	Eastman Chemical Switzerland LLC
v	Aromatic oil	P. S. P. Specialties Public Company Limited
vi	Carbon black (N330)	Birla Carbon (Thailand) Public Company Limited
vii	Precipitated silica (Tokusil 255)	OSC Siam Silica Co. Ltd.
viii	Bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT or Si69 coupling agent)	Briture Co. Ltd.
ix	Sulphur (S)	The Siam Chemical Public Company Limited
x	N-tert-butyl-2-benzothiazyl sulphenamide (TBBS)	Ningbo Actmix Rubber Chemicals Co., Ltd.

Table 2: Recipe of the tyre tread vulcanisate

Material/Sample code	Amount (phr)					
	Control	**A**	**B**	**C**	**D**	**E**
NR(STR20)	80	64	64	64	64	64
BR (01)	20	16	16	16	16	16
60 mesh size GTR	-	20	20	20	20	20
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
6PPD	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1	1
Aromatic oil	10	10	10	10	10	10
CB (N330)	60	60	60	55	50	45
Silica	-	-	-	5	10	15
Si69	-	-	-	0.5	1	1.5
S	2	2	2	2	2	2
TBBS	1.2	1.2	1.2	1.2	1.2	1.2

B. Mixing of the rubber compounds

The ingredients were weighed based on the recipe presented in Table 2. Two-step mixing as described in literature [4 -5] was used to carry out the mixing. The "control" and sample "A" were mixed following the description presented in Table 3 [4]. Internal mixer (500 ml Brabender plasticoder lab station, Germany) was used to carry out the mixing step 1. The mixing parameters for the step 1 were; temperature of 60℃, fill factor of 0.78 and rotor speed of 40 rpm. After dumping the rubber compound from the internal mixer, it was allowed to cool at room temperature until the temperature got to room temperature. Followed was mixing step 2 of the rubber compound using a two-roll mill at temperature 30℃ and the mixing time was 5 minutes. The mixing step 2 was to ensure homogenisation of the rubber compound. The same internal mixer was also used to carry out mixing step 1 for each of samples "B", "C", "D", and "E", at the same fill factor and rotor speed, but initial mixing temperature of 100℃ to ensure silanization reaction [9-10]. The mixing followed the sequence presented in Table 4 [4]. After dumping the compounds from the internal mixer, they were allowed to cool to room temperature before further mixing. The mixing step 2 for the samples (B-E) were carried out on a two-roll mill at temperature 30℃ and the mixing time was 6 minutes. TBBS and S which served as the curatives were added during mixing on two-roll mill at the 3rd minute and homogenised mixing was ensured. All the rubber compounds were kept at room temperature for 24 hours before further processing was carried out.

Table 3: Sequence of addition of materials during mixing step 1 for samples "control", and "A" [4].

Time (minute)	Operation
0	STR 20, BR150 and GTR (for sample A) were loaded in the mixer
1st	ZnO, 6PPD, TMQ, stearic acid, and ¼ of carbon black were added
3rd	¾ of the carbon black, and aromatic oil were added
6th	Sulphur and TBBS were added.
8th	The rubber compound was dumped from the mixer

Table 4: Sequence of addition of materials during mixing step 1 for samples "B to E" [4]

Time (minute)	Operation
0	STR 20, BR150 and GTR were loaded in the internal mixer
1st	ZnO, 6PPD, TMQ, stearic acid, ¼ of carbon black, and silica were added. Si69 was added in samples "C– E"
3rd	¾ of the carbon black and aromatic oil were added
6th	The compound was dumped from the mixer.

C. Moulding of the rubber vulcanisates

2 mm sheets rubber vulcanisates were moulded through hydraulic press compression moulding machine (Wabash MPI, USA). The moulding pressure was 20 tons-force and cure temperature was 150℃. The cure time (t_{c90}) earlier determined from rheometer [5] was used. The samples for flex fatigue test having thickness of 4.5 mm were moulded with their specified moulds and the cure time was t_{c90} + 3 minutes.

D. Characterisations of the rubber vulcanisates

i. Scanning electron microscopy (SEM) on the samples

Specimens for SEM analysis were cut from the 2 mm vulcanisates sheets using the cutting machine. The cut specimens were then cryogenically fractured using liquid nitrogen. The fractured specimens were mounted on the stub and installed in auto coater. They were sputter coated with platinum. The images of the fractured surfaces were obtained with the Hitachi field emission scanning electron microscope at applied voltage of 10 kv and magnification of 30,000.

ii. Measurement of flex fatigue resistance

The resistance to cracking under repeated flexing strain was studied using flex fatigue testing tester (GT-7011-D) according to ASTM D430-06 (2018) standard. The specimens were installed on the machine and flexed at frequency of 5 Hz (300 cycles per minute) at room temperature (23℃). The presence and grade of cracks based on ASTM D430-06 (2018) standard were initially checked after 500 cycles. Subsequently, at intervals of 1000 cycle until 10,000 cycles, the specimens were checked for presence and grade of cracks.

III. RESULTS AND DISCUSSION

A. Microstructure of the rubber vulcanisates

The SEM micrographs of the cryogenically fractured surface topography of the control sample and those filled with 20 phr GTR (A to E) are shown in Figure 1(a-f). The SEM micrograph of the fractured surface of the control sample (where GTR was not added) (Figure 1a) shows that the additives were well dispersed and distributed in the matrix. The fractured surface shows rough surfaces indicating high energy requirement to cause failure. This correlates with the good physic-mechanical properties of the control sample earlier reported [4-5]. The SEM micrograph of the fractured surface of sample A containing 20 phr GTR and mixed at initial temperature of 60℃ is shown in Figure 1b. The micrographs show detachment of the GTR from the rubber matrix and this resulted in the poor mechanical properties exhibited by sample. Earlier, it was reported that the introduction of unmodified GTR in butyl rubber resulted in lack of adhesion between the matrix and GTR [11]. Also, Colom *et al* (2018), [12] reported that the introduction of unmodified GTR in natural rubber matrix resulted in cracks, pores and many cavities in the rubber matrix. The micrograph of the sample A shows similar morphology in agreement with earlier reports. It has been suggested that modification of GTR can be used to improve its adhesion and dispersion in rubber matrix [13]. In the SEM micrograph of sample B (Figure 1c) containing 20 phr GTR and mixed at initial temperature of 100℃, microstructure appear more homogenous compared with sample A. The mixing of the GTR and the rubber matrix was improved. However, the fractured surface appears smooth, an indication of poor resistance to fracture. The properties of sample B are therefore better than those of sample A but generally not improved. The micrograph of sample C containing 20 phr GTR and 5 phr silica in a hybrid carbon black/silica (55/5) reinforcement system is shown in Figure 1d. Silica was trapped as agglomerates in the matrix due to their small amount and lack of shear force for better dispersion and distribution. Hence, sample C exhibited poor physic-mechanical properties. The best improvement in the properties were achieved in the samples containing 10 phr silica in hybrid carbon black/silica (50/10) filler reinforcement of the tyre tread compound containing GTR. The SEM micrograph of sample D (Figure 1e) shows that the materials were well dispersed and distributed in the matrix. Rough fractured surface observed is an indication that the properties of the rubber vulcanisate containing GTR were improved through hybrid carbon black/silica (50/10) reinforcement assisted by silane coupling agent. It was observed that increased silica content (from 10 to 15 phr) in the hybrid carbon black/silica (45/15) reinforcement (Figure 1f), also resulted to good dispersion as no agglomerations were observed in the SEM micrograph. All the results show that in a tyre tread compound containing GTR, the ratio of carbon black/silica for the best

improvement in the properties of the vulcanisate was 50/10 for 60 phr filler loading.

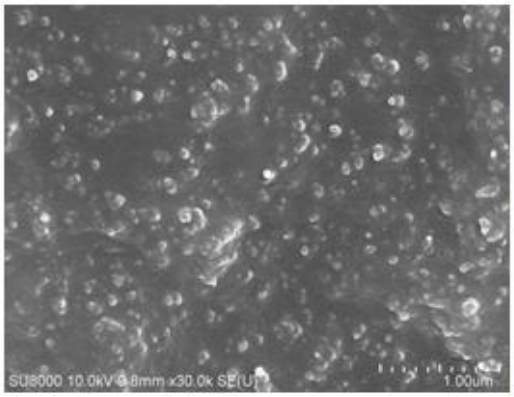

Figure 1a: SEM micrograph of the control sample

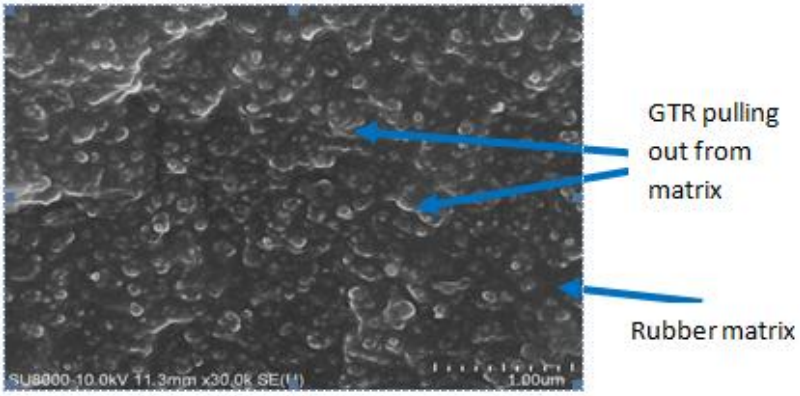

Figure 1b: SEM micrograph of sample A

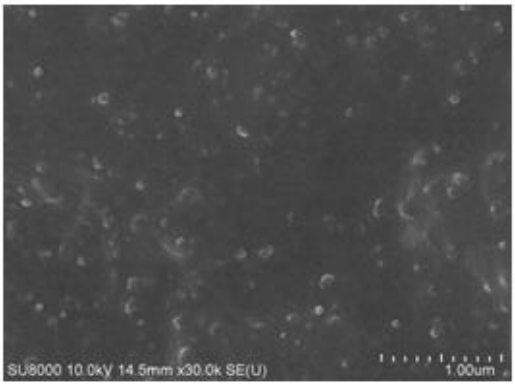

Figure 1c: SEM micrograph of sample B

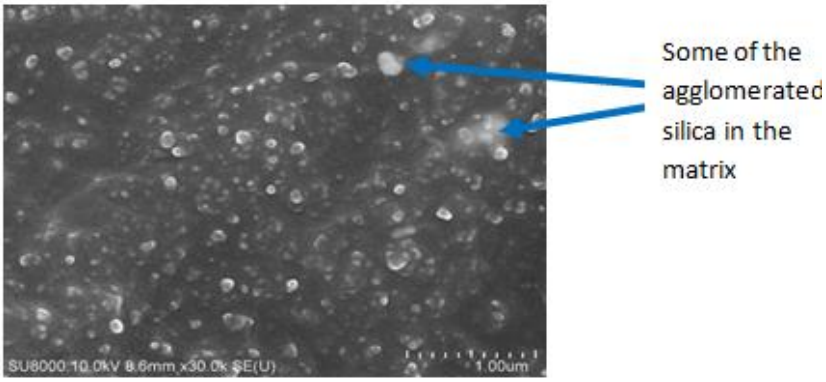

Figure 1d: SEM micrograph of sample C

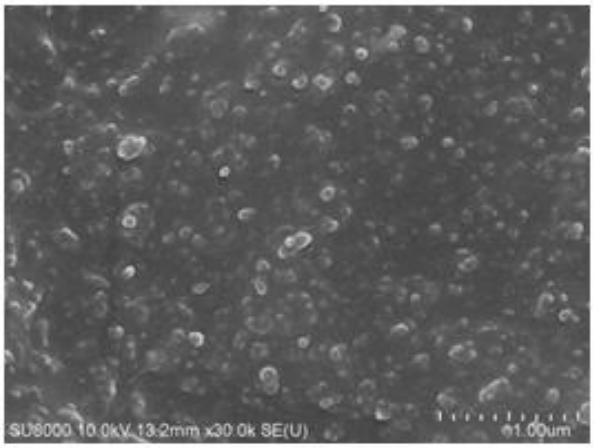

Figure 1e: SEM micrograph of sample D

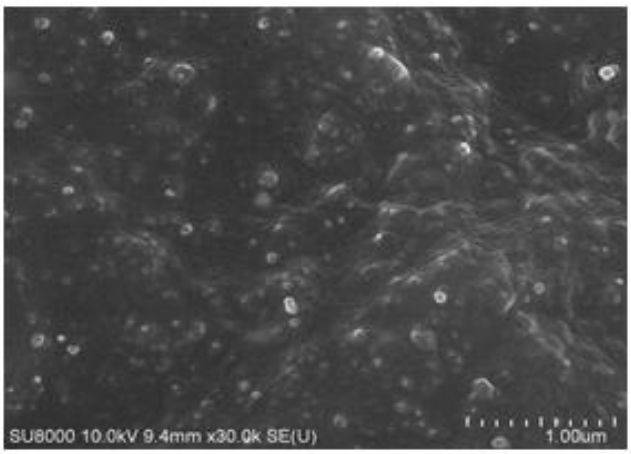

Figure 1f: SEM micrograph of sample E

B. Flex fatigue properties of the rubber vulcanisates

The flex fatigue resistance of the rubber vulcanisates are shown in Table 5. The control sample did not exhibit any crack. Also, the samples containing hybrid carbon black/silica reinforcement from 10-15 phr (samples D and E) exhibited no crack after 10,000 cycles due to good dispersion resulting from the synergistic effect of hybrid filler reinforcement in the tyre tread compound containing GTR.

Table 5: Flex fatigue resistance of the vulcanisate samples

Sample	Control	A	B	C	D	E
Number of cycle		Grade of Crack				
500	0	0	0	0	0	0
1000	0	0	0	1	0	0
2000	0	0	0	2	0	0
3000	0	1	0	3	0	0
4000	0	1	0	3	0	0
5000	0	1	0	3	0	0
6000	0	1	0	3	0	0
7000	0	1	1	3	0	0
8000	0	1	1	3	0	0
9000	0	1	1	3	0	0
10000	0	1	1	3	0	0

IV. Conclusion

This work has presented the results of SEM analysis of the microscructure of tyre tread compound containing GTR and reinforced with carbon black/silica hybrid filler. The SEM images show that GTR is not very compatible when incorporated in rubber matrix. The micrographs of the fractured surfaces of the rubber vulcanisates obtained from SEM show that the incorporation of silica at optimal amount in carbon black reinforced solid tyre compound containing GTR improved the dispersion as well as the distribution of materials in the rubber matrix. The improved dispersion and distribution resulted in the vulcanisates having more resistance to fracture and flex fatigue resistance.

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