

# Natural rubber and epoxidized natural rubber in combination with silica fillers for low rolling resistance tires

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## Abstract

Introducing silica into tire tread rubber compounds offers at least two advantages: a reduction in heat build-up as well as an improvement in mechanical properties, in particular tear strength, cut, chip, and chunking resistance, when compared with the use of carbon black. Silica itself gives a lower degree of reinforcement when compared to carbon black of the same primary particle size due to the different nature of the surface chemistry of the fillers. In general, silica can reinforce better in more polar rubbers when compared to nonpolar rubbers due to stronger silica-to-rubber interactions. The insufficient reinforcement efficiency of silica-filled nonpolar rubbers—general purpose rubbers, for example, natural rubber (NR)—can be improved by using silane coupling agents. The quality of silica-filled rubber compounds significantly depends upon mixing conditions and key ingredients in the compounds. These parameters are crucial and need to be optimized to obtain desirable hydrophobation and micro-dispersion of silica as well as appropriate filler–rubber and rubber–rubber networks in the compounds, leading to the optimum properties of the final vulcanizates. Epoxidized NR (ENR) is often quoted to be suitable for easy-dispersion precipitated silica-reinforced passenger car tire treads compounds, without the need to use a silane coupling agent. The epoxy-moieties on the ENR backbone enable a chemical reaction with the silanol groups on the silica, thereby creating a solid chemical bond between rubber and silica, similar to what the silane coupling agent can achieve. There are several approaches to this technology, each with their own merits and potential success: (1) The full use of ENR instead of NR, whereby the degree of epoxidation of the ENR plays an important dual role: first, there should be a high enough degree of epoxidation to guarantee sufficient reactivity toward the silica; on the opposite side the epoxidation raises the glass transition temperature of the NR, which tends to become too high for tire applications; (2) The use of ENR in small quantities as compatibilizer and/or reactive species between the silica and otherwise pristine NR as the main component. This enables to use ENR with higher epoxide contents without major adverse effects on the glass

transition temperature; (3) Epoxidized low molecular weight NR has a potential to improve both processing and vulcanizate properties, due to its plasticizing effect and epoxide–silica interactions; and (4) In all three cases the use of small amounts of silane coupling agents relative to the quantities used for pure NR–silica compounds helps to overcome eventual shortcomings. The present chapter provides a review of the developments over time, the advantages and disadvantages of the various approaches, highlighted on the basis of laboratory-scale compounding and characterizations, like Mooney viscosities, Payne effects, dynamic mechanical analyses, and vulcanized tensile mechanical properties.

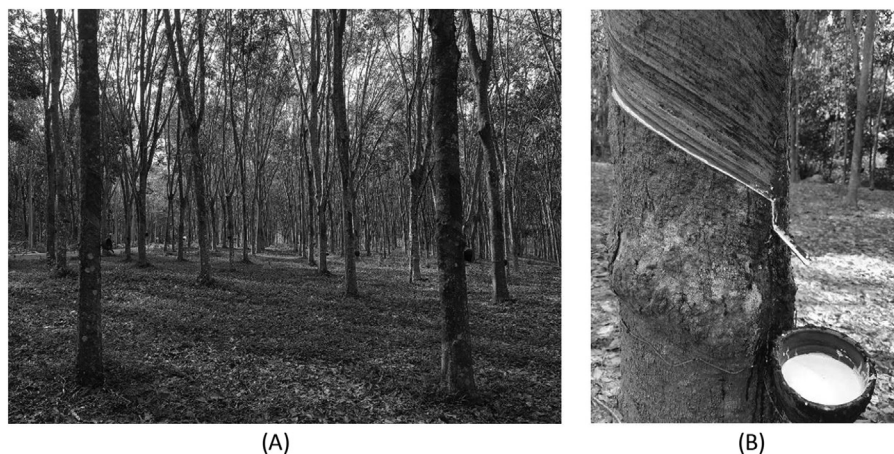
**Keywords:** Epoxidized natural rubber; silica; silane; tire; NR

## 9.1 Introduction

Natural rubber (NR) is widely used in all types of tires, especially for heavy trucks and aircraft, to keep the heat build-up at a low level. Passenger car tire treads are in general based on synthetic rubbers; heavy-duty truck tire treads contain 50%–100% NR and aircraft tires are almost wholly NR. Many components of passenger car tires are also made from NR such as the body compounds, sidewall, and the bead filler, because next to low heat build-up, it provides good flex fatigue and excellent mechanical properties [1]. Particulate reinforcing fillers such as carbon black and silica are most commonly used in combination with NR for tread applications. Use of silica instead of carbon black in combination with a synthetic solution–styrene–butadiene rubber (SSBR) with high-vinyl content, blended with high-*cis*-BR, after the patent of Michelin [2] for passenger car tires, offers lower rolling resistance and higher wet grip, so less fuel consumption and better driving safety. The successful use of silica in rubber compounds requires chemical bonding between the silica and the elastomers because of the large difference in polarity of the silica and the rubbers [3,4]. Silane coupling agents such as most commonly used bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) are commonly applied in such compounds vulcanized with a sulfur-cure system. It involves two subsequent chemical reactions [5]: (1) the reaction of the coupling agent with the silica surface, often called silanization reaction; and (2) the reaction of the sulfur moiety of the coupling agent with the elastomers, known as coupling reaction. The mechanism of these reactions is to be further elaborated in Section 9.1.3. To control these two reactions in a proper manner is a complicated challenge. In this context, the present introduction covers an overview of the state-of-the-art silica technology for NR and epoxidized NR (ENR).

### 9.1.1 Natural rubber as renewable and sustainable material

NR is a renewable material, which combines excellent mechanical and dynamic properties. It has superior mechanical properties over synthetic rubbers, due to its high molecular weight, and regular structure of *cis*-1,4-polyisoprene. NR



**Figure 9.1** (A) Natural rubber plantation in Surat Thani, Thailand, and (B) fresh natural rubber latex from a Pará rubber tree exuded into a collecting cup.

crystallizes when stretched by an external force, so-called strain-induced crystallization, which leads to a high tensile strength and elongation at break [6–8]. Fig. 9.1 shows an NR plantation in Thailand and NR latex exuded from a rubber tree.

NR has always been and is still in use in a variety of applications, mostly in the form of filled vulcanizates. In general, the properties of rubber goods depend significantly on the choice of the rubber type and the compound compositions: fillers, curing agents, and other additives, the production process, as well as the shape and design of the products [9,10]. In these respects, there has continuously been research to obtain rubber products with superior properties, more environmentally friendly and cost effective. The most commonly used raw NR for tire applications, in particular, heavy-duty tires for trucks and airplanes, is the Technically Specified Rubber grade 20, for example, Standard Thai Rubber (STR20) as illustrated in Fig. 9.2.

Owing to the depletion of petroleum oils and more stringent environmental and safety concerns, the use of renewable materials and less toxic substances to produce rubber products under more efficient energy use is one of the key directions at present and for the future [11]. One of the unique characteristics of NR is that it is a carbon dioxide ( $\text{CO}_2$ ) sequester. Carbon dioxide is taken from the air to produce this natural polymer by the rubber trees or plants. Studies were conducted to elucidate why the rubber trees produce this NR latex [12–14]. The conclusion was drawn that the role of NR latex is accredited as an essential protector for a rubber tree from potentially being attacked by diseases—antifungal substance. The rubber trees after their service life are normally used for furniture production. Therefore the useful features of NR which provide benefits to human and environmental needs should be further implemented to extend its use as a sustainable material.

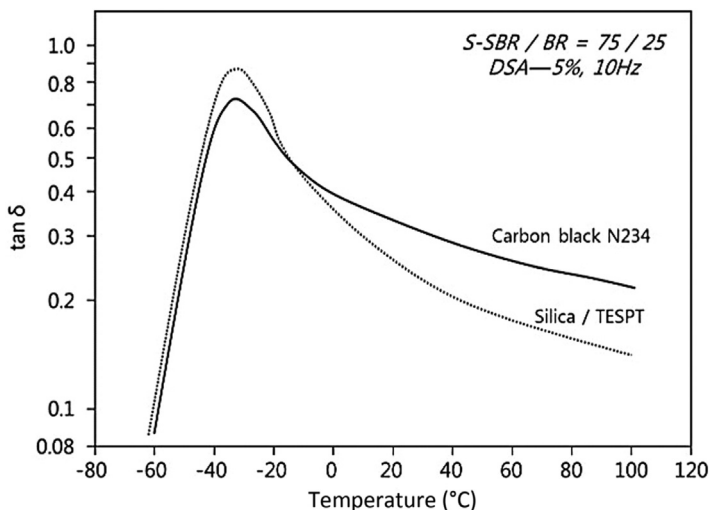


**Figure 9.2** STR20—one of the TSR, as the most commonly used raw NR for tire productions. *STR20*, Standard Thai Rubber grade 20; *TSR*, technically specified rubber.

### 9.1.2 Development and challenges of silica technology in tire applications

Silica as a reinforcing filler in compounds is growing tremendously in use, especially in the tire industry. The full replacement of carbon black by silica as reinforcing filler in passenger tire treads was first introduced by Michelin in 1992 [2], since it significantly reduces rolling resistance and improves wet traction of tires [15]. Fig. 9.3 depicts the loss tangent as a function of temperatures of silica- and carbon black – filled vulcanizates. The significant difference between the  $\tan \delta$  of these two compounds can be seen at the temperatures of 0°C and 60°C. The  $\tan \delta$  values at these two temperatures are basically considered as indirect indicators for wet grip and rolling resistance of a tire, respectively. In-depth information on the principle of the correlation between  $\tan \delta$  and tire performance can be further found in a publication of Nordsiek [15] and Wang [16]. By replacing carbon black with silica the  $\tan \delta$  at 60°C or hysteresis is reduced, leading to a desired lower rolling resistance. Higher  $\tan \delta$  values can be seen in the low temperature region for silica-filled compounds. This can result in advantages in terms of wet traction performance compared to carbon black – filled rubber compound. The difference between silica and carbon black on reinforcing mechanism is explicitly elucidated in the literature [16].

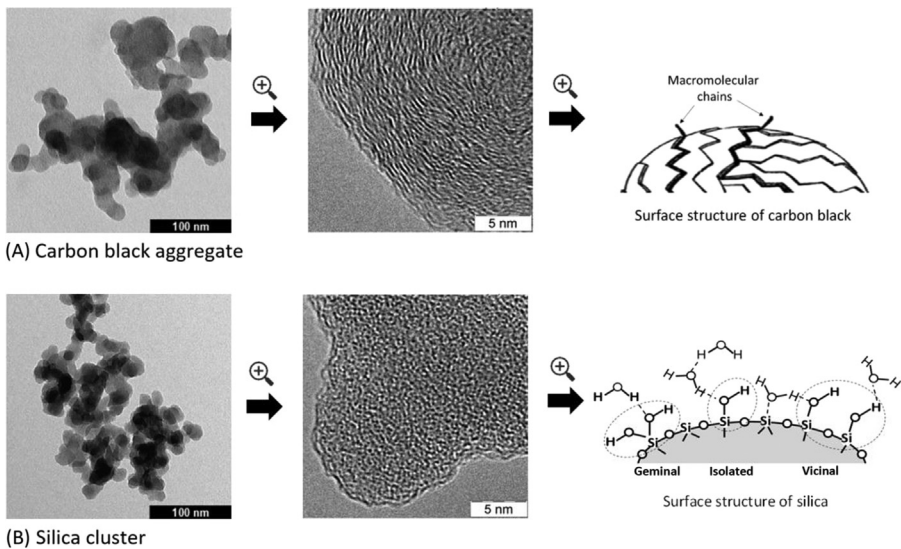
The use of silica reduces tire rolling resistance by approximately 30% relative to carbon black [17,18]. Assuming that correct tire pressures are maintained and making allowance for varying driving speeds and different driving conditions, a 30% reduction in rolling resistance corresponds to approximately 3%–6% fuel savings for passenger car tires, while a reduction of 20% of rolling resistance for truck tires results in a decreased fuel consumption of about 6% [18]. Moreover, silica provides substantial benefits in winter tires and all-season tires as the silica-reinforced



**Figure 9.3** Typical  $\tan \delta$  curves under temperature dependence for silica and carbon black – filled rubber vulcanizates. The particle sizes of silica and carbon black used in this investigation were comparable [16].

compounds are more elastic and flexible at lower temperatures leading to better grip and braking under winter conditions [17]. In addition to a better cost efficiency by reduced rolling resistance,  $\text{CO}_2$  emission can be diminished, leading to less air-pollution and reduced global warming.

Utilization of silica for rubber reinforcement differs from the use of carbon black since the polarity of the silica surface makes it incompatible with nonpolar rubbers, resulting in agglomeration or poor dispersibility of silica in the rubber matrix. Fig. 9.4 shows the microscopic images of carbon black (N330) and silica (with a specific surface area of  $158 \text{ m}^2/\text{g}$  measured by the cetyltrimethylammonium bromide or CTAB absorption method) in their initial form before mixing with rubber. The carbon black structure (Fig. 9.4A) has higher branches with an opened structure, whereas silica shows a denser and closed structure (Fig. 9.4B). This result is in line with the recent designation of silica structure, the so-called silica clusters, no aggregates or agglomerates like carbon black. The silica particles form a closed structure, attributed to the fact that the silica surface is highly polar due to hydroxyl groups on its surface, which generate hydrogen bonds between the silica particles/small clusters. Furthermore, at a magnification of 600,000, the surface of carbon black clearly shows aligned crystalline graphitic patterns, whereas the silica surface possesses a fully amorphous structure. This is an explicit proof that carbon black particles form aggregates/agglomerates mainly by physical interactions due to its coarse crystalline surface as well as van der Waals forces. This finding is consistent with the conclusions reported in the literature [19]. The reinforcement mechanism of carbon black occurs via an intermolecular interlocking interaction between the coarse surface of carbon black and macromolecular chains of polymers (Fig. 9.4A),



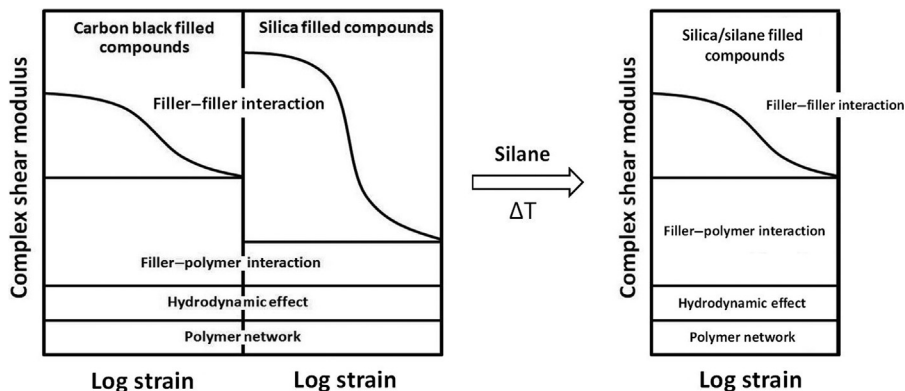
**Figure 9.4** Morphology of (A) carbon black (N330) and (B) silica (with a CTAB surface area of  $158 \text{ m}^2/\text{g}$ ) from a TEM and ATEM analysis at the magnifications of 100,000, that is, 100 nm, and 600,000, that is, 5 nm [19], along with the sketch of their surface characters [20,21]. *CTAB*, Cetyltrimethylammonium bromide; *TEM*, Transmission electron microscopy; *ATEM*, Analytical transmission electron microscopy.

while silica needs an intermediate substance to modify the hydroxyl groups on the surface prior to bonding with rubber molecules. The coupling technology of silica is to be discussed in the subsequent section.

Dispersibility of filler in a rubber compound is very important, as the mechanical properties are controlled by the degree of filler dispersion [22,23]. When a large amount of silica is added, the viscosity increases substantially, making the rubber compounds more difficult to process and causing excessive wear of the processing equipment [24]. In addition, the silanol groups present on the silica surface (Fig. 9.4B) are acids and cause adsorption of curatives, resulting in delay of the vulcanization reaction, and thus reduction of crosslink density. To solve these problems, various coupling agents are in use when mixing silica into rubber compounds [3–5,25,26].

A main drawback of silica comes from strong interparticle forces, making it difficult to obtain a good dispersion within the rubber matrix. The surface of precipitated silica exhibits a hydrophilic character with a number of silanol ( $\text{Si}-\text{OH}$ ) groups, see Fig. 9.4B, which causes the formation of hydrogen bonds between silica clusters [22,23]. These lead to a high filler–filler interaction, see Fig. 9.5 [27], which prevents easy dispersion during mixing and results in a poor compatibility between silica and hydrocarbon rubbers afterward. As a consequence, inferior final vulcanizate properties are usually obtained. These difficulties can be overcome by use of silane coupling agents (Fig. 9.5), which are able to react chemically with the





**Figure 9.5** Improved reinforcement of silica in rubbers by applying a silane coupling agent as well as a specifically adjusted mixing condition, in particular mixing temperature.

Source: Modified from A.R. Payne, The dynamic properties of carbon black loaded natural rubber vulcanizates. Part II, J. Appl. Polym. Sci. 6 (1962) 368-372.

silica and rubber polymers during the mixing and vulcanization stages, respectively [3–5]. Mixing of silica, silane, and rubber needs a high appropriate temperature to ensure the completion of the reaction between silica and silane, called “silanization reaction.” Therefore the mixing of silica-filled compounds is basically different from that of carbon black [23].

### 9.1.3 State-of-the-art coupling technology for silica-based compounds

#### 9.1.3.1 Mechanistic aspects of silane coupling agent

The chemical treatment of silica surfaces has become the most successful method to improve filler–rubber interaction and reduce filler–filler interaction. Among those chemical treatments, silane coupling agents are widely used to improve filler dispersion and to prevent chemical adsorption of curatives on the silica surface. This involves an increase in adhesion between rubber and silica, improvement in wetting of silica, rheology, and other handling properties [3]. The coupling agent also modifies the interface region to strengthen the organic and inorganic boundary layers. Silane coupling agents of basic structure  $X_3SiR_Y$  are characterized by dual functionalities.  $R_Y$  represents an organofunctional group and  $X$  represents a hydrolyzable alkoxy group attached to the silicium atom. The organofunctional groups are chosen for reactivity or compatibility with the polymer, while the hydrolyzable alkoxy groups are to react with silanol groups of silica forming a chemical bond to the silica surface [3–5]. However, silane chemistry is rather complicated because of the necessary in situ reactions during rubber processing.

The chemical bridge formation between the rubber and filler phases through the silanization reaction of the alkoxy groups of the silane with silanol groups on silica,

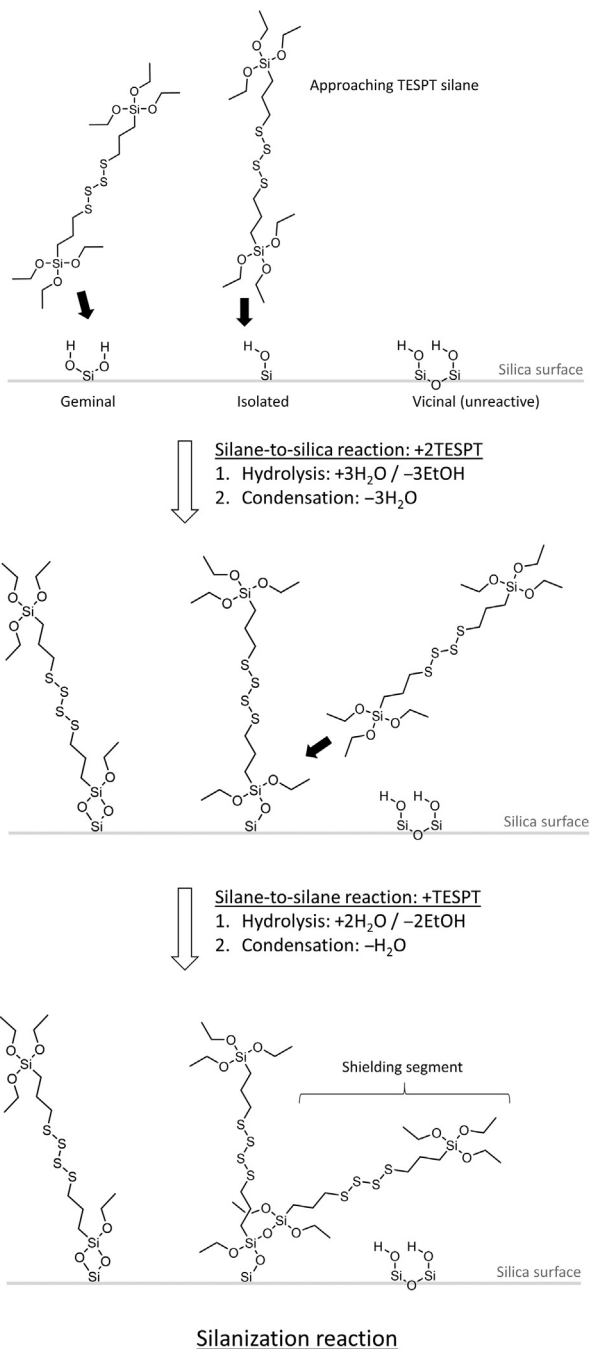
and the subsequent coupling reaction with the elastomer provides the vulcanized rubber good dynamic mechanical properties with low hysteresis. Among various types of silane coupling agents available, the state-of-the-art TESPT is the most commonly used and effective bifunctional silane for silica-filled rubber compounds [21]. The use of silane coupling agent not only decreases filler–filler interaction, that is, Payne effect (Fig. 9.5), but also increases the silica–rubber interaction and interfacial adhesion. The silanization reaction between the alkoxy groups in the silane molecules and the silanol groups on the silica surface proceeds through primary and secondary silanization reactions during mixing [21,28], see the reaction mechanism demonstrated in Fig. 9.6.

The primary silanization reaction takes place between a silanol group on the silica surface and one ethoxy group in the TESPT molecules. The secondary condensation between adjacent silane molecules reacted onto the silica surface then occurs. Thereafter, the polysulfide part in the silane molecules will react with elastomer molecules during vulcanization, leading to the full silica – silane – rubber bridge [4,5]. Based on model system studies [5,21], the primary reaction is about 10–20 times faster than the secondary reaction and the reaction can occur via two pathways: direct condensation and hydrolysis prior to condensation. During the silanization reaction, 1 mol of TESPT can release 6 mol of ethanol (EtOH) as a byproduct. Recently, it has been reported that only the isolated and geminal silanol groups on the silica are involved in the silica–silane reaction and that only approximately 25% of the Si–OH groups are able to react with silanes due to limited accessibility of the silanol groups for incoming silane molecules [28,29]. Due to the limited number of silanes that can be grafted on the silica surface [30], the additional use of small molecules such as alcohols and amines or silanes with high shielding potential to increase the hydrophobation of the silica surface is beneficial.

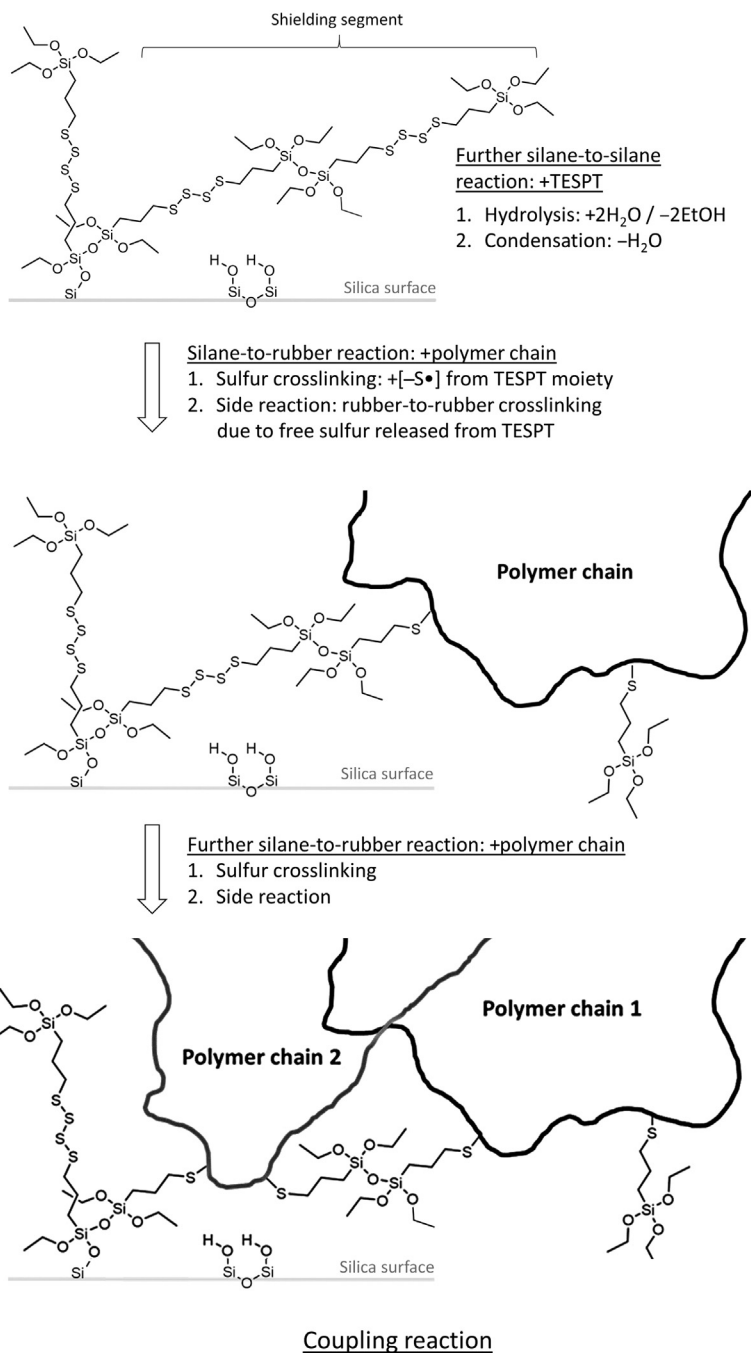
### 9.1.3.2 Development of silane coupling agents

Multiple commercial silanes are available in the market; each offers a specific influence on final properties of silica-filled vulcanizates, for example, mechanical and dynamic properties of the rubber compounds. Fig. 9.7 shows various chemical structures of silanes and their evolution steps. Silane coupling agents have evolved over time with the aim to further improve their performance for application in silica-based tire treads. The number of sulfur atoms in the molecule of the classical TESPT silane was reduced from four atoms to be two atoms on average, creating a new bifunctional silane, called TESPD (bis-(3-triethoxysilylpropyl) disulfide) with a better scorch safety of a compound [31,32]. This is because TESPT releases free sulfur into the system after its molecular bisection during mixing. The free sulfur can react with rubber molecules during the mixing stage, which significantly increases the compound viscosity of the compound, leading to processing problems. To continually improve the coupling reaction between silica and rubber, in particular with the silica with ultra-high surface area that poses more difficulties to disperse into the rubber matrix, the mercaptosilane coupling agents have been developed, for example, (3-mercaptopropyl)triethoxy silane, Si 363 as shielding





**Figure 9.6** The mechanism of the silanization reaction between silica and a bifunctional silane coupling agent [28].



**Figure 9.6** Continued.



routes for improving processability and utility of NR-based silica–rubber mixes have to be developed. Several publications have revealed that the silanol groups on the silica surface have potential to form physical interactions or even chemical bonds with functionalized elastomers such as chlorosulfonated polyethylene (CSM) [34], carboxylated nitrile rubber (XNBR) [35], and ENR [36,37]. Herein, the polar-modified rubbers can be used either as raw materials [38,39] or as compatibilizers [40,41].

#### **9.1.4 Evolution of silica reinforcement in tires based on epoxidized natural rubbers**

Some polar rubbers bearing functional groups that can interact with the silica surface have been studied as alternatives to silane coupling agents to enhance the interaction in silica-filled compounds [34–41]. A nonpolar rubber such as polybutadiene was chemically modified to have epoxy groups on the main chain and the interaction of such epoxidized rubber with silica was consequently improved, as observed by a decrease of the Payne effect [27] and a change of damping behavior in the glass transition region. The improvement of silica–rubber interaction was also demonstrated by a higher bound rubber content and better silica dispersion in the matrix [42]. Incorporation of silica into an epoxidized SBR showed a strong interaction between the silica and the epoxidized functional groups due to the highly polar character of the epoxidized rubber [43].

ENR has successfully been produced since the 1920s and there were many intensive studies on ENR-related subjects in the 1980s and 1990s, led by the research team from the Tun Abdul Razak Research Centre (TARRC) [44–48]. Recently, growing concerns regarding the increase of the rubber price, shortage of fuel-based materials as well as environmental issues led to an increasing interest in natural-based materials. Renewable materials like NR which can be modified into a variety of functionalized forms are of interest. In 2004 Sumitomo Rubber Industries Ltd. introduced a low rolling resistance “green tire” made from a silica-based ENR compound, which contained 70% nonpetroleum-based materials compared to 44% in the conventional synthetic rubber-based green tire [49]. It was claimed that ENR-containing tires provided better rolling resistance and thus improved fuel efficiency with a good balance of wet grip, when compared to conventional tires [2,44,49]. These conclusions are based on evidence shown in Table 9.1 which summarizes the key properties of the compounds based on silica-filled ENR/NR compared with silica-filled NR/SBR [49]. Tires produced by various companies have been reported to consist of ENR as part of the rubber components in their compound formulations [50–53] because ENR can essentially improve silica dispersion leading to improved processability, storage stability, and hence better tire performance [54,55]. There are two grades of ENR available in the market nowadays: ENR-25 and ENR-50 which possess epoxide contents of 25 and 50 mol.%, respectively. For tire applications, ENR-25 gives the most preferred properties, in particular rolling resistance and wet grip [40,44,55].

**Table 9.1** Compound formulations and tire performances of rubber treads based on silica-filled epoxidized natural rubber (ENR)/NR and silica-filled styrene–butadiene rubber (SBR)/NR as reference—Ref.

Composition (parts by weight)	Tread compounds							
	Ref.	A	B	C	D	E	F	G
Natural rubber	40	40	40	40	40	40	40	40
Epoxidized natural rubber with 25 mol.% epoxide content (ENR-25)	—	60	60	60	60	60	60	60
SBR	60	—	—	—	—	—	—	—
Silica	50	50	50	50	50	50	50	50
Silane coupling agent	5	5	5	5	5	5	5	5
Aromatic oil	10	—	—	—	—	—	—	—
Vegetable oil	—	10	10	10	10	10	10	10
Calcium stearate	—	—	5	5	—	—	5	—
Barium stearate	—	—	—	—	5	5	—	—
Anionic surfactant 1	—	—	1	—	1	—	—	1
Anionic surfactant 2	—	—	—	1	—	1	—	—
Antioxidant	1	1	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2	2	2
Zinc oxide	3	3	3	3	3	3	3	3
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Primary accelerator TBBS	1	1	1	1	1	1	1	1
Secondary accelerator DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
<b>Evaluation results</b>								
Processability (index)	100	80	120	116	116	113	110	90
Abrasion resistance (index)	100	80	105	104	104	102	95	95
Rolling resistance (index)	100	103	105	106	106	105	105	105
Wet grip performance (index)	100	105	106	105	105	104	103	103

These compounds were designed for investigating the effects rubber types, process oils, metal stearates, and surfactants [49]. *TBBS*, N-tert-butyl-2-benzothiazyl sulfenamide. *DPG*, 1,3-diphenylguanidine.

ENR is more polar than virgin NR due to the epoxide groups in its structure. The chemical and physical properties of ENR change according to the epoxide contents, such as the resistances toward heat and swelling [47]. By its polar functional groups, ENR interacts with hydroxyl groups on the silica surface [55]. It has been reported already that the mechanical properties of silica-filled ENR without coupling agent are higher than those of silica-filled virgin NR [38,56]. This was claimed to be due to improved interaction between ENR and the silica surface via hydrogen bonds. ENR as the rubber component in tire compounds has been reported to improve the silica dispersion leading to improved processability, better storage stability, and tire performance [52,54,55,57]. ENR was also used as

compatibilizer in silica-filled NR/NBR (acrylonitrile butadiene rubber) blends to enhance the mechanical properties [58]. In the case of silica-filled NBR vulcanizates the use of ENR as a compatibilizer improved tensile strength, tear strength, and abrasion loss [59], as well as lowered the loss tangent [60], as the ENR acts as a coupling agent because it can self-crosslink with NBR and also link with silica at the vulcanization temperature [59,60]. Furthermore, ENR was used as a compatibilizer in organoclay-filled NR composites wherein cure characteristics, tensile and dynamic mechanical properties were improved [61]. In Sections 9.3 and 9.4, the uses of ENR as raw material and compatibilizer in silica-filled compounds are discussed.

## 9.2 Silica-reinforced conventional natural rubber compounds

Because of the necessary in situ silanization reaction during rubber processing, the mixing temperature necessary for silica/silane-filled rubber requires a high energy input. In the present chapter the optimized mixing conditions and formulation for a silica/silane/NR system are described. Subsequently, a verification of the mechanistic aspects of silane coupling agents is carried out. Polar-modified NR is of interest in this context because it may lead to a reduction or a possible replacement of conventional silane coupling agents to be discussed in Sections 9.3 and 9.4.

### 9.2.1 Aspects of mixing conditions

The experiments described in the present section first focus on optimization of the mixing conditions, which are key parameters for silica reinforcement in rubber compounds. This section will provide a better understanding of the influence of mixing conditions on the properties of silica-filled NR compounds. The compound formulation and mixing procedure used in this study are given in Table 9.2 and Fig. 9.8A, respectively. The mixing was performed in an internal mixer, while the curatives were added on a two-roll mill. The internal mixer was operated at a fill factor of 70% and a rotor speed of 60 rpm. Initial temperature settings of the mixer were adjusted in the range of 50°C–140°C. The vulcanization of samples was carried out at 150°C with an optimum cure time at 90% vulcanization degree ( $t_{c90}$ ).

#### 9.2.1.1 Compound viscosities during mixing and after the final mixing stage

From Fig. 9.8A, in the second nonproductive stage, that is, from 430 to 700 s, the compounds with low initial mixer temperature settings (i.e., 50°C and 70°C) show a decrease of mixing torque, while the compounds with high initial mixer temperature settings (i.e., 110°C and 140°C) display rather constant mixing torques with a slight increase at the end of this mixing stage. In this latter case the lower mixture viscosity due to a higher temperature is balanced by the higher mixture viscosity



**Table 9.2** Formulation of silica-filled natural rubber (NR) compound used in this study [62,63].

Ingredients	Amount (phr)
NR (grade RSS 3) <sup>a</sup>	100
Silica (grade ULTRASIL 7005)	55
Silane coupling agent TESPT	5
Process oil TDAE <sup>b</sup>	8
Zinc oxide	3
Stearic acid	1
Antioxidant TMQ <sup>c</sup>	1
Secondary accelerator DPG <sup>d</sup>	1.1
Primary accelerator CBS <sup>e</sup>	1.5
Sulfur	1.5

DPG, 1,3-Diphenylguanidine; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide; TMQ, 2,2,4-trimethyl-1,2-dihydroquinoline. TDAE, Treated distillate aromatic extract.

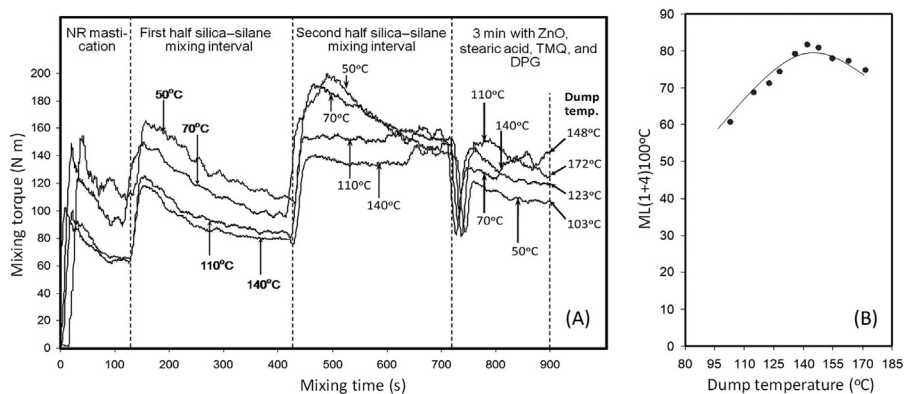
<sup>a</sup>Ribbed smoked sheet grade 3.

<sup>b</sup>Treated distillate aromatic extract.

<sup>c</sup>Poly(1,2-dihydro-2,2,4-trimethyl-quinoline).

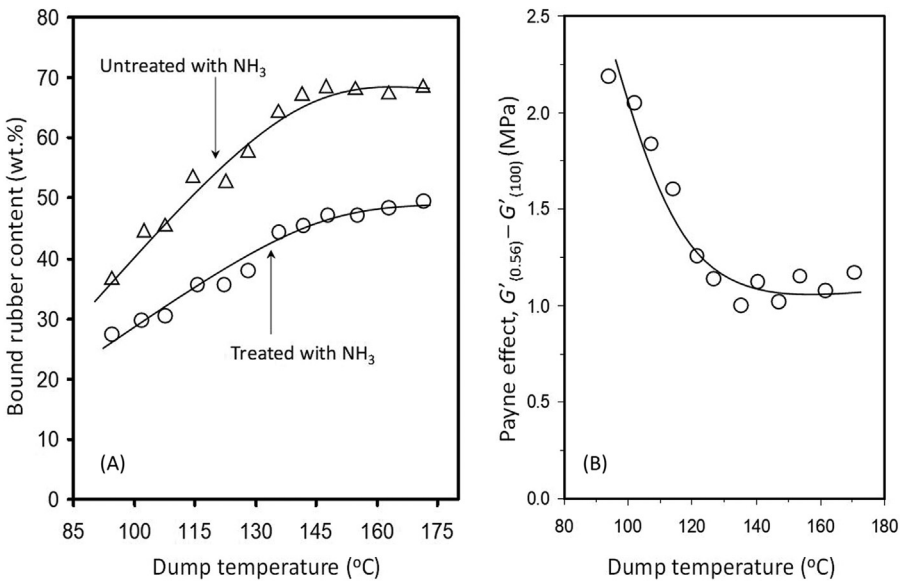
<sup>d</sup>1,3-Diphenylguanidine.

<sup>e</sup>N-Cyclohexyl-2-benzothiazole sulfonamide.



**Figure 9.8** (A) Mixing fingerprints of silica-filled NR masterbatches mixed at different initial mixer temperature settings: that is, 50°C, 70°C, 110°C, and 140°C and (B) Mooney viscosity as a function of dump temperatures of the final compounds (with curatives) [62,63]. NR, Natural rubber.

due to a better silanization reaction and some premature crosslinking caused by sulfur in TESPT. For mixing times larger than 600 s, a crossover of the curves can be observed. Fig. 9.8B illustrates that the Mooney viscosities initially increase with higher dump temperatures, after which the values gradually drop when the dump temperature is over 150°C. This result corresponds with the change in mixing torque as depicted in Fig. 9.8A. The results of bound rubber content and Payne effect

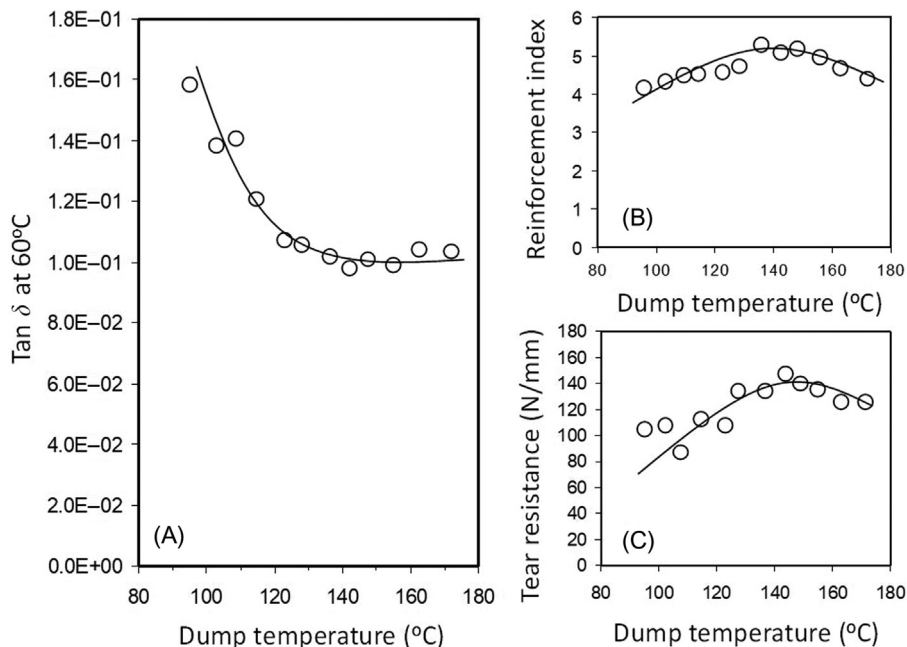


**Figure 9.9** Influence of dump temperatures on (A) bound rubber content and (B) Payne effect of silica-filled NR compounds. Chemically and physically bound rubber contents were measured with and without an ammonia (NH<sub>3</sub>) treatment, respectively [62,63]. NR, Natural rubber.

shown in Figs. 9.9 and 9.10 clearly demonstrate the influences of filler–rubber and filler–filler interactions on the material behavior during mixing and on the properties of compounds.

### 9.2.1.2 Optimizing filler–rubber and filler–filler interactions

The bound rubber contents of the silica-filled compounds were evaluated under two conditions, that is, with and without ammonia treatment. The ammonia treatment was used to cleave the physical linkages formed by physical adsorption, so that only the amount of chemically bound rubber, that is, strong filler–rubber interactions and covalent bonds, was determined. Fig. 9.9A shows the bound rubber contents as a function of dump temperature of the compounds measured without and with ammonia treatment. It is clear that the bound rubber content measured with ammonia treatment is lower than the total bound rubber content measured without ammonia treatment. With increasing dump temperature and larger silica–silane–rubber mixing intervals, both total and chemically bound rubber contents in the compounds significantly increase, but level off when the dump temperature exceeds 135°C. The Payne effects, that is, the storage modulus difference between small (0.56%) and large (100%) strains, are shown as a function of dump temperature in Fig. 9.9B. By increasing the dump temperature and mixing time, the Payne effect as a measure of filler–filler interaction decreases. However,



**Figure 9.10** Effect of dump temperatures on (A)  $\tan \delta$  at 60°C, (B) reinforcement index and (C) tear resistance of silica-filled NR compounds [62,63]. NR, Natural rubber.

for dump temperatures above 135°C, there is no further change of the Payne effect. These findings are in good agreement with mixing torques and Mooney viscosities as discussed in Section 9.2.1.1. This again confirms the optimum degrees of silanization and coupling reactions during mixing of the compounds.

### 9.2.1.3 Influence of mixing conditions on final vulcanizates

Regarding the  $\tan \delta$  at 60°C of the vulcanizates, which is commonly used as an indication of rolling resistance of tires for which a lower value indicates a lower rolling resistance or less fuel consumption, the compounds prepared with higher dump temperature and longer silica – silane – rubber mixing interval have the lowest  $\tan \delta$  at 60°C (Fig. 9.10A). The reduction of  $\tan \delta$  at 60°C levels off for dump temperatures above 135°C. Fig. 9.10B shows the reinforcement index (i.e., the ratio of the moduli at 300% and 100% elongations or M300/M100) and tear resistance of the silica-filled NR vulcanizates prepared with varying dump temperatures. The decrease of reinforcement index and tear resistance when the dump temperature exceeds 150°C is caused by inevitable NR degradation under high temperature and shearing forces. Degradation of NR with and without antioxidant after mixing in an internal mixer at 160°C and 180°C for 10 min was clearly demonstrated by Narathichat et al. [64] Considering the reinforcement index, an increasing dump temperature and a silica – silane – rubber mixing interval lead to an optimum at

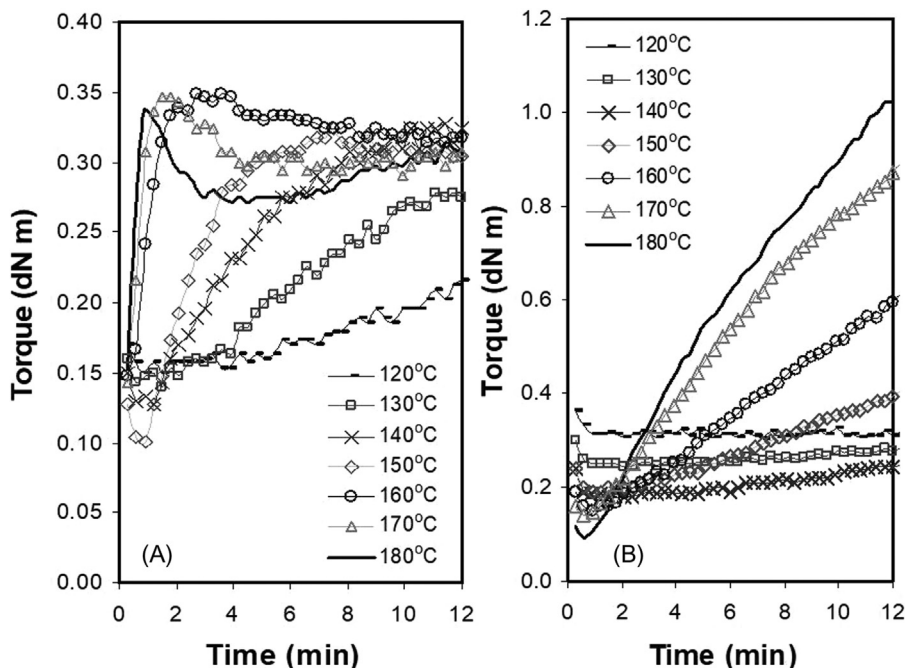
135°C; thereafter the values gradually decrease when the dump temperature exceeds 150°C. A change of tear resistance of the vulcanizates with varying dump temperatures and mixing times displays the same sort of dependence as that of the reinforcement index.

The present results clearly demonstrate that the properties of both unvulcanized compounds and vulcanizates show a strong dependence on mixing dump/discharge temperature, since the silanization reaction and silica dispersion are strongly dependent on this parameter. The optimal mixing conditions for silica-filled NR compounds with TESPT as coupling agent are a dump temperature in the range of 135°C–150°C, and 10 min mixing interval of silica – silane – rubber prior to addition of the other ingredients: zinc oxide (ZnO), stearic acid, stabilizer (polymerized 2,2,4-trimethyl-1,2-dihydroquinoline) and secondary accelerator diphenylguanidine (DPG). Mixing performed till dump temperatures above 150°C leads to a decrease in vulcanizate properties as a result of NR degradation. During mixing of silica-filled NR compounds with TESPT as coupling agent, it is seen that, in addition to the silanization reaction, premature crosslinking reactions take place since NR starts to react with sulfur released from TESPT beginning at a temperature above 120°C [4]. However, this phenomenon does not have an adverse effect on the eventual vulcanizate properties.

### **9.2.2 Competitive reactions between silanization, coupling, and degradation**

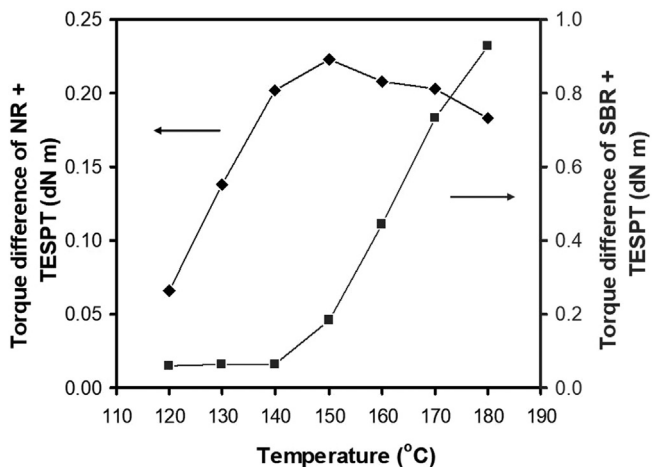
With respect to the change of the NR compound viscosities with dump temperature, as reflected in the mixing torques, Mooney viscosities, bound rubber contents, and Payne effect in Figs. 9.8 and 9.9, each separate property reveals the same trend. With increasing mixing temperatures, the compound viscosities initially increase, then reach a maximum for a dump temperature range of 135°C–150°C. For dump temperatures above 150°C the compound viscosity drops. This phenomenon is different from the work reported by Wolff [65], in which a steady decrease of viscosity with increasing dump temperature from 110°C to 170°C for silica-filled NR compounds was observed. However, it should be noted that only 20 phr of silica was used in combination with 40 phr of carbon black in that work. In the case of silica–TESPT-filled SBR/BR compounds, Reuvekamp et al. [26] reported a rather constant viscosity with increasing dump temperatures from 120°C to 150°C, but an increased Mooney viscosity when dump temperatures above 150°C were obtained, caused by premature scorch of the rubber by sulfur released from the TESPT. It is clear that the NR and SBR/BR compounds display remarkably opposite trends of compound viscosities with varying mixing conditions.

The mixing torque can be used as an indication of polymer softening and breakdown, the silanization and crosslinking reaction. During mixing times of 120–720 s in Fig. 9.8, which represent the first and second incorporations of silica, silane, and processing oil, the decrease in the mixing torques with increasing temperature, especially after the first incorporation, is due to several factors. These include



**Figure 9.11** Cure characteristics of (A) NR and (B) SBR compounds, in the presence of TESPT (5.0 phr) and DPG (1.5 phr) at different cure temperatures [62,63]. DPG, 1,3-Diphenylguanidine; NR, natural rubber; SBR, styrene–butadiene rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

softening of the rubber at high temperature, and the breakdown of NR chains and silica structures by the mixing due to mechanical energy input, in combination with the hydrophobation effect by the TESPT silica surface modification. However, interestingly, a crossover of mixing torques is noticed at the final stage of mixing. It demonstrates that, besides the silanization reaction between silica and silane, a coupling and/or crosslinking reaction of NR with sulfur released from TESPT is simultaneously taking place, that is, a bond between silica – silane–rubber and rubber–rubber is created in the compound and consequently causes a rise in the compound viscosity. To prove this, the cure characteristics of NR and TESPT were investigated in comparison with that of SBR as shown in Fig. 9.11. The test was performed with compounds without *n*-cyclohexyl-2-benzothiazole sulfenamide (CBS) and elemental sulfur. It is clearly seen that NR readily reacts with TESPT at a temperature as low as 120°C and the reaction rate increases rapidly at higher temperatures, as seen from a change of the cure curves. SBR shows a different behavior since it starts to react with TESPT only at a higher temperature, that is, 150°C. The rheometer torque differences, commonly used to indicate the extent of crosslinking of both compounds, are shown in Fig. 9.12. The value for the NR + TESPT compound increases substantially from a test temperature of 120°C up to 150°C and



**Figure 9.12** Rheometer torque difference of NR and SBR compounds as a function of cure temperature in the presence of TESPT (5.0 phr) and DPG (1.5 phr) [62,63]. DPG, 1,3-Diphenylguanidine; NR, natural rubber; SBR, styrene–butadiene rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

then gradually decreases at higher temperatures: a sort of reversion. On the other hand, the torque difference for the SBR + TESPT compound remains constant till a temperature of 140°C and then increases rapidly when the cure temperature exceeds 150°C. These results indicate that the viscosity of silica–TESPT-filled rubber compounds significantly depends on a premature crosslinking reaction that takes place during the mixing process due to available sulfur released from TESPT, in addition to the silanization reaction and the thermo-mechanical shearing action. The large difference between the torque scale variation for SBR and NR in Figs. 9.11 and 9.12 arises from the difference in molecular structures of NR and SBR. The torque increases observed in these rheometer curves are due to the light crosslinks caused by released sulfur from TESPT only. A combination of partial crosslinking and bulky phenyl groups in the styrene part of SBR causes a larger restriction in movement of molecular chains under shear and hence a larger torque increase for SBR, compared to NR. In this context, it is worth to mention that TESPT was first developed as a sulfur-cure accelerator with sulfur-donor properties, before it became commonly accepted as a coupling agent [66]. Therefore the increase of the silica-filled NR compound viscosities for dump temperatures in the range of 100°C–145°C (Fig. 9.8) is to a large extent due to the silica–silane–NR coupling reaction that occurs during the mixing process, and this reaction reaches its maximum at a dump temperature around 135°C–150°C. This premature crosslinking reaction dominates over the breakdown of rubber chains and silica structures.

As seen in Fig. 9.8B, the viscosities of the silanized silica–filled NR compounds tend to decrease again at dump temperatures above 150°C. This may be attributed to an optimum degree of silica–rubber and rubber–rubber interactions/reactions induced by the TESPT. Furthermore, degradation of rubber chains and/or



polysulfide linkages becomes prominent. This observation is confirmed by the change of bound rubber content in the compounds (Fig. 9.9). The chemically bound rubber reaches a plateau at a dump temperature of approximately 135°C, indicating that the silica–silane–rubber and rubber–rubber interactions/reactions remain intact at higher temperatures and shear force.

The mixing of silica–silane and NR cannot avoid this premature crosslinking/coupling when TESPT is used as coupling agent, as the NR starts to react with sulfur released from TESPT at a temperature as low as 120°C (Figs. 9.11 and 9.12). The increased Mooney viscosity is normally an undesired processing property since it leads to processing difficulties in extrusion and calendaring. Surprisingly, this phenomenon does not have an adverse effect on other properties of the compounds and vulcanizates. As reported elsewhere in Ref. [63], even better cure characteristics are obtained for compounds prepared with higher dump temperatures, as indicated by the faster cure rate and longer scorch time. The improvement in cure behavior could be the result of better silanization so that all silica surfaces are well covered with silane resulting in less acidity and polarity, which in turn prevents accelerator adsorption and cure retardation. Furthermore, when DPG is used in the formulation to enhance the silanization reaction [67] as well as to act as a secondary accelerator, the higher level of silanization could also mean that a smaller portion of CBS is adsorbed on the still uncovered silica surface, so that this accelerator is more efficiently used for the curing.

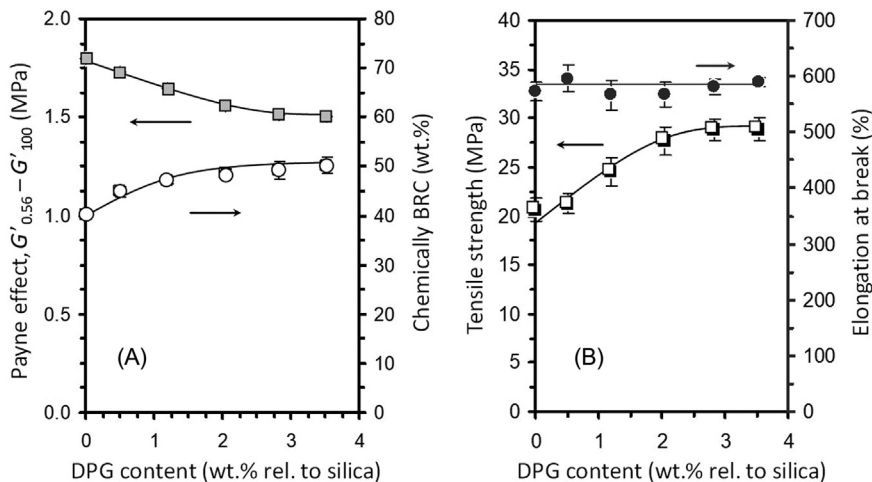
### 9.2.3 Key compound ingredients

Besides the production process, in particular, the mixing procedure, the properties of rubber goods also depend on the choice of rubber type and compound composition: fillers, curing agents, and other additives, as well as the shape and design of the articles. To obtain products with superior properties and more effective processing, this part discusses the rubber formulation that plays a significant role in silica-reinforced NR properties. Type and amount of silica and silane coupling agent as well as the amount of DPG need to be optimized.

#### 9.2.3.1 Tetrasulfide versus disulfide silane coupling agents

The results demonstrate that vulcanizate properties of the silica-filled NR are much improved by incorporating silane coupling agents. Fig. 9.13 shows that TESPT clearly gives better tensile strength than the disulfide-based silane (TESPD). The use of TESPT provides a greater extent of filler–rubber interactions and dispersion stability as indicated by flocculation rate constant [68] due to filler–rubber interaction and lightly rubber–rubber crosslinks, therefore better tensile strength, when compared to the use of TESPD. Both types of silane show optimal loadings at approximately 9.0 wt.% relative to the amount of silica. This result is consistent with the conclusion of Guy et al. [69] which led to a well-accepted Eq. (9.1) for estimating the optimum quantity of ethoxy-based silane coupling agents to be used in a silica-filled rubber compound. Furthermore, an equation for optimizing the





**Figure 9.14** Influence of DPG contents on (A) Payne effect, chemically bound rubber, (B) tensile strength and elongation at break of silica-filled NR compounds [62,68]. DPG, 1,3-Diphenylguanidine; NR, natural rubber.

zinc soaps, fatty acids, amine antioxidants, glycols, and accelerators in particular, have rather strong adsorptive interactions with the silica surface. Apart from lowering the crosslink density caused by the acidity of the silica surface and by adsorption of accelerators that affect the cure behavior, the adsorbed layer of chemicals prevents direct wetting between silica and rubber and then lessens the extent of silica–rubber interactions [3,23,70]. To minimize the accelerator adsorption on silica surface and hence to improve cure characteristics, either glycols or amines are normally added into the rubber compounds. In addition to diethylene glycol, the commonly used amine for this purpose is DPG, which itself is also acting as a synergistic secondary accelerator for sulfenamide accelerated sulfur vulcanization [23,71]. Furthermore, DPG facilitates as a catalyst the silanization reaction between silica and silane coupling agent [72].

DPG acts as a synergist to sulfenamide primary accelerators, as well as activator for the silanization reaction, because DPG decreases the Payne effect, taken as semiquantitative indication for reduced filler–filler interaction, and increases the bound rubber content as indicative for filler–rubber interactions, see Fig. 9.14A. Tensile strength increases with the addition of DPG up to its optimal amount of 2 wt.% relative to the silica content (Fig. 9.14B). Therefore the optimal quantities of both silane coupling agent and DPG required in the formulation are correlated to the CTAB-specific surface area of the silicas employed, as demonstrated in Eqs. (9.1) and (9.2).

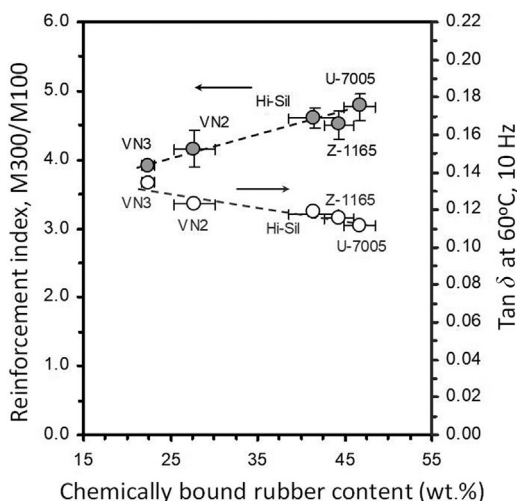
DPG is generally used as a secondary accelerator that gives a synergistic effect with primary sulfenamide type accelerators. As the silica surface is acidic and highly polar in nature, which interferes with the performance of basic accelerators during sulfur vulcanization and causes delayed curing, the addition of DPG into the

compounds improves the cure characteristics. In addition, DPG has been reported to act as a booster for the silanization reaction as amine can catalyze the condensation reaction [72]. The better silanization reaction results in more hydrophobicity of the silica surface and hence less interference with the vulcanization reaction.

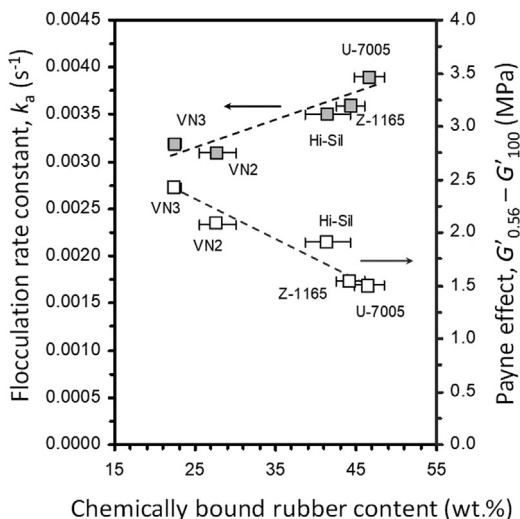
### 9.2.3.3 Different types of silica

Highly dispersible (HD) silicas provide higher bound rubber contents than conventional silicas and these are in accordance with the dibutylphtalate or DBP values, indicating higher silica structure. The use of higher structured silicas not only results in a lower Payne effect, that is, a better filler–rubber interaction, but also generates a faster flocculation process (demixing) or less dispersion stability when compared with conventional silicas. A higher silica structure leads to better dispersion, smaller cluster sizes, and thus faster flocculation. The HD silica-reinforced NR vulcanizates show better reinforcement index and lower  $\tan \delta$  at 60°C, indicative for lower rolling resistance if used in tire treads, compared to those based on conventional silica – filled compounds. The vulcanizate properties correlate with the chemically bound rubber contents before vulcanization.

HD silicas clearly give higher total and chemically bound rubber contents, see Fig. 9.15, indicating a better filler–rubber interaction and thus greater reinforcement power in comparison with conventional silicas. HD silicas have been developed originally for synthetic rubbers like SSBR and BR which develop lower shear forces than NR by lack of strain-induced crystallization so that this type of silica



**Figure 9.15** Correlations between chemically bound rubber, reinforcement index, and  $\tan \delta$  at 60°C of silica-filled NR compounds prepared based on the formulation shown in Table 9.2. The optimum amounts of TESPT silane and DPG were estimated following Eqs. (9.1) and (9.2) [62,68]. DPG, 1,3-Diphenylguanidine; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.



**Figure 9.16** Correlations between chemically bound rubber content, flocculation rate constant, and Payne effect of silica-filled NR compounds prepared based on the formulation shown in Table 9.2. The optimum amounts of TESPT silane and DPG were estimated following Eqs. (9.1) and (9.2) [62,68]. DPG, Diphenylguanidine; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

can be easily dispersed. The use of HD silica in rather highly viscous materials like NR will surely lead to better dispersion, compared to conventional silica. Hence, the compounds filled with HD silica shall consist of smaller aggregates, corresponding to less filler–filler interaction, that is, more filler–rubber interaction, compared to the conventional silicas, as indeed seen in the bound rubber contents in Figs. 9.15 and 9.16.

In general, the DBP value is a measure of reinforcing filler structures. The higher the DBP value, the higher the extent of bound rubber, in particular the chemically bound rubber. A high DBP value indicates structures with high branching of clusters [73,74] which provide a greater surface contact area between silica and rubber. For conventional silicas (CV), ULTRASIL VN2 with a lower CTAB-specific surface area but higher DBP value (see Table 9.3) gives a higher bound rubber content compared to ULTRASIL VN3. The HD silicas also show that filler–rubber interaction in the compound corresponds most clearly with filler structure, that is, DBP value and practically not with the Brunauer–Emmett–Teller (BET) or CTAB-specific surface areas. As reported by Blume [75], dispersion depends mainly on the DBP value, where higher DBP values lead to better filler dispersion. As the rubber molecular chains penetrate into the voids of silica clusters during mixing, a higher structure with a higher void volume allows more rubber molecules to penetrate into silica clusters, thus leading to a breakdown of the large clusters into smaller clusters. This accounts for better dispersion of silica in the rubber and hence higher filler–rubber interaction.

**Table 9.3** Types, suppliers, and technical data of silicas used in this study [62,68].

Silica	Supplier	Type	BET (m <sup>2</sup> /g)	CTAB (m <sup>2</sup> /g)	DBP (g/100 g)
ULTRASIL VN3 GR	Evonik Industries, Germany	CV	175	165	176
ULTRASIL VN2 GR	Evonik Industries, Germany	CV	127	125	185
ULTRASIL 7005	Evonik Industries, Germany	HD	180	171	217
Zeosil 1165MP	Solvay, France	HD	160	150	202
Hi-Sil EZ160	PPG Industries, the Netherlands	HD	160	150	192

CTAB, Cetyltrimethylammonium bromide; DBP, dibutylphtalate; HD, highly dispersible.

Fig. 9.16 shows that the compounds filled with HD silicas have poorer dispersion stability than the ones with conventional silicas, as faster flocculation can be observed in these compounds. Based on the bound rubber content depicted in Fig. 9.15, HD silicas provide higher filler–rubber interaction indicated by lower Payne effects. This should also provide better dispersion stability and suppress the flocculation process. However, this is not the case. A possible explanation may be in the diffusion of silica clusters as it plays a role in flocculation kinetics. It is well known for colloidal systems that the diffusion constant depends on temperature and inversely relates to viscosity and radius of the particles [76]. This has empirically been proven to apply to filled rubber compounds, as demonstrated by a change of carbon black flocculation with matrix viscosity [76]. The increase of flocculation rate constant in spite of increasing compound viscosity and chemically bound rubber, as well as with increasing DBP value (Figs. 9.15 and 9.16), may therefore be attributed to a smaller size of the silica clusters. The higher filler structure leads to a greater extent of cluster breakdown, resulting in smaller clusters that can easily migrate through the unvulcanized compound under thermal conditions. The results do suggest however that even though HD silica is employed, the flocculation process in the compounds cannot be prevented. This is because, in principle, the silica surface could not be fully hydrophobized by a silane; only 20%–30% of silica surface is modified [29,30]. Thus the silica clusters dispersed in a rubber with a silane used are still polar and capable of inducing the reformation of larger silica clusters in the compound. However, in this case, this feature does not give adverse effects on the Payne effect measured at 100°C. The HD silicas still display less filler–filler interactions than the conventional counterparts.

### 9.2.4 Mechanistic aspects of silane modifiers

To gain better insight in the chemical mechanisms of bifunctional organosilanes, especially TESPT in reaction with silica and NR, different types of modifying

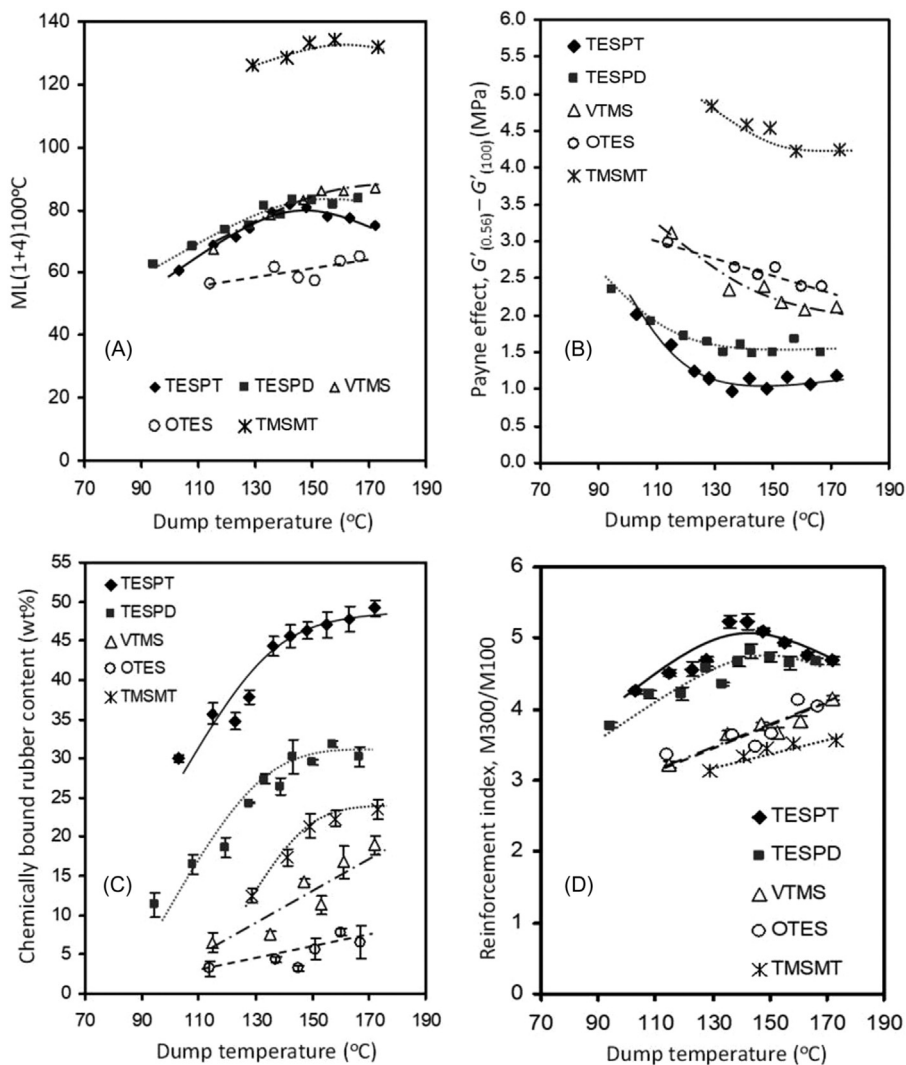


**Table 9.4** Silane modifiers used in this study [62,77].

Chemical name	Abbreviation	Structure
Bis-(3-triethoxysilylpropyl) tetrasulfide	TESPT	$\begin{array}{c} \text{H}_5\text{C}_2\text{O} \\   \\ \text{H}_5\text{C}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}_4-(\text{CH}_2)_3-\text{Si}-\text{OC}_2\text{H}_5 \\   \qquad \qquad \qquad   \\ \text{H}_5\text{C}_2\text{O} \qquad \qquad \qquad \text{OC}_2\text{H}_5 \\ \text{H}_5\text{C}_2\text{O} \qquad \qquad \qquad \text{OC}_2\text{H}_5 \end{array}$
Bis-(3-triethoxysilylpropyl) disulfide	TESPD	$\begin{array}{c} \text{H}_5\text{C}_2\text{O} \\   \\ \text{H}_5\text{C}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}_2-(\text{CH}_2)_3-\text{Si}-\text{OC}_2\text{H}_5 \\   \qquad \qquad \qquad   \\ \text{H}_5\text{C}_2\text{O} \qquad \qquad \qquad \text{OC}_2\text{H}_5 \\ \text{H}_5\text{C}_2\text{O} \qquad \qquad \qquad \text{OC}_2\text{H}_5 \end{array}$
Octyltriethoxysilane	OTES	$\begin{array}{c} \text{H}_5\text{C}_2\text{O} \\   \\ \text{H}_5\text{C}_2\text{O}-\text{Si}-(\text{CH}_2)_7-\text{CH}_3 \\   \\ \text{H}_5\text{C}_2\text{O} \end{array}$
Vinyltrimethoxysilane	VTMS	$\begin{array}{c} \text{H}_5\text{C}_2\text{O} \\   \\ \text{H}_3\text{CO}-\text{Si}-\text{CH}=\text{CH}_2 \\   \\ \text{H}_3\text{CO} \end{array}$
Bis-(3-trimethylsilylmethyl) tetrasulfide	TMSMT	$\begin{array}{c} \text{H}_3\text{C} \\   \\ \text{H}_3\text{C}-\text{Si}-\text{CH}_2-\text{S}_4-\text{CH}_2-\text{Si}-\text{CH}_3 \\   \qquad \qquad \qquad   \\ \text{H}_3\text{C} \qquad \qquad \qquad \text{CH}_3 \end{array}$

agents as illustrated in Table 9.4 are employed to investigate the role of key functionalities contained in the modifying chemicals. The properties of silica-filled NR compounds and vulcanizates prepared with different silane coupling agents are correlated with the phenomena of reinforcement. The mechanisms of the reactions that take place during processing of the silica-based NR compounds are defined in the present section. The compounds in this investigation were prepared and characterized as those described in Section 9.2.1.

As shown in Fig. 9.17A, the alkoxy-based organosilanes substantially reduce the compound viscosity, when compared to the nonalkoxy TMSMT (bis-trimethylsilylmethyl tetrasulfide), because of their hydrophobation power through the reaction of the alkoxy groups with the silanol groups of the silica, as already mentioned. In addition to the influence of the alkoxy groups, the sulfur moiety in the silane agents also plays a significant role. With increasing mixing dump temperature the Mooney viscosity of the compounds prepared with TMSMT, a sulfidic (nonalkoxy)-silane, gradually increases and reaches an optimum at dump temperatures in the range of 140°C–150°C. TESPT and TESPD, which are sulfidic alkoxy-type silanes, show a similar trend but at lower values. After the Mooney viscosities have reached the maximum value the compounds show some sort of reversion which could be linked to a change within the polysulfide linkages. According to the conclusions given in Section 9.2.1, this result is in good agreement with the fact that, apart from the silanization reaction, a certain amount of coupling and crosslinking reactions of active sulfur toward NR also takes place during mixing in the mixer, which results in a rise of the Mooney viscosity. Basically, all these reactions are temperature dependent. Higher mixing temperatures lead to a higher potential for silanization as well as for crosslinking [25,26,68].



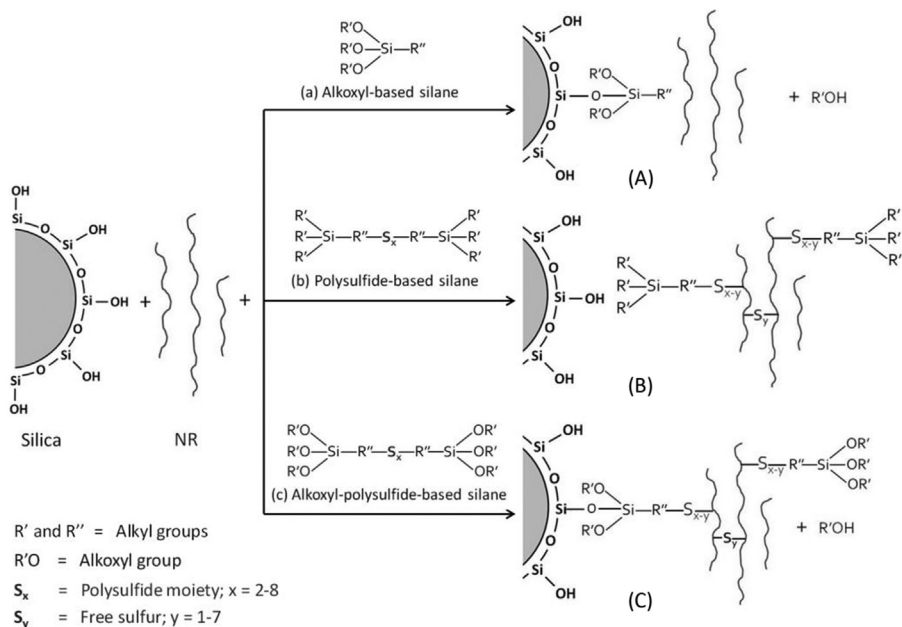
**Figure 9.17** Properties as a function of dump temperatures of silica-filled NR compounds with different silane modifiers. The quantities of alkoxy-based and nonalkoxy sulfide-based silanes were estimated based on the equimolar content of alkoxy or sulfide groups, respectively, relative to that of TESPT as reference [62,77]. *NR*, Natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

In general, an increase in the degree of silanization should lead to a decrease in compound viscosity as a consequence of improvement in silica dispersion [65,74,78]. However, this is apparently not the case for NR, for which the Mooney viscosity initially increases with increasing dump temperature, and then either levels off or decreases a little after reaching a certain dump temperature. This points

to a dominant effect of network contributions toward the compound viscosity, see Fig. 9.17C. These network contributions originate from premature crosslinking that mainly includes two possible features: (1) silica – silane – rubber linkages and (2) rubber–rubber cross-links. For the sulfide based silanes, that is, TESPT, TESP, and TMSMT, the crosslinks are formed via sulfur that is released and activated at the high temperatures. For vinyl silane, that is, VTMS (vinyltrimethoxysilane), the crosslinks can also occur via C = C and active radicals are generated during mixing. Surprisingly, for octyltriethoxysilane (OTES) that has alkoxy groups with an alkyl chain, there is also a slight increase of the compound viscosity with increasing dump temperature. Nonetheless, the OTES silane gives the lowest compound viscosity, as this system can generate only a silanization or hydrophobation reaction and no real crosslinks.

Based on the results of the Payne effects and reinforcement parameters as shown in Fig. 9.17B and D, it is clear that the alkoxy-based organosilanes reduce filler–filler interaction for silica-filled NR compounds, indicating that they can effectively transform the hydrophilic into a more hydrophobic silica surface to provide better compatibility between the silica and NR. This leads to improved silica dispersion. However, the different alkoxy-silanes show variable efficiency because of their differences in functionalities on the other side of the silane molecules, as depicted in Table 9.4. TESPT and TESP possess sulfur functionalities that can create crosslinks during mixing at high temperature and so strongly affect the compound viscosity, silica dispersion, and filler–filler interaction. The alkoxy nonsulfur silanes, that is, OTES and VTMS, show somewhat less reactivity compared to the sulfide types. Free sulfur released from TESPT can produce lightly crosslinked rubber during the nonproductive mixing stage [26,63,68]. These network contributions result in a better stability of the dispersed silica clusters as the chemical linkages restrict the silica mobility in the rubber matrix and hence suppress the reagglomeration of silica. The explanation was already elaborated in terms of the correlation between flocculation and network contributions in Sections 9.2.1 and 9.2.2. The sulfur moiety contained in the silanes provides additional aid for the improvement of the silica dispersion stability and Payne effect of silica-filled rubber systems. The use of TMSMT that has no alkoxy groups but only a sulfur functionality clearly demonstrates the ineffectiveness of this silane type, as it provides only a poor silica dispersion and very high extent of filler–filler interaction in the NR compounds. Not being able to silanize, TMSMT cannot chemically hydrophobize the silica surface and so the large difference in polarity between silica and NR is not overcome. The results demonstrate that it is necessary to utilize bifunctional organosilanes for silica-filled compounds.

The investigations clarify that when organosilanes bearing alkoxy- and sulfide-functional groups are used, there are three reaction mechanisms competitively taking place during primary compound mixing or in the nonproductive mixing stage. Fig. 9.18 describes the mechanistic aspects of three main different silanes used in silica-filled NR compounds. These mechanisms are all temperature dependent: (1) the silane-to-silica or silanization/hydrophobation reaction; (2) silane-to-rubber or coupling reaction; and (3) rubber–rubber crosslinking originating from active sulfur



**Figure 9.18** Interactions between silica, natural rubber molecule, and silanes with different functionalities including (A) alkoxy-based silane, (B) polysulfide-based silane and (C) alkoxy-polysulfide-based silane [77].

released by the polysulfide-based silanes. These simultaneous reactions reach an optimum at a dump/discharge temperature of approximately  $140^{\circ}\text{C}$ – $150^{\circ}\text{C}$ , as determined by filler–filler and filler–rubber interactions, and mechanical properties corresponding to the findings in the previous sections. The network structures between silica–silane–rubber and rubber–rubber primarily account for an increase of the Mooney viscosity and chemically bound rubber content, as well as improved silica dispersion with less filler–filler interaction. A silane bearing only alkoxy groups but no sulfur moiety and so cannot couple to the rubber shows that it can improve the processing properties—lower Mooney viscosity, better silica dispersion, lower Payne effect, and mechanical properties only for a very limited degree, relative to the better dispersion—when compared to the one without coupling agent. However, the best possible overall properties are only obtained when bifunctional coupling agents—TESPT and TESP—are used.

### 9.3 Epoxidized natural rubber as raw material for tire tread compounds

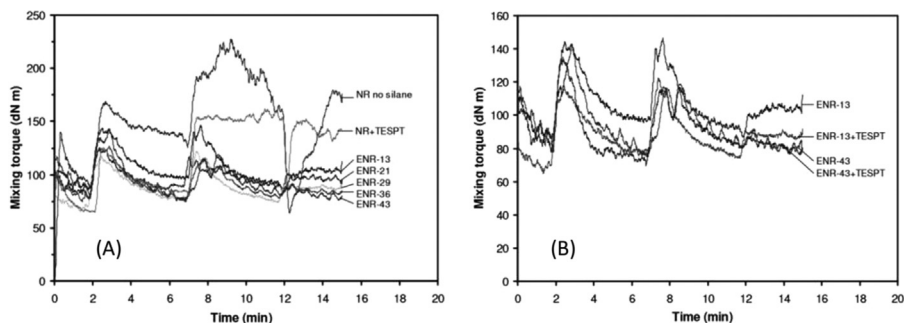
Besides the use of silica surface modifying agents and/or silane coupling agents, compatibilization between silica and hydrocarbon rubbers can be promoted by the

use of polar polymers. As reviewed in Section 9.1.4, the silanol groups on the silica surface have the potential to form physical interactions or even chemical bonds with functionalized rubbers [34–41]. In this part, the influence of epoxide contents in ENRs in the absence of a silane coupling agent and 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, dynamical and mechanical properties of the compounds, and vulcanizates are discussed. The mechanistic principles and optimal processing conditions for silica reinforcement in ENR as raw material and compatibilizer are discussed.

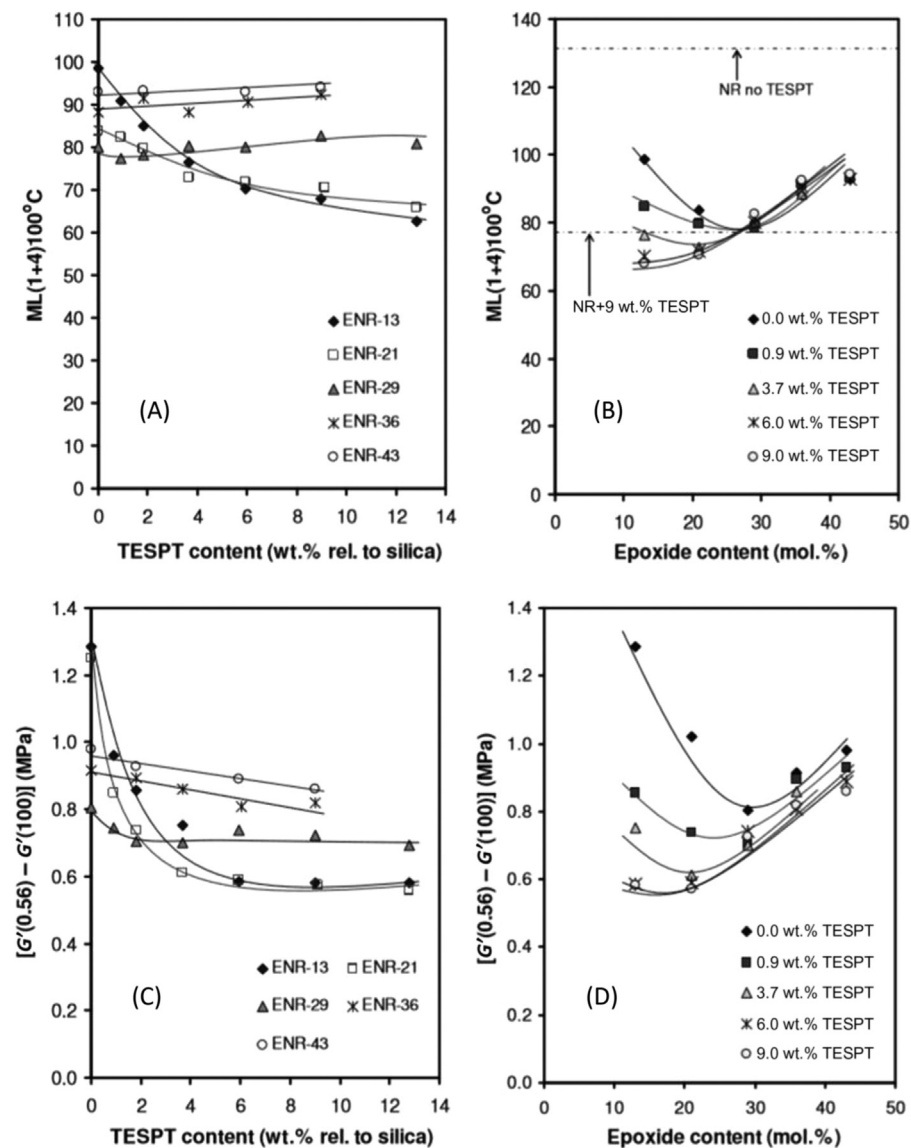
### 9.3.1 Influences of epoxidation degrees and silane coupling agent contents

This part focuses on the influence of epoxide functionality in ENR on the compatibility of silica-filled ENR compounds. Parallel studies with respect to various levels of epoxidation in ENR in the absence of TESPT as well as a combination of ENRs with different loadings of TESPT were carried out. The epoxide functionality on the NR molecules has a significant influence on both processing and end-use properties of silica-filled ENR-based compounds.

The mixing torque (Fig. 9.19), compound Mooney viscosity, and Payne effect (Fig. 9.20) decrease with the presence of epoxide functional groups up to 29 mol.% on ENR compared to silica-filled normal NR compounds, see Fig. 9.19A. A high content of epoxide groups, for example, ENR-36 and ENR-43, adversely affects the processability and most of the properties. Addition of TESPT into silica-filled ENRs with epoxide contents of 13 and 21 mol.% further improves compound processability (Fig. 9.19B) and vulcanizate properties (Fig. 9.20), while the use of TESPT has only a minor effect on the ENR-29 (i.e., 29 mol.% epoxide content) compound.



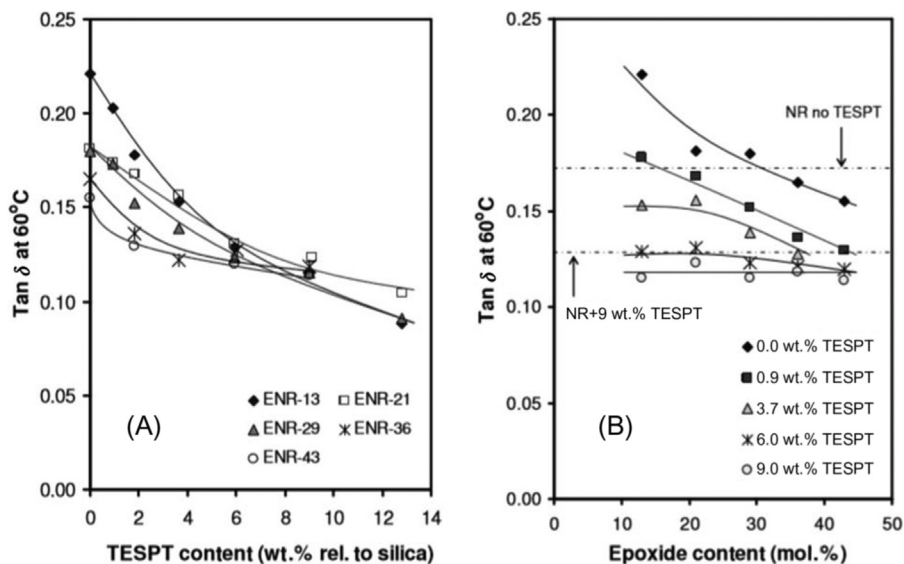
**Figure 9.19** Mixing fingerprints of silica-filled ENR compounds with different epoxide contents in ENR. Silica-filled virgin NR compounds with and without TESPT silane are references [62,79]. ENR, Epoxidized natural rubber; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.



**Figure 9.20** Influences of TESPT and epoxide contents on (A and B) Mooney viscosity and (C and D) Payne effect of silica-filled ENR compounds. The compounds with virgin NR are given as unmodified NR-based references [62,79]. *ENR*, Epoxidized natural rubber; *NR*, natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

The influence of silane content on  $\tan \delta$  at 60°C at a given epoxide level can be seen in Fig. 9.21. Increase of the TESPT loading results in a sharp decrease in  $\tan \delta$  at 60°C of the compounds based on ENRs with 13, 21, and 29 mol.% epoxide content, and a slight decrease for ENR-36 and ENR-43. Basically,  $\tan \delta$  relates strongly

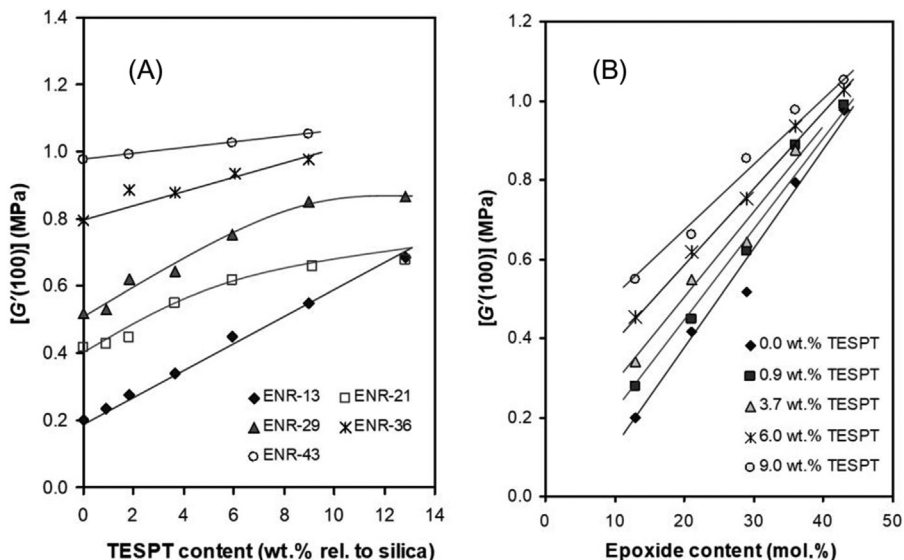




**Figure 9.21** Effects of (A) TESPT and (B) epoxide contents on  $\tan \delta$  at 60°C of silica-filled ENR compounds. The compounds with virgin NR are considered as unmodified NR-based references [62,79]. ENR, Epoxidized natural rubber; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

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 agreement with the storage modulus at 100% strain (Fig. 9.22). Without TESPT, an increase of epoxide contents leads to a strong decrease in  $\tan \delta$  at 60°C as visualized in Fig. 9.21. This can be linked to the greater filler–rubber interaction/network formation as reflected by the higher storage modulus at high strain in Fig. 9.22. The combinations of epoxide functionality with TESPT silane coupling agent jointly improve the  $\tan \delta$  at 60°C or rolling resistance of tires. Therefore, with ENR, there is a possibility to reduce the amount of TESPT needed compared to unmodified NR in silica-filled formulations.

Based on the overall properties, epoxide groups on ENR alone cannot provide the properties to match those of silica–TESPT-filled unmodified NR, but the right combination of epoxide groups and TESPT as silane coupling agent leads to similar levels of properties compared to the silica–TESPT filled unmodified NR system. With the cooperative effect of the polar epoxide groups, it can be concluded that the best possible combination to optimize processability, 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, that is, 2–4 wt.% relative to silica content. This leads to a significant reduction of approximately 60–80 wt.% of TESPT when compared to



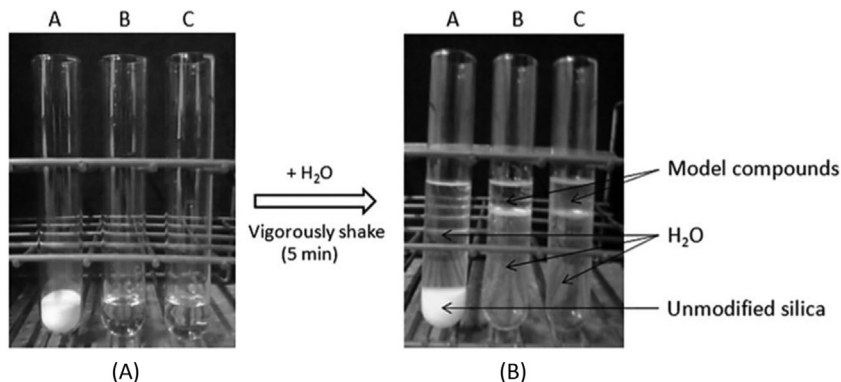
**Figure 9.22** Storage modulus at 100% strain as functions of (A) TESPT amount and (B) epoxide content in ENRs for the silica-filled ENR compounds [62,79]. ENR, Epoxidized natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

the conventional NR compounds, in which the optimal loading of TESPT was 9.0 wt.% relative to silica content [79].

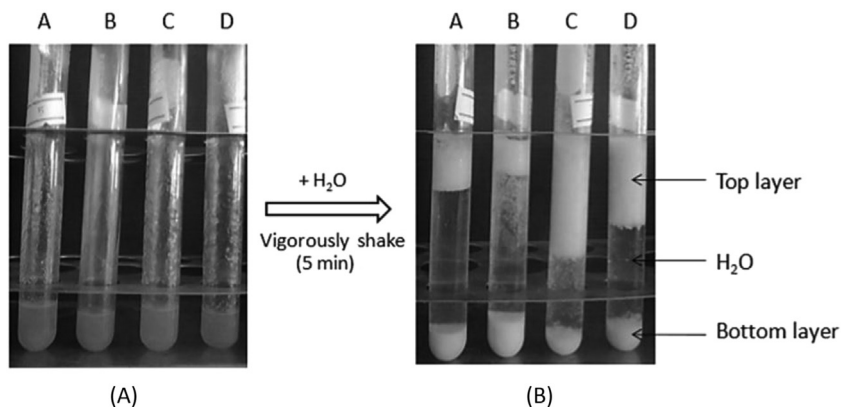
### 9.3.2 Verification of the interactions between epoxidized natural rubber, silica, and silane

Qualitative experiments were 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) were used as model compounds for NR and ENR, respectively. Reactions between model squalenes 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 the silica was surface modified by the model compounds and separated from the original silica which sinks in water, see Figs. 9.23 and 9.24.

The modified silica in the top layer was extracted with acetone to remove unbound hydrocarbons prior to characterization by the FTIR technique. In Fig. 9.25 the FTIR analytical data of the purified modified silicas separated from the mixture of Sq with TESPT, and ESq with and without TESPT displays 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 was used. This reflects the ability to create more strong/



**Figure 9.23** Pure forms of A: silica; B: Sq; and C: ESq; (A) before and (B) after addition of water [62,80].

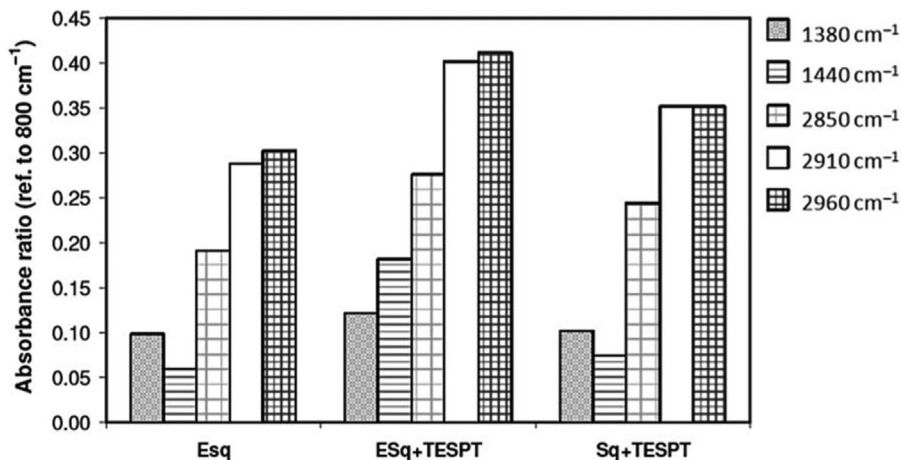


**Figure 9.24** Mixtures of silica and model compounds after heating 1 h at 145°C and with and without TESPT; (A) before and (B) after component separations with water. A: ESq + silica; B: Sq + silica; C: ESq + silica + TESPT; and D: Sq + silica + TESPT [62,80]. TESPT, Bis-(3-triethoxysilylpropyl) tetrasulfide.

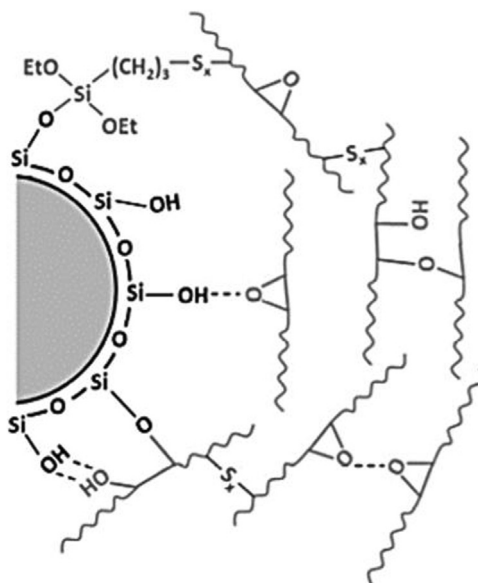
chemical filler–rubber interactions in silica-filled ENR compounds under high thermal conditions during mixing and vulcanization than in compounds based on unmodified NR, either in the presence or absence of TESPT. Fig. 9.26 shows postulated interactions/reactions between silica, silane, and epoxidized rubber molecules based on the evidence from this model compound investigation.

### 9.3.3 Factors affecting compound viscosity and reinforcement mechanism

With regard to the changes in Payne effect and compound viscosity as shown in Fig. 9.20A and B of Section 9.3.1, these phenomena apparently relate well to the

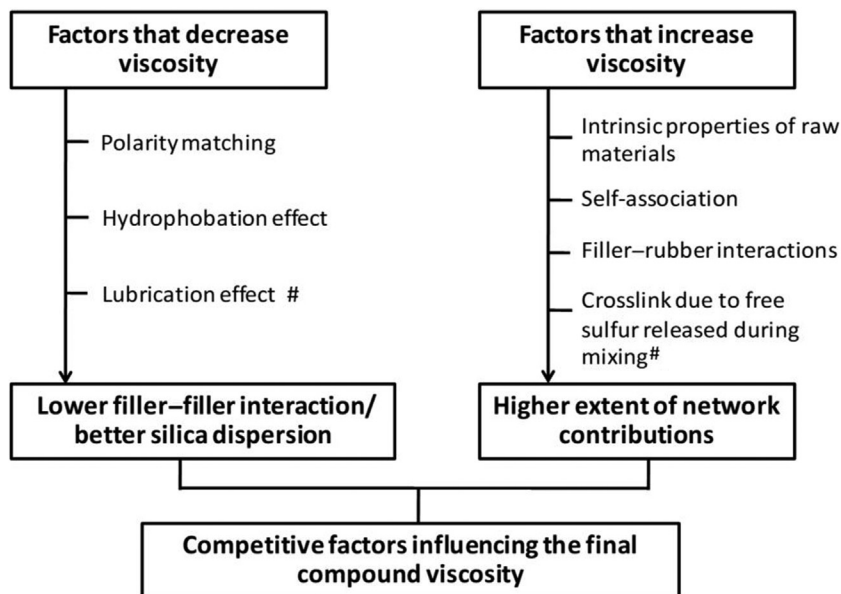


**Figure 9.25** Absorbance ratios for different peaks associated with vibrations of hydrocarbon bonds referred to Si–O bonds at  $800\text{ cm}^{-1}$  in modified silicas [62,80].



**Figure 9.26** Postulated interactions/reactions between silica and epoxidized squalene in the presence of TESPT as silane coupling agent [62,80]. TESPT, Bis-(3-triethoxysilylpropyl) tetrasulfide.

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 Fig. 9.27.



#These factors can only take place in the system with the presence of silane coupling agent.

**Figure 9.27** Competitive factors influencing compound viscosities of silica-filled ENR compounds with and without TESPT silane coupling agent [62,79]. ENR, Epoxidized natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

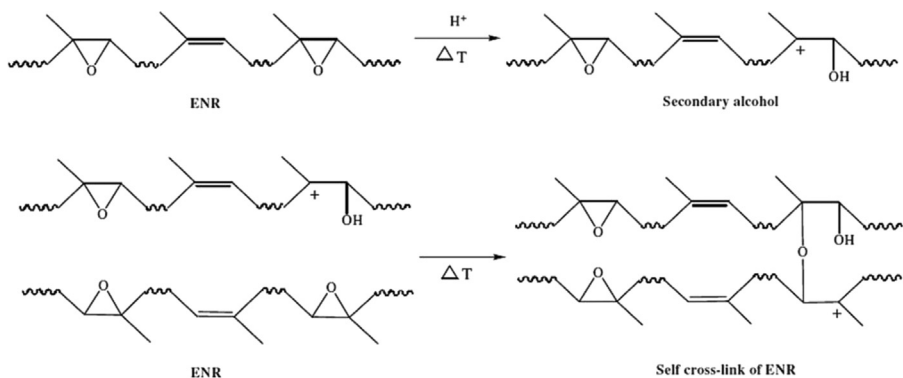
The change in compound viscosities as indicated by Mooney viscosity (Fig. 9.20A and B) can be discussed by considering several factors which are simultaneously and competitively taking place in the compounds. “A better silica dispersion” resulting from a lower filler-filler interaction or Payne effect 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.% (Fig. 9.20A and 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 the Payne effect, see Fig. 9.20C and D. 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 further addition of TESPT has only a minor additional effect on the properties.

After the compounds show their optimum low compound viscosities due to the presence of appropriate combinations of either epoxide functionality or TESPT,

**Table 9.5** ML(1 + 4)100°C of normal natural rubber (NR) and epoxidized NRs (ENRs) with various levels of epoxide functionality [62,79].

Rubber type	ML(1 + 4)100°C
Normal NR (i.e., RSS 3)	73
ENR-13 <sup>a</sup>	85
ENR-21 <sup>a</sup>	89
ENR-29 <sup>a</sup>	91
ENR-36 <sup>a</sup>	93
ENR-43 <sup>a</sup>	96

<sup>a</sup>mol.% epoxide content.



**Figure 9.28** Self-crosslinking of epoxidized natural rubber under acidic and high thermal conditions [81].

other factors play a dominant role toward increased compound viscosities. The rise of compound viscosity can be mainly attributed to “the increment of network contributions” (Fig. 9.22). The ENRs with various levels of epoxide functionality have different basic properties which certainly affect the compound viscosities. As shown in Table 9.5, 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 [81]. Fig. 9.28 shows the possible self-crosslinking of ENR. This network generation contributes to the increase of compound viscosity.

In addition to the possibility of physical interactions generated between ENR and silica via polar–polar interactions, chemical silica-to-ENR coupling has been proposed, as illustrated in Fig. 9.26 [80]. For the compounds with TESPT coupling agent, strong chemical filler–rubber interaction can be formed through silane chemistry contributing to network structures. Moreover, TESPT can additionally release free sulfur into the system and then cause light rubber–rubber crosslinking

during the high thermo-mechanical mixing conditions as indicated earlier in [Section 9.2](#). The combination of these factors that involve network formation leads to the increase in compound viscosities of silica-filled ENR systems.

## 9.4 Compatibilizing silica-filled natural rubber systems by epoxidized natural rubbers

ENR has higher polarity than virgin NR due to the epoxide groups in its structure. The chemical and physical properties of ENR change according to the epoxide contents, such as heat and swelling resistances [47]. By its polar functional groups, ENR interacts with hydroxyl groups on the silica surface [55]. It has been reported already that the mechanical properties of silica-filled ENR without a coupling agent are higher than those of silica-filled virgin NR [54,56]. This was claimed to be due to improved interaction between ENR and the silica surface via hydrogen bonds as also discussed in [Section 9.3](#). ENR as the rubber component in tire compounds has been reported to improve the silica dispersion leading to improved processability, better storage stability, and tire performance [52,54,55,57]. ENR was also used as a compatibilizer in silica-filled NR/NBR blends to enhance the mechanical properties [58]. In the case of silica-filled NBR vulcanizates the use of ENR as a compatibilizer improved tensile strength, tear strength, and abrasion loss [59], as well as lowering the loss tangent [61], as the ENR acts as a coupling agent because it can crosslink with NBR and also link with silica at vulcanization temperature [59,60]. Further, ENR was used as a compatibilizer in organoclay-filled NR composites, wherein cure characteristics, tensile, and dynamic mechanical properties were improved [61,62]. Even though ENR has been used to compatibilize silica and various rubber matrices, the use of ENR as compatibilizer for silica-filled virgin NR has not yet been extensively studied. In the present section a recent research is reported and conducted to verify the role of ENR as compatibilizer in silica-filled NR compounds. A combination of compatibilizing ENR and silane coupling agents was also investigated for its effectiveness in reinforcing a NR compound in comparison with a conventional silanized silica-filled NR compound.

### 9.4.1 *Optimized epoxide content of epoxidized natural rubber used as compatibilizer*

Particular attention in the present section is given to the use of chemically modified NR as compatibilizer for silica-reinforced NR compounds. ENRs with different mol.% of epoxide groups were used as compatibilizers in a range of 2.5–15 phr for virgin NR/silica compounds. The effects of ENR contents and mol.% of epoxide were investigated. The epoxide groups are supposed to interact with the silanol groups of the silica and so to improve silica–rubber compatibilization, while the unmodified parts of the ENR structure are compatible with the NR matrix. The compound formulations used for this investigation are shown in [Table 9.6](#).

**Table 9.6** Compound formulations used in this experiment [82,83].

Ingredients	Amounts (phr)		
RSS 3	100.0	100.0	97.5–85.0
ENRs	—	—	2.5–15.0
Zeosil 1165MP	55.0	55.0	55.0
TESPT <sup>a</sup>	—	4.5	—
TDAE oil	8.0	8.0	8.0
ZnO	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0
TMQ	1.0	1.0	1.0
DPG <sup>a</sup>	1.0	1.0	1.0
CBS	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5

*DPG*, 1,3-Diphenylguanidine; *ENR*, epoxidized natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide; *TMQ*, 2,2,4-trimethyl-1,2-dihydroquinoline; *CBS*, n-Cyclohexyl-2-benzothiazole sulfonamide; *TDAE*, Treated distillate aromatic extract.

<sup>a</sup>Amounts of TESPT and DPG were calculated according to Eqs. (9.1) and (9.2), respectively.

The compounds were prepared using an internal mixer with a fill factor of 70%, a rotor speed of 60 rpm and a controlled dump temperature at 145°C. A mixing procedure was applied following the same as given in Fig. 9.8. NR and ENR were first masticated. Then, other compositions were incorporated. Finally, curatives were added on a two-roll mill for 5 min and then the compound was sheeted out and kept for 24 h prior to property characterizations.

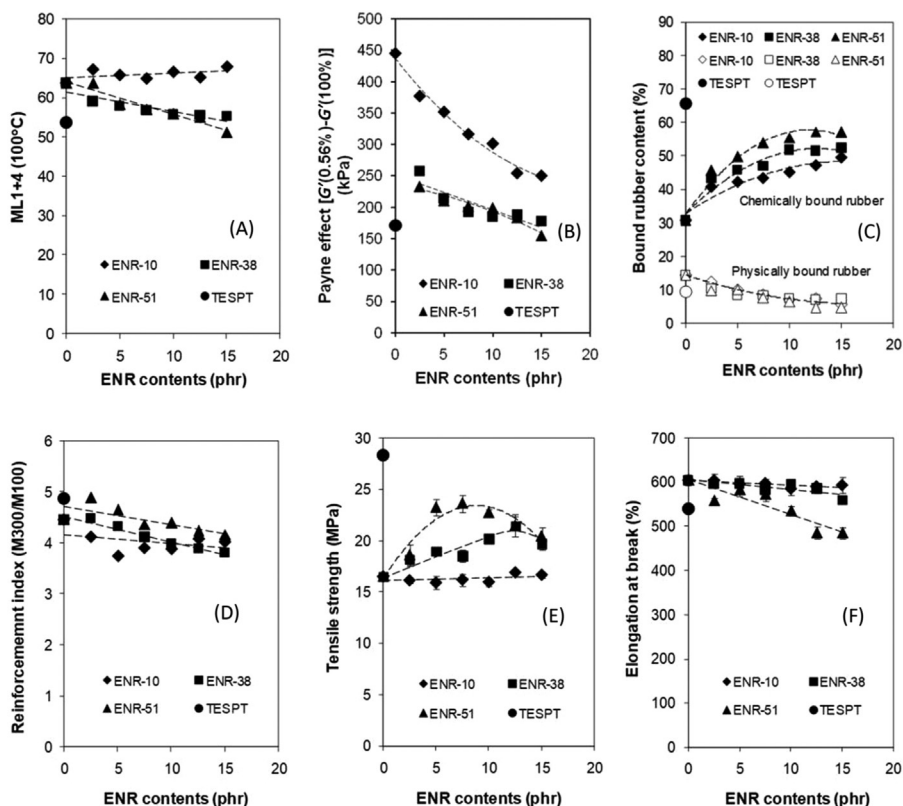
These amounts of ENRs investigated in this study were considered to be in a range of which they show only a compatibilizing effect with none/less blending effect involved in the system. Based on the results shown in Fig. 9.29, the use of ENR as compatibilizer improves the filler–rubber interaction, silica dispersion, and tensile strength. Increase of the ENR content and mol.% of epoxide groups decreases the filler–filler interaction and improves silica dispersion, as reflected in a lower Mooney viscosity and Payne effect (Fig. 9.29A and B). The addition of ENR-38 and ENR-51 (with 38 and 51 mol.% epoxide, respectively) leads to higher chemically bound rubber (Fig. 9.29C) and tensile strength (Fig. 9.29E).

The Mooney viscosities of the compounds with ENR-10 as compatibilizer show almost no change when the amount of ENR-10 is increased from 2.5 to 15 phr (Fig. 9.29A). Incorporation of ENR-38 and ENR-51 decreases the Mooney viscosities of the compounds to match the level of that of the TESPT-containing compound when the amount of ENRs used is  $\geq 10$  phr. The decrease of compound viscosity when ENR is used as compatibilizer implies an improvement of silica dispersion due to interactions between epoxide groups and silanol groups of the silica resulting in better compatibility and avoiding the re-clustering. However, the compound viscosities can also be affected by various factors including NR/ENR blend incompatibility. The presence of polar epoxy groups in the ENRs leads to a difference between the solubility parameters of NR and ENR and increases interfacial tension. It has been reported that NR/ENR blends exhibit two distinct glass

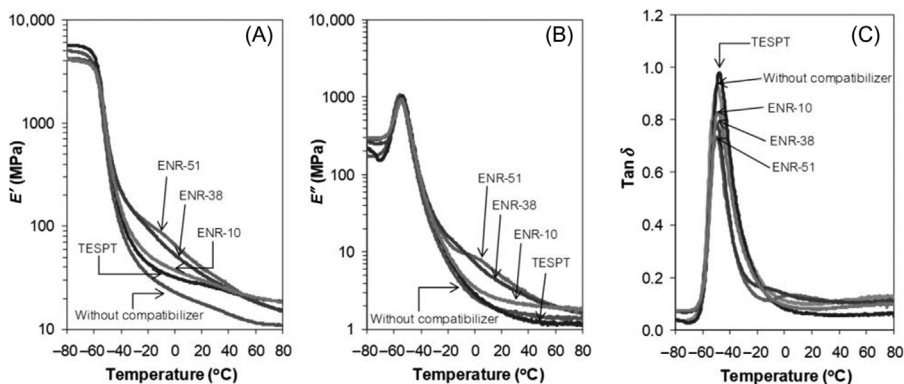


transition temperatures ( $T_g$ ) corresponding to the original polymers, as analyzed by differential scanning calorimetry [84].

The use of ENR-10 shows no positive effect on the tensile strength of the silica-filled NR, but the addition of ENR-38 and ENR-51 enhances the tensile strength, compared to the compound without compatibilizer (Fig. 9.29E). ENR-51 gives a higher tensile strength than ENR-38, and increasing the ENR content increases tensile strength to a maximum whereafter the property drops. The optimum value is observed at 7.5 phr for ENR-51 and 12.5 phr for ENR-38. The results support the proposition that the epoxide functional groups improve silica–rubber interaction in the compounds. This is in accordance with the increased bound rubber content in Fig. 9.29C and the decreased elongation at break as shown in Fig. 9.29F. When compared among the ENR types, the use of ENR-51 gives the highest reinforcement index. An increase of ENR content tends to decrease the reinforcement index



**Figure 9.29** Influence of ENR contents used as compatibilizer on (A) Mooney viscosity, (B) Payne effect, (C) bound rubber content, (D) reinforcement index, (E) tensile strength and (F) elongation at break of silica-filled NR compounds and vulcanizates [82,83]. ENR, Epoxidized natural rubber; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.



**Figure 9.30** (A) Storage modulus, (B) loss modulus and (C)  $\tan \delta$  as a function of temperature of silica-filled NR vulcanizates with 7.5 phr of ENRs as compatibilizer [82]. *ENR*, Epoxidized natural rubber; *NR*, natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

slightly (Fig. 9.29D). This may be caused by the presence of two different rubber phases in the system due to the incompatibility between NR and ENR [37,84], as discussed earlier for Mooney viscosities in Fig. 9.29A.

With respect to tire performance the presence of ENR-38 and ENR-51 as compatibilizer improves wet grip indicator but negatively affects rolling resistance indicator due to the increased glass transition temperature of the ENR. The addition of ENR-51 at 7.5 phr shows the best overall properties, however, still somewhat lower when compared to a compound with the commonly employed TESPT silane as coupling agent.

Fig. 9.30 shows the effect of ENR compatibilizers in silica-filled NR vulcanizates on the dynamic performance as a function of temperature. The addition of 7.5 phr of ENRs with different levels of mol.% epoxide results in a different response of the  $\tan \delta$  curves (Fig. 9.30C). The height of the  $\tan \delta$  peaks is decreased when the epoxide group level is increased. This is caused by the interactions between silica and ENRs in the NR matrix and between ENR molecules themselves, leading to a restriction of the molecular chain mobility and relaxation. Furthermore, the higher epoxide groups content leads to a possible self-crosslinking between the ENR itself and introduces an immobilization of the rubber chains. Second transitions of  $\tan \delta$  are observed when ENR-38 and ENR-51 are added into the silica-filled NR compounds, in accordance with the second step changes of  $E'$  and  $E''$  as observed in Fig. 9.30A and B. These may again be attributed to the glass transition temperatures of ENR-38 and ENR-51. The highest  $\tan \delta$  peak is observed for the silica/TESPT-filled vulcanizate, which can be described by its better silica dispersion causing a decrease of rubber trapped within the filler network and more mobility of rubber segments in the matrix that are involved in the relaxation process. The change of  $\tan \delta$  peak height with respect to compatibilizer types, that is, TESPT and ENR, is in accordance with the work previously reported by Saramolee et al. [85].

**Table 9.7** Glass transition temperatures taken from loss modulus and  $\tan \delta$  peaks, and values of  $\tan \delta$  at different temperatures of silica-filled natural rubber (NR) vulcanizates with various compatibilizers [82].

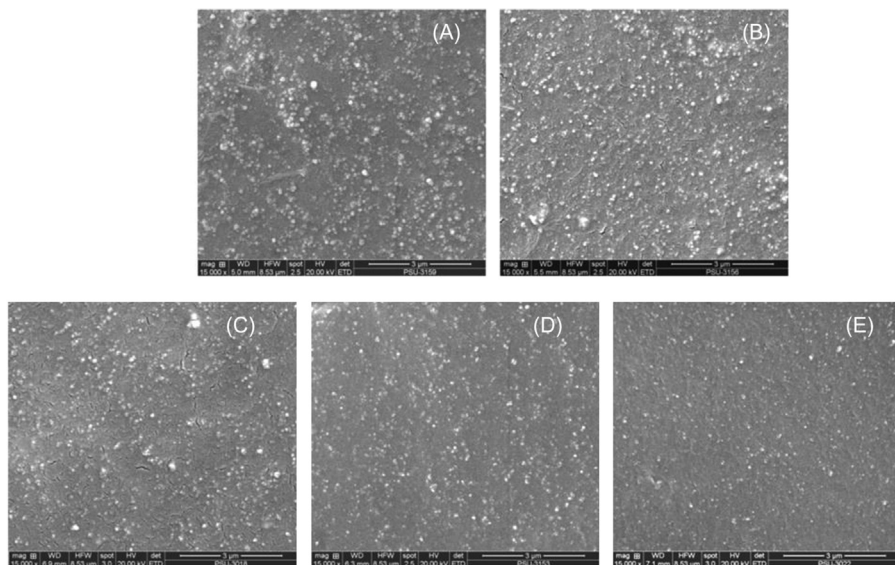
Compatibilizer types	Glass transition temperature (°C)	Values of $\tan \delta$			
	At $E''$ peak	At $\tan \delta$ peak	At 0°C	At 5°C	At 60°C
Without compatibilizer	-56	-50	0.11	0.11	0.12
ENR-10 7.5 phr	-55	-50	0.09	0.09	0.09
ENR-38 7.5 phr	-55	-50	0.14	0.13	0.10
ENR-51 7.5 phr	-54	-50	0.13	0.13	0.11
TESPT	-53	-48	0.08	0.07	0.06

ENR, Epoxidized natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

The temperatures at peak of loss modulus ( $E''$ ) and  $\tan \delta$  can be taken as glass transition temperatures ( $T_g$ ) of the materials. As reviewed by Robertson and Roland [86],  $T_g$  based on the  $\tan \delta$  peak can be problematic because  $\tan \delta$  in the glass-to-rubber softening region is influenced not only by the local segmental polymer dynamics but also by filler induced changes in both storage and loss moduli at higher temperatures. The present work reports the  $T_g$  values of silica-filled NR vulcanizates with and without compatibilizers taken from both  $E''$  and  $\tan \delta$  peaks, as shown in Table 9.7. It can be seen that the  $T_g$ 's taken from the  $E''$  peaks show a small but gradual change of values with compatibilizer types. The silica-filled NR without compatibilizer shows the lowest  $T_g$  and the presence of compatibilizers tends to shift the  $T_g$  slightly to slightly higher temperature in accordance with the degree of interactions as observed by bound rubber content in Fig. 9.29C. The silica/TESPT-filled NR vulcanizate has the highest  $T_g$ , while the ENR-compatibilized vulcanizates show similar  $T_g$  values. The shift of  $T_g$  to higher temperature is due to the strong interactions between filler and rubber phases leading to restricted movement of the rubber molecules at the interface [87].

$\tan \delta$  in the low temperature range, for example, in the range of 0°C–20°C can be used to indicate wet grip or resistance between a tire tread and road surface. A higher  $\tan \delta$  at low temperature indicates a better wet grip of a tire. The use of ENR-38 and ENR-51 as compatibilizers in silica-filled NR shows an increase of  $\tan \delta$  values at low temperature (Table 9.7) due to the effect of the glass transition temperatures and damping properties of ENR-38 and ENR-51 in the NR matrix. The incorporation of ENR-38 and ENR-51 therefore positively affects tire wet grip but negatively influences tire rolling resistance, as observed by the higher  $\tan \delta$  values at 60°C when compared to the silica-filled NR vulcanizate with TESPT.

From Fig. 9.31 the silica dispersion level of filled NR vulcanizates without any compatibilizer and with ENR-10 7.5 phr looks similar and poorer than that of the other compounds, as silica clusters can clearly be observed. The addition of ENR-38 and ENR-51 at 7.5 phr into the silica-filled compounds visibly shows an



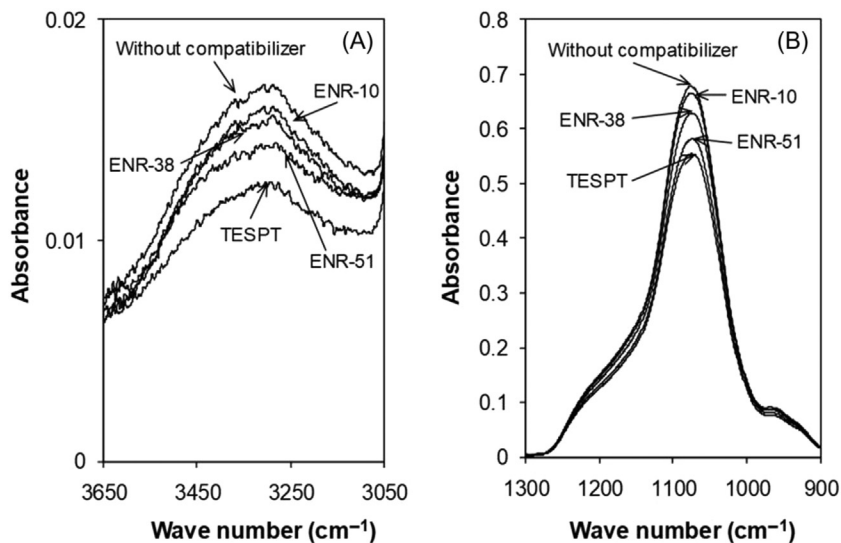
**Figure 9.31** SEM micrographs of silica-filled NR vulcanizates with various types of compatibilizers at 15,000 $\times$  magnification; (A) without compatibilizer, (B) ENR-10 7.5 phr, (C) ENR-38 7.5 phr, (D) ENR-51 7.5 phr, and (E) TESPT [82]. *ENR*, Epoxidized natural rubber; *NR*, natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

improvement of silica dispersion as shown in Fig. 9.31C and D, respectively. This improved silica dispersion again supports the occurrence of interactions and/or reaction between silanol groups on the silica surface and epoxy groups of ENR, according to the mechanism proposed in Fig. 9.26, leading to reduction of polar Si – OH groups. The silica-filled NR with TESPT silane coupling agent (Fig. 9.31E) shows the best silica distribution and dispersion which is in accordance with its superior properties.

ENR can thus be used as compatibilizer in silica-filled NR, as it results in improved filler–rubber interaction, silica dispersion, and tensile strength. Increase of ENR content and mol.% of epoxide groups increases the interactions between silica and rubber and decreases filler–filler interaction, as reflected by lower Mooney viscosity, Payne effect, and the higher filler–rubber interaction parameter, chemically bound rubber, tensile strength, and silica dispersion level. With respect to tire performance, the presence of ENR-38 and ENR-51 as compatibilizer improves wet grip but negatively affects rolling resistance. The addition of ENR-51 at 7.5 phr shows the best overall properties, however still somewhat lower when compared to a compound with TESPT silane as coupling agent.

#### 9.4.2 Evidence of interactions from FTIR spectra

As reflected in the changes of properties of both compounds and vulcanizates (Fig. 9.29), the epoxide groups of ENR interact with the silanol groups of silica and



**Figure 9.32** ATR-FTIR spectra at the wave number in the ranges of (A) 3050–3650  $\text{cm}^{-1}$  and (B) 900–1300  $\text{cm}^{-1}$  of silica-filled NR vulcanizates with 7.5 phr of ENR as a compatibilizer compared to vulcanizates with TESPT and without any compatibilizer [82,83]. ENR, Epoxidized natural rubber; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

promote compatibilization. To gain more evidence of such interactions between the epoxide groups of ENR and the silanol groups of silica, vulcanized sheets of silica-filled NR containing either no compatibilizer, TESPT, or 7.5 phr of ENR-10, ENR-38, and ENR-51 were subjected to a fourier-transform infrared spectroscopy (FTIR) analysis with an attenuated total reflectance (ATR) mode to look for a change of absorption peak intensities of the functional groups of silica. The spectra of the vulcanizates in the region of absorption bands that are associated with  $-\text{OH}$  and  $\text{Si}-\text{O}-\text{Si}$  stretching vibrations are shown in Fig. 9.32. Herein, Fig. 9.32A shows the  $-\text{OH}$  stretching region at 3500–3000  $\text{cm}^{-1}$  and Fig. 9.32B displays the absorption band of  $\text{Si}-\text{O}-\text{Si}$  asymmetric stretch in the range of 1300–900  $\text{cm}^{-1}$  [37,89].

The ATR-FTIR spectra in Fig. 9.32A show a reduction of  $-\text{OH}$  groups of silica with increase of mol.% epoxide and use of TESPT. In addition to hydrogen bonding between silanol groups and oxirane oxygen of ENR, as proposed in Fig. 9.26,  $-\text{OH}$  groups of silica can react with  $-\text{OH}$  groups of ENR after ring opening and form bonding during curing process. Therefore the free  $-\text{OH}$  of silanol groups decrease. According to Bertora et al. [90] and Zhuravlev [91], the surface silanol groups content of Zeosil 1165MP is 4.90  $\text{OH nm}^{-2}$ . As only part of these silanol groups are able to react or interact with epoxide groups of ENR for reason of steric hindrance, providing the same content of ENR compatibilizers with increasing mol.% epoxide leads to more epoxide groups available to interact, and less free silanol

groups remaining in the matrix. As a result, a lower intensity of the  $-OH$  peak with increasing mol.% of epoxide is observed in Fig. 9.32A.

The peak intensity of  $Si-O-Si$  asymmetric stretching of silica in the NR matrix at  $1080\text{ cm}^{-1}$  decreases with the addition of ENR as compatibilizer and TESPT as coupling agent. The higher the mol.% epoxide of ENR, the more the decrease of peak intensity, while TESPT shows the lowest peak intensity. In Fig. 9.32B the intensities of the peak shoulder at  $965\text{ cm}^{-1}$  arising from the  $Si-O$  of the  $Si-OH$  group also change in the same order as observed for the peak at  $1080\text{ cm}^{-1}$  when ENR and TESPT are added. This is also due to the reduction of the amount of  $Si-O-Si$  and  $Si-O$  bonds in the compounds. Thus the use of ENR and TESPT in the silica-filled NR compounds reduces silica-silica interaction leading to a lower number of silica clusters in the compounds.

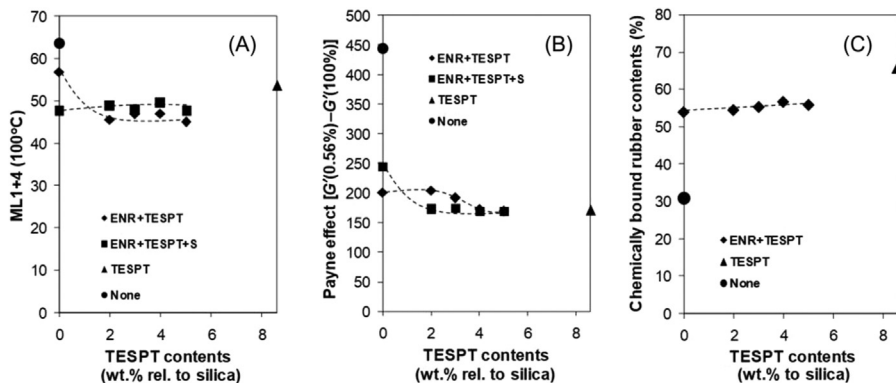
### 9.4.3 Hybridization of silane coupling agent and epoxidized natural rubber

As demonstrated in Section 9.4.1, the addition of ENR as compatibilizer in silica-filled NR compounds enhanced both processing and vulcanizate properties. The Payne effect was reduced and filler-rubber interaction was promoted leading to an improvement in mechanical properties. However, the properties were still lower compared to the reference compound that employed TESPT as coupling agent. One of the reasons can be attributed to the influence of network formation within the material. The TESPT-containing compounds obtain a contribution from sulfur that is released from TESPT and so have a higher network density. A cooperative effect of epoxide groups in ENR and TESPT on reinforcing efficiency of silica-filled ENR compounds was recently reported [79]. The use of epoxidized low molecular weight NR (ELMWNR) as compatibilizer in silica-filled NR compounds reduced the Payne effect and improved the mechanical properties when compared to an uncompatibilized system. 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  $60^\circ\text{C}$  [85]. This ELMWNR material is to be elaborated further in Section 9.4.5. Herein, an amount of extra sulfur was added to compensate for the sulfur in the TESPT molecules.

The use of 7.5 phr of ENR-51 as compatibilizer showed the best overall properties of the silica-filled NR compounds, but still inferior to those of the reference compound with TESPT. This part is therefore to present the use of 7.5 phr of ENR-51 in combination with TESPT at varying amounts from 2 to 5 wt.% relative to silica, without and with sulfur compensation. The compensation was applied by adding elemental sulfur into the compound to adjust the total sulfur content, to make it equal to the sulfur contained in the reference compound with 4.7 phr of TESPT.

The results depicted in Fig. 9.33 show that the use of ENR-51 at 7.5 phr in combination with TESPT at 2 wt.% relative to the silica further decreases the Mooney viscosity and Payne effect and increases bound rubber contents of the silica-filled



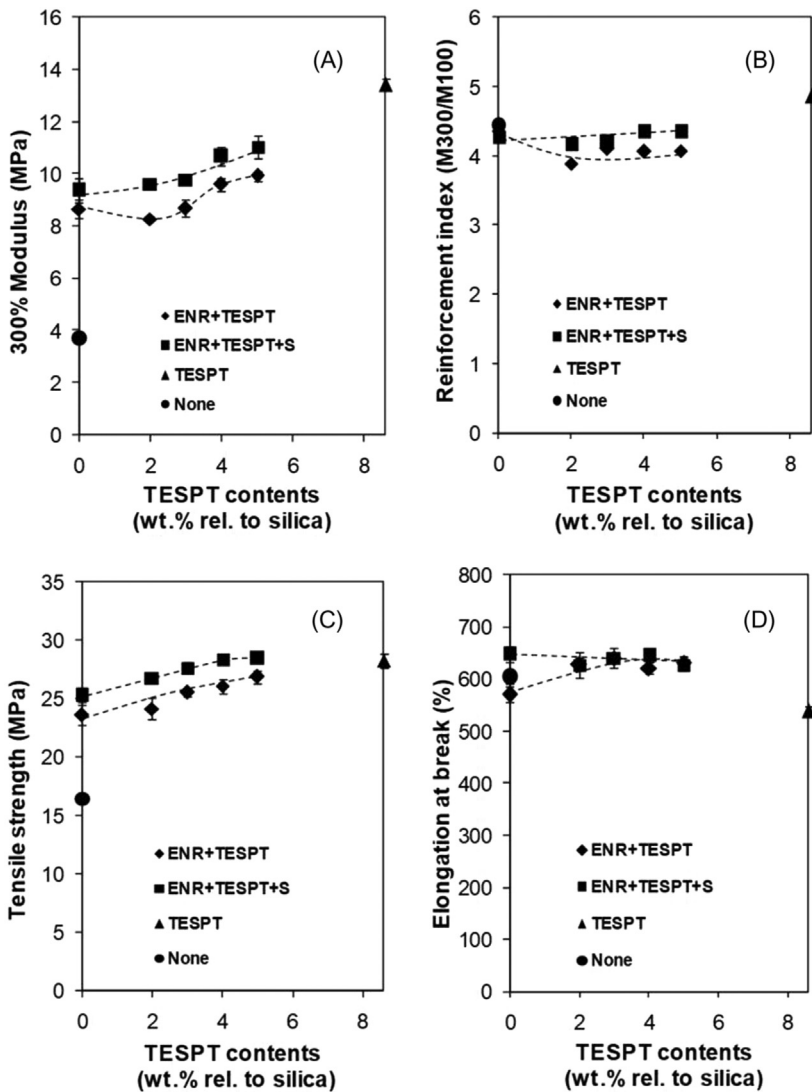


**Figure 9.33** (A) Mooney viscosity, (B) Payne effect, and (C) chemically bound rubber content of silica-filled NR compounds with 7.5 phr of ENR-51 as compatibilizer in combination with TESPT with and without sulfur compensation [82]. *ENR*, Epoxidized natural rubber; *NR*, natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

NR compounds, when compared to a silica-filled compound with ENR-51 alone. A further increase of TESPT-content has only a small additional effect on the compound properties.

Tensile strength and modulus of the vulcanizates increase with increasing TESPT contents and further improve by sulfur compensation relative to the reference compound with TESPT, to equilibrate the level of crosslink density (Fig. 9.34). The use of ENR-51 at 7.5 phr with TESPT at 4 wt.% relative to silica and sulfur compensation gives vulcanizates with the same level of tensile strength compared to vulcanizates with TESPT at 8.6 wt.% relative to silica.

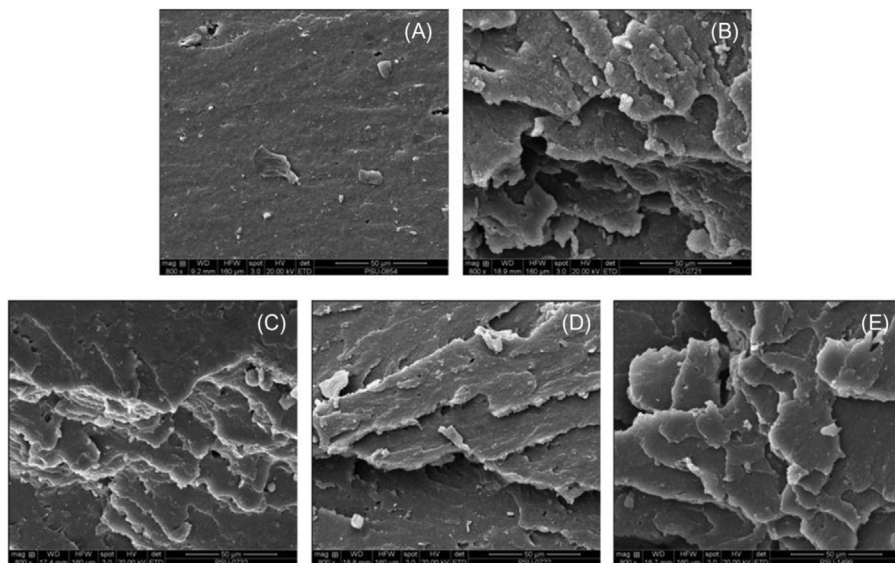
SEM micrographs of tensile fractured surfaces of the silica-filled NR vulcanizates containing different compatibilizers are shown in Fig. 9.35. The silica-filled NR vulcanizate without compatibilizer that has the lowest tensile strength because of the poor filler dispersion and filler–rubber interactions shows a smooth surface with some vacuoles on the fractured surface indicating de-wetting of silica by the NR matrix, as shown in Fig. 9.35A. The observation of these large silica clusters by SEM in silica-filled NR without compatibilizer was previously demonstrated by Pal and De [92]. The effective use of TESPT silane coupling agent in the silica-filled NR that leads to the highest modulus (Fig. 9.34A) and tensile strength (Fig. 9.34C) gives a rough fractured surface with many tear lines from ductile failure [93] as a result of good interfacial interactions between rubber and silica by 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 Fig. 9.35C – E, show a rough surface and tear lines pattern but at different degrees compared with the silica/TESPT system. The ENR-compatibilized vulcanizate with improved filler–rubber interactions via the interaction/reaction between the epoxide groups of ENR and the silanol groups on the silica surface has a considerably less complicated fractured surface when compared to the



**Figure 9.34** (A) 300% tensile modulus, (B) reinforcement index, (C) tensile strength, and (D) elongation at break of silica-filled NR compounds with 7.5 phr of ENR-51 as compatibilizer in combination with TESPT with and without sulfur compensation [82]. ENR, Epoxidized natural rubber; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

one with optimal content of TESPT. The silica-filled vulcanizates with TESPT and ENR/TESPT/extra sulfur show the same level of tensile strength as shown in Fig. 9.34C and show very similar tensile fractured surfaces, as shown in Fig. 9.35C and E, respectively. SEM micrographs of tensile fractured surfaces of filled NR



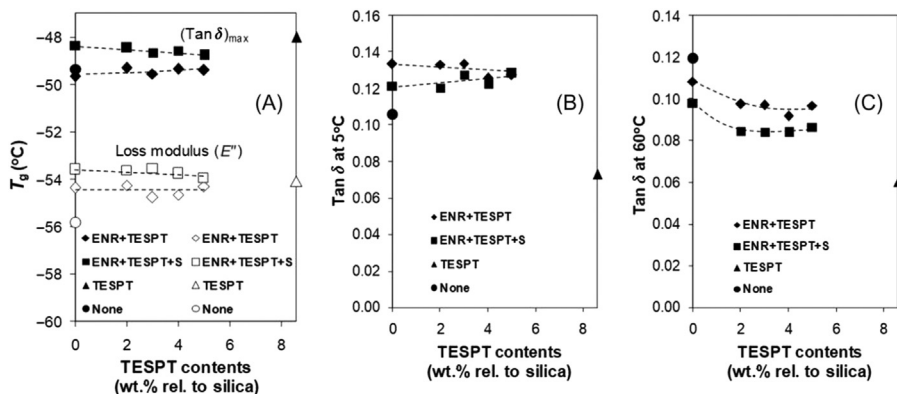


**Figure 9.35** SEM micrographs of tensile fractured surfaces of filled NR vulcanizates with 55 phr of silica at  $800\times$  magnification: (A) without compatibilizer; (B) with 8.6 wt.% TESPT rel. to silica; (C) with 7.5 phr ENR-51; (D) with 7.5 phr ENR-51 plus 4 wt.% TESPT rel. to silica; and (E) with 7.5 phr ENR-51, 4 wt.% TESPT rel. to silica and extra sulfur [82]. *ENR*, Epoxidized natural rubber; *NR*, natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

vulcanizates have also been used to demonstrate dispersion and wetting of filler by the matrix, such as in the work of Arayapraneet et al. [93] and Ismail et al. [94] in which the rough surfaces with tear lines indicated higher tensile strength.

As seen in Fig. 9.36, the presence of ENR in the silica-filled NR affects the dynamic mechanical properties. Above the glass-to-rubber transition, the ENR-containing vulcanizates show a higher mechanical loss factor  $\tan \delta$  compared to the silica/TESPT system. The addition of TESPT to the ENR-compatible compounds causes only a small change in glass transition temperature ( $T_g$ ) and  $\tan \delta$  at  $5^\circ\text{C}$  but lowers  $\tan \delta$  at  $60^\circ\text{C}$ , indicative for wet skid and rolling resistance, respectively, of tire treads made thereof. Furthermore, the addition of extra sulfur leads to an increase in  $T_g$  and lower  $\tan \delta$  at both  $5^\circ\text{C}$  and  $60^\circ\text{C}$  as a result of increased crosslink density. SEM micrographs clearly show good silica dispersion in all compatibilized vulcanizates, and the tensile fracture surfaces of the materials show different tear line patterns dependent on their tensile strengths.

Overall, the combination of ENR-51, TESPT, and sulfur compensation does not fully match the properties of a compound with TESPT alone at optimal quantity. However, if in the perspective of the “Magic Triangle of Tire Technology” the wet skid resistance needs to be boosted versus rolling resistance, for example, for “Winter Tires,” then the combination of ENR-51, TESPT, and sulfur compensation presents itself as a better option, which has to be confirmed in real tire tests.



**Figure 9.36** (A) Glass transition temperatures ( $T_g$ ) at the peaks of  $\tan \delta$  (solid symbols) and loss moduli (open symbols), (B)  $\tan \delta$  at 5°C, and (C)  $\tan \delta$  at 60°C of silica-filled NR vulcanizates with different compatibilizer combinations [82]. NR, Natural rubber. ENR, Epoxidized natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

#### 9.4.4 Suitable silane coupling agents as compatibilizers with epoxidized natural rubber

Silica is constantly gaining importance for energy-saving tires, there is also a steady development of alternative silanes. NXT has been introduced as a silane coupling agent offering a better scorch safety than TESPT, because of its blocking end-group on the mercapto function [95,96]. The blocked silane will couple with NR only during the curing period [96] and it has been reported that the NXT-silane needs a mixing temperature above 130°C to react with the silanol groups on silica. The longer scorch time of NXT-containing compounds is in accordance with the higher activation energy for premature scorch compared to that of TESPT [96]. A study on SBR compounds filled with silica that were modified by NXT in comparison with TESPT showed that the NXT compounds showed lower Payne effects and lower viscosities due to better filler dispersion, but poorer modulus because the silane contains only one sulfur atom in its structure [97]. Another new silane that was proposed for tire compounds is Si 363 which is a bifunctional organosilane having long dialkoxy-ethoxy-silyl groups and a mercapto function [98]. The “scorchy” nature of the mercapto function of this silane is suppressed by steric hindrance by the large side-arms [98]. As the silica–silane reaction proceeds via the ethoxy group, this silane type produces less ethanol emission during processing compared to the conventional TESPT or Si-69. A kinetic study by Blume [99] using a model system showed that the presence of –SH and long alkoxy groups enhances the rate of coupling reaction between silica and silane. Furthermore, the oxygen atoms inside the long alkoxy chain of Si 363 may increase the possibility of silane adsorption onto the silanol groups of the silica via hydrogen bonding and shield the free silanol groups.

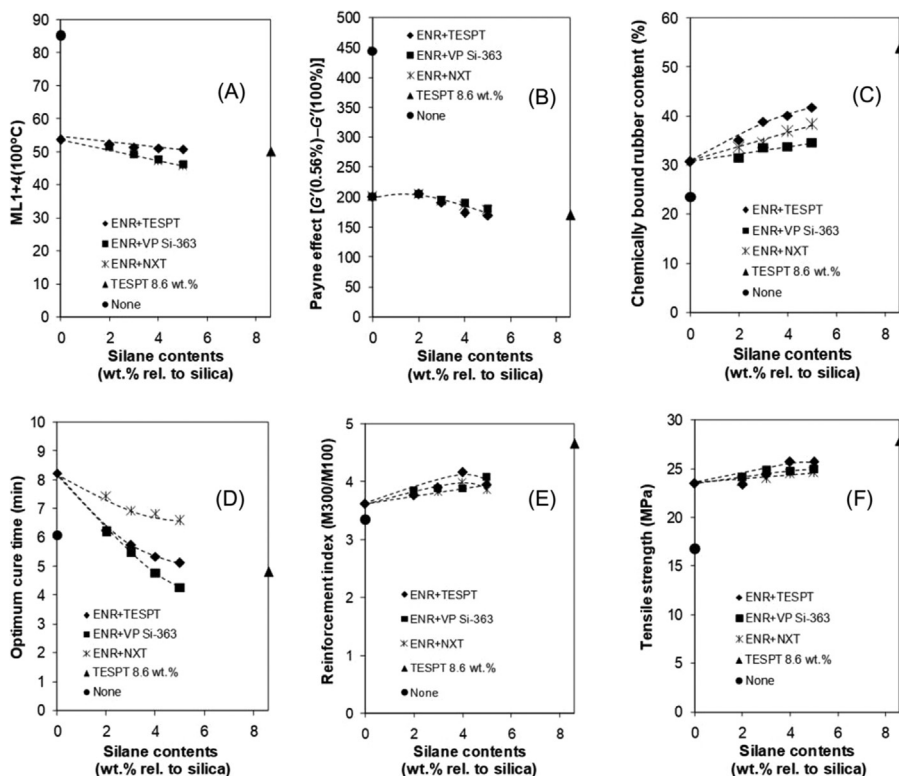
**Table 9.8** Information of the silane coupling agents used in this experiment [82,88].

Silane types	Chemical names	Structures	MW (g/mol)
TESPT	Bis-(3-triethoxysilyl-propyl) tetrasulfide	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{O} \qquad \qquad \qquad \text{OCH}_2\text{CH}_3 \\   \qquad \qquad \qquad \qquad \qquad   \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}_x-(\text{CH}_2)_3-\text{Si}-\text{OCH}_2\text{CH}_3 \\   \qquad \qquad \qquad \qquad \qquad   \\ \text{CH}_3\text{CH}_2\text{O} \qquad \qquad \qquad \text{OCH}_2\text{CH}_3 \end{array}$ <p style="text-align: center;">with <math>x = 3, 7, 0</math></p>	532.5
Si 363	3-Mercaptopropyl-di(tridecan-1-oxy-13-penta (ethyleneoxide)) ethoxysilane	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_5\text{O} \\   \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{SH} \end{array}$	987.5
NXT	3-Octanoyl-thio-propyltriethoxysilane	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_5\text{O} \\   \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_6\text{CH}_3 \\   \\ \text{CH}_3\text{CH}_2\text{O} \end{array}$	365

Based on the findings discussed in Section 9.4.1, the use of ENR containing 51 mol.% of epoxide (ENR-51) at 7.5 phr gave the best overall improvement in the Payne effect, bound rubber content, mechanical, and dynamic mechanical properties. With the aim to reduce the use of silane coupling agent and to reduce ethanol emissions, this section presents experiments exploring the combinations of ENR-51 at 7.5 phr with three different types of silane: TESPT, Si 363, and NXT in silica-filled NR compounds. The amount of ENR-51 is fixed at 7.5 phr based on the optimum properties as previously reported, and the silane contents are varied from 2.0 to 5.0 wt.% relative to the silica amounts. Later on, with the fixed amounts of both ENR-51 and silane, compensations are applied in the compound with elemental sulfur relative to the total sulfur contained in the reference TESPT compound, and the resulting properties are investigated in comparison with the normal formulation (Table 9.8) [82,88].

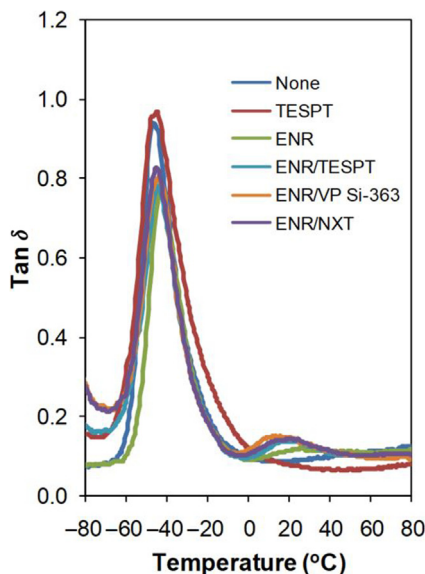
Based on the experimental results presented in Fig. 9.37, addition of silane reduces the compound viscosity slightly but clearly enhances the chemically bound rubber content and cure properties. Among the three different ENR-51/silane combinations, the use of ENR/TESPT gives the highest chemically bound rubber content and tensile properties, whereas the ENR/NXT combination gives higher chemically bound rubber content but similar tensile properties compared to the ENR/Si 363 system. The improvement of the overall properties by the use of TESPT over the other two types of silanes is due to the bis-(triethoxysilyl)- and tetrasulfide-functional groups that provide more ethoxy groups to react with the silanol groups on the silica surface, and the reactive free sulfur released by TESPT to involve in network formation. When the amount of silane coupling agent is fixed at 4.0 wt.% relative to silica in combination with 7.5 phr of ENR-51 as compatibilizer in the silica-filled NR compound, the addition of extra sulfur to correct the total sulfur content relative to the reference compound with TESPT leads to an increase in modulus and tensile strength while elongation at break decreases.

The results of  $\tan \delta$  in Fig. 9.38 show that the silica-filled NR with TESPT has the highest intensity of  $\tan \delta$  peak due to the improved silica dispersion and less rubber trapped in the silica network, leading to more rubber segments involved in the polymer segmental relaxation in the glassy region [100]. The addition of ENR



**Figure 9.37** (A) Mooney viscosity at 100°C, (B) Payne effect, (C) chemically bound rubber content, (D) optimum cure time, (E) reinforcement index and (F) tensile strength of silica-filled NR vulcanizates with 7.5 phr of ENR-51 as compatibilizer in combination with varying amounts of TESPT, Si 363 and NXT [82,88]. ENR, Epoxidized natural rubber; NR, natural rubber; NXT, 3-octanoyl-thio-propyltriethoxysilane; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

as compatibilizer in the silica-filled NR decreases the intensity of  $\tan \delta$  at  $T_g$  peak, as also shown in the values in Table 9.9. This reduction is caused by the silica–ENR interactions and intermolecular interactions between epoxy groups of adjacent ENR molecules, which results in a restriction of polymer chain relaxations and an increase in the material stiffness. These results are in accordance with the  $\tan \delta$  curves as previously shown in Fig. 9.30. The addition of silane coupling agents together with ENR-51 increases the ( $\tan \delta$ ) max values slightly when compared to the vulcanizate with only ENR-51, as summarized in Table 9.9, because of further improvement of filler dispersion and less occluded rubber. Among the different compatibilizer types, the  $\tan \delta$  peak of the TESPT compound is broader toward the rubbery region compared to that of the others as a result of a greater extent of filler–rubber interactions in this material.



**Figure 9.38** Loss tangent ( $\tan \delta$ ) of silica-filled NR vulcanizates compatibilized with 7.5 phr of ENR-51 and 4.0 wt.% of silanes relative to silica with sulfur compensation, in comparison with those vulcanizates without compatibilizer, respectively, with reference TESPT only and with ENR-51 alone [82]. ENR, Epoxidized natural rubber; NR, natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide.

The second glass transition peak corresponding to ENR-51 is clearly observed for the compounds that are compatibilized with either ENR only or with ENR/silane. According to Manna et al. [101], ENR with 50 mol.% of epoxy groups and 60 phr of silica has a  $T_g$  of about  $-3^\circ\text{C}$  to  $1^\circ\text{C}$ . It is observed in Fig. 9.38 that in the presence of silane coupling agents, the second  $\tan \delta$  peak intensity is increased and the peak position shifted toward lower temperature in comparison with ENR-51 alone. In the systems with ENR/silane combinations, silica–silane interactions are prevailing over epoxide–silica interactions. In this case, there is a competition of more free epoxide groups in the ENR compared to the silica-filled NR with only ENR as compatibilizer. In the combined system, ENR therefore exhibits its characteristic peak in a more prominent manner. For the compound with only ENR as compatibilizer the second  $\tan \delta$  peak is broader and less pronounced because of more interactions between epoxide groups of ENR and silanol groups on the silica, leading to a weaker characteristic peak of ENR. This observation of the change of  $\tan \delta$  peak of ENR as compatibilizer in silica-filled NR due to the level of filler–rubber interactions was also reported by Saramolee et al. [85].

The  $T_g$  values taken from both  $\tan \delta$  and loss modulus peaks are summarized in Table 9.9 together with the  $\tan \delta$  values at different temperatures. On comparing with the noncompatibilized material, the  $T_g$ 's of the vulcanizates with compatibilizers shifted to slightly higher temperature, due to an increase of silica–rubber interactions that restrict the rubber segmental relaxations in the transition region.

**Table 9.9**  $T_g$  and  $\tan \delta$  values of silica-filled natural rubber (NR) vulcanizates with 7.5 phr of epoxidized NR (ENR) 51 as compatibilizer in combination with varying amounts of bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT), Si 363, and 3-octanoyl-thio-propyltriethoxysilane (NXT) [82].

Compatibilizer types	$T_g$ (°C)	Values of $\tan \delta$			
	At $\tan \delta$ peak	At $E''$ peak	At peak	At 5°C	At 60°C
Without compatibilizer	-47	-58	0.94	0.09	0.11
TESPT	-45	-54	0.97	0.10	0.07
ENR-51	-44	-52	0.77	0.09	0.11
ENR-51 + TESPT + S	-45	-57	0.79	0.12	0.10
ENR-51 + Si 363 + S	-45	-57	0.80	0.13	0.09
ENR-51 + NXT + S	-45	-57	0.82	0.11	0.10

For the  $\tan \delta$  values at 5°C and 60°C summarized in Table 9.9, according to UNECE regulation no. 117 [102], wet grip grading of normal tires should be tested in the temperature range of 5°C–35°C. Table 9.9 shows the  $\tan \delta$  values at 5°C of the silica-filled vulcanizates containing different compatibilizers and without. The use of ENR-51 together with silane coupling agents gives the highest  $\tan \delta$  values in the temperature range of 5°C–35°C which is in the range of the second glass transition associated with the ENR, when compared to the use of TESPT, ENR only and no compatibilizer, respectively. The increased  $\tan \delta$  at low temperature indicates a better wet grip of tire compounds.

On the other side, the  $\tan \delta$  value at high temperature, commonly in the range of 40°C–80°C indicates tire rolling resistance. As shown in Table 9.9, the incorporation of ENR either with or without silane results in higher  $\tan \delta$  values at 60°C which are just slightly lower than that of the compound without compatibilizer. This damping property is again related to the  $T_g$  of ENR-51. The high mol.% of epoxide groups on the ENR introduces higher chain stiffness and lower elasticity. Moreover, the different polarity of the two rubber phases leads to blend incompatibility which causes an energy loss at their interface under dynamic deformation. Among the different compatibilizers studied, the use of conventional TESPT in silica-filled NR compounds provides a remarkably low  $\tan \delta$  at 60°C, indicating superior low rolling resistance for tire compounds.

The use of an ENR/silane combination increases the  $\tan \delta$  at 5°C and reduces the  $\tan \delta$  at 60°C compared to the use of ENR-51 alone, indicating an improvement in wet traction and rolling resistance of tires made thereof. However, overall the use of TESPT alone at optimum loading still gives the best mechanical and dynamic mechanical properties compared to the presence of ENR as compatibilizer.

Among the three types of silanes studied in combination with ENR-51 and sulfur compensation, the use of 2.2 phr TESPT together with 7.5 phr ENR-51 provides the best overall properties, but it does still not fully match the properties of a compound with TESPT alone at optimal quantity, that is, 4.7 phr as previously discussed.

However, in the perspective of the “Magic Triangle of Tire Technology” where wet skid resistance, rolling resistance, and wear are all to be optimized, the combination of ENR-51, TESPT, and sulfur compensation may become a better option for “Winter Tires” that demand good wet grip, providing that real tire tests have yet to confirm this.

#### **9.4.5 Use of epoxidized low molecular weight natural rubber**

ELMWNR constitutes a new family of polymers. It is a highly viscous rubber of relatively low molecular weight that is generally used as plasticizer or processing aid, and it also has a random distribution of epoxide groups along the polymer backbone [48]. The chemical structure contains both epoxide and unsaturated sites. Although the double bonds can be crosslinked by sulfur, the epoxide groups provide alternative sites for crosslinking or for chemically interacting with other functional chemicals. ELMWNR has been used as plasticizer during processing of some polymers, such as reinforced NBR and NR/NBR blends [103]. The results showed a decrease in total mixing energy and compound viscosity with increasing low molecular weight rubber content. George et al. [41] reported that an optimum concentration of about 15% of ENR relative to total rubber in a silica-filled NBR compound improved bound rubber content and mechanical and dynamic mechanical properties. The presence of the polar epoxide groups provides a good compatibility between rubber and silica. This compatibility involves hydrogen bonding and possibly also some chemical bonding [37], allowed by ring opening of the oxirane ring caused by the acidity of the siloxane groups on the silica surface at vulcanization temperature.

In the present context, enhancing the processing properties and compatibility between rubber and fillers by the use of ELMWNR is discussed, based on the investigations of Saramolee et al. [85] on the effect of ELMWNR with different degrees of epoxidation, that is, 12, 28, and 51 mol.%. ELMWNR with molecular weights in the range of 50,000–60,000 g/mol was employed in this investigation. Cure characteristics, processing properties, and mechanical and dynamic mechanical properties of silica- and carbon black–reinforced NR compounds were investigated. The results of an ELMWNR-compatible system are compared with those of a conventional silane coupling agent, e.g. TESPT, used in silica-filled compounds. For comparison, the use of LMWNR bearing no epoxide groups was studied. The investigated compounds were based on the formulations shown in Table 9.10. The silica compounds were prepared using an intermeshing internal mixer with a mixing procedure the same as that described in Section 9.2.1. For the carbon black – filled compounds, they were prepared using the mixing steps similar to the silica compounds to have the same total mixing time of 15 min, but different in the mixer temperature setting at 60°C.

Epoxide groups in ELMWNR play a major role in silica-filled NR compounds and affect both processing and vulcanizate properties, due to epoxide–silica interactions. The addition of ELMWNR to a carbon black – filled NR compound shows



**Table 9.10** Silica-filled and carbon black – filled compound formulations with different quantities of epoxidized low molecular weight natural rubber (NRs) containing three levels of epoxidation degrees [85,104].

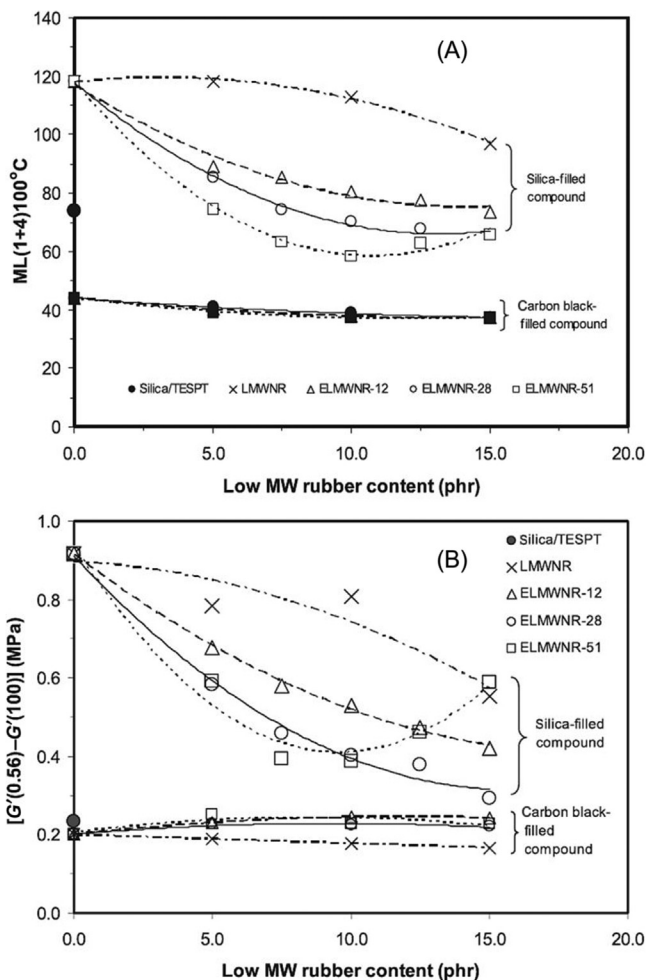
Ingredients	Dosage (phr)											
	Silica compounds							Carbon black Compounds				
	R-i	R-ii	I	II	III	IV	V	R-iii	I	II	III	
NR (RSS 3)	100	100	95	92.5	90	87.5	85	100	95	90	85	
ELMWRN <sup>a</sup>	–	–	5	7.5	10	12.5	15	–	5	10	15	
(or LMWRN)												
Silica (Zeosil 1165MP)	55	55	55	55	55	55	55	–	–	–	–	
Silane TESPT	4.4	–	–	–	–	–	–	–	–	–	–	
Carbon black (HAF N330)	–	–	–	–	–	–	–	55	55	55	55	
Process oil (TDAE)	5	The same amounts as that of the reference (R-i) compound						5	The same amounts as that of the reference (R-iii) compound			
ZnO	3							3				
Stearic acid	1							1				
TMQ	1							1				
DPG <sup>b</sup>	1.1							0.3				
CBS	1.2							1.2				
Sulfur	1.5							1.5				

ELMWRN, Epoxidized low molecular weight natural rubber; TESPT, bis-(3-triethoxysilylpropyl) tetrasulfide; TMQ, 2,2,4-trimethyl-1,2-dihydroquinoline; TDAE, treated distillate aromatic extract; DPG, 1,3-diphenylguanidine.

<sup>a</sup>ELMWRNs with 12, 28, and 51 mol.% epoxide were used; LMWRN was prepared for comparison.

<sup>b</sup>The amount of DPG used for silica- and carbon black–based compounds was different, because silica has an accelerator absorption effect which needs to be compensated.





**Figure 9.39** (A) Mooney viscosity and (B) Payne effect of silica- and carbon black – filled NR compounds with different amounts of low molecular weight rubbers [85,104]. NR, Natural rubber; ELMWNR, epoxidized low molecular weight natural rubber.

only a plasticizing effect. Blending of ELMWNR into a silica-filled NR compound decreases Mooney viscosity and Payne effect as can be seen in Fig. 9.39.

Fig. 9.39A shows Mooney viscosities of silica- and carbon black – filled NR compounds containing various amounts of low molecular weight rubber, compared with that of compounds with and without TESPT in the case of silica-filled compounds. The Mooney viscosity of carbon black – filled compound shows no significant change by the incorporation of either LMWNR or ELMWNR, whereas Mooney viscosities of the silica-filled compounds are clearly reduced by the addition of 5 phr of low molecular weight rubber bearing epoxide groups and further decreased with an increasing amount of ELMWNR. The use of LMWNR at 5

10 phr shows almost no effect on the viscosity of a silica-filled compound, and the increasing amount of LMWNR to 15 phr decreases the compound viscosity, which is mainly due to the plasticizing effect as the incorporation of smaller polymer molecules of polymer increases chain mobility. In addition, when a high loading of LMWNR (i.e., 15 phr) was used, the carbonyl groups at the chain ends [105] of the LMWNR can possibly interact with the silanol groups on the silica surface, thereby positively affecting filler dispersion and consequently lower Mooney viscosity. The use of a sufficient amount of ELMWNR-28 and ELMWNR-51 in silica-filled compounds can decrease the Mooney viscosity to match the level of the compound with TESPT. This is caused by the interactions between epoxide groups and silanol groups on the silica surface resulting in a better dispersion of silica in the NR matrix, and also by suppression of the reformation of larger silica clusters [106]. However, the use of ELMWNR-51 at a high concentration ( $> 10$  phr) results in an upward turn in Mooney viscosity that can be due to self-association of epoxide groups, leading to a decreasing amount of epoxide groups available to interact with silanol groups and resulting in poorer silica dispersion. The self-association itself also would increase viscosity as is visible in Fig. 9.28 and Section 9.3.3.

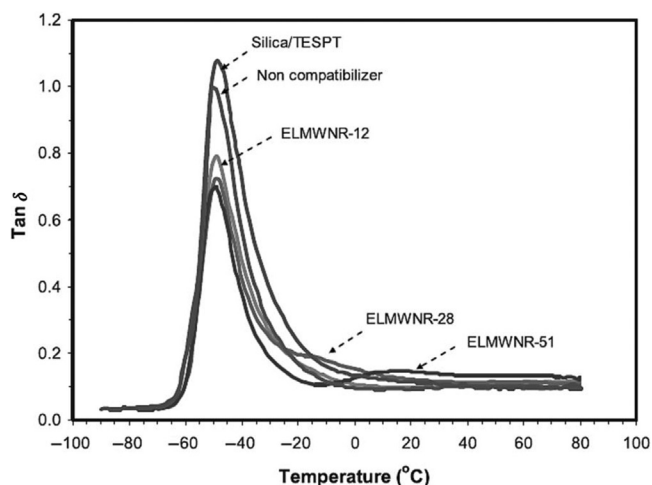
The effect of low molecular weight rubber in silica-filled and carbon black-filled compounds on the Payne effect can be clearly seen in Fig. 9.39B. The Payne effect of the silica-filled compound without compatibilizer is much higher than that of the carbon black-filled compound, attributed to the hydroxyl groups on the silica surface that form hydrogen bonds and result in strong filler-filler interaction. Carbon black is composed of graphitic layers with only a very small quantity of polar functional groups, such as hydroxyl, carboxyl, or ketone, on its surface [107]. Thus the filler-filler interaction of silica is much stronger than that of carbon black. Compared with the silica-filled compounds without compatibilizer, the storage modulus of carbon black-filled compounds gradually drops with increasing strain amplitude because of less filler-filler interactions. For silica-filled compounds the use of low molecular weight NR without epoxide groups slightly lowers the Payne effect compared with the effect with only original NR. However, the use of 10 phr ELMWNR with 28 and 51 mol.% epoxide significantly reduces the Payne effect by lowering the storage modulus of the compounds to a level close the silane-containing compound. This indicates that the incorporation of ELMWNR weakens the filler-filler interactions and can further imply the possible formation of hydrogen bonds between epoxide groups of ELMWNR and silanol groups of silica during the mixing stage, thereby promoting the filler-rubber interaction.

The Payne effect of the silica-filled compounds decreases with increasing amounts of low molecular weight rubber and epoxide content and can be explained by two different contributions. First, the low molecular weight rubber molecules act as internal plasticizers in rubber compounds, thereby improving the mobility of both rubber chains and fillers and facilitating filler dispersion. Second, the relatively strong interaction between the epoxide group of ELMWNR and the silanol groups on the silica surface via hydrogen bonds, chemical bonds, or both, formed after epoxide ring opening [108]. Covering of the silanol groups by the ELMWNR molecules prevents filler-filler interactions. For the silica-filled compound with 15 phr

of LMWNR a clear decrease of the Payne effect can also be attributed in part to the possible interaction between carbonyl groups at the rubber chain ends and silanol groups of silica, resulting in better filler–rubber interaction and filler dispersion. Increasing amounts of ELMWNR-12 and ELMWNR-28 further decrease the Payne effect, but the use of ELMWNR with 51 mol.% epoxide at high concentrations, that is, >10 phr, shows an upturn in Payne effect that is ascribed to self-association of the epoxide groups, leading to a reduced tendency of epoxide-silanol interactions. The incorporation of low molecular weight rubber without epoxide groups shows no effect in carbon black – filled compounds, and the level of storage modulus difference [ $G_0(0.56\%) - G_0(100\%)$ ] is comparable to that of the silica–TESPT compound.

The optimal mechanical properties of silica-filled NR vulcanizates can be obtained by using 10 phr of ELMWNR-28. ELMWNR shows its own  $T_g$  in the NR vulcanizates, but due to the interaction between epoxide and silanol groups, the  $T_g$  peak of ELMWNR in a silica-filled compound is less pronounced compared to that of the carbon black – filled compound.

The dynamic mechanical properties were determined with a dynamic mechanical analysis (DMA) viscoanalyzer in tension mode at a frequency of 10 Hz and dynamic strain of 0.1%. Fig. 9.40 shows the loss tangent ( $\tan \delta$ ) as a function of temperature in the range of  $-90^\circ\text{C}$  to  $80^\circ\text{C}$  of the silica-filled vulcanizates. Without any compatibilizer, the rubber vulcanizate shows a glass transition temperature,  $T_g$ , of  $-50^\circ\text{C}$ . The  $T_g$  is slightly shifted to a higher temperature,  $-48^\circ\text{C}$ , when using TESPT as a coupling agent in the vulcanizate. The increase in the  $T_g$  is due to a reduction in the molecular mobility of the polymer chains that are in contact with the silica surface [86,97]. For the silica–TESPT system, this is caused by

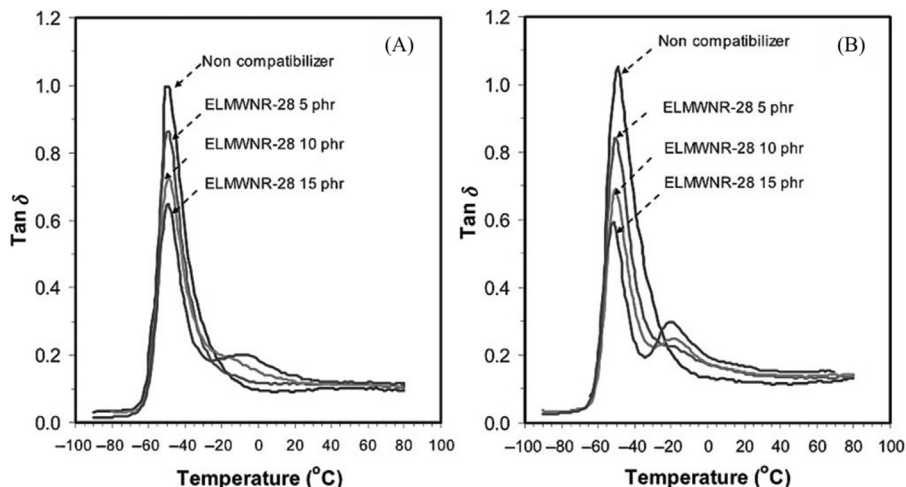


**Figure 9.40**  $\tan \delta$  curves of silica-filled NR vulcanizates containing 10 phr of low molecular weight rubber [85,104]. NR, Natural rubber; ELMWNR, Epoxidized low molecular weight natural rubber.

the increase of filler–rubber interactions and enhanced rubber network formation by additional sulfur in TESPT. The direct bonding of the rubber chains to the filler via the silane coupling reaction reduces local segmental mobility and influences  $T_g$  [86], as determined by using the loss tangent peak. However, the  $T_g$  value of the silica-filled NR with ELMWNRs as the compatibilizer remains unchanged compared to the vulcanizate without a compatibilizer. For the ELMWNR-compatible systems the filler–rubber interactions are mainly due to hydrogen bonding between epoxide groups and silanol groups of silica, with a possibly small fraction of directly bonded rubber chains on the filler surface via the condensation reaction between the  $-OH$  groups of ring-opened epoxidized rubber and silanol groups of silica [37]. Therefore it has no influence on the  $T_g$  of the vulcanizates.

The silica-filled vulcanizates containing ELMWNRs show a second peak of  $T_g$  associated with the  $T_g$  of ELMWNR, and a higher  $T_g$  at higher epoxide contents. The silica-filled vulcanizate with TESPT displays a larger peak height of  $\tan \delta$  compared to the vulcanizates without TESPT. It is well known that filled rubber compounds show a lower  $\tan \delta$  value at the maximum than gum compounds, because the viscous component of the compound decreases [97]. In the filled system, filler–polymer and filler–filler interactions lead to an effective immobilization of the elastomer segments. These segments lose their rubbery behavior, thereby increasing the effective volume of the filler and reducing the viscous component of the compound. When comparing the NR–silica vulcanizates with and without TESPT, the better filler dispersion of the rubbers containing TESPT reduces the formation of a secondary filler–filler network and thus decreases the amount of rubber trapped within that filler network. This means that more rubber molecules are involved in segmental relaxations. In contrast, the incorporation of 10 phr of ELMWNR in NR vulcanizates leads to lower  $\tan \delta$  values at the maximum of the curve due to the reduction of the NR proportion by the addition of ELMWNR and the lower chain mobility of the epoxidized rubber. The height of the  $\tan \delta$  peak for ELMWNR-51 compatibilized silica-filled vulcanizates is lower than that of the ELMWNR-28 and ELMWNR-12, respectively. This suggests a higher polar–polar interaction and a possible self-association of epoxide groups in ELMWNR that are less mobile to resonate with the externally applied sinusoidal stress in the glass transition regions. Consequently, the vulcanizates that contain the ELMWNR show higher hysteresis at normal service temperature, from which some applications such as damping materials, for example, rubber engine mounts, can benefit. However, it increases rolling resistance for tires as indicated by the  $\tan \delta$  value measured at 60°C. The use of ELMWNR with 12 mol% epoxide in the silica-filled compound shows only a small effect on  $\tan \delta$  at 0°C and 60°C, but the addition of ELMWNR with 28 mol% epoxide increases  $\tan \delta$  at both 60° and particularly 0°C (Fig. 9.40). The highest  $\tan \delta$  at 0°C of the vulcanizate with ELMWNR-28 indicates a better wet grip of a tyre tread made thereof when compared to the other compounds. On the other hand, for low rolling resistance tire tread applications, the vulcanizate needs to have a low  $\tan \delta$  at 60°C. However, ELMWNR-28 slightly increases the rolling resistance of tires.

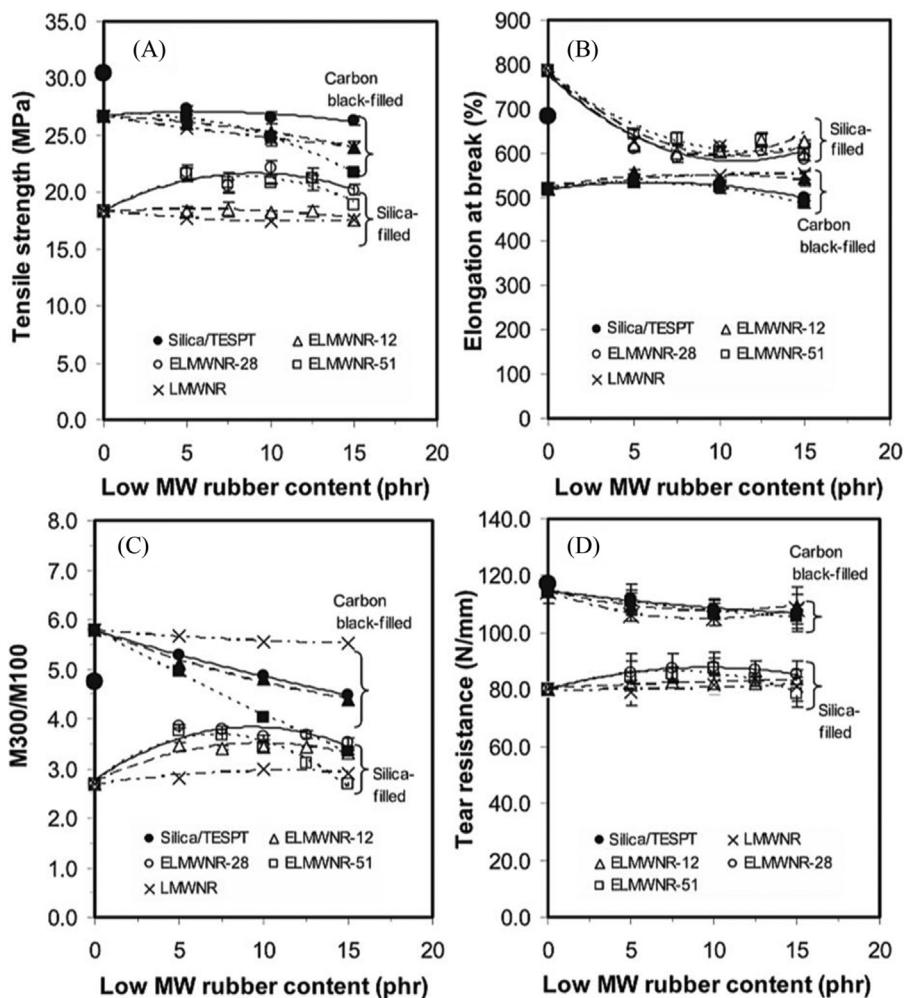
Fig. 9.41 shows the effect of the presence of ELMWNR with 28 mol.% epoxide as compatibilizer at various contents in silica- and carbon black – filled



**Figure 9.41** Variation of  $\tan \delta$  as a function of temperature for (A) silica-filled and (B) carbon black – filled NR vulcanizates with various amounts of ELMWNR-28 [85,104]. ELMWNR, Epoxidized low molecular weight natural rubber; NR, natural rubber.

vulcanizates on the  $\tan \delta$  curve. The same decreasing trend of  $\tan \delta$  values at maximum of the NR phase is observed with increasing ELMWNR-28 contents for both types of vulcanizates. Looking at the second peak of the  $\tan \delta$  curve, which represents the  $T_g$  of ELMWNR, this peak is broader and less pronounced in the silica compound compared with the carbon black – filled vulcanizate. The  $T_g$  also shifts to a higher temperature. The interactions between epoxide groups and silanol groups on the silica surface lead to a weaker characteristic peak of epoxidized rubber, and these interactions introduce more physical and chemical crosslinks that result in a shift of  $T_g$  to a higher value. In the carbon black – filled compounds, where weak physical interactions are dominant, the  $T_g$  peak of ELMWNR is clearly visible. The difference in the  $\tan \delta$  peaks of ELMWNRs in the silica- and carbon black – filled NR vulcanizates evidently supports the occurrence of the interactions between epoxide groups and silanol groups of silica, as also evidenced in the previous sections of this chapter.

The effect of ELMWNR on tensile strength, elongation at break, reinforcement index (M300/M100), and tear resistance of filled NR vulcanizates is presented in Fig. 9.42. The silica-TESPT vulcanizate shows the highest tensile strength, followed by the vulcanizates filled with carbon black and silica with ELMWNR. The efficient use of TESPT enhances the reinforcement activity of silica in NR through the silanization reaction of the silanol groups of silica with the ethoxy groups of silane during mixing and by the formation of crosslinks with the rubber molecules during vulcanization. It has also been proven that because of the availability of sulfur in the compound, TESPT can act as a sulfur donor and increase the crosslink density of the vulcanizates [21,25,26,33,63]. For silica-filled vulcanizates the tensile strength shows an increase up to 10 phr of ELMWNR with 28 and 51 mol.%



**Figure 9.42** Mechanical properties: (A) tensile strength, (B) elongation at break, (C) reinforcement index and (D) tear resistance, of silica-filled and carbon black – filled NR vulcanizates [85,104]. *NR*, Natural rubber; *ELMWNR*, Epoxidized low molecular weight natural rubber; *TESPT*, bis-(3-triethoxysilylpropyl) tetrasulfide.

epoxide and then tends to decrease. The reduction of tensile strength as well as reinforcement index, when ELMWNR-28 and -51 are used at high loadings, can be attributed to the incompatibility between the nonpolar NR matrix and more polar ELMWNR compatibilizer.

The addition of ELMWNR decreases compound viscosity and the Payne effect, the filler–filler interaction of the silica-filled compound. For the silica–silane compound and the compound with 28 mol.% epoxide (ELMWNR-28) the compound viscosities are comparable. The best mechanical properties of silica-filled

vulcanizates are obtained at an ELMWNR-28 loading of 10 phr. In contrast, the addition of ELMWNR to a carbon black – filled compound shows only a plasticizing effect. The incorporation of ELMWNR into NR compounds introduces a second glass transition temperature and affects their dynamic mechanical properties. Higher epoxide contents lead to higher loss tangent values of the rubber vulcanizates in the range of the normal service temperatures of a tire.

## 9.5 Summary

Overall, the reinforcement of rubber products by silica reinforcing fillers is not entirely novel, but it has been improved significantly during recent years after the introduction of the low rolling resistant tires by Michelin in 1992, promoting more efficient fuel consumption and an improved wet grip for automotive transport. Although this silica–silane technology provides numerous benefits, it is more susceptible to processing problems when compared to the use of conventional carbon black. To transfer the successful introduction of silica in SSBR/BR blend compounds used for passenger car tires to NR-compounds e.g. of interest for truck tire tread compounds is still an open issue. Many different aspects of the silica technology for NR have been explored in the past, new ones have been described in this chapter. Based on the results in this practical research, reinforcement of silica in NR is a versatile technology. Mixing parameters and chemical ingredients formulated in the compounds significantly govern the overall properties of silica-filled NR products. The findings presented in this chapter contribute to a much better understanding of the mechanistic aspects which provides an essential fundament as well as a better control of this technology. Furthermore, a reduction of the optimal quantity of silane coupling agents applied for conventional compounds can potentially be implemented by use of polar epoxy-modified NR.

A growing importance of silica-reinforced tire compounds for reduction of automotive fuel consumption motivates research and development of the relevant rubber technology. In addition to the commonly used silica/silane technology, alternative compatibilizers to totally or partially replace the silane for more “green” products are of interest. This present chapter provided an application of ENR as an alternative compatibilizer. The use of ENR alone or as compatibilizers clearly shows an enhancement already of the silica-NR compatibility, silica dispersion, and some mechanical properties. The properties can be further enhanced by using ENR in combination with only small amounts of silane coupling agents and sulfur compensation relative to a reference compound with TESPT. Even though the application of chemically modified NRs in the forms of ENRs as compatibilizers without further silanes results in inferior overall properties compared to the use of the state-of-the-art TESPT, the right combination of modified NR with only small amounts of TESPT and sulfur compensation offers an alternative system with the advantages of NR-based product usage and less ethanol emission from the silanization reaction. The presence of ELMWNRs as compatibilizers positively influences the



processability and wet grip indicator of NR tread compounds, but affects the rolling resistance slightly negatively; they can be applied as alternative compatibilizers in this system. All-in-all, the use of ENR brings in a good wet grip in the perspective of the “Magic Triangle of Tire Technology.”

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## References

- [1] K.P. Jones, P.M. Lewis, P. Mc.L. Swift, I.R. Wallace, Compounding for tyres, in: A.D. Roberts (Ed.), *Natural Rubber Science and Technology*, Oxford University Press, New York, 1988.
- [2] R. Rauline, Copolymer rubber composition with silica filler, tires having a base of said composition and method of preparing same, European Patent, EP0501227A1 (1992).
- [3] J.T. Byers, Silane coupling agents for enhanced silica performance, *Rubber World* 218 (1998) 38–47.
- [4] H.-D. Luginsland, J. Frohlich, A. Wehmeier, Influence of different silanes on the reinforcement of silica-filled rubber compounds, *Rubber Chem. Technol.* 75 (2002) 563–579.
- [5] U. Görl, A. Hunsche, A. Muller, H.G. Koban, Investigations into the silica/silane reaction system, *Rubber Chem. Technol.* 70 (1997) 608–623.
- [6] Y. Shimomura, J.L. White, J.E. Spruiell, A comparative study of stress-induced crystallization of guayule, hevea, and synthetic polyisoprenes, *J. Appl. Polym. Sci.* 27 (1982) 3553–3567.
- [7] G.R. Mitchell, A wide-angle X-ray study of the development of molecular orientation in crosslinked natural rubber, *Polymer* 25 (1984) 1562–1572.
- [8] S. Toki, I. Sics, S. Ran, L. Liu, B.S. Hsiao, S. Murakami, et al., New insights into structural development in natural rubber during uniaxial deformation by in situ synchrotron X-ray diffraction, *Macromolecules* 35 (2002) 6578–6584.
- [9] M. Morton, *Rubber Technology*, Van Nostrand Reinhold Company Inc, New York, 1987.
- [10] S.K. De, J.R. White, *Rubber Technologist's Handbook*, Rapra Technology Ltd., Shawbury, Shropshire, UK, 2001.



- [11] K. Ab-Malek, A.D. Roberts, *The Role of Natural Rubber: Turning Tyres Green*, Malaysian Rubber Board, Brickendonbury, Hertford, UK, 2015.
- [12] P. Fournier, Tuong-Chi-Cuong, The biosynthesis of rubber, *Rubber Chem. Technol.* 34 (1961) 1229–1305.
- [13] B.L. Archer, B.G. Audley, F.J. Bealing, Biosynthesis of rubber in *Hevea brasiliensis*, *Plast. Rubber Int.* 7 (1982) 109–111.
- [14] R. Giordani, C. Gachon, J. Buc, P. Regli, J.L. Jacob, Antifungal action of *Hevea brasiliensis* latex. Its effect in combination with fluconazole on *Candida albicans* growth, *Mycoses* 42 (1999) 465–474.
- [15] K.H. Nordsiek, The integral rubber concept – an approach to an ideal tire tread rubber, *Kautsch. Gummi Kunstst.* 62 (1985) 178–185.
- [16] M.-J. Wang, Effect of polymer-filler and filler-filler interaction on dynamic properties of filled vulcanizates, *Rubber Chem. Technol.* 71 (1998) 520–589.
- [17] J.E. Kogel, N.C. Trivedi, J.M. Barker, S.T. Krukowski, *Industrial Mineral & Rocks: Commodities, Markets, and Uses*, Society of Mining, Metallurgy, and Exploration Inc., Englewood, CO, 2006.
- [18] U.S. Department of Transportation, National Highway Traffic Safety Administration, Factors and considerations for establishing a fuel efficiency regulatory program for commercial medium- and heavy-duty vehicles, (2010). Available from: [https://www.nhtsa.gov/sites/nhtsa.dot.gov/files/nhtsa\\_study\\_trucks.pdf](https://www.nhtsa.gov/sites/nhtsa.dot.gov/files/nhtsa_study_trucks.pdf). (Accessed 10 February 2020).
- [19] F. Grunert, Analytical Method Development to Predict the In-Rubber Dispersibility of Silica (Ph.D. thesis), University of Twente, Enschede, 2018.
- [20] J.-B. Donnet, Fifty years of research and progress on carbon black, *Carbon* 32 (1994) 1305–1310.
- [21] A. Blume, L. Gatti, H.-D. Luginsland, D. Maschke, R. Moser, J.C. Nian, et al., Silica and silane, in: B. Rodgers (Ed.), *Rubber Compounding: Chemistry and Applications*, second ed., CRC Press, Taylor and Francis Group, Boca Raton, FL, 2015.
- [22] A.I. Medalia, Filler aggregates and their effect on reinforcement, *Rubber Chem. Technol.* 47 (1974) 411–433.
- [23] M.P. Wagner, Reinforcing silicas and silicates, *Rubber Chem. Technol.* 49 (1976) 703–774.
- [24] W.K. Dierkes, J.W.M. Noordermeer, K.-U. Kelting, A. Limper, Improving silica processing, *Rubber World* 229 (2004) 33–40.
- [25] J.W. ten Brinke, P.J. van Swaaij, L.A.E.M. Reuvekamp, J.W.M. Noordermeer, The influence of silane sulphur rank on processing of a silica-reinforced tyre tread compound, *Kautsch. Gummi Kunstst.* 55 (2002) 244–254.
- [26] L.A.E.M. Reuvekamp, J.W. ten Brinke, P.J. van Swaaij, J.W.M. Noordermeer, Effects of time and temperature on the reaction of TESPT silane coupling agent during mixing with silica filler and tire rubber, *Kautsch. Gummi Kunstst.* 75 (2002) 187–198.
- [27] A.R. Payne, The dynamic properties of carbon black loaded natural rubber vulcanizates. Part II, *J. Appl. Polym. Sci.* 6 (1962) 368–372.
- [28] A. Blume, J. Jin, A. Mahtabani, X. He, S. Kim, Z. Andrzejewska, New structure proposal for silane modified silica, *Kautsch. Gummi Kunstst.* 73 (2020) 19–24.
- [29] A. Blume, F. Thibault-Starzyk, Deciphering the silica/silane reaction mechanism for the development of a new generation of low rolling resistance tires: Part 1 – Characterization by in situ IR spectroscopy, *Rubber Fibres Plast. Int.* 12 (2017) 152–157.
- [30] A. Blume, F. Thibault-Starzyk, Deciphering the silica/silane reaction mechanism for the development of a new generation of low rolling resistance: Part 2 – Transfer of

- results from model examinations into practice, *Rubber Fibres Plast. Int.* 12 (2017) 236–241.
- [31] H.-D. Luginsland, C. Röben, The development of sulphur-functional silanes as coupling agents in silica-reinforced rubber compounds: their historical development over several decades, *Gummi Fasern Kunstst.* 68 (2015) 734–737.
- [32] H.-D. Luginsland, Reactivity of the sulfur chains of the tetra sulfane silane Si69 and the disulfane silane TESP, *Kautsch. Gummi Kunstst.* 53 (2000) 10–23.
- [33] M. Sato, Reinforcing Mechanisms of Silica/Sulfide-Silane vs. Mercapto-Silane Filled Tire Compounds (Ph.D. thesis), University of Twente, Enschede, 2018.
- [34] A. Roychoudhury, P.P. De, N. Roychoudhury, A. Vidal, Chemical interaction between chlorosulfonated polyethylene and silica—effect of surface modifications of silica, *Rubber Chem. Technol.* 68 (1995) 815–823.
- [35] S. Bandyopadhyay, P.P. De, D.K. Tripathy, S.K. De, Interaction between carboxylated nitrile rubber and precipitated silica: role of (3-aminopropyl)triethoxysilane, *Rubber Chem. Technol.* 69 (1996) 637–647.
- [36] S. Varughese, D.K. Tripathy, Chemical interaction between epoxidized natural rubber and silica: studies on cure characteristics and low-temperature dynamic mechanical properties, *J. Appl. Polym. Sci.* 44 (1992) 1847–1852.
- [37] A.K. Manna, P.P. De, D.K. Tripathy, S.K. De, D.G. Peiffer, Bonding between precipitated silica and epoxidized natural rubber in the presence of silane coupling agent, *J. Appl. Polym. Sci.* 74 (1999) 389–398.
- [38] F. Cataldo, Preparation of silica-based rubber compounds without the use of a silane coupling agent through the use of epoxidized natural rubber, *Macromol. Mater. Eng.* 287 (2002) 348–352.
- [39] K. Sahakaro, S. Beraheng, Reinforcement of maleated natural rubber by precipitated silica, *J. Appl. Polym. Sci.* 109 (2008) 3839–3848.
- [40] S.S. Choi, K.H. Chung, C. Nah, Improvement of properties of silica-filled styrene-butadiene rubber (SBR) compounds using acrylonitrile-styrene-butadiene rubber (NSBR), *Polym. Adv. Technol.* 14 (2003) 557–564.
- [41] K.M. George, J.K. Varkey, K.T. Thomas, N.M. Mathew, Epoxidized natural rubber as a reinforcement modifier for silica-filled nitrile rubber, *J. Appl. Polym. Sci.* 85 (2002) 292–302.
- [42] M.M. Jacobi, M.V. Braum, T.L.A.C. Rocha, R.H. Schuster, Lightly epoxidized polybutadiene with efficient interaction to precipitated silica, *Kautsch. Gummi Kunstst.* 60 (2007) 460–466.
- [43] T.L.A.C. Rocha, R.H. Schuster, M.M. Jacobi, D. Samios, Influence of epoxidation on physical properties of SBR and its interaction with precipitated silica, *Kautsch. Gummi Kunstst.* 57 (2004) 656–661.
- [44] C.S.L. Baker, I.R. Gelling, R. Newell, Epoxidized natural rubber, *Rubber Chem. Technol.* 58 (1985) 67–85.
- [45] I.R. Gelling, Modification of natural rubber latex with peracetic acid, *Rubber Chem. Technol.* 58 (1985) 86–96.
- [46] C.S.L. Baker, I.R. Gelling, S. Azemi, Epoxidised natural rubber, *J. Nat. Rubber Res.* 1 (1986) 135–144.
- [47] I.R. Gelling, M. Porter, Chemical modification of natural rubber, in: A.D. Roberts (Ed.), *Natural Rubber Science and Technology*, Oxford University Press, Oxford, UK, 1988.
- [48] I.R. Gelling, Epoxidised natural rubber, *J. Nat. Rub. Res.* 6 (1991) 184–205.
- [49] K. Muraoka, N. Yagi, Rubber composition for tread and pneumatic tire using the samein: European Patent, EP1484359A1, 2004.

- [50] T.J. Segatta, P.H. Sandstrom, J.J.A. Verthe, Sulfur cured rubber composition containing epoxidized natural rubber and silica filler, United States Patent, US5396940 (1995).
- [51] M.N. Nanni, A. Serra, Process for producing tyres, tyres thus obtained and elastomeric compositions used therein, European Patent, EP1144503A1 (2001).
- [52] C.J. Lin, W.L. Hergenrother, Tire compositions comprising epoxidized natural rubber and a functionalized polyolefin, United States Patent, US6845797B2 (2005).
- [53] K. Hochi, Rubber composition for tread and tire having tread using the same, European Patent, EP2019126B1 (2011).
- [54] S. Schaal, A.Y. Coran, S.K. Mowdood, Silica reinforced rubber compositions of improved processability and storage stability, United States Patent, US6482884B1 (2002).
- [55] A.V. Chapman, Natural rubber and NR-based polymers: renewable materials with unique properties, in: The 24th International H.F. Mark-Symposium, Vienna, Austria, November 15–16, 2007.
- [56] Y.Y. Luo, Y.Q. Wang, J.P. Zhong, C.Z. He, Y.Z. Li, Z. Peng, et al., Interaction between fumed-silica and epoxidized natural rubber, *Organomet. Polym.* 21 (2011) 777–783.
- [57] P.J. Martin, P. Brown, A.V. Chapman, S. Cook, Silica-reinforced epoxidized natural rubber tire treads - Performance and durability, *Rubber Chem. Technol.* 88 (2015) 390–411.
- [58] C. Kantala, E. Wimolmala, C. Sirisinha, N. Sombatsompop, Reinforcement of compatibilized NR/NBR blends by fly ash particles and precipitated silica, *Polym. Adv. Technol.* 20 (2009) 448–458.
- [59] K.M. George, J.K. Varkey, K.T. Thomas, N.M. Mathew, Epoxidized natural rubber as a reinforcement modifier for silica-filled nitrile rubber, *J. Appl. Polym. Sci.* 85 (2002) 292–306.
- [60] K.M. George, J.K. Varkey, B. George, S. Joseph, K.T. Thomas, N.M. Mathew, Physical and dynamic mechanical properties of silica filled nitrile rubber modified with epoxidised natural rubber, *Kautsch. Gummi. Kunstst.* 59 (2006) 544–549.
- [61] P.L. Teh, Z.A. Mohd Ishak, A.S. Hashim, J. Karger-Kocsis, U.S. Ishiaku, On the potential of organoclay with respect to conventional fillers (carbon black, silica) for epoxidized natural rubber compatibilized natural rubber vulcanizates, *J. Appl. Polym. Sci.* 94 (2004) 2438–2445.
- [62] W. Kaewsakul, Silica-Reinforced Natural Rubber for Low Rolling Resistance, Energy-Saving Tires: Aspects of Mixing, Formulation and Compatibilization (Ph.D. thesis), University of Twente, Enschede, 2013.
- [63] W. Kaewsakul, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Optimization of mixing conditions for silica-reinforced natural rubber tire tread compounds, *Rubber Chem. Technol.* 85 (2012) 277–294.
- [64] M. Narathichat, K. Sahakaro, C. Nakason, Assessment degradation of natural rubber by moving die processability test and FTIR spectroscopy, *J. Appl. Polym. Sci.* 115 (2010) 1702–1709.
- [65] S. Wolff, Optimization of silane-silica OTR compounds. Part 1: Variations of mixing temperature and time during the modification of silica with bis-(3-triethoxysilylpropyl)-tetrasulfide, *Rubber Chem. Technol.* 55 (1982) 967–989.
- [66] F. Thum, S. Wolff, Nouveaux organosilanes pour l'industrie des pneumatiques (fr), *Kautsch. Gummi Kunstst.* 28 (1975) 733–739.
- [67] C. Penot, Rubber composition for a tire comprising a reinforcing inorganic filler and an (inorganic filler/elastomer) coupling system, United States Patent, US6951897 (2005).

- [68] W. Kaewsakul, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Optimization of rubber formulation for silica-reinforced natural rubber compounds, *Rubber Chem. Technol.* 86 (2013) 313–329.
- [69] L. Guy, S. Daudey, P. Cochet, Y. Bomal, New insights in the dynamic properties of precipitated silica filled rubber using a new high surface silica, *Kautsch. Gummi Kunstst.* 62 (2009) 383–391.
- [70] Y. Bomal, P. Cochet, B. Dejean, J. Machurat, Influence of mixing procedures on the properties of a silica reinforced agricultural tire tread, *Rubber World* 208 (1993) 33.
- [71] H.-M. Issel, L. Steger, A. Bischoff, Application of dithiophosphates in silica reinforced elastomer compounds, *Kautsch. Gummi Kunstst.* 58 (2005) 529–533.
- [72] S. Mihara, R.N. Datta, A.G. Talma, J.W.M. Noordermeer, Rubber composition, United States Patent, US7923493 (2011).
- [73] B. Schwaiger, A. Blume, Silica/silane—a winning reinforcement formula, *Rubber World* 222 (2000) 32–38.
- [74] H.-D. Luginsland, W. Niedermeier, New reinforcing materials for rising tire performance demands, *Rubber World* 228 (2003) 34–45.
- [75] A. Blume, Analytical properties of silica a key for understanding silica reinforcement, *Kautsch. Gummi Kunstst.* 53 (2000) 338–345.
- [76] T. Wang, M.-J. Wang, J. Shell, The effect of compound processing on filler flocculation, *Kautsch. Gummi Kunstst.* 53 (2000) 497–505.
- [77] W. Kaewsakul, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Mechanistic aspects of silane coupling agents with different functionalities on reinforcement of silica-filled natural rubber compounds, *Polym. Eng. Sci.* 55 (2015) 836–842.
- [78] L. Wahba, M. D'Arienzo, R. Donetti, T. Hanel, R. Scotti, L. Tadiello, et al., In situ sol–gel obtained silica–rubber nanocomposites: influence of the filler precursors on the improvement of the mechanical properties, *RSC Adv.* 3 (2013) 5832–5844.
- [79] W. Kaewsakul, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Cooperative effects of epoxide functional groups on natural rubber and silane coupling agents on reinforcing efficiency of silica, *Rubber Chem. Technol.* 87 (2014) 291–310.
- [80] W. Kaewsakul, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Verification of interactions between silica and epoxidised squalene as a model for epoxidised natural rubber, *J. Rubber Res.* 17 (2014) 129–142.
- [81] S.-C. Ng, L.-H. Gan, Reaction of natural rubber latex with performic acid, *Eur. Polym. J.* 17 (1981) 1073–1077.
- [82] K. Sengloyluan, Silica-Reinforced Natural Rubber: Use of Natural Rubber Grafted With Chemical Functionalities as Compatibilizer (Ph.D. thesis), University of Twente, Enschede, 2015.
- [83] K. Sengloyluan, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber, *Eur. Polym. J.* 51 (2014) 69–79.
- [84] T.L.A.C. Rocha, C. Rosca, J. Ziegler, R.H. Schuster, Influence of polymer polarity on phase morphology of NR blends, *Kautsch. Gummi Kunstst.* 58 (2005) 22–29.
- [85] P. Saramolee, K. Sahakaro, N. Lopattananon, W.K. Dierkes, J.W.M. Noordermeer, Comparative properties of silica- and carbon black-reinforced natural rubber in the presence of epoxidized low molecular weight polymer, *Rubber Chem. Technol.* 87 (2014) 320–339.
- [86] C.G. Robertson, C.M. Roland, Glass transition and interfacial segmental dynamics in polymer-particle composites, *Rubber Chem. Technol.* 81 (2008) 506–522.
- [87] Y. Li, M.J. Wang, T. Zhang, Study on dispersion morphology of silica in rubber, *Rubber Chem. Technol.* 67 (1994) 693–699.

- [88] K. Sengloyluan, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer, Synergistic effects in silica-reinforced natural rubber compounds compatibilized by ENR in combination with different silane coupling agents, *J. Rubber Res.* 19 (2016) 170–189.
- [89] M.K. Kravlevich, J.L. Koenig, FTIR analysis of silica-filled natural rubber, *Rubber Chem. Technol.* 71 (1997) 300–309.
- [90] A. Bertora, M. Castellano, E. Marsano, M. Alessi, L. Conzatti, P. Stagnaro, et al., A new modifier for silica in reinforcing SBR elastomers for the tyre industry, *Macromol. Mater. Eng.* 296 (2011) 455–464.
- [91] L.T. Zhuravlev, The surface chemistry of amorphous silica. Zhuravlev model, *Colloids Surf. A Physicochem. Eng. Aspects* 173 (2000) 1–38.
- [92] P.K. Pal, S.K. De, Effect of reinforcing silica on vulcanization, network structure, and technical properties of natural rubber, *Rubber Chem. Technol.* 55 (1982) 1370–1388.
- [93] W. Arayaprane, N. Na-Ranong, G.L. Rempel, Application of rice husk ash as fillers in the natural rubber industry, *J. Appl. Polym. Sci.* 98 (2005) 34–41.
- [94] H. Ismail, R. Nordin, A.M. Noor, Cure characteristics, tensile properties and swelling behaviour of recycled rubber powder-filled natural rubber compounds, *Polym. Test.* 21 (2002) 565–569.
- [95] H. Yan, G. Tian, K. Sun, Y. Zhang, Y. Zhang, Effect of silane coupling agent on the polymer-filler interaction and mechanical properties of silica-filled NR, *J. Appl. Polym. Sci.* 43 (2005) 573–584.
- [96] H. Yan, K. Sun, Y. Zhang, Y. Zhang, Y. Fan, Effects of silane coupling agents on the vulcanization characteristics of natural rubber, *J. Appl. Polym. Sci.* 94 (2004) 1511–1518.
- [97] J.L. Valentín, I. Mora-Barrantes, A. Rodríguez, L. Ibarra, L. Gonzalez, Effect of oleyl amine on SBR compounds filled with silane modified silica, *J. Appl. Polym. Sci.* 103 (2007) 1806–1814.
- [98] O. Klockmann, The International Tire Exhibition & Conference (ITEC) 2006, September 12–14, 2006, Akron, OH, Paper No. 29B.
- [99] A. Blume, Kinetics of the silica-silane reaction, *Kautsch. Gummi Kunstst.* 64 (2011) 38–43.
- [100] L. Qu, G. Yu, L. Wang, C. Li, Q. Zhao, J. Li, Effect of filler–elastomer interactions on the mechanical and nonlinear viscoelastic behaviors of chemically modified silica-reinforced solution-polymerized styrene butadiene rubber, *J. Appl. Polym. Sci.* 126 (2012) 116.
- [101] A.J. Manna, P.P. De, D.K. Tripathy, Dynamic mechanical properties and hysteresis loss of epoxidized natural rubber chemically bonded to the silica surface, *J. Appl. Polym. Sci.* 84 (2002) 2171–2177.
- [102] The United Nations Economic Commission for Europe (UNECE), UNECE Regulation No 117: Testing method for measuring the wet grip index of C1 tyres - Proposed amendments, Informal Document No. GRRF-71-10 (2011). Available from: <https://unece.org/fileadmin/DAM/trans/doc/2011/wp29grrf/GRRF-71-10e.pdf> (Accessed 20 February 2020).
- [103] D. Wonkam, E. Ehabe, F. Ngolemasango, B. Nkouonkam, H. Livonnière, Effect of epoxidised liquid natural rubber on nitrile butadiene rubber based mixes, *Plast. Rubber Compos.* 29 (2000) 420–426.
- [104] P. Saramolee, Utilization of Functionalized Low Molecular Weight Natural Rubber to Improve Processing Property and Reinforcement in Silica-Filled NR Compounds (Ph.D. thesis), Prince of Songkla University, Pattani, 2014.

- [105] P. Phinyocheep, C.W. Phetphaisit, D. Derouet, I. Campistron, J.C. Brosse, Chemical degradation of epoxidized natural rubber using periodic acid: preparation of epoxidized liquid natural rubber, *J. Appl. Polym. Sci.* 95 (2005) 6–15.
- [106] H. Xu, J. Liu, L. Fang, C. Wu, In situ grafting onto silica surface with epoxidized natural rubber via solid state method, *J. Macromol. Sci. B* 46 (2007) 693–703.
- [107] S. Wolff, U. Gorl, The influence of modified carbon-blacks on viscoelastic compound properties, *Kautsch. Gummi Kunstst.* 44 (1991) 941.
- [108] T.L.A.C. Rocha, M.M. Jacobi, D. Samios, R.H. Schuster, Evaluation of the influence of the polymer-filler interaction on compounds based on epoxidized elastomeric matrix and precipitated silica, *Polimeros* 16 (2006) 111–115.