APPENDIX

VERIFICATION OF INTERACTIONS BETWEEN SILICA AND EPOXIDIZED SQUALENE AS A MODEL FOR EPOXIDIZED NATURAL RUBBER

Unmodified squalene (Sq) and epoxidized squalene (ESq), as models for natural rubber and epoxidized natural rubber, were mixed with silica in a reactor at 140 – 145 °C, which corresponds to the optimal mixing dump temperature of silica-filled NR or ENR compounds. The mixtures were prepared with and without TESPT silane coupling agent. The bound silica in the mixtures was extracted and checked for its composition by using Fourier-transform infrared (FT-IR) spectroscopy. The results indicate that Sq and ESq with the help of TESPT can chemically link to the silica surface, as the FT-IR spectra of purified bound silicas show absorption peaks of hydrocarbon structures. The epoxidized squalene also produces chemical interaction with silica in the absence of TESPT, but to a lesser extent compared to the one with TESPT, as indicated by the absorption intensity. On the other side, the silica in the Sq mixture without TESPT shows no traces of hydrocarbon, indicating that there is no noticeable chemical interaction involved.

INTRODUCTION

The main interactions between silica and polar rubbers come from hydrogen bonding or other interaction forces, e.g. polar-polar and Van der Waals forces.\textsuperscript{1-3} It has been reported in literature that polar rubbers can form strong chemical interaction or chemically link to silica particles at vulcanization temperatures, thus function as a coupling agent.\textsuperscript{4-8}

Manna \textit{et al.},\textsuperscript{7} and George \textit{et al.},\textsuperscript{8} have proposed a mechanism of reaction between epoxidized natural rubber (ENR) and silica, showing that at high temperature chemical linkages between the rubber and silica could be formed. In Chapter 8, the results showed that ENR with 20 – 30 mol% epoxidation as matrix requires less TESPT
silane coupling agent compared to TESPT needed for conventional NR compounds. The improvement in reinforcing efficiency of silica by using ENR can be mainly attributed to better silica dispersion as well as greater and stronger filler-rubber interaction enhanced by the polar epoxide groups. However, the evidence for filler-rubber interactions in polar rubber systems has not been clearly demonstrated.

The present experiments are executed to confirm the linkage type of filler-to-rubber interactions in silica-filled NR and ENR compounds in the presence and absence of TESPT silane coupling agent. Unmodified squalene (Sq) and epoxidized squalene (ESq) are used as model compounds for NR and ENR, respectively. The reactions between silica and model squalenes are carried out at high temperature to resemble the optimum rubber compound dump temperature. The bound silicas in the mixtures are extracted and analyzed for their compositions by using the FT-IR technique.

**EXPERIMENTAL**

**Materials**

Squalene, 98.0% (Alfa-Aesar, USA) was used as a model compound for NR. It contains 6 double bonds in a molecule as illustrated in Figure 1. Epoxidized squalene (ESq) was prepared in-house. The chemicals, i.e. formic acid, hydrogen peroxide, and Teric N30 used for ESq synthesis were the same as those applied for the preparation of ENR, as detailed in Chapter 8. Silica and bis-triethoxysilylpropyl tetrasulfide (TESPT) were the same as described in Chapter 3. Acetone (Lab-Scan, Ireland) and distilled water were also employed.

![Figure 1 Molecular structure of squalene.](image)

**Preparation and characterization of epoxidized squalene, ESq**

*Preparation of performic acid.* — For this reaction, the performic acid was separately prepared through the reaction between formic acid and hydrogen peroxide in a continuously stirred reactor at ambient temperature. 1 mol of formic acid was
added into the reactor which contains distilled water in a sufficient amount to dilute the obtained performic acid to 35% w/w. 1 mol of hydrogen peroxide was subsequently added dropwise. The entire amount of hydrogen peroxide was charged in a time period of about 3 h. The reaction was continued for 24 h.

**Epoxidation procedure.** — The epoxidation reaction of squalene was carried out in a stirred reactor at ambient temperature. 1 mol of squalene was charged into the reactor, followed by addition of 6 mol performic acid. The reaction mixture was continuously stirred over a time period of 24 h. After completion of the reaction, the resulting epoxidized squalene was neutralized by washing several times with water.

**Characterization of the ESq structure.** — The chemical structure and actual mol% epoxide of the product were characterized by means of the proton nuclear magnetic resonance (¹H-NMR) spectroscopic technique, as described in the experimental part of Chapter 8. The ¹H-NMR spectra of unmodified squalene and epoxidized squalene are shown in Figure 2.

![Figure 2](image)

**Figure 2** ¹H-NMR spectra of (a) unmodified squalene and (b) epoxidized squalene.

For the spectrum of pure squalene as shown in Figure 2(a), signal characteristics of the trans-1,4-isoprene unit appear at 1.6, 1.7, 2.1 and 5.1 ppm, which
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are assigned, respectively, to methyl-, methylene-, and alkene protons as indicated in the figure, according to Saito et al. After epoxidation of squalene two new peaks at 1.2 and 2.7 ppm are observed, which are assigned to protons associated with the epoxide ring as indicated in Figure 2(b). The epoxide content in ESq was calculated from the integral of absorption peaks at 2.7 and 5.1 ppm assigned to protons on the epoxide ring and on the double bonds, respectively, according to Equation 8.1. In this experiment, the integrals at chemical shifts of 2.7 and 5.1 ppm were 0.29 and 1.00, respectively. As a consequence, epoxidized squalene with 22.5 mol% epoxide content was achieved.

Reactions between squalene, epoxidized squalene and silica in the presence and absence of TESPT silica coupling agent

Reaction procedure. — Squalene and epoxidized squalene were used as the model compounds for NR and ENR, respectively. The reaction was performed at high temperature to mimic the mixing dump temperature that is required for silica-filled NR compounds, as reported in Chapter 3. The model compound was first introduced into a continuously stirred reactor which was positioned in an oil bath with the medium temperature of 145 °C. Subsequently, silica at 20 wt% relative to the amount of model compound was added and the reaction was continued for 1 h. In case of the compound with TESPT silane coupling agent, the silane was charged at 10 wt% relative to the silica content at the same adding moment as the silica.

Component separation. — After the reaction of the silica-model compound was completed, distilled water was added to separate the components in the mixture, since squalenes and silica are basically different in terms of specific gravity and degree of polarity. Squalene is a hydrocarbon molecule with a density of 0.86 g/cm³, so it is phase separated floating on water. Unmodified silica is hydrophilic, so silica will soon sink in water after water adsorption on its surface, as shown in Figure 3.
Verification of interactions between silica and functionalized natural rubber

Figure 3 Pure forms of A: silica; B: Sq; and C: ESq; (a) before and (b) after addition of water.

The separated layers in water of different compounds after heating at 145°C for 1 h are shown in Figure 4. The silica with its surface modified by squalene hydrocarbon moieties by chemical interaction or bonding is expected to be more hydrophobic and to be partly associated in the squalene or epoxidized squalene phase.

Figure 4 Mixtures of silica and model compounds after heating 1 h at 145°C and with and without TESPT; before (a) and after (b) component separations with water. A: ESq+silica; B: Sq+silica; C: ESq+silica+TESPT; and D: Sq+silica+TESPT.

The components in the silica-filled model compounds are clearly separated with water located in the middle as displayed in Figure 4. As previously demonstrated in Figure 3, the model squalene is separated as a top layer due to its lower specific gravity, while unmodified silica sinks into water due to its high hydrophilicity. However,
after the reaction, silica is visible in both the top and bottom layers in different proportions. The silica in the top layer, i.e. the squalene layer, indicates that the silica surface of these particles has been chemically modified by means of silica-to-model squalene interactions. A higher proportion of silica in the top layer implies that there is a greater extent of interaction/reaction in such a system.

Investigation of components present in the separate layers. — The divided layers of silica-filled model compounds in water as shown in Figure 4, were separately taken out of the reactor. Since squalene can well dissolve in acetone, the separated mixtures were washed 10 times by using 20 ml of acetone each time on filter paper with a fine particle retention of approximately 3 µm (grade no. 6). The residual solid on filter paper was dried in a vacuum oven at 100°C for 24 h. To make sure that the unbound squalene had been totally removed, the residual silica was further extracted with acetone using a Soxhlet extraction method for 24 h. After that the silicas obtained from both layers were again dried in a vacuum oven at 100°C for 24 h, and finally weighed.

The bound silicas obtained from the top layers under each condition were further analyzed by Fourier-transform infrared (FT-IR) spectroscopy in order to verify a trace of model squalenes, i.e. unmodified and epoxidized squalenes, chemically reacted onto the silica surface. The virgin forms of squalene, and modified squalene were also characterized. To characterize the original pure silica and purified bound silica obtained from the reactions, the potassium bromide or KBr disc sample preparation technique was used and the weight ratio between KBr powder and silica sample was kept constant to ensure an equal concentration in each sample analysis.

RESULTS AND DISCUSSION

Residual silica content in each separate layer

After purification of the residual silicas present in each layer of the mixtures, the quantities of silicas were determined, as illustrated in Figure 5.
Figure 5 shows the percent weight of silicas residing in each separated layer of mixtures. As discussed for Figure 4, the ability to float on water of silica particles/aggregates comes from the model compounds which are potentially either physically or chemically reacted onto the silica surface, and then assist the bound silica to move to the top layer, while unbound silica sinks to the bottom layer. In the absence of TESPT, the amount of silica in the top layer of epoxidized squalene is clearly higher compared to unmodified squalene. The results indicate that the epoxidized squalene has a greater or stronger interaction with silica than the unmodified squalene. The incorporation of TESPT significantly raises the bound silica in both unmodified and modified squalene, which can be seen in Figure 4, as well as reflected in the higher percentage of silica contained in the top layer compared to the mixtures without TESPT in Figure 5.

FT-IR spectra of unmodified, epoxidized squalenes and silica

The virgin forms of squalene, epoxidized squalene and silica as received were characterized for their molecular structures by the FT-IR technique.
**Figure 6** Absorbance spectra of virgin squalene and epoxidized squalene.

Comparing the FT-IR spectra of unmodified and epoxidized squalenes as depicted in Figure 6, epoxidized squalene shows additional peaks at 1240 and 870 cm\(^{-1}\) which are respectively assigned to C−O and \(\delta_{\text{C−CH}}\) vibrations on the oxirane rings in its structure. The absorption peak at 835 cm\(^{-1}\) is a characteristic peak of =C−H bending in the isoprene unit and the broad peak at 3400 cm\(^{-1}\) of epoxidized squalene is due to O−H stretching vibrations.

**Figure 7** FT-IR spectrum of pure silica.

The signals appearing in the spectrum of pure silica as shown in Figure 7 are listed in Table 1. The spectrum shows peaks at 800, 1110 and 1190 cm\(^{-1}\), which are
assigned to Si–O stretching vibrations. The signals of silanol groups (Si–OH) appear at 950 and 3400 cm\(^{-1}\). In addition, absorption bands at 3200 and 1610 cm\(^{-1}\) are observed as a result of stretching and deformation vibrations of adsorbed water molecules, respectively.

**Table 1** Infrared absorbance signals of silica and their assignments.\(^{10}\)

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>Si–O</td>
</tr>
<tr>
<td>950</td>
<td>Si–OH</td>
</tr>
<tr>
<td>1110, 1190</td>
<td>Si–O–Si</td>
</tr>
<tr>
<td>1610</td>
<td>O–H (water)</td>
</tr>
<tr>
<td>3200</td>
<td>O–H (water)</td>
</tr>
<tr>
<td>3400</td>
<td>Si–OH (hydrogen bonded)</td>
</tr>
</tbody>
</table>

**Characterization of bound silica**

The purified silicas obtained from the top layers were analyzed for their chemical structures by FT-IR; the infrared spectra are shown in Figure 8.

**Figure 8** Infrared spectra of silica, squalene, and purified bound silicas obtained from the top layer of silica and squalene mixtures, with and without TESPT.
All FT-IR analysis was carried out using an equal concentration of sample in the KBr powder to ensure that the intensity of the peaks is not affected by concentration according to the Beer-Lambert Law, but only influenced by the presence of different functional groups. In addition to the characteristic peaks of silica as summarized in Table 1, the modified silica from the mixture with TESPT shows weak absorption peaks at the wavenumbers of 1380, 1440, 2850, 2910 and 2960 cm\(^{-1}\) which correspond to the vibrations of C–H in the squalene structure. This indicates the presence of squalene bound to the silica surface. On the other side, squalene without TESPT does not react with silica as none of the characteristic peaks of C–H stretching and bending vibrations are observed. Based on this squalene model compound study, we can refer to the natural rubber that needs silane coupling agent to produce chemical filler-to-rubber bonds in the silica-filled system.

**Figure 9** Infrared spectra of silica, squalene, and purified bound silicas separated from the top layer of silica and epoxidized squalene mixtures with and without TESPT.

The FT-IR spectra of modified silicas that were separated from the mixtures of epoxidized squalene with and without TESPT are shown in Figure 9. The spectra of modified silicas from both mixtures display the signals of hydrocarbon bonds, i.e. at 1380, 1440, 2850, 2910, and 2960 cm\(^{-1}\) resembling the adsorption bands of squalene,
so indicating the chemical nature of the bond of model epoxidized squalene to silica. However, the intensities of the absorption bands are different from the virgin squalene case, reflecting a difference in concentration of epoxidized squalene bonds to the silica surface. The incorporation of TESPT into the ESq/silica mixture clearly enhances the content of hydrocarbon that is chemically attached to the silica surface. This implies that chemical interactions/bonding between silica and epoxidized natural rubber are increased by using TESPT in the practical rubber compounds.

Absorbance ratio between the signals of hydrocarbon bonds and Si-O in modified silicas

To compare the absorption intensity of hydrocarbon on silica, the absorbance ratio is calculated versus the peak at 800 cm$^{-1}$, which is assigned to Si-O of silica, as expressed in Equation 1:

\[
\text{Absorbance ratio} = \frac{A_x}{A_x + A_r}
\]

where $A_x$ is the absorbance peak height at $x$ cm$^{-1}$. 

$A_r$ is the absorbance peak height of a reference peak at 800 cm$^{-1}$.

An example of the measurement of absorbance peak height can be seen in Figure 10. The results of peak height ratios are shown in Figure 11.

**Figure 10** Example of measurement of absorbance peak height at 800, 1380, 1440, 2850, 2910 and 2960 cm$^{-1}$.
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Figure 11 Absorbance ratios at different peaks associated with vibrations of hydrocarbon bonds referred to Si-O bonds at 800 cm\(^{-1}\) in modified silicas.

The peaks at 1380 and 1440 cm\(^{-1}\) are assigned to C–H bending, while the ones at 2850, 2910, and 2960 cm\(^{-1}\) are due to C–H stretching vibrations. Figure 11 clearly shows that the systems with TESPT coupling agent provide a higher absorbance ratio indicating a higher extent of filler-rubber interaction, compared to the system which contains epoxide functional groups only, i.e. ESq. In the presence of TESPT, the absorbance ratios are larger when epoxidized squalene is used instead of unmodified squalene. The results support the conclusion drawn in Chapter 8 based on practical silica-filled epoxidized natural rubber compounds that the epoxide functional group and TESPT silane coupling agent provide synergistic effects on chemical filler-rubber interactions.

Proposed interactions of silica, model compounds, TESPT and water

With regard to the component separation of the mixtures as depicted in Figure 4, the characteristic features of silica aggregates/agglomerates dispersed in each layer can be proposed as shown in Figure 12.
Figure 12 Possible silica aggregates/agglomerates in each layer of the mixtures after component separation as experimentally observed in figure 4. A: ESq+silica; B: Sq+silica; C: ESq+silica+TESPT; and D: Sq+silica+TESPT.

Figure 12 shows different levels of silica in each layer of the mixtures as shown earlier in Figures 4 and 5. A spherical shape of silica aggregates/agglomerates is assumed as illustrated in Figures 12[i], 12[ii] and 12[iii]. With the evidence obtained from FT-IR analysis as shown in Figures 8 and 9, the interactions between silica-epoxidized squalene: Figure 12[i] and silica-squalene: Figure 12[ii] in the presence of TESPT silane coupling agent can be proposed as shown in Figure 13 and 14, respectively. In addition, hydrogen bonding between silica and water: Figure 12[iii] is also postulated in Figure 15.

Figure 13 Postulated interactions between silica and epoxidized squalene in the presence of TESPT as silane coupling agent.
CONCLUSIONS

Epoxidized squalene (ESq) with 22.5 mol% epoxidation was synthesized and used as a model compound for epoxidized natural rubber (ENR). Reactions between model squalenes, i.e. unmodified squalene (Sq) and ESq, and silica with and without TESPT silane coupling agent were carried out at 145°C according to the optimal mixing dump temperature for silica-filled NR or ENR compounds. Part of silica was surface modified by the model compounds and separated from the original silica which sank in water. The modified silica in the top layer was extracted with acetone to remove unbound hydrocarbons prior to characterization by the FT-IR technique. The FT-IR spectra of the purified modified silicas separated from the mixture of Sq with TESPT,
and ESq with and without TESPT display the characteristic absorption peaks of C–H in
the structure of model squalenes, indicating the presence of chemical silica-to-model
compound interactions or bonding, more so than when unmodified squalene is used.
This reflects the ability to create more strong/chemical filler-rubber interactions in silica-
filled ENR compounds under high thermal conditions during mixing and vulcanization
than in compounds based on unmodified NR, in either the presence or absence of
TESPT.

REFERENCES

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10. N. Hewitt, “Compounding precipitated silica in elastomers”, William Andrew Publishing,