

Material Properties

# Reinforcement of natural rubber with silica/carbon black hybrid filler

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## Abstract

Carbon black (CB) and silica have been used as the main reinforcing fillers that increase the usefulness of rubbers. As each filler possesses its own advantages, the use of silica/CB blends should enhance the mechanical and dynamic properties of natural rubber (NR) vulcanizates. However, the optimum silica/CB ratio giving rise to the optimum properties needs to be clarified. In this research, reinforcement of NR with silica/CB hybrid filler at various ratios was studied in order to determine the optimum silica/CB ratio. The total hybrid filler content was 50 phr. The mechanical properties indicating the reinforcement of NR vulcanizates, such as tensile strength, tear strength, abrasion resistance, crack growth resistance, heat buildup resistance and rolling resistance, were determined. The results reveal that the vulcanizates containing 20 and 30 phr of silica in hybrid filler exhibit the better overall mechanical properties.

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## 1. Introduction

Although natural rubber (NR) is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into NR in most cases in order to gain the appropriate properties for specific applications. A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinfor-

cement, reduction in material costs and improvements in processing [1]. Reinforcement is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness and modulus [2,3]. In most applications, carbon black (CB) and silica have been used as the main reinforcing fillers that increase the usefulness of rubbers. When CB is compounded with rubbers, tensile strength, tear strength, modulus and abrasion resistance are increased. For this reason, CB has been extensively exploited in numerous rubber engineering products [4]. In general, a CB-reinforced rubber has a higher modulus than a silica-reinforced one. However, silica provides a unique combination of tear strength, abrasion resistance, aging resistance and

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adhesion properties [5]. In tire treads, silica yields a lower rolling resistance at equal wear resistance and wet grip than CB [6]. Since CB and silica possess their own advantages, the utilization of hybrid filler or blends of silica and CB in rubber should give the benefits from each filler. It is stated that the addition of precipitated silica in CB-filled rubber components can be applied to tire treads, wire and fabric coating, conveyor belts, hoses, rubber-covered belts, engine mounts, bumper strips, and cable jackets [7,8]. One of the important commercial hybrid fillers is CB–silica dual phase filler (CSDPF). It is produced by pyrolyzing petroleum- and silicon-based feedstocks, a unique co-fuming by Cabot Corporation [9]. CSDPF features high surface activity of the carbon domain and high silica surface [10]. It has been shown to give better overall mechanical properties in comparison with the conventional CB and silica fillers. Some properties, such as abrasion resistance and low rolling resistance, of a typical truck-tread compound are superior to those of the vulcanizate filled with CB N110. This is due to its high polymer–filler interaction and lower filler–filler interaction. Compared to silica, the CSDPF is reported to have significant advantages in abrasion resistance and tear strength [11]. Nevertheless, the ratio of CB and silica in CSDPF has not been revealed. Although several past studies have been made to elucidate the hybrid filler systems, there is not much systematic scientific report on the effect of silica/CB ratio on the properties of NR vulcanizates. In this experiment, the hybrid filler was practically prepared from silica (Hisil 233) and CB (N330) at various ratios. The effects of filler ratio on various mechanical properties of NR vulcanizates were systematically studied and presented. The ratio of silica and CB giving better overall mechanical properties is also reported.

## 2. Experimental

### 2.1. Preparation of silica/CB-filled NR compounds

All compounds had the same composition, except for the amounts of silica (Hisil 233) and CB (N 330), which were varied to prepare compounds with different ratios of hybrid filler. However, the total amount of hybrid filler in each formulation was kept constant at 50 phr. Therefore, the amount of silica or CB ranged from 0 to 50 phr. The samples were named as S0, S10, S20, S30, S40 and S50. The

number followed the letter “S” indicates the amount of silica in the samples. For example, S20 contains 20 phr of silica and 30 phr of CB. The other ingredients in the rubber compound were (in phr): rubber, 100; stearic acid, 2.0; ZnO, 4.0; bis(3-triethoxysilylpropyl) tetrasulfide (Si-69), 3.0; poly(ethylene glycol), 2.0; *N*-(1, 3-dimethyl)-*N'*-phenyl-*p*-phenylenediamine (6-PPD), 2.0; wax, 2.0; *N*-tert-butyl-2-benzothiazolesulfenamide (TBBS), 1.6; sulfur, 1.4. All ingredients, except the curatives, were mixed with rubber in a laboratory-size internal mixer (Brabender Plasticorder) at a set temperature of 50 °C with a rotor speed of 50 rpm and a fill factor of 0.7. The total mixing time in the internal mixer was 8 min. After discharging, the compound was further mixed on a two roll-mill for 1 min. Then, the curatives were added and mixed for four more minutes. Finally, 10 end-roll passes were made before sheeting off.

### 2.2. Determination of cure characteristics

Cure characteristics, which are scorch time, cure time and minimum torque of the rubber compound were determined at 150 °C with an oscillating disk rheometer (ODR). About 10 g of rubber compound were used with a 1° arc. The cure time ( $t_{90}$ ) used for preparation of the cured samples was the time at which the rheometer torque increased to 90% of the total torque change on the cure curve.

### 2.3. Equilibrium swelling measurement of the vulcanizates

The vulcanizate having a thickness of 1.2 mm was cut into rectangular shape with weight about 0.7 g. Free organic materials were first extracted from the sample for 12 h using acetone as a solvent. Then, the sample was dried in a vacuum oven at room temperature. The sample was immersed in 100 ml toluene for 7 days. The swollen sample was removed from the toluene and the excess toluene was blotted with a paper towel. Then, the swollen sample was placed in a clean weighing bottle and weighed accurately. The swelling ratio ( $Q$ ) was determined using Eq. (1). The value of swelling ratio of each vulcanizate was the average of three specimens:

$$Q = (W_S - W_U) / W_U, \quad (1)$$

where  $W_S$  is the weight of swollen sample and  $W_U$  the weight of extracted and dried sample before swelling.

## 2.4. Mechanical property measurement

Compression molded sheets having a thickness of about 1.2 mm were used for tear and tensile testing. Tear and tensile properties of the specimens were measured according to ISO 34-1 and ISO 37, respectively. Crescent test pieces were used for determining the tear strength. The measurements were carried out using an Instron Universal Tester (Model 4301) with a crosshead speed of 500 mm/min and initial clamp separation of 65 mm. The values of tear and tensile properties were the average of 4–5 specimens.

The aging properties were carried out by placing five dumbbell specimens in air circulating oven at 100 °C for 22 h. Then, the specimens were cooled at room temperature for at least 16 h before testing. The tensile properties of aged specimens were determined in the same manner as the unaged specimens. Tensile strength retention was calculated using the equation:

$$\text{Tensile retention(\%)} = [(T_u - T_a)/T_u] \times 100, \quad (2)$$

where  $T_u$  and  $T_a$  are tensile strength of unaged and aged specimens, respectively.

Abrasion, heat buildup and crack growth resistance of the vulcanizates were measured, in accordance with ISO 4649, ISO 4666 (Goodrich flexometer) and ISO 132, respectively. Dynamic compression set was evaluated using the same specimens as for heat buildup testing. After heat buildup testing, the specimen was left at 25 °C for 1 h. Thereafter, its final height was measured and the compression set was calculated using the equation:

$$\text{Dynamic compression set (\%)} = [(H_o - H_f)/H_o] \times 100, \quad (3)$$

where  $H_o$  is the original height (mm);  $H_f$  the final height (mm).  $\tan \delta$  was measured using a dynamic mechanical thermal analyzer (Gabo, Explexor™ 25 N) with tension mode of deformation. The test frequency and dynamic strain amplitude used were 5 Hz and 0.5%, respectively. The temperature of measurement ranged from 30 to 90 °C, with a heating rate of 2 °C/min.  $\tan \delta$  at 70 °C was chosen for indicating the rolling resistance property of the rubber vulcanizates [12].

A rubber process analyzer (RPA 2000) was used to determine the dependence of storage modulus ( $G'$ ) on shear strain of the rubber compounds. The stronger dependence of storage modulus and shear

strain indicates the greater disruption of filler–filler interaction. About 5.2 g of the test specimen was used, and the experiment was carried out at a test frequency and temperature of 100 rad/s and 100 °C, respectively. The strain deformation ranged from 0.28% to 200%.

## 2.5. Scanning electron microscopy

Cryogenic fracture surfaces were prepared for observing filler dispersion. The specimens were sputter coated with Pt–Pd and investigated under a Hitachi (model S-2500) scanning electron microscope (SEM).

## 3. Results and discussion

### 3.1. Cure characteristics

Scorch time, cure time and minimum torque of NR compounds filled with silica/CB hybrid filler are depicted in Figs. 1–3, respectively. It should be noted that the total hybrid filler content in each vulcanizate is 50 phr and the amount of silica ranges from 0 to 50 phr. The results show that scorch time and cure time of the vulcanizates increase with increasing silica content up to 30 phr and then they slightly decrease when silica content is further increased. These results are consistent with the previous work showing an increase in scorch protection of the compound with increasing silica surface area [8]. This is due to the adsorption of accelerator by silanol groups on the silica surface. Although it is well established that the use of coupling agent (Si-69) would reduce the adsorption of accelerator on the silica surface, the amount of

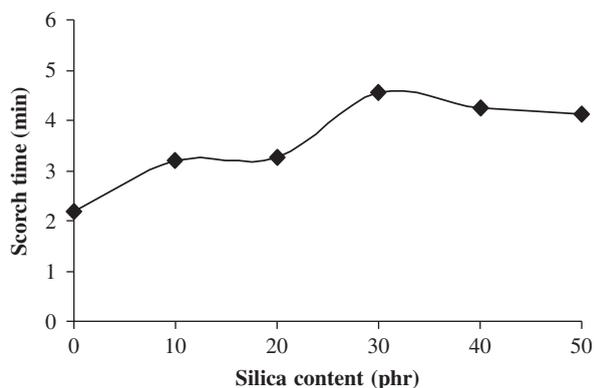


Fig. 1. Scorch time of silica/CB-filled NR vulcanizates at various filler ratios.

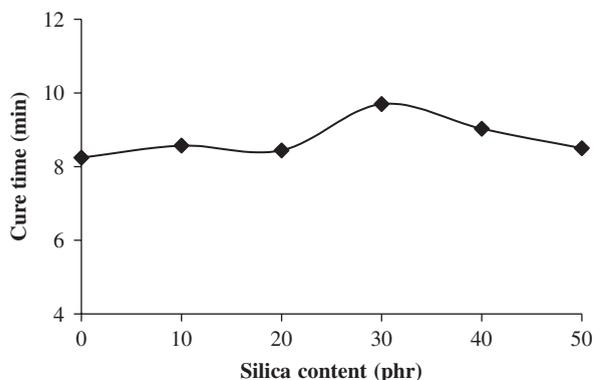


Fig. 2. Cure time of silica/CB-filled NR vulcanizates at various filler ratios.

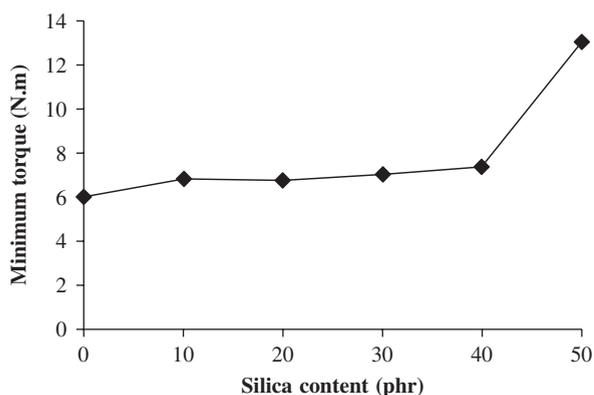


Fig. 3. Minimum torque of silica/CB-filled NR vulcanizates at various filler ratios.

Si-69 used in this experiment may not be sufficient when the silica content is high. In addition, the gradual decrease in scorch time and cure time when silica content is more than 30 phr might be because these compounds have experienced greater thermal history during mixing as a result of their higher compound viscosities. It is known that the shear heating during mixing increases when silica loading is increased due to the increase of compound viscosity. This explanation is supported by the value of minimum torque determined from rheometer cure curves. It can be seen in Fig. 3 that compounds having high silica loading give higher minimum torque, indicating higher viscosities compared to others.

### 3.2. Swelling resistance and mechanical properties

Fig. 4 presents the relationship between swelling ratio and silica content in hybrid filler. Swelling resistance of the vulcanizates, which is inversely

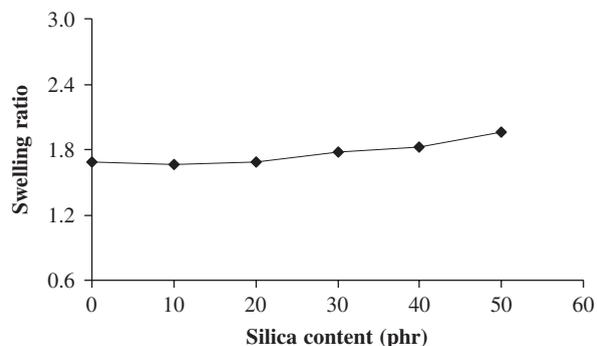


Fig. 4. Swelling resistance of silica/CB-filled NR vulcanizates at various filler ratios.

proportional to swelling ratio, decreases gradually when the silica content is higher than 20 phr. This indicates the reduction in crosslink density. As mentioned above, the amount of Si-69 used in this experiment may not be sufficient to reduce the adsorption of accelerator on silica surface when the silica content in the vulcanizates is high. Besides, the decrease in filler–rubber interaction is thought to be another cause for the reduction in swelling resistance as silica loading increases. It is well known that silica has strong filler–filler interaction [7]. Therefore, the increase in silica loading should lead to an increase in the silica–silica interaction and, hence, a decrease in filler–rubber interaction.

100% modulus, elongation at break before and after aging, are presented in Figs. 5 and 6. It is evident that the moduli of both unaged and aged samples tend to reduce when the silica content is increased. This is due to the decrease in crosslink density when silica loading is high. As a consequence, a rise in elongation at break is observed with increasing silica content. The increase in modulus and reduction in elongation at break of aged samples over those of the corresponding unaged samples indicates the increase of crosslink network as a result of post-curing during aging treatment. The increase in the crosslink density after aging reduces the mobility of the rubber chains. On the other hand, it appears that tensile strength shown in Fig. 7 does not significantly change with increasing silica content and tensile strength of unaged sample ranges from 29 to 31 MPa. Fig. 8 shows that tensile retention tends to be enhanced when the silica content is increased, except for S40.

Fig. 9 shows that tear strength of the vulcanizates is not much different at various filler ratios. However, it should be noted that tear strength of

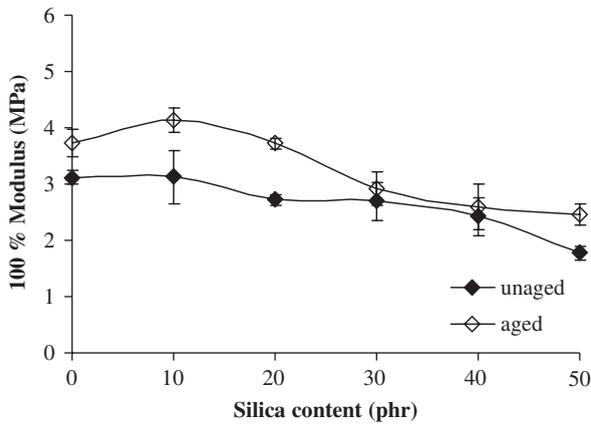


Fig. 5. 100% modulus of silica/CB-filled NR vulcanizates at various filler ratios.

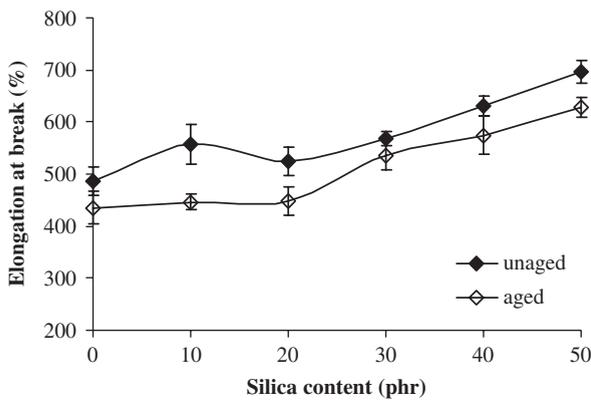


Fig. 6. Elongation at break of silica/CB-filled NR vulcanizates at various filler ratios.

the vulcanizates having 20 and 30 phr of silica is comparable to that of the vulcanizates having 0 and 50 phr of silica but slightly higher than that of the vulcanizates having 10 and 40 phr of silica. Abrasion resistance of the silica/CB-filled NR vulcanizates, expressed as abrasion loss, is presented in Fig. 10. The results show that abrasion resistance tends to decrease when silica content is more than 10 phr. It has been reported that abrasion resistance is controlled mainly by the modulus and the friction coefficient of the vulcanizate [13]. Higher modulus and lower friction coefficient give the vulcanizates with better abrasion resistance. Although the friction coefficient was not measured in this work, the results seem to agree well with the moduli. In addition, a vulcanizate with good filler dispersion is claimed to have a better wear property than that with poor filler dispersion [14]. Therefore, poor

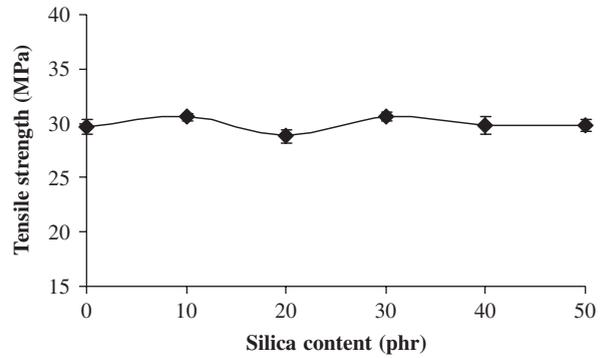


Fig. 7. Tensile strength of silica/CB-filled NR vulcanizates at various filler ratios.

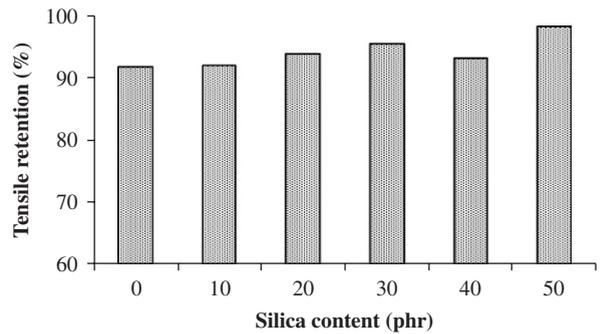


Fig. 8. Tensile retention of silica/CB-filled NR vulcanizates at various filler ratios.

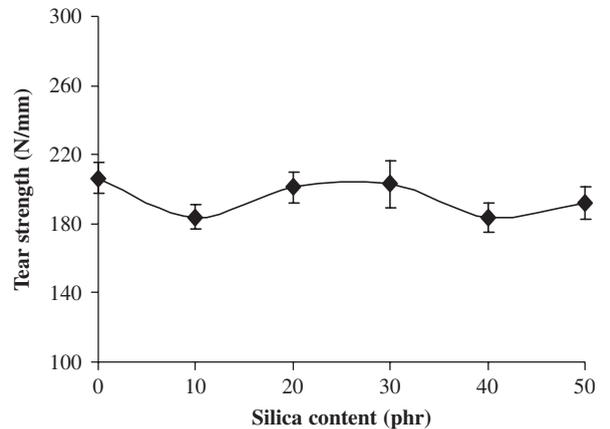


Fig. 9. Tear strength of silica/CB-filled NR vulcanizates with at filler ratios.

silica dispersion or strong silica–silica interaction is thought to be another reason for the dramatic reduction in abrasion resistance at high silica loading.

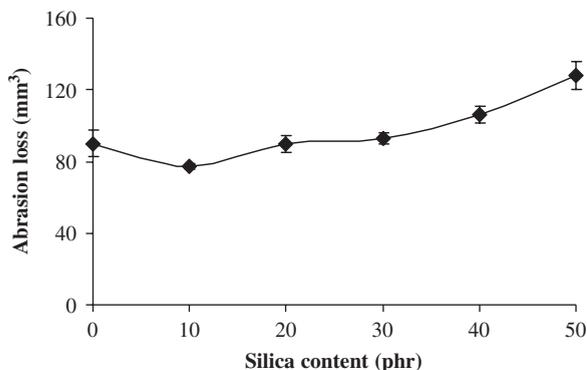


Fig. 10. Abrasion resistance of silica/CB-filled NR vulcanizates at various filler ratios.

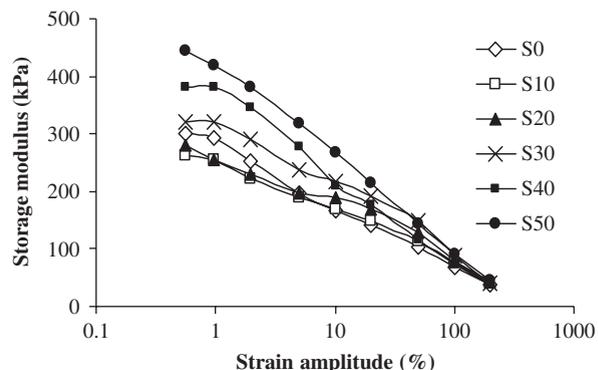


Fig. 11. Relationship between storage modulus ( $G'$ ) and strain amplitude of silica/CB-filled NR vulcanizates at various filler ratios as determined from RPA 2000.

It has been reported that the relationship between the storage modulus and shear strain of silica-filled rubber vulcanizates is governed by various factors, such as strong filler–filler interaction, filler–rubber interaction, rubber network properties and hydrodynamic effects. However, the increase in the storage modulus at small strains with increasing silica content is mainly caused by the increase in strong filler–filler interaction [15,16]. Therefore, the relationship of storage modulus and shear strain was investigated in this experiment in order to study the filler dispersion. It can be seen in Fig. 11 that the vulcanizates having higher ratio of silica to CB exhibit stronger dependence of storage modulus on shear strain, indicating the greater disruption of filler–filler interaction known as the Payne effect [17,18]. In other words, the greater filler–filler interaction is observed for the vulcanizates having higher ratio of silica to CB. The greater dependence of storage modulus on shear strain of the vulcanizate having 50 phr of silica compared to that of the vulcanizate having 0 phr of silica also implies the stronger filler–filler interaction in silica-filled compound compared to CB-filled compound. This result supports the poorer filler dispersion in the sample containing 50 phr of silica, thus giving rise to the lower abrasion resistance.

Fig. 12 shows SEM micrographs of NR vulcanizates filled with silica/CB hybrid filler. It can be seen that the extent of filler dispersion in vulcanizates containing 20 and 30 phr of silica is similar and greater than for other samples. However, it could not be distinguished between silica and CB. Compared to the sample having 50 phr of silica, better filler dispersion is observed in the samples containing 0, 10 and 40 phr of silica. These results

relate well with the dependence of storage modulus and shear strain showing the greatest filler–filler interaction or poor filler dispersion of the vulcanizates having 50 phr of silica.

Fig. 13 demonstrates the increase in crack growth resistance of the vulcanizates with increasing silica content up to 30 phr. The explanation is given as the reduction in modulus resulting in lower stress concentration at the crack tip [19]. On the other hand, a decrease in crack growth resistance is observed even though the modulus is decreased when silica content loading is more than 30 phr. In this case, poor silica dispersion is thought to be responsible for the reduction of crack growth resistance, and it overrides the effect of the modulus.

The influences of silica content in hybrid filler on dynamic compression set and heat buildup of NR vulcanizates are revealed in Figs. 14 and 15, respectively. It is evident that the compression set is low and comparable at low silica loading. Thereafter, it tends to increase when the silica content is more than 30 phr due to the decrease in crosslink density as well as poor filler–rubber interaction. In addition, heat buildup of the samples containing hybrid filler is not much different, while the samples in single filler system give the higher heat buildup. Theoretically, heat buildup is a measure of energy dissipated as heat during cyclic deformation or loss modulus ( $E''$ ) which can be represented as

$$\frac{E''}{E'} = \tan \delta, \quad (4)$$

where  $E'$  is the storage modulus [20]. Storage modulus and  $\tan \delta$  of the vulcanizates are shown

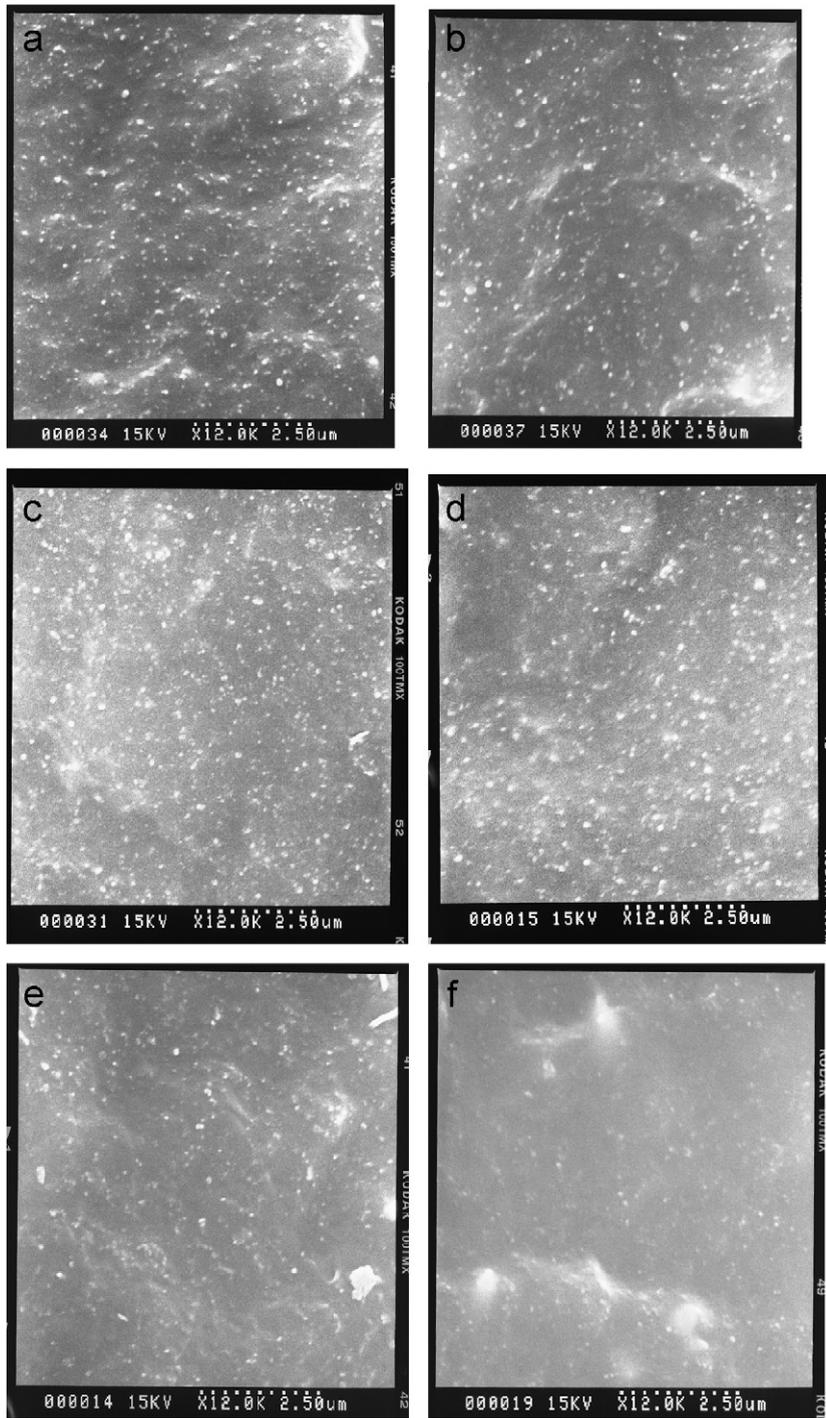


Fig. 12. SEM photomicrographs of fracture surface specimens filled with silica/CB at different ratios: (a) 0/50, (b) 10/40, (c) 20/30, (d) 30/20, (e) 40/10 and (f) 50/0.

in Figs. 16 and 17, respectively. It can be seen that both  $E'$  and  $\tan \delta$  of the vulcanizates having single filler are higher compared to those of vulcanizates containing hybrid filler. Also, it has been reported

that rolling resistance of tires is related to  $\tan \delta$  value at temperatures of 50–80 °C [12]. A low  $\tan \delta$  value is needed for achieving the low rolling resistance and saving energy. In this experiment,

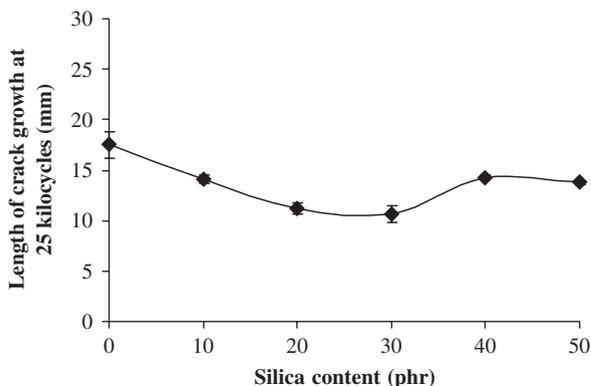


Fig. 13. Crack growth resistance at 25 kilocycles of silica/CB-filled NR vulcanizates at various filler ratios.

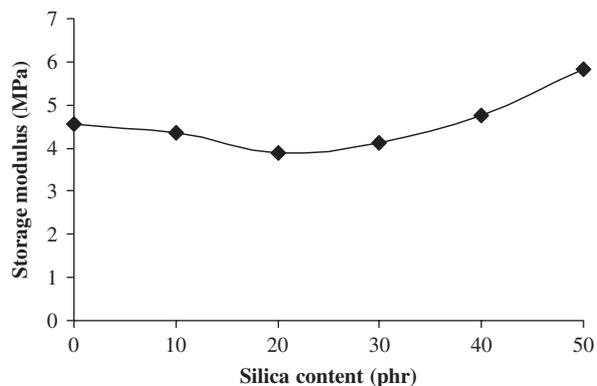


Fig. 16. Storage modulus ( $E'$ ) of silica/CB-filled NR vulcanizates at various filler ratios as determined from DMA Explexor™ 25 M.

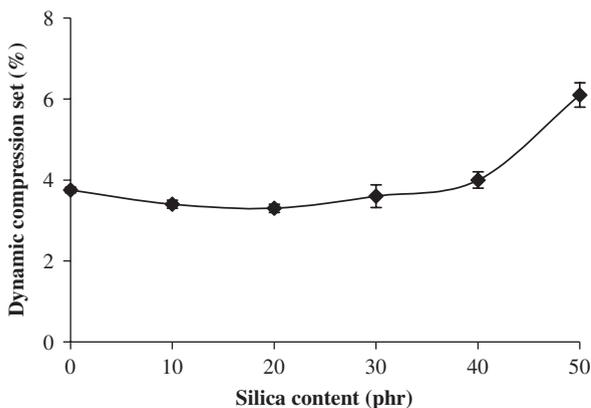


Fig. 14. Dynamic compression set of silica/CB-filled NR vulcanizates at various filler ratios.

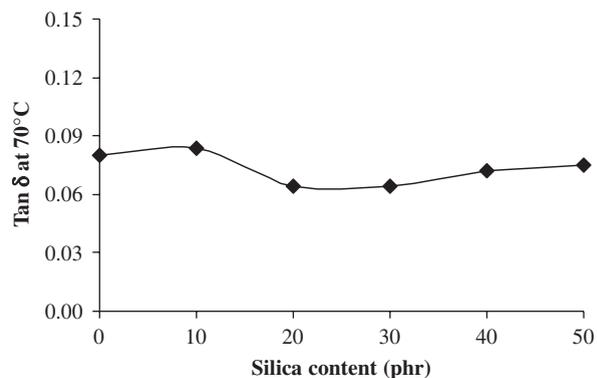


Fig. 17. Tan  $\delta$  at 70 °C of silica/CB-filled NR vulcanizates at various filler ratios.

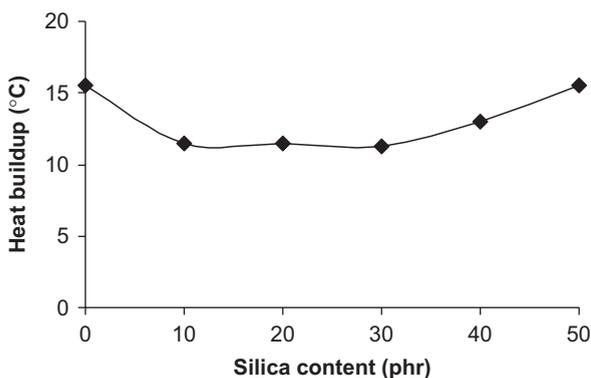


Fig. 15. Heat buildup of silica/CB-filled NR vulcanizates at various filler ratios.

tan  $\delta$  of the vulcanizates having various filler ratios was determined at 70 °C. The result shows that tan  $\delta$  of the vulcanizates tends to reduce when silica is

more than 10 phr and subsequently goes up when silica loading is higher than 30 phr. The result obviously suggests the lowest rolling resistance in the vulcanizates containing silica 20 and 30 phr.

#### 4. Conclusions

It can be concluded that vulcanizates containing 20 and 30 phr of silica in the hybrid filler give better overall mechanical properties. The explanation is given as the better filler dispersion as a result of the lowest development of filler network in these vulcanizates. However, mixing of the compound containing 20 phr of silica is more practical than the compound containing 30 phr of silica. This is because the higher amount of CB (N 330) is incorporated into NR more easily than silica (Hisil 233) at the initial stage of mixing.

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