CHAPTER 8

SYNERGISTIC EFFECTS OF EPOXIDE FUNCTIONAL GROUPS ON
NATURAL RUBBER AND SILANE COUPLING AGENTS ON
REINFORCING EFFICIENCY OF SILICA

Polar functionality attached onto natural rubber has a significant impact on the reinforcing efficiency of silica. Parallel studies involving various levels of epoxidation on natural rubber (ENR) in the absence of TESPT coupling agent, as well as a combination of ENRs with different loadings of TESPT, provide a better understanding of the various factors which influence the properties of silica-filled ENR compounds. Based on the overall properties, the best possible combination to optimize processibility, to reduce filler-filler interaction, and improve vulcanization rate as well as vulcanizate properties, is to utilize ENR with an epoxide content in the range of 20 – 30 mol%, together with a small portion of TESPT, i.e. 2 – 4 wt% relative to the silica content. This leads to a reduction of approximately 60 – 80 % of TESPT when compared to the conventional NR compounds, where the optimal loading of TESPT was 9.0 wt% relative to the silica content.

8.1 INTRODUCTION

In addition to the use of silica surface modifying agents and/or silane coupling agents, compatibilization between silica and hydrocarbon rubbers can be promoted by the use of polar polymers. As reviewed in Chapter 2, the silanol groups on the silica surface have potential to form physical interactions or even chemical bonds with functionalized rubbers such as chlorosulfonated polyethylene (CSM),\textsuperscript{1} carboxylated nitrile rubber (XNBR),\textsuperscript{2} and epoxidized natural rubber (ENR).\textsuperscript{3-5} The polar-modified rubbers can be used either as raw material\textsuperscript{6,7} or as compatibilizer.\textsuperscript{8,9}

In this chapter, the influences of epoxide content in ENRs in the absence of a silane coupling agent, resp. a combination of ENRs with TESPT at varying loadings are evaluated on the overall properties of silica-filled ENR compounds. Filler-filler
interaction, network contributions, Mooney viscosity, cure characteristics, dynamic and mechanical properties of the compounds and vulcanizates are investigated.

8.2 EXPERIMENTAL

8.2.1 Materials

The ENRs with various epoxide levels were prepared in-house and are used as raw material. The chemicals employed for the synthesis of ENRs were high ammonia (HA) NR latex (Yala Latex, Thailand), formic acid (Fluka Chemie, Switzerland), hydrogen peroxide (Riedel-De Haën, Germany), alkylphenol ethoxylate or Teric N30 (Huntsman Corp. Australia Pty., Australia), and commercial grade methanol (J.T. Baker, USA).

The ingredients used for the rubber formulations, i.e. silica, TESPT silane coupling agent, TDAE oil, zinc oxide, stearic acid, TMQ, CBS, sulfur, and DPG were the same as those described in Chapter 3.

8.2.2 Preparation and characterization of epoxidized natural rubber

8.2.2.1 Modification procedure. — The ENRs were prepared using HA latex with a dry rubber content (DRC) of approximately 60 wt% via an in-situ performic epoxidation reaction in which the performic acid was generated by a reaction between formic acid and hydrogen peroxide ($\text{H}_2\text{O}_2$) inside the reactor. The recipe used for this synthesis is given in Table 8.1.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity</th>
<th>mole</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA latex (60 wt% DRC)</td>
<td></td>
<td>2.0</td>
<td>226.7</td>
</tr>
<tr>
<td>Hydrogen peroxide (50% w/w)</td>
<td></td>
<td>4.0</td>
<td>272.0</td>
</tr>
<tr>
<td>Formic acid (94% w/w)</td>
<td></td>
<td>1.0</td>
<td>48.9</td>
</tr>
<tr>
<td>Teric N30 (10% w/w)</td>
<td></td>
<td>-</td>
<td>15.0a</td>
</tr>
</tbody>
</table>

*approximately 1.0 phr

The epoxidation reaction as shown in Figure 8.1 was carried out in a continuously stirred reactor, at a temperature of 40°C. The latex was first diluted to
Synergistic effects of epoxide functional groups on natural rubber and silane coupling agents

have a DRC of approximately 20 wt% and then stabilized against coagulation by adding a non-ionic surfactant, i.e. Teric N30, and held for 15 minutes. After that, formic acid was added dropwise, followed by the hydrogen peroxide. The entire quantity of each reagent was charged into the reactor over a time period of 1.5 hours. Because the degree of epoxidation depends significantly on the reaction time, the modification times were varied at 2.5, 4.5, 6.0, 9.5 and 14.5 hours, in order to obtain different concentrations of epoxide functionality in a variety of ENRs.

![Chemical Reaction](image)

**Figure 8.1** Mechanism of epoxidation reaction in the preparation of the ENRs.

After the modification reaction was finished, the ENR latex was coagulated with methanol, thoroughly washed with water and then dried in a vacuum oven at 40°C for approximately 72 hours.

**8.2.2.2 Characterization of the ENR structure.** — The ¹H-NMR technique as previously described in Chapter 5 was performed to analyze the molecular structure
and to determine the exact level of epoxide content in the ENRs. Deuterated chloroform (CDCl₃) was used to dissolve the ENR samples. The ¹H-NMR spectra of the ENRs are shown in Figure 8.2.

![Figure 8.2 ¹H-NMR spectra of the ENRs with various levels of epoxide functionality.](image)

The absorption peaks at chemical shifts of 2.7 and 5.1 ppm indicate the resonances of a proton in an oxirane ring and isoprene unit, respectively (see Figure 8.1). The integral values under these peaks at 2.7 and 5.1 ppm are taken to calculate the epoxide content in ENR according to Equation 8.1:\(^2\)

\[
\text{Epoxide content (mol\%)} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \quad (8.1)
\]

where \( I_{2.7} \) and \( I_{5.1} \) are the integrals of the absorption peaks at the chemical shifts of 2.7 and 5.1 ppm, respectively.
In the present work, five levels of epoxide content in the ENRs were prepared. The different mol% epoxide contents in the ENRs prepared by using different reaction times are given in Table 8.2 and Figure 8.3.

Table 8.2 Degree of epoxidation of ENRs at varying reaction times.

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Mol% epoxide (by $^1$H-NMR)</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>12.8</td>
<td>ENR-13</td>
</tr>
<tr>
<td>4.5</td>
<td>21.4</td>
<td>ENR-21</td>
</tr>
<tr>
<td>6.0</td>
<td>28.7</td>
<td>ENR-29</td>
</tr>
<tr>
<td>9.5</td>
<td>36.1</td>
<td>ENR-36</td>
</tr>
<tr>
<td>14.5</td>
<td>43.3</td>
<td>ENR-43</td>
</tr>
</tbody>
</table>

![Figure 8.3](image.png)  
**Figure 8.3** Epoxide content in ENRs as a function of epoxidation reaction time.

8.2.3 Compound preparation

The effect of the degree of epoxidation in the ENRs was investigated in parallel with variation of the TESPT concentrations. Table 8.3 shows the compound formulation used in this study.
Table 8.3 Compound formulation.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Dosage (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber (ENRs&lt;sup&gt;a&lt;/sup&gt; or NR)</td>
<td>100.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>TMQ</td>
<td>1.0</td>
</tr>
<tr>
<td>Ultrasil 7005</td>
<td>55.0</td>
</tr>
<tr>
<td>TESPT</td>
<td>Variable&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>TDAE oil</td>
<td>8.0</td>
</tr>
<tr>
<td>DPG</td>
<td>1.1</td>
</tr>
<tr>
<td>CBS</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> ENRs with 12.8, 21.4, 28.7, 36.1, and 43.3 mol% epoxide were studied.

<sup>b</sup> The quantity of TESPT used for each ENR compound was varied from 0 – 12 wt% relative to the silica content.

All silica-filled ENR compounds were prepared following the same methods as described in Chapter 4. The unmodified NR (i.e. Ribbed Smoked Sheet 3, RSS 3) compounds with and without TESPT were prepared and treated as a reference.

8.2.4 Property analysis and testing

Mooney viscosity, Payne effect, cure characteristics, tensile and dynamic mechanical properties of the compounds were investigated according to the methods and instruments as described in Chapter 3.

8.3 Results

8.3.1 Mixing torque and mixing temperature

The processibility of silica-filled ENR compounds can initially be determined by monitoring the mixing torque during mixing in the internal mixer.
Figure 8.4 Mixing torques of silica-filled ENR compounds with various epoxide contents, as indicated for each line. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are considered as references.

All ENR compounds show lower mixing torques compared to normal NR either with or without TESPT used, as observed in Figure 8.4. The reduced mixing torque is more pronounced when the epoxide content in ENRs increases. The mixing torques in the mastication step, i.e. the first 2 mins., show similar values, but after the addition of silica, the mixing torques of the ENR and unmodified NR compounds are clearly separated. This indicates an effect of filler dispersion. The epoxide functionality on NR molecules increases their polarity, and then enhances the compatibility with the polar active silica, leading to lower shear forces during compound mixing and so decreased mixing torque. The effect of epoxide groups on ENR and TESPT in unmodified NR results in similar mixing torques in the first interval of silica mixing. However, in the second half-addition of silica, NR with TESPT shows higher mixing torques compared to ENRs compounds which may be attributed to premature crosslinks by sulfur in the TESPT, as discussed in Chapter 3.
Figure 8.5 Mixing temperatures developed during compound mixing in the internal mixer of silica-filled ENR compounds with various epoxide contents. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are considered as references.

The mixing torques correspond well with the heat generation during compound mixing in the internal mixer as seen in the temperature profiles given in Figure 8.5. The ENR compounds show lower mixing temperatures than those of the compounds prepared with unmodified NR both with and without TESPT.

Figure 8.6 Mixing torques of silica-filled ENR compounds with 13 and 43 mol% epoxide contents, compared between the ones with and without TESPT at 9 wt% relative to the silica content, as indicated for each line.
The epoxide groups in the ENRs are expected to react with the silanol groups of the silica and compatibilize the two phases. However, the possibility of a synergistic effect between the epoxide groups and the silane coupling agent is also studied in this work. Figure 8.6 shows the mixing torques of the silica-filled ENR compounds with and without TESPT as silane coupling agent. The addition of TESPT into the ENR-13 based compounds clearly reduces mixing torque, whilst the ENR with 43 mol% epoxide content exhibits no significant difference in mixing torques between the compounds with and without TESPT. These results indicate that the ENR with low mol% epoxide content has not enough polar functional groups to hydrophobize the silica surface and the addition of TESPT helps to improve hydrophobation and silica dispersion. The ENR with high concentration of epoxide groups: ENR-43, can improve the silica dispersion due to a better polarity matching without the need for silica surface modifying agents.

8.3.2 Filler-filler interaction and network contributions

8.3.2.1 Payne effect. — In order to determine filler-filler interaction in the compounds, the storage moduli at 0.56 and 100% strain were measured as the difference in moduli at small and large deformation indicates the level of filler-filler interactions in the compounds. The Payne effect of the silica-filled ENR compounds with and without TESPT is shown in Figure 8.7. Figure 8.7(a) shows that ENR-13, and ENR-21 incur a strong decrease in Payne effect with increasing TESPT content up to 6.0 and 3.7 wt% relative to the silica content, respectively, and thereafter level off. The ENR-29 compounds show only a slight decrease in Payne effect when TESPT at 1.8 wt% relative to silica is added and thereafter a more or less constant value. Therefore, the minimal levels of TESPT content required to optimize the Payne effect for each compound are different, depending on the availability of functional groups in the rubber matrix, as seen in Figure 8.7(b). The combination of epoxide groups in ENR-13 and ENR-21 with TESPT results in the lowest Payne effects. The higher levels of the storage modulus difference in ENR-29, ENR-36, and ENR-43, in the presence of TESPT may be attributed to the presence of the large amounts of epoxide groups which can create additional interactions and/or linkages between themselves. The epoxide groups can be ring-opened and form crosslinks between adjacent molecules, as reported by NG and Gan. For ENR-36 and ENR-43, the Payne effect slightly decreases with increasing TESPT loading, as a result of a dilution effect.
Figure 8.7 Payne effect as functions of (a): TESPT content; and (b): epoxide content in the ENR compounds.

With respect to the influence of epoxide content, the compounds without TESPT show a decrease in Payne effect when the epoxide functionality is increased from 13 – 29 mol%, and then Payne effect increases again with a further rise in epoxide content, as shown in Figure 8.7(b). This observation suggests that only a specific level of epoxide groups is required to interact with the silanol groups on silica surface. The presence of a too high concentration of epoxide groups has an adverse effect. The addition of TESPT can still clearly lower the Payne effect or filler-filler interaction in the ENR-13 and ENR-21 based compounds, but it shows only a small influence on the Payne effect of the compounds based on ENR-29, ENR-36 and ENR-43. Based on the minimum Payne effect observed for each set of compounds, a shift of the minimum points is noticeable in the sense that: the higher the epoxide content, the lower the TESPT loading required. Furthermore, it can be seen that after the optimum level, all the compounds show a rise in Payne effect.

To demonstrate the intrinsic properties of the different types of rubbers used as raw materials, the storage moduli of these matrices were additionally tested under strain variation. The results are given in Figure 8.8.
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Figure 8.8 (a) Storage modulus at varying deformations, and (b) storage modulus differences at 0.56 and either 30% ($\Delta G'_1$) or 100% ($\Delta G'_2$) strain of neat unmodified NR, and ENRs with various levels of epoxide functionality.

Figure 8.8 shows the storage moduli from small to large deformations of unmodified NR and the ENRs. The ENRs with a greater degree of polarity have significantly higher storage moduli at small deformation, i.e. below 10% strain, as seen in Figure 8.8(a), as a result of interactions between their epoxide functional groups. In order to determine the degree of intrinsic interaction forces in each rubber, the storage modulus difference was calculated and plotted against epoxide content, as shown in Figure 8.8(b). The results reveal that a higher epoxide content leads to higher interaction forces as the storage modulus differences at 0.56 and 30 or 100% strain linearly increase. Till 30% strain the pure NR keeps a constant modulus, to decrease for higher strains due to non-linearity. On the other hand, for the ENRs these non-linear effects already start to be visible at lower strain. Therefore, the increase of Payne effect after the optimum level of about 25 mol% epoxide on the NR: Figure 8.7, is mainly because of a dominant effect of interaction forces associated with the polar nature of ENR itself. At low epoxide levels in the case of ENR-13 and ENR-21, the interactions between the epoxide moieties and silanol groups on the silica are still playing the main role, causing the reduction of filler-filler interactions.
8.3.2.2 Network contributions. — The network contributions can be further evaluated by the storage moduli at 100% strain, since the entire physical filler-filler linkages are assumed to be destructed, as depicted in Figure 8.9.

![Figure 8.9 Storage modulus at 100% strain as functions of (a): TESPT amount; and (b): epoxide content in ENRs for the silica-filled ENR compounds.](image)

It can be seen that higher amounts of TESPT and stronger polarity of the ENRs: Figures 8.9(a) and 8.9(b), respectively, result in higher network contributions in the compounds. These network structures can originate from several factors: 1) filler-to-rubber interactions; 2) self-association of polar materials; and 3) rubber-rubber bonding by free sulfur released from TESPT. When TESPT is excluded, the ENR-36 and ENR-43 clearly show higher storage moduli, mainly attributed to self-association of epoxide groups. These two ENRs show the least dependence on TESPT loading.

8.3.3 Compound viscosity and cure characteristics

8.3.3.1 Mooney viscosity. — Mooney viscosities of the compounds prepared with the various ENRs containing different levels of epoxide functionality are shown in Figure 8.10.
The influence of silane loading at a given epoxide content can be seen in Figure 8.10(a). The ENR-13 and ENR-21 compounds show a sharp decrease in compound viscosity when the TESPT amounts are increased from 0 – 6.0 phr or 0 – 3.7 wt% relative to the silica content, respectively. After those ranges of TESPT concentration, the Mooney viscosities do not change much anymore. ENR-29 shows a marginal drop in Mooney viscosity when TESPT is added from 0 – 1.8 wt% relative to the amount of silica, and after that it slightly increases. For ENR-36 and ENR-43, the Mooney viscosities of the compounds tend to increase slightly with increasing TESPT content.

The effect of epoxide groups available on the ENRs on Mooney viscosity at a given amount of TESPT is shown in Figure 8.10(b). Considering the compounds without TESPT, an increase of epoxide content from 13 – 29 mol% results in a sharp decrease in Mooney viscosity, after that the Mooney viscosity increases again. TESPT at 6.0 and 3.7 wt% relative to the silica content is the optimal quantity which can minimize the viscosities of ENR-13 and ENR-21 based compounds, respectively. The addition of TESPT into ENR-29, ENR-36 and ENR-43 based compounds does not
affect the Mooney viscosities much, as seen in the overlapping data points in Figure 8.10(b).

The change of Mooney viscosities with regard to epoxide group contents and TESPT loading as shown in Figure 8.10 resembles very much the various Payne effects as displayed in Figure 8.7. As previously discussed for the Payne effects, the ENRs with low content of epoxide groups can not completely hydrophobize the silica surface and the addition of TESPT still has a positive effect for hydrophobization and compatibilization. The compounds therefore have a lower Mooney viscosity as well as Payne effect. When the ENRs contain a high concentration of epoxide groups, in addition to interaction with the silanol groups of silica these polar groups tend to associate among themselves causing an increase in Mooney viscosity.

8.3.3.2 Cure characteristics of the compounds. — Figure 8.11 shows that the changes of cure rheometer minimum torques with regard to TESPT and epoxide contents exhibit again the same trend as with the Mooney viscosities (Figure 8.10), since the rheometer minimum torque is also an indication for compound viscosity.

**Figure 8.11** Rheometer minimum torques as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.
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Figure 8.12 Rheometer maximum torques as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.

Rheometer maximum torques of the compounds are shown in Figure 8.12. This parameter reflects the entire extent of network contributions in the reinforcing filler-based compounds, including both chemical and physical entities: i.e. rubber crosslinks; filler-rubber interactions; as well as the filler-filler network. These results demonstrate similar trends to the Payne effects and compound viscosities as shown in Figures 8.7, 8.10 and 8.11, because these complex network contributions also simultaneously determine the rheometer maximum torques of the compounds.
Optimum cure times $t_{c,90}$ as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.

Figure 8.14 Cure rate index as functions of (a): TESPT loading; and (b): epoxide content in the ENRs.

Optimum cure times of the compounds are shown in Figure 8.13 and are reworked in terms of cure rate index as illustrated in Figure 8.14. The ENR compounds with different levels of epoxide groups show different responses towards TESPT
addition with regard to cure rate index. The cure rate index of the ENR-13 and ENR-21 compounds initially decreases with increasing TESPT amount, but then tends to increase after the TESPT exceeds 3.7 wt% relative to the silica amount. The ENR with 29 mol% epoxide content exhibits a rather constant cure rate index with TESPT loading. ENR-36 and ENR-43 show decreasing trends when TESPT is increased. These different cure behaviors are also observed in Figure 8.14(b) in which the cure rate index increases when the epoxide contents are in the range of 13 – 21 mol%, but tends to decrease after the epoxide content exceeds 29 mol%. For the silica-filled ENR compounds in which two polar functional groups, i.e. epoxide and silanol groups play a role, the cure properties can be affected by chemical adsorption of highly polar basic accelerators. The silanol group on silica itself is acidic in nature and retards the curing reaction. Further, the greater extent of double bond transformation into epoxide rings reduces the number of active available double bonds for sulfur curing, and therefore reduces the cure reactivity. With these various factors involved, the cure behavior of this silica-filled ENR system is complicated. Considering the compounds based on ENRs with 13 – 29 mol% epoxide but without TESPT, see Figure 8.12, polar interactions between silanol and epoxide groups provide better polarity matching, reduce filler-filler interaction and so improve the cure rate index. This is because chemical adsorption on the silica surface can be minimized. A further increase of epoxide content, i.e. 36 – 43 mol%, significantly reduces the cure rate index. This can be either because of self-association of epoxide groups leaving the silanol groups free to adsorb curatives, or interference of excess epoxide groups with the vulcanization reaction. The addition of TESPT in the system with excess epoxide further decreases the cure rate index as the excess polar TESPT will also interfere with the curatives and hence slow down the curing reaction.

8.3.4 End-use properties of the compounds

8.3.4.1 Dynamic mechanical properties. — Tan δ at 60°C is well-known as an indication for rolling resistance of tires made from the compounds. The use of ENR as matrix for silica-filled compounds in the presence and absence of TESPT results in changes of tan δ at 60°C as shown in Figure 8.15.
The influence of silane content on $\tan \delta$ at 60°C at a given epoxide level can be seen in Figure 8.15(a). Increase of the TESPT loading results in a sharp decrease in $\tan \delta$ at 60°C of the compounds based on ENRs with 13, 21 and 29 mol% epoxide content, and a slight decrease for ENR-36 and ENR-43. Basically, $\tan \delta$ relates strongly to network contributions in the compounds. The dynamic mechanical test was performed at 3.5 % strain and a frequency of 10 Hz, where the filler network begins to break. The results are therefore strongly influenced by network contributions originating from filler-rubber interactions and physical/chemical crosslinks. These results are in good correspondence with the storage modulus at 100% strain (Figure 8.9). Without TESPT, the increase of epoxide contents leads to a strong decrease in $\tan \delta$ at 60°C as visualized in Figure 8.15(b). This can be linked to the greater filler-rubber interaction/network formation as reflected by the higher storage modulus at high strain in Figure 8.9. The combination of epoxide functionality with TESPT silane coupling agent jointly improve the $\tan \delta$ at 60°C or rolling resistance of tires. Therefore, there is a possibility to reduce the amount of TESPT needed in silica-filled ENR formulations.

**8.3.4.2 Mechanical properties.** — Tensile properties of the vulcanizates are shown in Figure 8.16.
The tensile strength clearly shows effects of TESPT loading and epoxide content, as depicted in Figures 8.16(a) and 8.16(b), respectively. Without TESPT, the ENR-21 and ENR-29 compounds show the best possible tensile strength obtained by the utilization of the epoxide functional groups only for the silica-filled system. As seen in Figure 8.16(b), the tensile strength of ENR-21 and ENR-29 compounds without the use of TESPT lies almost in the middle between the tensile strength of NR compounds with and without TESPT. A further increase in degree of polarity by more epoxide functionality shows an adverse effect towards tensile properties. The use of ENR-13 clearly requires TESPT to enhance its tensile strength, as seen in a substantial increase of this property with TESPT loading. The optimum tensile strength for ENR-13 is observed when it is used in combination with 6.0 wt% TESPT relative to silica content. Under this condition, the property reaches more or less the same level as that of unmodified NR with optimal TESPT loading. The tensile strength of the ENRs with higher degree of epoxidation shows less dependence on silica coupling agent addition, and this property is decreasing especially when the epoxide content exceeds 29 mol%. The self-association\textsuperscript{13,15} of epoxide groups that creates another type of crosslink and contributes to a higher degree of crosslinking, as observed by the high storage modulus.
at 100 % strain (Figure 8.9) and Mooney viscosity (Figure 8.10 and Table 8.3), subsequently has an adverse effect on the ultimate tensile properties.

**Figure 8.17** Elongation at break as functions of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references.

Figure 8.17(a) shows that all ENR compounds, except ENR-13, have a decrease in elongation at break with increasing TESPT loading, whilst the ENR-13 compounds show a slight increase of elongation at break when the TESPT content is increased up to 9.0 wt% relative to the silica content. Considering the effect of epoxide content as shown in Figure 8.17(b), the increase of epoxide content leads to a sharp decrease in elongation at break, and all ENR compounds have lower elongation at break than NR both with and without TESPT. These results correspond with the tensile modulus at 100 % elongation as shown in Figure 8.18. Again, the network contribution as described for the dynamic modulus (Figure 8.9) can significantly affect the extensibility and flexibility of the vulcanizates.
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Figure 8.18 Tensile modulus at 100 % strain as function of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references.

Figure 8.19 Reinforcement index as functions of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references.

The compounds based on ENR-13, ENR-21 and ENR-29 show their optimum reinforcement indices when TESPT amounts at 9.0, 3.7, and 3.7 wt% relative to the
silica content are combined, respectively, as shown in Figure 8.19(a). A further increase of TESPT loading results in a decrease in reinforcement index. In Figure 8.19(b), the ENR compounds without TESPT show an increase of reinforcement index with increasing epoxidation degree up to 29 mol% to match more or less the same level as that of an unmodified NR compound in the presence of TESPT. However, a further increase of epoxide content leads to a decrease again in reinforcement index. With the presence of TESPT, the results show the same trends as the tensile strength: Figure 8.16. The compounds based on ENR-13, ENR-21 and ENR-29 in combination with suitable TESPT contents, show higher reinforcement index compared to that of silica/TESPT filled NR compound. This reflects a good synergistic effect between epoxide groups and TESPT towards enhanced reinforcing efficiency of silica in ENR compounds.

8.4 DISCUSSION

With regard to the changes in Payne effect and compound viscosity, the phenomena apparently relate well to the overall properties of silica-filled ENR compounds and vulcanizates. There are several factors competitively influencing the compound viscosities of silica-filled polar-modified NR systems as can be summarized in Scheme 8.1.

Scheme 8.1 Competitive factors influencing compound viscosities of silica-filled ENR compounds with and without TESPT silane coupling agent.
The change in compound viscosities as indicated by Mooney viscosity and rheometer minimum torque, Figures 8.10 and 8.11, respectively, can be discussed by considering several factors which are simultaneously and competitively taking place in the compounds. “A better silica dispersion” resulting from a lower filler-filler interaction or Payne effect is a key factor that strongly reduces the viscosity of the compounds. Considering the ENRs with epoxide contents in the range of 13 – 29 mol% in Figures 8.10(b) and 8.11(b), the compounds without TESPT show a decrease in compound viscosities, due to a dominant effect of silica dispersibility. Epoxide groups can result in polar-polar interactions with silanol functionalities on the silica, and then lead to better compatibility of the mixes resulting in a lower filler-filler interaction and hence a reduction of compound viscosity as corresponding to Payne effect: see Figure 8.7. Apart from the polarity matching between silica and ENR, when TESPT is additionally applied in the compounds, the enhanced hydrophobation and additional lubrication effects in the ENR-13 and ENR-21 compounds also lead to a strong reduction in compound viscosity. The only slight change of compound viscosity in ENR-29 with varying TESPT contents points to the fact that this level of epoxide content is just enough to hydrophobize the silica surface and the addition of TESPT has only a minor additional effect on the properties.

Table 8.4 ML(1+4)100°C of normal NR and ENRs with various levels of epoxide functionality.

<table>
<thead>
<tr>
<th>Rubber type</th>
<th>ML(1+4)100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal NR (i.e. RSS 3)</td>
<td>72.9</td>
</tr>
<tr>
<td>ENR-13*</td>
<td>85.4</td>
</tr>
<tr>
<td>ENR-21*</td>
<td>89.0</td>
</tr>
<tr>
<td>ENR-29*</td>
<td>90.8</td>
</tr>
<tr>
<td>ENR-36*</td>
<td>93.4</td>
</tr>
<tr>
<td>ENR-43*</td>
<td>96.0</td>
</tr>
</tbody>
</table>

* mol% epoxide content

After the compounds show their optimum low compound viscosities due to the presence of appropriate combinations of either epoxide functionality or TESPT, other factors play a dominant role towards increased compound viscosities. The rise of compound viscosity can be mainly attributed to “the increment of network
contributions": Scheme 8.1. The ENRs with different levels of epoxide functionality have variable basic properties which certainly affect their compound viscosities. As shown in Table 8.4, the Mooney viscosities of the ENRs increase with increasing epoxide content, as the ENRs themselves possess a relatively high polarity in their structures, and so tend to form self-association via hydrogen bonding or polar interactions between either the same or neighboring molecules, and even self-crosslink due to the opening of the oxirane rings. Figure 8.20 shows the possible self-crosslinking of epoxidized natural rubber. This network generation contributes to the increase of compound viscosity.

Figure 8.20 Self-crosslinking of epoxidized natural rubber under acidic and high thermal conditions. In addition to the possibility of physical interactions generated between ENR and silica via polar-polar interactions, chemical silica-to-ENR coupling has been proposed, as reviewed in Chapter 2. For the compounds with TESPT coupling agent, strong chemical filler-rubber interaction can be formed through silane chemistry contributing to network structures. Moreover, TESPT can additionally release free sulfur into the system, and then cause light rubber-rubber crosslinking during the high thermo-mechanical mixing conditions as indicated earlier in Chapters 3 and 5. The combination of these factors which involve network formation leads to the increase in compound viscosities of silica-filled ENR systems.
8.5 CONCLUSIONS

The epoxide functionality on natural rubber molecules has a significant influence on both processing and end-use properties of silica-filled ENR compounds. The mixing torque, Payne effect, and compound viscosity remarkably decrease with the presence of epoxide functional groups up to 29 mol% on ENR compared to silica-filled normal NR compounds. A high content of epoxide groups, e.g. ENR-36 and ENR-43, adversely affects the processibility and most of the properties. Addition of TESPT into silica-filled ENRs with epoxide contents of 13 and 21 mol% further enhances compound processibility and vulcanizate properties, whilst the use of TESPT has the least effect on the ENR-29 compound. Based on the overall properties, epoxide groups on ENR alone can not provide the properties to match with those of silica-TESPT filled unmodified NR. But, the right combination of epoxide groups and TESPT as silane coupling agent leads to similar level of properties compared to the TESPT-normal NR system. With the synergistic effect of polar epoxide groups, the silane coupling agent loading needed can be reduced down to half or even lower compared to conventional silica-filled NR compounds.

8.6 REFERENCES