# The Effects of Silica/Carbon Black Hybrid Filler Contents on Natural Rubber Composite Properties Using Conventional Vulcanization System

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Received May 29, 2020; Revised November 5, 2020; Accepted December 9, 2020

## Abstract

The physical properties and mechanical properties of rubber composite were improved by reinforcing with silica and carbon black (S/CB) hybrid filler. The amounts of S/CB hybrid filler were varied from 30 to 60 phr of NR. Maximum torque and minimum torque of NR compound grew continuously with increasing the amount of hybrid filler. The NR compounds were vulcanized for 90 % of cure time at 150 °C. Physical and mechanical properties, e.g., hardness, volume change, abrasion loss, tensile strength, tensile modulus, elongation at break, tear strength and compression set of NR composite were investigated. The overall properties of the NR composite went up with increasing S/CB hybrid filler until 50 phr but they decreased after increasing S/CB hybrid filler of > 50 phr. This is mainly due to the agglomeration of S/CB hybrid filler. Moreover, hybrid filler content loaded NR composites hardly affects properties of aged NR composites. The results reveal that the optimum amount of S/CB hybrid filler added 50 phr in NR composites is suitable for application.

**Keyword:** Natural rubber; Hybrid filler, Physical properties; Mechanical properties; Aging resistance

## 1. Introduction

Natural rubber (NR) is one of the bio-based polymers which is used to prepare compounding rubber for many applications and products, including automobile tires, outdoor sealing and aerospace engineering. The properties of NR is known to exhibit outstanding such as good oil resistance, high strength and low gas permeability and it can be improved for specific applications (Heinrich et al., 2002; Pal et al., 2010; Schué, 2000). NR plays a major role in rubber industry, especially for the production of truck tyres, because it strengthens the rubber in highly strained regions and, therefore, impedes the formation of cracks (Nair & Joseph, 2014). One of the most important NR design is the fillers which commonly is added into rubbers as a reinforcing agent to improve mechanical properties (tensile strength, tear strength, abrasion resistance, and aging resistance). For example, the carbon blacks (CB), silica (S) and resins reduce material costs and improve mechanical properties. The carbon black and silica are used as the main reinforcing-fillers that increase the usefulness of rubber (Al-Hartomy et al., 2016; Flanigan et al., 2012; Kato et al., 2013; Rattanasom et al., 2009; Rattanasom et al., 2007; Ulfah et al., 2015). Production of some mechanical rubber goods requires rubbers with multifunctional properties, such as strength, barrier properties, resistance to oxidative aging.

The properties of rubber compounds are strongly influenced by the incorporation of carbon black and silica. Although the carbon black-reinforced rubber exhibits higher modulus, strength and abrasion resistance when compared to a silica-reinforced one, silica provides a unique combination of tear strength, aging resistance and adhesion properties. To improve the properties of NR product, silica was used as an important reinforcing agent in rubber composite together

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with carbon black (Li et al., 2008; Sae-Oui et al., 2014; Thaptong et al., 2014). The surfaces of both reinforcing fillers are very different. It is known that silica contains predominantly the hydroxyl group on the surface, which results in highly polar or hydrophilic and strong filler–filler interaction via hydrogen bonds. Intramolecular hydrogen bonds of silica are very strong and it can form a tight aggregate (Wang et al., 2016; Xu et al., 2015). Therefore, the surface of silica was modified by using two coupling agents, polyethylene glycol (PEG) and bis (3-triethoxysilylpropyl) tetrasulfide (Si-69), as previously reported in numerous studies. Each coupling agent has a different function. PEG can be used as a permanent buffer between silica and the ingredients coated on the surface of silica to remove the cure hindering adsorptions. The added PEG improves the properties of NR including cure rate, scorch, viscosity, hardness, trouser tear, compression set, heat buildup and abrasion index (Kralevich & Koenig, 1997). The Si-69 is needed to improve the filler-to-rubber bonds or interaction between the particles of silica and elastomer (Pal et al., 2010; Kralevich & Koenig, 1997; Fröhlich et al., 2005; Kaewsakul et al., 2014; Kaewsakul et al., 2016). It was reported that the presence of Si-69 simultaneously worked as the surface capping agent at the mixing temperature between 50 to 110 °C (Rattanasom et al., 2009; Rattanasom et al., 2007; Choi & Park, 2001; Tabsan et al., 2010).

The ratio between carbon black and silica as the hybrid filler of NR was previously studied in order to determine the optimum proportions (Rattanasom et al., 2009; Rattanasom et al., 2007). The results showed that the composite containing carbon black and silica of 30:20 and 20:30 in hybrid filler had the better overall mechanical properties and, therefore, these ratios were chosen for the subsequent study. The degree of reinforcement depends on the amount of the hybrid filler. In this study, the S/CB ratio of hybrid filler was kept condition of proportions at 3:2, when the total hybrid filler to NR composite was varied from 30 to 60 phr. The effects of the filler content on the physical properties, mechanical properties, morphology property and aging resistance of rubber composite were investigated. The NR composite would be potentially used to produce a rubber corner guard to protect wall corners from accidental damage. It is suitable for parking garages, basement parks and commercial warehouses.

## 2. Materials and Methods

### 2.1 Materials

Natural rubber (STR 5L) has Mooney viscosity ($ML_{1+4}$ at 100 °C) of 81.3. Properties of carbon black N220 are iodine adsorption 121 mg/g, DBP adsorption 114 $cm^3$/100g and pour density 350 g/$dm^3$. Silica US-M were investigated by BET surface area as 175 $m^2$/g, bulk density 0.19 g/$cm^3$. The silicon dioxide ($SiO_2$, Hydrated Base) was 93.0%. The other additives such as zinc oxide (ZnO), stearic acid, poly(ethylene glycol) bis(3-triethoxy silylpropyl) tetrasulfide (Si-69), N-(1,3-di methyl)-N'-phenyl-*p*-phenylendiamine (6-PPD), gum resin, naphthenic oil, 2,2,4-Trimethyl-1,2-Dihydroquinoline polymer (TMQ), Tetramethyl thiuram Disulfide (TMTD), N-tert-butyl-2-benzothiazole sulfenamide (TBBS), and sulfur ($S_8$) were also of commercial grades. STR 5L rubber and all mixing additives were obtained from suppliers in Bangkok, Thailand.

### 2.2 Preparation of S/CB hybrid filler NR composites

All composites were prepared at the same composition of NR and additives, except for the amount of silica (US-M) and carbon black (N220), that were varied based on the formulation shown in Table 1. In this research, reinforcement of NR with silica/CB hybrid filler at various ratios was maintained constantly at 3:2 and the total amount of hybrid filler was varied from 30 to 60 phr. The formulations were named as S/CB30, S/CB40, S/CB50, S/CB55 and S/CB60. Silica surface was modified with a silane coupling agent as 8% wt. of silica. Then, NR was masticated in an internal mixer (Brabender Plasticorder, Yongfong) firstly at 70 °C for 5 min and rotor speed of 60 rpm. After that, the other ingredients, except the curatives: TBBS, TMTD and $S_8$, were added and mixed for 8 min at the same temperature and rotor speed. Finally, the curatives were poured and admixed for 5 min using the two roll-mill to prepare NR compound. NR compound of each formulation was kept at least 16 h at room temperature before testing. The curing time (tc90), maximum torque and minimum torque for preparing the NR composites or NR vulcanizates were measured using the moving die rheometer (MDR) on the cure curve at 150 °C. The schematic diagram of the NR composites experiment procedure was shown in Figure 1.

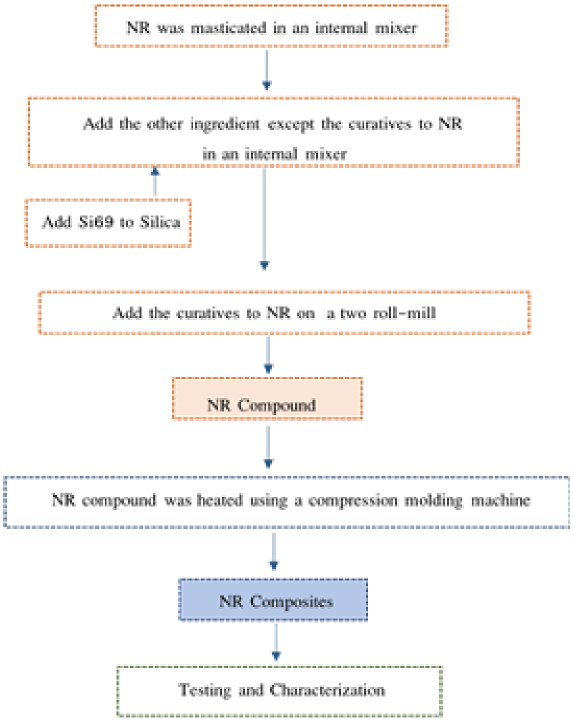

**Figure 1.** The schematic diagram of NR composites experiment procedure.

**Table 1.** Formulation of the rubber composites (in phr of total rubber content)

| Ingredients | Composition (phr) | | | | |
|---|---|---|---|---|---|
| | S/CB30 | S/CB40 | S/CB50 | S/CB55 | S/CB60 |
| STR 5L | 100 | 100 | 100 | 100 | 100 |
| ZnO | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 |
| Carbon Black N220 | 12 | 16 | 20 | 22 | 24 |
| Silica US-M | 18 | 24 | 30 | 33 | 36 |
| Si69 (8 % wt. of silica) | 1.44 | 1.92 | 2.4 | 2.64 | 2.88 |
| PEG4000 (5 % wt. of silica) | 0.9 | 1.2 | 1.5 | 1.65 | 1.8 |
| Naphthenic Oil | 6 | 6 | 6 | 6 | 6 |
| Gum Rosin | 5 | 5 | 5 | 5 | 5 |
| 6 PPD | 2 | 2 | 2 | 2 | 2 |
| TMQ | 1 | 1 | 1 | 1 | 1 |
| TBBS | 1 | 1 | 1 | 1 | 1 |
| TMTD (Sulfur donor) | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Sulfur | 2 | 2 | 2 | 2 | 2 |

### 2.3 Testing and Characterization

#### 2.3.1 Maximum torque and minimum torque

Maximum torque and minimum torque of NR composites were determined using Moving Die Rheometer (Monsanto, MDR2000) at 150 °C. The 10 g of samples were used with a 0.5° arc. The cure time (tc90) of the cure samples was used to measure the total torque change on the cure curve.

#### 2.3.2 Hardness and Volume change tests

Hardness values were conducted using a Shore A type from universal hardness tester (Bareiss Digi test II) under conditions according to ISO 7619 Part 1. Additionally, the volume change of products in water was carried out following ISO 1817.

#### 2.3.3 Tensile tests

The tensile modulus values at 100% (M100) and 300% (M300) of elongation at break, tensile strength and elongation at break were tested on dumbbell-shaped specimens using a universal mechanical testing machine (Shimadzu Intron Universal Testing Machine) following ISO 37:2011 (Type 1) at a crosshead speed of 500 mm/min.

#### 2.3.4 Compression set and Tear properties tests

Compression set values were measured using the compression set test fixtures according to method B specified in ASTM D395-03 (2008) at 70 °C for 24 h. Tear strength of specimens was carried out on die B shaped specimens using a universal mechanical testing machine (Shimadzu Intron Universal Testing Machine) according to ISO 34 (Method B)

#### 2.3.5 Abrasion loss tests

Abrasion loss of cylinder specimens was carried out using abrasion tester following DIN 53516. Abrasion loss is measured by moving a test piece of rubber composite across the surface of an abrasive sheet mounted on a revolving drum. It is expressed as a volume loss in cubic millimeters.

#### 2.3.6 The aging properties

The aging properties of samples were measured by placing dumbbell-shaped five specimens in the air circulating oven at 70 °C during 96 h. After that, the samples were cooled at room temperature for at least one day before the measurement of hardness and tensile properties of samples. The tensile and hardness properties of aged samples were investigated in the same method as the unaged samples. Tensile strength retention was calculated from the equation[9]:

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

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

#### 2.3.7 Scanning electron microscopy

The morphology of fracture surfaces of NR composites was investigated using scanning electron microscopy (SEM JEOL 6340F) at an accelerating voltage of 10 kV. The specimens were sputter-coated with gold to prevent charging on the surface before the examination.

## 3. Results & Discussion

### 3.1 Maximum torque and minimum torque

Maximum torque and minimum torque at various S/CB hybrid filler contents are displayed in Figure 2. The minimum torque of NR compound grows up continuously with increasing the amount of hybrid filler up to 60 phr due to the increase of NR compound viscosity. Furthermore, the maximum torque dramatically increased when S/CB hybrid filler content went up from 30 phr to 60 phr. It is already reported that maximum torque depends on the three-dimensional crosslinking density and chain entanglements. This result can be explained that S/CB hybrid filler affects the crosslinking density by reacting with the chemical ingredients of formulation thus leading to a higher torque[25].

### 3.2 Physical properties

#### 3.2.1 Hardness and volume change of NR composites

Figure 3. presents the effect of S/CB hybrid filler contents on the hardness of NR composites. The hardness of NR composite increased upon raising the content of S/CB hybrid filler because the increment of hard phase from silica and carbon black were more loaded in NR composites thus leading to a decrease of NR matrix phase. The volume change of NR composites

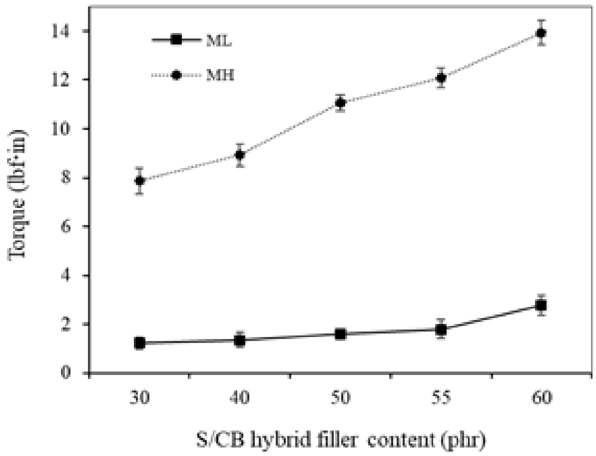

**Figure 2.** Maximum torque and minimum torque of NR compound with various S/CB hybrid filler contents

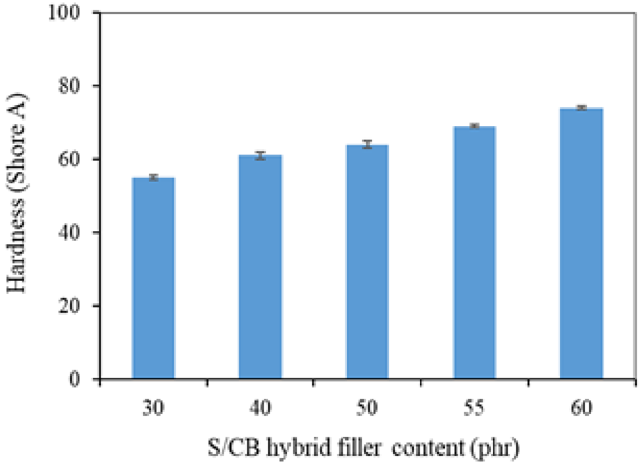

**Figure 3.** Hardness of NR composites with various S/CB hybrid filler contents

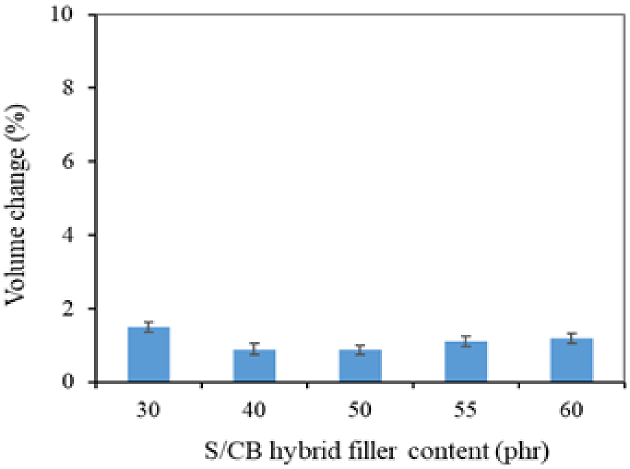

**Figure 4.** Volume change of NR composites with various S/CB hybrid filler contents

with different loading of S/CB hybrid filler are shown in Figure 4. The volume change of NR composite is slightly changed as the contents of S/CB hybrid filler increased from 30 to 60 phr. This means that adding S/CB hybrid filler in the range of 30 to 60 phr less affected the volume change of NR composite. This is due to cross-link bond density in NR composites after curing NR compound.

### 3.3 Mechanical properties

#### 3.3.1 The modulus of NR composites

Figure 5. is presented the modulus of NR composites at various S/CB hybrid filler content. The modulus is the force at a specific elongation value, ie 100% or 300% elongation. The increase of S/CB hybrid filler content was affected continuously increase the 100% and 300% modulus. This is due to the increment of the hard phase from the added silica and carbon black. Moreover, the increase in modulus with S/CB hybrid filler content is explained by the stiffening effect caused by the interaction between the filler and rubber particles. Additionally, the hardness properties of NR composites also follow the same trend as the modulus.

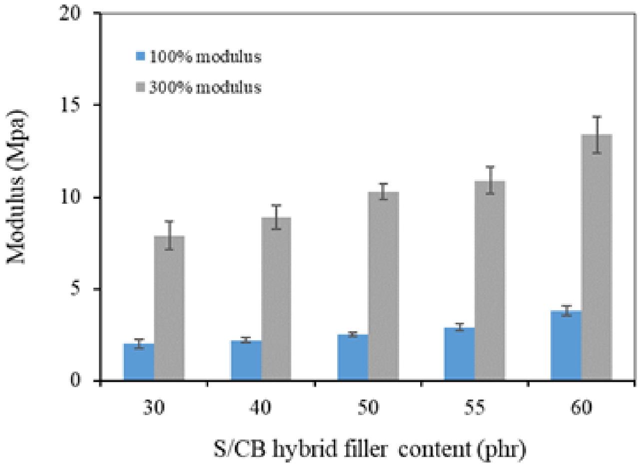

**Figure 5.** 100 % and 300 % Modulus of NR composites with various S/CB hybrid filler contents

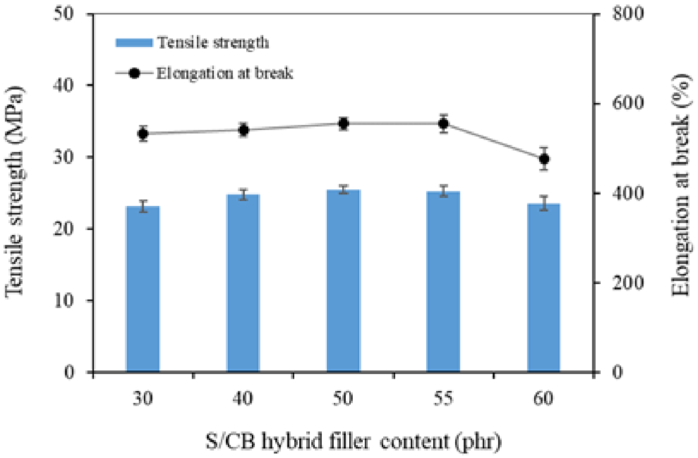

**Figure 6.** Tensile strength and Elongation at break of NR composites with various S/CB hybrid filler contents

#### 3.3.2 The tensile strength and elongation at break

The comparison of results between the tensile strength and elongation at break with various S/CB hybrid filler contents is shown in Figure 6. The tensile increase with increasing S/CB hybrid filler up to 50 phr and then they slightly decrease when silica content is further increased. On the other hand, it appears that elongation at break does not significantly change with increasing S/CB hybrid filler from 30 phr to 55 phr. Both results are started to decrease as the content of S/CB hybrid filler at 55 phr. This is due to the high S/CB hybrid filler at > 50 phr tended to coalesce leading to poor dispersion. This could restrict molecular chain mobility when NR composites were stretched which lowered the tensile strength and elongation at break.

### 3.3.3 Tear strength and the abrasion loss

The tear strength and the abrasion loss of NR composites at various amounts of S/CB hybrid filler are shown in Figure 7. The tear strength first increased when adding S/CB hybrid filler to 50 phr. After that, tear strength decreased with further loading S/CB hybrid filler up to 60 phr. It is significantly seen that the tear strength drop with increasing S/CB hybrid filler over 50 phr because of formation of hybrid filler agglomeration in NR composite. This result that the interaction between hybrid filler and NR is weak, so the increment in the filler loading has further reduced this interaction. Moreover, the hybrid filler agglomerated also prevent molecular chains movement of NR. Furthermore, the decline of abrasion loss could be explained by the increase in hard phase filler thus leading to high abrasion resistance of NR composite. This result supports the slightly decreased abrasion loss with increasing S/CB hybrid filler content from 30-60 phr. Moreover, it corresponded with hardness properties.

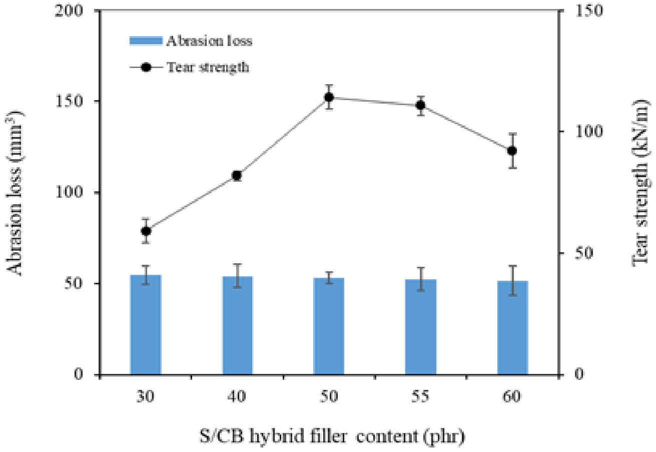

**Figure 7.** Tear strength and Abrasion loss of NR composites with various S/CB hybrid filler contents

### 3.3.4 Compression set

Figure 8. is shown the compression set of the NR composites. The compression set is a test of the ability of the rubber to retain their elastic properties after extended compression at a constant strain under a specified set of conditions (Smith, 1993; Othman, 2001). The compression set value of NR composite was varied upon the amount of hybrid filler. Low amounts of hybrid filler from 30 to 40 phr give a low compression set of NR composite but compression set of NR composite slightly increased with increasing hybrid filler content over 40 phr. The result suggests that the increase in compression set values confirms that the elasticity of cured NR composite is impaired in the presence of hybrid filler at higher contents. It could be resulted from the agglomeration of hybrid filler, leading to the loss of

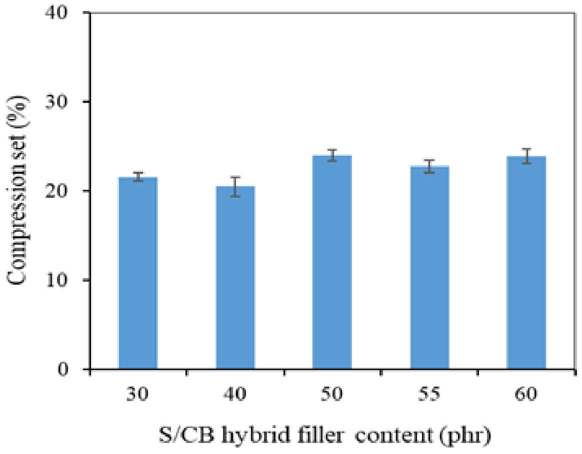

**Figure 8.** Compression set of NR composites with various S/CB hybrid filler contents

the NR composite elasticity.

### 3.4 Morphology property

The fractured surfaces of NR composites loaded with S/CB hybrid filler are shown in Figure 9. It indicates that hybrid filler was well dispersed in NR composite and no critical agglomeration of hybrid filler was visible at low loading level. Nevertheless, the increase of hybrid filler content more than 50 phr, the particles tended to agglomerate. It can be seen that good dispersion of S/CB hybrid filler is considered as a factor to achieve good mechanical properties (Ghari & Azam, 2016) which according to the results of the mechanical properties of NR composites.

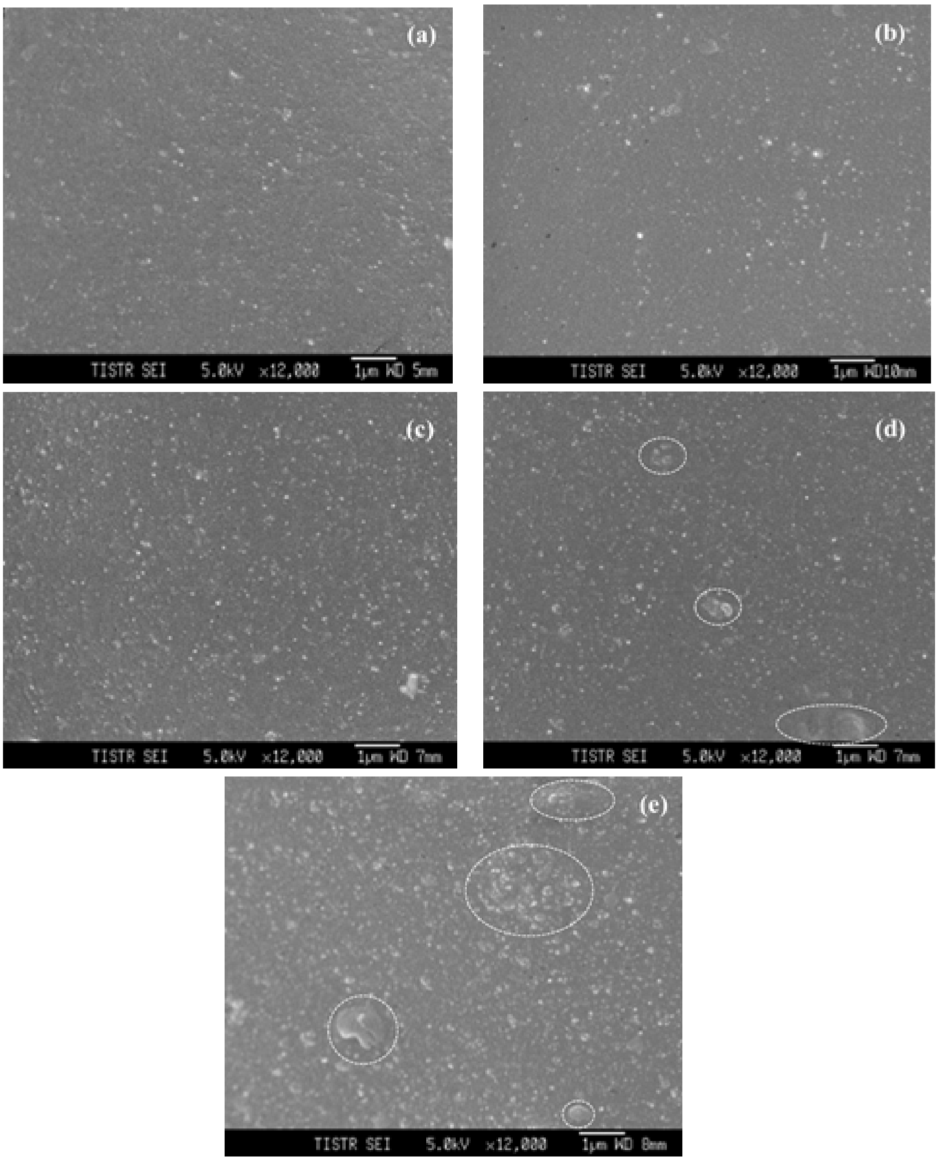

**Figure 9.** The fractured surfaces of NR composites with various S/CB hybrid filler contents; (a) 30 phr, (b) 40 phr, (c) 50 phr, (d) 55 phr and (e) 60 phr

### 3.5 Aging resistance

Aging is the degeneration of desirable properties during storage or usage that it is a phenomenon common of NR because it is susceptible to thermal-oxidative ageing  due to unsaturated carbon-carbon double bonds in molecular structure. Moreover, various changes can occur in rubber component as a result of the conditions under which it is used or stored. This research studied changing properties of NR composites under accelerated aging.

The hardness change with various S/CB hybrid filler contents is shown in Figures 10. The hardness of all NR composites formulation slightly increased as the heat aging temperature grew at 70 °C for 168 h. Besides, the loading of hybrid filler increases the hardness retention of NR composites hardly changed. The tensile test results for the heat-aged specimen at 70 °C for 168 h are presented in Figures 11 and 12. It can be seen that the tensile strength and elongation at break of aged NR composites at 70 °C for 168 h less went up when they were compared with tensile strength and elongation at break for unaged NR composites (virgin). Moreover, tensile strength retention, elongation at break retention of NR composites slightly increase when the hybrid filler content increase because the heating effect could destroy the remaining molecular chain of unsaturated NR and initiates the movement of the filler within the matrix. Hence, degradation occurred inside of the NR matrix thus leading to the breaking of filler, filler-rubber and rubber-rubber bonding.  Nevertheless, they are also evident that hybrid filler content added NR composites hardly affect hardness change, tensile strength retention and elongation at break retention of aged NR composites.

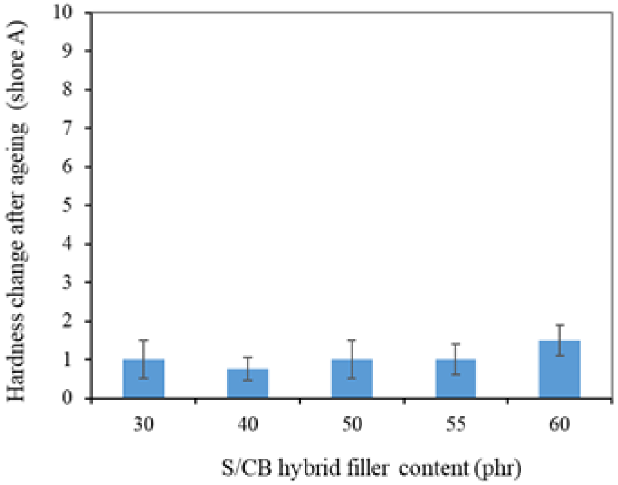

**Figure 10.** Hardness change after aging of NR composites with various S/CB hybrid filler contents at 70 °C for 168 h.

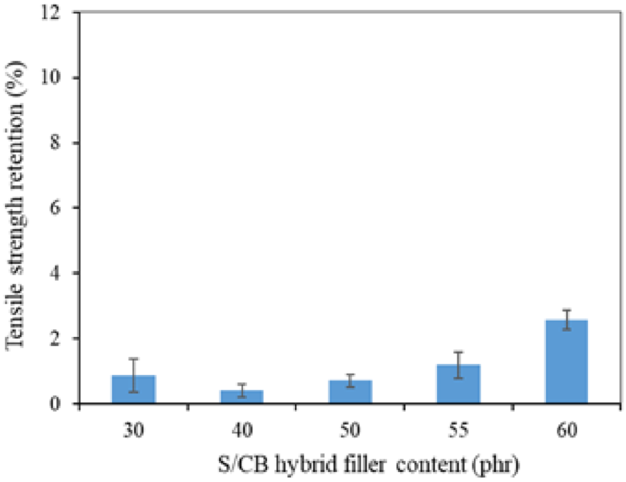

**Figure 11.** Tensile strength retention of NR composites with various S/CB hybrid filler contents at 70 °C for 168 h.

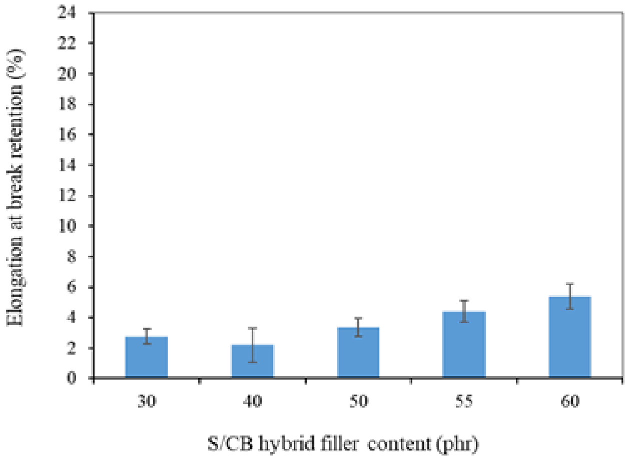

**Figure 12.** Elongation at break retention of NR composites with various S/CB hybrid filler contents at 70 °C for 168 h.

## 4. Conclusion

It can be concluded that maximum torque and minimum torque of NR compound increases continuously with increasing the amount of hybrid filler. The mechanical properties, physical properties of NR composites can be improved by using silica/carbon black hybrid filler. The properties of NR composites were dependent on the amount of hybrid filler. The results reveal that high S/CB hybrid filler content over 50 phr resulted in poor dispersion and the more large agglomeration formed. This non-uniform mixture could affect the mechanical and physical properties by increasing hardness, modulus and lowering of elasticity. Nevertheless, the amount of S/CB hybrid filler hardly affects the physical and mechanical properties of aged NR composites. The results suggest that the optimum amount of hybrid filler is suitable at 50 phr on the application of NR composites.

## Acknowledgements

The author would like to thank National Research Council of Thailand (NRCT) and Thailand Institute of Scientific and Technological Research (TISTR) for financial support.

## References

Al-Hartomy, O. A., Al-Ghamdi, A. A., Farha Al Said, S. A., Dishovsky, N., Mihaylov, M., Lvanov, M. (2016). Effect of the Carbon-Silica Reinforcing Filler Obtained from the Pyrolysis-Cum-Water Vapour of Waste Green Tyres upon the Properties of Natural Rubber Based Composites. J. Compos. Mater, 50, 377-386.

Choi, S-S., Park, S. (2001). Silane grafted natural rubber and its compatibilization effect on silica-reinforced rubber tire compounds. Polym Kor, 9, 92-99.

Flanigan, C. M., Beyer, L., Klekamp, D., Rohweder, D. (2012). Comparative study of silica, carbon black and novel fillers in tread compounds. Rubber World, 245, 18-31.

Fröhlich, J., Niedermeier, W., Luginsland, H. D., (2005). The effect of filler–filler and filler–elastomer interaction on rubber reinforcement. Compos Part A Appl Sci Manuf, 36, 449-460.

Ghari, H.S., Azam, J.A. (2016). Nanocomposites based on natural rubber, organoclay and nano-calcium carbonate: Study on the structure, cure behavior, static and dynamic-mechanical properties. Appl. Clay Sci, 119, 348-357.

Heinrich, G., Kluppel M., Vilgis, T. (2002). Reinforcement of elastomers. Curr Opin Solid State Mater Sci, 6, 195–203.

Kaewsakul, W., Sahakaro, K., Dierkes, W. K., Noordermeer, J. W. M. (2014). Cooperative effects of epoxide functional groups on natural rubber and silane coupling agents on reinforcing efficiency of silica. Rubber Chem. Technol, 87, 291-310.

________ (2016). Factors influencing the flocculation process in silica-reinforced natural rubber compounds. J Elastom Plast, 48, 426-441.

Kato, A., Ikeda, Y., Tsushi, R., Kokubo, Y. (2013). Viscoelastic properties and filler dispersion in carbon black-filled and silica-filled cross-linked natural rubbers. J. Appl. Polym. Sci, 130, 2594-2602.

Kralevich, M. L., Koenig, J. L. (1997). The effects of polyethylene glycol and the coupling agent bis-($\gamma$-triethoxysilyl-propyl)-tetrasulfide (Si-69) on the interactions of silica-filled natural rubber. Compos Interface, 5, 125-135.

Li, Z. H., Zhang, J., Chen, S. J. (2008). Effects of carbon blacks with various structures on vulcanization and reinforcement of filled ethylene-propylene-diene rubber. Express Polym Lett, 2, 695-704.

Nair, A. B., Joseph, R. (2014). Eco-friendly bio-composites using natural rubber (NR) matrices and natural fiber reinforcements. Woodhead Publishing Limited; Cochin University of Science and Technology, 249-283.

Othman, A. B. (2001). Property profile of a laminated rubber bearing. Polym Test, 20, 159-166.

Pal, K., Rajasekar, R., Kang, D. J., Zang, Z. X., Pal, S. K., Das, C. K., Kim, J. K. (2010). Effect of fillers on natural rubber/high styrene rubber blends with nano silica: Morphology and wear. Mater. Des, 31, 677-686.

Ramesan, M.T. (2004). The effects of filler content on cure and mechanical properties of dichlorocarbene modified styrene butadiene rubber/carbon black composites. J. Polym. Res, 11, 333-340.

Rattanasom, N., Prasertsri, S., Ruangritnumchai. (2009). Comparison of the mechanical properties at similar hardness level of natural rubber filled with various reinforcing-fillers. T. Polym Test, 28, 8-12.

Rattanasom, N., Saowapark, T., Deeprasertkul, C. (2007). Reinforcement of natural rubber with silica/carbon black hybrid filler. Polym Test, 26, 369-377.

Sae-Oui, P., Thepsuwan, U., Thaptong, P. (2014). Comparison of reinforcing efficiency of carbon black, conductive carbon black, and carbon nanotube in natural rubber. Adv Polym Tech, 33, 21422(1 of 7).

Schué, F. (2000). Blends of natural rubber. Novel techniques for blending with speciality polymers. Polym Int, 49, 472-472.

Smith, L. P. (1993). The language of rubber. Londpl: B9utterworth Heinemann.

Tabsan, N., Wirasate, S., Suchiva, K. (2010). Abrasion behavior of layered silicate reinforced natural rubber. Wear, 269, 394-404.

Thaptong, P., Sirisinha, C., Thepsuwan, U., Sae-Oui. (2014). Properties of natural rubber reinforced by carbon black-based hybrid fillers. P. Polym Plast Technol Eng, 53, 818-823.

Ulfah, I. M., Fidyaningsih, R., Rahayu, S.; Fitriani, D. A., Saputra, D. A., Winarto, D. A., Wisojodharmo, L. A. (2015). Influence of carbon black and silica filler on the rheological and mechanical properties of natural rubber compound. Procedia Chem, 16, 258-264.

Wang, Y., Liao, L., Zhong, J., He, D.; Xu, K., Yang, C., Luo, Y., Peng, Z. (2016). The effect of epoxidized natural rubber on mechanical properties of siliceous earth/natural rubber composites. J Appl Polym Sci, 133, 43571(1 of 9).

Xu, T., Jia, Z., Luo, Y., Jia, D., Peng, Z. (2015). Interfacial interaction between the epoxidized natural rubber and silica in natural rubber/silica composites. Appl Surf Sci, 328, 306-313.