

FUNCTIONALIZED SBRs IN SILICA-REINFORCED TIRE TREAD COMPOUNDS: EVIDENCE FOR INTERACTIONS BETWEEN SILICA FILLER AND ZINC OXIDE

S. MAGHAMI, W. K. DIERKES, J. W. M. NOORDERMEER*

UNIVERSITY OF TWENTE, ELASTOMER TECHNOLOGY AND ENGINEERING, 7500 AE ENSCHEDE, THE NETHERLANDS

RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 89, No. 4, pp. 559–572 (2016)

ABSTRACT

Unlike carbon black, silica is polar and naturally not compatible with nonpolar hydrocarbon elastomers. This lack of interaction or compatibility between the filler and the elastomer typically causes lower properties compared with carbon black-filled compounds. A common approach to deal with this problem is to use silane coupling agents in the system to link the silica and the polymer chains via covalent bonds. An alternative is the introduction of polar functional groups or chemically reactive groups into the elastomer chains, which can improve the compatibility of elastomers with fillers such as silica. In this article, the effect of three functionalized SBRs, one backbone modified with carboxylate moieties, one modified with dithiol groups, and one partially Si-coupled, on the dynamic and mechanical properties of a silica-reinforced tire tread compound will be discussed and compared with a reference compound that contains unmodified s-SBR as the main polymer. The results show the significant potential of two of these modified SBRs to reduce the rolling resistance of tire treads made thereof, while no major change in wet grip occurs. Zinc oxide is known as the best activator for sulfur vulcanization. Zn ions combine with accelerators to form an active complex that catalyzes the vulcanization process. However, in silica-filled compounds, ZnO may interfere with the silanization process because of its alkaline nature, and it may compete with the silanes in reacting with the acidic –OH groups on the surface of silica particles. When functionalized SBRs with higher polarity are used in silica compounds, ZnO may interact with these moieties as well. To investigate the effect of ZnO on the properties of the silica-reinforced tread compound, a series of compounds have been prepared, in which the addition of ZnO in a later stage was compared with conventional mixing. The dynamic and mechanical properties of the final compounds are discussed. [doi:10.5254/rct.16.84810]

INTRODUCTION

With the introduction of silica technology in passenger car tire tread applications, filler–polymer interactions have become of key importance. Besides the silane coupling agents and control of the silanization process, polymer functionality can play an essential role in polymer–filler interactions. The main research subjects over the past years have focused on the design of functionalities in elastomers, especially s-SBRs.^{1–7} The aim is to reduce the hydrophobic characteristics of the hydrocarbon polymers and make them more compatible with hydrophilic silica, thereby providing better silica dispersion and better polymer–filler interactions.

Alkoxysilane functionalized SBR prepared through terminating the anionic polymerization with tetraethylorthosilicate in silica containing tire tread recipe is claimed to yield reduced rolling resistance and improved wear compared with the similar nonfunctionalized polymer.⁸

The introduction of epoxy groups is another prosperous method in this field. It has been reported that the use of an epoxidized SBR with just 7 mol% of epoxidation groups in the main chain results in a reduction of about four times in the value of storage modulus at low strains, G_0 , compared with an untreated SBR–silica mixed compound. This has been attributed to the weaker filler network, which is itself a result of hydrogen bonding, more than chemical bonds between the epoxidized SBR and silica surface groups.⁹

Thiele et al. prepared a series of functionalized s-SBRs using some coupling agents and chain-end and backbone modifiers; the polymer preparation and modification pathways can be seen

*Corresponding author. Ph: 0031-53-4892529; email: j.w.m.noordermeer@utwente.nl

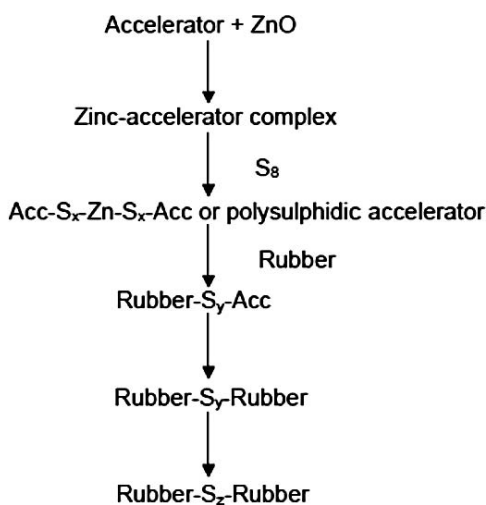


FIG. 1. — General scheme for sulfur vulcanization.

elsewhere.⁵ Using chain-end-modified polymers in vulcanizates made thereof leads to an improvement of dynamic characteristics, particularly to a reduced hysteresis.⁴ Thiele et al. also prepared some backbone-modified SBRs and reported that all of these polymer vulcanizates have an increased tensile strength and modulus 300 value compared with the reference compound polymers. The $\tan\delta@60^\circ\text{C}$ indicative of the rolling resistance property of a tire improved for all backbone-modified polymer vulcanizates by 19% to 32%, whereas the $\tan\delta@0^\circ\text{C}$ (indicative of wet grip characteristic) deteriorated slightly: 3% to 15%.⁵ Overall, a predominantly rolling resistance improvement was measured for backbone-modified polymers compared with both unmodified and chain-end-modified reference polymers. The vulcanizate heat buildup decreased accordingly. Therefore, the authors concluded that the excellent hysteresis properties of a chain-end-modified polymer can be further improved by the application of the backbone modification technology.

Zinc oxide (ZnO) has been used in rubber compounds since 1905, when it was used as reinforcing filler and not as an activator. Only in the early 1920s was its role as activator for sulfur vulcanizates discovered; it was found that using ZnO in combination with stearic acid reduces the vulcanization time and improves the properties of rubber. Fatty acids such as stearic acid are used to solubilize the zinc in the system and set zinc ions free to form complexes with accelerators.^{10,11} Besides these properties, other functionalities such as reduced heat buildup, improved tire abrasion resistance, and decreased shrinkage of molded rubber products have been reported for compounds containing ZnO.¹¹

The general reaction path of accelerated sulfur vulcanization is proposed as follows: The activated accelerator reacts with sulfur to give polysulfides of the structure $\text{Acc-S}_x\text{-Acc}$, where Acc is an organic group derived from an accelerator.^{12,13} The polysulfides interact with allylic hydrogen atoms of the elastomer to form polymeric polysulfides, such as $\text{rubber-S}_x\text{-Acc}$ (sulfurated rubber). Finally, the rubber polysulfides react, either directly or through an intermediate, to give cross-links ($\text{rubber-S}_x\text{-rubber}$). These reactions are catalyzed by zinc-accelerator complexes, although they can also occur in the absence of ZnO, albeit at significantly lower reaction rates. The initial cross-links may eventually desulfurate to form shorter cross-links or degrade to cyclic sulfides. It has been reported that also in this stage of the vulcanization process, zinc ions play a role.¹⁴ These steps are illustrated in Figure 1.

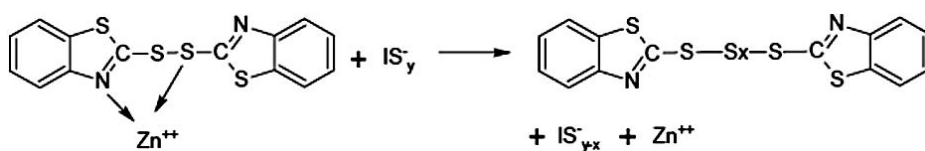


FIG. 2. — Formation of polysulfidic MBTS via a complex with zinc.

Many mechanisms have been proposed for the reaction of activators in sulfur-cured systems. Generally accepted is that in many vulcanization systems, ZnO is a precursor to zinc-derived accelerators.¹⁵ It reacts with most of the accelerators to form a highly active zinc salt. A preceding reaction with stearic acid forms hydrocarbon soluble zinc stearate and liberates water before the onset of cross-linking. Then the released zinc ion reacts with the accelerator to form an active accelerator complex.

The exact activation role of ZnO is very much dependent on the type of accelerator present in the system. Figure 2 graphically shows the formation of a sulfur-rich complex in a system with 2-mercaptobenzothiazole-disulfide (MBTS) as accelerator and an ionized form of linear sulfur (IS_y) in the presence of a zinc ion. It has been frequently reported that in a sulfenamide-sulfur accelerated system in the presence of ZnO, the vulcanization reactions are of radical or ionic nature.¹⁶⁻¹⁸

The presence of zinc in the system catalyzes the formation of macromolecular complexes. The rate of increase of the amount of sulfur atoms embedded in the accelerator (e.g., MBTS) is increased when ZnO is present because of the interaction of Zn^{+2} with the accelerator. Also, an increase in the concentration of fatty acid, with the accompanying increase in the concentration of available Zn^{+2} ions, raises the overall rate in the early reaction steps, which lead to the formation of the rubber- S_x -accelerator complex.¹²

ZnO does not react with sulfenamide accelerators themselves such as N-cyclohexylbenzothiazole-2-sulfenamide and N-tert-butylbenzothiazole-2-sulfenamide.^{19,20} In case of sulfenamide accelerators, as in the formulation of a tire tread, the accelerator first needs to be decomposed to form MBT and later MBTS, as shown in Figure 3, and then the complex formation continues as described before.

The silanol groups on the surface of silica are acidic in nature and therefore can react with an alkali, such as ZnO. This will lead to a reduced availability of the silanol groups for reaction with the

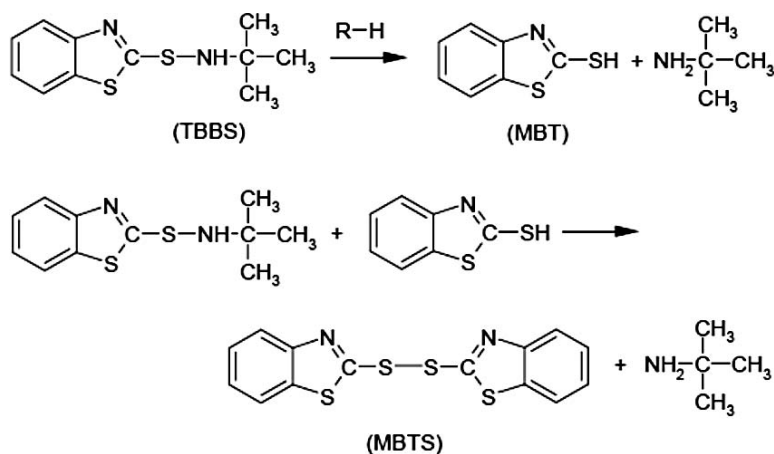


FIG. 3. — Thermal decomposition of N-tert-butylbenzothiazole-2-sulfenamide and formation of MBTS.

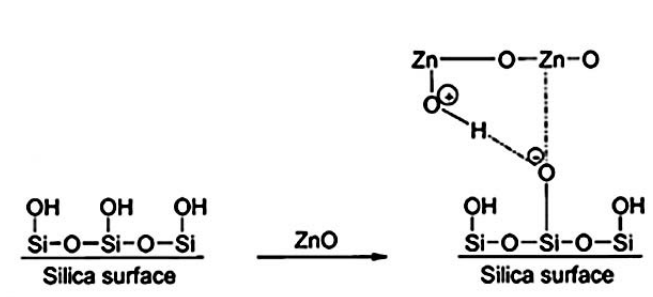


FIG. 4. — Possible reaction between silica and ZnO.

coupling agent. Several authors have stated that ZnO affects the reaction between silica and coupling agent.^{21–23} Reuvekamp et al.²³ observed that a lower tendency to scorch is seen when ZnO is omitted during the internal mixing stage and added only later together with the curing additives on a cold two-roll mill. The presence of ZnO in the mixer provokes premature scorch of the compound due to its catalytic effect on the reaction between coupling agent and rubber. When mixing a compound without ZnO in the first mixing step, the scorch effect is largely reduced, and it is possible to mix until higher dump temperatures without prescorch problems. Furthermore, an overall better hydrophobation of the silica surface is obtained, which is attributed to the fact that the coupling agent bis(triethoxysilylpropyl)tetrasulfide does not have to compete with ZnO over the silanol groups on the silica surface. An acid–alkali reaction of ZnO with the silica surface via the silanol groups was proposed, as illustrated in Figure 4.²³

When functionalized elastomers with carboxylic or dithiol modifications are employed, the same type of acid–alkali reactions would be expected in the compound formulation. In this article, the effect of adding ZnO in different stages of mixing on the final properties of the compounds are discussed for two different modified SBRs, compared with a reference compound.

EXPERIMENTAL

MATERIALS AND COMPOUND PREPARATION

Blends of different solution styrene–butadiene rubbers (S-SBR) and high-cis polybutadiene (BR) with a weight ratio of 70/30 and 80 phr silica loading were prepared. A highly dispersible silica was used as reinforcing filler, and the compound containing BUNA VSL 5025-2HM (Lanxess, Leverkusen, Germany) was taken as the reference. Three types of functionalized SBR were used in this study: SPRINTAN SLR-4602 (Styron, Schkopau, Germany) is described to be dithiol-modified for improved polymer–filler interaction with carbon black as well as with silica.⁵ It is claimed to be statistically modified along the entire polymer chain. Buna VSL VP PBR 4003 (Lanxess) is also statistically modified along the polymer chain with COOH groups with a concentration of 35 mEq/kg. SPRINTAN SLR-4630 (Styron) is partially Si-coupled and contains a nonstaining stabilizer.²⁴ There are no further details provided on whether this coupling is randomly along the chain, or—more likely—chain-end. Properties of these elastomers and their suppliers are as shown in Table I.

All other ingredients and suppliers are as listed in Table II. Four compounds (Ref, CS8, P8, and S8) were prepared based on the formulations given in Table II. In the compound CS8, an extra amount of oil was added to compensate for the lack of oil in this elastomer compared with the other two.

TABLE I
SBR TYPES USED IN THIS STUDY

SBR type	SLR 4630	SLR 4602	PBR 4003	Buna VSL 5025-2 HM
Supplier	Styron	Styron	Lanxess	Lanxess
Functionalization	Part. Si-coupled	Di-thiol	COOH	none
Compounds code	S8	CS8	P8	Ref.
Vinyl, wt. %	63	63	48	50
Styrene, wt. %	25	21	24	25
T_g (DSC), °C	-29	-25	-26	-29
Mooney viscosity ML(1+4) 100 °C, MU	55	65	53	62
Oil content (TDAE), phr	37.5	0	37.5	37.5

The compounds were prepared in a 350 mL Brabender 350S internal mixer, operating at 110 and 130 rpm with a fill factor of 0.7 in three-step mixing. The total mixing time was 10 min, while the dump temperature for the first two stages was adjusted to 155 ± 5 °C by changing the initial temperature, as explained in Table III.

To assess the effect of ZnO, three compounds (one reference and two based on the new SBRs) were prepared according to the same formulation, but with a small difference: ZnO in the first stage of mixing was eliminated and added later on in the third stage with the curatives. Two of the new SBR types, which showed promising rolling resistance properties (SPRINTAN SLR-4602-Schkopau and Buna VSL VP PBR 4003), were chosen for these series of experiments. These compounds are presented by the acronyms Ref-Z, CS8-Z, and P8-Z.

TABLE II
RUBBER COMPOUND COMPOSITION (PHR)

Ingredient	Supplier	Compound Code			
		S8	CS8	P8	Reference
S-SBR		96.3	70	96.3	96.3
BR		30	30	30	30
Silica		80	80	80	80
TESPT ^a	Evonik Degussa GmbH	7	7	7	7
TDAE ^b	BP Belgium	6.7	33	6.7	6.7
Zinc oxide	Sigma Aldrich	2.5	2.5	2.5	2.5
Stearic acid	Sigma Aldrich	2.5	2.5	2.5	2.5
6PPD ^c	Flexsys	2	2	2	2
TMQ ^d	Flexsys	2	2	2	2
Sulfur	Sigma Aldrich	1.4	1.4	1.4	1.4
TBBS ^e	Flexsys	1.7	1.7	1.7	1.7
DPG ^f	Flexsys	2	2	2	2

^a Coupling agent bis(triethoxysilylpropyl) tetrasulfide.

^b Treated distillate aromatic extract oil, ENERTHENE 1849 F.

^c Antiozonant N-phenyl-N'-1,3-dimethylbutyl-p-phenylenediamine.

^d Antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline.

^e Accelerator N-tert-butylbenzothiazole-2-sulfenamide.

^f Accelerator difenyl guanidine.

TABLE III
MIXING PROCEDURE

First stage
Rotor speed: 110 RPM
Initial temperature: 50 °C
Min.
0.0 Add polymers
1.0 Add ½ silica, ½ silane, ZnO + stearic acid
2.0 Add ½ silica, ½ silane, oil, TMQ, 6PPD
3.0 Sweep
4.0 Dump @ ~155 °C
Second stage
Rotor speed: 130 RPM
Initial temperature: 50 °C
Min.
0.0 Add I-stage batch
3.0 Dump @ ~155 °C
Third stage
Rotor speed: 75 RPM
Initial temperature: 50 °C
Min.
0.0 Add batch from the second stage
1.0 Add curatives (mixed together)
3.0 Dump @ ~100 °C

The samples were cured in a Wickert press WLP 1600 at 160 °C to sheets with a thickness of 2 mm according to their t_{90} optimum vulcanization time as determined in a rubber process analyzer RPA 2000 from Alpha Technologies.

MEASUREMENTS

The rubber process analyzer RPA 2000 was used to evaluate cure properties and dynamic loss properties at high strain (6%). For cure properties, the measurement was performed under 2.79% strain, a frequency of 0.833 Hz, at 160 °C and for 30 min. Hardness of the vulcanized compounds was measured with a Zwick 3150 Shore A Hardness Tester. Mechanical properties of the samples were tested using a Zwick Z020 tensile tester according to ISO-37 at a cross-head speed of 500 mm/min. Bound rubber tests were done by immersing approximately 0.2 g of the still uncured compound in 50 mL of toluene for 7 days to obtain equilibrium swelling. In addition, samples immersed in toluene were treated under an ammonia atmosphere in order to separate them physically from chemically bound rubber. The mass of the samples before and after the test was used to calculate the bound rubber. Payne effect measurements were performed in shear mode in a Metravib DMA2000 dynamic spectrometer. The samples were cut from the cured sheets of the rubber compounds. Dynamic rebound was measured in a Zwick/Roell Rebound Resilience Tester 5109 according to DIN13014 at room temperature and at 70 °C.

A Laboratory Abrasion Tester 100 (LAT 100, VMI, The Netherlands) was used to measure the side force coefficient (SFC) as an indication for the wet traction of tires. Wheel samples were made by compression molding in a special mold using a Wickert laboratory vulcanization press WLP 1600. Testing was performed with water of five different temperatures (2, 8, 15, 22, and 30 °C) and

TABLE IV
COMPOUND MOONEY VISCOSITIES ML(1+4) 100 °C

Reference	Ref-Z	CS8	CS8-Z	P8	P8-Z	S8
65	76	63	66	63	69	74

at a constant slip angle of 15°. Water is needed to simulate the wet traction as well as to keep the temperature at the right level because of heating of the rubber wheel. An electrocorundum disc with a relative roughness value of 180 was used to simulate the tire–road interface. Tests were performed at a constant speed of 1.5 km/h and a load of 75 N for a distance of 33 m. The SFC is measured as

$$\text{SFC} = \frac{F_y}{F_z}, \quad (1)$$

where F_y is the side force and F_z is the normal load on the wheel sample. The higher the SFC, the higher the expected wet grip or traction.

RESULTS AND DISCUSSION

To protect the intellectual property rights of one of the project sponsors, all data presented in this article are ranked in a relative manner, normalized to the reference compound values.

Table IV gives the compound Mooney viscosities for the various samples. Despite the known beneficial effect of adding ZnO at the latest stages of mixing together with the other curatives,²³ it is in actual practice often not done because the omission of ZnO in the early mixing stages tend to raise the compound Mooney viscosity, hampering further processing. Although the small mixing equipment used for the present study is far more effective in mixing than large industrial mixers, this tendency of higher compound Mooneys for late ZnO addition can still be seen to some extent. A mutual comparison between the various polymers is of little value because of their wide variation in polymer Mooney viscosities to start with.

Bound rubber is the rubber portion that can no longer be separated from the filler when the still unvulcanized rubber batch is extracted with a good rubber solvent such as toluene over a specific period of time, usually at room temperature.^{25,26} Bound rubber is composed of three different types of polymer–filler interactions: a part that is chemically bound to the filler, physically bound polymer, and occluded rubber. The determination of the chemically bound rubber is done after ammonia treatment, which is carried out on the samples according to the procedure explained earlier. Ammonia splits the adsorptive physical bonds between rubber and silica; therefore, only the covalently bound elastomer portion remains attached to the filler.

Figure 5 shows the bound rubber test results of the compounds. As is observed, in the reference compound, the difference between the total (i.e., the sum of the physically and chemically bound rubber) and the chemically bound rubber is very large compared with the other compounds. In other words, adding functional groups to the rubber chains promotes chemical filler–polymer connections already in the unvulcanized stage. As expected, the polar functionalization (compounds CS8 and P8) has the highest effect on the chemically bound rubber portion. It is hard to assign a quantitative number to the chemically bound filler–polymer portion, as usually the errors in bound rubber measurements are high. But it can definitely be used as a good indication for polymer and filler chemical connections. Bound rubber tests were also performed for the compounds with ZnO added in the later stage of mixing, but as the results were too confusing and the errors were high, they are not presented here.

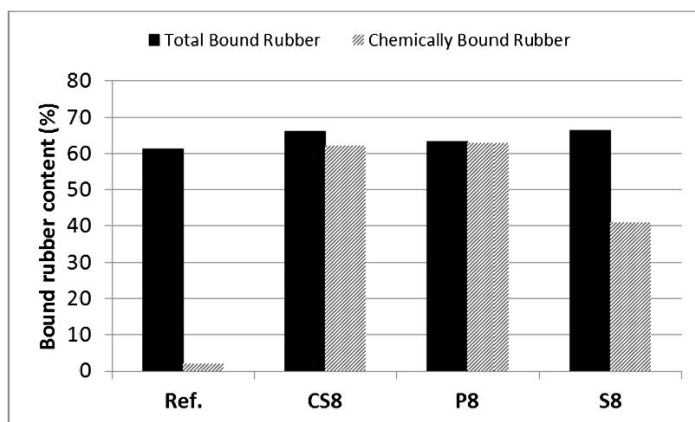


FIG. 5. — Bound rubber content (total and chemically) in the different compounds.

The relative hardness values of the cured compounds are given in Figure 6. As is clearly seen, the hardness values of all the compounds are lower than the reference one, which had an early addition of ZnO. Using functionalized polymers, generally, results in lower hardness values than the reference compound, with compound CS8 showing the lowest hardness value. Omission of ZnO in the first stage of mixing also has a diminishing effect on the hardness values compared with the conventionally prepared compounds, and this may affect the other properties of the compounds such as the SFC or tensile properties. To avoid possible misconceptions, a series of compounds with adjusted hardness values have been prepared and will be reviewed in a separate article.

The tensile properties of the compounds are presented in Figure 7. As illustrated in the figure, the compounds with lower hardness show lower stress and strain at break values. It seems that besides the effect of functionalized SBRs, the absence of ZnO does not affect the tensile properties much.

Figure 8 shows the relative $\tan\delta@60^\circ\text{C}$ values of the compounds. It is well accepted that the $\tan\delta$ value measured at 60°C , at a frequency of 10 Hz and 6% strain, correlates well with the rolling resistance performance of a tire tread. A lower $\tan\delta$ indicates lower hysteresis, which results in less energy dissipation.²⁷ By replacing the unmodified SBR by the functionalized SBRs, a great reduction of the loss tangent value $\tan\delta$ at 60°C is achieved. As shown, compound CS8 has the lowest $\tan\delta$ value (between the conventionally prepared compounds) with 16% reduction, followed by P8 with 12% reduction in the loss tangent value compared with the reference compound. From a mechanistic

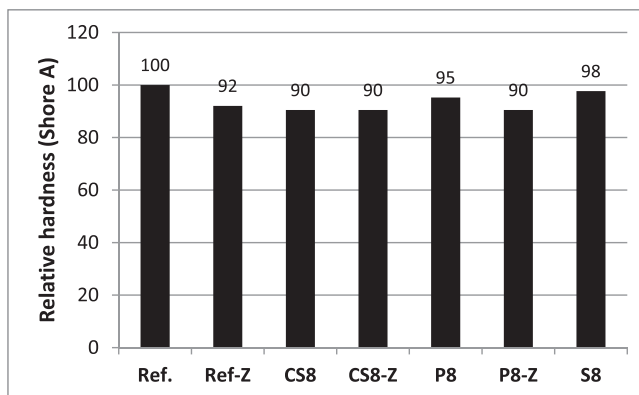


FIG. 6. — Hardness values of the cured compounds.

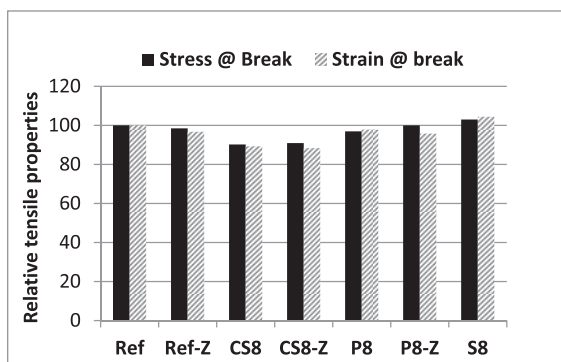


FIG. 7. — Relative tensile properties of the compounds.

perspective, the decrease in the hysteresis at this temperature of 60 °C can be attributed to a less developed filler–filler network, as the major source of energy dissipation at this temperature is the breakdown and reformation of this network.^{28,29} Besides, some authors suggest that slippage of polymer chains on the filler particle surface is a source of energy dissipation, too.^{30,31} Either mechanism works well in the interpretation of the obtained results. Polar functionalized SBRs (compounds CS8 and P8) show a lower loss tangent at 60 °C, whereas Si-coupled SBR (compound S8) shows a bit higher $\tan\delta$ value compared with the reference compound. It seems that good affinity between polar silica particles and partially polar SBR chains (in compounds CS8 and P8) leads to better filler dispersion or a less developed filler network, something that does not occur in the case of Si-coupled SBR (compound S8). In addition, when strong interactions occur between silica particles and polymer chains, which is indicated by the bound rubber test results (see Figure 5, movement of polymer chains), a source of energy dissipation is restricted. In addition, in the case of polar polymers, part of the ZnO can be involved in interactions with acidic moieties of the partially polar polymer chains and therefore interferes less with the silanization process, which again helps in better dispersion of the silica particles.

Comparing the dithiol modifications and carboxyl modifications, it looks like dithiol is more eager to couple to silica particles or is more reactive toward ZnO, resulting in the lowest $\tan\delta@60^\circ\text{C}$ for the two.

When ZnO is left out of the early stages of mixing and added at a later stage to the compound, the decrease in the loss tangent is even larger. Although it is observed in case of the reference

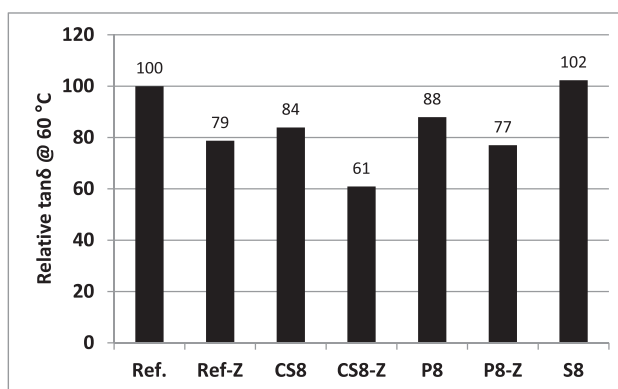


FIG. 8. — Relative $\tan\delta@60^\circ\text{C}$ values for different compounds.

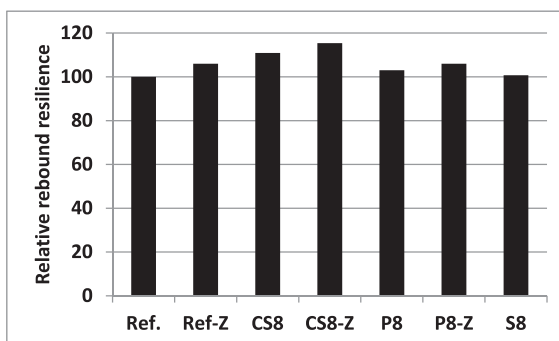


FIG. 9. — Relative rebound resilience data measured at 70 °C.

compound too, the decrease is much larger in the case of compound CS8-Z and reaches 39% relative to the reference compound. When there is no ZnO present in the compound intervening with the silanization and captivating the polar moieties of the polymer chains, it can be expected that besides improved silanization, all polar moieties of the polymer chains are free to come into contact with silica particles, which leads to much better filler dispersion and less filler–filler interaction. Considering the reduction achieved in compounds CS8-Z and P8-Z compared with their conventionally mixed compounds (CS8 and P8), again it can be concluded that mercapto functionalities are more reactive toward ZnO and/or more eager to react with silica particles than the carboxyl functionalities.

Rebound resilience tests confirm the loss tangent data (see Figure 9). The higher the rebound resilience, the more elastic the compound and therefore the lower the hysteresis, which favors lower rolling resistance. The two compounds CS8 and P8 show higher rebound resilience values compared with the reference: 11% and 3%, respectively. The rebound value of compound S8 remains almost unchanged compared with the reference compound, in that it showed little change in the $\tan\delta@60\text{ °C}$ as well. Absence of ZnO during the early stages of mixing by itself already brings about a more than 6% increase in the rebound resilience value in the case of the reference compound, but the highest value in rebound resilience is found for compound CS8-Z, with a 15% increase, all corresponding with the lowest $\tan\delta$ value.

Figure 10 represents the relative storage modulus data as a function of strain for the different compounds with ZnO present in the first stage of mixing. The difference between the storage

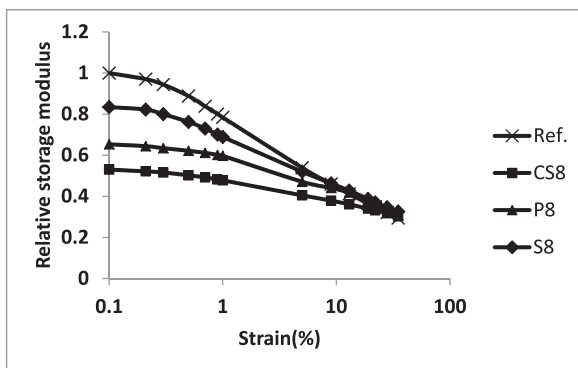


FIG. 10. — Relative storage modulus versus strain measured at 80 °C for the different compounds with ZnO present during mixing.

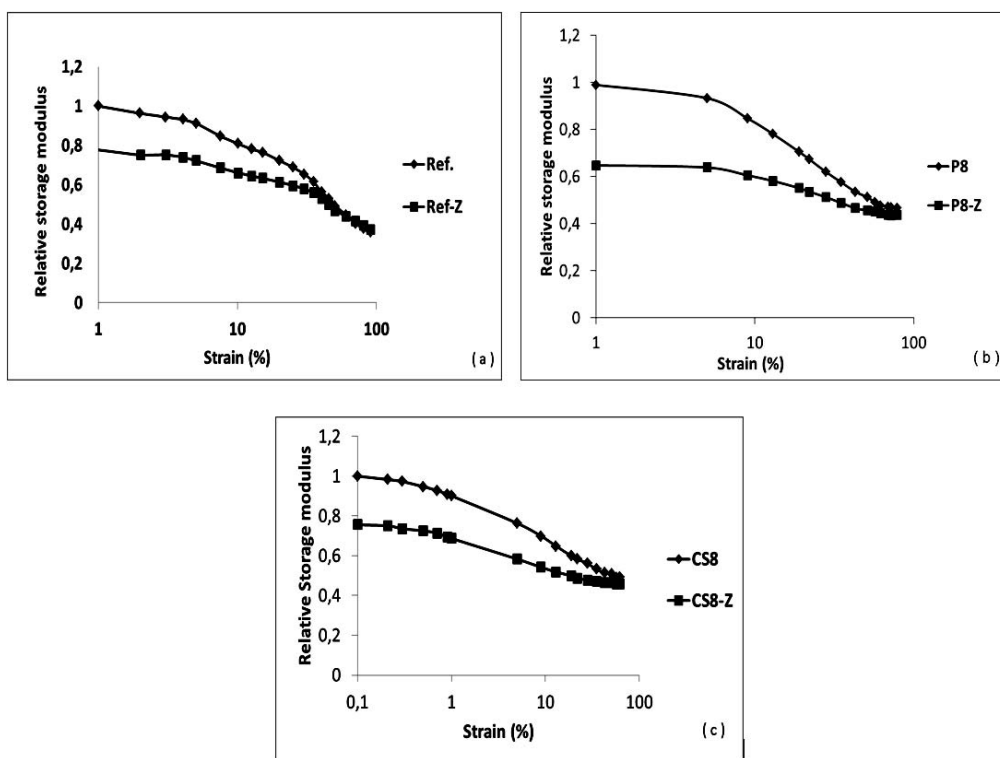


FIG. 11. — Relative storage modulus versus strain measured at 80 °C for the different compounds with and without ZnO added in stage I: (a) reference, (b) P8, (c) CS8.

moduli at low strain and high strain is defined as the Payne effect.^{31,32} As is seen, compound CS8 has the lowest Payne effect value and thus the lowest filler–filler interactions. Compounds P8 and S8 show lower Payne effects compared with the reference compound, too. Therefore, functional SBRs generally help in improving filler dispersion and reducing filler–filler interaction.

A significant change is observed in absence of ZnO in the first and second stages of mixing. By leaving out the ZnO during stage I, a large decrease in the low strain storage modulus values is seen. As was mentioned already, ZnO may interfere with the silanization reaction. So by leaving it out during silanization, more mature silanization can occur, which leads to lower filler–filler interaction and consequently a lower Payne effect, as is seen in the case of the reference compound (Figure 11a). Incorporation of functionalized polymers into the compound recipe helps diminish the filler network even more; these results can be seen in Figures 11b and c.

The LAT100 results of the three compounds with and without ZnO present in the first stage of mixing are shown in Figures 12 and 13a–c. The principle of the LAT100 measurements is explained elsewhere. Measured is the SFC, which is correlated to wet skid resistance, and a higher value implies better wet grip on the road surface. On average, SFC values of the functionalized polymer compounds are 5–10% lower than the reference. This decrease in SFC of the modified polymer compounds can be related to a lower hardness of the material as well. As seen in Figure 6, the hardness of the compounds CS8, P8, and S8 is lower than the reference compound by 8%, 5%, and 2% reduction, respectively, which will also affect the performance of the samples in the LAT100 test. Besides, a negative effect of the acidic functionalized elastomer on the vulcanization and therefore cross-link density may influence the material properties as well. The four polymers

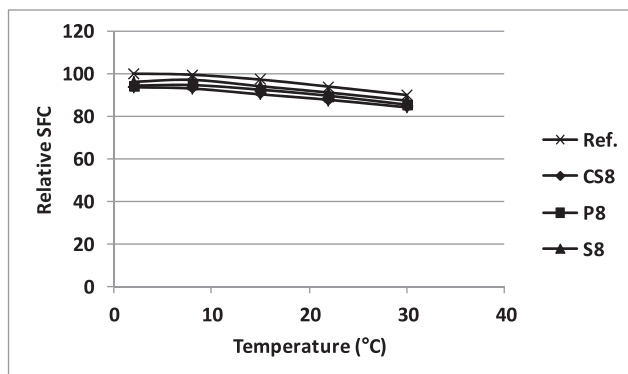


FIG. 12. — Relative side force coefficient (SFC) versus temperature.

investigated are quite different in nature. Besides the functionalization, they differ substantially in composition, particularly their vinyl content, and although only slightly different in Mooney viscosities, one polymer, SLR 4602, is non-oil extended whereas the others are oil extended. This must be related to quite large differences in molecular weight, molecular weight distribution, and branching. It made no sense to try to gain a deeper understanding of the observed effects without further details about the polymer structures.

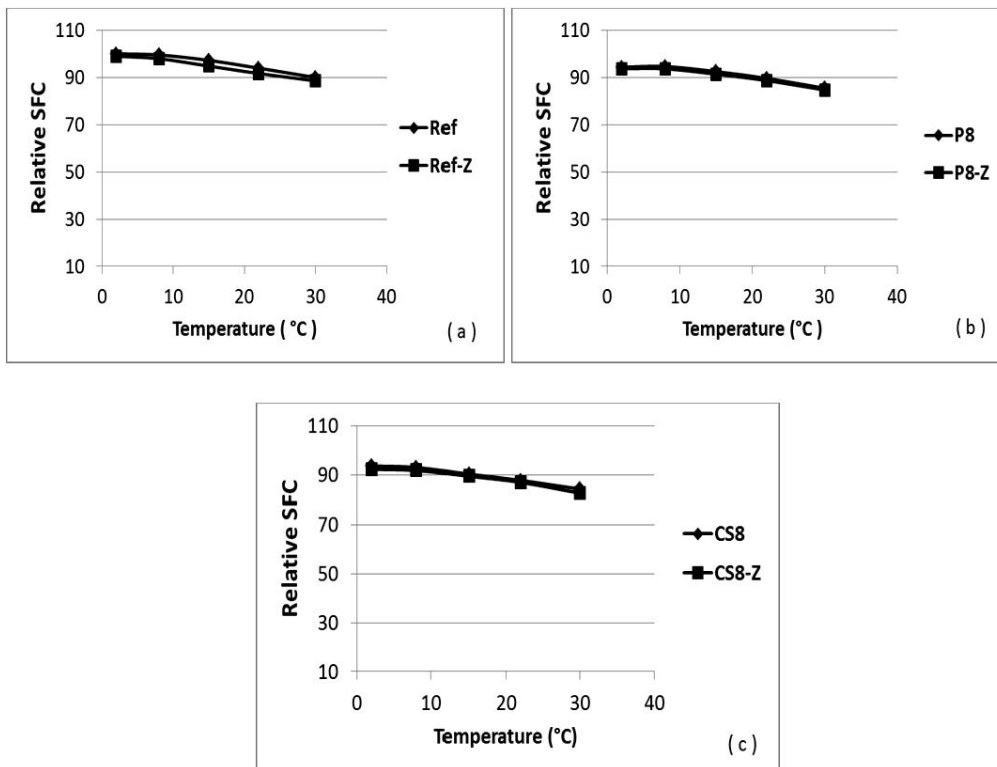


FIG. 13. — Relative side force coefficients measured at different temperatures for the different compounds with conventional and late addition of ZnO: (a) reference, (b) P8, (c) CS8.

Leaving ZnO out during the early mixing steps and adding it at a later stage does not have a significant effect on the SFC values. Therefore, the same traction performance on a wet road is expected for these compounds if implemented in tires. This indicates that a lower filler–filler interaction, as observed for the compounds with ZnO added in stage III of mixing, does not particularly contribute to a better friction performance of the compounds. This has been experienced in other work as well, where compounds with the same Payne effect values, hence similar filler–filler interactions, show different LAT100 behavior.³³ Therefore, it can be stated that there is not a clear relation between SFC and filler–filler interaction. However, it should again be considered that the reduced hardness observed for the compounds based on the functionalized elastomers may have also contributed to this effect.

CONCLUSIONS

Silica has a polar structure and is not compatible with the hydrophobic rubber by nature. Adding functional groups into the polymer chains may help to improve compatibility. The effect of three different functionalized SBR types in the formulation of a green tire tread was studied. Grafting polar groups, carboxyl (–COOH) or mercapto (–SH), onto the polymers increases the affinity between the elastomers and silica, whereas an Si-coupled elastomer does not have a specific positive effect. The largest improvement, a decrease of 16% in loss tangent at 60 °C, was achieved for the compound based on SBR with mercapto functionalities.

Bound rubber and Payne effect tests were performed to monitor the filler–polymer and filler–filler interactions, confirming the lowest filler–filler interaction, especially for the two compounds containing polar functionalities.

The LAT100 test results showed little difference in the SFC values of the different compounds. This implies a comparable wet grip performance on the road. However, the mechanical properties of the compounds with polar functionalities onto the SBR are slightly lower than the properties of the nonmodified reference compound.

ZnO has a significant influence on the loss properties and filler dispersion of the compounds based on the modified SBRs. With dithiol-modified SBR and ZnO added at a later stage of mixing, a large improvement with 39% decrease in the loss tangent value at 60 °C was obtained compared with the reference compound. The rebound resilience data for these compounds show the same trend. This decrease in hysteresis is expected to result in a strongly reduced rolling resistance of tire treads based thereon.

The SFCs measured on the LAT100 as indication for the wet skid resistance were independent of the time of ZnO addition. Therefore, the same wet traction performance as the conventionally processed compounds is expected for these compounds if used in tire treads. However, the somewhat reduced hardness observed for the compounds based on the functionalized elastomers may also have had some effect on these results.

ACKNOWLEDGEMENTS

This project was carried out in the framework of the innovation program “GO Gebundelde Innovatiekracht” and funded by the European Regional Development Fund. The project partners Apollo Tyres Global R&D, Enschede, The Netherlands; University of Twente (Tire-Road Consortium), Enschede, The Netherlands; and Elastomer Research and Testing (ERT), Deventer, The Netherlands are gratefully acknowledged. Specifically, we would like to thank Tanya Tolpekina and Steven Schultz from Apollo Tyres for their valuable contribution to this work.

REFERENCES

- ¹D. C. Edwards and K. Sato, *RUBBER CHEM. TECHNOL.* **53**, 66 (1980).
- ²F. Romani, E. Passaglia, M. Aglietto, and G. Ruggeri, *Macromol. Chem. Phys.* **200**, 524 (1999).
- ³S. Thiele, D. Bellgardt, and M. Holzleg, *Kautsch. Gummi Kunstst.* **5**, 244 (2008).
- ⁴S. Thiele, D. Bellgardt, and M. Holzleg, “Polymer Functionalization - Novel Rubber for Tire Tread Applications,” Paper presented at the 172nd Fall Meeting of the Rubber Division, ACS, Cleveland, October 16–18, 2007.
- ⁵S. Thiele and D. Bellgardt, “Novel Functionalized Oil Extended SBR for Silica and Carbon Black Containing Tires,” Paper presented at the 176th Fall Meeting of the Rubber Division, Pittsburgh, October 13–15, 2009.
- ⁶S. Thiele and J. Kiesekamp, “Modified Synthetic Rubber for Silica and Carbon Black Containing Tires,” Paper presented at the 9th Fall Rubber Colloquium of the “Deutsches Institut für Kautschuk Technologie (DIK),” Hannover, November 3–5, 2010.
- ⁷S. Thiele, J. Kiesekamp, S. Rulhoff, and D. Bellgardt, *Kautsch. Gummi Kunstst.* **64**, 36 (2011).
- ⁸T. E. Hogan, A. Randall, W. L. Hergenrother, and C. J. Lin, *Rubber World* **242**, 38 (2010).
- ⁹T. Rocha, R. H. Schuster, M. M. Jacobi, and D. Samios, *Kautsch. Gummi Kunstst.* **57**, 656 (2004).
- ¹⁰M. R. Kresja and J. L. Koenig, “The Nature of Sulfur Vulcanization,” in *Elastomer Technology Handbook*, N. P. Cheremisinoff and P. N. Cheremisinoff, Eds., CRC Press, Boca Raton, 1993.
- ¹¹G. Heideman, R. N. Datta, J. W. M. Noordermeer, and B. van Baarle, *RUBBER CHEM. TECHNOL.* **77**, 512 (2004).
- ¹²A. Y. Coran, *J. Appl. Polym. Sci.* **87**, 24 (2003).
- ¹³R. H. Campbell and R. W. Wise, *RUBBER CHEM. TECHNOL.* **37**, 635 (1964).
- ¹⁴M. Porter, “Rubber Vulcanization,” in *Organic Chemistry of Sulfur*, S. Oae, Ed., Plenum Press, New York, 1977.
- ¹⁵R. F. Ohm, “Rubber Chemicals,” in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, 1970.
- ¹⁶S. P. Manik and S. Banerjee, *RUBBER CHEM. TECHNOL.* **43**, 1311 (1970).
- ¹⁷J. R. Shelton and E. T. McDonel, *RUBBER CHEM. TECHNOL.* **33**, 342 (1960).
- ¹⁸E. Morita and E. J. Young, *RUBBER CHEM. TECHNOL.* **36**, 844 (1963).
- ¹⁹M. H. S. Gradwell and W. J. McGill, *J. Appl. Polym. Sci.* **51**, 177 (1997).
- ²⁰F. Ignatz-Hoover, *Rubber World* **24**, 220 (1999).
- ²¹S. H. Laning, M. P. Wagner, and J. W. Sellers, *J. Appl. Polym. Sci.* **2**, 225 (1959).
- ²²F. Thurn and S. Wolff, *Kautsch. Gummi Kunstst.* **28**, 733 (1975).
- ²³L. A. E. M. Reuvekamp, S. C. Debnath, J. W. ten Brinke, P. J. van Swaaij, and J. W. M. Noordermeer, *RUBBER CHEM. TECHNOL.* **77**, 34 (2004).
- ²⁴Trinseo, http://www.styron.com/eu/en/products/syntheticrubber/s_sbr.htm.
- ²⁵S. Wolff and M. J. Wang, *RUBBER CHEM. TECHNOL.* **65**, 329 (1992).
- ²⁶S. Wolff, *RUBBER CHEM. TECHNOL.* **69**, 325 (1996).
- ²⁷A. Scurati and C. J. Lin, *RUBBER CHEM. TECHNOL.* **79**, 170 (2006).
- ²⁸M. J. Wang, *RUBBER CHEM. TECHNOL.* **71**, 520 (1998).
- ²⁹S. Maghami, W. K. Dierkes, T. V. Tolpekina, S. Schultz, and J. W. M. Noordermeer, *RUBBER CHEM. TECHNOL.* **85**, 513 (2012).
- ³⁰G. Heinrich and M. Klüppel, *Adv. Polym. Sci.* **160**, 1 (2002).
- ³¹A. R. Payne, *J. Appl. Polym. Sci.* **6**, 57 (1962).
- ³²A. R. Payne and R. E. Whittaker, *RUBBER CHEM. TECHNOL.* **44**, 440 (1971).
- ³³E. Cichomski, T. V. Tolpekina, S. Schultz, W. K. Dierkes, and J. W. M. Noordermeer, “Silica-Silane Reinforced Passenger Car Tire Treads—Effect of Silica Morphology, Silica-Polymer Interface and Rubber Matrix Network on Tire-Performance Indicators,” Paper presented at the 184th Fall Technical Meeting of the Rubber Division, ACS, Cleveland, October 8–10, 2013.