Carbon black alternative

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Carbon black alternative

Optimizing the reaction between the sulfur in mercaptosilane on the surface of kaolin and natural rubber chains improves mechanical properties of the rubber

by Saad H Sheikh and Ali Ansarifar, Loughborough University, UK

Carbon black (CB) is one of the most widely used additives in industrial rubber compounds. Most CBs have a large surface area, ranging from 30-140 m²/g, which makes them highly reinforcing, and they are used extensively in tires. Mechanical properties such as hardness, tensile strength, tear strength, fatigue life and Young's modulus improve greatly when CB is added to rubber. However, CB is toxic and health risk is associated with its use in rubber compounds. There is a need to replace CB with other less harmful solid fillers. Several studies have looked into potential replacement of CB with kaolin (China clay) in rubber compounds. Kaolin has a plate-like structure (Figure 1) whereas CB is spherical.

A small amount of kaolin - 10 parts per hundred rubber (phr) by weight - was modified with sodium salt of rubber seed oil (SSRO) and mixed with natural rubber (NR). The SSRO-modified kaolin was more strongly bound in a constraint environment within the lamellae of kaolin. The rubber filled with SSRO-modified kaolin cured faster than that of a similar mix containing unmodified kaolin. In addition, the NR vulcanizates containing SSRO-modified kaolin showed considerable increase in tensile modulus, tensile strength, and elongation at break, indicating its potential as an organo-modified nanofiller.

NR nanocomposites reinforced with 20-50 phr of saline-modified kaolin exhibited outstanding mechanical properties and much higher thermal stability compared with the pure NR. The hardness and tensile properties improved with increasing filler loading and an optimum tensile strength was achieved at the highest loading of the modified kaolin. The cure systems in these compounds consisted of one accelerator, two activators and elemental sulfur. Clearly, after surface treatment, kaolin performed better in rubber.

Kaolin surface possesses OH groups (Al, Si, O, (OH)), which make it polar and moisture absorbing. To improve dispersion of the filler particles in rubber, the filler surface is treated with silane. One commonly used silane is 3-mercaptopyrroltrimethoxysilane (MPTS), which contains less than 2 wt% of sulfur (Figure 2). When sulfur reacts with rubber chains in the presence of an accelerator and activator, it produces stable covalent sulfur bonds. This in turn enhances the rubber/filler interaction and is immensely beneficial to the rubber reinforcement.

Using kaolin pretreated with MPTS, a new method has been developed that optimizes the reaction between the sulfur in MPTS on the kaolin surface and natural rubber chains. This reduces excessive use of chemical curatives and improves mechanical properties of the rubber vulcanizate. The Mooney viscosity, cure properties, hardness, tensile properties and Young's modulus, tear strength, and compression set of NR filled with MPTS pretreated kaolin were measured. The preliminary results indicate that when the reaction between the rubber and kaolin was optimized, the addition of elemental sulfur was the key factor in controlling the rubber properties. This made the MPTS pretreated kaolin an ideal replacement for CB in tires.

The raw rubber used was standard Malaysian natural rubber grade L (98wt% 1, 4-cis content, SMRL). The reinforcing filler was Mercap 100 (Imerys Ceramics, USA). Mercap 100 is kaolin, the surface of which had been pretreated with MPTS and has a 25 m²/g surface area measured by nitrogen adsorption (Imerys Ceramics). The silanization improved dispersion of the kaolin particles in the rubber. Mercap 100 contains approximately 90ppm of sulfur, which primarily comes from trace secondary minerals, mainly pyrite (FeS₂), which has a melting point of 1,100°C. In addition to
the raw rubber and kaolin, the other ingredients were N-tert-
butytyl-2-benzothiazole sulfenamide (a fast-curing delayed-action
accelerator) (Santocure TBBS, Sovereign Chemicals, USA), zinc
oxide (ZnO, an activator, Sigma-
Aldrich Ltd, UK), and elemental sulfur (curing agent, Solvay Barium
Strontium, Hanover, Germany).

The compounds were prepared in a Haake Rheocord 90 (Berlin,
Germany), a small size laboratory mixer with counter rotating rotors.
In these experiments, the Banbury rotors and the mixing chamber were
initially set at ambient temperature (23°C) and the rotor speed was set
at 45rpm. The volume of the mixing chamber was 78cm³, and it was 58% full
during mixing. Polylab monitor
4.17 software was used to control the mixing condition and store data.

Addition of TBBS to the kaolin-filled rubber
To activate the sulfur in MPTS, TBBS was added. The loading of
TBBS in the kaolin-filled rubber was increased from 6phr to 30phr

to measure the amount needed to react the sulfur in MPTS with the rubber chains to produce cross-
links and optimize the chemical bonding between the two. The idea was to add a minimum amount of
TBBS to the rubber and produce the largest effect on the Δtorque. Δtorque (the difference between the
maximum and minimum torque values on the cure trace of the rubber – Figure 3a) is an indication of
cross-link density changes in the rubber.15-17 The formation of cross-
links strengthened the interaction between the rubber and filler, which was greatly beneficial to the rubber
reinforcement.10,16 In total, seven rubber compounds were made.

Addition of ZnO and elemental sulfur
The loading of ZnO was increased progressively from 0phr to 4phr
to evaluate its effect on the cure properties of the kaolin-filled rubber compound with TBBS (Figure
3c), and the kaolin-filled rubber compound with TBBS and ZnO (Figures 4a, 4b and 4c). In total, four rubber compounds were made.

After these measurements were completed, five rubber compounds
were prepared for further tests (compounds 1-5, Table 1). The raw rubber was placed in the mixing
chamber and mixed for two minutes, and then kaolin was put in and
mixed for another eight minutes. Finally after 10 minutes of mixing,
TBBS, ZnO and elemental sulfur were added and mixed for another
five minutes. The total mixing time of 15 minutes was enough to
fully disperse the kaolin particles in the rubber matrix (Figure 5).

When mixing ended the compound was removed from the mixer and allowed to cool to ambient
temperature (21°C). Temperature of the compounds during mixing was
48-58°C. The compounds were kept at ambient temperature (±2°C) for at

<table>
<thead>
<tr>
<th>Formulation (phr)</th>
<th>Compound number</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>Kaolin</td>
<td>60</td>
</tr>
<tr>
<td>TBBS</td>
<td>16</td>
</tr>
<tr>
<td>ZnO</td>
<td>0</td>
</tr>
<tr>
<td>Elemental sulfur</td>
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</tr>
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</table>

Table 1: Rubber formulations

ODR test results at 160°C

<table>
<thead>
<tr>
<th>Minimum torque (dNm)</th>
<th>7</th>
<th>8</th>
<th>6</th>
<th>7</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum torque (dNm)</td>
<td>33</td>
<td>80</td>
<td>41</td>
<td>67</td>
<td>88</td>
</tr>
<tr>
<td>Δtorque (dNm)</td>
<td>26</td>
<td>72</td>
<td>35</td>
<td>60</td>
<td>81</td>
</tr>
<tr>
<td>Scorch time, tₙ (min)</td>
<td>35</td>
<td>5</td>
<td>34</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Optimum cure time, tₙ (min)</td>
<td>64</td>
<td>12</td>
<td>65</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Cure rate index (min')</td>
<td>3.5</td>
<td>14.3</td>
<td>3.2</td>
<td>3.5</td>
<td>11.3</td>
</tr>
</tbody>
</table>
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least 24 hours before their viscosity and cure properties were determined. They were later cured at 160°C for 64 minutes to produce sheets of rubber approximately 2.4 mm thick and cylindrical samples 5.9 mm thick and 15.3 mm in diameter for measuring mechanical properties and hardness.

Results

Figure 4 shows a torque as a function of TBBS loading for the kaolin-filled rubber. Torque increased from 6.5 dNm to 26 dNm as the loading of TBBS was raised from 6phr to 16phr, and it continued to rise at a much slower rate to about 27 dNm when the loading of TBBS reached 30phr. Evidently the addition of 16phr TBBS to the kaolin-filled rubber was sufficient to react the sulfur in MPTS with the rubber chains to form cross-links or chemical bonds between the two.

To enhance the efficiency of TBBS in the kaolin-filled rubber, ZnO was added. Torque increased from 26dNm to 35dNm when 0.2phr ZnO was included, and it continued to rise at a much slower rate to 40dNm, when the loading of ZnO reached 2phr (Figure 7). The inclusion of 0.2phr ZnO was sufficient to optimize the efficiency of TBBS and increase chemical bonding between MPTS and the rubber.

Torque increased from 26dNm to 72dNm when 4phr of elemental sulfur was added to the kaolin-filled rubber with 16phr TBBS. The cure characteristics were also affected (Table 1). The scorch time, tₙₛ, and optimum cure time, tₒ, decreased from 35 to 5 minutes and from 64 to 12 minutes, respectively. The rate of cure increased sharply, with the cure rate index rising from 3.5 to 14.3min⁻¹ (cf. Figures 3a and 3c).

Probably the most interesting feature in Figures 3a and 3c was the fact that the sulfur in MPTS had a much longer reaction cycle (longer optimum cure time) than elemental sulfur at the same temperature (cf. compound 1 and compound 2 – Table 1). This highlighted a fundamental problem with the use of sulfur-bearing silanes in rubber compounding. In tire making, often silica, liquid silane, for example Bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT), and elemental sulfur are used to reinforce and cure rubber compounds. Previous studies have shown that silica-filled rubber compounds containing liquid TESPT had short optimum cure times when elemental sulfur was present and this did not allow sufficient time for the sulfur in TESPT to react fully with the rubber chains to produce strong stable sulfur covalent bonds, which were essential for rubber reinforcement.

In this study, a similar problem albeit more acute, was also encountered in the use of MPTS-pretreated kaolin in NR. In addition to compounds 1 and 2, three more kaolin-filled compounds containing 16phr TBBS and 0.2phr ZnO with 0phr, 1.5phr and 3.0phr elemental sulfur were also prepared (compounds 3-5, Table 1) and cured for 64 minutes. This allowed sufficient time for the sulfur in MPTS to react fully with the rubber chains, and at the same time the compounds also...
Table 2: Mooney viscosity, ODR test results at 160°C, hardness, tensile properties, Young’s modulus, tear strength and compression set carried out on the three rubber compounds shown in Table 1

<table>
<thead>
<tr>
<th>Compound number</th>
<th>3º</th>
<th>4º</th>
<th>5º</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mooney viscosity ML(1+4) at 100°C</td>
<td>26</td>
<td>27</td>
<td>28</td>
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<tr>
<td>ODR test results</td>
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</tr>
<tr>
<td>Minimum torque (dNm)</td>
<td>6</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Maximum torque (dNm)</td>
<td>41</td>
<td>67</td>
<td>88</td>
</tr>
<tr>
<td>Moerne (dNm)</td>
<td>35</td>
<td>60</td>
<td>81</td>
</tr>
<tr>
<td>τ_b (min)</td>
<td>34</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>τ_t (min)</td>
<td>65</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Cure rate index (min⁻¹)</td>
<td>3.2</td>
<td>3.5</td>
<td>11.1</td>
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</table>

<table>
<thead>
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<th>Property</th>
<th>3º</th>
<th>4º</th>
<th>5º</th>
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<tbody>
<tr>
<td>Hardness (Shore A)</td>
<td>36</td>
<td>53</td>
<td>58</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>11.7</td>
<td>12.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>1025</td>
<td>721</td>
<td>668</td>
</tr>
<tr>
<td>Stressed energy density at break (MJ/m³)</td>
<td>50.4</td>
<td>45.0</td>
<td>29.4</td>
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<tr>
<td>Young’s modulus (MPa)</td>
<td>2.3</td>
<td>3.5</td>
<td>3.9</td>
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<tr>
<td>Tear energy (kJ/m²)</td>
<td>9.8</td>
<td>7.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Range of values (kJ/m²)</td>
<td>9.2-10.1</td>
<td>6.6-7.8</td>
<td>6.4-9.6</td>
</tr>
<tr>
<td>Compression set (%)</td>
<td>76</td>
<td>47</td>
<td>42</td>
</tr>
</tbody>
</table>

*Compounds 3, 4 and 5 were cured for 64 minutes

References

The authors would like to thank Imerys Ceramics, USA, for supplying the kaolin filler. The scanning electron microscopy of the samples was carried out at the Loughborough Materials Characterisation Centre in the UK. tire

Figure 7: Torque vs ZnO loading for the kaolin-filled rubber with 16phr TBBS. Each point on the graph corresponds to one compound

was incorporated into the rubber (cf. compound 3 with compound 4 and compound 5 – Table 2). Clearly the MPTS pretreated kaolin could be a viable replacement for CB in tire applications and besides, adding elemental sulfur is the key factor in controlling the mechanical properties of the rubber.

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benefitted from cross-links formed between the rubber chains when elemental sulfur was added. The mechanical properties of compounds 3-5 were later measured (Table 2). Compounds 1 and 2 were excluded from further work. Note that only one accelerator, one activator and elemental sulfur were used to cure the rubber compounds. Traditionally two accelerators and two activators have been used with elemental sulfur to cure rubber compounds for tires.1

The properties that gained the largest benefit from the addition of elemental sulfur to the kaolin-filled rubber with 16phr TBBS and 0.2phr ZnO were hardness, Young’s modulus and compression set. The hardness increased by 61%, the Young’s modulus by 70%, and the compression set decreased by 45% when the full amount of elemental sulfur was added. The tensile strength showed a marginal improvement, for example 9% when 1.5phr of elemental sulfur was included, but deteriorated by 32% when the amount of elemental sulfur reached its full amount. The elongation at break, stored energy density at break, and tear energy reduced by almost 41%, 42% and 29%, respectively, when up to 3phr elemental sulfur