Interactions between Silica and Epoxidized Natural Rubber with and without Silane

by Anke Blume*[1], Wisut Kaewsakul[1,2,], Kannika Sahakaro[2], Wilma K. Dierkes[1] and Jacques W.M. Noordermeer[1]

[1]Department of Elastomer Technology and Engineering, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

[2]Department of Rubber Technology and Polymer Science, Prince of Songkla University, Pattani Campus, 94000 Thailand

* Speaker

ABSTRACT

Unmodified squalene (Sq) and epoxidized squalene (ESq), as models for natural rubber and epoxidized natural rubber, were mixed with silica in the presence or absence of TESPT silane coupling agent. The results indicate that Sq and ESq with the help of TESPT can chemically link to the silica surface. 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. 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. Further 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.

INTRODUCTION

The introduction of the silica / silane technology in passenger car tires leads to a significant improvement in in-rubber properties like rolling resistance and wet traction but also to a challenge in processing. The challenge of using this technology is the combination of the polar silica-filler with a non-polar polymer blend. The most common way is to use a silane which can couple to the silica as well as to the polymer. But this implies that the tire manufacturers have to control to a greater extent a chemical reaction during the mixing process, the coupling of the silica to the silane. Therefore, many investigations were carried out to find alternatives. The chemical pre-treatment of silica surfaces is one [1, 2].

Another possibility is the use of polar polymers. The main interactions between silica and polar rubbers such as chlorosulfonated polyethylene (CSM),[3] carboxylated nitrile rubber (XNBR),[4] and epoxidized natural rubber (ENR)[5-7] come from hydrogen bonding or other interaction forces, e.g. polar-polar and Van der Waals forces.[8-10] 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.[11-15] The polar-modified rubbers can be used either as raw material[6,7] or as compatibilizer.[16, 17]

Polar polymers are normally not used in tire compounds. But especially for truck tires which contain mainly natural rubber (NR) the successful introduction of the silica / silane system has not been reached yet. Therefore, the use of functionalized NR could be an interesting alternative. Manna *et al.*,[14] and George *et al.*,[15] 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. 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. Even though filler-rubber interaction is generally analyzed by bound rubber measurement following the work of Wolff *et al.*[18] but in practical highly filled compounds in the presence of high molecular weight rubber, the bound rubber content can be deviated by the presence of filler network and gel. Furthermore, solubility of polar rubber in toluene will be differed from that of the non-polar ones. This work is therefore designed to simply demonstrate the occurrence of filler-rubber interaction through the use of model compounds having only low loading of silica without interference from any other compounding ingredients.

The first part of this study is 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.

In the second part of the study, 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.

EXPERIMENTAL SET-UP

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. Teric N30 is a non-ionic surfactant that was used to provide the squalene emulsion in water medium for epoxidation reaction. The silica ULTRASIL® 7005 and bis-triethoxysilylpropyl tetrasulfide (TESPT, Si 69®) were used for both parts of the study. Acetone (Lab-Scan, Ireland) and distilled water were also employed.

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 (50% w/w, Riedel-De Haën, Germany), alkylphenol ethoxylate or Teric N30 (Huntsman Corp. Australia Pty., Australia), and commercial grade methanol (J.T. Baker, USA).
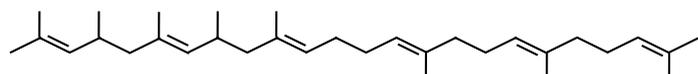

FIG. 1 – Molecular structure of squalene

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 10 °C in an ice-cooled water bath. M-CPBA was used as a catalyst. 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 diluted with 1 wt% Teric N30 in water to reach a 50 wt% concentration. This dilution 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 the reaction was reached, the resulting epoxidized squalene was washed several times with water till its pH-value is constant at 7.

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 (^{1}H-NMR) spectroscopic technique. The spectra were recorded with a Fourier Transform NMR spectrometer (500 MHz, Unity Inova, Varian, Germany) at room temperature using deuterated chloroform as a solvent for sample preparation. The ^{1}H-NMR spectra of unmodified squalene and epoxidized squalene are shown in Figure 2.
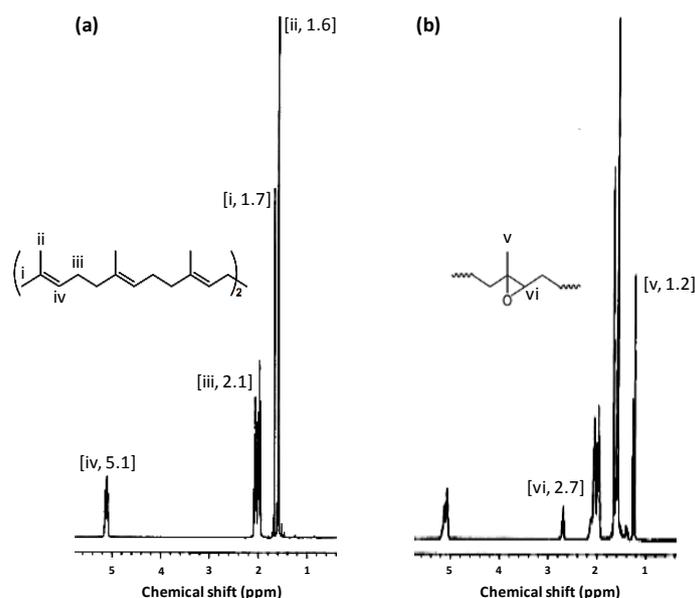
FIG. 2 – ^{1}H-NMR spectra of (a) unmodified squalene and (b) epoxidized squalene

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 are assigned, respectively, to methyl-, methylene-, and alkene protons as indicated in the figure, according to Saito *et al.*[19] 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 1[21]:

$$Epoxide\ content\ (mol\%) \quad = \quad \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \quad x \quad 100 \quad (Equation\ 1)$$

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 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. The epoxidized squalene contains different structures like a terminal epoxidized unit, an internal epoxidized unit or both.

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. Firstly, the epoxidized squalene was dried in a vacuum oven at 60 °C for 48 h until constant weight. Secondly, the model compound was 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/cm^3, 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.
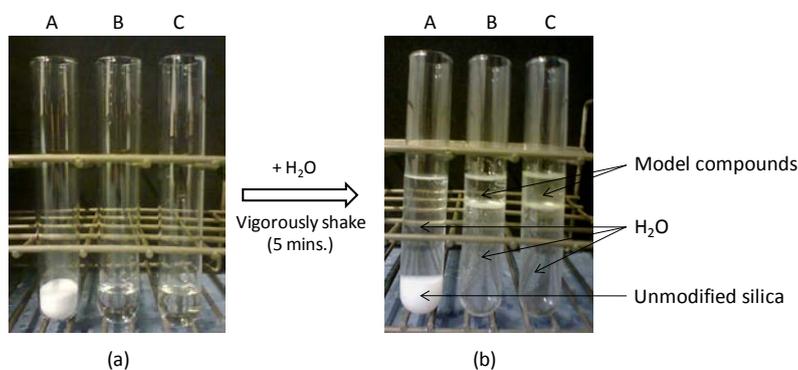

FIG. 3 – Pure forms of A: silica; B: Sq; and C: ESq; (a) before and (b) after addition of water

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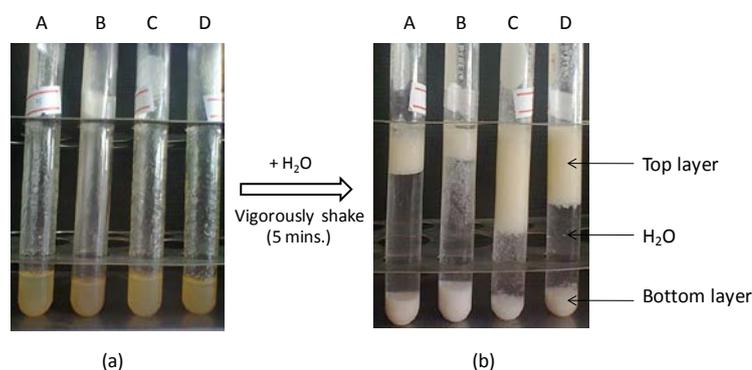
FIG. 4 – Mixtures of silica and model compounds after heating 1 h at 145 °C and with and without TESPT; before (a) and after (b) component separations with water. A: ESq+silica; B: Sq+silica; C: ESq+silica+TESPT; and D: Sq+silica+TESPT

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 (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 silica obtained from both layers were again dried in a vacuum oven at 100 °C for 24 h, and finally weighed.

The bound silica 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.

Preparation and characterization of epoxidized natural rubber

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 (H_2O_2) inside the reactor. The recipe used for this synthesis is given in Table 1.

The epoxidation reaction as shown in Figure 5 was carried out in a continuously stirred reactor, at a temperature of 40°C. The latex was first diluted to 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,[10] 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.
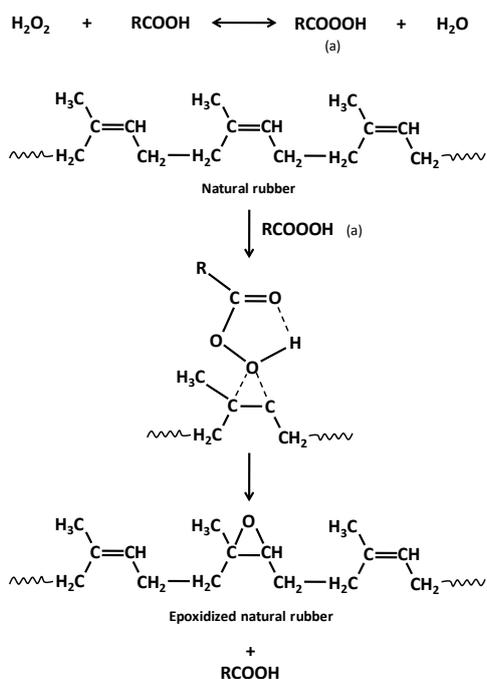

FIG. 5 – Mechanism of epoxidation reaction in the preparation of the ENRs[22]

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.
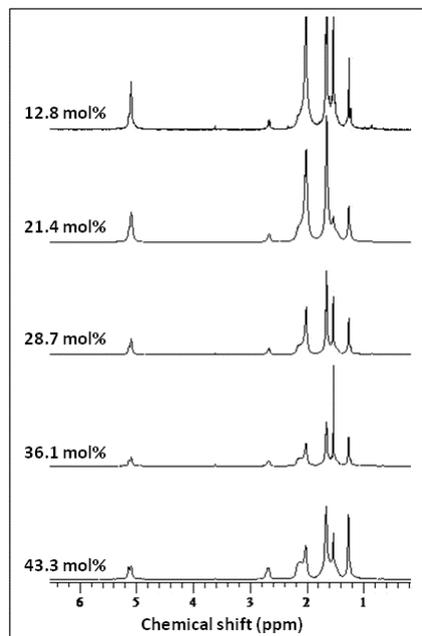

FIG. 6 – ¹H-NMR spectra of the ENRs with various levels of epoxide functionality

Characterization of the ENR structure. — The ¹H-NMR technique was used 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 6. 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 6). 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 1[21].
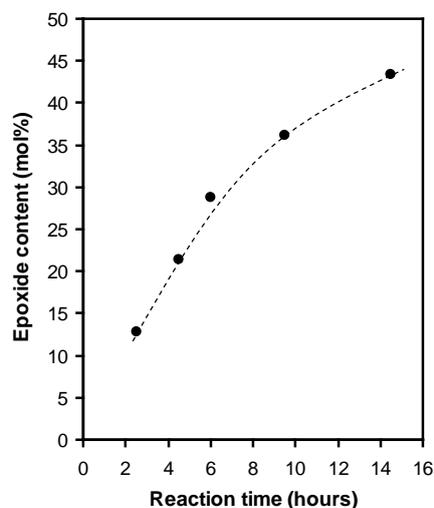
FIG. 7 – Epoxide content in ENRs as a function of epoxidation reaction time

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 2 and Figure 7.

Compound preparation

The effect of the degree of epoxidation in the ENRs was investigated in parallel with variation of the TESPT concentrations. Table 3 shows the compound formulation used in this study. All silica-filled ENR compounds were prepared in an internal mixer with a chamber of 500 cm³ (Chareon Tut Co., Thailand), fill factor = 0.7, rotor speed = 60 rpm, initial temperature at 100 °C and controlled dump temperature at 140 – 145 °C. NR or ENR was initially masticated for 2 min. Then, half of the silica and silane was added and mixed for 5 min, prior to adding the second half of the silica and silane together with TDEA oil and mixed for another 5 min. Subsequently, ZnO, TMQ and DPG were added and mixed for 3 min. The compounds were then dumped, sheeted out on a two-roll mill and kept overnight. The accelerators and the sulfur were added in a second stage on a luke-warm two-roll mill. The unmodified NR (i.e. Ribbed Smoked Sheet 3, RSS 3) compounds with and without TESPT were prepared in the same way and treated as a reference.

RESULTS

Residual silica content in each separate layer of the model experiments

After purification of the residual silicas present in each layer of the mixtures with squalene or epoxidized squalene in the model study, the quantities of silicas were determined, as illustrated in Figure 8.
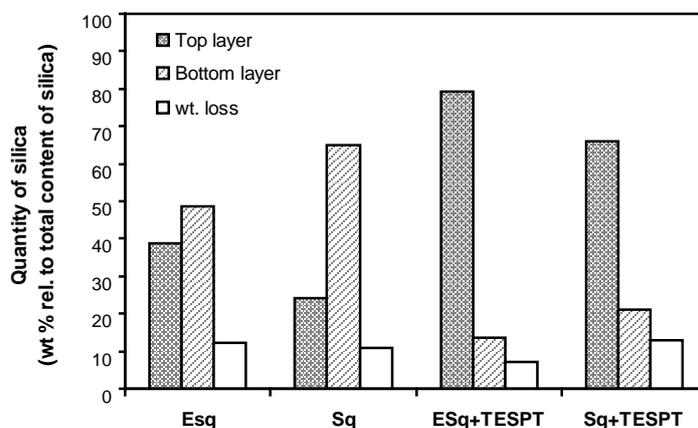

FIG. 8 – Quantity of residual silicas consisting in each separated layer of the mixtures

Figure 8 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 8.

The FT-IR study confirmed that the systems with TESPT coupling agent provide 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. This means that the epoxide functional group and TESPT silane coupling agent provide synergistic effects on chemical filler-rubber interactions.

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. All ENR compounds show lower mixing torques compared to normal NR either with or without TESPT used, as observed in Figure 9. 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 min, 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.
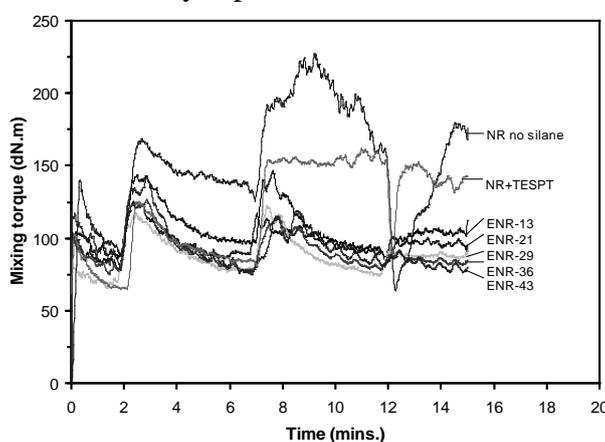
FIG. 9 – Mixing torques of silica-filled ENR compounds with various epoxide contents, as indicated for each line. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are considered as references

The epoxide functionality on NR molecules increases their polarity,[23] 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.
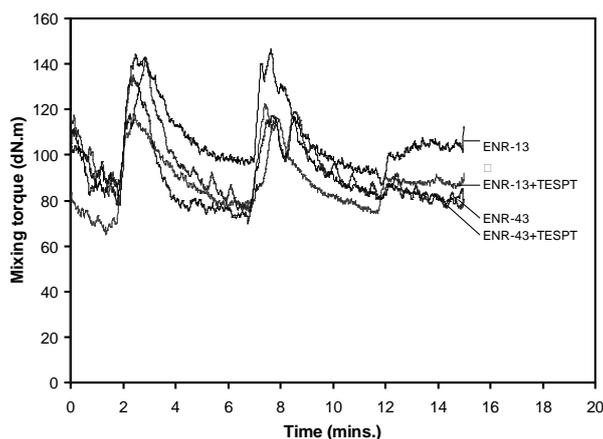
FIG. 10 – Mixing torques of silica-filled ENR compounds with 13 and 43 mol% epoxide contents, compared between the ones with and without TESPT at 9 wt% relative to the silica content, as indicated for each line

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 10 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.

Filler-filler interaction and network contributions

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.[24] The Payne effect of the silica-filled ENR compounds with and without TESPT is shown in Figure 11. Figure 11(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 11(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.[25] For ENR-36 and ENR-43, the Payne effect slightly decreases with increasing TESPT loading, as a result of a dilution effect.
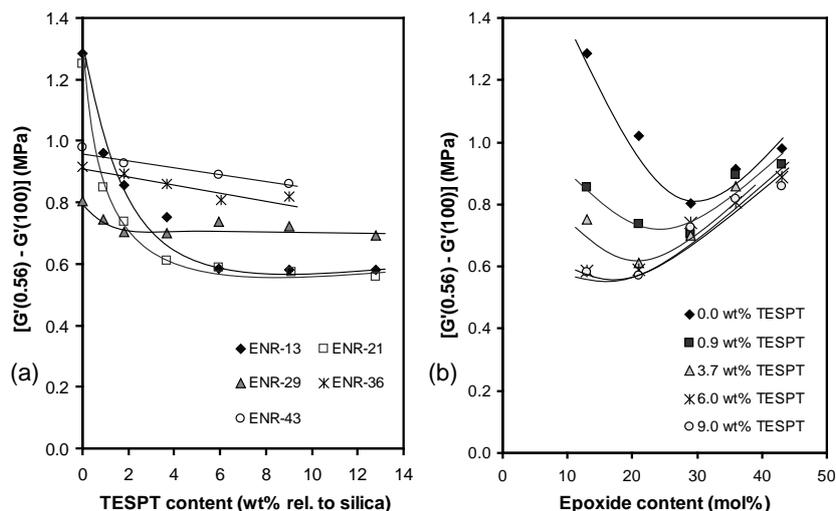
FIG. 11 – Payne effect as functions of (a): TESPT content; and (b): epoxide content in the ENR compounds

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 11(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.

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,[24] as depicted in Figure 12.
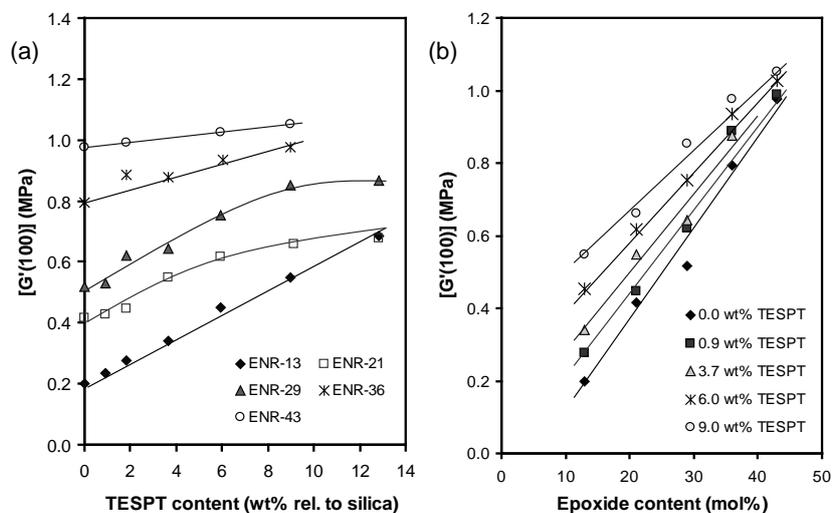
FIG. 12 – Storage modulus at 100% strain as functions of (a): TESPT amount; and (b): epoxide content in ENRs for the silica-filled ENR compounds

It can be seen that higher amounts of TESPT and stronger polarity of the ENRs: Figures 12(a) and 12(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.

Compound viscosity and cure characteristics

Mooney viscosity. — Mooney viscosities of the compounds prepared with the various ENRs containing different levels of epoxide functionality are shown in Figure 13.
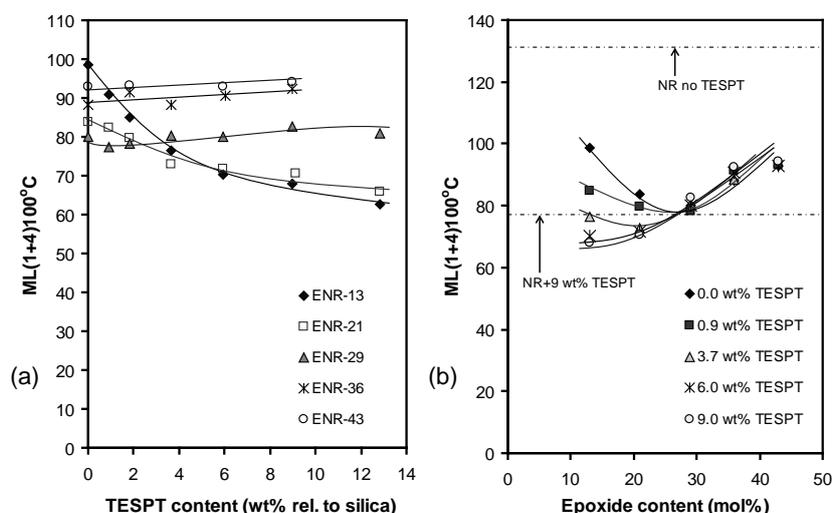
FIG. 13 – Mooney viscosities as functions of (a): TESPT content; and (b): epoxide content in ENRs. Silica-filled normal NR compounds without and with TESPT at 9 wt% relative to the silica content are shown as references by dashed lines

The influence of silane loading at a given epoxide content can be seen in Figure 13(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 13(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 13(b).

The change of Mooney viscosities with regard to epoxide group contents and TESPT loading as shown in Figure 13 resembles very much the various Payne effects as displayed in Figure 11. 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.

End-use properties of the compounds

Dynamic mechanical properties. — Tan δ at 60 ^{o}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 ^{o}C as shown in Figure 14.
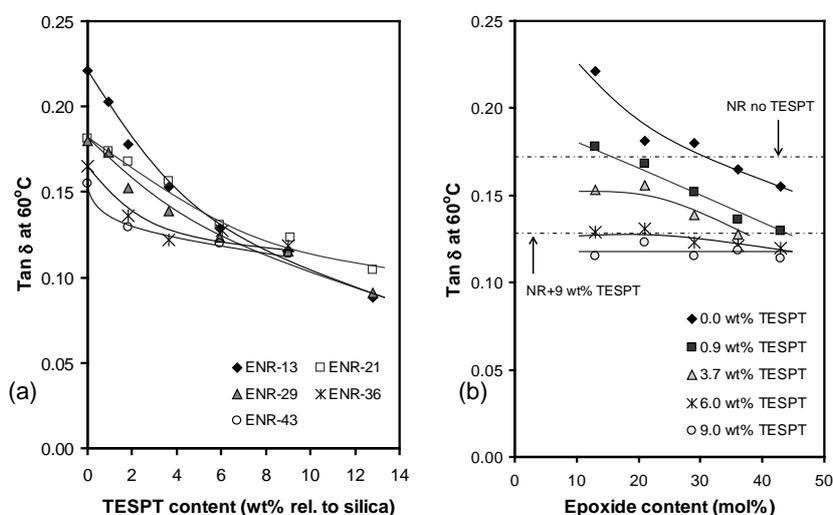
FIG. 14 – Tan δ at 60 °C as functions of (a): TESPT amount; and (b): epoxide content in ENRs

The influence of silane content on tan δ at 60 ^{o}C at a given epoxide level can be seen in Figure 14(a). Increase of the TESPT loading results in a sharp decrease in tan δ at 60 ^{o}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 δ 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. Without TESPT, the increase of epoxide contents leads to a strong decrease in tan δ at 60 ^{o}C as visualized in Figure 14(b). This can be linked to the greater filler-rubber interaction/network formation. The combination of epoxide functionality with TESPT silane coupling agent jointly improve the tan δ at 60 ^{o}C or rolling resistance of tires. Therefore, there is a possibility to reduce the amount of TESPT needed in silica-filled ENR formulations.

Mechanical properties. — 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 15(a). A further increase of TESPT loading results in a decrease in reinforcement index. In Figure 15(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. 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.
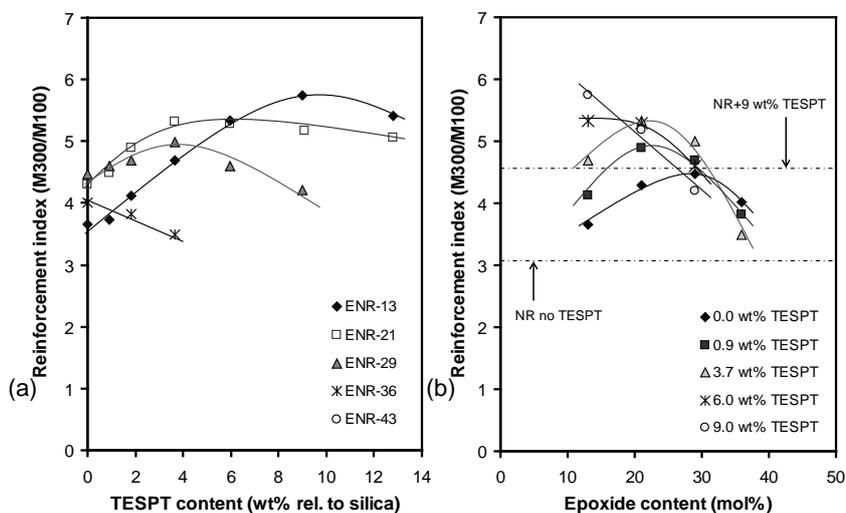

FIG. 15 – Reinforcement index as functions of (a): TESPT amount; and (b): epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references

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 1.
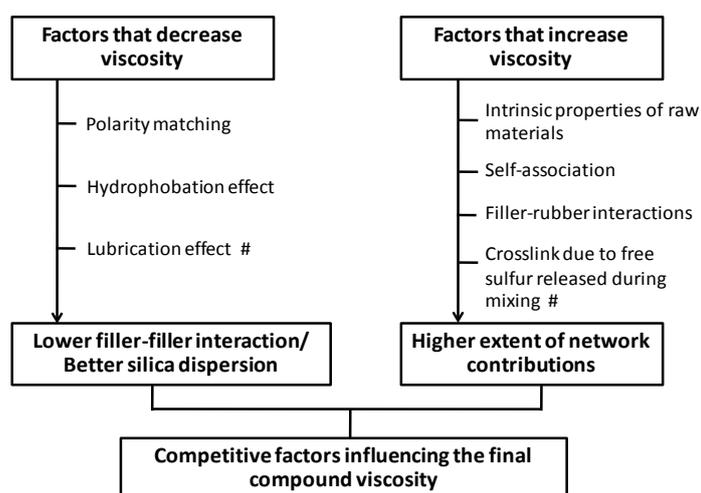
SCHEME 1 – Competitive factors influencing compound viscosities of silica-filled ENR compounds with and without TESPT silane coupling agent

The change in compound viscosities as indicated by Mooney viscosity and rheometer minimum torque 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 Figure 13(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 11. 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. In general, 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.[25] Figure 16 shows the possible self-crosslinking of epoxidized natural rubber. This network generation contributes to the increase of compound viscosity.
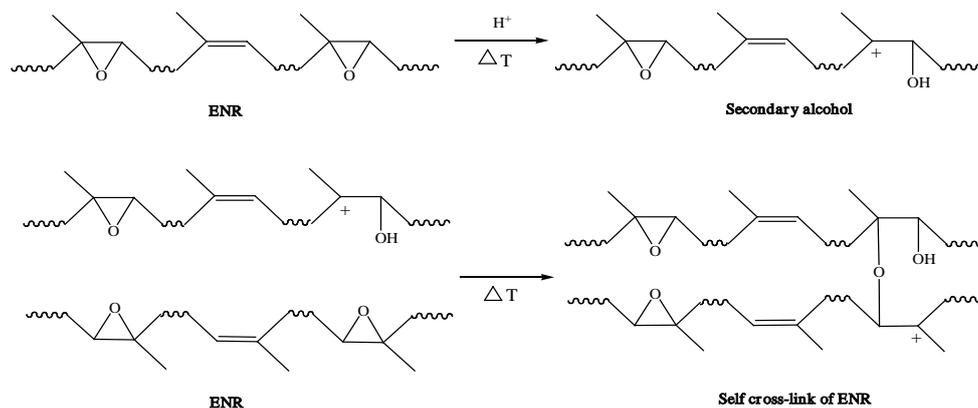
FIG. 16 – Self-crosslinking of epoxidized natural rubber under acidic and high thermal conditions[25]

In addition to the possibility of physical interactions generated between ENR and silica *via* polar-polar interactions, chemical silica-to-ENR coupling can occur.[6,7] 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. The combination of these factors which involve network formation leads to the increase in compound viscosities of silica-filled ENR systems.

SUMMARY AND 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 investigated at 145°C according to the optimal mixing dump temperature for silica-filled NR or ENR compounds. The FT-IR spectra of the purified modified silicas separated from the mixture of Sq with TESPT, and ESq with and without TESPT indicated the presence of chemical silica-to-model compound interactions or bonding, even more when

ummodified squalene was 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.

With the evidence obtained from FT-IR analysis, the interactions between silica and epoxidized squalene or squalene respectively can be proposed as shown in Figure 17 and 18.
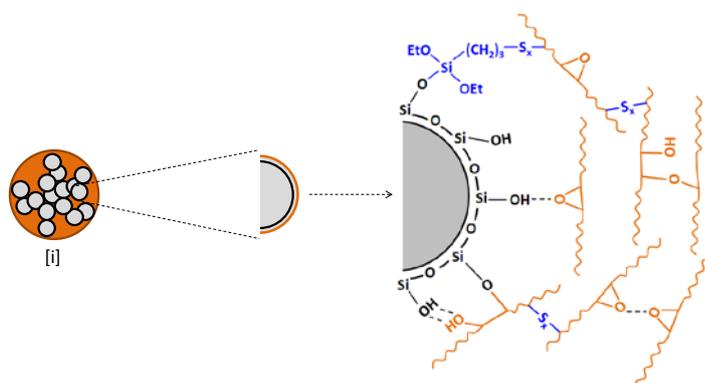

FIG. 17 – Postulated interactions between silica and epoxidized squalene in the presence of TESPT as silane coupling agent
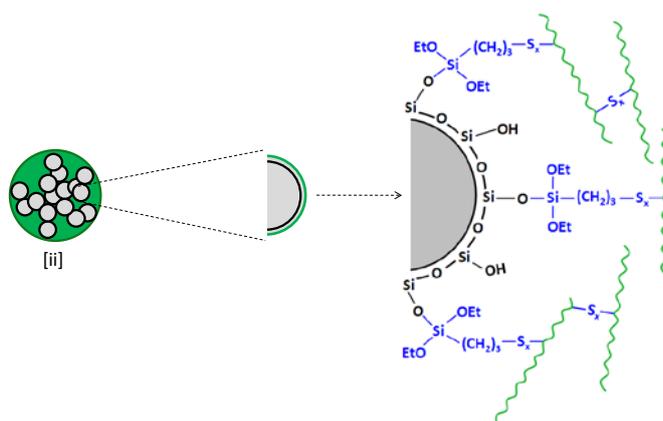
FIG. 18 – Postulated interactions of silica and squalene in the presence of TESPT as silane coupling agent

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 cannot 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 in-rubber properties compared to the TESPT-normal NR system but by having a significant improved processing behavior. 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.

Tab. I

Recipe for ENR synthesis

Ingredients	Quantity	
	mole	g
HA latex (60 wt% DRC)	2.0	226.7
Hydrogen peroxide (50% w/w)	4.0	272.0
Formic acid (94% w/w)	1.0	48.9
Teric N30 (10% w/w)	-	15.0[a]

[a] *approximately 1.0 phr*

Table II

Degree of epoxidation of ENRs at varying reaction times

Reaction time (h)	Mol% epoxide (by ^{1}H-NMR)	Notation
2.5	12.8	ENR-13
4.5	21.4	ENR-21
6.0	28.7	ENR-29
9.5	36.1	ENR-36
14.5	43.3	ENR-43

Table III
Compound formulation

Ingredient	Dosage (phr)
Rubber (ENRs[a] or NR)	100.0
ZnO	3.0
Stearic acid	1.0
TMQ	1.0
Ultrasil 7005	55.0
TESPT	Variable[b]
TDAE oil	8.0
DPG	1.1
CBS	1.5
Sulfur	1.5

[a] *ENRs with 12.8, 21.4, 28.7, 36.1, and 43.3 mol% epoxide were studied.*
[b] *The quantity of TESPT used for each ENR compound was varied from 0 – 12 wt% relative to the silica content.*

REFERENCES

[1] H.-D. Luginsland, J. Fröhlich, and A. Wehmeier, RUBBER CHEM. TECHNOL. **75**, 563 (2002)

[2] Y. Bomal, P. Cochet, B. Dejean, and J. Machurat, *Rubber World* **208**, 33 (1993)

[3] A. Roychoudhury, P.P. De, N. Roychoudhury, and A. Vidal, *Rubber Chem. Technol.*, **68**, 815 (1995).

[4] S. Bandyopadhyay, P.P. De, D.K. Tripathy, S.K. De, *Rubber Chem. Technol.*, **69**, 637 (1996).

[5] S. Varughese, D.K. Tripathy, *J. Appl. Polym. Sci.*, **44**, 1847 (1992).

[6] A.K. Manna, A.K. Bhattacharyya, P.P. De, D.K. Tripathy, S.K. De, D.G. Peiffer, *Polymer*, **39**, 7113 (1998).

[7] A.K. Manna, P.P. De, D.K. Tripathy, S.K. De, D.G. Peiffer, *J. Appl. Polym. Sci.*, **74**, 389 (1999).

[8] F. Cataldo, *Macromol. Mater. Eng.*, **287**, 348 (2002).

[9] K. Sahakaro, S. Beraheng, *J. Appl. Polym. Sci.*, **109**, 3839 (2008).

[10] S.S. Choi, K.H. Chung, C. Nah, *Polym. Adv. Technol.*, **14**, 557 (2003).

[11] A. Roychoudhury, P.P. De, N. Roychoudhury, A. Vidal, *Rubber Chem. Technol.*, **68**, 815 (1995).

[12] S. Bandyopadhyay, P.P. De, D.K. Tripathy, S.K. De, *Rubber Chem. Technol.*, **69**, 637 (1996).

[13] S. Varughese, D.K. Tripathy, *J. Appl. Polym. Sci.*, **44**, 1847 (1992).

[14] A.K. Manna, A.K. Bhattacharyya, P.P. De, D.K. Tripathy, S.K. De, D.G. Peiffer, *Polymer*, **39**, 7113 (1998).

[15] K.M. George, J.K. Varkey, K.T. Thomas, N.M. Mathew, *J. Appl. Polym. Sci.*, **85**, 292 (2002).

[16] K.M. George, J.K. Varkey, K.T. Thomas, N.M. Mathew, *J. Appl. Polym. Sci.*, **85**, 292 (2002).

[17] S.S. Choi, K.H. Chung, C. Nah, *Polym. Adv. Technol.*, **14**, 557 (2003).

[18] Wolff, S., Wang, M.J., and Tan, E.H. (1993) Filler–elastomer interaction. Part VII. Study on bound rubber. Rubber Chem. Technol.,66, 163-177.

[19] T. Saito, W. Klinklai, S. Kawahara, *Polymer*, **48**, 750 (2007).

[20] N. Hewitt, "Compounding precipitated silica in elastomers", William Andrew Publishing, New York, p.15 (2007).

[21] S.N. Gan, A. Hamid, *Polymer*, **38**, 1953 (1997).

[22] A.S. Hashim, S.K. Ong, R.S. Jessy, *Natuurrubber,* **28** (2002).

[23] I.R. Gelling, A.L. Tinker, H.B.A. Rahman, *J. Nat. Rub. Res.*, **6**, 20 (1991).

[24] A.R. Payne, *Rubber Plast. Age*, **42**, 963 (1961).

[25] S.C. NG, L.H. Gan, *Eur. Polym. J.*, **17**, 1073 (1981).