

Functionalized SBRs in Silica-reinforced Hardness-adjusted Tire Tread Compounds:
Interactions with Filler and Zinc Oxide

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ABSTRACT

The silica/silane system is nowadays well established in the passenger car tire tread. The use of this system leads in combination with a SSBR/BR blend to a significant improvement in wet traction and rolling resistance by maintaining the same abrasion resistance compared to the traditionally used carbon black. But due to the fact that silica is polar and naturally not compatible with non-polar hydrocarbon elastomers, a compatibilizer has to be additionally introduced. Silane coupling agents are added to the compound to couple first during the mixing process to the silica and second during the vulcanization phase to the polymer. An alternative is the introduction of polar functional groups or chemically reactive groups into the elastomer chains which can give improved compatibility of elastomers with the silica.

In this article, the effect of silica-filled compounds of two functionalized SBRs, one backbone modified with carboxylate moieties and the other one modified with dithiol groups, on the dynamic and mechanical properties of a silica-reinforced tire tread compound will be discussed and compared to a reference compound which contains unmodified s-SBR as the main polymer. Zinc oxide is known as the best activator for sulfur vulcanization. Zn-ions combine with accelerators to form an active complex which catalyzes the vulcanization process. However, in silica filled compounds, ZnO may interfere with the silanization process due to 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. In order to investigate the effect of ZnO on the properties of the silica-reinforced tread compound, a series of compounds have been prepared, in which ZnO addition in a later stage was compared to conventional mixing. This leads to promising results favoring rolling resistance of tires made thereof, but brings along lower hardness values, which can affect other properties of the compounds, such as tire traction which leads to misinterpretations. Therefore, compounds with adjusted hardness are prepared through an oil adjustment. Dynamic and mechanical properties of these compounds are studied and compared with the original data without hardness adjustment.

The results show the significant potential of especially one of these modified SBRs to reduce the rolling resistance of tire treads made thereof, while no major change in wet grip occurs.

INTRODUCTION

The filler-polymer interactions have become of key importance with the introduction of the silica technology in passenger car tire treads. Besides the silane coupling agents and control of the silanization process, a polymer functionality can play an essential role in the polymer-filler interactions. The main research subjects over the last years were 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 giving better silica dispersion and better polymer-filler interactions.

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

Introduction of epoxy groups is another prosperous method in this field. It has been reported that the use of an epoxidised SBR with just 7 mol% of epoxidation groups in main chains results in a reduction of around four times in the value of storage modulus at low strains, G_0 , compared to 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 epoxidised 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 elsewhere.⁵ Using chain-end modified polymers in vulcanizates made thereof leads to an improvement of dynamic characteristics, particularly to a reduced hysteresis.⁴ They have also prepared some backbone modified SBRs and reported that all 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%, while the $\tan\delta@0^\circ\text{C}$ (indicative of wet grip characteristic) deteriorated slightly: 3-15%.⁵ Overall, predominantly a rolling resistance improvement was measured for backbone-modified polymers compared with both unmodified and chain-end modified reference polymers. The vulcanizate heat build-up decreased

accordingly. Therefore, they concluded that 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 utilized in rubber compounds since 1905, when it was used as reinforcing filler and not as an activator. Only in the early 1920s, its role as activator for sulfur vulcanizates was discovered; it was found that using ZnO in combination with stearic acid reduces the vulcanization time and improves the rubber properties. Fatty acids like 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-build-up, 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 Acc-S_x-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 Rubber-S_x-Acc (sulfurated rubber). Finally, the rubber polysulfides react, either directly or through an intermediate, to give crosslinks (Rubber-S_x-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 crosslinks may eventually desulfurate to form shorter crosslinks 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.

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 crosslinking. Then the released zinc ion reacts with the accelerator to form an active accelerator complex.

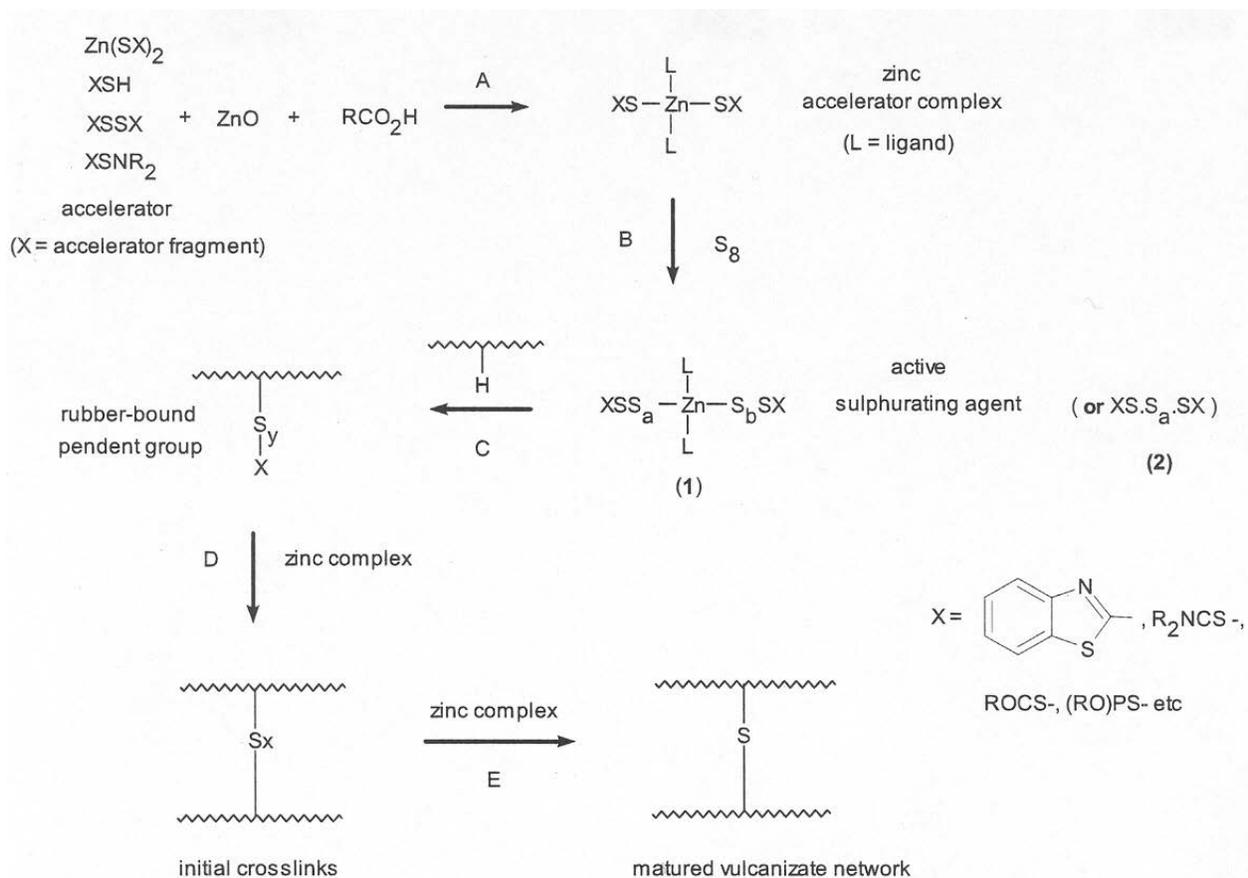


Fig. 1.- General scheme for sulfur vulcanization³⁴

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 presence of ZnO, the vulcanization reactions are of radical or ionic nature.¹⁶⁻¹⁸

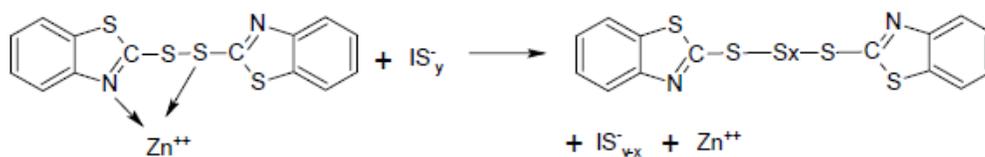


Fig. 2.- Formation of polysulfidic MBTS via a complex with zinc¹¹

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 like N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and N-tert-butylbenzothiazole-2-sulfenamide (TBBS).^{19,20} In case of sulfenamide accelerators, like 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.

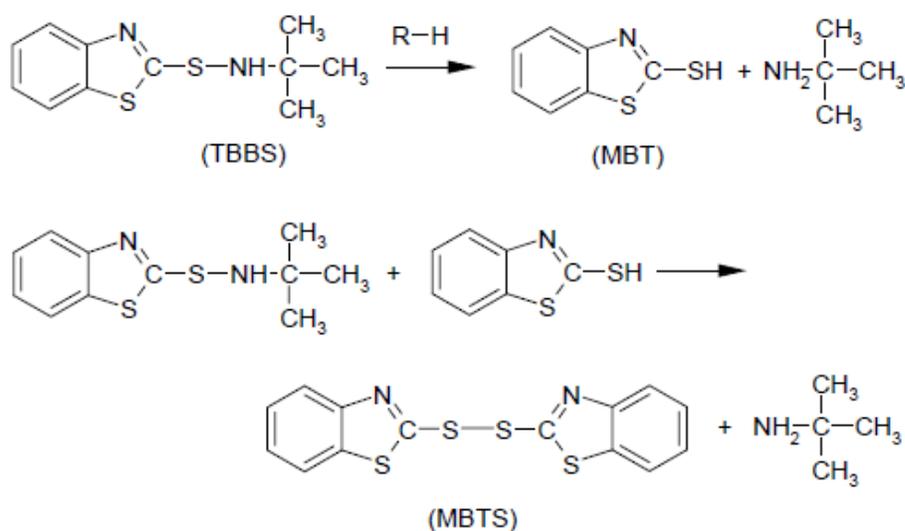


Fig. 3.- Thermal decomposition of TBBS and formation of MBTS¹¹

The silanol groups on the surface of silica are acidic of 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 coupling agent. Several authors have stated that zinc oxide affects the reaction between silica and coupling agent.²¹⁻²⁴ Reuvekamp et al. observed that a lower tendency to scorch is seen when zinc oxide is omitted during the internal mixing stage and added only later together with the curing additives on a cold two roll mill.²³ Presence of zinc oxide 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 zinc oxide in the first mixing step, the scorch effect is largely reduced and it is possible to mix until higher dump temperatures

without pre-scorch 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 (TESPT) does not have to compete with zinc oxide over the silanol groups on the silica surface. An acid-alkali reaction of zinc oxide with the silica surface via the silanol groups was proposed as illustrated in Figure 4.²³

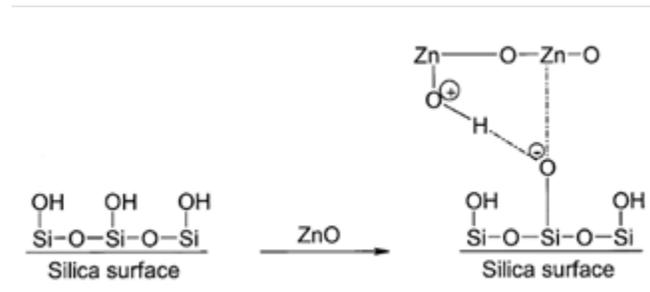


Fig. 4.- Possible reaction between silica and ZnO

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 the present work, 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 to a reference compound. Furthermore, the hardness of the compounds were adjusted to make a fair comparison of the compounds possible.

Hardness of the tread compound plays an important role in the performance of a tire. Hardness which is directly related to the static modulus of a compound²⁵, influences the other properties of the compound²⁶⁻²⁷, and is therefore used as the first guiding principle in practical applications. A higher hardness value of the tread compound may cause rapid irregular wear and stress cracking of the tread and lower riding comfort and shock absorbing capacity of the tire²⁶. Hardness will also affect the traction performance of the tire. The effect is sometimes controversial: on dry roads a softer compound may yield better traction due to increased true contact area, while under wet conditions where hydrodynamic lubrication predominates, a higher hardness produces an increased traction level²⁸. Figure 5 indicates that the hardness of a particular rubber used for the tread will influence the wet traction coefficient. Hardness can also affect the hysteresis properties of the compound, as a softer material undergoes more deformation, hence possibly a higher hysteresis.

As was shown earlier²⁹, leaving the ZnO out of the early stages of mixing and adding it later on with the other curatives resulted in markedly lower hysteresis ($\tan\delta@60^\circ\text{C}$), predicting a

lower rolling resistance and comparable side force coefficient (SFC) values, which may be correlated with the wet skid resistance of a tire. But it was also seen that hardness values of these compounds were lower than the accepted range of tire tread compound's hardnesses. Therefore, to avoid misinterpretations new compounds with adjusted hardness values were prepared and their dynamic and mechanical properties evaluated.

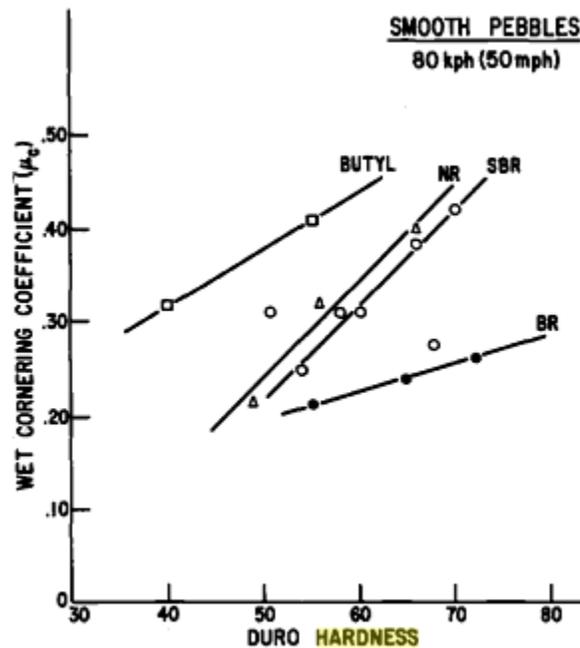


Figure 5. - Wet traction vs. Durometer hardness for several tread and butyl rubbers²⁸

EXPERIMENTAL

Two type of functionalized SBRs were used in this study: SPRINTAN SLR-4602 (Trinseo, Schkopau, Germany) is described to be dithiol-modified for improved polymer-filler interaction with carbon black as well as with silica.⁵ Buna VSL VP PBR 4003 (Arlanxco, Leverkusen, Germany) is statistically modified along the entire polymer main chain with COOH-groups with a concentration of 35 [meq./kg]. Their characteristics can be found in Table 1.

Tab. 1: SBR types used in this study

SBR Type	SLR 4602	PBR 4003	Buna VSL 5025-2 HM
Supplier	Trinseo	Arlanxeo	Arlanxeo
compounds code	CS8	P8	Ref. (reference)
Vinyl (wt.%)	63	48	50
Styrene (wt.%)	21	24	25
T_g (DSC) [°C]	-25	-26	-29
Mooney Viscosity ML(1+4) 100°C [MU]	65	53	62
Oil content (TDAE) [phr]	0	37.5	37.5

A highly dispersible silica was used as reinforcing filler, and the compound containing regular S-SBR BUNA VSL 5025-2HM (Arlanxeo, Leverkusen, Germany) was taken as the unmodified reference. 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 according to the formulations given in Table 2.

Table 2: Rubber compounds formulations (phr)

	Supplier	Ref.	Ref-Z	P8-Z	P8-Z-oil	CS8-Z	CS8-Z-oil
SBR BunaVSL 5025-2		96,3	96,3				
BR		30	30	30	30	30	30
PBR 4003				96,3	96,3		
SLR-4602						70	70
Silica		80	80	80	80	80	80
TESPT^a	Evonik	7	7	7	7	7	7
TDAE^b oil	BP Belgium	6,7	6,7	6,7	-	33	15
Zinc oxide	Sigma Aldrich	2,5	2,5	2,5	2,5	2,5	2,5
stearic acid	Sigma Aldrich	2,5	2,5	2,5	2,5	2,5	2,5
6PPD^c	Flexsys	2	2	2	2	2	2
TMQ^d	Flexsys	2	2	2	2	2	2
Sulfur	Sigma Aldrich	1,4	1,4	1,4	1,4	1,4	1,4
DPG^e	Flexsys	2	2	2	2	2	2
TBBS^f	Flexsys	1,7	1,7	1,7	1,7	1,7	1,7

^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-di-hydroquinoline

^e Accelerator diphenyl guanidine

^f Accelerator N-tert-butylbenzothiazole-2-sulfenamide

The “-Z” incorporated in acronyms refers to the ZnO-study compounds which were prepared according to the same formulation and mixing procedure, but with a small difference: ZnO was left out in the Ist stage of mixing and added later on in the IIIrd stage with the curatives in order to evaluate the effect of ZnO. In order to adjust to the same hardness as the reference compound, the amount of oil in the formulation was changed (compounds P8-Z-oil and CS8-Z-oil). The compounds were prepared in a 350 ml Brabender 350S internal mixer, operating at 110 and 130 rpm rotor speed with a fill factor of 0.7 in three step mixing (Table 3). The total mixing

time was 10 minutes while the dump temperature for the first two stages was adjusted to 155±5 °C by changing the initial temperature.

Table 3: Mixing procedure

Ist Stage	
Rotor speed: 110 RPM	
Initial temp.: 50 °C	
Min.	
0.0	Add polymers
1.0	Add ½ Silica, ½ Silane, Stearic acid
2.0	Add ½ Silica, ½ Silane, Oil, TMQ, 6PPD
3.0	Sweep
4.0	Dump @ ~ 155 °C
IInd Stage	
Rotor speed: 130 RPM	
Initial temp.: 50 °C	
Min.	
0.0	Add I-stage batch
3.0	Dump @ ~ 155 °C
IIIrd Stage	
Rotor speed: 75 RPM	
Initial temp.: 50 °C	
Min.	
0.0	Add batch from the II nd stage
1.0	Add ZnO + 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 t₉₀ optimum vulcanization time as determined in an Alpha Technologies Rubber Process Analyzer RPA 2000.

MEASUREMENTS

The RPA 2000 was used to evaluate the cure properties under 2.79% strain, at a frequency of 0.833Hz, at 160°C and for 30 minutes. The dynamic loss properties tanδ @ 60°C were measured after pre-curing the compounds according to their t₉₀ optimum vulcanization time at 160°C in the RPA 2000, subsequently cooling the RPA 2000 to 60°C and measuring the dynamic

properties at a frequency of 10 Hz and 6% strain. Hardness of the vulcanized compounds was measured with a Zwick 3150 Shore A Hardness Tester according to ASTM D 2240. Mechanical properties of the samples were tested at room temperature using a Zwick Z020 tensile tester according to ISO-37 at a crosshead speed of 500 mm/min.

Abrasion tests were performed in an DIN Rubber Abrasion test machine 564C from Karl Frank GmbH according to ISO 4649. The weight loss was measured and recalculated to a volume loss for each sample. Relative storage modulus as a function of strain, or Payne effect measurements were performed at 80°C in the 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 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 at five different water temperatures: 2, 8, 15, 22 and 30 °C, and at a constant slip angle of 15°. An electro-corundum disc with a relative roughness value of 180 was used to simulate the tire-road interface. Tests were performed at constant speed of 1,5 km/h and load of 75 N for a distance of 33 meters. The Side Force Coefficient is measured as:

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

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

RESULTS AND DISCUSSION

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.^{30,31} Bound rubber is composed of three different types of polymer-filler interactions: a part which 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 6 shows the bound rubber test results of the compounds. As is observed, in the reference compound the difference between the total, that is the sum of the physically and chemically bound rubber, and the chemically bound rubber, is very large compared to 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 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.

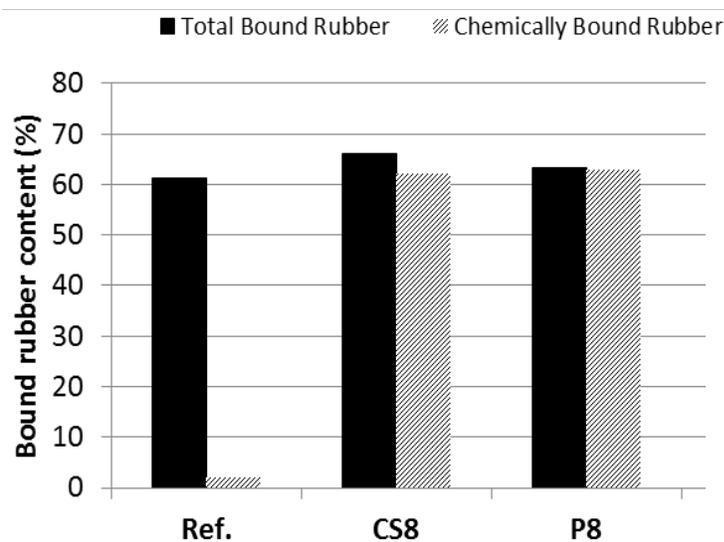


Fig. 6.- Bound rubber content (total and chemically) in the different compounds

The cure characteristics of the six compounds are shown in Figure 7, the relative hardness values of the compounds in Figure 8. Clearly, decreasing the amount of oil has resulted in increased hardness values, almost to the level of the reference. Reducing 6.7 phr and 18 phr of oil dosage for the compounds P8-Z and CS8-Z, respectively, has resulted in 7 and 13% increase in relative hardness: compounds P8-Z-Oil and CS8-Z-Oil. These changes in hardness values correlate with lower strain at break of the cured compounds (Figure 9). Increasing the hardness by oil-reduction has an increasing effect on tensile strength. The M300/M100 modulus ratio,

known as the reinforcing index, is higher for the compounds with higher hardness, except for the compound CS8-Z-Oil which breaks before reaching 300% elongation.

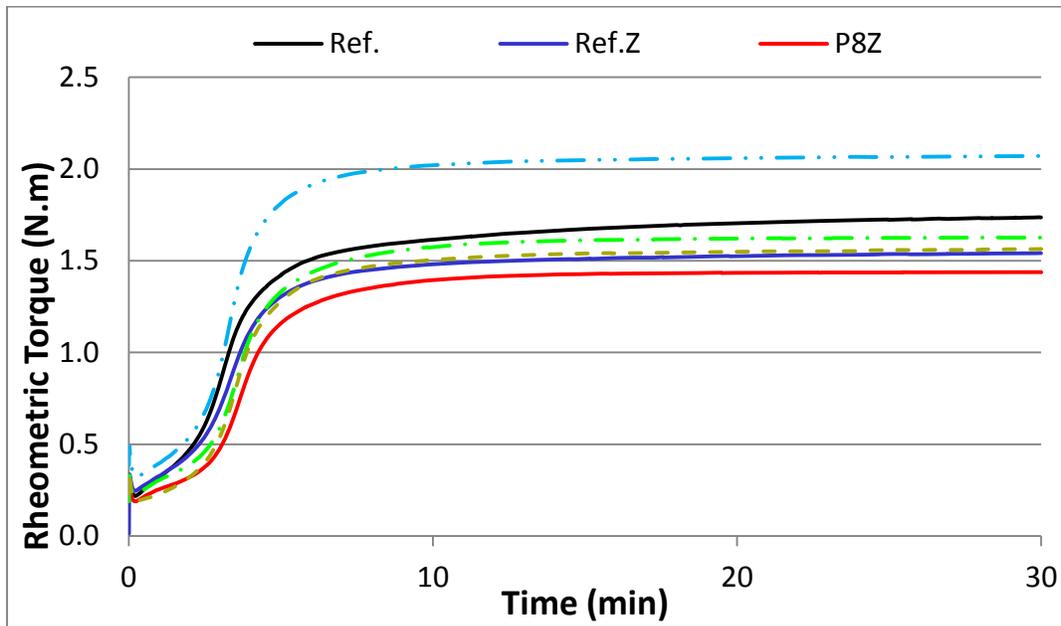


Fig. 7.- Cure characteristics (RPA rheograms) of the compounds at 160°C

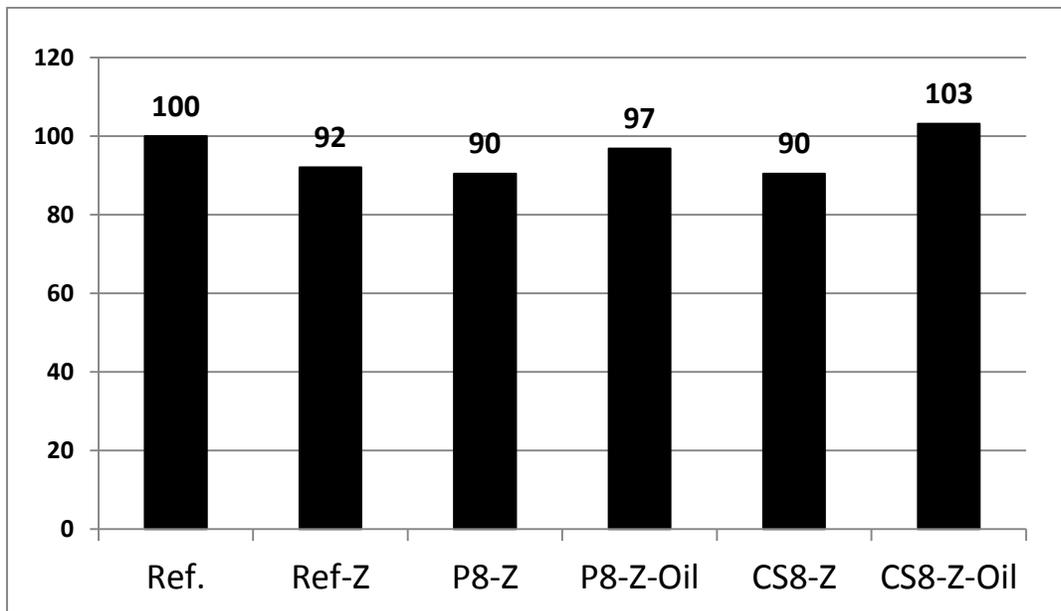


Fig. 8.- Relative hardness value of the compounds

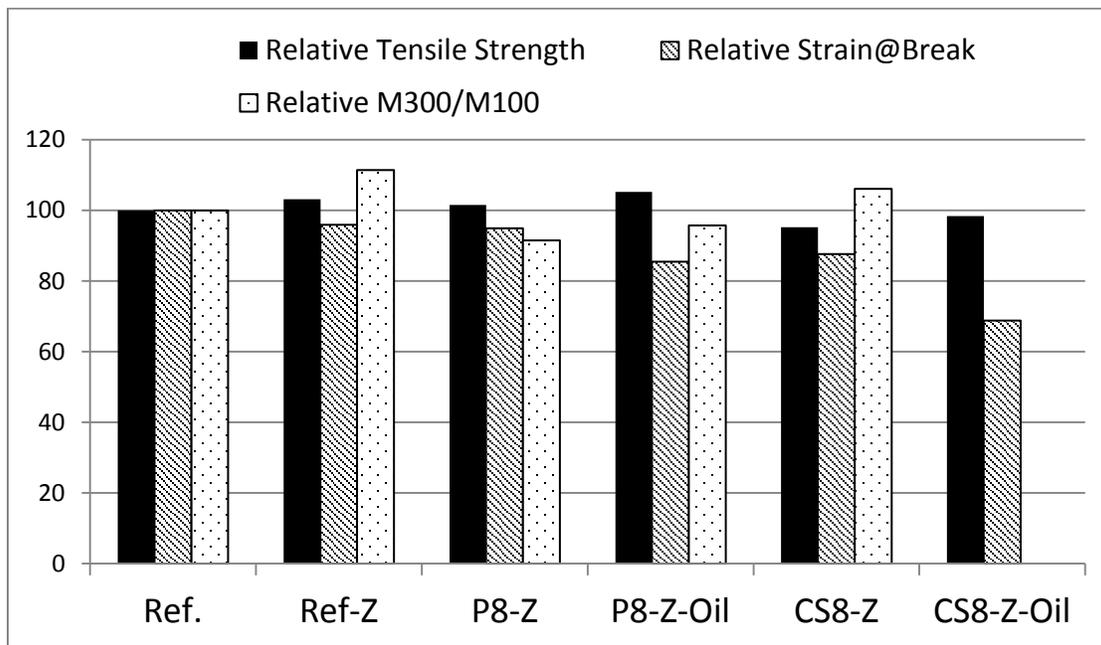


Fig. 9.- Relative mechanical properties of the compounds

The abrasion resistance of the cured compounds was assessed with the DIN abrader instrument. Relative volume loss values are presented in Figure 10. The lower the volume loss, the higher the abrasion resistance. The compounds containing SPRINTAN SLR-4602 polymer, the CS8-Z series, show significantly lower volume loss, therefore the highest abrasion resistance. The compounds containing Buna VSL VP PBR 4003, the P8-Z series, display virtually the same volume loss as the reference compound. It has been reported that the wear resistance of filled rubber is affected to a high degree by the polymer-filler interaction. For fillers having similar morphologies, the increase in polymer-filler interaction, either through enhancement of physical adsorption of polymer chains on the filler surface or via creation of chemical linkages between filler and polymer, is crucial to the enhancement of wear resistance⁹. In addition, it is accepted that the abrasion volume increases with rise of the tire surface temperature¹⁰; therefore a compound with lower heat build-up, here CS8-Z series, is expected to cause lower abrasion. Anyhow, it seems that adjusting the hardness values of the compounds, does not have a significant effect on the abrasion resistance of the compounds within a series of the same rubber used.

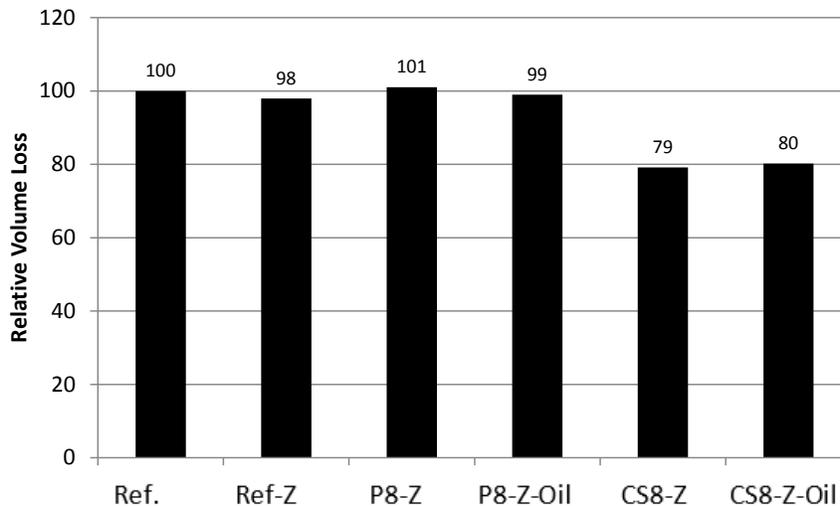


Fig. 10.- Relative volume loss of the different compounds

Relative loss tangent values measured at 60°C are presented in Figure 11. It is commonly accepted that the $\tan\delta$ -value of a compound measured at 60°C, at a frequency of 10 Hz and 6% strain, correlates with the rolling resistance performance of a tire tread made therefrom. Lower $\tan\delta$ indicates lower hysteresis, which results in less energy dissipation^{11,35}. 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-Z has the lowest $\tan\delta$ value (between the conventionally prepared compounds), followed by P8-Z. From a mechanistic 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 network³²⁻³³. Besides, some authors suggest that slippage of polymer chains on the filler particle surface is a source of energy dissipation, too³⁸. Either mechanisms work well in interpretation of obtained results. Polar functionalized SBRs (compounds CS8 and P8) show a lower loss tangent compared to the unmodified 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 less developed filler network. In addition, when strong interactions occur between silica particles and polymer chains - which is indicated by Bound Rubber test results, see Figure 6 - movement of polymer chains, hence a source of energy dissipation would be restricted. Additionally, in case of polar polymers, part of the ZnO can be involved in interactions with acidic moieties of the partially polar polymer chains and therefore less interferes with the

silanization process, which helps in better dispersion of the silica particles, again. Comparing the dithiol-modifications and carboxyl-modifications, it looks like the dithiol is more eager to couple to silica particles or more reactive towards ZnO, resulting in the lowest $\tan\delta$ at 60°C for the two.

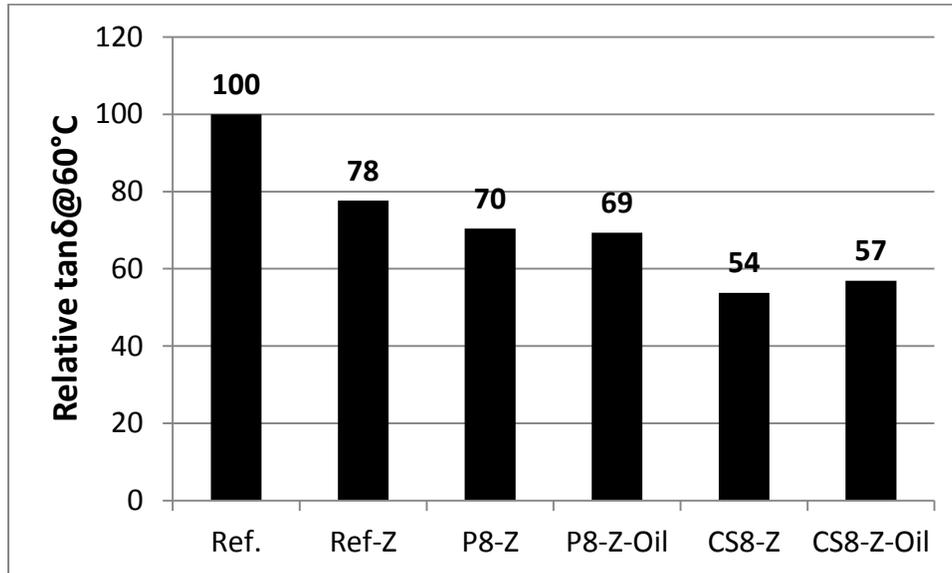


Fig. 11.- Relative $\tan\delta$ at 60°C values for different compounds

The compounds containing SPRINTAN SLR-4602 polymer show the lowest $\tan\delta$ -values @ 60°C. Hardness adjustment leads to a little increase in $\tan\delta$ -value. The same trend is noticed for the P8-Z series, as the compounds with higher hardness values show a bit higher $\tan\delta$ @ 60°C too. Loss properties and in particular the loss tangent originate from the ability of turning dynamic input energy into heat. Any changes induced in the system which hinders the segmental movements of molecules results in lower loss tangent values¹². Taking some amount of oil out of the compound formulations may increase the internal friction, either between filler particles or between filler particles and adjacent polymer chains. This effect is rather small in case of the P8-Z-Oil compound, but larger for the CS8-Z-Oil compound. Nevertheless, at similar hardness values, still the compounds with SPRINTAN 4602 are the best choices from a rolling resistance point of view.

Rebound resilience results confirm the $\tan\delta$ at 60°C data (Figure 12). The higher the rebound resilience, the more elastic the compound and therefore the lower the hysteresis, which favors lower rolling resistance. Compounds including SPRINTAN SLR-4602 polymer present

the highest rebound resilience. It seems that taking some amount of oil out of the compounds does not have a significant effect on the rebound resilience results, for either polymers.

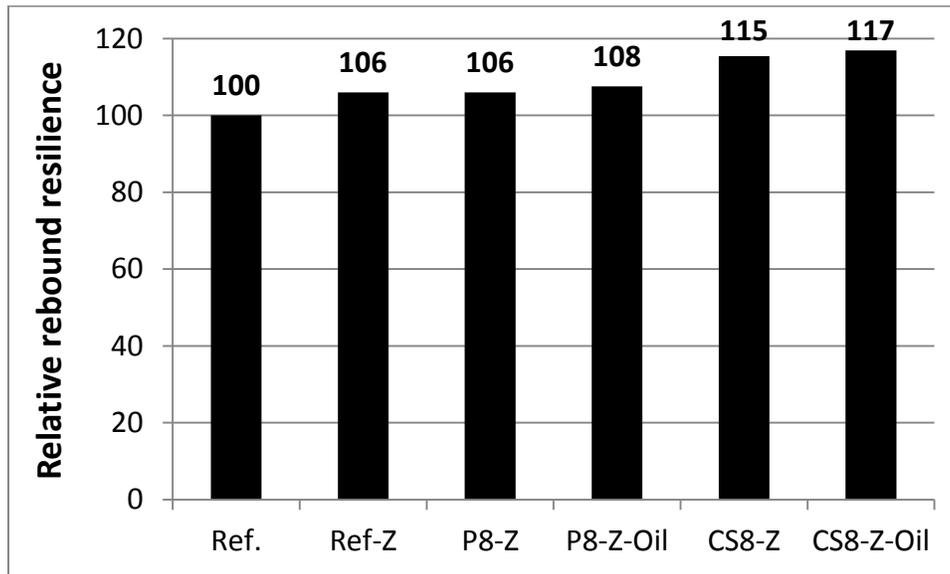


Fig. 12.- Relative rebound resilience data measured at 70°C

Figure 13 represents the relative storage modulus data as a function of strain for the different compounds. The difference between the storage moduli at low strain and high strain is defined as the Payne effect^{36,37}. The compounds including the SPRINTAN SLR-4602 and Buna VSL VP PBR 4003 polymers show lower modulus values, therefore lower Payne effects compared to the reference compound. . Therefore, functional SBRs generally help in improving filler dispersion and reducing filler-filler interaction. Taking out some amount of oil gives rise to some increase in the storage modulus values relative to the original compounds. An increased Payne effect value can be taken as a sign of poorer filler-filler dispersion and/or higher filler-filler interactions. The increase is most pronounced in the compounds with lower oil content.

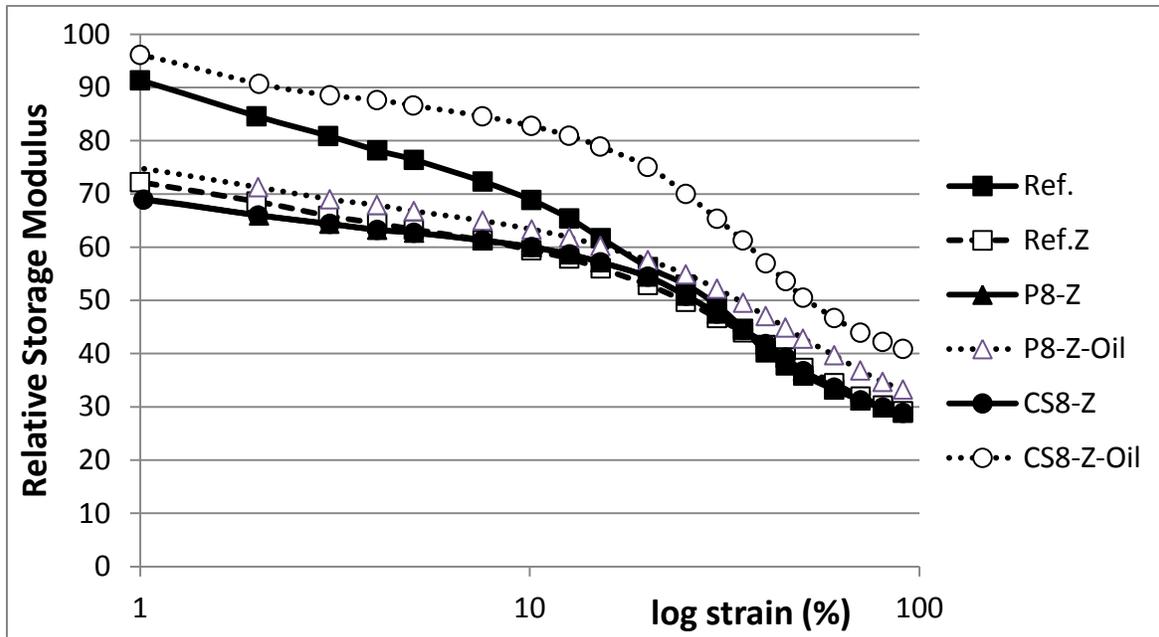


Fig. 13.- Relative storage modulus versus strain measured at 100°C for the different compounds

Figure 14 represents the LAT100 test results for the different compounds. As is clearly seen, adjusting the hardness values of the compounds by removing some amount of oil (P8-Z-Oil and CS8-Z-Oil) resulted in increased side force coefficients (SFC) compared to their original compounds (P8-Z and CS8-Z), however the values are still lower than for the reference compound. To summarize, hardness adjustment by removing some amount of oil, causes an increase in SFC for the compounds with ZnO added in the later stage of mixing relative to their original formulations. Nonetheless, it should be mentioned that all these changes are in a small range of 3-7% and might not really be determining, in practice, for the skid performance of the tires made out of these compounds. Practical tire tests must confirm the results observed.

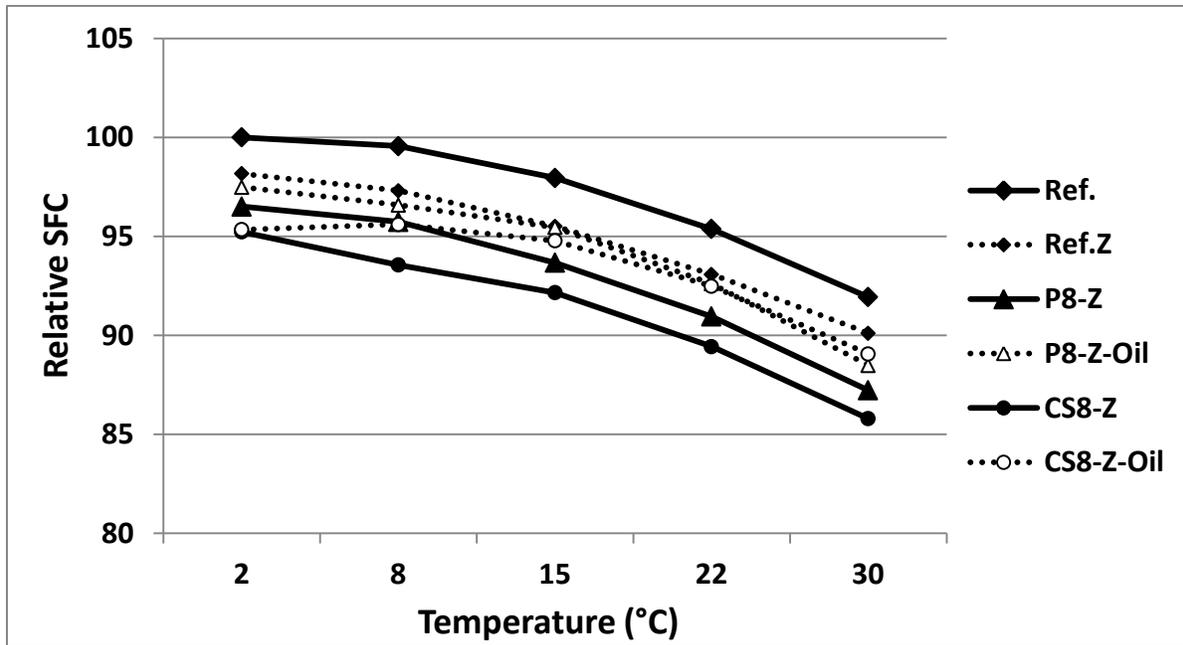


Fig. 14.- Relative side force coefficients measured at different temperatures for the different compounds

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 the 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. 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 in order to monitor the filler-polymer and filler-filler interactions, confirming the lowest filler-filler interaction, especially for the two compounds containing polar functionalities.

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 to 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.

A series of compounds were prepared in which ZnO was omitted from the first mixing stages and added later on with the curatives. In order to adjust the hardness level of these compounds to the reference one, some amount of oil was removed from the formulation.

The alteration in the amount of oil in the Zn-series formulations delivers new compounds with similar hardness values as the reference compound. The CS8-Z series shows the best abrasion resistance overall, but adjusting the hardness levels did not have a significant effect on the abrasion resistance of all compounds. The CS8-Z series compounds show the lowest $\tan\delta @ 60^\circ\text{C}$. Higher hardness led to a small increase in $\tan\delta @ 60^\circ\text{C}$ values which can be attributed to the fact that taking out some oil increases the internal friction between the filler particles or fillers and polymer chains. The Payne effect test results confirm higher filler-filler interactions in the compounds with lower amount of oil. Looking at the side force coefficient values, it seems that taking some amount of oil out of the formulations leads to a little increase in the friction coefficient of the compounds. Anyhow, the changes in SFC values are very small and within a range of 3-7%, therefore might be not really significant in real tire practice.

To summarize, the excellent performance of the SPRINTAN SLR-4602 polymer in the tread formulation does not change much by changing the hardness value of its compounds as it performs at a large distance better than the other polymers used.

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