COMPATIBILIZED SILICA-REINFORCED NATURAL RUBBER TIRE
TREAD COMPOUNDS BY EPOXIDIZED RUBBER IN COMBINATION
WITH SILANE COUPLING AGENT

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This work aims to at least partially replace the use of large quantities of silane coupling agent bis-(3-trithoxysilylpropyl) tetrasulfide (TESPT) in silica-reinforced natural rubber (NR) compounds in an attempt to reduce the ethanol emissions released during the silanization reaction. The results show that the use of 7.5 phr of epoxidized natural rubber (ENR-51) as compatibilizer between NR and silica already enhances the properties, which can be further improved by half or even lower amounts of TESPT than needed with the silane alone. Due to TESPT donates reactive elemental sulfur in the compound during vulcanization, sulfur compensation is needed in the case of use of ENR.

Introduction

Silica-reinforced passenger tire tread compounds offer better wet traction and lower rolling resistance, compared to their counterparts filled with carbon black [1]. A silane coupling agent is normally used to bridge between silica and non-polar rubbers, but polar rubber such as Epoxidized Natural Rubber (ENR) [2] can be also used as compatibilizer to enhance the compatibility between silica and rubbers. The most widely used silane coupling agent in silica-filled compounds cured with a sulfur system is bis-(3-trithoxysilylpropyl) tetrasulfide (TESPT) which is known to also act as a sulfur donor to promote crosslinking. The use of TESPT causes the release of substantial amounts of ethanol during mixing [3] and later during vulcanization. The addition of ENR as compatibilizer in silica-filled NR compounds enhanced both processing and vulcanize properties [4], but the properties were still inferior compared to the reference compound with TESPT as coupling agent. This can partly be attributed to the contribution from reactive elemental sulfur that is released from TESPT during mixing and later vulcanization resulting in a higher network density. Based on our previous report [4] in which the use of 7.5 phr of ENR with 51 mol% of epoxide (ENR-51) as compatibilizer was found to give the best overall properties of the silica-filled NR compounds, this present work is therefore to investigate the use of 7.5 phr of ENR-51 in combination with TESPT at varying amounts, without and with sulfur compensation in order to further enhance the properties.

The compensation is applied by adding elemental sulfur into the compound to adjust the total sulfur content, equal to the sulfur contained in the reference system.

Experimental

Materials

The rubbers used were NR (Ribbed Smoked Sheet (RSS) #3) and ENR-51. The latter one was in-house prepared as described in our previous report [4]. The compounding ingredients were Zeosil 1165MP highly dispersible silica (Solvay, France), bis-(3-trithoxysilyl-propyl)tetrasulfide (TESPT) (Evonik, Germany), treated distillate aromatic extract oil (TDAE oil) (Hansen & Rosenthal, Germany), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Belgium), ZnO, stearic acid and sulfur (all from Sigma-Aldrich Chemie, Germany).

Compound preparation

The formulations are as shown in Table 1. The rubber compounds were mixed using two step mixing procedures. The first step was carried out in an internal mixer (Brabender Plasticorder 350S, operated at an initial mixer temperature setting of 110°C, rotor speed of 60 rpm and a fill factor of 0.7). NR and ENR were firstly masticated for 2 mins, then half of silica and TESPT (if any) was added and mixed for 5 mins, followed by another half of silica and silane (if any) for another 5
mins, and finally ZnO, stearic acid and TMQ were added and mixed for 3 mins before the compound was discharged. The second step was to mix DPG, CBS and sulfur into the compounds by using a two roll mill. The silica-filled NR compounds with and without TESPT and without ENR were prepared and treated as reference.

Table 1 – Compound formulations.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts per hundred parts of rubber (phr)</th>
<th>None</th>
<th>TESPT</th>
<th>ENR+TESPT</th>
<th>ENR+TESPT+S</th>
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<tr>
<td>NR (RSS3)</td>
<td>100.0</td>
<td>100.0</td>
<td>92.5</td>
<td>92.5</td>
<td></td>
</tr>
<tr>
<td>ENR-51</td>
<td>-</td>
<td>-</td>
<td>7.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>TESPT</td>
<td>-</td>
<td>-</td>
<td>4.7*</td>
<td>1.1-2.7**</td>
<td>1.1-2.7**</td>
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<tr>
<td>Silica</td>
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<td>55.0</td>
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<tr>
<td>TDAE oil</td>
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<tr>
<td>ZnO</td>
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<td>3.0</td>
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<tr>
<td>TMQ</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Stearic acid</td>
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<td>1.0</td>
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<tr>
<td>DPG</td>
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<td>1.0</td>
<td>1.0</td>
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<tr>
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<td>1.5</td>
<td>1.5</td>
<td>2.3-1.9**</td>
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<tr>
<td>Sulfur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>2.3-1.9**</td>
<td></td>
</tr>
</tbody>
</table>

Remarks: * TESPT 4.7 phr equals 8.6 wt% relative to silica; ** TESPT 1.1-2.7 phr equals 2-5 wt% relative to silica; *** sulfur contents were adjusted to compensate for the sulfur in the TESPT molecules by taking the compound with 4.7 phr of TESPT as reference.

Testing of compounds and vulcanizates

The Mooney viscosity (ML(1+4) 100°C) of the uncured silica-filled compounds was tested using a Mooney viscometer (MV 2000VS, Alpha Technologies, Akron, USA) according to ASTM D1646. The Payne effect or filler-filler interaction was studied by using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 100°C, frequency 0.5 Hz and varying strains in the range of 0.56 to 100%. The difference of storage moduli at low strain (i.e. 0.56%) and high strain (i.e. 100%) is reported. Then, the compounds were vulcanized to their respective optimum cure times (tc90) that were determined by using the RPA at 150°C, frequency 0.833 Hz and 2.79% strain, by using a Wickert WLP 1600 laboratory compression press (Wickert Machinenbau GmbH, Germany) at 150°C into 2 mm thick sheets. Type 2 dumb-bell test specimens were die-cut from the press-cured sheets and tensile tests were carried out with a Zwick tensile tester Model Z1.0/TH1S at a crosshead speed of 500 mm/min according to ASTM D412. The tensile-fractured test pieces were gold-coated before being analyzed by SEM (Quanta 400, FEI). Dynamic mechanical properties of the vulcanizates were characterized with a Metravib Viscoanalyzer VA 2000 (ACOEM, Paris, France) in tension mode with a temperature sweep from -80°C to 80°C at a frequency of 10 Hz and 0.1% strain.

Results and Discussion

Mooney viscosities of the silica-filled NR compounds with ENR-51 as compatibilizer in combination with varying contents of TESPT, with and without extra sulfur, in comparison with that of the compounds with no compatibilizer at all and with only 4.7 phr of TESPT as reference are shown in Figure 1(a).

![Figure 1](image-url) – Mooney viscosity and Payne effect of silica-filled NR compounds.

Without extra sulfur, the incorporation of 2 wt% TESPT relative to silica into the silica-filled NR compounds decreases Mooney viscosity, and a further increase of TESPT content shows no additional effect on this property. The compounds with extra sulfur show no change in Mooney viscosity with increasing silane content and the values are marginally higher than that of the compounds with no extra sulfur. All of the compounds with ENR-51/TEPST combinations, either with or without extra sulfur, show lower Mooney viscosities when compared to the reference compound with 4.7 phr TESPT. As the sulfur was added in the second step of mixing on a two-roll mill, a premature crosslinking reaction is unlikely to take place. Nevertheless, the compounds with TESPT and extra sulfur show a slightly higher Mooney viscosity compared to the mixes with lower sulfur content. In the absence of ENR and TESPT, the ENR-compatibilized compound shows the highest Mooney viscosity.

The filler-filler interaction or Payne effect of the silica-filled NR compounds is shown in Figure 1(b). The addition of 7.5 phr of ENR-51 already remarkably decreases the filler-filler interactions in the compounds when compared to the non-compatibilized one due to interaction between silanol groups on the silica surface and epoxy groups of ENR. The use of extra sulfur in the silica-filled NR compounds with ENR-51 as compatibilizer results in a somewhat higher Payne effect compared to the mixes with normal sulfur content. This may be due to their lower Mooney viscosities that cause a tendency of silica re-agglomeration. The Payne effect
The tensile strength of the vulcanizates is improved by adding TESPT on top of the ENR-51 as compatibilizer, and further enhanced by the addition of extra sulfur, as shown in Figure 3. The use of TESPT at 4 wt% relative to the silica with ENR-51 and extra sulfur gives the same level of tensile strength as that of the silica/TESPT reference compound. The results show that, in combination with the ENR, the amount of TESPT needed to optimize the silica-filled compound properties can be reduced, compared to a conventional TESPT-silanized silica filled system. Herein Figure 3, SEM micrographs of tensile fractured surfaces of some vulcanizates containing different compatibilizers are displayed.

The silica-filled NR vulcanizate without compatibilizer that has the lowest tensile strength shows a smooth surface with some vacuoles on the failure surface that may be caused partly by de-wetting of the silica from the NR matrix. The fractured surfaces of silica-filled NR with ENR-51 as compatibilizer alone had a considerably less complicated fracture surface when compared to the one with optimal content of TESPT. The silica-filled vulcanizates with TESPT and ENR/TESPT/extra sulfur that exhibit the same level of tensile strength, show very similar rough tensile fractured surfaces with many tear lines as a result of good interfacial interactions between rubber and silica. The SEM micrographs of tensile fractured surfaces of filled NR vulcanizates, in which the rough surfaces with tear lines indicated higher tensile strength, have also been used to demonstrate dispersion and wetting of fillers by the matrix, such as in the work of Arayapranee et al. [7].

Figure 2 – Possible interactions and bonding in the silica-filled NR compounds compatibilized with ENR/TESPT.

Figure 3 – Tensile strength and SEM images of tensile fractured surface.

of the silica-filled NR compounds with 2 wt% TESPT relative to silica and extra sulfur decreases to the same level as that of the reference compound with TESPT only. This further reduction of filler-filler interaction by the addition of TESPT indicates that even though epoxy-groups of ENR interact with the silanol-groups on the silica surfaces, there are still free silanol-groups present in the system. With regard to an ability to cap the free silanol groups on the silica surface, the ability of the epoxide-groups in ENR-51 is obviously lower than for TESPT due to their difference in molecular size. TESPT is a relatively low molecular weight substance, which enables it to migrate through the unvulcanized compound towards the silica surface, whereas ENR-51 is a macromolecule with low diffusion mobility and a steric hindrance that may prevent it to penetrate into the macro porosity of the silica. For the ENR-compatibilized silica-filled NR compounds, the use of just small amounts of TESPT therefore further decreases the filler-filler interactions through the silanization reaction of the remaining silanol-groups. The compound without TESPT with extra sulfur, which has a lower Mooney viscosity, shows a higher Payne effect, whilst the one with both TESPT and extra sulfur that has higher Mooney viscosities exhibits lower Payne effects. The results indicate an influence of Mooney viscosity on re-agglomeration of silica aggregates which relates to the Payne effect.

In the silica-reinforced NR compounds with ENR as compatibilizer in the presence of small amount of TESPT, there are several possible interactions and/or reactions within the system, as shown in Figure 2, including interaction between hydroxyl-groups of ring-opened ENR [2]; interaction between hydroxyl-groups of ring-opened ENR with the silanol groups of silica [5]; bonding between silica and rubber molecules via silane molecules [6]; interaction between epoxy and silanol groups [2]; and bonding between silanol and hydroxyl groups [5]. These interactions/reactions contribute to the decreased silica-silica interactions.
Figure 4 – Storage modulus and loss tangent as functions of temperature of silica-filled NR vulcanizes.

The storage modulus ($E'$) and tan δ as functions of temperature of the silica-filled NR vulcanizates are shown in Figures 4 (a-b) in which the results of the vulcanizates with 8.6 wt% TESPT relative to silica, with 7.5 phr ENR-51, with 7.5 phr ENR-51 plus 4 wt% TESPT relative to silica, and with 7.5 phr ENR-51 plus 4 wt% TESPT relative to silica plus extra sulfur, are comparatively displayed. In the glassy state, the addition of the different types of compatibilizers into the silica-filled NR vulcanizates has little effect on the storage modulus. But, the material properties are clearly different in the rubbery region where the vulcanizates that contain ENR-51 as compatibilizer, either without or with TESPT, show higher storage modulus than the ones with TESPT and without any compatibilizer. The presence of ENR-51 with high epoxide-content causes chain stiffness, therefore, results in a higher elastic modulus.

When compared to the uncompatibilized rubber vulcanize, the use of the optimal content of 4.7 phr TESPT results in the highest tan δ peak due to improvement of silica dispersion, leading to less trapped rubber in the silica aggregates and so more rubber segments to respond to the dynamic deformation. Conversely, the use of ENR as compatibilizer results in a decrease of the tan δ peak intensity, even in combination with TESPT, which is partially caused by the ENR which at this temperature is still in the glassy state. The interactions between the ENR and silica as well as self-crosslinked ENR also cause a restriction of chain mobility. In the rubbery region, the silica/TESPT system provides the lowest tan δ value due to the good chemical bonding between silica and rubber via silane bridges.

The presence of ENR-51 that possesses higher damping properties results in the higher tan δ in the temperature range of 0 to 80°C above its glass transition temperature of around 0°C. The silica-filled NR vulcanize with TESPT shows the lowest tan δ at 5°C implying the lowest tire wet skid resistance. The chemical bonds between silica and rubber via silane molecules give an additional contribution to the crosslink network that is normally generated by the vulcanization reaction to result in a better elastic response and lower energy loss. This double network also causes the lowest tan δ at 60°C which indicates a low rolling resistance for tires, as shown in Figure 4(b). The presence of ENR-51 leads to a significantly higher tan δ at 60°C compared to the use of TESPT alone, but is still lower than for the non-compatibilized compound. The addition of ENR together with TESPT with and without extra sulfur gives an improvement in tan δ at 60°C due to the improved filler dispersion and network formation.

Conclusions

The use of 7.5 phr of ENR-51 in combination with TESPT decreases Mooney viscosity and filler-filler interactions, compared to the silica-filled compound with ENR-51 alone. Tensile strength of the vulcanizates increases with increasing TESPT-contents and further improves by sulfur compensation relative to the reference compound with TESPT alone. The use of ENR-51 at 7.5 phr, with TESPT at 4 wt% relative to the silica and extra sulfur gives vulcanizates with the same levels of tensile strength compared to the vulcanizates with TESPT at optimum 8.6 wt% relative to the silica, but without ENR. The ENR-containing vulcanizates show higher storage modulus and tan δ compared to the silica/TESPT system due to the higher Tg of ENR compared with NR. The addition of TESPT to the ENR-compatibilized compounds causes a small change in tan δ at 5°C, but lower tan δ at 60°C, and the addition of extra sulfur leads to a lower tan δ at both temperatures as a result of increased crosslink density. Overall, the combination of ENR-51, TESPT and sulfur compensation nearly matches the properties of a compound with TESPT alone at optimal quantity. But, with only half or smaller amount of TESPT is needed when ENR-51 is included, the amounts of ethanol released from such a compound with ENR-51 can be substantially reduced.

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References


