Influence of Carbon Black/Silica Hybrid Ratio on Properties of Passenger Car Tire Sidewall

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Abstract

Influence of carbon black (CB)/precipitated silica (SiO_2) hybrid ratio on properties of a passenger car tire (PCT) sidewall based on natural rubber (NR) and butadiene rubber (BR) blend was investigated. Rubbers filled with various hybrid filler ratios at a constant loading of 50 phr were prepared and tested. The filler reinforcement efficiency in association with crucial properties of the tire sidewall were of interest. Results show the enhanced rubber–filler interaction with increasing SiO_2 fraction leading to the improvement in many vulcanizate properties including hardness, tensile strength, tear strength and fatigue resistance, at the expense of cure efficiency and hysteretic behaviors (i.e., reduced heat build-up resistance and increased dynamic set). The results also suggest the improvement in tire sidewall performance of the NR/BR vulcanizates reinforced with CB/SiO_2 hybrid filler, compared to that of the CB-filled vulcanizate.

Keywords

hybrid filler, filler reinforcement, tire sidewall, mechanical properties, viscoelastic properties

1 Introduction

Reinforcing filler is one of the most critical ingredients in tire production. Typically, tire formulations contain approximately 30 % by weight of reinforcing fillers, mainly carbon black (CB) and precipitated silica (SiO_2) [1]. Reinforcing fillers not only reduce the product cost, but also improve the overall performance of the tires. Generally, CB can increase resistances to tensile, tear and abrasion at the expense of a drastic increase of energy dissipation and thus the undesirably increased heat build-up of the tires under service conditions. Precipitated SiO_2 is also another important reinforcing filler widely used in the rubber industry. Due to the existence of hydroxyl groups on its surface, SiO_2 is not compatible with most non-polar rubbers, including natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). With the advent of a silane coupling agent, the reinforcement of SiO_2 has been dramatically improved due to the enhancement of rubber-filler interaction and better filler dispersion [2–8].

Typically, car tire consists of many components, including tread, belt plies, inner liner, beads and sidewall. As tread is the only part of the tire contacting the road surface [9], it is engineered to provide many specific features, including high wear resistance, excellent wet traction and braking ability and low rolling resistance. Extensive research and development has been focused on tire tread compounds to improve tire performance through the application of various hybrid fillers. A partial replacement of CB with silane-treated SiO_2 has recently gained much attention from many tire manufacturers. This is because of its many benefits over the sole use of CB including the greater resistance to chipping and chucking, better wet-grip, lower rolling resistance and reduced heat build-up [10, 11]. Different ratios of CB/SiO_2, in association with the use of silane coupling agent, have been used in the tread production to balance tire wear resistance, rolling resistance and wet grip index, leading to an optimal tire performance [12, 13].

Apart from the tire tread, tire sidewall is one of the critical tire components because it helps absorb the shock generated by hitting road bumps and, thus, provides the ride comfort. Also, the sidewall offers lateral stability and protection of the body plies. The most desirable properties of tire sidewall are high resistance to flex cracking and low

heat build-up [14, 15]. The sidewall compounds are, therefore, mostly made from NR/BR blends filled with medium-reinforcing CB, particularly N550 [16] or N660 [17]. Surprisingly, disclosure of the compounding technology concerning the property improvement of tire sidewall is still limited. To date, there are published works focusing on the crack-growth resistance improvement of tire sidewall by blending CB-filled NR with BR [18] and on the fatigue resistance enhancement with reduced heat build-up by the use of a reactive multifunctional compatibilizer in CB-filled NR/BR blends [19]. Unlike in the tread applications, little attention has been paid to the use of CB/SiO$_2$ hybrid filler technology for improving crucial properties of the tire sidewall compounds. Thus, the present work attempted to close the gap by focusing on the application of CB/SiO$_2$ hybrid filler to improve the properties of the tire sidewall compounds. The reinforcement efficiency provided by various SiO$_2$/CB loading ratios was of interest, and the optimal hybrid loading ratio demonstrating the synergistic effect was drawn and discussed.

2 Experimental

2.1 Materials

2.1.1 Preparation of the sidewall compounds

Table 1 discloses the compounding ingredients used in this work. A blend of 60/40 NR/BR was selected to offer an optimum crack growth resistance, as previously reported [20, 21]. While the total amount of hybrid filler was kept constant at 50 phr, the weight ratios of CB to SiO$_2$ were varied as follows: 50/0, 40/10, 30/20, 20/30, 10/40 and 0/50 and designated as CB/SiO$_2$ 50/0, CB/SiO$_2$ 40/10, CB/SiO$_2$ 30/20, CB/SiO$_2$ 20/30, CB/SiO$_2$ 10/40 and CB/SiO$_2$ 0/50, respectively. Details of the compounding recipe are shown in Table 2. Rubber compounds were prepared using an internal mixer (Brabender-Plasticorder 350E, Germany) equipped with tangential rotors. The two-step mixing technique was used as follows. In the first step, the mixer was set at a fill factor of 0.75, a rotor speed of 40 rpm and a set chamber temperature of 70 °C. After filler incorporation, the rotor speed was raised to 70 rpm during the last 240 s of the mixing process to increase the batch temperature for accelerating the silanization reaction between coupling agent (TESPT) and silica. The total mixing time was kept constant at 900 s. The compounds were then sheeted on a two-roll mill and cooled down. In the second step, the compounds were mixed with curatives at a set temperature of 50 °C for 240 s before being sheeted and kept overnight at room temperature. Details of the mixing sequence are illustrated in Tables 3 and 4.

2.2 Characterization

Characterization of the uncured compounds included the measurements of bound rubber content (BRC), Mooney viscosity and cure characteristics. The BRC measurement was performed by extracting the unbound rubber with toluene at room temperature [22, 23]. Approximately 0.2 g of the uncured sample was cut into small pieces and placed into a metal cage. The sample was then immersed in 25 mL of toluene at room temperature for 168 hrs, and the solvent was renewed every 3 days. The sample was subsequently filtered, dried at room temperature for one day, and then at 75 °C until a constant weight was gained. The calculation of BRC is expressed in Eq. (1) [22–27]. Although the Eq. (1) is intentionally established for rubber filled with only filler(s), it is practically applicable for conventional compounds containing other ingredients such as sulfur, accelerators, and anti-degradants because these chemicals are soluble in toluene and, thus, do not interfere with the accuracy of the BRC measurement.

$$\mathrm{BRC}(\%) = \frac{W_{\mathrm{fg}} - W\left[m_{\mathrm{f}}/\left(m_{\mathrm{f}} + m_{\mathrm{p}}\right)\right]}{W\left[m_{\mathrm{f}}/\left(m_{\mathrm{f}} + m_{\mathrm{p}}\right)\right]} \times 100, \tag{1}$$

where W_{fg} is the weight of fillers and gel, m_{f} is the weight of the fillers in the compound, m_{p} is the weight of the polymer in the compound, and W is the weight of the specimen.

Mooney viscosity (ML (1+4) @100 °C) was measured using a Mooney viscometer (GOTECH model MV-3000U, Taiwan) according to ISO 289-1:2015 [28]. Cure behavior was monitored using a moving die rheometer (MDR, TechPro MD+, USA) at 160 °C following ISO 6502-3:2018(en) [29]. Also, the cure test under 100 % strain was conducted to impede the formation of the filler-filler network during the cure test by the use of Rubber Process Analyzer (Alpha Technologies model RPA2000, USA). Payne effect was determined by using the RPA2000 at a frequency of 1.7 Hz and temperature of 100 °C. A strain sweep test was carried out, and the difference of storage shear moduli ($\Delta G'$) at 0.56 % and 100.0 % was selected to represent the Payne effect magnitude. After the cure test, the vulcanized samples were prepared using a compression molding technique at 160 °C for the optimum cure time ($t'_c(95)$) as predetermined from the MDR cure curve.

After vulcanization, a swelling test was performed by soaking the weighed test pieces with a dimension of approximately $1 \times 1 \times 0.2$ cm^3 in toluene at room temperature for 120 hrs. Thereafter, the swollen test pieces were taken out, blotted gently by filter paper and weighed (W_2). The test pieces were then dried in an oven at 70 °C until a

Table 1 List of materials used in the present study

Ingredients	Suppliers
Natural rubber (STR 5L, 88 ML(1+4)@100 °C)	Union Rubber Product Co., Ltd., Thailand
Butadiene rubber (BR-150 with 43 ML(1+4)@100 °C, 98 wt% of *cis* content, 1wt% of *trans* content, and 1 wt% of vinyl content)	UBE Industries, Ltd., Japan
N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD)	Monflex Pte. Ltd., Singapore
2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)	Monflex Pte. Ltd., Singapore
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)	Monflex Pte. Ltd., Singapore
Bis (triethoxysilylpropyl) tetrasulfide (TESPT)	Innova (Tianjin) Chemical Co., Ltd., China
Carbon black (N660) with BET specific surface area of 35 ± 5 m^2/g	Thai Carbon Black Public Co., Ltd., Thailand
Silica (Tokusil 255) with BET specific surface area of 166 m^2/g	OSC Siam Silica Co., Ltd., Thailand
Naphthenic oil	PSP Specialties Co., Ltd., Thailand
Microcrystalline wax	Petch Thai Chemical Co., Ltd., Thailand
Stearic acid	Kij Paiboon Chemical Ltd., Part., Thailand
Zinc oxide (ZnO)	Thai-Lysaght Co., Ltd., Thailand
Sulfur	Siam Chemicals Public Co., Ltd., Thailand

Table 2 Compounding recipes

Ingredients	CB/SiO_2 Loading (phr/phr)					
	50/0	40/10	30/20	20/30	10/40	0/50
NR	60.0	60.0	60.0	60.0	60.0	60.0
BR-150	40.0	40.0	40.0	40.0	40.0	40.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Microcrystalline wax	3.0	3.0	3.0	3.0	3.0	3.0
Naphthenic oil	4.0	4.0	4.0	4.0	4.0	4.0
Carbon black (N660)	50.0	40.0	30.0	20.0	10.0	0.0
Silica (Hisil 255)	0.0	10.0	20.0	30.0	40.0	50.0
TESPT (10 % w/w of SiO_2)	0.0	1.0	2.0	3.0	4.0	5.0
IPPD	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	1.0	1.0	1.0	1.0	1.0	1.0
TBBS	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0

Table 3 Mixing sequence used in this study; **1ˢᵗ mixing step**: Fill factor: 0.75; set temperature: 70 °C, rotor speed: 40 rpm (0–660 s) and 70 rpm (661–900 s)

Time (s)	Ingredients added
0	NR + BR
	1. ZnO + stearic acid and microcrystalline wax
120	2. ½CB + ½SiO$_2$ + ½TESPT + naphthenic oil
	3. ½CB + ½SiO$_2$ + ½TESPT
660	IPPD + TMQ
900	Discharge

Table 4 Mixing sequence used in this study; **2ⁿᵈ mixing step**: Rotor speed: 40 rpm; set temperature: 50 °C

Time (s)	Ingredient added
0	NR/BR mix
60	TBBS and sulfur
240	Discharge

constant weight was obtained (W$_1$). Swelling ratio (S) was calculated by Eq. (2):

$$S(\%) = (W_2/W_1) \times 100. \tag{2}$$

Hardness test was performed according to ISO 48-4:2018 [30] using a durometer (Wallace Shore A, UK). At least five measurements were carried out for each sample at different locations. Elastic modulus (G') at 1.95 % strain of the vulcanizate was measured using the RPA2000 at a frequency of 1.7 Hz and a temperature of 100 °C.

Tensile properties (i.e., tensile strength, stress at 100 % elongation or 100 % modulus (M100), elongation at break) and tear strength were measured using a universal testing machine (Instron 3366 series, USA) as per ISO 37:2017(en) [31] (die type 1) and ISO 34-1:2010 [32] (method B), respectively. Determination of heat build-up (HBU) was carried out in accordance with ISO 4666-3:2010 [33] by using a Goodrich flexometer (BF Goodrich Model II, USA). The temperature increases at the specimen's base were recorded. Values of the dynamic set were also reported together with the heat build-up results. Fatigue resistance was determined according to ISO 132:2017 [34] using a De Mattia flexing machine (GOTECH model GT-7011-D, Taiwan).

3 Results and discussion

Fig. 1 demonstrates bound rubber content (BRC) results of the compounds filled with various CB/SiO$_2$ hybrid ratios. As expected, the SiO$_2$-filled system (i.e., CB/SiO$_2$=0/50) possesses the highest BRC, whereas the CB-filled
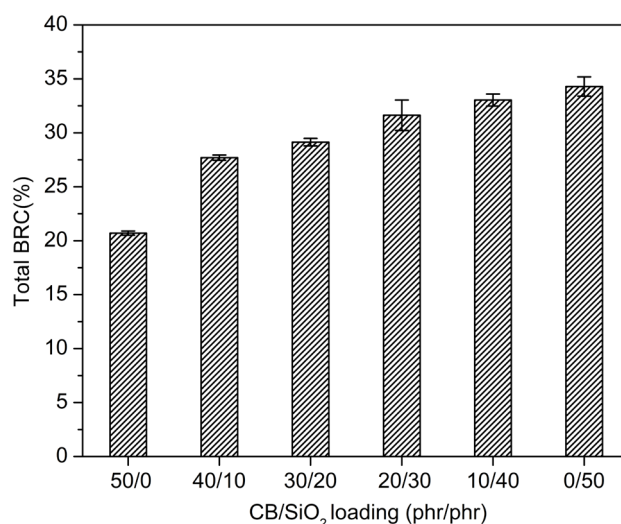
Fig. 1 Bound rubber content of the compounds filled with various CB/SiO$_2$ hybrid loadings

system (CB/SiO$_2$ = 50/0) shows the lowest BRC. The result is not uncommon because SiO$_2$ used in this work possesses a much greater specific surface area than CB (BET specific surface area: 166 vs. 35 m^2/g) meaning that there is much higher contacting surface area and, thus, rubber-filler interaction in the SiO$_2$-filled system. In the case of hybrid filler systems, as one can expect, the BRC increases continuously with increasing SiO$_2$ fraction due to a dilution effect.

Fig. 2 depicts the Payne effect magnitude of the compounds. The Payne effect or filler-filler interaction tends to increase with increasing SiO$_2$ fraction. The result trend is in line with that of the BRC results, as mentioned earlier. Again, the explanation is given by the considerably higher specific surface area of SiO$_2$, compared to CB, which leads
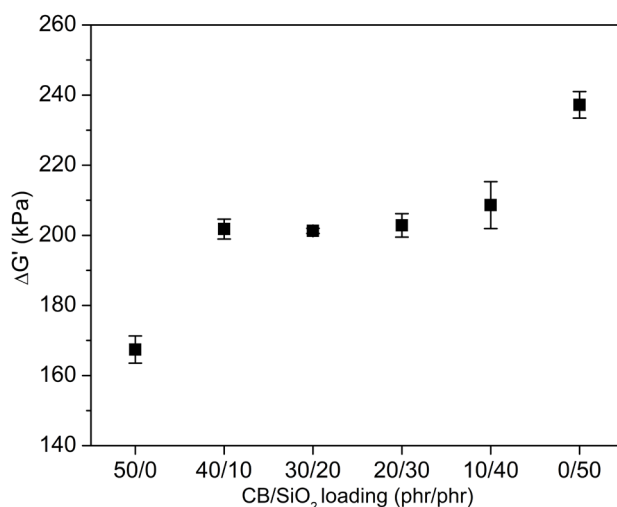
Fig. 2 Payne effect of the compounds filled with various CB/SiO$_2$ hybrid loadings

to the increase in rubber-filler interaction (as evidenced from the BRC results) and the enhanced filler-filler interaction.

Mooney viscosity results of the compounds are illustrated in Fig. 3. As CB (N660) used in this work has a relatively low specific surface area (35 m²/g) compared to SiO$_2$ (166 m²/g), the SiO$_2$-filled compound shows much higher viscosity than the CB-filled compound. Surprisingly, in the hybrid filler systems, the viscosity values of the compounds are approximately the same and do not follow the mixture rule. This might be explained by the difference in the degree of filler dispersion. In the CB-rich filled systems, shearing force during mixing was relatively low due to the low specific surface area of CB, resulting in a relatively poor SiO$_2$ dispersion when compared to the SiO$_2$-rich systems. Viscosity values of the CB-rich filled system are therefore unexpectedly high. It is also noticeable that the Mooney viscosity results are analogous to the Payne effect results (see Fig. 2).

Cure curves of the compounds are shown in Fig. 4 and the extracted data are summarized in Table 5. Both t_{s2} and $t'_c(95)$ tend to increase with increasing SiO$_2$ fraction. A similar observation is reported elsewhere [35, 36] as explained by the cure retardation effect. It is widely accepted that the hydroxyl groups on the SiO$_2$ surface, particularly the ones that do not react with TESPT, can adsorb zinc complex and curatives from the matrix. Interestingly, both t_{s2} and $t'_c(95)$ measured from MDR at low strain (ca. 7 %) are longer than those measured from RPA at high strain (100 %). Such difference could be explained as follows. At low strain (in MDR), there is a slow torque rise as a function of time or the so-called marching phenomenon, which is more pronounced in the SiO$_2$-rich systems. Such phenomenon is, to some

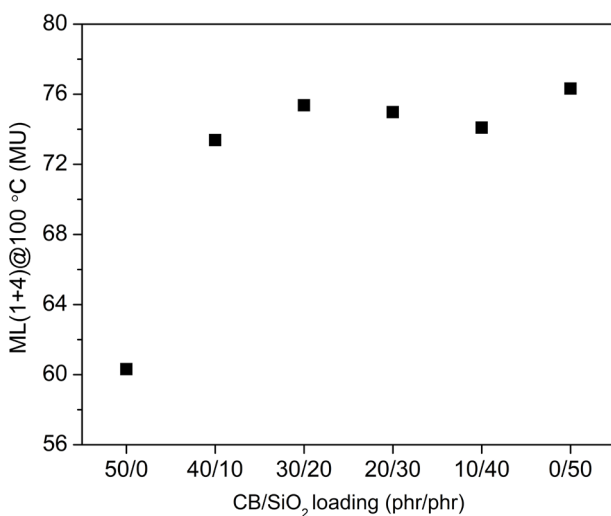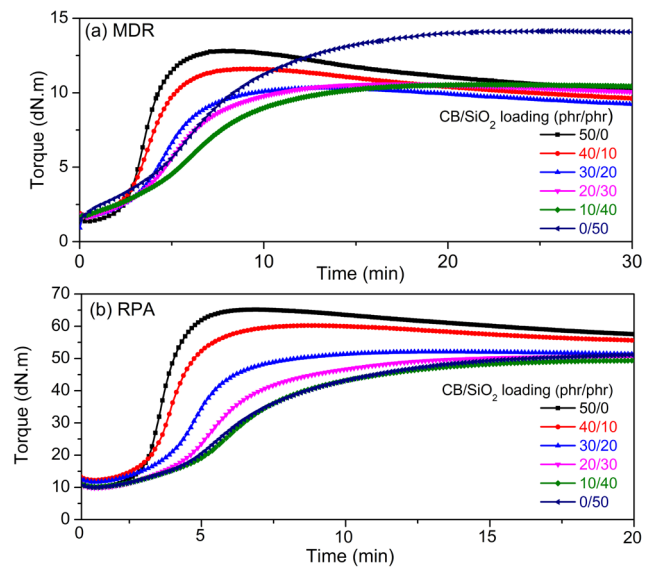**Fig. 4** Cure characteristics of the compounds as measured by (a) MDR at low strain (7 % strain) and (b) RPA at high strain (100 % strain)

extent, caused mainly by the SiO$_2$ transient network formation via the highly reactive silanol groups on the SiO$_2$ surface. Since the SiO$_2$ network formation is a time-consuming process and, thus, causes a delay of maximum torque (M_H), $t'_c(95)$ is therefore prolonged in this case. On the contrary, at a relatively high strain of the RPA test (i.e., 100 %), the SiO$_2$ network formation is impeded [37–39], and therefore no delay of $t'_c(95)$ is observed.

Generally, the torque difference (M_H–M_L) is directly proportional to *crosslink density*. One might expect the lower torque difference values found in the SiO$_2$-filled vulcanizates due to the cure retardation phenomenon as previously mentioned [2, 40, 41]. Unexpectedly, the torque difference value of the SiO$_2$-filled system measured from MDR is comparable to that of the CB-filled one, as illustrated in Table 5. This unexpected finding is caused by the unusual increase in M_H value of the SiO$_2$-filled vulcanizate resulting from the formation of SiO$_2$ transient network, apart from the chemical crosslinks developed in the rubber matrix. In contrast, by performing the cure test using RPA, the torque interference by the transient filler network is eliminated. The torque difference values become in the proper order, i.e., they decrease with increasing SiO$_2$ fraction, which is in good accordance with the cure retardation phenomenon via the curative adsorption on the SiO$_2$ surface as discussed earlier.

Fig. 5 displays the swelling ratio of the vulcanizates filled with the hybrid filler. As tightly bound rubber is more restricted to swelling by solvent, theoretically, the vulcanizate having higher BRC should have a lower swelling ratio,

Fig. 3 Mooney viscosity of the compounds filled with various CB/SiO$_2$ hybrid loadings

Table 5 Cure characteristics of the compounds as determined from MDR and RPA

CB/SiO$_2$ Loading (phr/phr)	M_H (dN·m)		M_H–M_L (dN·m)		t_{s2} (min)		t_c'(95) (min)	
	MDR	RPA	MDR	RPA	MDR	RPA	MDR	RPA
50/0	12.72 ± 0.13	65.13 ± 0.04	11.35 ± 0.13	55.01 ± 0.08	2.77 ± 0.02	1.49 ± 0.01	5.43 ± 0.07	3.44 ± 0.04
40/10	11.46 ± 0.21	60.16 ± 0.07	9.75 ± 0.16	48.05 ± 0.08	2.94 ± 0.04	1.50 ± 0.01	6.36 ± 0.09	3.57 ± 0.07
30/20	10.28 ± 0.08	52.09 ± 0.01	8.57 ± 0.10	40.44 ± 0.01	3.52 ± 0.01	1.59 ± 0.02	9.11 ± 0.44	4.51 ± 0.01
20/30	10.72 ± 0.18	50.63 ± 0.03	9.01 ± 0.08	40.82 ± 0.10	3.64 ± 0.05	2.03 ± 0.02	11.22 ± 0.10	6.29 ± 0.03
10/40	10.68 ± 0.18	49.43 ± 0.03	8.89 ± 0.11	39.40 ± 0.22	4.00 ± 0.08	2.11 ± 0.01	14.11 ± 0.05	7.40 ± 0.03
0/50	14.11 ± 0.06	51.62 ± 0.04	11.46 ± 0.19	41.29 ± 0.44	4.04 ± 0.04	2.11 ± 0.03	16.29 ± 0.80	8.17 ± 0.04
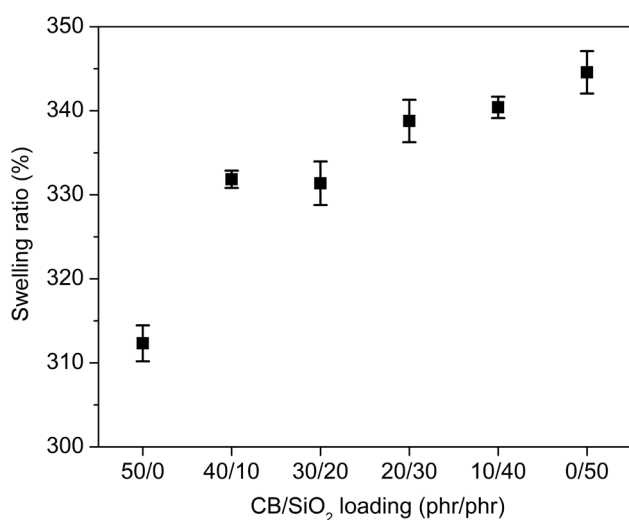
Fig. 5 Swelling ratio of the vulcanizates filled with various CB/SiO$_2$ hybrid loadings

when compared at a given crosslink density. However, in this work, the highest swelling ratio is found in the SiO$_2$-filled system despite its highest BRC. The lowest crosslink density as evidenced from the torque difference results obtained from RPA might be a possible reason for the finding. Likewise, the lowest swelling ratio of the CB-filled system, despite its lowest BRC, can be explained by the its highest crosslink density. In addition, the cage effect of the grape-like structure of CB might be another reason to restrict the swelling of rubber molecules trapped within the CB structure. With increasing SiO$_2$ fraction, the rubber vulcanizates exhibit a continuous increase in swelling ratio due possibly to the dilution effect.

Hardness is a measure of the resistance of rubber against surface deformation [42]. Fig. 6 shows the hardness results of the rubber vulcanizates filled with different CB/SiO$_2$ hybrid fractions. The hardness increases continuously with increasing SiO$_2$ fraction despite the reduced crosslink density. The results imply that the higher rubber-filler interaction (BRC) and the stronger filler-filler network in the SiO$_2$-rich systems play a greater role in the

hardness of rubber vulcanizates than the crosslink density. As it is widely known that hardness is closely related to modulus at low strain, shear modulus (G') at 1.95 % strain of the vulcanizates follows the same trend as the hardness results (see also Fig. 6).

Table 6 illustrates the tensile and tear properties of the rubber vulcanizates. With increasing SiO$_2$ fraction, the improvements in tensile strength and 100 % modulus (M100) are revealed, indicating the greater magnitude of filler reinforcement which could be explained by the enhanced rubber-filler interaction due to the increase of the total contacting surface area of fillers in the vulcanizates. Notably, despite the increased magnitude of filler reinforcement effect, deformability of the vulcanizates represented by the elongation at break value is unexpectedly increased. Such an increase could be explained by the reduced crosslink density, as discussed previously. For the tear test, the result trend is in a similar manner to the tensile test but with a stronger magnitude of enhancement. The substantial improvement in tear strength is caused by the combination of:

1. the filler reinforcement as evidenced by BRC results (see Fig. 1) and
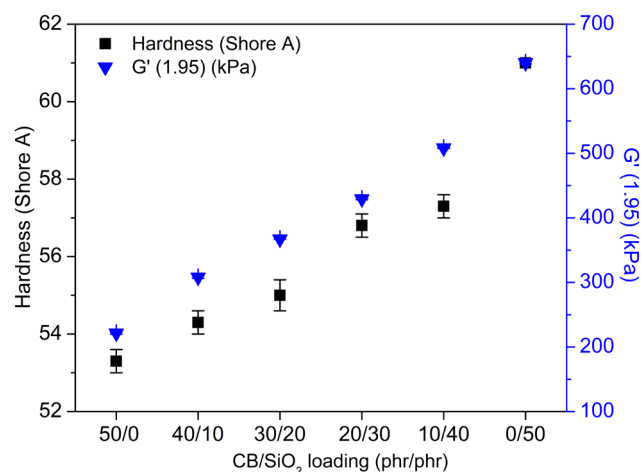
Fig. 6 Hardness and storage modulus (G') of the vulcanizates filled with various CB/SiO$_2$ hybrid loadings
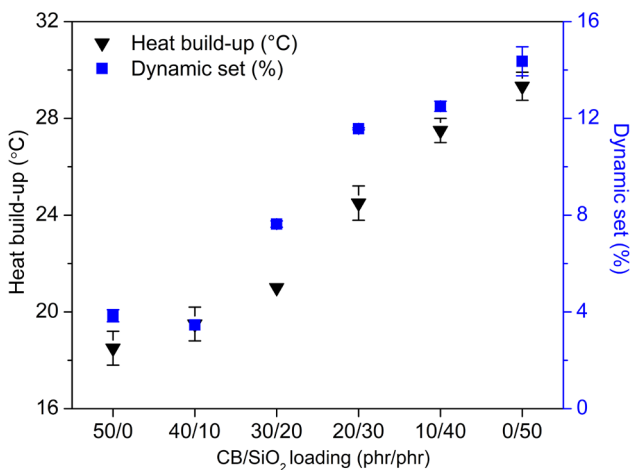
Table 6 Tensile properties and tear strength of the vulcanizates filled with various CB/SiO$_2$ hybrid loadings

| CB/SiO$_2$ Loading (phr/phr)	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	Tear strength (N/mm)
50/0	18.4±1.3	511±29	2.09±0.08	21.9±1.7
40/10	20.1±1.0	550±31	1.92±0.10	46.1±4.0
30/20	20.6±0.4	600±41	2.48±0.06	57.6±1.8
20/30	20.9±0.5	650±24	2.40±0.13	60.5±0.4
10/40	21.6±1.0	734±40	2.76±0.19	63.2±2.6
0/50	21.5±0.7	660±23	2.94±0.33	65.0±6.5

2. the decreased crosslink density. Generally, the vulcanizates with relatively low crosslink density tend to give relatively high tear strength due to the greater energy dissipation through the higher molecular motion [43].

Fig. 7 illustrates heat build-up (HBU) and dynamic set of the vulcanizates. With increasing SiO$_2$ fraction, there are undesirable increases in both HBU and dynamic set, demonstrating a rise in viscous response (or a reduction in elastic contribution). Such augmented viscous response is caused by a combination of the reduced crosslink density and the increase in the total contacting filler surface area, facilitating the greater slippage of the rubber molecules on the filler surface. This leads to the increased energy dissipation during the cyclic deformation and, thus, the rise in HBU [44].

Fig. 8 demonstrates fatigue resistance of the rubber vulcanizates, represented in terms of the number of kilocycles required to cause 2 mm. crack length. Clearly, the fatigue resistance tends to increase continuously with increasing SiO$_2$ fraction. The explanation is given to the improvement in rubber–filler interaction in association with the reduced crosslink density, facilitating the energy dissipation at the crack tip during the cyclic operation [45, 46].
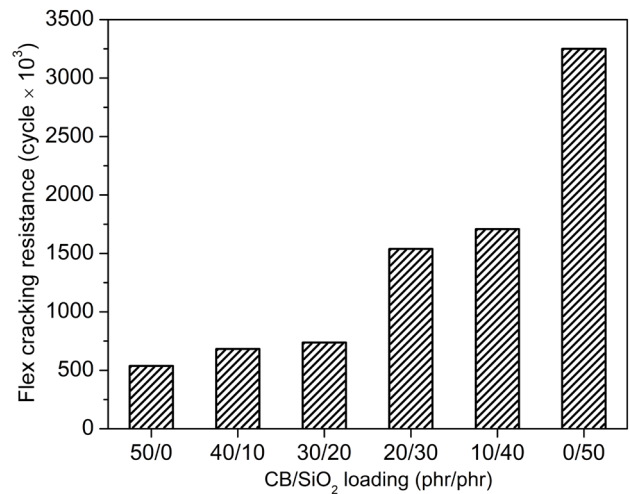

Fig. 8 Fatigue resistance of the vulcanizates filled with various CB/SiO$_2$ hybrid loadings

From the overall results, it is possible to summarize the effect of hybrid filler ratio on tire sidewall performance as illustrated in Fig. 9 in which the properties of the CB-filled vulcanizate were employed as references for normalization. Clearly, the SiO$_2$-filled system (0/50) has higher strengths and fatigue resistance than the CB-filled system (50/0). Meanwhile, the use of sole SiO$_2$ in the tire sidewall compound might lead to a significant increase in heat build-up, which is undesirable for tire sidewall. A proper selection of CB/SiO$_2$ ratio to achieve a good balance of the tire sidewall performance is therefore recommended.

Fig. 7 Heat build-up (HBU) and dynamic set of the vulcanizates filled with various CB/SiO$_2$ hybrid loadings
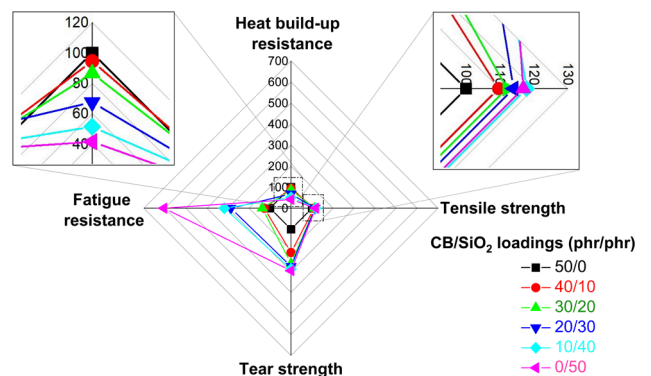
Fig. 9 Normalized graph of tire sidewall performance at various CB/SiO$_2$ hybrid loadings

4 Conclusions

The tire sidewall compounds reinforced with a hybrid filler system of carbon black (CB) and precipitated silica (SiO_2) were prepared by varying the SiO_2 fraction, and their properties were investigated. Results demonstrate the increases in hardness, modulus, tensile strength, tear strength as well as fatigue resistance with increasing SiO_2 fraction, at the expense of the hysteretic behavior (i.e., impaired heat build-up and dynamic set). The overall results provide the advantages and disadvantages of using CB/SiO_2 hybrid filler over the sole use of CB in the production of tire sidewall compound. With a proper selection of CB/SiO_2 ratio, optimal performance of tire sidewall can be achieved. Practically, the hardness of the tire sidewall should be maintained constant after the formulation adjustment. Substantial replacement of medium reinforcing CB (N660) by a superior reinforcing SiO_2 (Hisil 255) therefore permits the reduction of total filler loading in the compound formulation which could reduce the undesirable increases in heat build-up and dynamic set of the SiO_2-rich systems.

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