REDUCED ETHANOL EMISSIONS BY A COMBINATION OF EPOXIDIZED NATURAL RUBBER AND SILANE COUPLING AGENT FOR SILICA-REINFORCED NATURAL RUBBER-BASED TIRE TREADS

K. SENGLOYLUAN,[1,2] K. SAHAKARO,[1,2*] W. K. DIERKES,[2] J. W. M. NOORDERMEER[2]

[1]DEPARTMENT OF RUBBER TECHNOLOGY AND POLYMER SCIENCE, FACULTY OF SCIENCE AND TECHNOLOGY, PRINCE OF SONGKLA UNIVERSITY, PATTANI CAMPUS 94000, THAILAND

[2]DEPARTMENT OF ELASTOMER TECHNOLOGY AND ENGINEERING, FACULTY OF ENGINEERING TECHNOLOGY, UNIVERSITY OF TWENTE, 7500AE ENSCHEDE, THE NETHERLANDS

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ABSTRACT

In an attempt to reduce the high volatile organic compound (ethanol) emissions from silica-reinforced NR compounds, this work aimed to, at least partially, replace the use of large quantities of silane coupling agent bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT). The use of 7.5 phr of epoxidized natural rubber (ENR-51) as compatibilizer between NR and silica enhances the properties, which can be further improved by half or even lower amounts than required with TESPT alone. The properties obtained with TESPT are nearly matched, except for steric limitations imposed upon the ENR molecules to cap the silanol groups on the silica surface to the same extent as TESPT can do. Furthermore, TESPT donates reactive elemental sulfur to the compound during vulcanization, which needs to be compensated for in use with ENR. [doi:10.5254/rct.16.84813]

INTRODUCTION

Silica-reinforced rubber compounds offer better wet traction and lower rolling resistance for passenger tire treads compared with their carbon black–filled counterparts.[1,2] However, silica mixing requires longer times and higher temperatures than does carbon black–containing compounds. Moreover, silica-filled, hydrocarbon rubber compounds, without any coupling agent as a compatibilizer, suffer from poor silica dispersion because of the strong filler–filler interactions, which result in inferior mechanical properties. To enhance the compatibility between silica and nonpolar rubbers, a silane coupling agent or polar rubber, such as NBR,[3] CR,[4] and epoxidized natural rubber (ENR),[5] can be used as compatibilizer. The most widely used silane coupling agent in silica-filled compounds cured with a sulfur system is bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT). This sulfur-containing, silane coupling agent also acts as a sulfur donor to promote crosslinking. Under optimal mixing conditions, the use of TESPT effectively reduces filler–filler interaction and enhances silica–rubber interaction.[6,7] The silica–silane combination leads to good silica dispersion and significant improvement in mechanical and dynamic properties because of the rubber–silica bonds bridged by TESPT.[8] However, the use of TESPT causes the release of substantial amounts of volatile organic compounds (ethanol) during mixing and later during vulcanization, which are an environmental burden and are a potential cause for porosity in cured vulcanizates. The removal of this ethanol is a major technical challenge.[9]

Epoxidized NR shows a higher polarity than original NR because of the epoxy groups in its structure. Its viscosity and polarity increase with increasing epoxy content.[10] Epoxidized NR has been used as compatibilizer in filled systems, such as NR–organoclay nanocomposites[11,12] in which the use of ENR improved the filler–rubber interaction and the filler dispersion in the matrix. The improved compatibility between filler and rubber subsequently improved the physical and mechanical properties of the nanocomposites.[11,12] Silica-filled ENR shows significantly improved

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*Corresponding author. Ph: +66-7-331-2213; email: kannika.sah@psu.ac.th

mechanical properties when compared with a silica-filled NR counterpart without silane because of the interaction of ENR and silica through hydrogen bonds.[13] In addition, chemical bonding between epoxy groups of ENR and silanol groups of silica can take place during molding at high temperatures[3] or during mixing at 150–170 °C.[5,14]

In prior studies, the addition of ENR as compatibilizer in silica-filled NR compounds enhanced both processing and vulcanizate properties.[15] However, the properties were still inferior compared with the reference compound with TESPT as the coupling agent. This can partly be attributed to the influence of network formation within the material: the TESPT-containing compounds obtain a contribution from the reactive, elemental sulfur that is released from the TESPT during mixing and later during vulcanization, resulting in greater network density. A cooperative effect of epoxide groups in ENR and TESPT on the reinforcing efficiency of silica-filled ENR compounds was recently reported.[16] The use of epoxidized low molecular weight natural rubber (ELMWNR) as a compatibilizer in silica-filled NR compounds reduced the Payne effect and improved the mechanical properties when compared with an uncompatibilized system.[17] In addition, the effect of extra sulfur added into the silica-filled NR compounds compatibilized with ELMWNR was reported to enhance modulus and tensile strength as well as to reduce the loss tangent at 60 °C.[18]

As shown in our previous report,[15] the use of 7.5 phr of ENR with 51 mol% of epoxide (ENR-51) as a compatibilizer showed the best overall properties of the silica-filled NR compounds but was still somewhat inferior to those of a reference with TESPT alone. This present work, therefore, investigated the use of 7.5 phr of ENR-51 in combination with TESPT at varying amounts, without and with sulfur compensation to further enhance the properties. The compensation was applied by adding elemental sulfur into the compound to adjust the total sulfur content, equal to the sulfur contained in the reference system.

EXPERIMENTAL

MATERIALS

The rubbers used were NR (ribbed smoked sheet number 3), locally produced in Thailand, and ENR-51, which was prepared in-house, as described in our previous report.[15] The compounding ingredients were highly dispersible silica (Zeosil 1165MP, Solvay, Collonges-au-Mont-d'O, France), TESPT (Evonik Industries, Essen, Germany), treated distillate aromatic (TDAE) extract oil (Hansen & Rosenthal, Hamburg, Germany), *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Brussels, Belgium), ZnO, stearic acid, and sulfur (all from Sigma-Aldrich Chemie, Darmstadt, Germany).

COMPOUND PREPARATION

Rubber compounds were prepared using the formulations as shown in Table I. Mixing was carried out using an internal mixer (Brabender Plasticorder 350S, Brabender, Duisburg, Germany) with an initial mixer temperature of 110 °C, rotor speed of 60 rpm, according to the mixing procedure shown in Table II. The silica-filled NR compounds, with and without TESPT, and without ENR, were prepared and treated as references.

MOONEY VISCOSITY, PAYNE EFFECT, AND FLOCCULATION RATE CONSTANT OF UNCURED COMPOUNDS

The Mooney viscosity [ML (1+4), 100 °C] of the uncured silica-filled compounds was tested using a Mooney viscometer (MV 2000VS, Alpha Technologies, Akron, OH, USA) according to ASTM Standard D 1646. The Payne effect or filler–filler interaction was studied by using a rubber

TABLE I
COMPOUND FORMULATIONS

Ingredients	Parts,[a] phr			
	None	TESPT	ENR + TESPT	ENR + TESPT + S[b]
RSS3, Natural Rubber	100.0	100.0	92.5	92.5
ENR-51	—	—	7.5	7.5
TESPT	—	4.7*	1.1–2.7**	1.1–2.7**
Zeosil 1165MP	55.0	55.0	55.0	55.0
TDAE oil	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0
TMQ	1.0	1.0	1.0	1.0
Stearic acid	1.0	1.0	1.0	1.0
DPG	1.0	1.0	1.0	1.0
CBS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	2.3–1.9***

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

[b] S, sulfur.

process analyzer (RPA 2000, Alpha Technologies) at 100 °C and a frequency of 0.5 Hz, with varying strains in the range of 0.56 to 100%. The differences in storage moduli at low strain (i.e., 0.56%) and high strain (i.e., 100%) are reported.

The flocculation rate constant (k_a) was studied with the RPA at 100 °C, strain 0.56%, frequency 1.00 Hz, and the test time was 12 min. The k_a value[19] was calculated as follows in Eqs. 1 and 2:

$$x = \frac{G'(t) - G'(i)}{G'(f) - G'(i)} \tag{1}$$

where x is the degree of flocculation, $G'(t)$ is the storage modulus at 0.56% strain at test time t, $G'(i)$ is the storage modulus after preheating for 1 min, and $G'(f)$ is the storage modulus after heating for 12 min.

$$k_a = \frac{\ln(1 - x_1) - \ln(1 - x_2)}{t_2 - t_1} / \text{min} \tag{2}$$

TABLE II
TWO-STEP MIXING PROCEDURE

Mixing procedure	Time, min
Step 1: internal mixer	
· NR and ENR mastication	2
· Addition of the first half of silica + TESPT	5
· Addition of the second half of silica + TESPT and TDAE oil	5
· Addition of ZnO, stearic acid, and TMQ	3
Step 2: two-roll mill	
· Addition of DPG, CBS, and sulfur	5

where x_1 and x_2 are the degrees of flocculation at different heating times, namely, t_1 and t_2, respectively.

MEASUREMENT OF BOUND RUBBER CONTENT

Bound rubber content was measured according to the method described in details in our previous report,[15] following the work of Wolff et al.[20] The ammonia treatment was done to cleave the physical linkages between rubber and silica to determine the chemically bound rubber.

CURE CHARACTERISTICS AND TENSILE PROPERTIES

Vulcanization or cure properties of the compounds were studied with the RPA at 150 °C, frequency 0.833 Hz, and 2.79% strain for 30 min. The compounds were then vulcanized to their respective optimum cure times (t_{c90}) with a Wickert WLP 1600 laboratory compression press (Wickert Maschinenbau GmbH, Landau in der Pfalz, Germany) at 150 °C and 100 bar into 2-mm-thick sheets. Type 2 dumbbell test specimens were die-cut from the press-cured sheets, and tensile tests were carried out with a Zwick Roell Group (Ulm, Germany) tensile tester (model Z1.0/TH1S) at a crosshead speed of 500 mm/min according to ASTM Standard D 412.

DYNAMIC MECHANICAL PROPERTIES

Dynamic mechanical properties of silica-filled NR vulcanizates were characterized with a Metravib Viscoanalyzer VA 2000 (ACOEM, Paris, France). The samples were cut into 6- × 4- × 2-mm^3 specimens and tested in tension mode with a temperature sweep from –80 °C to 80 °C at a frequency of 10 Hz and 0.1% strain.

SCANNING ELECTRON MICROSCOPE ANALYSIS OF SILICA-FILLED NR VULCANIZATES

Scanning electron microscope (SEM) analysis was performed with two different sets of specimens. First, compounds containing 30 phr of silica and (1) without any compatibilizer, (2) with 7.5 phr ENR-51, (3) with 7.5 phr ENR-51 and TESPT 4 wt% relative to silica, and (4) with TESPT 8.6 wt% relative to silica were prepared using the formulation shown in Table I, except for the lower amount of silica. The compounds were vulcanized to their optimum cure times to produce a thin sheet of 1–2 mm thickness, immersed in liquid nitrogen, and cryogenically cracked. The newly cracked surface was gold-coated before being analyzed by SEM (Quanta 400, FEI, Hillsboro, OR, USA). A second set of vulcanized specimens was taken from tensile-fractured test pieces, which contained 55 phr of silica, that is, the normal silica content used in this study. The tensile-fractured surface was also coated with gold before being analyzed.

RESULTS AND DISCUSSION

MOONEY VISCOSITY, PAYNE EFFECT, AND FLOCCULATION TENDENCY

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

Without extra sulfur, the incorporation of 2 wt% TESPT relative to silica into the silica-reinforced NR compounds leads to a decrease in Mooney viscosity. A further increase of TESPT content shows no additional effects on this property. The compounds with extra sulfur showed no

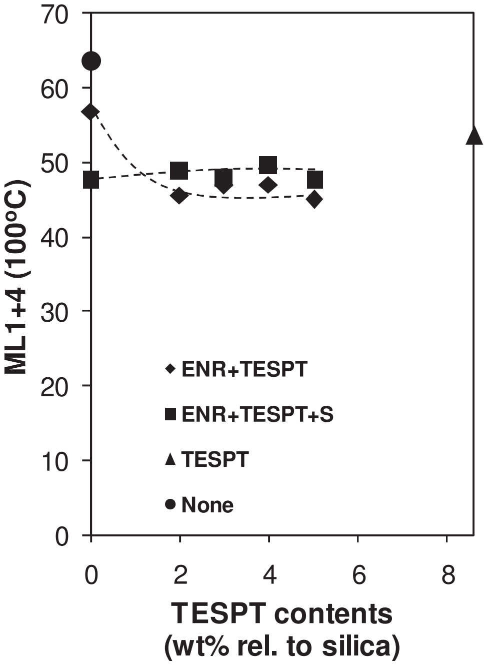

FIG. 1. — Mooney viscosity of silica-filled NR compounds with 7.5 phr of ENR-51 as compatibilizer in combination with TESPT with and without sulfur compensation.

change in Mooney viscosity with increasing silane content, and the values were marginally higher than that of the silica-filled NR compounds with no extra sulfur. All of the compounds with ENR-51/TESPT combinations, either with or without extra sulfur, showed lower Mooney viscosities when compared with the reference compound at 4.7 phr TESPT. The lower Mooney viscosity may be attributed to a better filler distribution causing smaller silica aggregates and less resistance to flow. As the sulfur was added in the second step of the mixing on a two-roll mill, a premature crosslinking reaction is unlikely to have taken place, which is the case if the addition of extra sulfur into the internal mixer is at a high temperature.[7] Nevertheless, the compounds with TESPT and extra sulfur showed a slightly higher Mooney viscosity compared with the mixes with lower sulfur content. In the absence of TESPT, the ENR-compatibilized compound with higher sulfur content showed a lower Mooney viscosity.

Silica particles and aggregates commonly form a filler–filler network to their neighbors because of the polar silanol groups on the surface.[21] The filler–filler interaction or Payne effect of the silica-filled NR compounds is shown in Figure 2a. The addition of 7.5 phr of ENR-51 remarkably decreased the filler–filler interactions in the silica-filled NR compounds when compared with the noncompatibilized sample because of the interaction between the silanol groups on the silica surface and the epoxy groups of the ENR. The use of extra sulfur in the silica-filled NR compounds with ENR-51 as compatibilizer results in a somewhat higher Payne effect compared with the mixes with normal sulfur content. This may be due to their lower Mooney viscosities (Figure 1), which increases the tendency of the silica to reagglomerate, that is, to flocculate, which is in agreement with the flocculation rate constant in Figure 2b. The flocculation process is the reformation of silica–silica interactions in the compound under heat treatment to regenerate a silica network.[22] The flocculation behavior of silica-filled NR compounds containing ENR-51 as

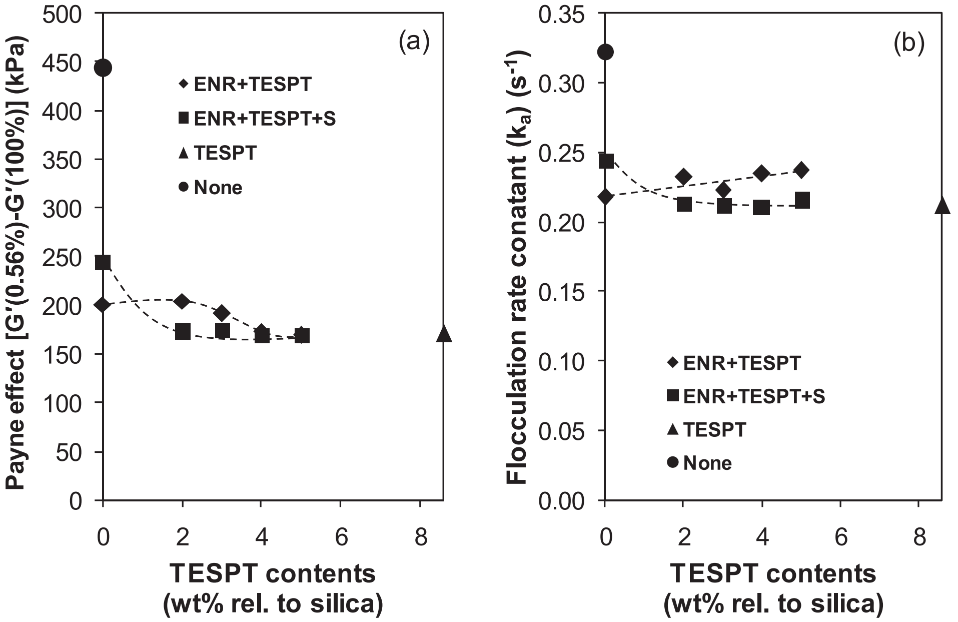

FIG. 2. — (a) Payne effect and (b) flocculation rate constant of silica-filled NR compounds with 7.5 phr of ENR-51 as the compatibilizer in combination with TESPT with and without sulfur compensation.

compatibilizer in combination with TESPT and extra sulfur shows the same trend as the Payne effect.

The Payne effect (Figure 2a) and the flocculation rate constant (Figure 2b) of the silica-filled NR compounds with 2 wt% TESPT relative to silica and extra sulfur decreased to the same levels as that of the reference compound with TESPT only. This further reduction of the filler–filler interaction by the addition of TESPT indicates that, even though epoxy groups of ENR interact with the silanol groups on the silica surfaces, there are still free silanol groups present in the system. It is well-known that even TESPT can only cap part of the approximately six free silanol groups per square nanometer on the silica, leaving many of these groups free. Because TESPT largely decreases the hydrophilicity of silica and so enhances silica dispersion and silica–rubber interaction, the leftover silanol groups are abundant enough to kill the sulfur vulcanization by their acidic nature. Consequently, DPG must be added to the curing package to deactivate these leftover silanol groups.

The ability of the epoxide groups in ENR-51 to cap the silanols on the silica surface is obviously less than it is for TESPT. The TESPT is a relatively low molecular weight substance, which enables it to migrate through the yet unvulcanizated compound toward the silica surface. The ENR-51 is a macromolecule with a much lower diffusion mobility. Furthermore, the ENR-51 macromolecule has an intrinsic steric rigidity, which may prevent it, more than it would the TESPT, to follow the intricate surface unevenness and to penetrate into the macroporosity of the silica used.

Based on these arguments, the reduced ability of ENR-51 to cap silanol groups, in comparison to TESPT, can be well understood. The use of just small amounts of TESPT further decreases the filler–filler interactions through the silanization reaction of the remaining silanol groups. Without TESPT, the compound with extra sulfur, which has a lower Mooney viscosity, shows a higher Payne effect and a higher flocculation rate constant. In the presence of both TESPT and extra sulfur, however, the compounds that have higher Mooney viscosities exhibit lower Payne effects and

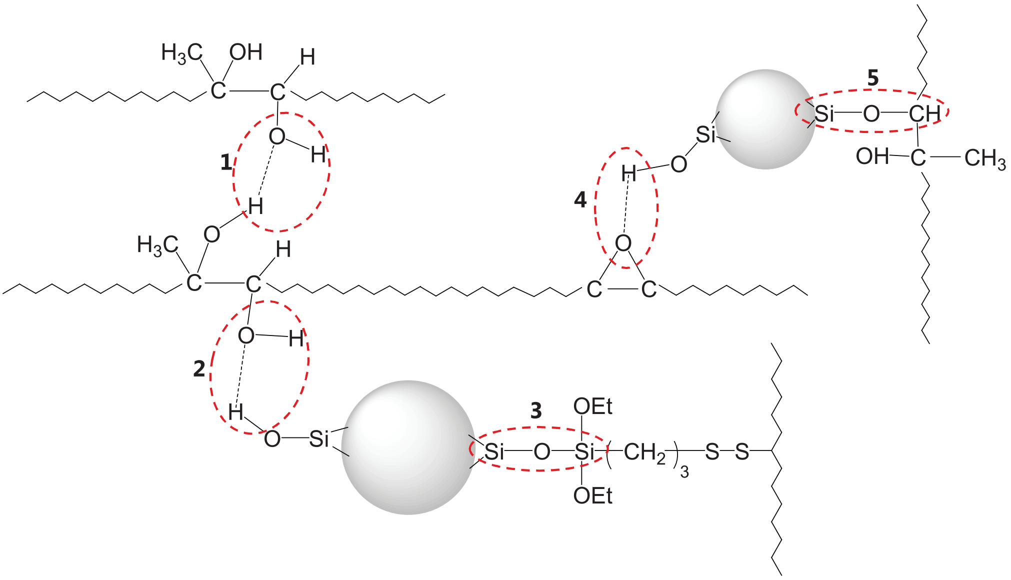

FIG. 3. — Various possible interactions and bondings in the silica-filled NR compounds compatibilized with ENR in combination with TESPT.

lower flocculation rate constants, and the values are similar to that of the reference silica/TESPT system. The results indicate an influence of Mooney viscosity on the flocculation rate constant, which in turn, relates to the Payne effect.

There are several possible interactions and/or reactions within the system, which include (1) an interaction between hydroxyl groups of ring-opened ENR,[5] (2) an interaction between hydroxyl groups of ring-opened ENR with the silanol groups of silica,[23] (3) a bonding between the silica and rubber molecules via the silane molecules,[7] (4) an interaction between the epoxy and the silanol groups,[5] and (5) a bonding between the silanol and hydroxyl groups,[23] as shown and numbered in Figure 3. The interactions/reactions between the epoxy or hydroxyl groups of the ENR and silanol groups of the silica contribute to the decreased silica–silica interactions.

FILLER-RUBBER INTERACTIONS

The bound rubber content can optionally be used as an indication for filler–rubber interactions[20] in the silica-reinforced rubber compounds. The results of silica-filled NR compounds compatibilized with ENRs and TESPT are shown in Figure 4. The silica-filled compound without compatibilizer shows the lowest chemically bound rubber content because of high filler–filler interactions through hydrogen bonding between the silica aggregates and the poor interactions between silica and rubber because of their differences in polarity. The reference, the silica-filled NR compound with 4.7 phr TESPT, gives the highest chemically bound rubber content, which is distinctly higher than the value for the noncompatibilized compound because of the good interfacial interaction via the silanization reaction. The ENR-compatibilized, silica-filled NR compounds also show an improvement in bound rubber content compared with the uncompatibilized one because of the interactions/reactions between epoxy and silanol groups. The chemically bound rubber contents increase slightly with the addition of TESPT and with increasing TESPT contents because of an increase in chemical bonds between the silica and the rubber matrix through the silane bridge.[24] However, the level of chemically bound rubber does not reach the value observed for 4.7 phr

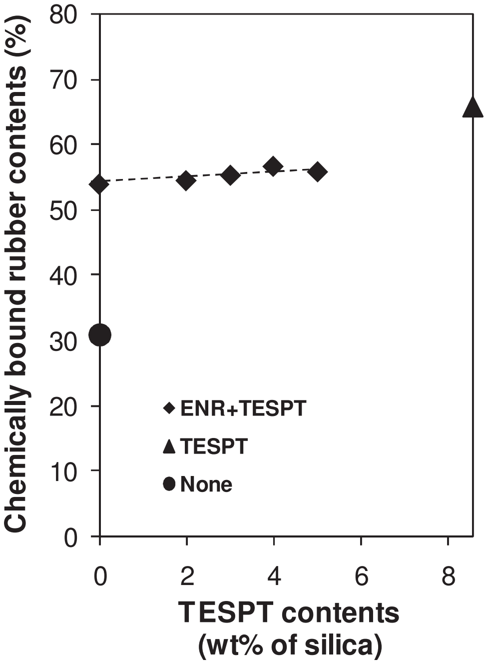

FIG. 4. — Chemically bound rubber content of silica-filled NR master batches with 7.5 phr of ENR-51 as the compatibilizer in combination with TESPT.

TESPT. Apparently, the bound ENR blocks, to some extent, the ability of the added TESPT to reach the remaining silanol groups compared with the use of TESPT alone.

CURE CHARACTERISTICS

Scorch and optimum cure times of the silica-filled NR compounds with 7.5 phr of ENR-51 in combination with TESPT, without and with extra sulfur, are shown in Figure 5a,b, respectively. The use of ENR-51 alone as compatibilizer in the silica-filled NR compound shows the longest scorch and cure times because of the remaining free silanol groups and polar epoxide groups that can adsorb polar curatives and so retard the vulcanization reaction, as previously described. Residual acid left in the ENR may also take part in the cure retardation. The incorporation of TESPT in the silica-filled compound helps to reduce the remaining polar moieties through the silanization reaction. In addition, TESPT acts as a sulfur donor to the vulcanization reaction,[7] leading to a faster cure time compared with the silica-filled NR with ENR alone as compatibilizer. The addition of extra sulfur in the systems results in shorter scorch times with increasing TESPT concentrations, compared with the compounds with normal sulfur content because of the presence of higher concentrations of curatives that can generate crosslinks. The compounds with different sulfur contents, however, show more or less the same optimum cure times, which decrease with increasing TESPT loadings. Interestingly, the noncompatibilized compound shows similar scorch and cure times to that of the silica/TESPT system despite the polar and acidic silanol groups. This can be attributed to the occurrence of the filler–filler network, as seen by its highest Payne effect and flocculation rate constant in Figure 2, which results in a smaller surface area and less available silanol groups. The TESPT system has good filler dispersion and the aggregate size is smaller, providing more surface area and free silanol groups to have a role in the vulcanization reaction. With

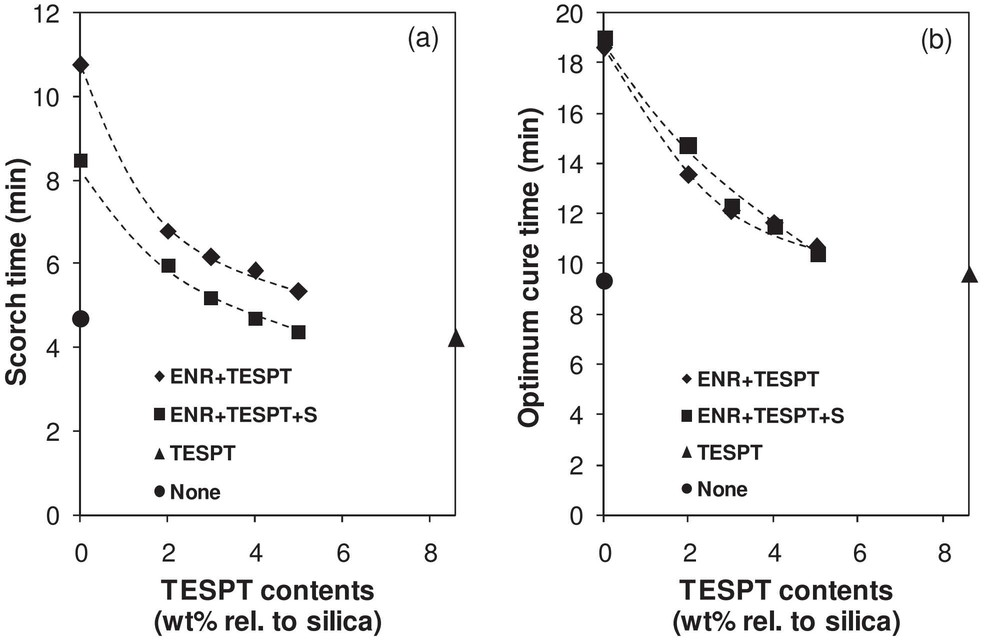

FIG. 5. — Scorch and cure times of silica-filled NR compounds with ENR-51 at 7.5 phr in combination with TESPT without and with sulfur compensation.

this competitive balance, the compounds with no compatibilizer and with optimal TESPT content show equal optimum cure times, as shown in Figure 5b.

TENSILE PROPERTIES

The incorporation of TESPT without sulfur compensation clearly enhances the 300% modulus, as shown in Figure 6a, because of an increase in silica–rubber interactions/reactions in the system. The introduction of more elemental sulfur to match the level available in the reference TESPT/silica system significantly increased the tensile modulus of the vulcanizates because of an increased amount of crosslinking agent and, consequently, a higher crosslink density. With ENR/TESPT and extra sulfur, the vulcanizates still show a lower 300% modulus when compared with the compound with the optimal TESPT content of 4.7 phr. The reinforcement index (M300/M100) of the silica-filled NR vulcanizates is improved when TESPT and extra sulfur are added; however, increasing the amount of TESPT has no clear effect on the reinforcement index of the vulcanizates (Figure 6b). All compatibilized compounds show a remarkable improvement in modulus compared with the one without, but with little dependence on the TESPT content.

The tensile strength (Figure 7a) of the vulcanizates is improved by adding TESPT on top of the ENR-51 as compatibilizer and is further enhanced by the addition of extra sulfur. The use of TESPT at 4 wt% relative to the silica with ENR-51 and extra sulfur gives the same level of tensile strength as that of the silica/TESPT reference compound, whereas the elongation at break remains more or less unchanged (Figure 7b). In combination with the epoxy groups that can interact and/or react with the silanol groups of silica, the amount of TESPT needed to optimize the silica-filled compound properties can be reduced, compared with a conventional TESPT-silanized silica filled system. The different levels of modulus and tensile strength caused by the difference in sulfur content because of

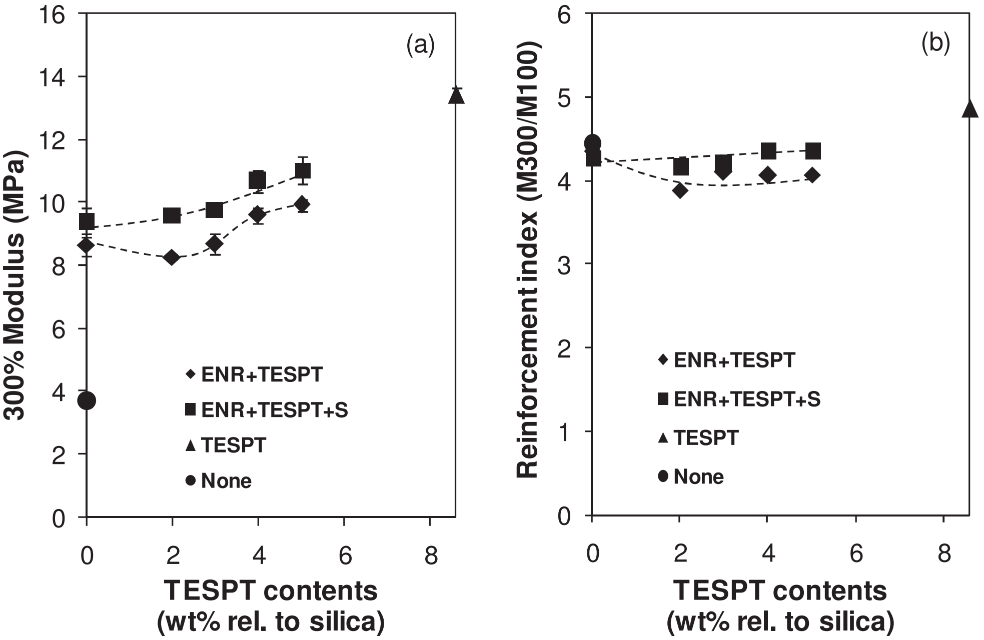

FIG. 6. — Modulus 300% and reinforcement index (M300/M100) of silica-filled NR compounds with 7.5 phr of ENR-51 in combination with TESPT without and with sulfur compensation.

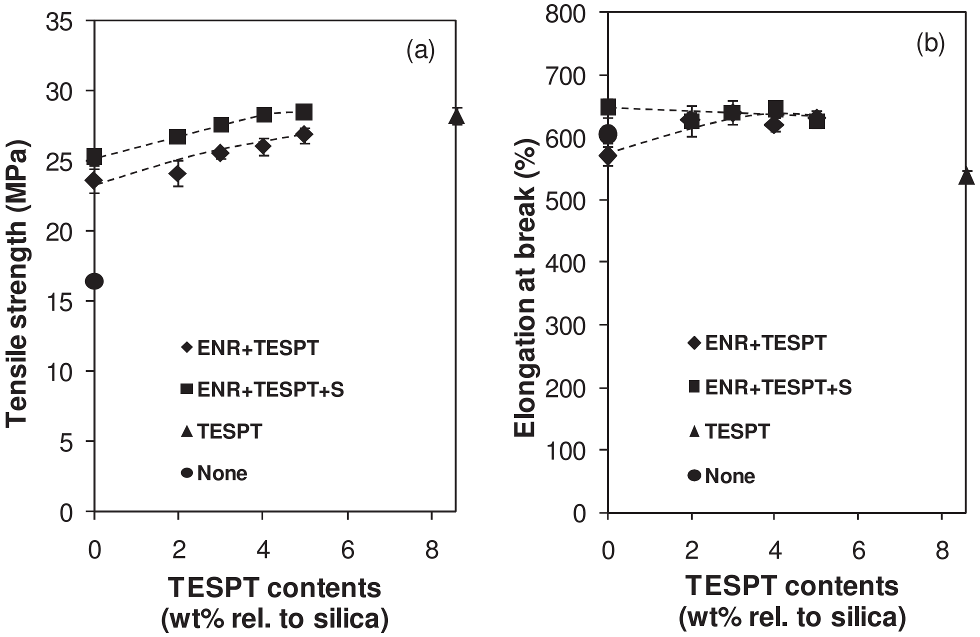

FIG. 7. — (a) Tensile strength and (b) elongation at break of silica-filled NR compounds with 7.5 phr of ENR-51 in combination with TESPT without and with sulfur compensation.

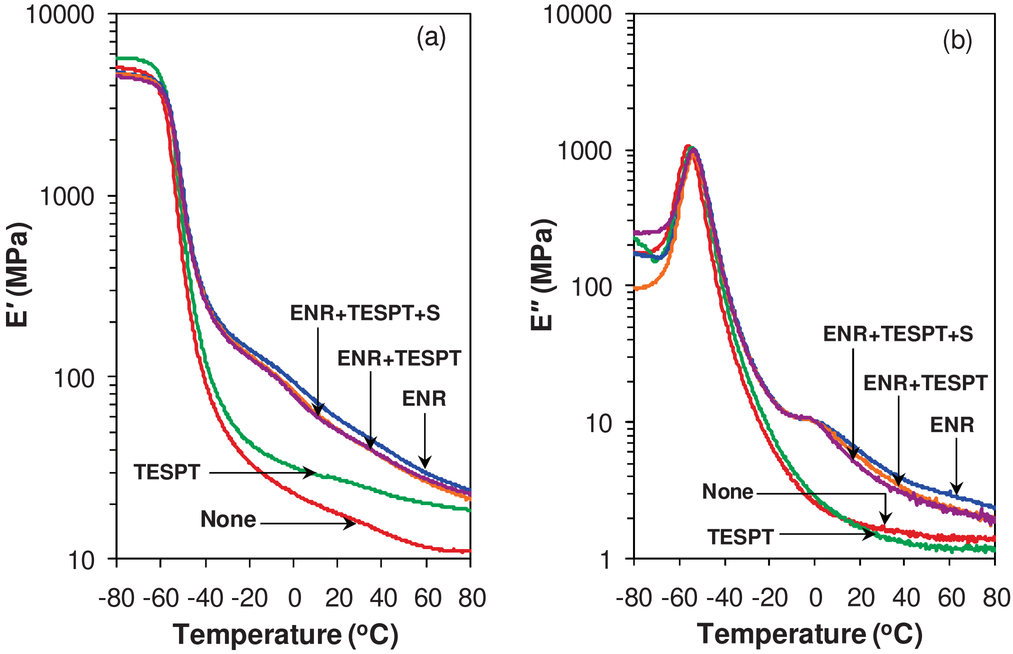

FIG. 8. — (a) Storage modulus and (b) loss modulus of silica-filled NR vulcanizates containing different compatibilizer types and combinations.

the sulfur donation of the TESPT can be further improved by introducing more crosslinks generated by the extra elemental sulfur added.

DYNAMIC MECHANICAL PROPERTIES

Silica-filled NR vulcanizates with various types of compatibilizers have different viscoelastic properties, as shown in Figures 8–10. These properties depend on polymer characteristics, reinforcing filler type and content, process oil, and crosslink density, among others. In tire technology, the viscoelastic properties of the rubbers are intrinsic characteristics related to tire performance, that is, wet traction and rolling resistance.[25]

The storage modulus, loss modulus, and tan δ, as functions of temperature of the silica-filled NR vulcanizates, are shown in Figures 8a,b and 9. In these figures, the results of the vulcanizates with 8.6 wt% TESPT relative to silica, with 7.5 phr ENR-51, with 7.5 phr ENR-51 plus 4 wt% TESPT relative to silica, and with 7.5 phr ENR-51 plus 4 wt% TESPT relative to silica plus extra sulfur, are comparatively displayed.

Figure 8a,b clearly show that the addition of the different types of compatibilizers into the silica-filled NR vulcanizates has little effect on the storage (E') and loss (E') moduli in the glassy state and in the glass-to-rubber softening region but significantly affects the material properties in the rubbery region. The different extent of the interactions between the various components, the presence of the ENR blended with the NR, and the filler dispersion all have a role in the ability of the rubber chains to move and respond to deformation. After passing through the glass transition, the vulcanizates that contain ENR-51 as a compatibilizer, either without or with TESPT, show greater storage and loss moduli than do the ones with TESPT and without any compatibilizer. The presence of 7.5 phr ENR-51 with high epoxide content and a glass transition temperature of ±0 °C causes a certain chain stiffness. Therefore, the NR with the ENR-51 as compatibilizer has a higher elastic

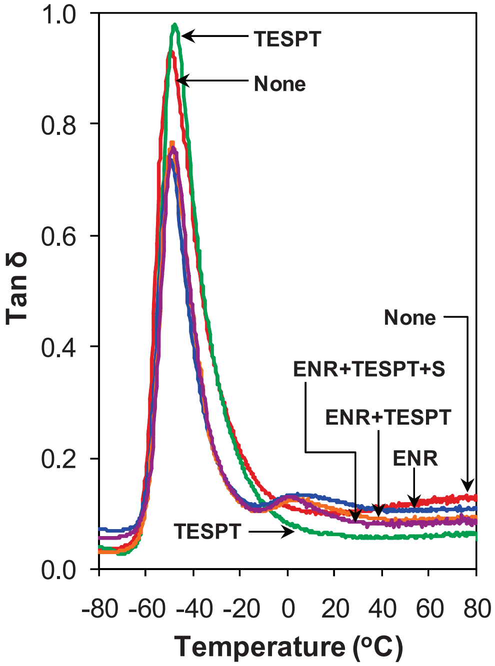

FIG. 9. — Tan δ of the silica-filled NR vulcanizates containing different compatibilizer types and combinations.

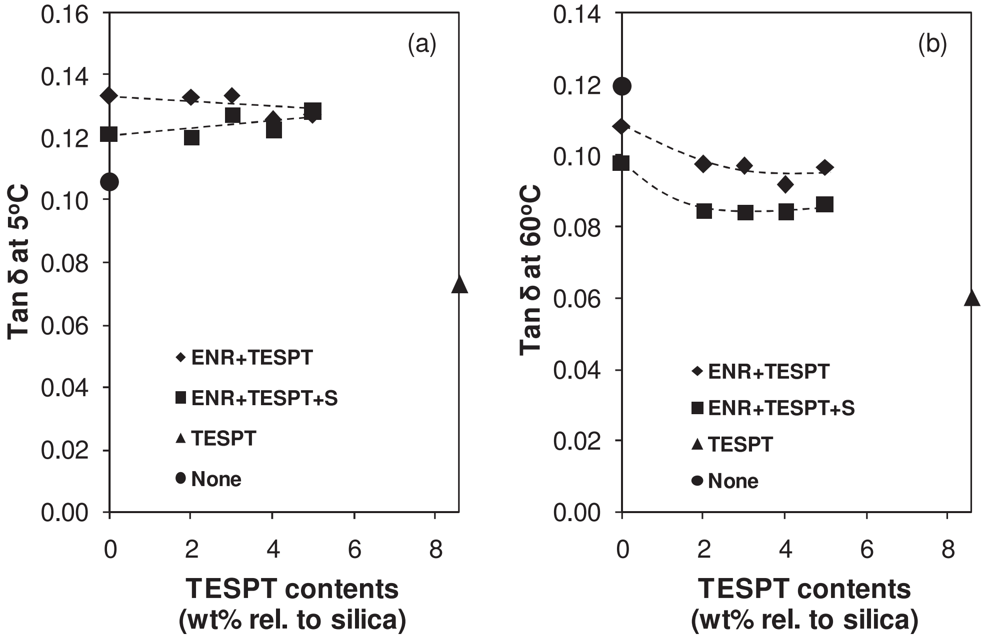

FIG. 10. — Tan δ at (a) 5 °C and (b) 60 °C of silica-filled NR vulcanizates without and with different compatibilizer combinations.

modulus and also shows a higher viscous or loss modulus because of lessened chain flexibility, as shown in Figure 8.

The use of the optimal content of 4.7 phr TESPT results in vulcanizates with the highest tan δ peak because of the improvement in the silica dispersion, leading to less trapped rubber in the silica aggregates and, therefore, more rubber segments to respond to the dynamic deformation in this region. On the other hand, the use of ENR as compatibilizer results in a decrease of the tan δ peak intensity, even in combination with TESPT. This is partially caused by the ENR, which at this temperature is still in the glassy state, but may also result from interactions between the ENR and silica and the self-crosslinked ENR, which restrict the motions of the rubber segments. In the rubbery region, the silica/TESPT system provides the lowest tan δ value because of the good chemical bonding between the silica and rubber via the silane bridges, which help to reduce energy loss under dynamic conditions. The higher network density enhances the elasticity further, resulting in a lower loss tangent as well. The presence of ENR-51 that possesses greater damping properties results in the higher loss tangent in the temperature range of 0 to 80 °C above its glass transition temperature of around 0 °C. The compound without any compatibilizer also shows an increasing trend toward the loss tangent with a rise in the test temperature.

By dynamic mechanical analysis, the glass transition temperature (T_g) of the polymers can be determined by using the peak temperatures of either the tan δ or the loss modulus (E''). The best point to represent T_g is still a subject of debate. Robertson et al.[26] discussed the tan δ in the glass-to-rubber softening transition as being determined not only by the local segmental motions of the polymer, as reflected in the loss modulus toward the lower temperature, but also by the filler reinforcement effect on both the storage and loss moduli at higher temperatures. They reported that the loss modulus peak that corresponds to the segmental relaxation process is not significantly affected by the particle surface area of the filler or the degree of filler–polymer interactions,[26] whereas the shape and magnitude of the tan δ peaks are influenced by these parameters associated with the nature of the filler.

The present work reports the T_g of silica-filled NR vulcanizates containing no TESPT and different levels of TESPT, in combination with 7.5 phr of ENR-51, with and without sulfur compensation, as determined by the tan δ peaks, as shown in Figure 9. The compounds with different degrees of filler–rubber interactions, as indicated by their bound rubber contents in Figure 4, show different shapes and magnitudes of the tan δ vs temperature peaks (Figure 9). The T_g of the vulcanizate with the optimal content of 4.7 phr TESPT, which has the highest chemically bound rubber content as well, is the highest. The vulcanizates with extra sulfur that have a higher crosslink density compared with the ones with normal sulfur content show a slightly higher T_g, and samples with increasing TESPT contents in the ENR-compatibilized NR show an insignificant effect on T_g.

A study[27] on the viscoelastic properties of crosslinked NR by dynamic mechanical analysis showed that the T_g depended on both the crosslink density and the crosslink types. A higher crosslink density increased the T_g because of the greater restrictions on molecular-chain motions, as is commonly observed. Furthermore, higher sulfur content leads to an increased proportion of polysulfidic crosslinks and cyclic sulfidic structures, which has a greater influence on T_g than does monosulfidic or carbon–carbon crosslink types.[27] The chemically bound rubber via silane bridges to the silica surface further restricts the movement of the polymer chains and increases the T_g. This is in accordance with the work that reported the shift of T_g toward higher temperatures by polymer-filler coupling bonds.[5]

In the test method for wet grip grading of C1 tires, according to the United Nations Economic Commission for Europe (UNECE) regulation R117,[28] the wet surface temperature range for normal or summer tires is 5–35 °C, and for winter tires, it is 2–20 °C. Figure 10a,b shows tan δ values at 5 °C and 60 °C tested at a frequency of 10 Hz for the silica-filled NR-vulcanizates with different compatibilizers. A higher tan δ at low temperature indicates a better tire wet grip. As shown in

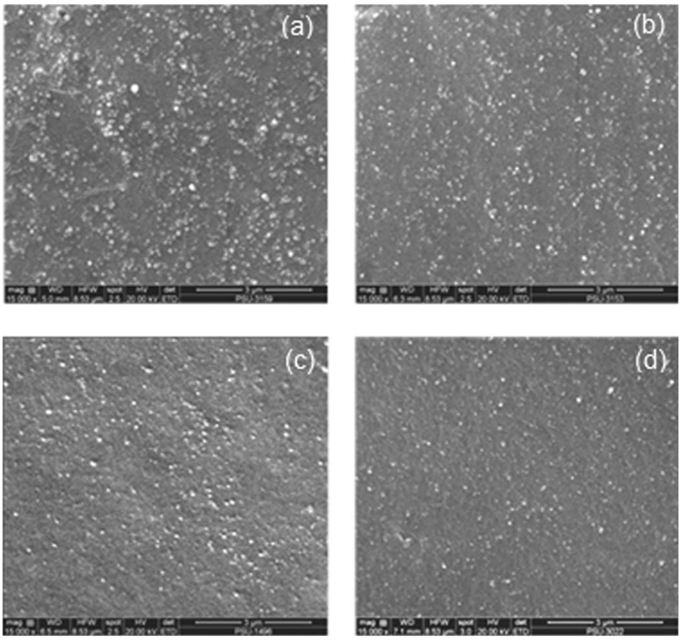

FIG. 11. — SEM micrographs of filled NR vulcanizates with 30 phr of silica at 15 000× magnification: (a) without compatibilizer, (b) with 7.5 phr ENR-51, (c) with 7.5 phr ENR-51 plus 4 wt% TESPT relative to the silica, and (d) with 8.6 wt% TESPT relative to the silica.

Figure 10a, the tan δ at 5 °C for the silica-filled NR vulcanizates is substantially increased with ENR added as compatibilizer because of the damping behavior of epoxidized rubber influenced by its T_g, as exhibited in Figure 9. The use of TESPT in the range of 2–5 wt% relative to the silica content, in combination with ENR, has only little effect on the tan δ. The silica-filled NR vulcanizate with TESPT showed the lowest tan δ at 5 °C, implying the lowest tire wet-skid resistance. The chemical bonds between silica and rubber via silane molecules contribute to the crosslink network that is normally generated by the vulcanization reaction. This results in a better elastic response and lower energy loss. This double network also causes the lowest tan δ at 60 °C, which indicates low rolling resistance for tires, as shown in Figure10b. The presence of ENR-51 leads to a significantly higher tan δ at 60 °C compared with the use of TESPT alone, but is still lower than for the noncompatibilized compound. The addition of only 2 wt% TESPT relative to the silica shows an improvement in tan δ at 60 °C because of the improved filler dispersion and cure behavior. The correction of the sulfur content in the ENR-compatibilized compounds decreases the tan δ of the vulcanizates at both 5 °C and 60 °C because of the increase in crosslink density, leading to better rubber elasticity.

SEM IMAGES

Filler dispersion level is one of the parameters that affect the properties of filled compounds and vulcanizates. The silica dispersion in the NR matrix containing different types of compatibilizers was studied by the SEM technique using two different sets of specimens. For the cryogenically cracked surfaces, as shown in Figure 11, the compounds contain only 30 phr of silica to be better able to observe the silica dispersion. For the regular formulation with 55 phr of silica, tensile fractured surfaces were used, and the SEM micrographs are shown in Figure 12.

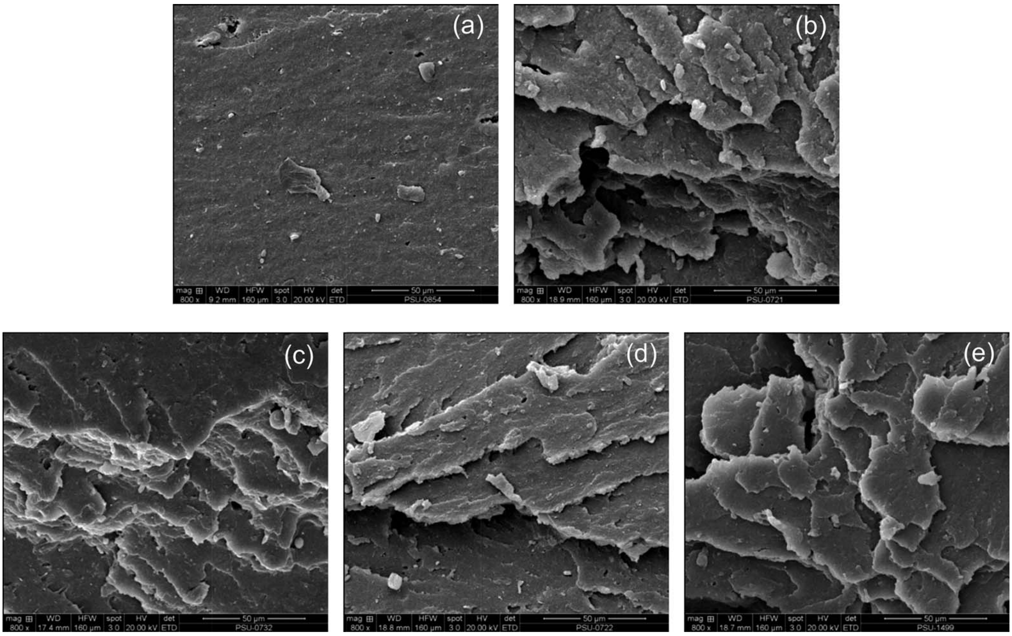

FIG. 12. — SEM micrographs of tensile fractured surfaces of filled NR vulcanizates with 55 phr of silica at 800× magnification: (a) without compatibilizer, (b) with 8.6 wt% TESPT relative to the silica, (c) with 7.5 phr ENR-51, (d) with 7.5 phr ENR-51 plus 4 wt% TESPT relative to the silica, and (e) with 7.5 phr ENR-51, 4 wt% TESPT relative to the silica and extra sulfur.

Because of the many silanol groups on the silica surface, breaking of the silica agglomerates and dispersion of the aggregates into the rubber matrix are difficult because of hydrogen bonding. The silica dispersion of the filled NR vulcanizate without compatibilizer (Figure 11a) is clearly poorer than the vulcanizates that contain compatibilizers because the silica is less homogeneously dispersed in the matrix and the aggregates/agglomerates sizes are larger than that observed in the other compounds. The incorporation of ENR-51 into the silica-filled NR improves the silica dispersion in the matrix, as shown in Figure 11b, because of interactions between the silanol groups of the silica and epoxide groups of the ENR leading to hydrophobation of the silica. The dispersion of silica is further improved by the use of ENR in combination with TESPT at 4 wt% relative to the silica, as shown in Figure 11c, where the silica is finely dispersed to more or less the same level as that in the silica-filled NR vulcanizate with the optimal content of 4.7 phr TESPT (Figure 11d). The SEM results are in accordance with the Payne effect (Figure 2a), and the resulting vulcanizate properties, with the noncompatibilized system being the worst. The addition of TESPT to react with free silanol groups through the silanization reaction and the bound silane on the silica surface suppress the filler–filler interactions and prevent the silica from re-agglomeration. The better silica dispersion in NR with the TESPT silane coupling agent, compared with vulcanizates without silane, was also clearly demonstrated by the SEM images of the cutoff surfaces by Choi et al.[29]

The SEM micrographs of the tensile fractured surfaces of the 55 phr silica-filled NR vulcanizates containing different compatibilizers are shown in Figure 12. The silica-filled NR vulcanizate without a compatibilizer, which has the lowest tensile strength because of poor filler dispersion and filler–rubber interactions, shows a smooth surface with some vacuoles on the failure surface, which may be partly caused by the de-wetting of the silica from the NR matrix, as shown in Figure 12a. The silica agglomerates shown by SEM in silica-filled NR without a compatibilizer was previously demonstrated by Pal and De.[30] The effective use of the TESPT silane coupling agent in the silica-filled NR leads to the highest modulus (Figure 6a) and tensile strength (Figure 7a), which provides a rough fractured surface with many tear lines from the ductile failure[31] because of the good interfacial interactions between the rubber and the silica with silane coupling. All of the fractured surfaces of silica-filled NR with ENR-51, ENR-51 in combination with TESPT, and ENR-51 in combination with TESPT and extra sulfur as compatibilizers, as shown in Figure 12c–e, respectively, show a rough surface and tear line pattern but at different degrees compared with the silica/TESPT system (Figure 12b). The ENR-compatibilized vulcanizates with filler–rubber interactions only via the interaction/reaction between the epoxide groups of ENR and the silanol groups on the silica surface (Figure 12c,d) had a considerably less-complicated fracture surface when compared with the one with the optimal content of TESPT (Figure 12b). The silica-filled vulcanizates with TESPT and ENR/TESPT/extra sulfur show the same level of tensile strength as shown in Figure 7a, and they show very similar tensile fractured surfaces, as shown in Figure 12b,e, respectively. The SEM micrographs of tensile fractured surfaces of filled NR vulcanizates have also been used to demonstrate dispersion and wetting of fillers by the matrix, such as in the work of Arayapranee et al.[31] and Ismail et al.,[32] in which the rough surfaces with tear lines indicate higher tensile strength.

CONCLUSIONS

This work clearly demonstrates that it is extremely complicated to balance the many, partially opposing, chemical, physical, mechanical, and ecological factors involved in silica reinforcement of tire rubbers. Each component has a balanced role and a one-to-one replacement of such a component is not possible. The use of ENR-51 at 7.5 phr in combination with the TESPT silane coupling agent increases the rubber–silica interactions, when compared with a silica-filled compound with ENR-51 alone. A further increase of TESPT content has only a small additional effect. The tensile strength and modulus of the vulcanizates increase with increasing TESPT content and are further improved by sulfur compensation relative to the reference compound with TESPT alone. The use of ENR-51 at 7.5 phr, with TESPT at 4 wt% relative to the silica, and extra sulfur gives vulcanizates the same level of tensile strength as the vulcanizates with TESPT at the optimum 8.6 wt% relative to the silica but without ENR. The dynamic mechanical properties of the silica-filled NR vulcanizates are significantly affected by the presence of ENR-51, which has a higher damping effect than NR does. The ENR-containing vulcanizates showed a higher storage modulus and tan δ compared with the silica/TESPT system because of the higher T_g of the ENR compared with the NR. The addition of TESPT to the ENR-compatibilized compounds causes a small change in the T_g and the tan δ at 5 °C but a lower tan δ at 60 °C. The addition of extra sulfur leads to an increase in T_g and a lower tan δ at both 5 °C and 60 °C because of the increased crosslink density. The SEM micrographs clearly show good silica dispersion in all compatibilized vulcanizates, and the tensile fracture surfaces of the materials show different tear line patterns depending on their tensile strengths.

Overall, the combination of ENR-51, TESPT, and sulfur compensation nearly matches the properties of a compound with TESPT alone at optimal quantity, double what is needed with ENR-51 included. Consequently, the amount of volatile organic compound released from such a compound with ENR-51 is reduced by at least half, which was the main objective of this study. From the perspective of the “Magic Triangle of Tire Technology,” when the wet skid resistance needs to be boosted vs the rolling resistance, for example, with winter tires, the combination of ENR-51, TESPT, and sulfur compensation presents itself as a better option, which remains to be confirmed in real tire tests.

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