Improvement of Natural Rubber Composite Properties Using Silica/Carbon Black Hybrid Filler

Borwon Narupai¹, Malinee Leekrajang¹, Siwaruk Chotiwan¹,², Nattaporn Chutchairattanaphum¹, Jate Panichpakdee¹, Sarut Nudchapong¹, Siriporn Larpkiattaworn¹
¹Expert Centre of Innovative Materials, Thailand Institute of Scientific and Technological Research, Pathum Thani 12120, Thailand
²Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
*E-mail: borwon@tistr.or.th

Abstract:
The physical and mechanical properties of natural rubber (NR) composite using silica and carbon black (SC/CB) hybrid filler were studied. The amounts of SC/CB hybrid filler with ratio of 3:2 added to NR were varied from 30 to 60 phr of NR and the optimum SC/CB hybrid filler content was examined. After being vulcanized for 90 % of cure time at 150 °C, the 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. It was found that the overall properties of the composite tended to decrease with the increasing SC/CB hybrid filler of > 50 phr due to the agglomeration of SC/CB hybrid filler.

1. Introduction
Natural rubber (NR) is one of the green polymer materials which is used to prepare compounding rubber for many applications and products. The mechanical properties of NR, e.g., modulus, hardness and abrasion resistance, can be improved for specific applications.¹⁻³ 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.⁴ For this purpose, fillers, commonly carbon blacks (CB), silica (SC) and resins, are necessarily added into rubbers as reinforcing agent to improve mechanical properties (tensile strength, tear strength, and abrasion resistance) and reduce the material costs. In general, carbon black and silica are used as the main reinforcing-fillers that increase the usefulness of rubber.⁵⁻¹⁰

The surface of rubber compound is strongly influenced by the incorporation of carbon black and silica. It is known that silica is highly polar or hydrophilic which results in strong filler–filler interaction via hydrogen bonds.¹¹⁻¹² 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.¹³ The Si-69 is needed to improve the filler-to-rubber bonds or interaction between the particles of silica and elastomer.²,¹⁻³,¹⁶ 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.⁸,⁹,¹⁷,¹⁸

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 with carbon black.\textsuperscript{19,21}

The ratio between carbon black and silica as the hybrid filler of NR was previously studied in order to determine the optimum proportions.\textsuperscript{8,9} The results showed that the composite containing carbon black and silica of 30:20 and 20:30 in hybrid filler had better overall mechanical properties and, therefore, these ratios were chosen for the subsequent study.

In this work, the total hybrid filler to composite was varied from 30 to 60 phr. The silica/carbon black ratio of hybrid filler in each rubber composite was kept constant at 3:2. The effects of total hybrid filler on various mechanical properties of composite rubber were studied. The effects of the filler content on the tensile strength, abrasion resistance, hardness of composite rubber were investigated. The rubber composite would be potentially used to produce rubber corner guard to protect wall corners from accidental damage. It was suitable for parking garages, basement parks and commercial warehouses.

2. Materials and Methods

2.1 Materials

Rubber and all mixing ingredients were obtained from suppliers in Bangkok, Thailand. Natural rubber (STR 5L) has Mooney viscosity (ML\textsubscript{1+4} at 100 °C) of 81.3. Properties of carbon black (N220) are iodine adsorption 121 mg/g, DBP adsorption 114 cm\textsuperscript{3}/100g and pour density 350 g/dm\textsuperscript{3}. Silica (US-M) were investigated by BET surface area as 175 m\textsuperscript{2}/g, bulk density 0.19 g/cm\textsuperscript{3}. The SiO\textsubscript{2} (Hydrated Base) was 93.0%. Stearic acid, zinc oxide (ZnO), poly(ethylene glycol) bis(3-triethoxysilylpropyl) tetrasulfide (Si-69), N-(1,3-di methyl)-N’-phenyl-p-phenylenediamine (6-PPD), gum resin, naphthenic oil, 2,2,4-Trimethyl-1,2-Di hydroquinoline polymer (TMQ), N-tert-butyl-2-benzothiazolesulfenamide (TBBS), Tetramethyl thiuram Disulfide (TMTD) and sulfur (S8) were commercial grade.

2.2 Preparation of SC/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), which were varied based on the formulation given in Table 1. The silica/carbon black ratio of hybrid filler in each rubber composite was kept constant at 3:2 and the total amount of hybrid filler was varied from 30 to 60 phr. The formulations were named SC/CB30, SC/CB40, SC/CB50, SC/CB55 and SC/CB60 as presented in Table 1. The amount of silane coupling agent was 8% wt. of silica. All mixing ingredients, except the curatives, with NR were prepared in internal mixer (Barbender Plasticorder) at 70 °C and rotor speed of 60 rpm. After the NR STR5L was masticated for 5 min, the ingredients was added and mixed for 8 min. After that, the NR compound was mixed with the curatives on a two roll-mill. After mixing, various NR compounds were kept overnight at room temperature prior to testing. The curing time (tc90) for preparing the NR composites or NR vulcanizates was the time at which the moving die rheometer (MDR) increased 90 % of the total torque change on the cure curve at 150 °C. The NR compounds were then compressed and cured at 150 °C and tc90 in order to produce NR composite samples.
Table 1. Formulation of the rubber compound

<table>
<thead>
<tr>
<th>Rubber and Chemical</th>
<th>SC/CB30</th>
<th>SC/CB40</th>
<th>SC/CB50</th>
<th>SC/CB55</th>
<th>SC/CB60</th>
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<tbody>
<tr>
<td>STR 5L</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>ZnO</td>
<td>5</td>
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<td>Stearic acid</td>
<td>2</td>
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<td>2</td>
<td>2</td>
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<tr>
<td>Carbon Black N220</td>
<td>12</td>
<td>16</td>
<td>20</td>
<td>22</td>
<td>24</td>
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<tr>
<td>Silica US-M</td>
<td>18</td>
<td>24</td>
<td>30</td>
<td>33</td>
<td>36</td>
</tr>
<tr>
<td>Si69 (8 % wt. of silica)</td>
<td>1.44</td>
<td>1.92</td>
<td>2.4</td>
<td>2.64</td>
<td>2.88</td>
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<tr>
<td>PEG4000 (5 % wt. of silica)</td>
<td>0.9</td>
<td>1.2</td>
<td>1.5</td>
<td>1.65</td>
<td>1.8</td>
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<tr>
<td>Naphthenic Oil</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
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<tr>
<td>Gum Rosin</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
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</tr>
<tr>
<td>6 PPD</td>
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</tr>
<tr>
<td>TBBS</td>
<td>1</td>
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<td>1</td>
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<tr>
<td>TMTD (Sulfur donor)</td>
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<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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<td>Sulfur</td>
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<td>2</td>
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</tbody>
</table>

2.3 Testing of NR composites

The tensile and tear strength of NR composites were tested following ISO 37 (die type 1) and ISO 34 (die B), respectively. The aging properties of elongation at break and tensile strength were determined following ISO 37. Compression set was tested according to ASTM D395-03. Volume change was investigated following ISO 1817. Hardness and abrasion tests were carried out according to ISO 7619 Part 1 (Wallace Shore A durometer) and DIN 53516, respectively.

The morphology 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 prior to the examination.

3. Results & Discussion

Figure 1 shows morphology of fractured surfaces NR composites loaded with SC/CB hybrid filler. It can be seen that hybrid filler was well dispersed in NR composite at low loading level. However, at high loads of hybrid filler of > 50 phr, the particles tended to agglomerate. This non-uniform mixture could affect the properties of NR composites, which will be reported in the next section.

The effects of SC/CB hybrid filler contents on the hardness and the volume change of NR composites are presented in Figure 2. The volume change in water can be determined according to ISO 1817. The hardness of NR composite increased upon raising the content of SC/CB hybrid filler due to the hard phase of the hybrid filler. Volume is slightly changed as the contents of SC/CB hybrid filler increased from 30 to 60 phr. This can be explained that adding SC/CB hybrid filler in the range of 30 to 60 phr hardly affected the volume change of NR composite.

The modulus of NR composites at various SC/CB hybrid filler contents is presented Figure 3. The 100 % and 300 % modulus of NR composites continued to increase with increasing SC/CB hybrid filler content. This is due to the increment of hard phase from the added silica and carbon black. Tensile strength and elongation at break increased as the contents of SC/CB hybrid filler increased from 30 to 50 phr, and stared to decrease as the content of SC/CB hybrid filler reached 55 phr, (Figure 4). This may be explained that SC/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 because of the agglomeration of hybrid filler in NR composite. The abrasion loss slightly decreased with increasing SC/CB hybrid filler content from 30-60 phr. The decline of abrasion loss could be resulted from the increase in hard phase filler and make NR composite has high abrasion resistance.

**Figure 1.** SEM micrographs of NR composites with various SC/CB hybrid filler contents; (a) 30 phr, (b) 40 phr, (c) 50 phr, (d) 55 phr and (e) 60 phr

**Figure 2.** Hardness and Volume change of NR composites with various SC/CB hybrid filler contents

Figure 5 shows the tear strength and the abrasion loss of NR composites at various amounts of SC/CB hybrid filler. It was found that the tear strength was dropped at the hybrid filler content over 50 phr

**Figure 3.** 100 % and 300 % Modulus of NR composites with various SC/CB hybrid filler contents

**Figure 4.** Tensile strength and Elongation at break of NR composites with various SC/CB hybrid filler contents

The compression set of the NR composites is shown in Figure 6. 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. The compression set value of NR composite is...
varied upon the amount of hybrid filler. Low amounts of hybrid filler from 30 to 40 phr give low compression set of NR composite. The compression set of NR composite increased by increasing hybrid filler contents due to a decrease in the molecular chain movement of NR composite. It could be resulted from the agglomeration of hybrid filler at higher contents, leading to the loss of the NR composite elasticity. Therefore, the optimum amount of hybrid filler was selected depending on the application of NR composite.

4. Conclusion
The mechanical and 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 amount of SC/CB hybrid filler over 50 phr resulted in poor dispersion and formation of more agglomerate. This phenomena affected the mechanical properties by increasing hardness and modulus and lowering of elasticity. It is important to select the optimum amount of SC/CB hybrid filler to fit NR composite application.

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References